

**The Rational Development of Improved
Methods for the Removal of Oil Contamination
from Wildlife and Rocky Foreshore Utilizing
Magnetic Particle Technology**

A thesis submitted for the degree of Doctor of Philosophy

by

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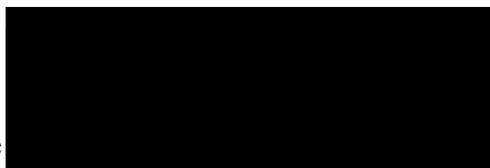
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September 2015

Declaration

I, Munaweera Thanthirige Kasup Munaweera, declare that this thesis entitled “The Rational Development of Improved Methods for the Removal of Oil Contamination from Wildlife and Rocky Foreshore utilizing Magnetic Particle Technology” is no more than 100,000 words in length, exclusive of tables, figures, appendices, bibliography, references and footnotes. This thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. This research has been conducted in collaboration with a number of partners, whose contributions have been appropriately acknowledged throughout. Thus, except where otherwise indicated, this thesis is my own work.

Signature



Date: 03 September 2015.....

Journal publications, conference proceedings and conference presentations relevant to the scope of this thesis

Refereed Journal Publications

Bigger, SW, **Munaweera, K**, Ngeh, LN, Dann, P, Orbell, JD 2013, 'Mathematical model for the sequential pick-up of chemical contaminants by magnetic particles', *Journal of Environmental Engineering*, vol. 139, pp. 796-802.

Ngeh, LN, Orbell, JD, Bigger, SW, **Munaweera, K**, Dann, P 2012, 'Magnetic cleansing for the provision of a quick clean to oiled wildlife', *World Academy of Science and Technology*, vol. 72, pp. 1091-1093.

Conferences

Orbell, JD, Bigger, SW, Ngeh, LN, **Munaweera, K**, Dann, P, Jessup, R, Healy, MT, 'Providing a 'quick wash' to oil contaminated wildlife using magnetic particle technology', Effects of Oil on Wildlife, 10th International Conference, Tallinn, Estonia, 5–9th October, 2009. *Platform presentation*.

Munaweera, K, Le, O, Ngeh, LN, Bigger, SW, Orbell, JD, Jessop, R, Dann, P, 'An assessment of the relative effectiveness of olive oil, methyl oleate and methyl soyate as pre-treatment agents for the rehabilitation of oiled birds', the Oamaru Penguin Symposium, Kingsgate Hotel Brydone, Oamaru, New Zealand, 24–25th June, 2009. *Poster presentation*.

Orbell, JD, Bigger, SW, Ngeh, LN, **Munaweera, K**, Jessop, R, Healy, R, Dann, P, 'The development of prototype magnetic particle technology (MPT) equipment for providing a "quick clean" to oil contaminated wildlife', the 7th International Penguin Conference, Boston, Massachusetts, USA, 29 Aug - 4 Sept, 2010. *Poster presentation*.

Munaweera, K, Ngeh, LN, Bigger, SW, Orbell, JD, Dann, P, ‘*Towards a rational choice of pre-treatment agents for the cleansing of oiled wildlife*’, the Australian Wildlife Rehabilitation Conference (“Continuous Improvement”), Townsville, Australia, 16–20th July, 2012. *Platform presentation and refereed proceedings*.

Ngeh, LN, Orbell, JD, Bigger, SW, **Munaweera, K**, ‘*Magnetic cleansing*’ for the provision of a ‘quick clean’ to oiled wildlife. *International Conference on Wildlife Ecology*, Rehabilitation and Conservation, Phuket, Thailand, 24–25th December, 2012. *Platform presentation and refereed proceedings*.

Media output

‘The Project’, *Channel 10*, Telecast on 23 May 2013.

‘Science dust off penguins for an 80th birthday’, *The Age*, 04 March 2011.

Awards

The collaborative research teams based at Victoria University and the Phillip Island Nature Parks, of which this research program formed a part, were awarded the 2013 Banksia Award (Business and Not-for-Profits – In Collaboration Award; “Magic Wand” Oiled Penguin Recovery Technology). The following statement was released: “*This initiative stood out in the Judge’s opinion based on its innovation, effectiveness and opportunity for a broad-scale solution to a global problem. Combined with its effective communication techniques to educate the public on the risks of oil spills and recovery strategies*”.

The above collaboration also contributed to the award of a \$250K grant to the the Penguin Foundation to further develop this technology in via the joint research and development program that is ongoing between Victoria University and the Phillip Island Nature Parks.

Note: Conference presentations and several oil removal videos using MPT are provided in one of the pocketed CDs.

Abstract

Oil contamination of ecosystems and wildlife presents a formidable challenge to environmental remediators, including wildlife rescuers and rehabilitators. Quite apart from the diversity of polluting events, existing clean-up methods and technologies have remained essentially unchanged over the years. For example, the method of choice for the treatment of oiled wildlife is still based on the transportation of affected animals to treatment facilities and the use of surfactants and copious amounts of warm water to remove the contamination. Although such techniques have themselves been developed to a high degree over the years, with a number of notable success stories, such operations are often very labour intensive and, not being portable, cannot be applied to the animals upon first encounter, either at remote locations or in holding bays. This means that victims are often left for long periods of time in contact with toxic and/or corrosive chemicals. In spite of such requirements for improvements in wildlife rehabilitation methods and technologies, there is a paucity of scientific and engineering research into alternatives.

This thesis is part of a program that exploits the use of oil ad(b)sorbing magnetic particle technology (MPT) in order to research the best methods and equipment to remove oil from a number of relevant substrates - including feathers, fur and rock surfaces. In this regard, the refinement of portable MPT equipment for the provision of a 'quick clean' to contaminated wildlife in the field has been pursued. This includes the development and testing of an optimal magnetic harvesting device, an investigation of the particle characteristics that promote a high initial removal of contaminant and the development, in collaboration with industrial design advisors, of the 'backpack concept' for a portable kit. Thus the final iteration of the magnetic harvesting device "the wand" is considered to be perfected and prototype equipment is ready for implementation in the event of an incident. The most appropriate particle size distribution and grade for the most efficient "quick removal" of the most volatile constituents has been established.

A more sophisticated understanding of the contaminant removal phenomenon is crucial to the development of improved magnetic particles e.g. that have both enhanced initial removal characteristics for the 'quick clean' approach, as well as for achieving an optimum final removal (ideally 100%). This has been addressed via the development of a mathematical model, benchmarked to experimental data, for the sequential pick-up of chemical

contaminants – as is appropriate for such applications. As well as providing insight into the physical basis for the pick-up phenomenon, this model also suggests an effective means for assessing the efficiency of removal.

Experiments have been conducted in order to further investigate what physical and chemical characteristics of the particles themselves are important for determining critical pick-up properties, such as initial pick-up efficiency and final removal. Hence, properties such as average particle size, particle size distribution, surface characteristics, surface coating, porosity and apparent density have been investigated. In this regard, an optimal average particle size range (i.e. preferably $> 5\mu\text{m}$ and $< 100\mu\text{m}$) and the importance of capillary effects (as reflected in the mathematical form of the removal isotherm) have been characterized.

In practice, related to the problem of efficient removal is the frequent necessity to use pre-treatment agents (PTAs) for recalcitrant contaminants. Where the use of a PTA is indicated, existing detergent-based protocols usually rely on anecdotal evidence for the choice of a suitable agent - such as olive oil or methyl soyate. There have been very few, if any, scientific investigations into what the optimum PTA for a given scenario (of contaminant type and bird species) might be and what might be the most appropriate point of PTA application during the cleansing process. This thesis has researched the further development of a *quantitative* assay, based on MPT together with the mathematical modelling, whereby the relative efficacy of potential PTAs can be conveniently assessed for specific situations. This method has been applied to the evaluation of a range of pre-treatment candidates with respect to the removal of different oil types from feathers. This work has clearly demonstrated that the choice of the most appropriate PTA is both oil and substrate dependent and also depends upon the point of PTA application. It has also been demonstrated that the PTA assay may be used to develop potentially more effective PTAs, including PTA blends, for specific applications.

An important consideration for this work is to test the hypothesis that the relative PTA efficacies - as determined by the MPT assay, carry over with fidelity to PTA-assisted detergent based methods; so that recommendations can be reliably made to the rehabilitation community at large. Experiments have therefore been designed and conducted in order to test this hypothesis for eight different PTAs. Thus parallel, semi-quantitative, detergent-based and, fully quantitative, MPT-based experiments have been designed and conducted for the

PTA assisted removal of a representative contaminant (a Bunker Oil) from the feathers of Mallard Duck, *Anas platyrhynchos*. These experiments have successfully confirmed the above hypothesis. This assay has also been applied to the identification of the most appropriate point of PTA application during the treatment process. The potential for this assay to be used for making recommendations to wildlife rehabilitators and for the screening and rational development of a wide range of pre-treatment candidates, for various feather types and contaminants, has been established.

The application of the above principles to the removal of various contaminants from other substrates such as fur and rock has also been investigated. Thus effective removal from mammalian fur has been demonstrated and the effect of different fur microstructures in relation to the penetration of the contaminant through the fur and onto the skin has been elucidated. It was demonstrated by comparing rabbit fur to seal fur that oil removal efficacies are dependent upon the fur microstructure and hence fur type. The effect of PTA application at various treatment stages has also been examined and compared to a feather substrate. In regards to removal from rock surfaces, the problem of oil penetration into porous rock has been examined in relation to the use of various PTAs. It has been found that the extent of oil penetration may also be quantified by this method.

The outcomes and significance of the above research may be summarized as follows:

- Appropriate technology and techniques for a quick clean of contaminated wildlife in the field have been successfully refined and developed.
- A mathematical model that furthers our understanding of the MPT pick-up phenomena has been successfully developed.
- Our knowledge of critical particle characteristics for efficient sequestration has been significantly advanced.
- A quantitative method based on MPT for the evaluation of relative PTA efficacy has been further developed and validated - to the extent where recommendations can now be made to wildlife rehabilitators worldwide.

- The potential of extending this technology to other substrates such as fur and rock surfaces has been established.

The above outcomes clearly represent significant advances with respect to applying this technology in the field. This is particularly the case with respect to utilizing this technology in remote locations for the quick and efficient removal of the toxic and corrosive volatile components of oil contamination via a “quick clean”.

Acknowledgements

I would like to convey my deepest gratitude to Professor John Orbell, my principal supervisor at Victoria University, for this opportunity and for all his support and tremendous encouragement for the completion of this thesis. His friendly, humble nature and excellent guidance has helped me, not only to overcome the challenging nature of the research, but also to become a complete and mature person. He has also helped me to see things in creative way. I appreciate all of the skills gained from him and it was a privilege to work with him.

I also would like to thank Dr. Lawrence Ngeh, my associate supervisor at Victoria University, for his great support towards the completion of this research. His help and guidance combined with his warm friendly nature provided me with the courage to complete this research. It was a pleasure to work with him and also to socialize with him.

My sincere thanks are extended to Professor Stephen Bigger, my associate supervisor at Victoria University, for his enthusiastic support, encouragement, commitment and patient guidance throughout this project. His high level contribution to my understanding of science is most appreciated and it was a great honour for me to work with and learn from him.

I would also like to thank Dr. Peter Dann, my associate supervisor based at the Phillip Island Nature Parks Research Centre, Victoria, Australia, for providing wide-ranging assistance including expertise, facilities and biological specimens.

My special thanks also go to Professor Authur De Bono, Dr. Selby Coxon and Mr. Alex Matthews at Monash University and Ms. Chathuri Piyadasa of the School of Engineering and Science at Victoria University for assistance in the design and building of prototype field equipment.

I am very grateful to the Australian Research Council for granting me a post-graduate stipend under an ARC Linkage grant and thanks are also extended to the Phillip Island Nature Parks and the Penguin Foundation for providing financial and in-kind assistance as industrial partners for this research project.

I also would like to thank Hoganas AB, Sweden and their Australian representative, Mr. Stephen Weir at Australian Metal Powder Suppliers Pty. Ltd., for the supply of technical advice and iron powder.

I sincerely thank our laboratory technical staff, Ms. Stacey Lloyd, Mr. Joseph Pelle, Ms. Min Nguyen and Dr. Suddina Hewakapuge for all of their unfailing support and assistance throughout the course of this project.

This thesis is dedicated to my loving parents and relatives

List of Abbreviations

A100S	Atomised fine un-annealed grade of iron powder
A40S	Atomised coarse un-annealed grade of iron powder
AMO	Arab Medium Crude Oil
AMSA	Australian Maritime Safety Authority
ASC100.29	Atomised fine annealed grade of iron powder
ASC300	Atomised superfine annealed grade of iron powder
<i>B</i>	Constant used in the hyperbolic pick-up model
BD1	De-oiler
BIO	Biodespersol
BO	Blended Oil
BO1	Bunker Oil 1
BO2	Bunker Oil 2
BPTA	Blended Pre-Treatment Agents
c_1	Proportionality constant allowing for deviation from idealized behaviour in the exponential pick-up model
C100.29	Spongy fine un-annealed grade of iron powder
c_2	Proportionality constant allowing for deviation from idealized behaviour in the hyperbolic pick-up model
CO	Canola Oil
CSIRO	Commonwealth Science and Industrial Research Organisation
DFC	Duck Feather Cluster
DFO	Diesel Fuel Oil
DMP	Data Modelling Program
DO	Diesel Oil
ENO	Engine Oil
EO	Ethyl Oleate
f_1	Mass of feather cluster
f_2	Mass of feather cluster plus excess contaminant
f_3	Mass of contaminated feather cluster
f_4	Mass of magnetically stripped feather cluster
GCO	Gippsland Crude Oil

gl	gallons
IO	Isopropyl Oleate
IP	Iron Powder
JCO	Jasmine Crude Oil
k_1	Proportionality constant used in the exponential pick-up model
k_2	Proportionality constant used in the hyperbolic pick-up model
m_1	Exponential constant allowing for deviation from idealized behaviour in the exponential pick-up model
m_2	Exponential constant allowing for deviation from idealized behaviour in the hyperbolic pick-up model
M40	Spongy coarse un-annealed grade of iron powder
mb	million barrels
MH300.29	Spongy superfine annealed grade of iron powder
MO	Methyl Oleate
MPT	Magnetic Particle Technology
MS	Methyl Soyate
Mg. T	Magnetic Tester
MT	Massage Technique
N	Number of Treatments
N=1	Pre-treatment Agent used at 1 st Treatment
N=3	Pre-treatment Agent used at 3 rd Treatment
N=5	Pre-treatment Agent used at 5 th Treatment
N=6	Pre-treatment Agent used at 6 th Treatment
N=7	Pre-treatment Agent used at 7 th Treatment
N ₉₀	Effective Number of Treatment (relative value of N ₉₀ intercept with the 90% horizontal axis)
N ₉₅	Effective Number of Treatment (relative value of N ₉₅ intercept with the 95% horizontal axis)
N ₉₉	Effective Number of Treatment (relative value of N ₉₉ – intercept with the 99% horizontal axis)
NC100.24	Spongy fine annealed grade of iron powder
NMT	Non-Massage Technique
NPTA	No Pre-conditioning Agent

NT	Number of Treatments
Oleo	Oleophobol
OO	Olive Oil
OSF	Original Seal Fur
P%	Percentage pick-up of contaminant
P_{∞}	Cumulative percentage pick-up after an infinite number of treatments
$P(n)$	Cumulative percentage pick-up of contaminant from the system upon treatment n
$P_1(n)$	The difference between P_{∞} and $P(n)$ expressed in the exponential pick-up model
PFC	Penguin Feather Clusters
PF	Penguin Foundation
PINP	Phillip Island Nature Parks
$P_o\%$	Final percentage contaminant
PS	Particle Size
PTA	Pre-Treatment Agent
r	Linear regression coefficient
RC	Rock
r_1	Mass of residual contaminant
R12	Niagara Fall grades iron powder
RF	Rabbit Fur
Rho	Rhodorsil
RSF	Recycled Seal Fur
RSQA	Relative Semi-Quantitative Assessment
RT	Room Temperature
R_x	Replicate Number
SANCCOB	South African Foundation for the Conservation of Coastal Birds
Sco	Scotchgard
SDF	Single Duck Feather
SE	Standard Error
SEM	Scanning Electronic Microscope
SF	Seal Fur
SPF	Single Penguin Feather

SSA	Specific Surface Area
T	Temperature
t	tonnes
TMS	Methoxitrimethylsilane
ν_1'	Contaminant pick-up efficiency after one treatment derived from the hyperbolic pick-up model
ν_1	Contaminant pick-up efficiency after one treatment derived from the exponential pick-up model
ν_{\max}	Maximum gradient of the $P(n)$ versus n isotherm as fitted by the hyperbolic pick-up model
ν_0'	Initial contaminant pick-up efficiency derived from the ideal hyperbolic pick-up model
ν_0	Initial contaminant pick-up efficiency derived from the ideal exponential pick-up model
VO	Vegetable Oil (Blended)
WND	Magnetic Wand
μm	Microns

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Chapter 1: Introduction

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Chapter 1: Introduction

1.1 Oil and the modern world

The history and the use of petroleum and petroleum products in the modern world, and the sustainability of this resource, are well documented in numerous excellent publications (Laws 1993; Congressional Digest 2000; Jones and Pujadó, 2008; Ghosh and Prelas, 2009; Fingas 2010; Laxer 2011; Gold 2012). The actual quantity of conventional¹ oil that is currently being produced and consumed is staggering, Figure 1.1, and this is projected to increase significantly over the course of the 21st century, especially with the unrelenting industrialization of highly populated developing countries such as China and India (Rogowska and Namieśnik, 2010; Read 2011).

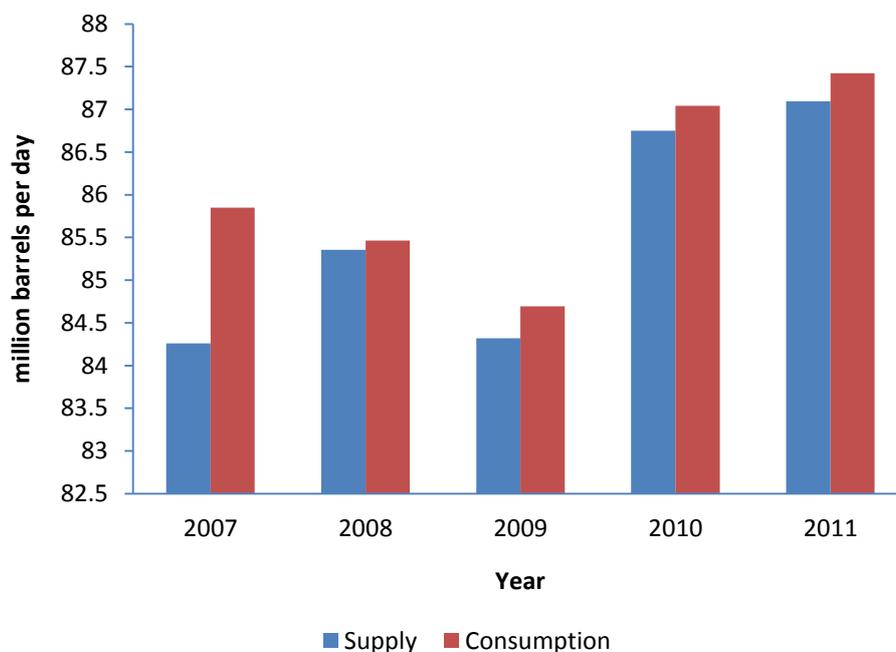


Figure 1.1 Global oil Supply and Consumption from 2007 to 2011; US Energy Information Administration [US Energy Statistics (2007-2011)].

Quite apart from the deleterious impact on the Earth's climate due to increasing petroleum consumption (Laxer 2011), the extraction and transportation of crude oil results in the

¹Conventional oil is a liquid mixture of hydrocarbons that is extracted from underground reserves via drilling. Non-conventional oil is oil obtained by other, usually indirect methods, such as from coal, sand, shale or by processing natural gas. The latter production activities are also expanding rapidly. The Earth's total recoverable oil reserves are estimated at around 2,330 billion barrels [Congressional Digest 2000].

frequent occurrence of devastating oil spills that endanger wildlife and delicate ecosystems. Some well-known examples of these are listed in Table 1.1 - although for many spills the statistics on bird mortality are unavailable and many other significant events undoubtedly go unreported.

Table 1.1 Examples of major documented oil spill events over the last 50 years.

Year	Ship Name	Location	Amount	Estimated Bird Mortality	Reference
2011	MS Olivia	Tristan da Cunha	80,500t	1,577	Oil Spills Intelligent Report 2011
2010	Deepwater Horizon	USA	4.9 m/b	2,303	Mascareli 2010; Schrope 2011; Barron 2012, US Fish & Wildlife Service 2011
2003	Tasman spirit	Pakistan	30,000t	Not available	Janjua et al. 2013
2002	Prestige	Spain	77,000t	24,000	Zuberogoitia <i>et al.</i> 2007; Fingas 2010
2001	New Amity	USA	50,000gl	Not available	Helm <i>et al.</i> 2008
2000	Westchester	USA	550,000gl	582	Michel, J, Henry, CBJR and Thumm,S 2002; Helm <i>et al.</i> 2008
1999	New Carissa	USA	70,000gl	3,137	Owen et al. 2002; Goodman 2003; Oil Spill Intelligence Report 2007; Helm <i>et al.</i> 2008
1998	Command	California	3,000gl	1,900	Hampton <i>et al.</i> 2003; Helm, Ford and carter 2008
1997	Kure	California	4,537t	5,206	Hampton <i>et al.</i> 2003; Helm, Ford and carter 2008
1997	Kuroshima	Alaska	39,000gl	>2,000	Martine <i>et al.</i> 1998; Helm, Ford and carter 2008
1996	Cape Mohican	USA	40,000gl	593	Helm, Ford and carter 2008
1996	North Cape	Rhode Is.	828,000gl	2,292	Hampton <i>et al.</i> 2003; Helm <i>et al.</i> 2008
1996	Sea Empress	UK	72,000t	3,640	Clark, Evans and Palmer 1997; Etkin 1999
1993	MV Braer	UK	85,034t	<1500	Etkin 1999; Fingas 2010; Jernelöv 2010; Höfer 1998, Cheong 2012
1991	Min Al Ahmadi	Kuwait	857,143t	Not available	Travos and Saier 2010; Fingas 2010; Etkin 1999
1991	700 oil wells	Kuwait	71,428,571t	Not available	Fingas 2010; Travos and Saier 2010
1991	Persian gulf	Kuwait	83,897t	Not available	Travos and Saier 2010
1991	Al Qadasiyah	Kuwait	139,690t	Not available	Fingas 2010; Travos and Saier 2010
1991	Hileen	Kuwait	139,690t	Not available	Travos and Saier 2010; Fingas 2010
1991	Al-Mulanabbi	Kuwait	117,239t	Not available	Fingas 2010; Travos and Saier 2010
1991	Tariq Ibn Ziyad	Kuwait	106,325t	Not available	Fingas 2010; Travos and Saier 2010
1991	Haven	Italy	144,000t	Not available	Fingas 2010; Jernelöv 2010; Cheong 2012
1991	ABT Summer	Angola	260,000t	Not available	Etkin 1999; Jernelöv 2010
1990	American Trader	USA	416,598gl	3,400	Card and Meehan 1991; Hampton <i>et al.</i> 2003; Helm, Ford and carter, 2008
1989	Exxon Valdez	USA	38,000t	~ 350,000	Piatt <i>et al.</i> 1990; Etkin 1999; Anderson 2002; Travos & Saier 2010; Peterson <i>et al.</i> 2003
1988	Nestucca	USA	230,000gl	52,000-78,000	Yaroeh 1991; Helm, Ford & carter 2008
1988	Odyssey	Canada	146,599t	Not available	Etkin 1999; Fingas 2010; Jernelöv 2010
1986	Apex Houston	USA	25,9000gl	9,856	Helm, Ford & carter 2008; Hampton <i>et al.</i> 2003; Carter <i>et al.</i> 2003
1985	Arco Anchorage	USA	239,000gl	~ 4,000	Helm, Ford & carter 2008
1985	Puerto Rican	USA	1,250,000gl	4,815	Helm, Ford & carter 2008; Hampton <i>et al.</i> 2003
1983	Castillo de	South	267,007t	Not available	Jernelöv 2010

	Bellver	Africa			
1979	Independentza	Turkey	98,255t	Not available	Etkin 1999; Fingas 2010; Jernelöv 2010
1979	Atlantic Empress	West Indies	286,354t	Not available	Etkin 1999; Travos & Saier 2010; Fingas 2010; Jernelöv 2010
1978	Amoco Cadiz	France	233,565t	4,500	Etkin 1999; Lamy <i>et al.</i> 2001; Fingas 2010; Cho and Oh 2012; Höfer 1998
1978	Esso Bernica	Scotland	1,200t	3,700	Höfer 1998
1977	Borag	Taiwan	35,357t	Not available	Etkin 1999; Fingas 2010
1976	Sansinena	USA	1,260,000gl	Not available	Helm, Ford & carter 2008
1975	B. Ambassador	Japan	48,214t	Not available	Etkin 1999; Fingas 2010
1972	Sea Star	Gulf of Oman	128,891t	Not available	Etkin 1999; Fingas 2010; Jernelöv, 2010; Rogowska & Namieśnik 2010
1971	San Francisco	USA	810,000gl	7,000-20,000	Helm, Ford & carter 2008
1970	Arroe & Irving	Chedabucto Bay	6,500t	>12,000	Höfer 1998
1969	Palva	Finland	150t	3,000	Höfer 1998
1967	Torrey Canyon	UK	129,857t	>30,000	Etkin 1999; Rogowska & Namieśnik 2010; Jernelöv 2010; Höfer 1998
1966	Seestern	UK	17,000t	5,000	Helm <i>et al.</i> 2008

t – tonnes ; gl – gallons ; m/b – million barrels

From the information shown in Table 1.1, it may be seen that such events may occur almost anywhere on Earth and are very unpredictable in terms of their location, magnitude, types of contaminant and varieties of wildlife and ecosystems affected.

1.2 The impact of oil spills on the environment

It is estimated that half of the World's crude oil production is transported by sea with the other half being transported overland by pipelines and vehicles (Clark 1992). For example, in 2007, out of approximately 72,000 ocean-going vessels in service, approximately 11,000 were oil tankers (Rogowska and Namieśnik, 2010). From 1974 to 2008, of the 4,369 oil spill events, 7% were classified as large spills (>700 t), 18% were medium spills (7-700 t) and 75% were small spills (< 7 t) (ITOPF 2009). Quite apart from the occasional accidents that result in the rupture of a tanker's hull, these vessels, and other types of sea-going vessels, also discharge oil into the environment during their normal operation. For example, oil tankers have to fill empty compartments with seawater (ballast) when their cargo is unloaded. These compartments may have between 800 t to 200,000 t residual oil in such compartments that contaminate the ballast - that is subsequently discharged to the sea (Clark 1992).

Spillage can also emanate directly from drilling on-land or off-shore. Again, apart from accidents, normal operations can also release significant amounts of pollution into the

environment. For example, oil originating off-shore contains water referred to as ‘production water’, which needs to be extracted/separated before it is transported to a refinery. This results in some discharge to the sea that is usually less than 40 ppm (Clark 1992). Also, drilling muds (which sometimes contain oil) are pumped back into the well to prevent catastrophic blowouts (Clark 1992). In addition, many oil refineries, that are usually located in coastal areas, still use old-fashioned refining processes such as stream-cracking. Such processes may also discharge oil contaminated water to nearby waterways with levels of up to 100 ppm. More modern facilities, with more advanced processes, may reduce the level of oil in their waste streams to around 25 ppm (Clark 1992).

Accidental oil spills can occur due to operational errors, structural failures, human errors and negligence, terrorism or vandalism, earthquakes and weather related events (Fingas 2010). Around 30 to 50% of anthropogenic oil spills are caused by human error, either directly or indirectly, and 20 to 40% are thought to be caused by equipment failure or malfunction (Fingas 2010). It is estimated that human activities contribute 53% to the total of oil contamination entering the sea annually (NRC 2003), with 47% being caused by natural seepage (IPIECA, 2005). It has been estimated that seepage is between 200,000 t to 2,000,000 t per year (Kvenvolden and Cooper, 2003). Accidents at off-shore oil wells, in particular, are often devastating with an enormous release of contamination. One of the more notorious events of this kind was the Deep-Water Horizon incident in the Gulf of Mexico in April, 2010 (Jevenelöv 2010). This event has been described as the worst environmental disaster in American history with thousands of birds being contaminated or killed by the end of June 2010 (Jevenelöv 2010).

Some of the more notorious oil spill accidents of recent times that involve tankers include the Exxon Valdez disaster where 11.2 million gallons of crude oil affected 1,750 km of Alaskan shoreline (Tumeo *et al.* 1994) and cost more than 300,000 seabird lives (Höfer 1998). The Prestige oil spill that occurred in November 2002 is yet another example that contaminated 1,900 km of shoreline in Spain and France resulting in 4,000 dead birds with 40,000 birds affected. It is estimated that between 80,000 to 150,000 seabirds died during the Erica oil spill in the Bay of Biscay (Peterson *et al.* 2003; Cadiou *et al.* 2004). More recently, the grounding and break-up of the bulk carrier MS Oliva in Tristan da Cunha on the 14th March 2011, which was carrying 1,400 t of fuel oil, 1,500 t of heavy crude oil and 65,266 t of soybeans, brought a huge environmental disaster to the Rockhopper penguin (*Eudyptes*

crestatus moseleyi) population, contaminating around 20,000 birds (Oil Spill Intelligence Report 2011).

As alluded to previously, the worldwide production and consumption of oil is likely to increase over the next 50 - 100 years (Fingas 2011). This increases the risk of oil spill events with further adverse consequences for living creatures and the environment (Dils 2011). Such events cause a wide variety of rapid, short-term (acute) and long-lasting (chronic) impacts on coastal and marine habitats. Oil spills may also cause irreversible damage to flora and fauna out at sea and even on the sea bed itself (Rogowska and Namieśnik 2010).

Crude oil contains a large number of different organic compounds that originate from naturally occurring organic matter that has been chemically transformed under various geological conditions for long periods of time (Wang *et al.* 2011). Thus different oil deposits may vary greatly in their composition and the toxicity as well as the polluting profile of an oil spill can depend to some extent on the actual chemical characteristics of the oil. The location of the spill is also an important factor since the prevailing weather can also affect the characteristics of the event. Thus the impact of an oil spill depends on the physical and chemical characteristics of the oil itself and its interaction with the immediate environment. When oil is released, it also undergoes a range of complex processes such as weathering, spreading, sinking, emulsification, dispersion, evaporation, photo-oxidation, microbial degradation and interaction with sediment (Wang *et al.* 2011; Al-Majed *et al.* 2012).

The impact of oil spills on shoreline may be exacerbated by temperature, wind, currents and waves, and may affect many diverse areas, including sensitive ecosystems and wildlife populations (Pereira and Mudge, 2004). Some effects may be quite subtle, but equally devastating. For example, fish eggs and larvae that are in surface water are particularly sensitive to toxins and are highly likely to be affected (Clark 1992).

Animals that are most visibly affected by oil spills include birds, marine mammals, whales and smaller marine organisms. Oil results in immediate external harm to birds and mammals, including hypothermia, by disrupting their feather and fur microstructure that is responsible for maintaining water repellency and maintaining heat insulation (Rogowska and Namieśnik, 2010; EPA 1999). It also affects the bird's ability to fly or float since the damaged feathers lose their capacity to trap air. The toxicity of the contaminant(s) is also a major problem and

can lead to conditions such as pneumonia and impaired fertility (Welte and Frink, 1991; Camphuysen and Hubeck, 2001; Rogowska and Namieśnik, 2010). Some petroleum hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), are also toxic to humans (Clark 1992). Humans are also adversely affected with respect to disruptions to their livelihoods, and by the impact to coastal industries such as tourism and fisheries (NOAA 2007).

The weathering of spilled oil is a particular problem with respect to environmental remediation and wildlife rehabilitation (Leighton 2003; Dao *et al.* 2006). This process usually results in a more viscous sticky substance that presents significant cleaning challenges, such as increased costs or the need for specialized conditioning agents (USEPA 2004). Sometimes an inappropriate cleaning strategy may result in even more environmental damage (Harris 1995). Occasionally, *in-situ* burning is used as a technique to reduce the immediate hazard of a thick oil slick on the surface of water. This is carried out before significant evaporation or dispersion has occurred. (Al-Majed *et al.* 2012).

1.3 Environmental remediation and wildlife rehabilitation

Humans must attempt to ameliorate the enormous damage caused to marine and coastal environments by oil spills (Ventikos *et al.* 2004). Clean-ups may be categorised as marine and/or shore-line operations (Tsocalist *et al.* 1994). Such operations are invariably challenging and expensive. For example, the Exxon Valdez disaster incurred costs of more than US\$630 million to ‘clean’ approximately 10.8 million gallons of released oil. The Deepwater horizon spill, involving more than 200 million gallons of released oil, incurred costs estimated in the tens of billions of dollars with an estimated social cost of between US\$60 to 100 billion (Taylor *et al.* 1997; Cohen *et al.* 2010). In general, oil contaminated shoreline is cleaned by ‘brute force’ techniques such as washing with high-pressure water or chemical spray and removal of oiled sediments (Leacock 2005; Canha *et al.* 2006). Such methods can result in additional environmental damage. More information on such methods for the remediation of oil spills are described in detail elsewhere (Dao 2007).

Part of the response to an oil spill involves the cleansing and rehabilitation of (usually) large numbers of contaminated animals, which are generally birds (Al-Majed *et al.* 2012) but

which may also include mammals (Jessup *et al.* 2012). When human intervention is possible, such events are often in remote areas that are difficult to access, resulting in a significant time lag between oiling and capture/treatment. Furthermore, rehabilitation facilities and equipment are often far away or have to be set up from the beginning at the nearest possible location. Even when the logistics are relatively favourable, large numbers of oil-contaminated birds may remain in holding bays for long periods of time awaiting treatment, Figure 1.2.



Figure 1.2 Oiled African penguins in a holding bay; June 23, 2000, Treasure oil spill, Cape Town, South Africa. Photo by Tony Van Dalsen.

Although traditional techniques for the treatment of oiled wildlife, based on detergent cleansing, have been highly refined with many successful outcomes (Bryndza *et al.* 1991; Bassères *et al.* 1994; Clark *et al.* 1997; Parsons and Underhill, 2005; Tegtmeier and Miller, 2007) such methods remain very labour intensive and require cumbersome and expensive equipment and facilities (Walte and Frink, 1991; Lamy *et al.* 2001). Such methods are also extremely stressful to the affected animal. With a view to optimising the survival, subsequent health and reproductive success of released animals, there is scope for the introduction of new and/or complementary methods and technologies for wildlife rescue and rehabilitation that could offer significant advantages over traditional methods.

One such alternative approach, that offers the possibility of significant improvements in efficiency and outcomes, involves the application of Magnetic Particle Technology (MPT) to the problem of contaminant removal, both from wildlife as well as from environmental domains such as rocky foreshore (Orbell *et al.* 1999, 2004, 2007; Ngeh 2001, Dao 2007).

This approach involves the application of contaminant-sequestering magnetic particles to an affected animal or surface, followed by subsequent magnetic harvesting, to simultaneously remove both contaminant and cleansing agent. This is essentially a dry cleansing process and may be referred to as “magnetic cleansing”. The principle is conceptually very simple and is represented schematically in Figure 3.

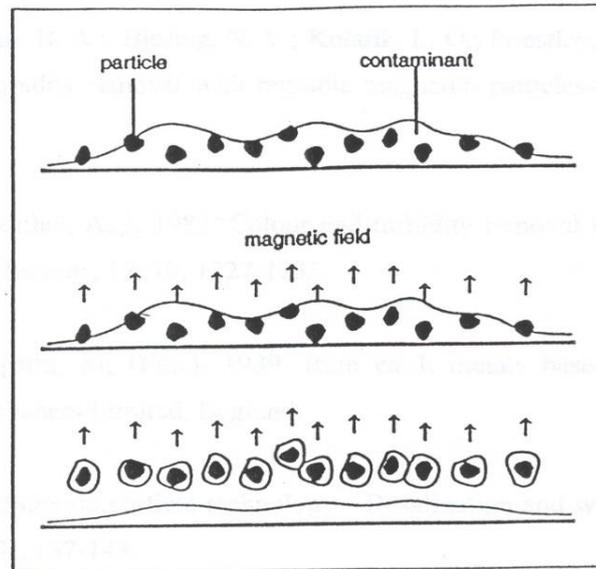


Figure 1.3 A schematic representation of the use of magnetic particles to remove a contaminant from a substrate – Ngeh 2001.

There are a number of potential advantages to this (magnetic cleansing) approach. For example, the worker has full control over the disposal of the contaminant, and magnetic cleansing is relatively benign compared to traditional detergent-based techniques for wildlife remediation, and compared to the range of relatively aggressive methods for the removal of oil from domains such as rocky foreshore (Orbell *et al.* 2007). In the case of its application to wildlife remediation, magnetic cleansing also offers the possibility of removing the bulk of the contaminant upon first encounter since it lends itself to portability. This is not possible with traditional detergent-based techniques due to the size and the nature of the equipment required. This could also offer significant survival advantages, especially when large numbers are involved or the contaminant contains toxic/corrosive components that can be ingested, inhaled or absorbed through the skin. If appropriately employed, this method could also significantly reduce the stress to the animal, since less handling is expected to be required. Improved portability and precision of application is also an important consideration for the remediation of ecologically sensitive terrain such as rocky foreshore.

In the context of the above discussion, the application of MPT to environmental remediation (Orbell *et al.* 1997) has been under investigation by researchers at Victoria University and Phillip Island Nature Park Research Centre (PINP-RC) for more than a decade. Since a seminal publication in 1999 (Orbell *et al.* 1999), demonstrating the effectiveness of finely divided iron powder in the removal (*via* magnetic harvesting) of up to 97% of a range of oil contamination from feathers, various proof-of-principle investigations by the VU/PINP-RC team have been published in the peer-reviewed literature (Orbell *et al.* 2004, 2005, 2006, 2007). An investigation into the particle characteristics that influence the efficiency of contaminant removal has established that 100% removal of a range of contaminants can be achieved (Orbell *et al.* 2006). Utilizing such optimised particles, the problem of magnetically removing weathered/tarry contamination has also been successfully addressed (Orbell *et al.* 2005, 2006) and an investigation into the role of pre-conditioners (or pre-treatment agents, PTAs) in facilitating more problematic oil removal has been undertaken (Orbell *et al.* 2006). More recently, the effectiveness of MPT in the removal of oil contamination from rock surfaces has also been demonstrated by the VU research group (Orbell *et al.* 2007).

Environmental remediators often use PTAs to enhance the removal of contamination (usually oil) from a variety of matrices and, in this regard, various substances and formulations of substances have been trialled by groups worldwide (Berkner *et al.* 1977; Randall *et al.* 1980; Bryndza *et al.* 1991; Walraven 1992, 2004; OWCN, 1999, 2003; Hills 1999, USFWS 2002; Gregory 2006; Dao *et al.* 2006, Massey *et al.* 2006; Dao 2007). Unfortunately, it has been impossible to adequately quantify their relative effectiveness with respect to detergent-based cleansing, since everything is washed away in the process. Consequently, the relative effectiveness of such candidates is currently only qualitative and pre-conditioners considered to be superior for particular applications tend to be communicated anecdotally, based on subjective assessments. Therefore, there is a need for a method whereby the effectiveness of existing PTAs (and potential candidates) may be quantified with respect to their relative abilities to enhance the removal of different contaminants from plumage, fur, or from substrates such as rock surfaces (either by traditional detergent-based techniques or by other methods such as magnetic cleansing).

In relation to this problem, our program to investigate the application of MPT to environmental remediation has led to the ‘spin off’ development of such a method: namely a

gravimetric methodology based on MPT that can be employed to quantitatively assay for the relative effectiveness of various pre-conditioning agents. Preliminary investigations have demonstrated that there is considerable scope for the improvement of existing pre-conditioners and for the tailoring of these agents to specific applications. The invention of this assay represents the first time that it has been possible to quantify the relative ability of pre-conditioning agents to enhance the removal of a given substance from a given substrate (Orbell *et al.* 2012). This method and its further development are described in more detail in Chapter 4.

1.4 The “quick clean” concept

Upon first encountering a contaminated animal, some stabilization measures are essential (Frink *et al.* 1986; Massey *et al.* 2006). These usually involve measures such as rehydration and/or the administration of antibiotics (Lamy *et al.* 2001). Such treatment contributes to the survival chances of an animal in the longer term thereby helping to ensure subsequent health and reproductive success post release (Welte and Frink, 1991; Massey *et al.* 2006; Barros *et al.* 2014). As an adjunct to initial stabilization, the development of portable equipment, based on MPT that could enable a ‘quick clean’ to be provided to the animal upon first encounter is highly desirable. This could be particularly advantageous when the contaminant contains toxic and/or corrosive components that can be ingested, inhaled or absorbed through the skin and/or where there is a delay in transporting the victim to a treatment centre. The method could also be useful as part of the stabilization protocol when a large number of affected animals are awaiting treatment within a holding bay of a rehabilitation facility, Figure 1.2. The successful implementation of this treatment would be reflected in a further improvement in initial and post-release survival rates and reproductive success. The exploitation of the magnetic cleansing method to develop and trial prototype quick clean equipment (the “kit”) is the subject of Chapter 2. Thus the development and refinement of the various components of such a portable kit have been explored in this project and include the development of a portable, hand-held, magnetic device, the “magnetic harvester”, that can safely and efficiently strip the oil laden magnetic particles from the animal and which can allow the waste to be disposed of in a controlled way. The design, development and testing of this device and the other various kit components is described in more detail in Chapter 2. Concomitant with the above work is the further refinement of the oil-sequestering magnetic particles themselves.

Thus Chapters 4 and 5 describe various approaches that relate to understanding and improving the efficacy of the particles themselves with respect to their initial pick-up and/or the final removal. To this end, the pick-up phenomenon itself has been mathematically modelled and the effect on oil removal of various parameters such as particle porosity, particle size and particle coating (with hydrophobic or super hydrophobic surfaces) has been explored (Ngeh 2002).

1.5 Objectives of the research

The overall objective of this thesis is reflected in its title: *“The Rational Development of Improved Methods for the Removal of Oil Contamination from Wildlife and Rocky Foreshore utilizing Magnetic Particle Technology”*.

The initial aim was based on the recommendations of a 2007 Australian Maritime Safety Authority (AMSA)/Phillip Island Nature Park (PINP) funded project entitled: “An Investigation into the Feasibility of Applying Magnetic Particle Technology to the Cleansing of Oiled Wildlife in the Field” (AMSA 2007). This report recommended the further development of magnetic particle technology for the cleansing of oiled wildlife primarily as part of an initial stabilization protocol (i.e. the provision of a quick clean); given that this is a role that cannot be filled by conventional detergent-based cleansing methods. Thus it was suggested that there is an imperative to advance the development of the appropriate technology and enhance the techniques for the provision of a ‘quick clean’ to contaminated wildlife in the field, utilizing MPT. This involves an investigation of the factors that contribute to an enhanced initial (as well as final) removal of contaminant, the further development of the magnetic particles themselves, the development of the most appropriate magnetic harvesting device, laboratory testing of equipment on whole bird models and logistical considerations. Thus Chapter 2 of this thesis describes the development of the “backpack” concept in consultation with industrial design staff at Monash University. This work has been carried out concomitant with the design and testing of an optimum magnetic harvesting device (subsequently dubbed the magnetic ‘wand’). Testing of the various components of the kit were carried out in a laboratory setting and a prototype kit has been assembled which is now located at the Phillip Island animal hospital in anticipation of being able to trial this equipment in the event of a contamination incident. This chapter also

describes a detailed study of the particles themselves in terms of their size and surface characteristics and how these relate to the initial (and final) removals. Thus the specific aims here were to refine the magnetic harvesting device, to optimize the efficacy of the magnetic particles in relation to the initial removal and to suggest an appropriate kit design for implementation in the field.

Another aim of this project was to advance the mathematical modeling of the pick-up phenomenon in order to provide more insight into its physical basis and to develop improved parameters for assessing the efficacy of removal. This work is described in detail in Chapter 3. Thus the specific aim here was to develop this mathematical model and to bench-mark it to contaminants of varying viscosities.

A major objective involved the further development of a previously devised assay, based on MPT, for the relative quantification of pre-treatment agent (PTA) efficacy. An important consideration for this work was the extent to which the relative PTA efficacies, as determined by the MPT assay, carry over with fidelity to PTA-assisted detergent based methods. It is essential to establish that this is the case so that PTA recommendations based on the MPT assay are transferrable to the wildlife rehabilitation community, who overwhelmingly employ detergent-based methods. Experiments were designed and conducted in order to test this hypothesis. This work is described in detail in Chapter 4. This chapter tests and refines the assay against a wide range of PTAs and blended PTAs and establishes sample recommendations based on the application of a wide range of potential PTAs to the assisted removal of a viscous oil contaminant from duck and penguin feathers. Thus the specific aim here was to validate the PTA assay to the extent where recommendations can be made to wildlife rehabilitators worldwide.

Chapter 5 extends the above principles to the removal of various contaminants from other substrates such as fur and rock. Thus the removal of oil contamination from two different types of mammalian fur has been demonstrated and the effect of different fur microstructures in relation to the penetration of the contaminant through the fur and onto the skin has been elucidated. These results have been benchmarked against removal from feathers. The effect of PTA application at various treatment stages has also been examined and compared to the outcomes for feather substrates. In regards to removal from rock surfaces, the problem of oil penetration into porous rock has been examined in relation to the use of various PTAs to

facilitate removal. Thus the specific aim here was to extend this technology to other substrates such as fur and rock and to demonstrate its potential for such applications.

1.6 References

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Chapter 2: The development of magnetic particle technology (MPT) equipment and methods for providing a “quick clean” to oil contaminated wildlife

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2.8.6 Surface features associated with physically coating the MH300.29 particles with Rhodasil[®]/SiO₂-nanoparticles

2.9 Relating the nature of the different SEM surfaces to the various removal isotherms

2.9.1 A comparison between the surface features and the JCO removal isotherms for the untreated MH300.29 particles, the TMS-functionalized, Oleophobol[®]-coated, Scotchgard[®]-coated MH300.29 and Rhodasil[®]/SiO₂-coated particles

2.9.2 A comparison between the JCO removal isotherms for untreated A100S particles, TMS-functionalized and Oleophobol[®]-coated A100S particles

2.9.3 A comparison between the JCO removal isotherms for Oleophobol[®]-coated and Scotchgard[®]-coated A40S particles

2.9.4 The effect of increasing particle size whilst maintaining the same coating

2.10 Conclusions

2.11 References

Chapter 2: The development of magnetic particle technology (MPT) equipment and methods for providing a “quick clean” to oil contaminated wildlife

2.1 Introduction

Acute exposure of wildlife to oil contamination continues to be a matter of worldwide concern - as evidenced by the recent grounding and break-up of the MS Olivia in Tristan da Cunha on 14th March 2011. Such events invariably result in the oiling of large number of animals, especially birds, often threatening endangered species such as the Northern Rock Hopper Penguin colonies that habitat the islands of Tristan Da Cunha (Oil Spill Intelligence Report 2011), Figure 2.1.



Figure 2.1 Oil contaminated Northern Rock Hopper Penguins in Tristan Da Cunha, from the recent grounding and break-up of the MS Olivia in Tristan da Cunha on 14th March 2011. Photo by: Kent Koberseen/Getty.

Such events are usually in remote areas that are difficult to access, resulting in a significant time lag between oiling and capture/treatment. Rehabilitation facilities and equipment are often far away or have to be set up from scratch at the nearest possible location. Even when the logistics are relatively favourable, large numbers of oiled birds may remain in holding bays awaiting treatment for long periods of time.

Although traditional techniques for the treatment of oiled wildlife, based on detergent cleansing, have been highly refined with many successful outcomes, such methods remain very labour intensive and require cumbersome and expensive equipment and facilities (Walte and Frink 1991; Bryndza *et al.* 1991; Bassères *et al.* 1994; Clark *et al.* 1997; Tegtmeier and Miller 2007; Lamy *et al.* 2001). With a view to optimizing the survival, subsequent health and re-productive success of released animals, there is scope for the introduction of new and complementary methods and technologies for wildlife rescue and rehabilitation that may offer significant advantages over traditional methods.

In this regard, for more than a decade, scientists at Victoria University and the Phillip Island Nature Parks have been engaged in a collaborative program aimed at advancing the science and technology involved in the rescue and rehabilitation of oiled wildlife (Orbell *et al.* 1997, 1999, 2004, 2005, 2006, 2007(4) & 2009; Ngeh 2001; Dao *et al.* 2006(3), 2007(2); Dao 2007). At the forefront of this research is the development of the so-called “magnetic cleansing” approach. This innovative development involves the use of oil sequestering magnetic particles for the removal of contaminants from plumage (Orbell *et al.* 1999 & 2007). This is effectively a benign dry cleaning process - with demonstrable minimal feather damage compared to detergent based cleansing.

2.2 The concept of a “quick clean” based on MPT

Being inherently portable, the application of magnetic particle technology (MPT) to the removal of oil contamination from plumage and fur also offers a number of advantages over conventional detergent-based methods, including the possibility of providing a “quick clean” to an animal upon first encounter (Ngeh *et al.* 2012). This could be particularly advantageous when the contaminant is toxic and/or corrosive, or where there is a delay in transporting the victim to a treatment facility. The method could also be useful as part of a stabilization protocol when large numbers of affected animals are awaiting treatment. This concept requires the development of a dedicated portable kit that would enable the most efficient manual transportation of the technology to the affected animal(s) by a trained rehabilitator(s). The basic elements of such a kit that has been under development as part of this project are shown in Figure 2.2.

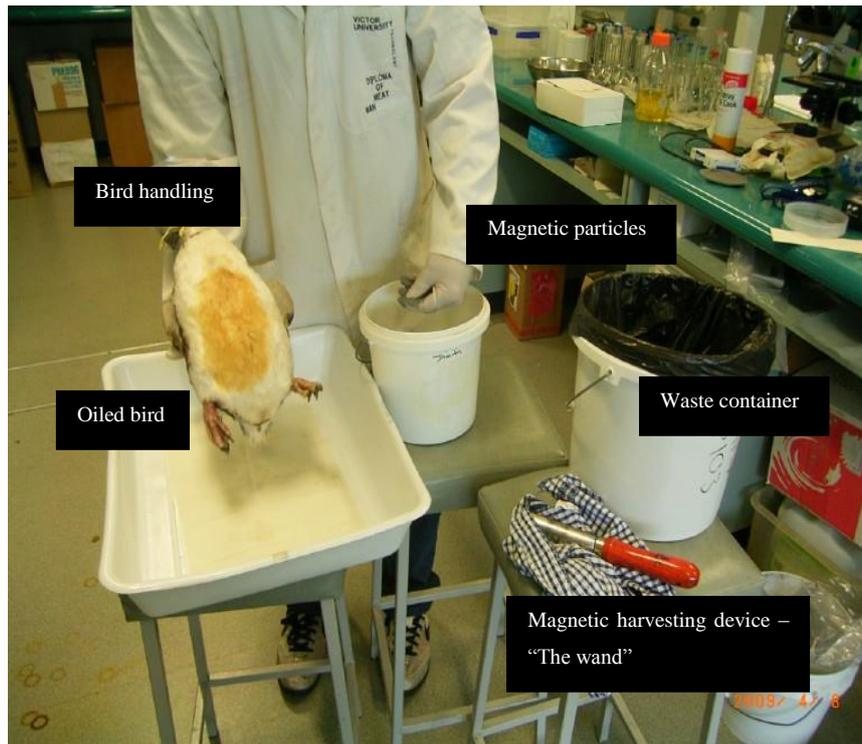


Figure 2.2 The basic elements of a “Quick Clean” kit based on MPT. Other items, such as a portable corral or a ‘bird cradle’ might also be included.

In order to advance this concept, a collaborative venture between the College of Engineering & Science, Victoria University, the Phillip Island Nature Parks Research Centre, and the Department of Design, Monash University², was undertaken in conjunction with this research project for the purpose of bringing industrial design expertise to bear on designing a prototype field kit for providing a “quick clean” to contaminated wildlife in the field, Figure 2.3. The actual construction and testing of such a prototype however is beyond the scope of this thesis.

The design of such an integrated portable kit must take into consideration such factors as the weight of the various components, including the weight of particles required, amount of waste produced, storage of particles and waste, ergonomic factors, the numbers of persons required in the quick clean team (e.g. one person would be required to handle the animal whilst the other carries out the operation) and their specific roles etc. Other considerations

²A collaborative venture between *the School of Engineering & Science, Victoria University* (Kasup Munaweera, John Orbell, Stephen Bigger and Lawrence Ngeh), *the Phillip Island Nature Park Research Centre* (Peter Dann) and *the Department of Design, Monash University* (Arthur De Bono, Selby Coxon and Alex Matthews) was initiated for the purpose of designing and building such a prototype field kit.

include the need for ancillary items and equipment such as appropriate clothing etc. Any such prototype would then have to be tested and evaluated both in the lab and in the field. Planning for such further development is underway within the group.

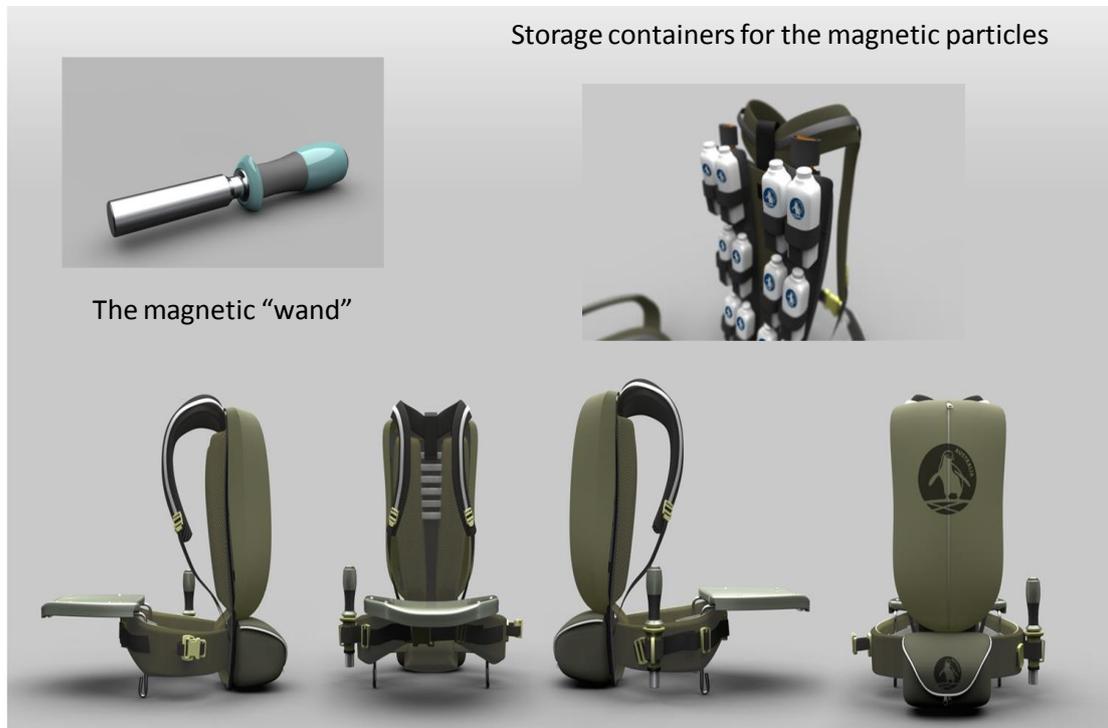


Figure 2.3 The “backpack” concept for a portable “Quick Clean” Kit based on MPT, see Footnote 1.

A “quick clean” is envisaged to involve one or two treatments - taking a matter of minutes. Characteristic oil removal isotherms, shown schematically in Figure 2.4, demonstrate how variations in one or more factors such as oil type, feather type, percentage coverage, use of pre-treatment agents, magnetic particle characteristics and temperature, may affect the efficiency of the *initial* removal after one or two treatments (i.e. after a quick clean). Although factors such as the oil type, the feather (substrate) type and the percentage coverage cannot be controlled in a field situation; other factors such as choice of pre-treatment agent, the particle temperature upon application, or a judicious modification of the magnetic particles themselves (e.g. average particle size/particle size distribution and/or surface modification), or particle and/or pre-treatment agent temperature, can influence the initial removal.

Although magnetic cleansing is conceptually simple, as described in Chapter 1, Figure 1.3, it is evident that the refinement of this technology for application in the field presents considerable challenges; some of which have been addressed as part of this thesis.

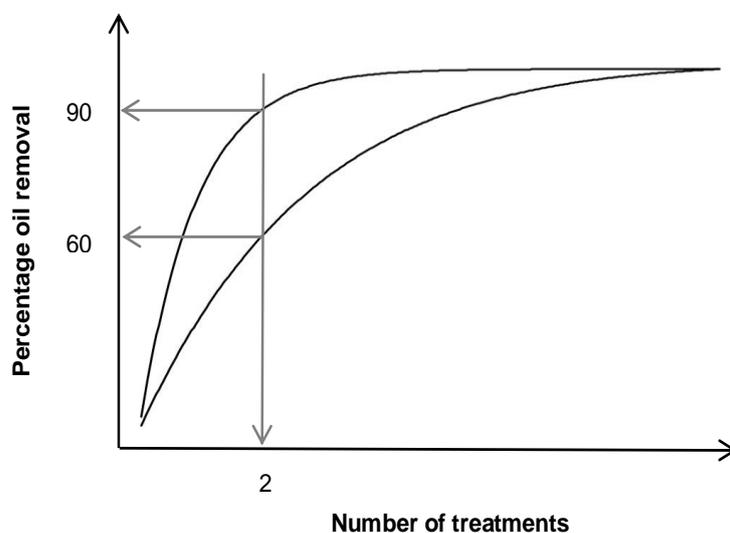


Figure 2.4 Different conditions, as described above, can lead to different profiles for the oil removal isotherms resulting in different initial removal efficiencies (e.g. at 1 or 2 treatments). This is an important consideration for the optimization of the “quick clean” concept. For example, introducing a different particle type for a given contaminant might result in an initial pickup after 2 treatments of 90% as opposed to 60%, even though the final removals might be comparable. These two types of pick-up are represented schematically by the two isotherms in the above graph.

These challenges include the optimization of the particles themselves with respect to factors such as size distribution, surface properties and possible surface coatings, the development of a magnetic harvesting device in terms of its design for a specific application, the optimum magnetic field strength of such a device, the ease of cleaning, the choice and use of pre-treatment agents, waste disposal issues and the integration of the various components into a portable kit, as described above – which requires overall design considerations (involving industrial design expertise), laboratory and field testing, logistics and costs, training and consideration of animal handling as well as integration into existing (detergent-based) protocols³.

Although the actual construction of a fully refined, industrially designed prototype kit, based on the components that have been developed to date, is beyond the scope of this study, a

³ This also includes the mathematical modelling of the pick-up phenomenon (as described in Chapter 3) as a means of better understanding the phenomenon and defining pick-up efficacy.

“non-backpack” prototype kit has been constructed from commercially available materials, depicted in Figures 2.5 (a) to (c). This has been located at the Animal Hospital at the Phillip Island Nature Park. This equipment will enable tests to be performed should a local oil spill result in contaminated wildlife becoming available – subject to the appropriate ethical procedures. This kit comprises two main storage sections, Figures 2.5 (b) & (c). The lower compartment (c) has the wheels and stores the iron powder, waste disposal bags and gloves. The upper section (b), also consisting of two parts, stores the magnetic harvester (e.g. the ‘wand’), paper towels and a weighing scale.



Figure 2.5 (a) Prototype “non-backpack” portable Oiled Wildlife Magnetic Cleansing Kit



Figure 2.5 (b) Upper compartment



Figure 2.5 (c) Lower compartment

2.3 Optimizing the various components of the “quick clean kit”

Part of this research project has involved the optimization of the various individual components that are required for incorporation into an eventual, industrially-designed, “quick clean” kit, as described previously, Figure 2.3. This includes work directed toward producing a customized magnetic harvester that is the most suitable for this application. In fact, after four design iterations, this has resulted in the so-called magnetic “wand”, as shown in Figures 2.2 & 2.3 - the development of which is described on page 38. Also of importance is the improvement of the efficacy of the magnetic particles themselves so as to optimize their *initial* removal in particular, see Figure 2.4. This latter work on particle optimization is also described within this Chapter.

2.3.1 Optimization of the magnetic harvester for a “quick clean”

For the application of a quick clean in the field there are a number of requirements for such a device. For example, optimum magnetic field strength, ease of portability, ease of handling, production cost and ease of cleaning the contamination from plumage. The process of refining the magnetic harvester device for this purpose is described as follows.

2.3.1.1 The basic “magnetic tester”

Nominated as the “1st generation” magnetic harvester in the development of the quick clean kit, a commercially available (Alpha Magnetics Pty. Ltd., Boronia, Victoria, Australia) “magnetic tester”, Figure 2.6, for which the magnetic field is turned on and off by a mechanical plunger, was trialled. This device contains a moveable rare earth magnet and requires two hands to operate. After testing on oiled bird carcasses, this device was considered to be slightly underpowered in terms of its magnetic field strength of ~ 3022 Gauss⁴, Figure 2.7, with respect to its contaminant removal efficacy. Initial trials with this device also led to the conclusion that it is too unwieldy for field application. However, this remains the preferred device for laboratory-based experiments.

⁴The DC Gauss meter Model 1-ST employed was manufactured by Alpha Lab Inc, U.S.A. (www.trifield.com) and purchased from Alpha Magnetics Pty. Ltd., 22/15/ Macquarie Place, Boronia, Vic. 3155, Australia, Tel +61 3 97298633.

2.3.1.2 A potential “2nd generation” device (powered by compressed air)

This device was designed to exploit the mechanical on/off mechanism of the magnetic tester described above, with the possible incorporation of a more powerful rare earth magnet. However, the focus here was to convert the device into one-handed operation via a powered on/off mechanism – in this case, powered by compressed air under the control of a trigger, Figure 2.8.



Figure 2.7 The “magnetic tester”



Figure 2.6 Measuring the magnetic field strength of the magnetic tester



Figure 2.8 Compressed air magnetic tester

Further investigation and experimentation has led to the conclusion that, whilst the above device could be suitable for use in a lab or within a treatment facility, the necessity of transporting available compressors or compressed air cylinders would make the whole kit too heavy and bulky for application in the field, especially where agility and flexibility of movement would almost certainly be required.

2.3.1.3 A potential “3rd generation” device (electromagnetic harvester)

A one-handed solenoid-based magnetic harvester was constructed to avoid the difficulties of the 2nd generation magnetic harvester, Figure 2.9. This was designed to be much more compact and portable, incorporating a rechargeable portable battery pack.



Figure 2.9 Electromagnetic harvester

Here, problems were identified relating to the required strength of the magnetic field, battery life and the weight of the battery pack. From experimental testing, it was estimated that a magnetic field strength well in excess of 3,000 Gauss (preferably in excess of 5,000 Gauss) is required for effective field applications. In this regard, for the solenoid-based device depicted above, the maximum magnetic field strength that can be achieved with a 12 volt power pack is 468 Gauss, Figure 2.10. It was found not to be possible to increase the voltage beyond this due to heating effects.



Figure 2.10 The maximum magnetic field strength achievable for the solenoid-based device.

2.3.1.4 The “4th generation” device – the “wand”

After consultation with Alpha Magnetics Victoria, Australia (the local supplier of all of our magnetic equipment) and, after a detailed consideration of the technology and their engineering capabilities, it was decided to order the construction of a magnetic cylinder of specific dimensions (100 mm in length; 25 mm diameter - and with 35 mm at the end of the tube being non-magnetic) that could generate a highly localized magnetic field of up to 10,000 Gauss. Furthermore, the tube could be adapted to fit a simple screw-on handle and to have a non-magnetic region at one end so that harvested oil-laden magnetic particles could be simply wiped off into a waste container. The final constructed device is depicted in Figure 2.11 (a).



Figure 2.11 (a) The “wand”, magnetic harvester **(b)** measuring the magnetic flux density (Gauss) of the magnetic region of the wand’s cylinder, reading 10,576 Gauss.

The magnetic field strength is considerably more than what was previously available, at more than 10,000 Gauss, Figure 2.11 (b). For the wand, the magnetic field cannot be turned off, as with the other permanent magnet devices or the electromagnetic device.

As indicated above, utilizing the wand, a series of laboratory experiments on contaminated penguin carcasses, Figure 2.12, have demonstrated that oil laden magnetic powder can effectively be removed and the waste conveniently disposed of by running a cloth or paper towel along its length. It was found that the paper towel was more effective than a cloth and could be easily disposed of together with the waste, Figure 2.13. Note that, for the experiments depicted in Figure 2.12, the removal efficacy for both oil types after two treatments (a quick clean) exceeds 85%. These results suggested that the wand is the most suitable field device that meets the requirements of portability, utility and high field strength. A DVD demonstrating the magnetic removal of blue-dyed diesel oil from a duck feather and the subsequent removal of the contaminant-laden particles from the wand is provided in one of the DVD pockets of this thesis. In summary, the comparative features of the four devices described previously are given in Table 2.1.

Table 2.1 Comparative features of the harvesting devices investigated

Name of the devise	Advantages	Disadvantage
1 st generation device (The basic “Magnetic Tester”)	Can be turned on and off mechanically, can penetrate deep into plumage. Suitable for laboratory experiments and for removing oil from flat surfaces.	Requires two hands to operate.
2 nd generation device (Compressed air-powered magnetic tester)	One-handed, simple trigger operation.	Heavy and bulky, suitable for use in treatment facility only.
3 rd generation device (Electromagnetic harvester)	One-handed, simple trigger operation. Relatively compact and portable.	Low magnetic field strength, heavy battery pack required. Could be affected by salt water.
4 th generation device (“wand”)	High magnetic field strength. Highly portable and easily manipulated. Highly effective waste disposal. Considered most suitable for use on wildlife in the field.	Potential effect of magnetic field on bird – trials being conducted.

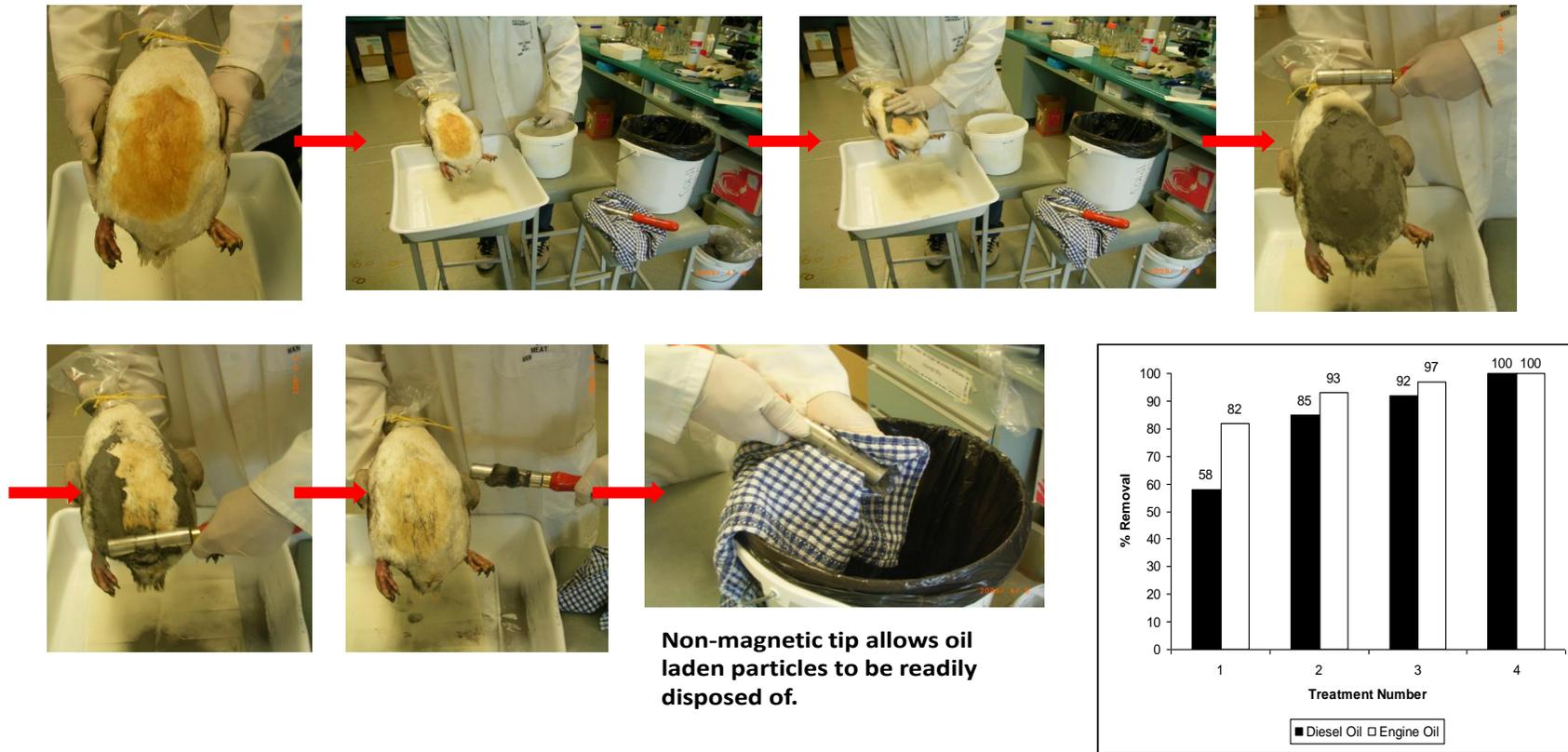


Figure 2.12 Laboratory trial of prototype quick clean equipment utilizing the ‘wand’ magnetic harvester to remove viscous engine oil (shown) and diesel oil from a Little Penguin (*Eudyptula minor*) carcasses.

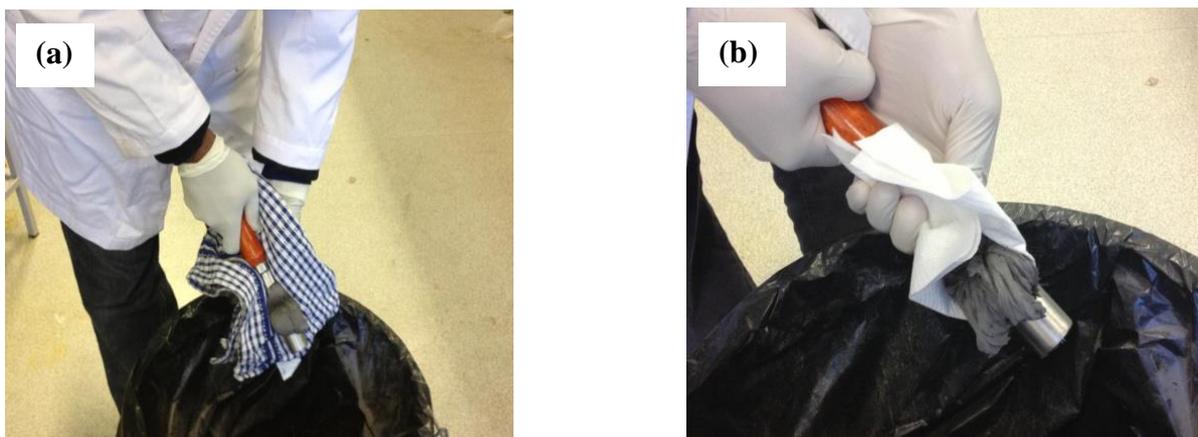


Figure 2.13 (a) Use of cloth to remove oil-laden particles from wand (b) Use of paper towel to remove oil-laden waste from wand.

2.4 The effect of particle heating on the removal of Jasmine Crude Oil from duck feather clusters

2.4.1 Temperature dependent isotherms

Materials used were Jasmine Crude Oil (JCO), Grade MH 300.29 iron powder and duck feather clusters. The experiment methodology for generating contaminant removal isotherms that is applied here is well established and is described in detail elsewhere in this thesis Section 2.6.2.2. The iron powder was heated to different temperatures levels (21°C , 32°C and 55°C) before being used to generate the isotherms shown in Figure 2.14.

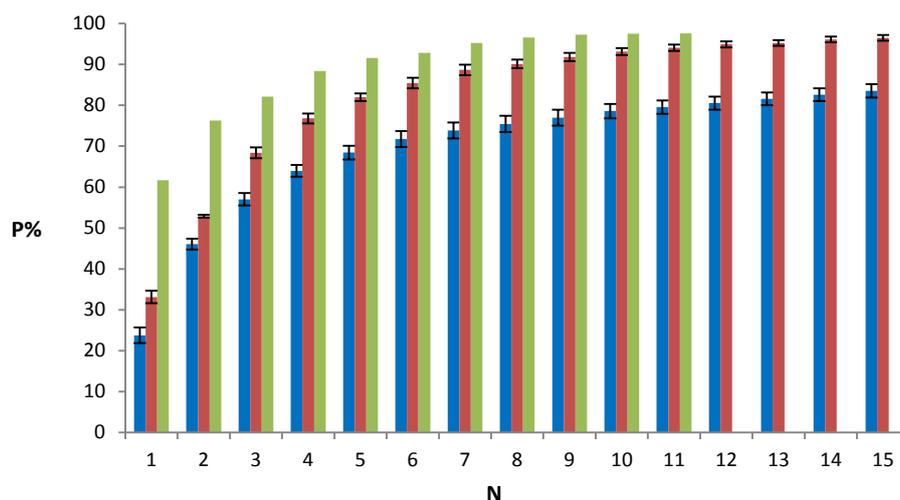


Figure 2.14 Comparison of JCO removal, P%, from duck feathers as a function of the number of treatments, N, using MH300.29 at 21°C (blue), 32°C (red) and 55°C (green). Error bars represent the SE for five replicates. The full data are provided in Appendix 2.1 (Table 1). Individual data profiles are presented in Appendix 2.1 (Table 2 and 3).

2.4.2 Commentary

From the data in Figure 2.14, and the derived critical parameters summarized in Table 2.2, it may be seen that the effect of pre-heating the particles had a dramatic impact on the initial and final removals. Work is in progress within the group to exploit this for practical applications.

Table 2.2 Initial (P% at N=1 and 2) and final (P_o%) removals of JCO from duck feathers with MH300.29 iron powder pre-heated to 21°C, 32°C and 55°C.

Temperature °C	P% at N=1	P% at N=2	P _o %
21	23%	47%	82%
32	32%	53%	94%
55	62%	77%	98%

2.5 Removal of oil blends using different iron powders

The removal of high viscosity JCO and a lower viscosity 4:1 v/v JCO:DO blend from duck breast-feather clusters were compared for two widely different average magnetic particle sizes in order to check the level of reproducibility (triplicates) of such blend experiments and the effect of widely different average particle sizes on different viscosities.

2.5.1 Materials and methods

Materials used are, Jasmine Crude Oil (JCO); viscosity, 682 cSt at 50°C; supplied by Leeder Consulting, Victoria, Australia. Diesel Oil (DO), 5.5 cSt at 40°C, was obtained from a local service station. For the purpose of this experiment the JCO and DO were blended 4:1 v/v. Iron powders were supplied by Höganäs AB, Sweden, and were described by the manufacturer as “spongy annealed superfine” (Grade MH 300.29, average particle size ~ 41µm) and “coarse atomised un-annealed” (Grade A40S, average particle size ~ 281µm). The feathers used in this study were the breast/contour feathers of the Mallard Duck (*Anas platyrhynchos*). The methodology applied in these experiments for the generation of the removal isotherms, Figure 2.15, is analogous to that described in Section 2.6.2.2.

2.5.2 Commentary

It may be seen from Figure 2.15 that there is a high level of reproducibility - such that statistical differences may be easily identified. Changing the viscosity is observed to have a more profound effect, especially with respect to initial removal, than changing the particle size. Specifically, lower viscosity and smaller average particle size favour a greater initial and final removal efficacy.

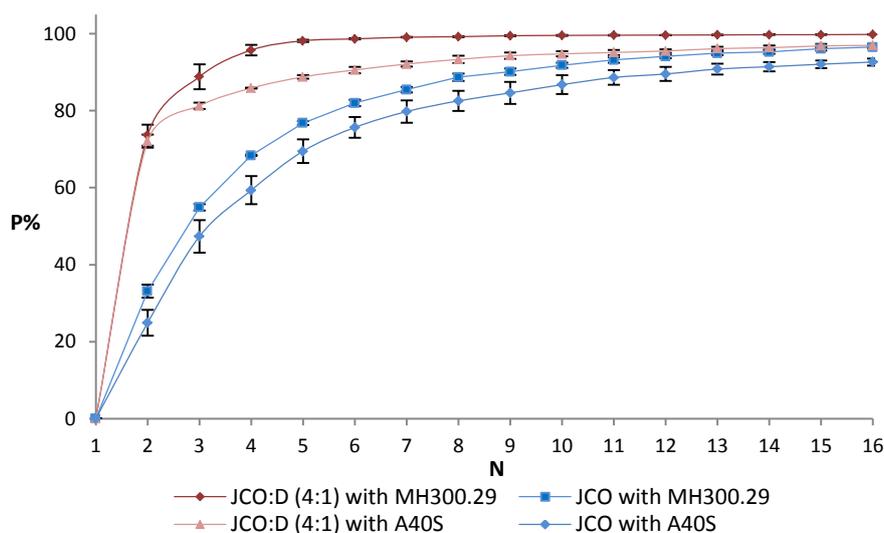


Figure 2.15 The removal, P%, of JCO and 4:1 blended JCO:DO from duck feather clusters as a function of the number of treatments, N; utilizing MH300.29 and A40S magnetic particles. All experiments were conducted at 22 C. Error bars represent the SE for triplicates. The full data sets are provided in Table 4 in Appendix 2.1 and the individual data profiles are provided in Tables 3, 5, 6 and 7 in Appendix 2.1.

2.6 Towards the optimization of magnetic particle grade with respect to a “quick clean”, in relation to the contaminants to Jasmine Crude Oil (JCO) and Diesel Oil (DO)

2.6.1 The effect of particle “grade” on initial removal

Iron powder is available in a wide range of grades that differ in particle size and particle size distributions, surface characteristics and porosities. Previous work within this group has demonstrated that such physical properties influence the efficacy of contaminant removal for a variety of oil types (Dao 2007). The focus of this previous work was on the *final* achievable removal, P₀%, and it was established that 100% removal (within experimental error) of Arab Medium Crude Oil (AMCO) from *feather clusters* is achievable with the judicious selection

of an appropriate grade of iron powder, namely MH300-29 (“superfine/spongy/annealed”)⁵. However, this work was prior to the development of the “quick clean” concept and no consideration was given to the effect of the grade type on the *initial* removal (P% at N=1 or 2).

An examination of the data from these previous experiments, specifically in relation to removals at N=1 or 2, and data from analogous experiments, conducted as part of this thesis, utilizing JCO and DO as the contaminants, Figures 2.16 and 2.17, shows that the *initial* removal is also affected by the grade of iron powder - and hence by the physical characteristics of the particles. Critical efficacy parameters for removal at N=1, N=2 as well as for the final removal are summarized in Table 2.3 and are also represented as comparative histograms in Figure 2.18.

2.6.2 Materials and methods

2.6.2.1 Materials

JCO, viscosity 682 cSt at 50°C, was supplied by Leeder Consulting, Victoria, Australia. DO, viscosity 5.5 cSt at 40°C was obtained from a local service station. Most iron powders were supplied by Höganäs AB, Sweden and the 5µm (average size) particles were sourced from the internet (Alibaba). The feathers used were the breast/contour feathers of the Mallard Duck (*Anas platyrhynchos*). The solidified JCO (at RT) was melted and retained in a small beaker (using a warm water bath) prior to contaminating the feathers for experimentation.

2.6.2.2 Method

For a given feather type, a number of individual feathers (usually, but not limited to, four or five) were tied together to form a cluster and then weighed, f_1 . The feather cluster was then completely immersed in the contaminant to achieve saturation. The cluster was removed and allowed to drain for 10 min prior to being re-weighed, f_2 , on a tared Petri dish. The residual quantity of contaminant, r , recorded after the cluster was removed from the dish. Hence, the

⁵ Note that 100% removal might not be feasible for actual plumage but these experiments demonstrated the important proof of principle that the grade of iron powder influences removal efficacy.

weight of the contaminant-laden feathers, f_3 , for further experimentation was given by the equation:

$$f_3 = f_2 - r \quad (2.1)$$

The contaminated feathers were then completely covered with iron powder in order for absorption and/or adsorption of the contaminant to occur. This takes only a few seconds. The contaminant-laden magnetic particles were then harvested from the feathers using a magnetic tester. The cleaned feather cluster was then weighted, f_4 . The percentage removal of the contaminant (This represents the first treatment, $N = 1$), $P\%$, was calculated using the equation:

$$P\% = [(f_3 - f_4)/(f_3 - f_1)] \times 100\% \quad (2.2)$$

The feather cluster was again completely covered with iron powder and the above magnetic harvesting procedure was repeated. The stripped feather cluster was weighed, and a $P\%$ value was calculated for $N = 2$. This procedure was repeated until a constant (optimal) value of $P\%$ was achieved (Ngeh 2001; Dao 2007).

2.6.3 Commentary

From Figures 2.16 to 2.17 and Table 2.3, it is evident that, across all the grades investigated, the removal at $N=1$ for AMCO (viscosity = 50.1 cSt at 22 °C) ranged from 70.97% (A40S) to 94.68% (MH300.29) and at $N=2$ from 83.11% (A40S) to 98.03% (MH300.29); the removal at $N=1$ for JCO ranged from 13.00% (M40) to 33.13% (MH300.29) and at $N=2$ from 26.18% (M40) to 52.89% (MH300.29); the removal at $N=1$ for DO ranged from 91.98% (A40S) to 98.94% (ASC300) and at $N=2$ from 95.31% (A40S) to 99.36% (ASC300).

These results demonstrate the profound effect that particle grade (and hence the particle size distribution and the surface characteristics) has on the initial removal of various oil types. Thus the preferred grade for initial removal at both $N=1$ and $N=2$ for both AMCO and JCO is MH300.29 and for DO the preferred grade for removal at $N=1$ and $N=2$ is ASC300.

These studies complete a comprehensive picture of the effect of particle grade on *initial removal* for light (DO), medium (AMCO) and heavy (JCO) contaminants. The data in Figures 2.16 to 2.18 indicate that the final removal is much less sensitive to particle grade for lower viscosity oil, but initial removal is grade sensitive for both high and low viscosities.

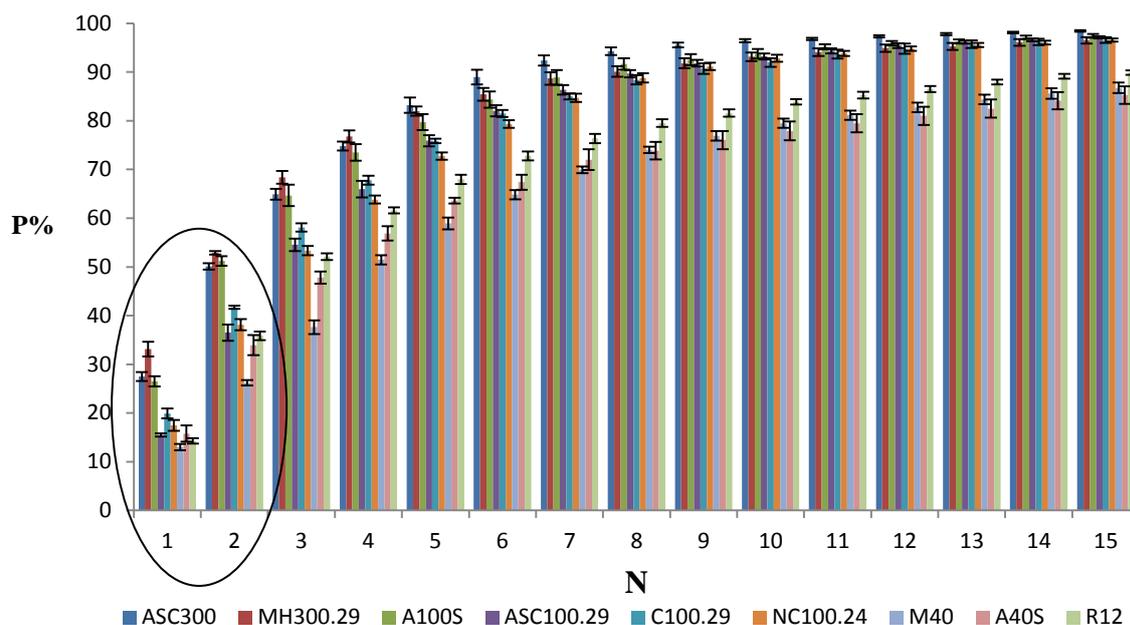


Figure 2.16 Jasmine Crude Oil (JCO) removal, P%, from duck feather clusters as a function of the number of treatments, N, using different grades of iron powder, at 22°C. Error bars represent the SE for five replicates. Note: the N=1 and 2 removals are circled. The full data sets are provided in Table 8 and individual profiles for each iron powder are presented in Tables 3, 9 to 16 in Appendix 2.1.

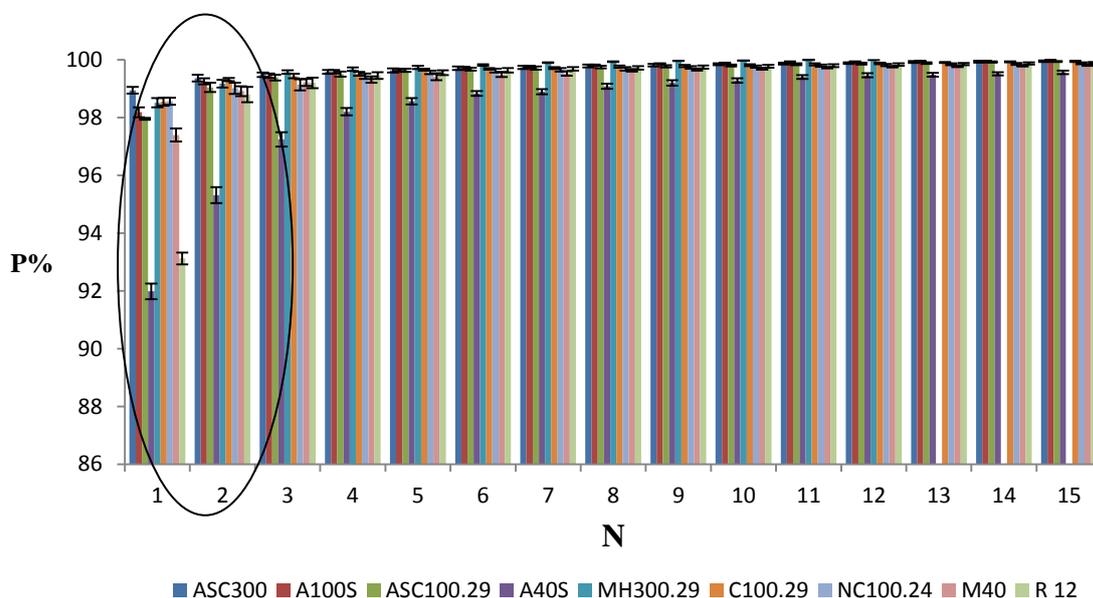


Figure 2.17 Diesel Oil (DO) removal, P%, from duck feather clusters as a function of the number of treatments, N, using different grades of iron powder, at 22°C. Error bars represent the SE for five replicates. Note: the N=1 and 2 removals are circled. The full data sets are provided in Table 17 and individual profiles for each iron powder are presented in Tables 18 to 26 in Appendix 2.1.

Table 2.3 Contaminant removal at treatments N=1 and 2 using different grades of iron powder for three different contaminants; namely, AMCO – Arab Medium Crude Oil (medium viscosity)⁶; JCO - Jasmine Crude Oil (high viscosity); DO – Diesel Oil (low viscosity). The physical characteristics for these oils and particle types are summarized in Tables 27 and 28 in Appendix 2.1. These parameters represent both those of the suppliers and those determined as part of this research.

Iron Powder Grade	Oil Contaminant	% Removal at,		
		Treatment N=1	Treatment N=2	Final Treatment
ASC300	JCO	27.47	50.08	98.45
	DO	98.94	99.36	99.95
	AMCO	91.37	94.44	99.59
A100S	JCO	26.48	51.21	97.41
	DO	98.18	99.25	99.98
	AMCO	84.72	92.56	98.76
ASC100.29	JCO	15.48	36.50	97.12
	DO	97.95	99.04	99.94
	AMCO	89.07	93.11	99.09
A40S	JCO	15.78	33.94	85.29
	DO	91.98	95.31	99.56
	AMCO	70.97	83.11	98.11
MH300.29	JCO	33.13	52.89	96.51
	DO	98.51	99.17	99.99
	AMCO	94.68	98.03	99.88
C100.29	JCO	19.91	41.72	96.59
	DO	98.54	99.31	99.94
	AMCO	90.20	92.22	99.22
NC100.24	JCO	17.46	38.11	96.57
	DO	98.56	99.01	99.87
	AMCO	91.47	94.51	99.42
M40	JCO	13.00	26.18	86.78
	DO	97.39	98.91	99.80
	AMCO	85.76	92.00	98.70
R12	JCO	14.28	35.87	89.89
	DO	93.12	98.79	99.89
5 µm	JCO	16.95	27.43	88.73
	DO	97.09	97.54	99.94

⁶ Note that these data were from a previous study carried out in this group by Dao et al, 2007

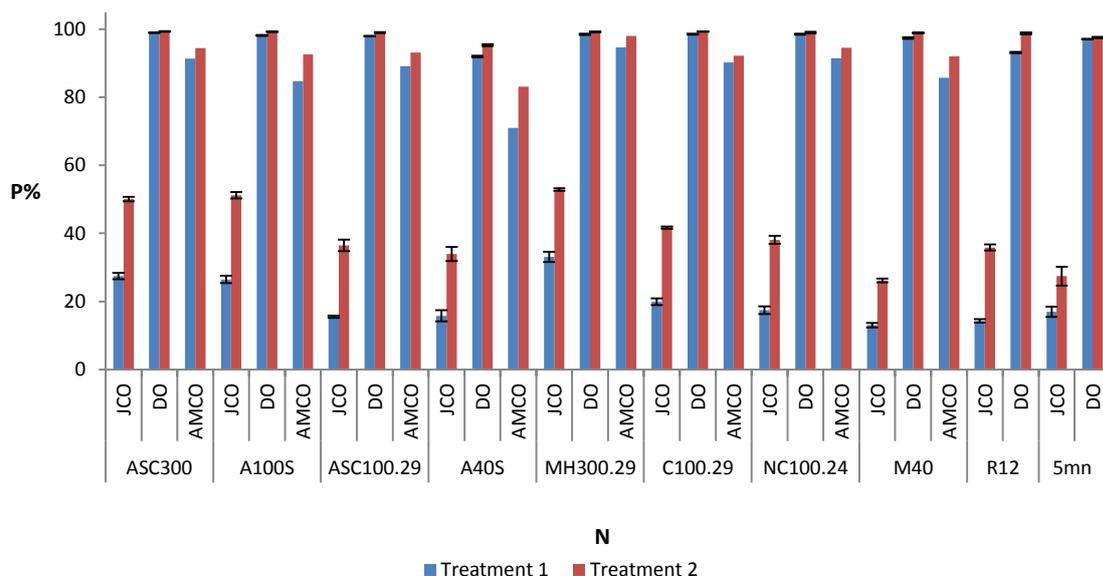


Figure 2.18 Comparison of three types of oil removal, P%, at treatments N=1 (blue) and N=2 (red), from duck feather clusters using different grades of iron powder at 22⁰C. Error bars represent the SE for five replicates. The removal data at N=1 and N=2 are presented in Table 2.3. The full sets of experimental data relating to the JCO and DO isotherms (five-fold replicates) are provided in Appendix 2.1.

2.6.4 Particle size considerations with respect to initial removal

As indicated in Table 28 in Appendix 2.1, the various particle grades that were under consideration differed with respect to a number of parameters including particle size and particle size distribution, surface properties (such as roughness - influenced by ‘annealing and atomization’) – related to specific surface area, and apparent density (potential porosity). Probably the most influential of these is the average particle size⁷ and this parameter has been investigated with respect to the *initial removals* for AMCO, JCO and DO, *vide supra*.

The particle suppliers (Höganäs) have provided data on the average particle sizes and the available surface areas (BET). We have independently checked these parameters through an assessment carried out by the CSIRO⁸ (Process Science & Engineering Division), data provided in Appendix 2.2. These analyses also provide additional information on the spread of the particle size distributions. It has been found that a good correlation exists between the supplier’s data and that of the CSIRO with respect to the average particle size, Figure 2.19.

⁷Another factor to be considered is the spread of the particle size distribution. This has been initially addressed in this thesis, but not rigorously - due to time constraints

⁸Equipment used: Mastersizer S Ver. 2.19 (Serial Number 32418/17), Malvern Instruments Ltd., Malvern Rd, UK.

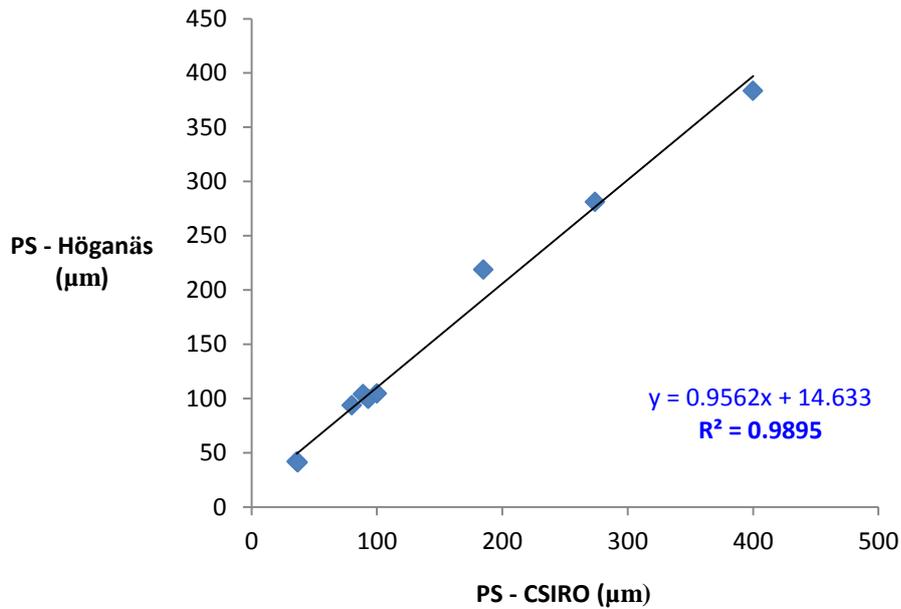


Figure 2.19 Average particle size (PS) as provided by the supplier (Höganäs) compared to the values obtained from the CSIRO. The CSIRO full analyses and particle size distributions for these iron powders are provided in Table 28 in Appendix 2.1.

However, when the BET values (m^2/kg) provided by Höganäs are compared to the specific surface area values (m^2/g), as determined by the CSIRO, essentially no correlation is obtained, Figure 2.20. This suggests that one of the sets of data relating to surface area were unreliable.

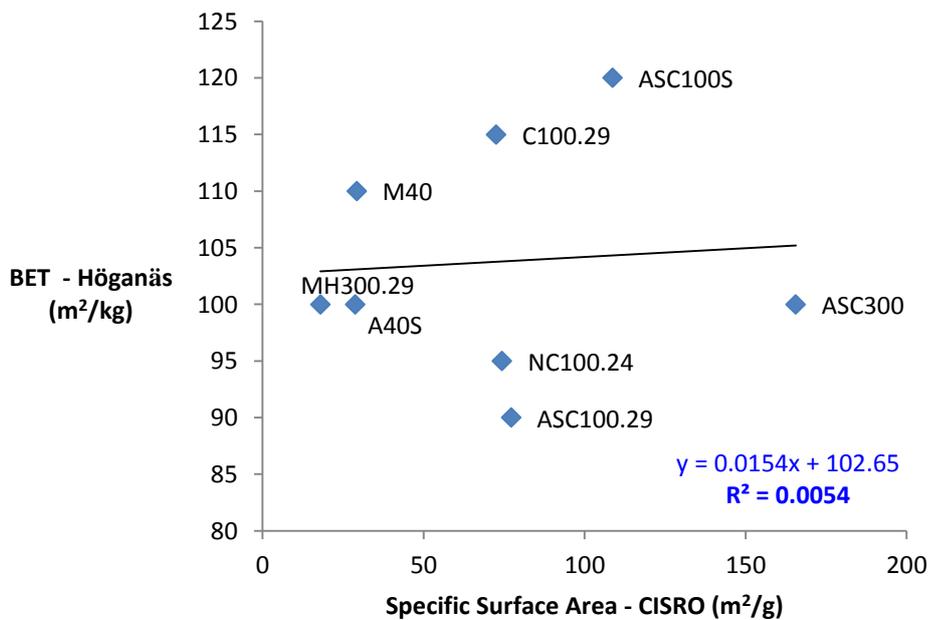


Figure 2.20 The supplier's surface area values (BETs) versus the surface area values (Specific Surface Area) values as determined by the CSIRO.

To establish which set is correct, the average particle size was plotted against the BET values (Höganäs) and the Specific Surface area (CSIRO) in turn, Figure 2.21 and 2.22.

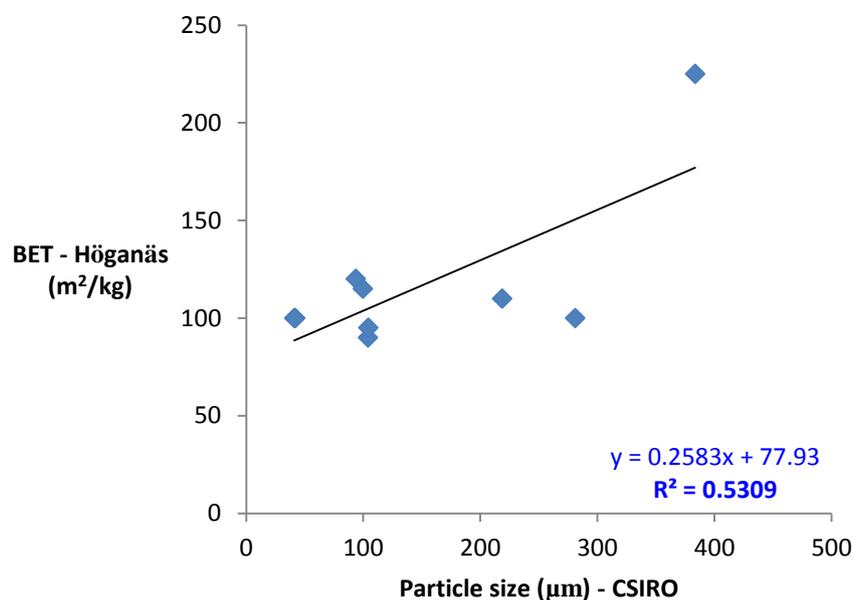


Figure 2.21 The BET (Höganäs) values plotted against the average particle size.⁹

The lack of correlation in Figure 2.21 compared to the reciprocal plot generated in Figure 2.22 established that the CSIRO data for specific surface area were the correct values for these iron powders. Therefore the latter values were subsequently used for our investigations.

It may also be reasonably surmised from the faithfully reproduced reciprocal relationship in Figure 2.22 that, over the range of iron powder grades that were used in these studies, the degree of surface roughness was essentially similar from grade to grade. This assumption assists in interpreting our investigations into the dependence of the initial removal efficacy on the average particle size alone.

⁹ The CSIRO values are used for the average particle size values - although the Höganäs values could also be used given that they are essentially the same, see Figure 2.19.

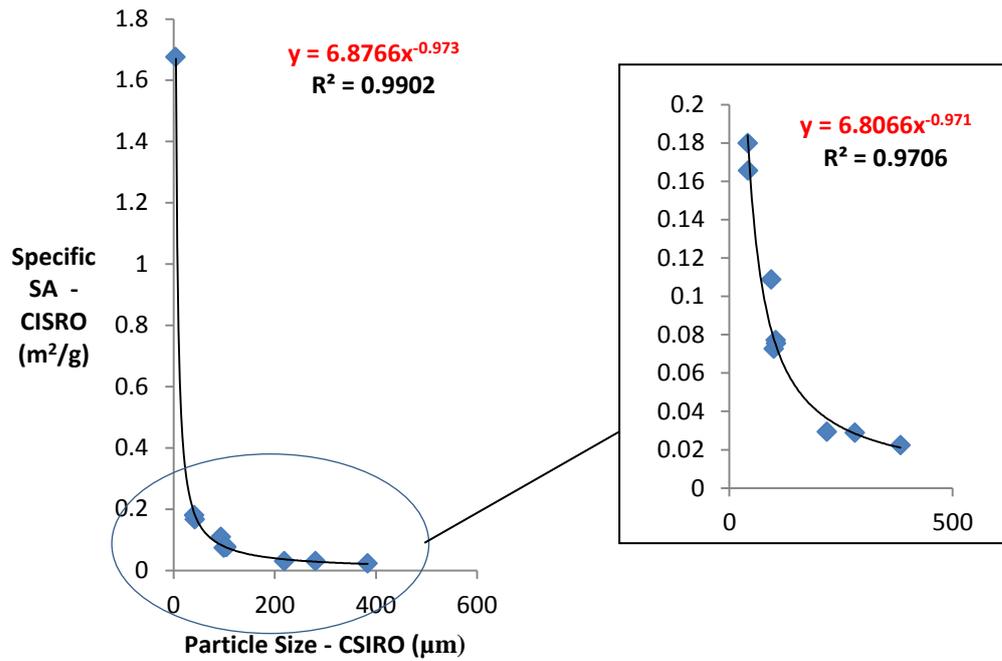


Figure 2.22 The Specific Surface Area, as determined by the CSIRO versus the average particle size. Note the excellent reciprocal relationship displayed. The inset, where the very small 5 µm particle data was excluded also retains the relationship.

2.6.5 The dependency of initial contaminant removal on average particle size and particle size distribution

For the removal of JCO from duck feather clusters, a comparison was made between the removal isotherms for 41 µm particles (MH300.29) and 5µm particles¹⁰ – both of which have essentially symmetrical (normal) distributions (Appendix 2.3), and a 50/50 blend of the two. By blending the two grades we can observe the effect of lowering the average particle size distribution (assumed to be between 5 and 37 µm after mixing) and also broadening the distribution (albeit with a negative skew) - see schematic diagram below, Figure 2.23. The relevant isotherms are shown in Figure 2.24.

¹⁰ Average values

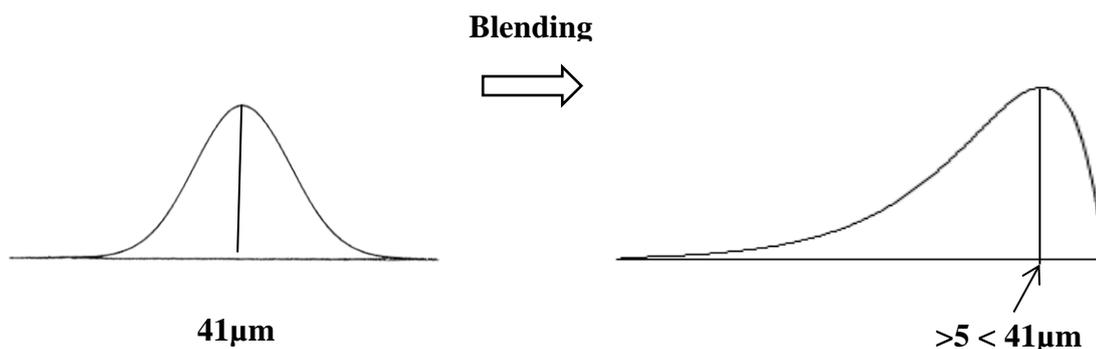


Figure 2.23 The expected effect of blending two particle size distributions

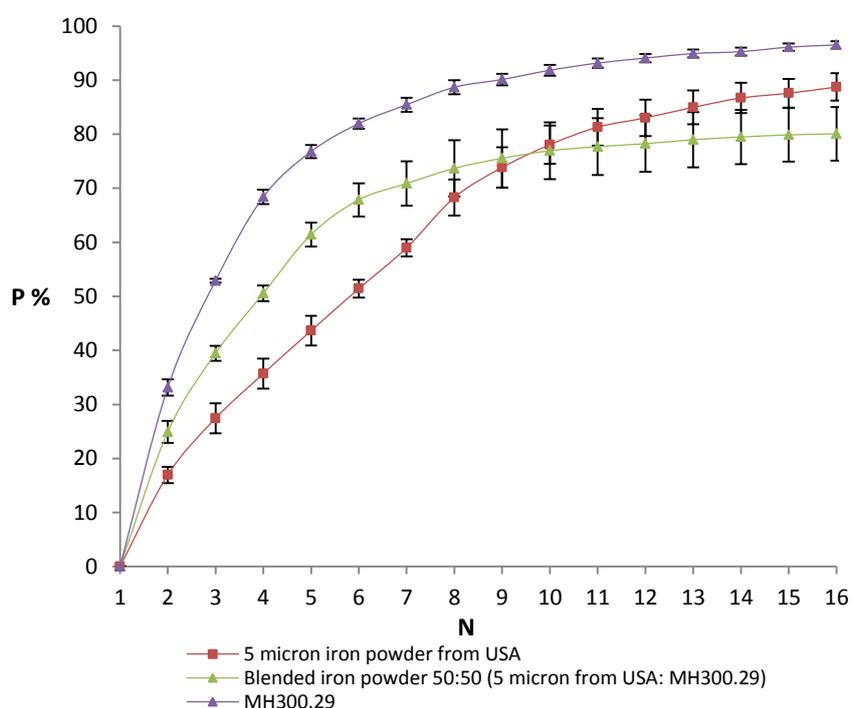


Figure 2.24 Jasmine Crude Oil (JCO) removal, P%, from duck feather clusters as a function of the number of treatments, N, using iron powders with different average particle sizes and distributions, at 22°C. Error bars represent the SE for five replicates. The full data sets are provided in Table 1 Appendix 2.3 and the individual data profiles are provided in Tables 3 in appendix 2.1 and Table 2 and 3 in Appendix 2.3.

It may be observed from Figure 2.24 that the removal isotherm for the particles with an average size of 41 μm (MH300.29 – the optimum grade) is a typically shaped removal isotherm. On the other hand, the removal isotherm for the 5 μm particles (sourced from the USA) shows a significant depression of the initial removal. Interestingly, the 50/50 blend is somewhere in-between. These results suggest that there was a lower limit (between 5 and 41 μm) below which the initial removal is compromised. Although not pursued in this study, further enquiry is required into this effect in relation to the average particle size and the

particle size distribution itself. This would require a supply of particles whereby the average particle size as well as the width of the particle size distribution could be controlled. Apart from sieving, a technique is suggested whereby from a standard stock of iron powder, batches of particles may be obtained with altered average sizes and narrower distributions. This suggested technique is represented in Figure 2.25. Thus a stream of ‘standard’ particles is subjected to a magnetic field perpendicular to the direction of flow. According to mass (size) the particles are diverted to different extents and the fractions with altered distributions are then harvested at the base.

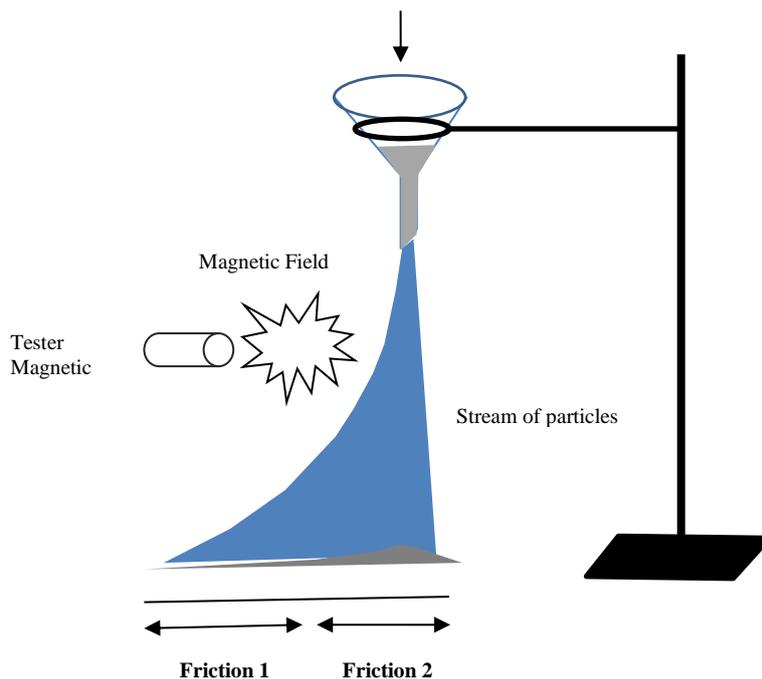


Figure 2.25 Schematic diagram of suggested method for manipulating the particle size distribution of a stock supply of iron powder.

A preliminary experiment on particles with an average particle size of 41 μm showed Fraction 1 to have an increased average particle size of 43 μm and a slightly narrower distribution, Appendix 2.2. Therefore, in principle, this technique could be feasible and remains to be refined.

Table 2.4 Iron powder grades with estimated average particle sizes (CSIRO) and Specific Surface Areas (SSA -CSIRO).

Grade of IP	Estimated particle size (μm)	SSA (m^2/g)
5 μm	4.3	1.6750
ASC300	42.1	0.1656
MH300.29	41.2	0.1812
A100S	93.7	0.1087
ASC100.29	104.1	0.0772
C100.29	99.7	0.0726
NC100.24	104.5	0.0754
M40	218.9	0.0293
A40S	281.1	0.0228
R12	383.7	0.0223

The average particle size, PS, and the Specific Surface Area, SSA, for each grade of iron powder (atomised and spongy) is given in Table 2.4. The initial removals, P% at N=1, for each particle grade have been plotted against PS for the three different oil types in Figures 2.26 to 2.28. It may be seen that for DO and AMCO, the initial removal tends to decrease with an increase in average particle size. However, for the more viscous JCO, the data is clustered into groups where the initial removal is distinctly compromised for smaller particles ($< \sim 41 \mu\text{m}$) and for larger particles ($> \sim 200 \mu\text{m}$).

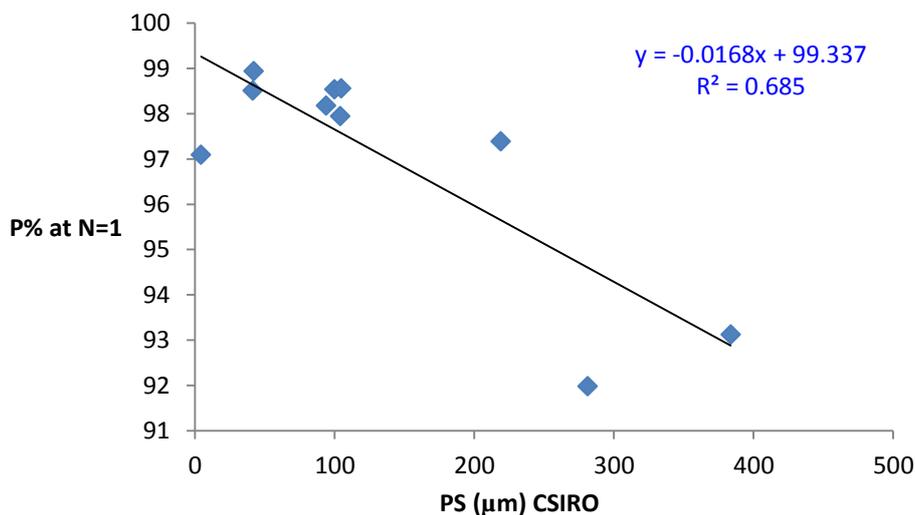


Figure 2.26 The percentage (%) removal of Diesel Oil (DO) at treatment 1 (N=1) versus the Particle Size (PS) values (as determined by the CSIRO). The data are provided in Table 4 in Appendix 2.3.

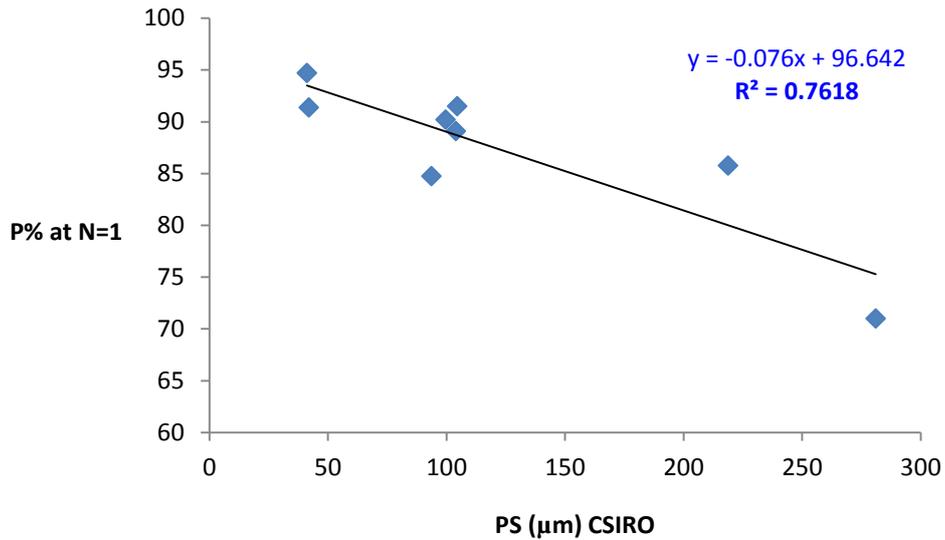


Figure 2.27 The percentage (%) removal of Arab Medium Crude Oil (AMCO) at treatment 1 (N=1) versus the Particle Size (PS) values (as determined by the CSIRO). The data are provided in Table 5 in Appendix 2.3.

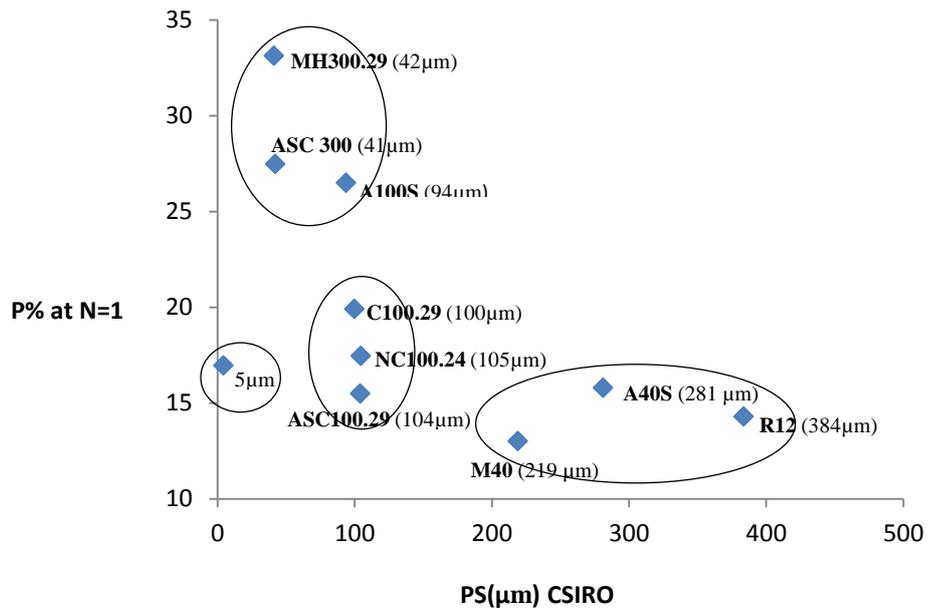


Figure 2.28 The percentage (%) removal of Jasmine Crude Oil (JCO) at treatment 1 (N=1) versus the average particle size. Note that for this more viscous oil, the maximum removal appears to be in a fairly narrow range. The data are provided in Table 6 in Appendix 2.3.

It may be seen from Figure 2.29 that, over a range of approximately 40 to 220 μm, the average particle size may be considered as being directly proportional to the specific surface area. Notably, it is outside of this range that the initial removal appears to be compromised for the JCO, in particular.

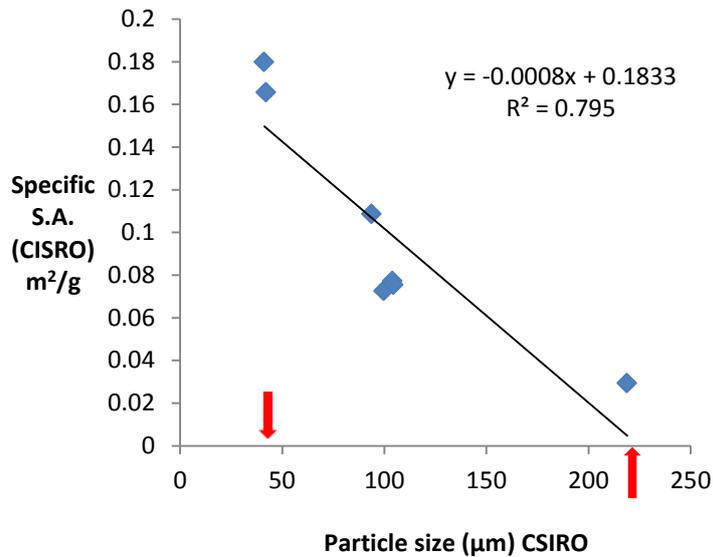


Figure 2.29 A plot of Specific Surface Area (S.S.A) versus the Particle Size (PS) values as determined by the CSIRO.

2.7 The effect of iron particle native surface characteristics (i.e. particle grade) on the initial removal

2.7.1 The effect of spongy versus atomized grades on the removal of DO, AMCO and JCO from feather clusters

The different grades of iron powder may be broadly divided into atomised and spongy. These two classes of particle are manufactured according to different processes - resulting in different physical (surface) attributes (Höganäs AB, 2003). From SEM studies (Dao 2007), see e.g. Figure 2.30, it can be seen that spongy grades have more voids and holes than atomized grades and this was expected to affect capillary action and hence pick-up (especially initial). This fundamental structural difference was also reflected in the available “apparent densities” (ADs) of the particles as provided by the particle manufacturer, Table 2.5, where the AD values tend to be $\sim 0.5 \text{ g.cm}^{-3}$ less, on average, for the spongy grades. In order to ascertain the effect of these different features, with due consideration to different average particle sizes on the removal of various oil types, such as DO (light), AMCO (medium) and JCO (heavy), from duck feather clusters, the oil pick-up isotherms of (spongy/atomised) pairs of particle grades have been generated and compared, Appendix 2.3 (Figures 1 to 3). The pairs were selected so that their average particle sizes and specific surface areas were

roughly comparable¹¹; namely - M40 (spongy) and A40S (atomized), being > 200 μm ; C100.29 (spongy) and A100S (atomized), being $\sim 100 \mu\text{m}$; NC100.24 (spongy) and ASC100.29 (atomized), also being $\sim 100 \mu\text{m}$ and MH300.29 (spongy) and ASC300 (atomized), being $\sim 40 \mu\text{m}$. Previous work of this kind focused on the removal of the medium viscosity contaminant, AMCO (Dao 2007) - with an emphasis on the final removal. The results presented here focus on the lighter and heavier contaminants, namely DO and JCO, with an emphasis on the *initial* removal - in relation to the “quick clean” concept, *vide supra*. However, for all three contaminants, the relevant data for a comprehensive analysis with respect to the initial removal (at N=1 and N=2) can be extracted from Table 2.6 and analysed for trends. Thus this work completes the picture for investigating the effect of spongy/atomized on initial removal for all three oil types, namely light (DO), medium (AMCO) and heavy (JCO).

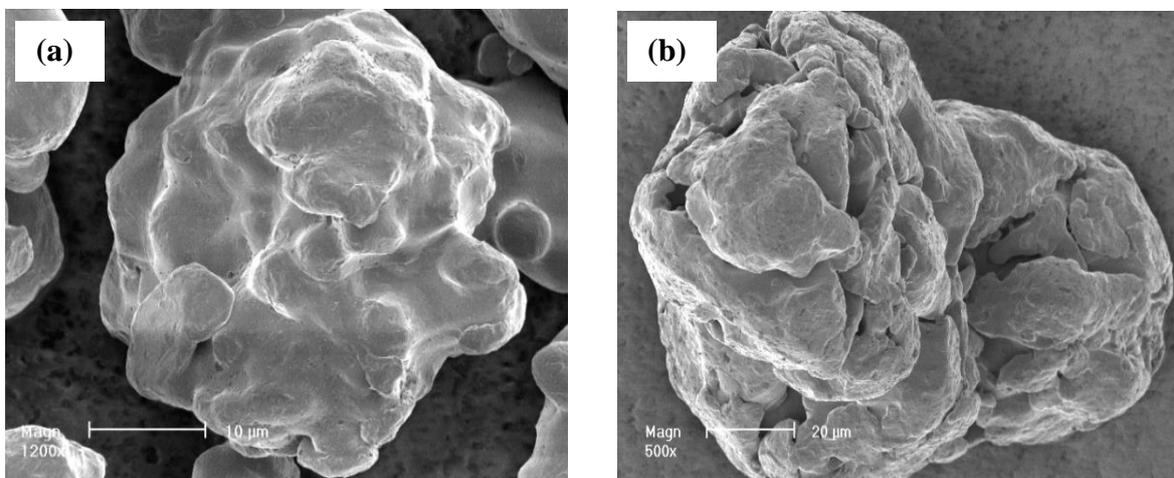


Figure 2.30 (a) Scanning electronic micrograph of *atomised* grade ASC100.29 (Dao 2007); (b) Scanning electronic micrograph of *spongy* grade NC100.24 (Dao 2007).

2.7.2 Data analysis

A typical set of nested isotherms for the removal of DO and JCO from duck feather clusters, comparing, for example, the M40 (spongy)/A40S (atomized) pair, from which the relevant data in Table 2.6 has been extracted, are shown Figure 2.31. All the other relevant isotherms and full data sets are given in Appendix 2.3. A comparison between the four Spongy (S) and Atomized (A) pairs of comparably sized particles, with respect to differences (S-A) between the P% values at N=1 and N=2 for each contaminant type (DO-light; AMCO-medium and JCO-heavy) is given in Table 2.6; see Figure 2.31 (a). This data has been drawn from Table 2.3.

¹¹ Each of the four pairs is self-consistent with respect to being annealed or un-annealed.

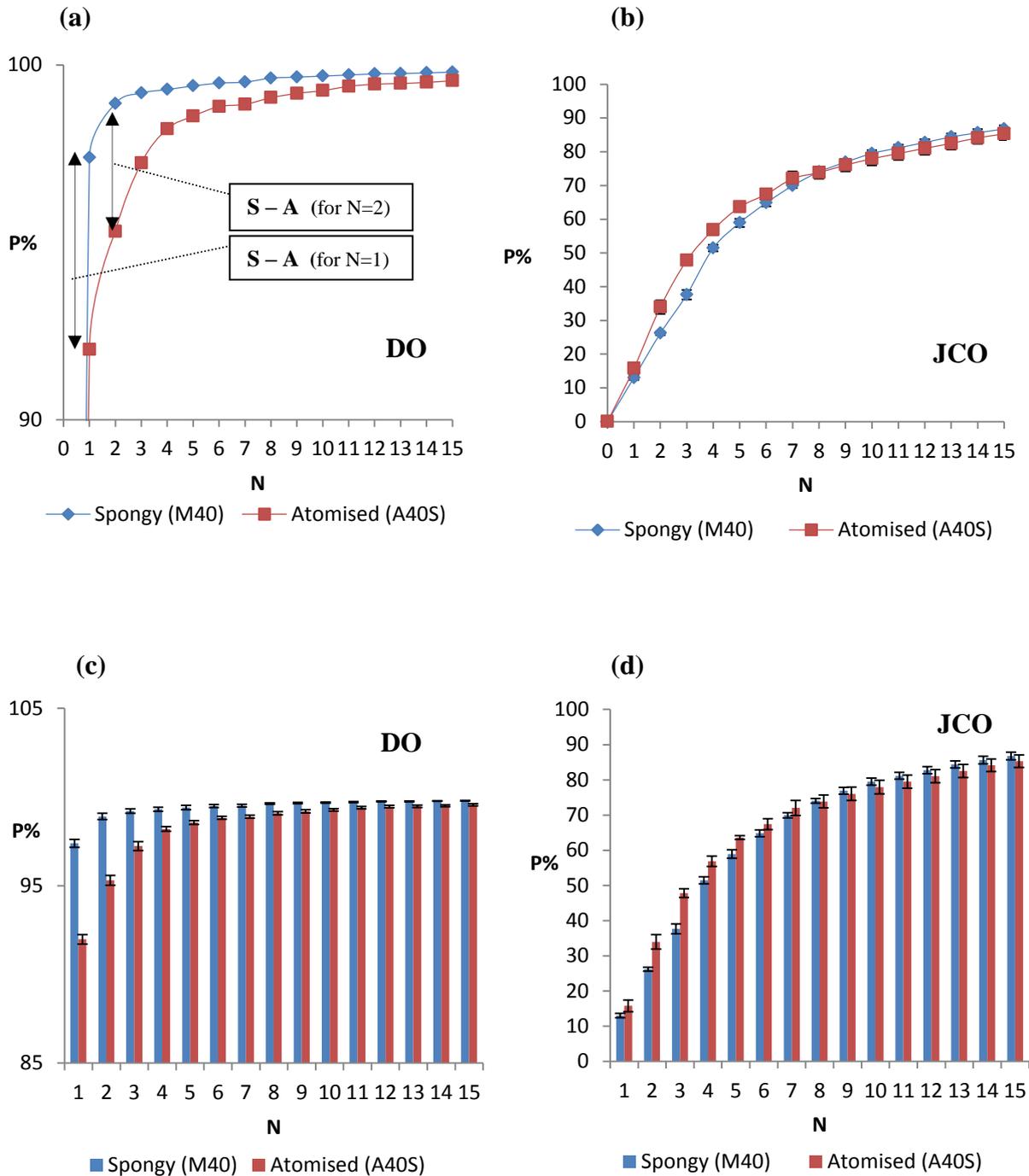


Figure 2.31 (a) & (c) Comparison of DO pick-up, from duck feather clusters as a function of number of treatments, N, between the spongy and atomised grades M40 and A40S, respectively (both are coarse and un-annealed). Error bars represent the SE for five replicates. **(b) & (d)** Corresponding comparison of JCO pick-up, from duck feather clusters as a function of number of treatments, N, between spongy and atomised grades (both coarse and un-annealed). Error bars represent the SE for five replicates. Full data are provided in Table 7 and 8, Appendix 2.3 and the individual data profiles are provided in Tables 14, 15, 24 and 25 in Appendix 2.1.

Table 2.5 Iron powder grades with estimated average particle sizes (CSIRO), Specific Surface Areas (SSA-CSIRO) and Apparent Densities (AD -Höganäs).

IP Grade	Iron Powder (IP)	Particle Size (PS)	Specific Surface Area (SSA) m ² /g	Apparent Density (AD), g/cm ³
Atomised	A40S	281.11	0.0288	-
	A100S	93.73	0.1087	2.90 - 3.40
	ASC100.29	104.05	0.0772	2.99
	ASC300	42.07	0.1656	-
Spongy	M40	218.90	0.0293	2.30 - 2.55
	C100.29	99.74	0.0726	-
	NC100.24	104.54	0.0754	2.43
	MH300.29	41.18	0.1812	2.2 - 2.8

Table 2.6 A comparison between the four Spongy (S) and Atomized (A) pairs of comparably sized particles, with respect to differences (S-A) between the P% values at N=1 and N=2 for each contaminant type (DO-light; AMCO-medium and JCO-heavy), see Figure 2.29 (a). This data was drawn from Table 2.3.

Oil type		Diesel Oil (DO)		Arab Medium Crude Oil (AMCO)		Jasmine Crude Oil (JCO)	
IP Type	IP Grade	N=1	N=2	N=1	N=2	N=1	N=2
S	M40	97.39	98.91	85.76	92	13	26.18
A	A40S	91.98	95.31	70.97	83.11	15.78	33.94
(S-A)		5.41	3.6	14.79	8.89	-2.78	-7.76
S	C100.29	98.54	99.31	90.2	92.22	19.91	41.72
A	A100S	98.18	99.25	84.72	92.56	26.48	51.21
(S-A)		0.36	0.06	5.48	-0.34	-6.57	-9.49
S	NC100.24	98.56	99.01	91.47	94.51	17.46	38.11
A	ASC100.29	97.95	99.04	89.07	93.11	15.48	36.5
(S-A)		0.61	-0.03	2.4	1.4	1.98	1.61
S	MH300.29	98.51	99.17	94.68	98.03	33.13	52.89
A	ASC300	98.94	99.36	91.37	94.44	27.47	50.08
(S-A)		-0.43	-0.19	3.31	3.59	5.66	2.81

Table 2.7 S-A values (red), averaged over treatments N=1 and N=2, as a function of approximate particle size and oil type. The more positive the value, the more significant was the spongy over the atomized with respect to the initial removal (up to N=2).

Oil	Approximate Average Particle Size		
	> 200 µm	~ 100 µm	~ 40 µm
DO (Light)	4.5	1.03	-0.84
AMCO (Medium)	11.84	2.24	3.45
JCO (Heavy)	-5.27	-3.12	4.24

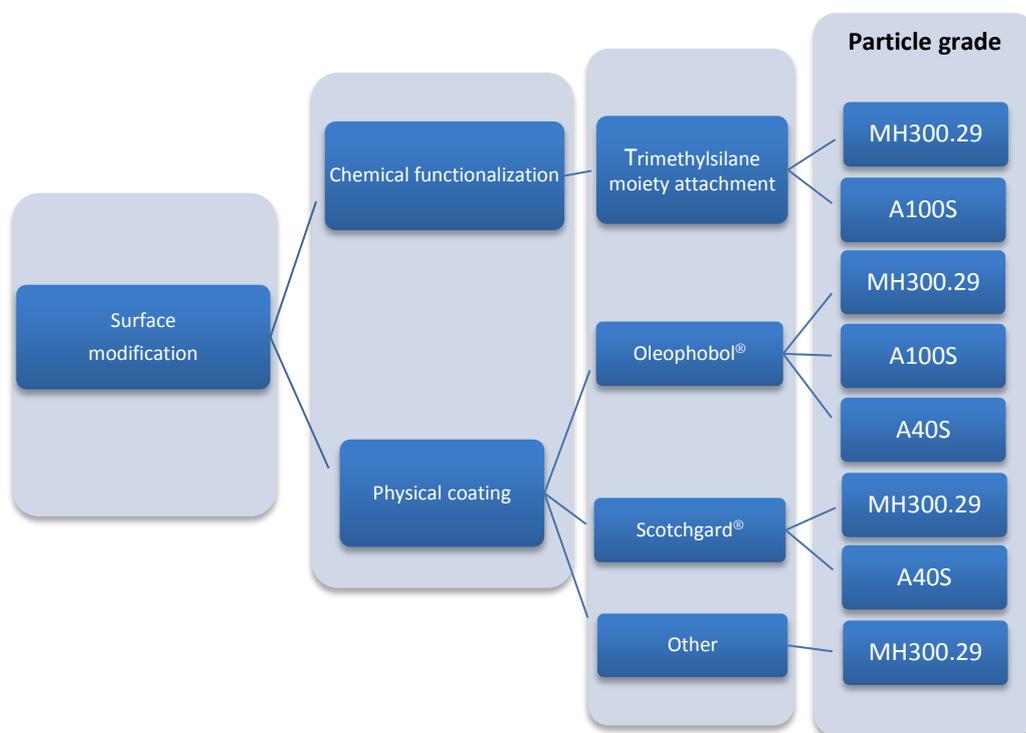
S-A values (red), averaged over treatments N=1 and N=2, see Figure 2.29 (a), as a function of approximate particle size and oil type have been extracted from Table 2.6 and summarized in Table 2.7. The more positive the value, the more significant was the spongy over the atomized with respect to the initial removal (up to N=2).

As can be seen from Table 2.7, for the light contaminant (DO), the influence of “sponginess” upon initial removal (up to N=2) decreases as the average particle size decreases from >200 μm to 40 μm . For the medium viscosity contaminant (AMCO), sponginess was dominant over atomized for a larger particle size (>200 μm) and less important, but also still better than atomised, for the smaller particle sizes (~100 μm and ~40 μm). For the heavy contaminant (JCO), the reverse trend was apparent, whereby “atomization” gave better initial removal for particles from 200 μm to 100 μm , but spongy was preferred for smaller particles of ~40 μm . For a given particle size, from ~200 μm , the initial removal was better for spongy grades for DO (light) and AMCO (medium – especially) but atomised was preferred for JCO (heavy). For ~100 μm , initial removal was better for spongy grades for DO (light) and AMCO (medium) but atomised was preferred for JCO (heavy). For a particle size of ~40 μm , initial removal of DO (light) was better for atomized but spongy was better for AMCO (medium) and JCO (heavy).

2.8 The effect of particle surface hydrophobicity and other surface modifications on the initial and final removal of JCO from feathers

Hydrophobic and super-hydrophobic surfaces can be found either naturally or can be created artificially. For example, such surfaces can be seen in nature on water-repellent plant leaves, butterfly wings and water-strider insect legs - and these naturally occurring nanostructures may be mimicked to produce such surface characteristics for practical applications (Bhushan *et al.* 2007; Sun *et al.* 2009; Crick and Parkin, 2010). The phenomenon of hydrophobicity may arise from surface chemical composition and/or surface structure (Cao and Gao, 2010). In order to achieve more insight into the effect on contaminant removal (especially with respect to initial removal for quick clean applications) of surface properties such as pores, cavities, smoothing, nano- and micro-roughness and hydrophilicity/hydrophobicity, the surfaces of selected particle grades have been modified by several different methods in an attempt to make them more hydrophobic and to alter the surface topology, Scheme 2.1.

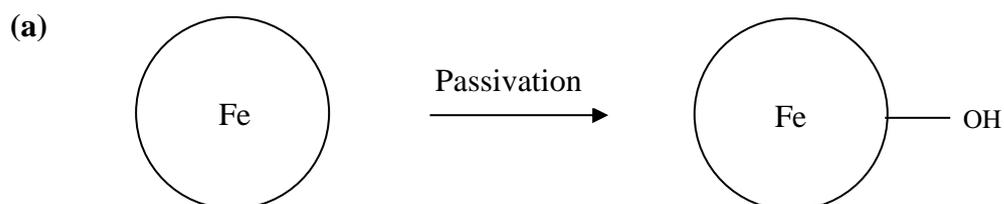
The removal isotherms of the functionalized or coated particles with respect to the contaminant JCO have then been generated and evaluated and qualitatively compared to the SEM images of the various surfaces.



Scheme 2.1 Strategy for probing the effect of surface modification on the removal of JCO from duck feather clusters. Isotherms for the removal of JCO from duck feathers have been determined for all eight modified (and unmodified) types of particle and these have been discussed with respect to the SEM images of the particles' surfaces.

2.8.1 Chemical functionalization of an iron surface with trimethylsilane (TMS) moieties

Chemical functionalization of the iron surface using the method described Taghvaei *et al.* (2009) is a three step process. The three steps are represented schematically in Figures 2.32 (a) to (c), below.



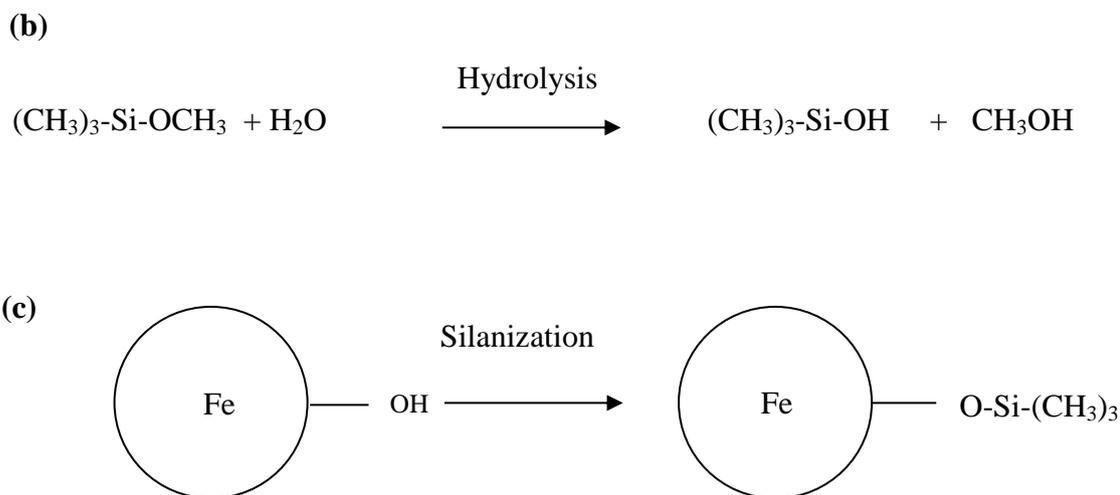


Figure 2.32 Schematics for the (a) passivation of the iron particle surface (b) hydrolysis of TMS (c) silanization of the particle surface.

2.8.1.1 Methods

2.8.1.1.1 Passivation

The MH300.29 grade of iron powder was selected for functionalization with trimethylsilane (TMS), Figure 2.32. The purity of this iron grade was reported by the manufacturer to be: Fe total - 99.0%; Fe metallic - 98.5%; C - 0.01% and S - 0.006%. To create a unified passive-oxide layer coating on the iron particles, 100g of the iron powder was washed in acetone, filtered, and dried in an oven overnight at 50 °C. The degreased iron powder was then mixed into an alkaline aqueous solution of 5M sodium nitrite (NaNO_2) (Sigma Aldrich) with pH monitoring. After stirring for a few minutes, the pH of the solution was observed to increase, as expected, to a value of 10.8 (literature, 10.5). 1M acetic acid was then added drop-wise to lower the pH to 7.6 (literature, 8.0) and the mixture was stirred for 20 minutes. The pH profile of the reaction over this time, Figure 2.33, was characteristic for surface passivation having taken place, Figure 2.32 (a).

2.8.1.1.2 Hydrolysis

Two drops of methoxy-trimethylsilane (Sigma-Aldrich) were added to 50 mL of H_2O (distilled water) and subjected to hydrolysis, Figure 2.32(b), by rapidly stirring for 20 min at 60 °C.

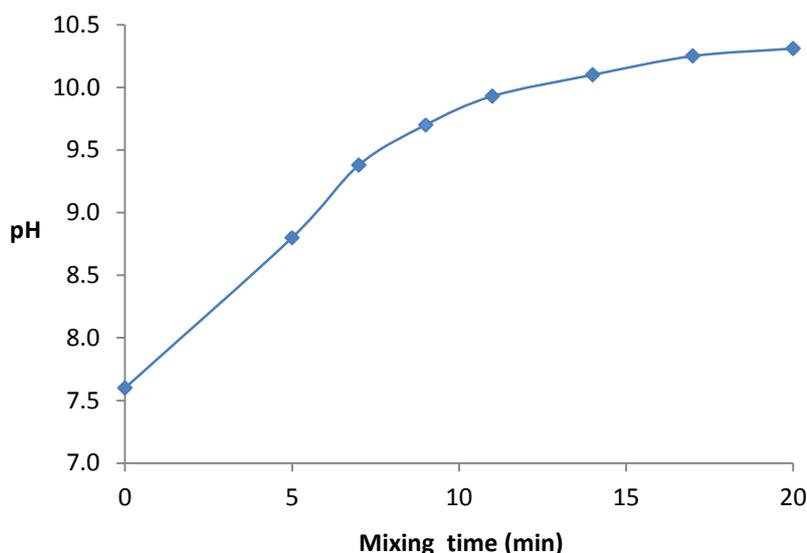


Figure 2.33 Observed (characteristic) pH vs time profile for the passivation of the iron surface. Data are provided in Table 15 in Appendix 2.3.

2.8.1.1.3 Salinisation

The passivated iron powder was added to 100 mL of a mixture of 95% alcohol and 5% distilled water. The hydrolysed methoxy-trimethylsilane solution was then added and the mixture was mechanically stirred at 60°C for 2 hrs. The particles were then filtered and washed 3 times with ethanol. The functionalized iron particles, Figure 2.32(c), were dried at 50°C.

2.8.2 Surface features of MH300.29 particles functionalised with TMS moieties

The original and functionalized MH300.29 particles were characterized using SEM, Figures 2.34 (a) to (c). Surface modification was clearly visible from these images. Figure 2.34 (a) shows that this grade of particle, when unmodified, has sizeable cavities and voids, but otherwise the surface appears smooth, as discussed previously for spongy grades. These cavities and voids were less pronounced (presumably filled in) after surface functionalization as shown in Figure 2.34 (b) and the surface texture was now more granular (exhibiting “nano-roughness”) - as is apparent in Figures 2.34 (b) and (c); also see Table 2.8. It was estimated that the nano-granulation is of the order of ~ 20 - 50 nm.

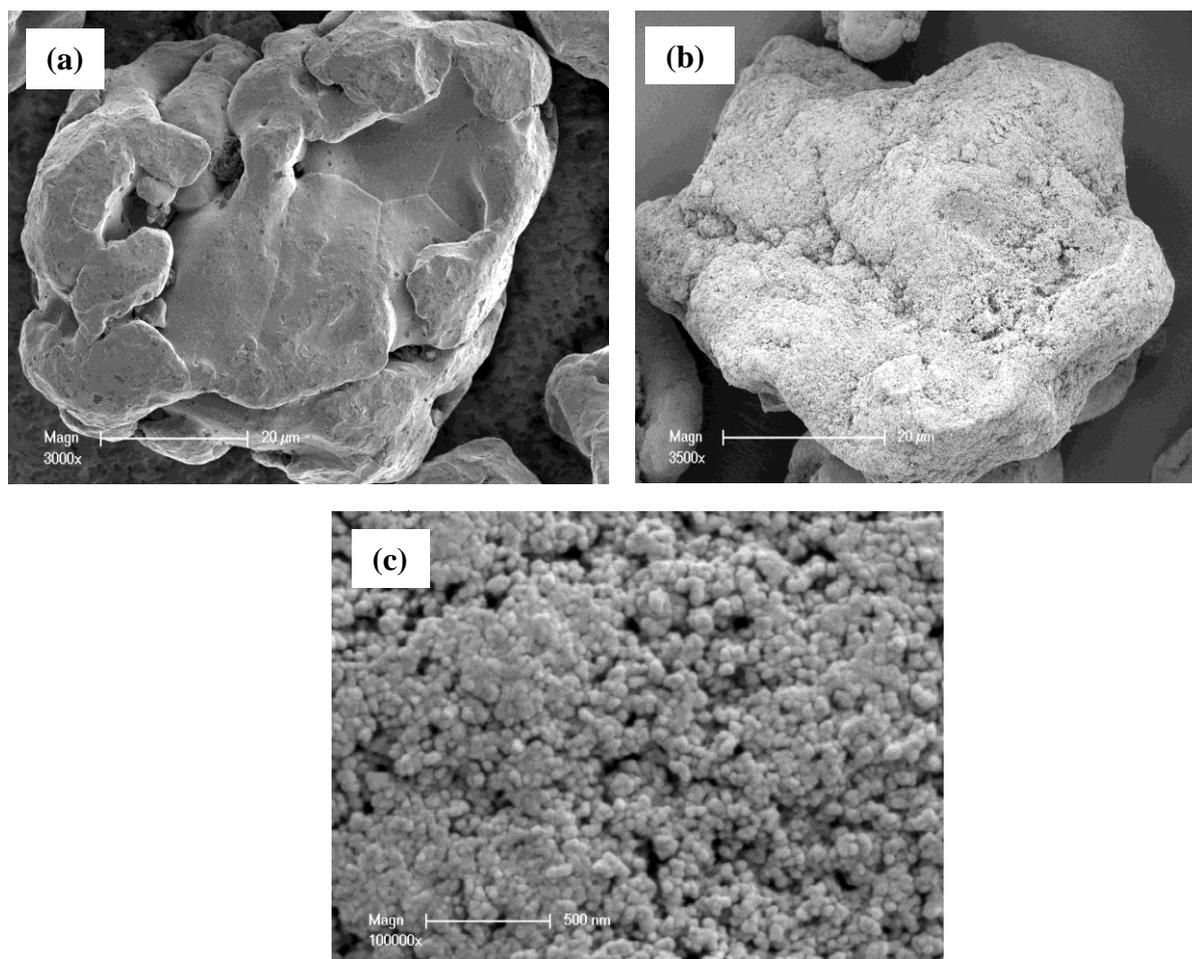


Figure 2.34 SEM images of (a) the original MH300.29 grade (b) the TMS-functionalized MH300.29 grade (c) finer detail of image (b).

2.8.3 Surface features of A100S particles functionalized with TMS moieties

Figure 2.35 (a) shows that this grade of particle, i.e. A100S, when unmodified, does not have the sizeable micro cavities and voids of the unmodified MH300.29, but it does possess extensive nano-pitting. The same method for functionalizing the spongy MH300.29 grade (average particle size $\sim 41\mu\text{m}$) was applied to the larger atomized A100S grade (average particle size $\sim 94\mu\text{m}$). This was to ascertain the effect of increasing the particle size whilst maintaining a hydrophobic, uniform and granular surface - as above. In spite of the observed nano-pitting, it was anticipated that the resulting surface coating of the A100S particles would be similar to that of MH300.29 (above) and that the only difference between the two would be in size. Indeed, qualitatively, a similar surface modification of A100S is achieved, Figure 2.35 (b) & (c), - but with coarser, and not quite as dense, granulation. Also, the nano-granulation here is larger and less uniform - within a 50 to 200 nm range, see Table 2.8.

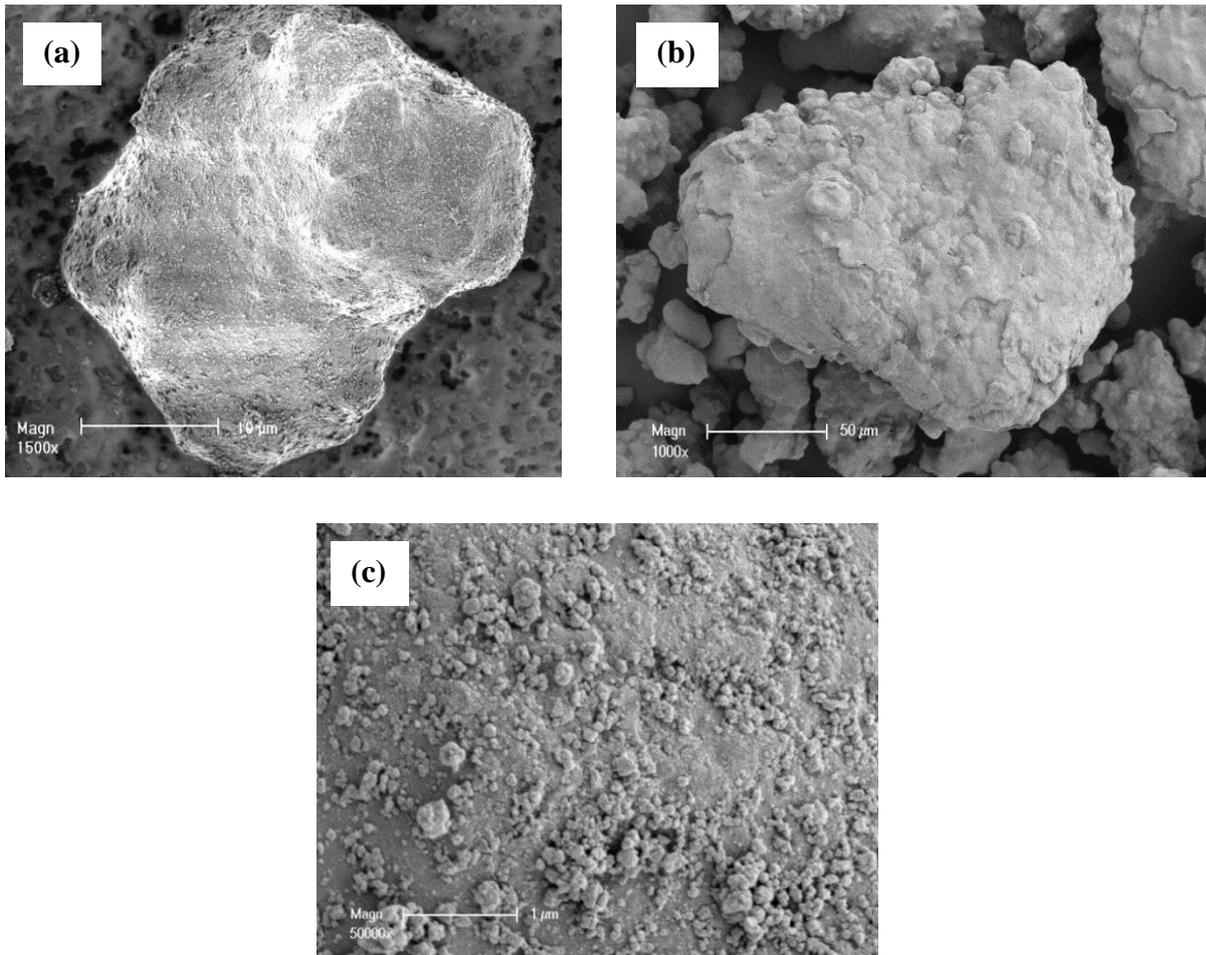


Figure 2.35 SEM images of (a) un-treated atomised grade A100S (Dao, 2007) (b) A100S grade functionalized with TMS moieties (c) finer detail of image (b).

2.8.4 Surface features associated with physically coating the MH300.29, A100S and A40S particles with hydrophobic Oleophobol®

A suspension of 100 g of each of the three grades of iron powder (MH300.29, A100S and A40S) were stirred in Oleophobol® (150 mL) for 40 minutes, using a mechanical stirrer. The coated particles were filtered and dried in an oven overnight at 40°C. The original and coated MH300.29 particles were characterized using SEM, Figure 2.36 (a) & (b). Again, surface modification is clearly visible from these images. Figure 2.36 (a) again shows the sizeable voids and cavities that are characteristic of spongy grades – *vide supra*. These voids and cavities are essentially obliterated by this coating and, unlike the TMS functionalization; the coated surface appears smooth - without any apparent granular nano-texture. It was anticipated that Oleophobol® coating of the A100S and A40S particles would be similar to that of the MH300.29 and that the only difference between the three would be in their relative sizes. However, this was found not to be the case. From the SEM images for these two

particle types as shown in Figure 2.37 (a) to (c) and Figure 2.38 (a) to (c), it may be seen that the resultant surfaces display micro-roughness estimated to be from 10-50 μm and nano-roughness granulation estimated to be from 50-1000 nm, see Table 2.8.

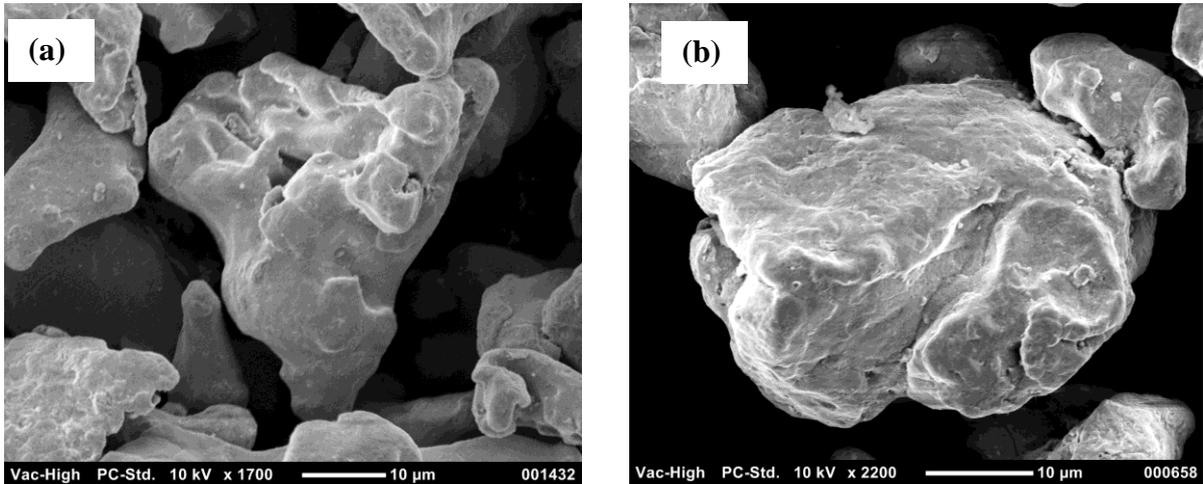


Figure 2.36 (a) un-treated MH300.29 particles (b) Oleophobol[®]-coated MH300.29 particles

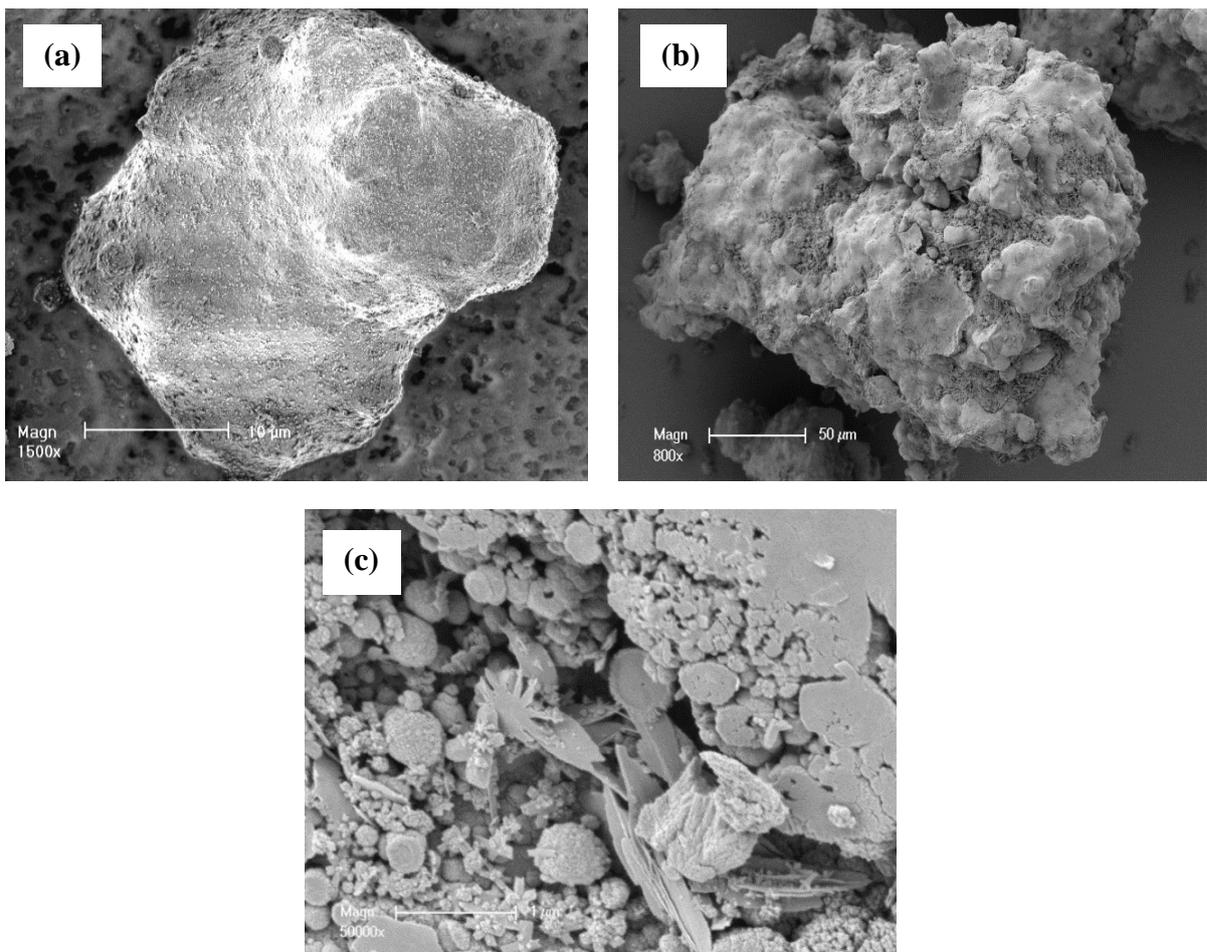


Figure 2.37 SEM images of (a) un-treated atomised grade A100S (Dao, 2007) (b) the A100S grade coated with Oleophobol[®] (c) finer detail of image (b) – scale is 1 μm . Micro-roughness estimated from 10-50 μm and nano-roughness granulation estimated from 50-1000 nm.

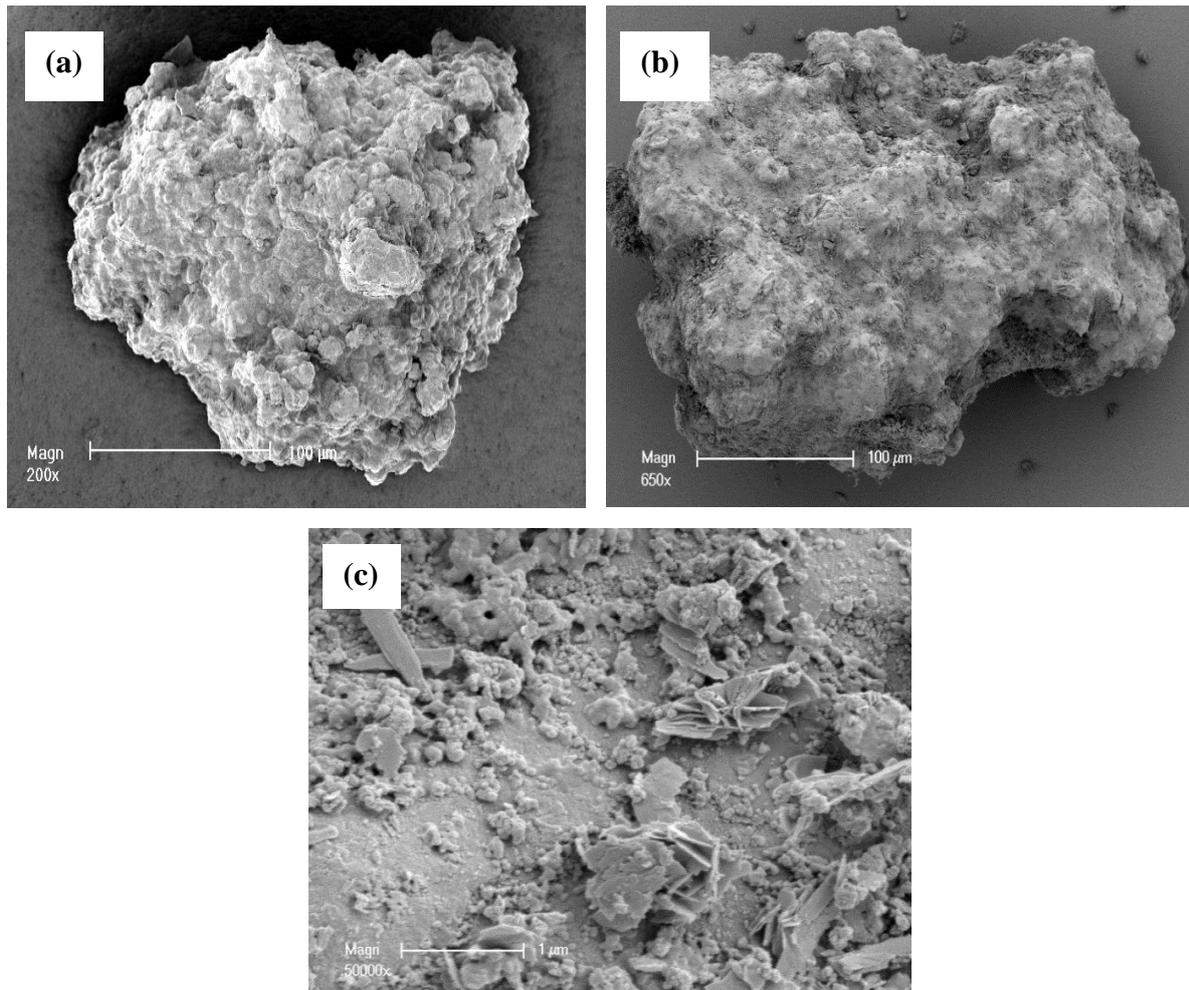


Figure 2.38 SEM images of (a) un-treated atomised A40S (Dao, 2007) (b) the A40S grade coated with Oleophobol (c) the finer texture of image (b). Micro-roughness estimated from ~10-50 μm and nano-roughness granulation estimated from ~50-1000 nm.

2.8.5 Surface features associated with physically coating A40S and MH300.29 iron particles with hydrophobic Scotchgard[®]

This represents a “spray-on” method for coating particles and is expected to produce a thinner, more conformal, surface coating. Thus 100 g each of A40S and MH300.29 particles were baked at 72 °C for two hours and left to cool for 20 minutes. The respective iron powders were then spread evenly on a tray and *lightly* sprayed with commercially available Scotchgard[®], and left for 6 hours to dry. The iron powder was then re-spread evenly on the tray and *lightly* sprayed again, being left for another six hours in a fume hood to dry at room temperature. SEM images of the coated A40S and MH300.29 particles were obtained and are shown in Figures 2.39 (a) & (b) and 2.40 (a) & (b), respectively. It was evident that this method leads to smooth and conformal coatings, see Table 2.8.

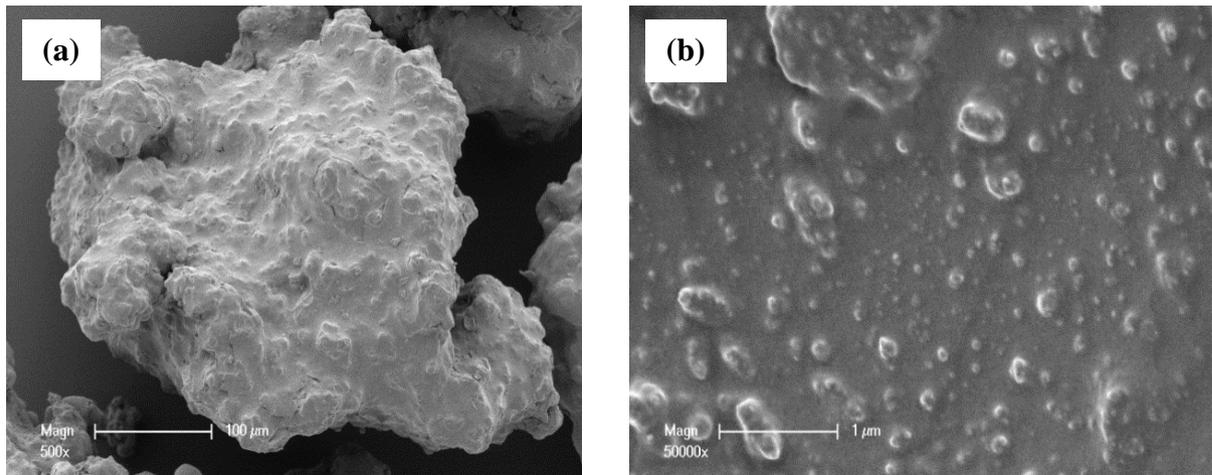


Figure 2.39 SEM images of (a) the A40S grade coated with Scotchgard® (b) finer detail of (a).

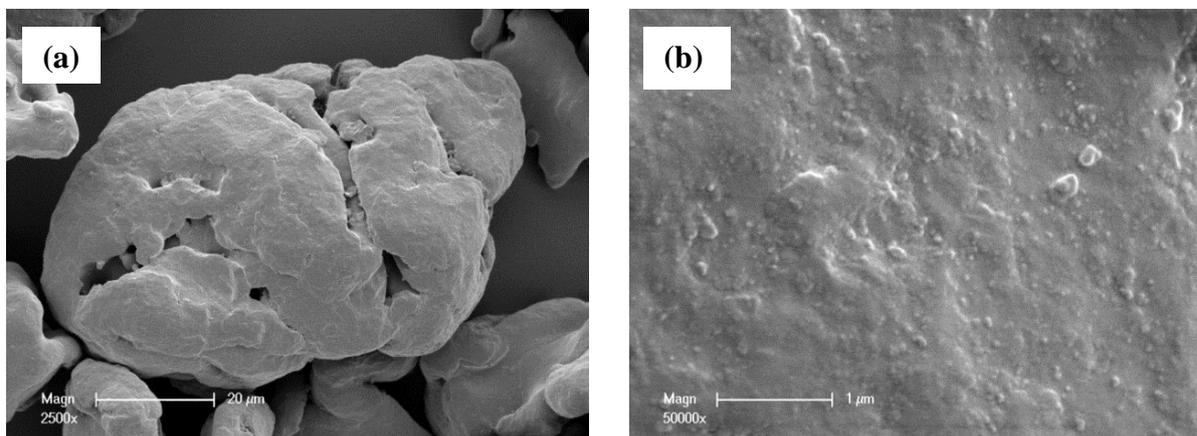


Figure 2.40 SEM images of (a) the MH300.29 grade coated with Scotchgard® (b) finer detail of (a).

2.8.6 Surface features associated with physically coating the MH300.29 particles with Rhodasil®/SiO₂-nanoparticles

As a further benchmark, a sample (100g) of MH300.29 was sent to the Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece for surface modification by a Rhodasil®/SiO₂-nanoparticle film (Manoudis *et al.* 2008). The SEM image of these coated particles, Figure 2.41, is consistent with their previously published data and, interestingly, is intermediate between the above TMS and Oleophobol® surfaces. Thus this surface has regions of granular nano-texture and regions of smoothness, see Table 2.8.

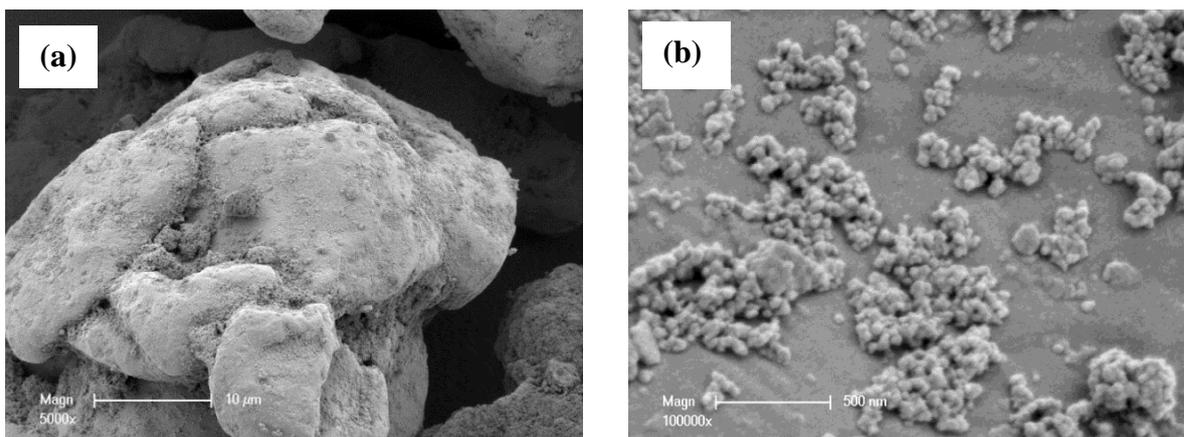


Figure 2.41 SEM images of MH300.29 particle coated with (a) Rhodosil®/SiO₂ (b) the finer detail of image (a). Shows around 50% nano-rough granulation (SiO₂ nanoparticles (~ 50nm) on a smooth surface.

Table 2.8 Qualitative summaries of the characteristics of the surface-modified iron particles.

Surface	MH300.29	A100S	A40S
Uncoated	Sizeable micro cavities and voids, surface otherwise smooth.	No micro cavities or voids. Extensive nano-pitting of surface.	Micro-rough with pitting & protuberances.
TMS	Dense granular, granular, nano-rough surface, estimated granule size 20-50 nm. Expect enhanced surface area and surface hydrophobicity.	Less dense and less uniform (than MH300.29), granular, nano-rough surface, estimated granule size 50-200 nm. Expect enhanced surface area and hydrophobicity.	-
Oleophobol®	Smoothing effect, obliteration of micro cavities and voids, no evidence of nano-roughness or granulation.	Micro-roughness estimated from 10-50 μm and nano-rough, non-uniform, granulation estimated from 50-1000 nm.	Micro-roughness estimated from 10-50 μm and nano-roughness, non-uniform, granulation estimated from 50-1000 nm.
Scotchgard®	Smooth conformal surface. Essentially nano-smooth with some sparse granulation.	-	Conformal coating showing micro-rough hydrophobic surface. Essentially nano-smooth with some sparse granulation.
Rhodosil®/SiO₂	~50% coverage of nano-rough granulation (SiO ₂ nanoparticles ~50 nm) on a smooth background surface.	-	-

2.9 Relating the nature of the different SEM surfaces to the various removal isotherms

For each of the functionalized and coated surfaces described above, see Scheme 2.1, the corresponding isotherms for the removal of JCO from duck feather clusters have been generated, compared and interpreted. The methods used for generating these isotherms have been described previously in Section 2.6.2.2. The full data sets are provided in Appendix 2.3. Representative comparative histograms are shown in Figures 2.42 - 2.44 and relevant comparative efficacy parameters for all plots, for initial ($P\%$ at $N=1$ and 2) and final ($P_o\%$) removals, are summarized in Tables 2.9 - 2.11.

2.9.1 A comparison between the surface features and the JCO removal isotherms for the untreated MH300.29 particles, the TMS-functionalized, Oleophobic[®]-coated, Scotchgard[®]-coated MH300.29 and Rhodosil[®]/SiO₂-coated particles

The SEM images of the surfaces to be compared are shown in Figures 2.34 (untreated and TMS-coated MH300.29), 2.36 (Oleophobic[®]), 2.40 (Scotchgard[®]) and 2.41 (Rhodosil[®]/SiO₂), *vide supra*. The relevant comparative isotherms, represented as histograms, are shown in Figure 2.42. The relative qualitative summaries of the surface characteristics are given in Table 2.8.

As can be seen in Figure 2.42 and Table 2.9, the initial removal of JCO (at $N=1$ and 2) was significantly lower for the surface treated particles than for the original particles. However, it can be seen that the final removal was significantly improved with the TMS functionalized particles and with the Oleophobic[®] coated particles.

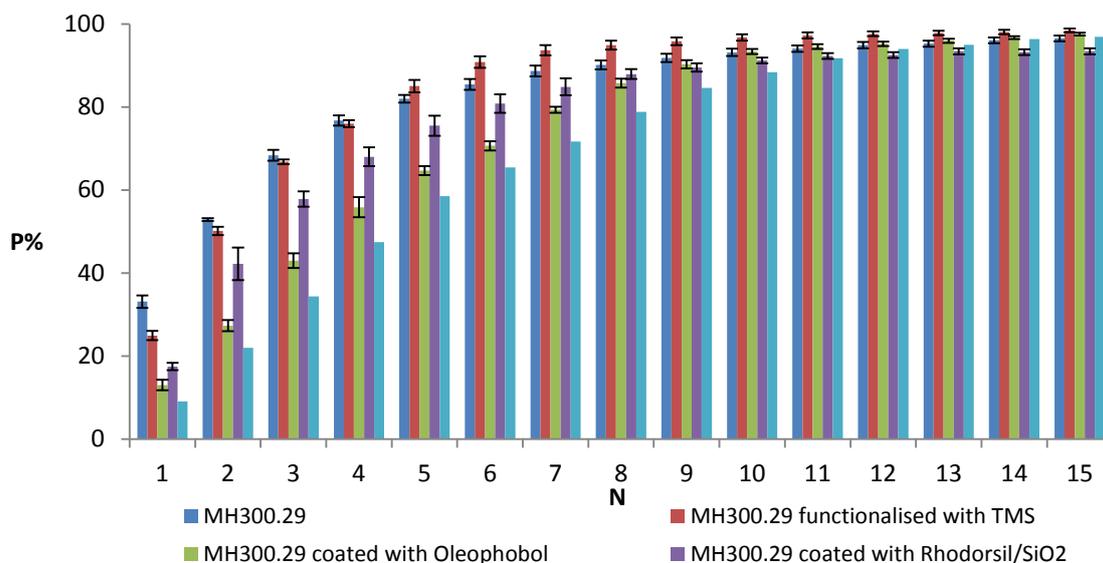


Figure 2.42 Comparison of JCO removal, P%, from duck feather clusters as a function of the number of treatments, N. Using - untreated MH300.29 particles, TMS-functionalized, Oleophobol[®]-coated, Rhodosil[®]/SiO₂-coated and Scotchgard[®]-coated MH300.29 particles. All experiments were conducted at 22 °C. Error bars represent the SE for five replicates, except for Scotchgard where single measurements were made – however, the reproducibility may be assumed to be similar to the others. Full data are provided in Table 16 and the individual data are provided in Table 17, 18 and 19 in Appendix 2.3.

Table 2.9 Comparison of the relevant % initial and final removal parameters for uncoated, TMS-functionalized, Oleophobol[®]-coated, Scotchgard[®]-coated and Rhodosil[®]/SiO₂-coated MH300.29 particles.

SURFACE	P% at N=1	P% at N=2	P ₀ %
TMS	24.9	50.2	98.5
Oleophobol [®]	13.0	27.3	97.6
Scotchgard [®]	9.2	22.0	96.9
Rhodosil [®] /SiO ₂	17.5	42.3	93.4
Uncoated	33.1	52.9	96.5

Initial Removal (N=1 & 2): Uncoated>TMS>Rhodosil[®]/SiO₂>Oleophobol[®]>Scotchgard[®]

Final Removal (P₀%): TMS>Oleophobol[®]>Scotchgard[®]≥Uncoated>Rhodosil[®]/SiO₂

These results suggest that the open cavities and voids (micro-rough surface) of the uncoated MH300.29 particles were more important for a better *initial* removal (at N=1 and 2) than the features of the fabricated surfaces. However, the importance of a degree of surface roughness (albeit nano-roughness) for initial removal was also suggested by the superiority of the TMS functionalized particles over the Oleophobol[®] or Scotchgard[®] coated particles. This was

supported by the fact that the Rhodosil[®]/SiO₂-coated particles were in-between these two in terms of initial removal - as was the surface texture, *vide supra*. The differences between the final removals were closer and more difficult to rationalize, although it would appear that a nano-rough, hydrophobic surface, as in the TMS functionalized particles, gave the best result. In this way, capillary effects *and* surface effects work together to yield a better overall removal.

2.9.2 A comparison between the JCO removal isotherms for untreated A100S particles, TMS-functionalized and Oleophobol[®]-coated A100S particles

Here, the relevant surfaces to be compared are shown in Figures 2.35 (untreated and TMS-coated A100S) and 2.37 (Oleophobol[®]). It was anticipated that the TMS-functionalized and the Oleophobol[®]-coated surfaces of the A100S particles would have the same characteristics as the surfaces shown in Figures 2.35 and 2.37 respectively. The relevant comparative isotherms, represented as histograms, are shown in Figure 2.43. The relative qualitative summaries of the surface characteristics are given in Table 2.8.

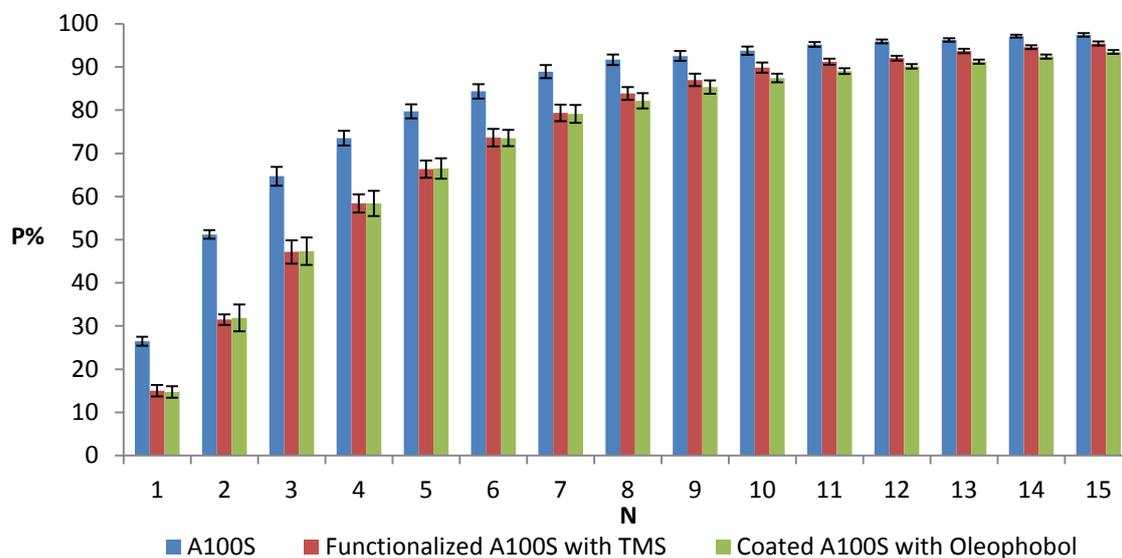


Figure 2.43 Comparison of JCO removal, P%, from duck feather clusters as a function of the number of treatments, N. Using - untreated A100S particles, TMS-functionalized and Oleophobol[®]-coated A100S particles. All experiments were conducted at 22°C. Error bars represent the SE for five replicates. Full data are provided in Table 20 and the individual data are provided in Tables 21, 22 and 23 in Appendix 2.3.

As can be seen from Figure 4.43 and Table 2.10, the initial removal of JCO (at N=1 and 2) was again significantly lower for the surface treated particles than for the original particles. It can also be seen that the final removal was also significantly less for the coated particles.

Table 2.10 Comparison of the relevant % initial and final removal parameters for uncoated, TMS-functionalized and Oleophobol[®]-coated A100S particles.

SURFACE	P% at N=1	P% at N=2	P_o%
TMS	15.0	31.5	95.5
Oleophobol[®]	14.7	31.9	93.5
Uncoated	26.5	51.2	97.4

Initial Removal (N=1 & 2): **Uncoated>TMS=Oleophobol[®]**

Final Removal (P_o%): **Uncoated>TMS>Oleophobol[®]**

It may be seen that, over the entire removal process, the original A100S particles were significantly more effective than the TMS functionalized or Oleophobol[®]-coated particles. In particular, the initial (N = 1 and 2) and final (P_o%) removals, Table 2.10, were significantly compromised by both surface treatments compared to the un-treated particles. The A100S particles do possess nano-roughness, Figure 2.35 (a), but this was due more to a “pitting” of the surface rather than the nano-protuberances evident on a TMS-functionalized surface, Figure 2.35 (b). Given that the initial removals were essentially the same for the nano-rough TMS and smooth Oleophobol[®]-coated surfaces, and that both of these surfaces were much less effective throughout than for the untreated particles, the “pitting” of the un-treated A100S particles could represent an special important structural feature for removal efficacy.

2.9.3 A comparison between the JCO removal isotherms for Oleophobol[®]-coated and Scotchgard[®]-coated A40S particles

Here, the relevant surfaces to be compared are shown in Figures 2.38 (a) (uncoated A40S), 2.38 (b) (Oleophobol[®]) and 2.39 (a) & (b) (Scotchgard[®]). The Oleophobol[®]-coated A40S particles appeared to be conformally coated displaying the micro-roughness of the original. In fact, the surface of the un-treated A40S can be described as considerably micro-rough, with both pitting and protuberances. This micro-roughness was estimated to be in the range of ~ 10-50 μm. At a finer level, the surface appeared to possess nano-roughness granulation in the

range of ~ 50-1000 nm. The Scotchgard[®]-coated A40S particles also displayed a degree of conformality but the surface was noticeably smoother than for Oleophobol[®] - both at the micro and the nano levels. Notably, this was also the case for the Scotchgard[®]-coated MH300.29 particles, Figure 2.40, where strict conformality was observed and the surface was quite smooth, also both at the micro and nano levels.

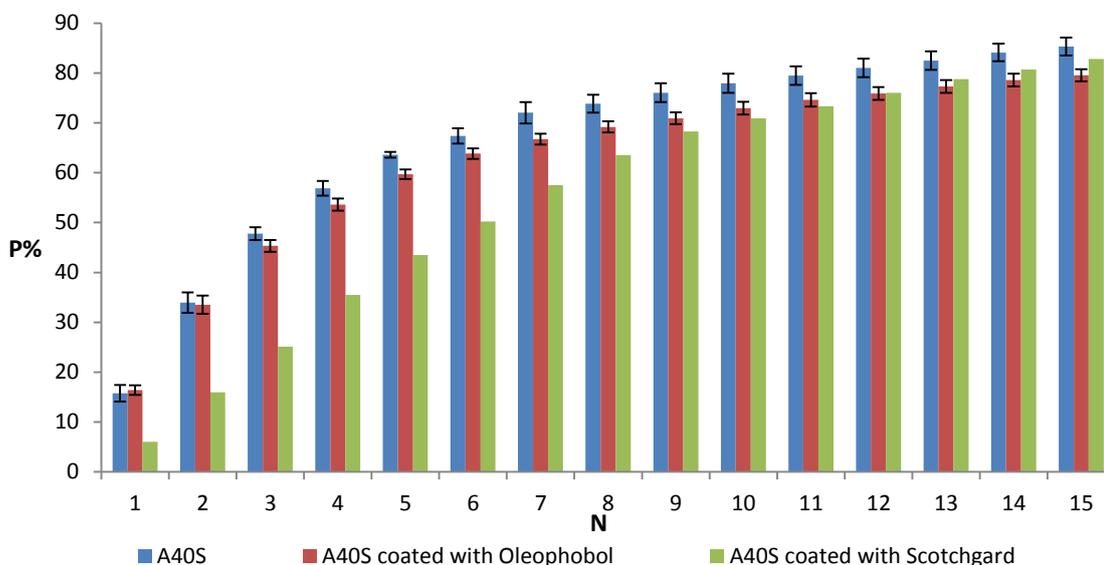


Figure 2.44 Comparison of JCO oil removal, P%, from duck feather clusters as a function of the number of treatments, N, using uncoated A40S particles, Figure 2.38 (a), Oleophobol[®]-coated A40S particles, Figure 2.38 (b) and Scotchgard[®]-coated A40S particles, Figure 2.39 (a) & (b). All experiments were conducted at 22 °C; error bars represent the SE for five replicates. Full data are provided in Table 24 in Appendix 2.3. The individual data are provided in Table 15 in Appendix 2.1 and Table 25 in Appendix 2.3.

Table 2.11 Comparison of the relevant % initial and final removal parameters for uncoated, Oleophobol[®]-coated and Scotchgard[®]-coated A40S particles.

SURFACE	P% at N=1	P% at N=2	P _o %
Oleophobol [®]	16.4	33.5	79.6
Scotchgard [®]	6.0	15.9	82.8
Uncoated	15.8	33.9	85.3

Initial Removal (N=1 & 2): Uncoated=Oleophobol[®]> Scotchgard[®]

Final Removal (P_o%): Uncoated> Oleophobol[®]≥Scotchgard[®]

The relevant comparative isotherms, represented as histograms, are shown in Figure 2.44. Focussing initially on the Oleophobol[®]-coated particles, it may be observed that for the initial removals at N=1 and N=2, there were no significant differences to the uncoated particles. Given that these particles, with an average particle size of ~280 µm, were considerably larger than the A100S (~94 µm) and MH300.29 (~41 µm), and that the surface of the un-treated particles was considerably micro-rough, these results could be explained by the Oleophobol[®]-coating actually being more conformal in this case – rather than smooth and obliterating - as with the smaller particles. This was confirmed by the SEM images. The fact that the removal for the untreated particles becomes superior at higher treatment levels could suggest that micro-roughness is actually less desirable with respect to final removal than a hydrophobic character. This is consistent with the previous comparisons.

2.9.4 The effect of increasing particle size whilst maintain the same coating

The above data may be arranged in different ways in order to glean further information. Thus Tables 2.12 shows the effect on the key parameters of increasing the uncoated particle size and Tables 2.13 - 2.15 compare these parameters for different sizes of the TMS-functionalized and the Oleophobol[®] and Scotchgard[®]-coated particles. A composite of all the key parameters is given in Table 2.16.

Table 2.12 Effect on key parameters of particle size for uncoated parameters

PARTICLE	P% at N=1	P% at N=2	P₀%
MH300.29 (~41µm)	33.1	52.9	96.5
A100S (~94 µm)	26.5	51.2	97.4
A40S (~280 µm)	15.8	33.9	85.3

The data of Table 2.12 show that, as expected, increasing the particle size tends to compromise the removal overall. However, this data also illustrates that other factors are at play (since doubling, tripling or more the particle size does not lead to correspondingly large changes in removal efficacy). Thus the logarithmic relationship of surface area to particle size, see Figure 2.22, and the different surface textures/features, Table 2.8, also play a role, *vide supra*.

Table 2.13 Effect on key parameters of particle size for TMS-functionalized parameters

PARTICLE	P% at N=1	P% at N=2	P_o%
MH300.29	24.9	50.2	98.5
A100S	15.0	31.5	95.5

For Table 2.13, the two surfaces are very similar and the differences here probably, predominantly, reflect the effect of relative particle size. Thus comparisons of this kind provide a benchmark of sorts. Thus increasing the particle size by a factor of ~ 2.3 reduced initial removal by ~ 1.6, all else being equal. Given this, “all else” is obviously not equal with reference to the situation represented by Table 2.12.

The fact that the final removals in Table 2.13 remain high and fairly close in value reflects the importance of the surface hydrophobicity rather than capillary effect at the final removal stages.

Table 2.14 Effect on key parameters of particle size for Oleophobol[®]-coated parameters

PARTICLE	P% at N=1	P% at N=2	P_o%
MH300.29	13.0	27.3	97.6
A100S	14.7	31.9	93.5
A40S	16.4	33.5	79.6

With reference to Table 2.14, a size effect was not apparent at all for the initial removals in these cases, all of which are compromised by this coating - which was characterized by hydrophobic micro-roughness. The seriously compromised final removal for the A40S was more difficult to rationalize although it was possible that at this size, given the micro-rough surface, that actual surface-to-surface contact could be compromised.

Table 2.15 Effect on key parameters of particle size for Scotchgard[®]-coated parameters

PARTICLE	P% at N=1	P% at N=2	P_o%
MH300.29	9.2	22.0	96.9
A40S	6.0	15.9	82.8

From Table 2.15 it may be seen that the initial removal in both cases was greatly compromised by the conformal hydrophobic coatings. In spite of the seven-fold increase in particle size the initial removals were probably very similar due to the effect of the micro-roughness of the A40S surface. As in Table 2.14, the micro-roughness of the large A40S could also compromise actual surface-to-surface contact, hence lowering the final removal.

Table 2.16 Jasmine Crude Oil (JCO) removal at treatments (N=1, N=2 (initial) and N=15 (final)) using surface modified iron particles.

Process	Chemicals & other	IP Grade	P% at N=1	P% at N=2	P _o %
Chemical Functionalization	TMS	MH300.29	24.9%	50.2%	98.5%
		A100S	15.0%	31.5%	95.5%
Particle coating	Oleophobol®	MH300.29	13.0%	27.3%	97.6%
		A40S	16.4%	33.5%	79.6%
		A100S	14.7%	31.9%	93.5%
	Scotchgard®	MH300.29	9.2%	22.0%	96.9%
		A40S	6.0%	15.9%	82.8%
	Other	MH300.29	17.5%	42.3%	93.4%
Untreated particle	-	MH300.29	33.1%	52.9%	96.5%
	-	A100S	26.5%	51.2%	97.4%
	-	A40S	15.8%	33.9%	85.3%

2.10 Conclusions

Some of the work of this thesis has been directed towards the further development of the “quick clean” concept in collaboration with an extended team of researchers. Thus laboratory work has been directed at identifying the key elements of a potential portable kit based on MPT and work has also been directed at the refinement of these key elements in consultation with industrial design specialists at Monash University and wildlife biologists at the Phillip Island Nature Parks. Thus the “backpack” concept has emerged and a prototype portable “non-backpack” kit has been devised and assembled. This has been stored at the Phillip Island Nature Parks Animal Hospital, together with back-up supplies, to enable rapid in-field testing in the event of an incident occurring in the locality.

Work on the development of the most suitable “quick clean” magnetic harvesting device has resulted in the development of the “wand”. This device has been tested on oiled Little Penguin carcasses with respect to several different oil types and was considered to be the

most appropriate device for incorporation into a quick clean kit. During these tests, the most effective method of implementation and contaminant removal has also been established.

Controlled experiments have demonstrated that pre-heating the magnetic particles significantly improved the initial and final removal efficacies. This has considerable implications for the treatment of oiled wildlife in cold environments.

Previous investigations within the group on the effect of particle grade on removal have been extended to include a wide range of different oil types. These results demonstrate the profound effect that particle grade (and hence the particle size distribution and the surface characteristics) has on the initial removal of various oil types. The results also indicate that the final removal was much less sensitive to particle grade for lower viscosity oil, but initial removal was sensitive for both high and low viscosities. Thus in selecting the best particle grade for a particular application, the viscosity of the oil must also be taken into consideration. Thus it was shown that for the medium to high viscosity oils AMCO and JCO the preferred grade for initial removal is MH300.29 but for the low viscosity oil DO, the preferred grade is ASC300

Other factors that affect contaminant removal, especially the initial removal, such as the modification of the particles themselves (particle size distribution, surface properties, surface coating) have been investigated. Thus it has been demonstrated that, in general, a greater initial and final removal was achieved for smaller particles and for lower viscosity contaminants. A more detailed investigation into the dependency of initial contaminant removal on the average particle size and particle size distribution was also undertaken. It may be seen that for low to medium viscosity oil, the initial removal tended to decrease with an increase in average particle size. However, for more viscous oil, the data was clustered into groups where the initial removal was distinctly reduced for smaller particles ($< \sim 41 \mu\text{m}$) and for larger particles ($> \sim 200 \mu\text{m}$).

These investigations suggest a lower limit on particle size, especially as the viscosity increases, below which the initial removal is seriously compromised. It is clear from the particle blending experiment that this effect is also related to the spread of the particle size distribution and a novel technique has been suggested whereby a given particle size distribution may be experimentally manipulated with respect to average particle size and the symmetry/spread of the distribution.

In addition to the detailed investigation of the effect of particle grade on the removal of a full range of oil types from feathers, the effect of other physical characteristics have been specifically examined with respect to the initial removal in particular. For example, the effect of particle “atomization” versus “sponginess” for different particle sizes has been investigated with respect to low, medium and high viscosity contaminants. This work has

built on previous work within the group where only medium viscosity oil had been considered, and clearly demonstrates that particle size, atomized versus spongy and oil type must all be carefully considered with respect to achieving an optimal initial removal. For example, it was demonstrated that for a particle size of $\sim 100\ \mu\text{m}$, spongy grades were better for the initial removal of light and medium viscosity contaminants whereas an atomised grade was preferable for heavy contaminants. On the other hand, for a particle size of $\sim 40\ \mu\text{m}$, atomized grades were better for the initial removal of light oil whereas a spongy grade was better for medium and heavy oils. It is notable that such detailed information, both qualitative and quantitative, may be obtained by the MPT technique.

An equally detailed investigation into the effect of various particle surface properties has been undertaken whereby different particle grades have been surface-functionalized or coated with hydrophobic materials. Such particles have been characterized by SEM and the qualitative surface features have been compared to the quantitative, initial and final, removal parameters derived from their respective contaminant removal isotherms. These studies clearly demonstrate the interplay between particle size and surface properties such as smoothing effects, conformal coating, particle cavities and voids, micro-pitting, micro- and nano-roughness, micro- and nano-granulation and surface hydrophobicity. In particular, the interplay between capillary and surface effects in relation to the initial and final stages of the removal process has been clearly demonstrated.

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Chapter 3: Mathematical model for the sequential pick-up of chemical contaminants by magnetic particles

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Chapter 3: Mathematical model for the sequential pick-up of chemical contaminants by magnetic particles

3.1 Introduction

MPT has well-established and emerging applications across a wide range of discipline areas (Safarikova and Safarik, 2001; Orbell *et al.* 2007). For example, in the medical arena, functionalized magnetic particles have been applied to diagnostics (Nakamura and Matsunaga, 1993), the separation of cancer cells (Wang *et al.* 1993) and the mechanical conditioning of bone cells *in vitro* (Cartmell *et al.* 2002). Magnetic particle technology has also been applied to water clarification and decolorization (Anderson and Priestley, 1983), sewage treatment (Priestley 1990; Booker *et al.* 1991), the separation of radioactive materials (Nunez *et al.* 1996), the removal of pesticides from water (Lawruk *et al.* 1993) and as catalyst supports (Wang *et al.* 2000). Other workers have reported that magnetite and maghemite particles exhibit high removal efficiency for the remediation of dispersants and oil (Chun and Park, 2001).

A more specific environmental application of this technology, that shows great promise in a series of published proof-of-principle experiments, involves the use of oil sequestering (zero valence) iron powder for the magnetic removal of oil from contaminated wildlife. This work demonstrated the effective removal of a wide range of oil contaminants, including an oil/seawater emulsion, from feathers and plumage (Orbell *et al.* 1999; Orbell *et al.* 2004), the ability to optimize contaminant removal from feathers by varying the physical properties of the iron particles themselves (Dao *et al.* 2006a), the effectiveness of “magnetic cleansing” for the removal of weathered and tarry contamination from feathers and plumage and the role of pre-conditioners in this process (Orbell *et al.* 2005; Dao *et al.* 2006) as well as the acute temperature dependency and the thermodynamics of the pick-up phenomenon (Dao *et al.* 2006b). The potential of this technology to remove oil contamination from the surface of rock has also been demonstrated (Orbell *et al.* 2007).

Traditional detergent-based methods for cleansing oiled wildlife remain very labor intensive and require expensive equipment and facilities (Massey 2006). The so-called “wet” detergent-based methods also damage the feathers necessitating lengthy periods of rehabilitation and the waste disposal is difficult to manage. On the other hand, the application of magnetic particle technology to this problem, *vide supra*, is a relatively inexpensive “dry” cleansing process that offers significant advantages, since iron powder is both non-toxic and a non-irritant and has been shown not to damage feather microstructure as a consequence of the cleansing process (Orbell *et al.* 1999). It also enables full control over both contaminant and cleansing agent and, importantly, offers portability of equipment that could enable a “quick clean” to be provided to the animal in the field (either upon first encounter or within a holding bay) thereby removing the worst of the contamination as quickly as possible. This would be particularly advantageous when, as is often the case, the contaminant contains toxic and/or corrosive components that can be ingested, inhaled or absorbed through the skin.

In order to facilitate the development and realization of the above field application, it is essential to develop a rigorous quantitative assessment of the relative efficiency of contaminant removal, especially with respect to initial contaminant removal (the “quick clean”). Depending upon a particular application, the characteristics of contaminant pick-up may be assessed experimentally by measuring the percentage of contaminant harvested by the particles, P , and plotting this as a function of a parameter such as the particle-to-chemical ratio, R , (non-sequential pick-up) (Orbell *et al.* 1997) or as a function of the number of treatments or applications, n , (sequential pick-up) (Orbell *et al.* 1999); the latter being more relevant to the use of this technology for the cleansing of oiled wildlife since the oiled substrate is saturated with the particles at each treatment.

With the primary aim of gaining greater insight into the physico-chemical basis for the pick-up phenomenon, previous work has derived a mathematical model for the *non-sequential* pick-up of a range of liquid organic compounds from a glass substrate, together with associated computer software that successfully applied the model to experimental data (Bigger *et al.* 2010). In developing the *non-sequential* model, it was recognized that real systems depart significantly from idealized behavior and so allowance was made within the model to account for this. Such an approach to processing the data also gives rise to a quantitative estimate of the extent to which a given system departs from idealized behavior.

This, in turn, is related to the efficiency of sequestration. The approach thus enables the relative pick-up efficiencies of various systems to be quantitatively determined, albeit for *in vitro* experiments in which the parameter P is monitored as a function of the variable R . However, this method does not provide information about the pick-up efficiency when such particles are applied *sequentially* to contaminated substrates such as feathers, fur or rocks, where the most convenient basis for experimentation is the number of successive treatments, n , rather than the R parameter.

Thus, in view of the need to assess the efficiency of pick-up of contaminants from various substrates on successive treatments with magnetic particles, and buoyed by the success of the previous non-sequential modeling, it was decided to explore the simplest mathematical model that would enable such experimental data to be processed and compared. To date there exists no quantitative method of assessment for such systems that enables a single parameter to be derived that comprehensively (i.e. based on all experimental data) reflects the efficiency of contaminant removal. Such an assessment and parameter will be essential in the future exploration and refinement of contaminant removal systems, such as the "quick clean" technology described previously.

The aim of this chapter is therefore to examine conceivable mathematical models that can be applied to real pick-up systems of this type and to test the respective merits of these when applied to a wide data range that is indicative of the extremes of expected system behavior. The experimental data set used here to test the mathematical model is a series of P versus n isotherms, representing the use of iron powder to magnetically remove eight different contaminant mixtures, ranging from low to high viscosity, from feather clusters.

3.2 Theory

Notation;

For the purpose of deriving and publishing the model, the notation used throughout the thesis has been modified as follows. Percentage removal 'P%' was defined as ' $P(n)$ ' and Number of treatment 'N' defined as ' n '.

3.2.1 The contaminant pick-up data fitting protocol

A set of $\{n, P(n)\}$ data pairs where n is the number of treatments and $P(n)$ is the cumulative percentage pick-up of contaminant upon treatment n in a contaminant pick-up experiment for a given contaminant-substrate system, can be empirically modeled by observing that: (i) the efficiency of pick-up as defined by the gradient of the $P(n)$ versus n plot decreases with an increasing number of treatments and (ii) such a plot passes through the origin. These experimental observations are the basis of the following two alternate approaches that have been identified and which lead to mathematical models that describe the variation of $P(n)$ with n .

3.2.2 Exponential model

An exponential model can be derived by assuming that the efficiency of pick-up of the remaining contaminant after n treatments is proportional to the amount of contaminant remaining to be picked up at that point in the treatment process. If the efficiency of pick-up is taken to be the gradient of the pick-up curve at any point in the treatment process, equation (1) applies under the assumption used as the basis of this model:

$$dP_1(n)/dn = -k_1P_1(n) \quad (1)$$

where $P_1(n) = P_\infty - P(n)$ which is the difference between P_∞ , the percentage pick-up after an infinite number of treatments and $P(n)$, the percentage pick-up after n treatments, and k_1 is a constant. The negative sign in this equation accounts for the decreased pick-up efficiency as n increases, which is in accordance with the experimentally observed behavior. Integrating equation (1) between the corresponding limits $\{n = 0, P_1(0) = P_\infty\}$ and $\{n, P_1(n) = P_\infty - P(n)\}$ yields:

$$P(n) = P_\infty[1 - \exp(-k_1n)] \quad (2)$$

In a previous study (Bigger *et al.* 2010) involving the derivation of a pick-up function, the initial pick-up efficiency was identified as a useful criterion for comparing the efficiencies of different systems. In the case of the current exponential model, this can be derived by

differentiating equation (2) with respect to n and finding an expression for the derivative at $n = 0$. This enables the initial pick-up efficiency for the ideal exponential model, v_0 , to be obtained as $v_0 = k_1 P_\infty$. This approach has the advantage of utilizing the entire $\{n, P(n)\}$ data set collected during a given contaminant pick-up experiment to derive a single number that reflects the pick-up efficiency of the system.

The model can be empirically adjusted to accommodate any deviation from idealized behavior that may be experimentally observed in the case of real systems by allowing the constant k_1 to vary with n in an empirical power law relation. Whence:

$$k_1 = f(n) = c_1 n^{m_1} \quad (3)$$

where c_1 and m_1 are constants. Equation (4) can be readily derived from equations (2) and (3) thus:

$$P(n) = P_\infty [1 - \exp(-c_1 n^{m_1+1})] \quad (4)$$

The incorporation of an empirical power law relation to account for non-idealized behavior renders a derivative function of equation (4) with respect to n that vanishes at $n = 0$ and so the derived function cannot be used to obtain the initial pick-up efficiency of a non-ideal system. Nonetheless, other efficiency parameters can be defined such as v_1 , the pick-up efficiency after one treatment (i.e. $n = 1$). In the case of an exponential model, v_1 can, in principle, be calculated from experimental data and is given by:

$$v_1 = [dP(n)/dn]_{n=1} = c_1(m_1 + 1)P_\infty \exp(-c_1) \quad (5)$$

3.2.3 Hyperbolic model

A hyperbolic model can be derived by assuming that the difference between the percentage pick-up after an infinite number of treatments, P_∞ , and the function $P(n)$ is inversely proportional to n in which case:

$$P_{\infty} - P(n) \propto 1/n \quad (6)$$

Re-arranging equation (6) and allowing for the function $P(n)$ to be finite at $n = 0$ gives rise to equation (7):

$$P(n) = P_{\infty} - k_2/(n + b) \quad (7)$$

where k_2 and b are constants.

Considering equation (7) and the required condition that $P(0) = 0$ it is clear that $b = k_2/P_{\infty}$ and so equation (8) can be derived:

$$P(n) = nP_{\infty}^2/(nP_{\infty} + k_2) \quad (8)$$

The derivative function of equation (8) with respect to n can be obtained and evaluated at $n = 0$ to obtain an expression for v_0' the initial pick-up efficiency for the ideal hyperbolic model. In this case $v_0' = P_{\infty}^2/k_2$.

Using a similar approach to the case of the exponential model, the deviation of a real system from idealized behavior can be taken into account by allowing k_2 to vary with n in an empirical power relation thus:

$$k_2 = f(n) = c_2 n^{m_2} \quad (9)$$

where c_2 and m_2 are constants. In this case, equation (8) can be re-written as follows:

$$P(n) = nP_{\infty}^2/(nP_{\infty} + c_2 n^{m_2}) \quad (10)$$

Similarly to the case of the non-ideal exponential model, the derivative of the non-ideal hyperbolic model equation vanishes at $n = 0$. Nonetheless, the derivative function of equation (10) with respect to n can be evaluated for $n = 1$ to render an expression for an efficiency parameter, v_1' :

$$v_1' = [dP(n)/dn]_{n=1} = c_2 P_\infty^2 (1 - m_2) / (P_\infty + c_2)^2 \quad (11)$$

Thus, v_1' is a single parameter that represents the pick-up efficiency after a single treatment in the case of the non-ideal hyperbolic model. Indeed, defined efficiency parameters such as v_0 , v_1 , v_0' and v_1' can be used as arbitrary measures to compare the efficiencies of different systems where the $\{n, P(n)\}$ data have been collected under standardized conditions.

3.3 Materials and methods

Jasmine Crude Oil (JCO) (viscosity, 682 cSt at 50°C) was supplied by Leeder Consulting, Victoria, Australia. Diesel was obtained from a commercial service station. Iron powder was supplied by Höganäs AB, Sweden, and was described by the manufacturer as "spongy annealed superfine" (Grade MH300.29). The feathers used in this study were the breast/contour feathers of the Mallard Duck (*Anas platyrhynchos*).

The JCO is a solid at ambient temperature and a stock quantity of 30 g was melted at 50°C (over a water bath) for the purpose of applying the more viscous contaminants to the feather clusters and for preparing Diesel/JCO mixtures. A series of these mixtures was prepared in order to access a range of contaminant viscosities, i.e. 0:100 (pure JCO), 20:80 (viscosity, 174 cSt at 22°C), 30:70, 40:60, 50:50, 60:40, 70:30 and 80:20, by volume. All contamination and removal experiments were subsequently conducted at 22°C.

Four feathers were tied into a cluster and weighed (f_1). The feather cluster was then dipped into a beaker of a liquid contaminant to achieve saturation. The cluster was allowed to drain on a tared Petri dish for 10 min prior to being re-weighed (f_2). The cluster was then removed from the dish and the residual mass, r_1 , was recorded. Hence, the mass of the contaminant-laden feathers, f_3 , for further experimentation is given by equation (12):

$$f_3 = f_2 - r_1 \quad (12)$$

At ambient temperature (22°C), the contaminated feathers were then completely covered with the iron powder in order for absorption and adsorption of the contaminant to occur. At least a

minute was provided for this although a previous study has indicated that the absorption/adsorption process was almost instantaneous (unpublished results). The contaminant-laden iron particles were then harvested from the feathers using a magnetic tester (Alpha Magnetics, Victoria, Australia). The stripped feather cluster was then reweighed (f_4). The percentage pick-up of the contaminant, P , was calculated in accordance with equation (13):

$$P = [(f_3 - f_4)/(f_3 - f_1)] \times 100\% \quad (13)$$

A number of applications, n , were performed until a constant value of P was achieved. Isotherms, such as that shown below in Figure 3.1, are generated by plotting $P(n)$ versus n .

3.4 Results and discussion

3.4.1 General considerations

To explore each of the above models, a computer program was written to read $\{n, P(n)\}$ data sets generated during contaminant pick-up experiments and to produce the best fit to the data in accordance with the model under investigation. The program incorporates a linear regression analysis to evaluate the c and m parameters where appropriate and consequently generate a $P(n)$ versus n isotherm that was fitted to the experimental data. The various models proposed above were applied to two cases that represent extreme system behavior with regard to the experimentally observed efficiency of contaminant pick-up.

The first case was the pick-up isotherm observed for the removal of 100% Jasmine Crude Oil (JCO) from duck feather clusters at 22°C using MH 300.29 iron particles. This system was representative of one with a relatively low efficiency where the function $P(n)$ gradually approached an asymptotic upper limit of close to 100% after *ca.* $n = 16$ contaminant removal treatments. The second case that was chosen was the isotherm for the removal of an 80:20 Diesel/JCO mixture from the same substrate and under the same experimental conditions. This system exhibited a very high pick-up efficiency where the function $P(n)$ rapidly approached the asymptotic upper limit after *ca.* $n = 1$ treatment.

Figure 3.1 shows plots of $P(n)$ versus n for the removal of 100% JCO and the 80:20 Diesel/JCO mixture from duck feather clusters at 22°C. The solid lines are the computer-generated fits to the data using the exponential model for an ideal system depicted by equation (2) with fit parameters. It is clear from the plots that the ideal exponential model fits neither set of experimental data satisfactorily despite the seemingly reasonable values of the regression coefficients calculated in the fitting routine using $\{n, \ln((1 - P(n))/P_\infty)\}$ transformed data in accordance with equation (2).

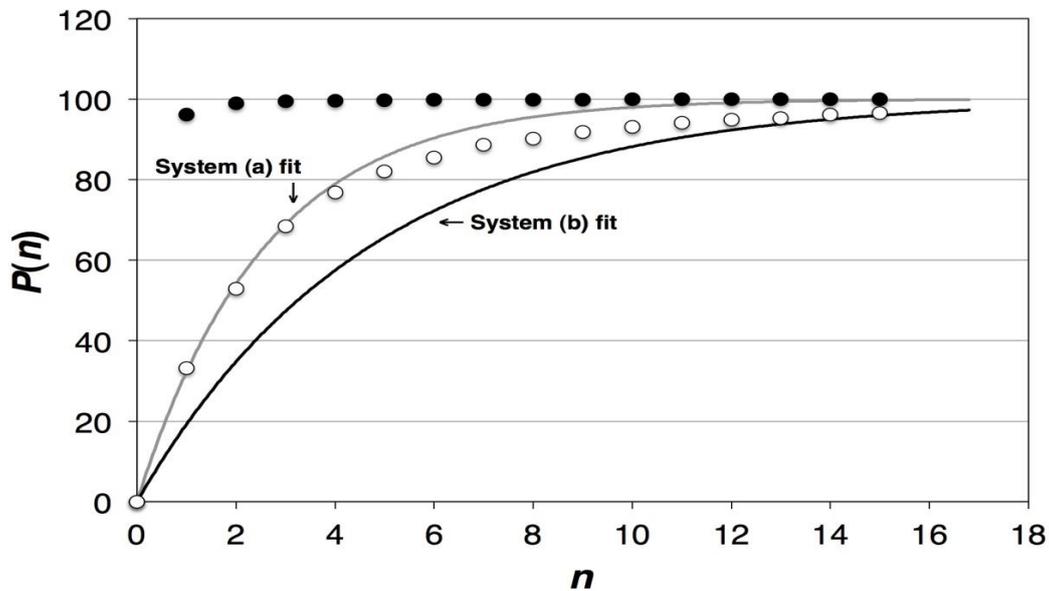


Figure 3.1 Plots of $P(n)$ versus n for the removal of: (a) 100% JCO (open circles) and (b) a 80:20 mixture of Diesel and JCO (filled circles) from duck feather clusters using MH300.29 iron particles at 22°C. Solid lines are the computer-generated fits to the data using the exponential model for an ideal system depicted by equation (2) with fit parameters $k_1=0.214$, $r^2 = 0.960$ (System (a)) and $k_1 = -0.253$, $r^2 = 0.922$ (System (b)). The raw data are provided in Table 1 in Appendix 3.1.

Making an allowance for non-ideal behavior in the exponential model by invoking a power law relationship for the variation of k_1 (see equations (3) and (4)) had little effect on the quality of fit of the experimental data. Figure 3.2 shows the fit that was achieved for the 100% JCO data when the non-ideal model was applied. The fit for the ideal model is also shown for comparison. These data suggest that although there is a slight improvement in the fit obtained by allowing for non-ideal behavior in the exponential model the fit remains quite poor suggesting that the exponential model was not applicable to these systems. Consequently, the pick-up efficiency defined as in, say, equation (5) may have limited value

for these systems. The regression coefficient calculated in the non-ideal exponential model fitting routine using the $\{\ln(n), \ln(\ln(P_\infty/(P_\infty - P(n))))\}$ transformed data in accordance with equation (4) suggests the fit was better than that obtained in the ideal case and this is reflected in the fitted line appearing slightly closer to the experimental data than that for the ideal case.

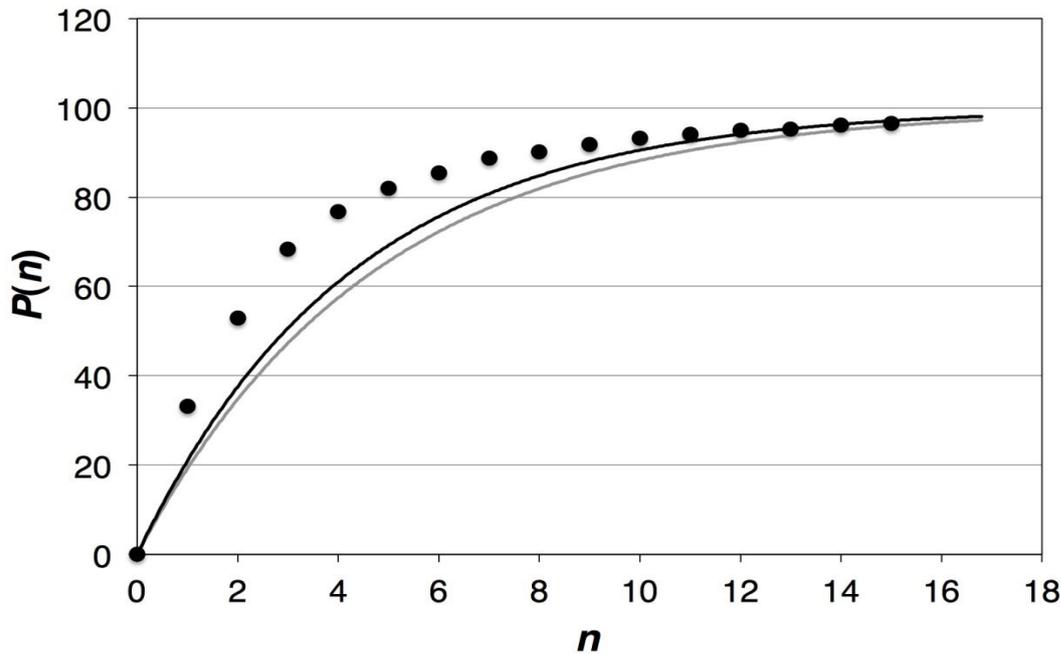


Figure 3.2 Plots of $P(n)$ versus n for the removal of 100% JCO from duck feather clusters using MH 300.29 iron particles at 22°C. The experimental data are fitted using the exponential model assuming: (a) an ideal system in accordance with equation (2) that produces fit parameters $k_1 = -0.214$, $r^2 = 0.960$ (grey solid line) and (b) a non-ideal system in accordance with equation (4) that produces fit parameters $m_1 = -0.238$, $c_1 = 0.462$ and $r^2 = 0.987$ (black solid line). The raw data are provided in Table 2 in Appendix 3.1.

Figure 3.3 shows plots of $P(n)$ versus n for the removal of 100% JCO and the 80:20 Diesel/JCO mixture from duck feather clusters at 22°C where the data have been fitted with the ideal hyperbolic model in each case (see equation (8)). It is clear that a much more satisfactory fit was achieved compared with the ideal and non-ideal exponential models. Nonetheless, the visual fit of the 100% JCO data in particular together with the regression coefficients calculated from the $\{n, nP_\infty(P_\infty - P(n))/P(n)\}$ transformed data in accordance with equation (8), suggests the ideal hyperbolic model still does not produce an optimal fit. Furthermore, the seemingly better visual fit of the 80:20 Diesel/JCO data is attributed to the apparently high removal efficiency exhibited by this system where the initial rapid rise in the $P(n)$ data is followed by little variation in those data that lie close to the 100% asymptote.

For these systems it appears that the pick-up efficiencies as defined by parameters such as v_0 may only be close approximations to what in reality are the true values. Thus a further refinement of the fitting model by allowing for a deviation from ideal behavior has been invoked in order to deliver a more acceptable fit to the data and thereby enable a more accurate assessment of pick-up efficiencies to be made.

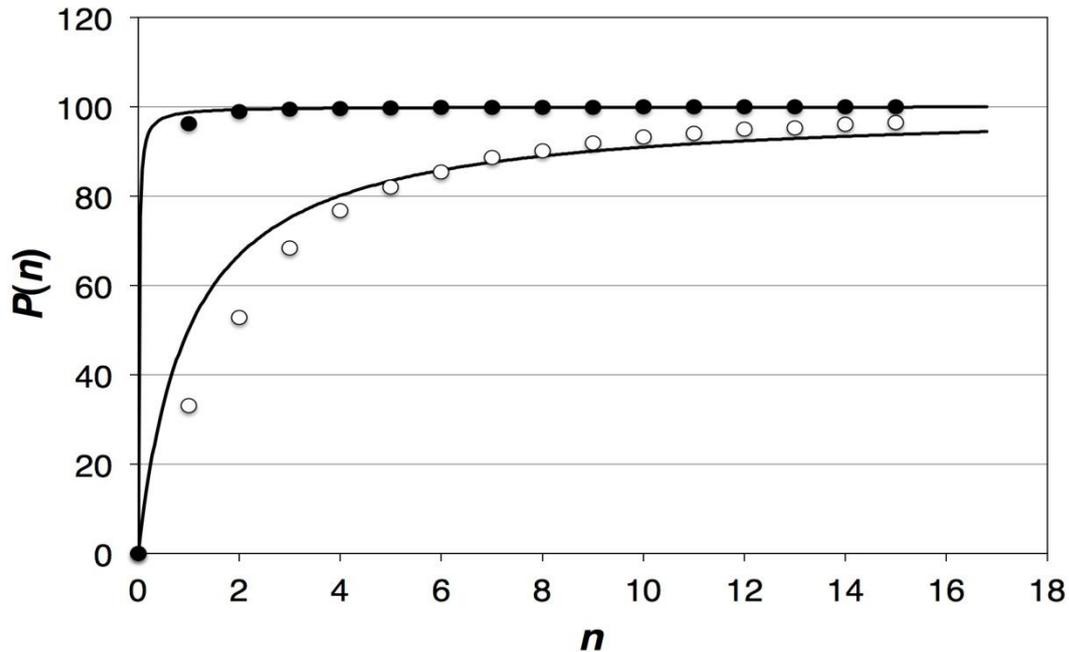


Figure 3.3 Plots of $P(n)$ versus n for the removal of: (a) 100% JCO (open circles) and (b) a 80:20 mixture of Diesel and JCO (filled circles) from duck feather clusters using MH 300.29 iron particles at 22°C. Solid lines are the computer-generated fits to the data using the hyperbolic model for an ideal system depicted by equation (8) with fit parameters $k_2 = 99.4$, $r^2 = 0.848$ (System (a)) and $k_2 = 1.31$, $r^2 = 0.723$ (System (b)). The raw data are provided in Table 3 in Appendix 3.1.

In contrast to the case of the exponential model the allowance for a deviation from ideal behavior *via* a power law relationship between k_2 and n (see equation (10)) produced a comparatively acceptable fit of the experimental data for the two extreme systems that are under investigation. This is apparent in Figure 3.4 where the non-ideal hyperbolic model has been applied to both the 100% JCO and the 80:20 Diesel/JCO data. Furthermore the regression coefficient data calculated from the $\{\ln(n), \ln(nP_\infty(P_\infty - P(n))/P(n))\}$ transformed data in accordance with equation (10) showed a considerable improvement on the respective data generated from the ideal hyperbolic model depicted in Figure 3.4. In order to investigate further the apparent better fit of the non-ideal hyperbolic model compared to the ideal hyperbolic model a statistical analysis was performed on the calculated average regression

coefficient obtained when each model was applied in fitting each of the contaminant systems studied. At the 95% confidence limit the average regression coefficients are $r^2_{av}(\text{ideal hyperbolic model}) = 0.579 \pm 0.038$ and $r^2_{av}(\text{non-ideal hyperbolic model}) = 0.816 \pm 0.034$ which demonstrates that the better fit obtained with the non-ideal hyperbolic model is statistically significant. The above observations collectively suggest that of the various models examined, the non-ideal hyperbolic model provided the best fit to the experimental data and thus equation (11) might be applied to such experimental data in order to evaluate contaminant pick-up efficiencies in these systems.

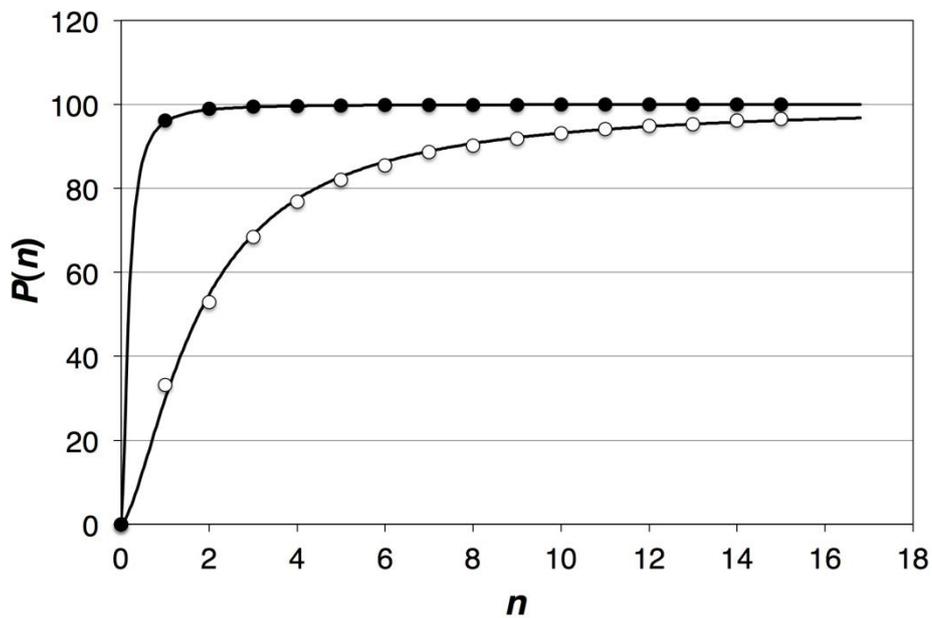


Figure 3.4 Plots of $P(n)$ versus n for the removal of : (a) 100% JCO (open circles) and (b) a 80:20 mixture of Diesel and JCO (filled circles) from duck feather clusters using MH 300.29 iron particles at 22°C. The experimental data have been fitted using the hyperbolic model assuming a non-ideal system in accordance with equation (10). Fit parameters: $m_2 = -0.507$, $c_2 = 236$, $r^2 = 0.972$ (System (a)) and $m_2 = -0.761$, $c_2 = 4.43$, $r^2 = 0.834$ (System (b)). The raw data are provided in Table 4 in Appendix 3.1.

In order to investigate the latter assertion more fully the computer fitting software was used to generate an expanded section of the non-ideal hyperbolic fitted function for the 100% JCO system in the range $n = 0$ to 2.0. These data are shown in Figure 3.5 and illustrates clearly the sigmoidal nature of the function particularly for systems such as the 100% JCO that exhibit relatively low pick-up efficiency at a correspondingly low number of treatments. Thus the pick-up efficiency as defined by the gradient of the fitted function close to the origin will not give a true indication of the efficiency of the system. For example, the gradient of the fitted

function in Figure 3.5 at the theoretical point $n = 0.04$ which is denoted $[dP(n)/dn]_{n=0.04}$ is significantly less than that at the point of inflexion of the function, $[dP(n)/dn]_{\max}$. Furthermore, as the fitted function changes along with the different systems under investigation the inflexion point may move particularly with regard to its abscissa value. In such cases equation (11) will render an inaccurate estimate of the pick-up efficiency. In recognition of these features of the non-ideal hyperbolic fitted function the computer analysis software was modified to include it finding the maximum gradient, $v_{\max} = [dP(n)/dn]_{\max}$, and reporting this as the preferred measure of the pick-up efficiency of the system.

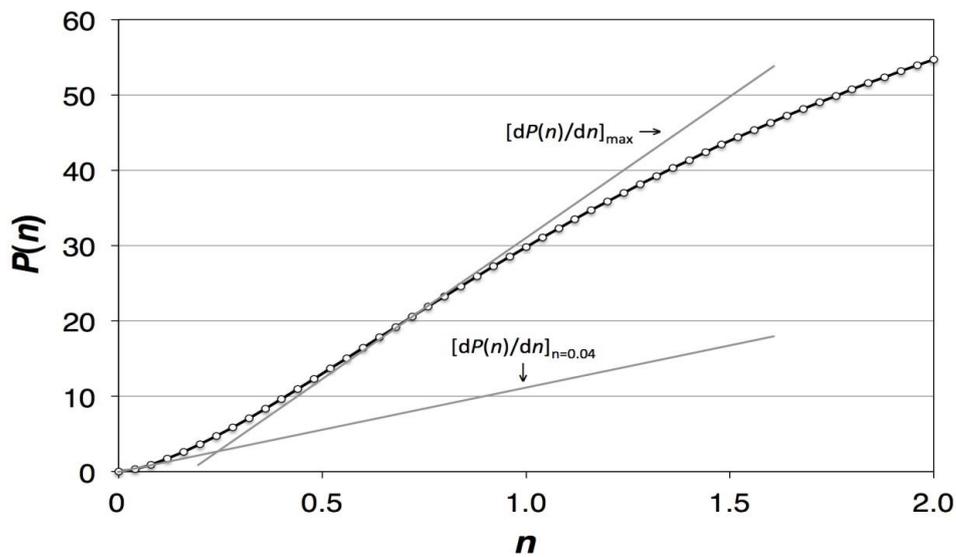


Figure 3.5 Expanded plot of the computer fitted curve for System (a) in Figure 4 showing the sigmoidal nature of the function depicted by equation (10). The small open circles are the data points generated by the program in its iterative calculations performed at a step interval of $\delta n = 0.04$ units. The solid line is the continuous function drawn through the points. The raw data are provided in Table 5 in Appendix 3.1.

The hyperbolic model is based on the assumption that the difference between the percentage pick-up after an infinite number of treatments, P_{∞} , and the function $P(n)$ is inversely proportional to n , the number of treatments in the removal process. Such a mathematical treatment is consistent with a mechanism involving a sequential series of equilibria where at each step the contaminant is partitioned between the surfaces of the substrate and the high surface area iron powder particles. This process can be viewed as being analogous to a Soxhlet extraction process in which a target compound is shifted from one phase to another (or from one physical location to another) in a sequence of cycles each of which involves the setting of a new equilibrium that is governed by a constant partition coefficient at constant

temperature. For the current system, it is suggested that the removal of the contaminant mixture from the surface of the substrate (feathers) is achieved *via* a surface adsorption/absorption phenomenon that is, in turn, driven by the lowering of the surface free energy of the iron particles when the contaminant mixture is transferred. However, the nature of the experiments performed in the current work clearly cannot unequivocally ascertain this mechanism.

Under some circumstances, the point of inflexion identified in Figure 3.5 might be interpreted as a transition from one type of mechanism to another. However, in reference to the current work it is suggested that the point of inflexion is an inherent feature of the non-ideal mathematical fitting function and does not necessarily indicate a transition in the removal mechanism. Evidence for this is twofold: firstly, over the extensive range of system viscosities studied in the current work the inflexion point only becomes significant for high viscosity (low removal efficiency) systems and secondly, when the point of inflexion is of significance with regard to calculating the initial pick-up efficiency, it occurs at $n < 1$. This is clearly in the theoretical domain as far as assigning a physical meaning to the result is concerned and would thus suggest that a single mechanism prevails for $n \geq 1$.

The variation of the non-ideal hyperbolic model fitting parameters c_2 and m_2 together with the maximum pick-up efficiency between the two extreme limits of 100% JCO (i.e. zero % (v/v) Diesel) and 80:20 Diesel/JCO (i.e. 80% (v/v) Diesel) was explored for the removal of a selection of different Diesel/JCO mixtures from duck feather clusters using MH 300.29 iron particles at 22°C. The results are given in Table 3.1 along with the regression coefficient r^2 pertaining to each analysis. In analyzing the experimental data to produce Table 3.1, it became apparent that wide variability in the calculated c_2 and v_{\max} parameters in particular occurred in systems of high pick-up efficiency, requiring in some cases experimental measurements to be reproducible to within *ca.* $\pm 0.2\%$ in order to obtain meaningful trends. This is consistent with the observation that in highly efficient systems $P(n)$ rises rapidly to *ca.* 100% after only one or two treatments rendering the few data in this region of the pick-up isotherm critical in the ultimate determination of the fit parameters. These observations are reflected in the apparent deviation from the overall trend exhibited by the 70% (v/v) Diesel data in Table 3.1.

Table 3.1 Non-ideal hyperbolic model parameters c_2 and m_2 together with the maximum pick-up efficiency v_{\max} and regression coefficient for the removal of various Diesel/JCO mixtures from duck feather clusters using MH 300.29 iron particles at 22°C.

% Diesel (v/v)	c_2	m_2	v_{\max}	r^2
0	236.00	-0.507	34.5	0.972
20	175.00	-0.671	43.9	0.967
30	120.00	-0.615	54.6	0.977
40	55.30	-0.548	89.1	0.827
50	19.20	-0.496	182.0	0.850
60	8.87	-0.462	317.0	0.655
70	5.03	-0.122	474.0	0.443
80	4.43	-0.761	354.0	0.834

Consideration of equation (10) in comparison with the ideal equation (8) reveals that the parameters c_2 and m_2 both express the deviation of a given system from idealized behavior with parameter c_2 expressing the "magnitude" or indeed "efficiency" with which this occurs and the parameter m_2 expressing the "order" of the deviation. In the limiting case where $m_2 = 0$, equation (10) collapses to give equation (8) with $c_2 = k_2$ and the system is considered to behave ideally. The data in Table 3.1 indicate that the parameter c_2 is large in cases where the system exhibited a relatively low efficiency and vice versa. This apparent correlation was tested further by plotting the reciprocal of v_{\max} as a function of c_2 and is shown in Figure 3.6.

It is clear from Figure 3.6 that the two parameters v_{\max} and c_2 are highly correlated suggesting that the parameter c_2 is also a measure of the pick-up efficiency of a given system. The data in Table 3.1 also suggest that the value of m_2 across the various runs fluctuates around a mean of $m_2 = -0.52 \pm 0.13$, implying almost an inverse square root order exists with respect to the variable n , the number of treatments. It remains to be seen whether the value of m_2 fluctuates within these limits for other systems and whether values of c_2 outside the limits observed in this study are possible indicating the existence of more extreme system behavior. However, this is the subject of ongoing investigations in our laboratory.

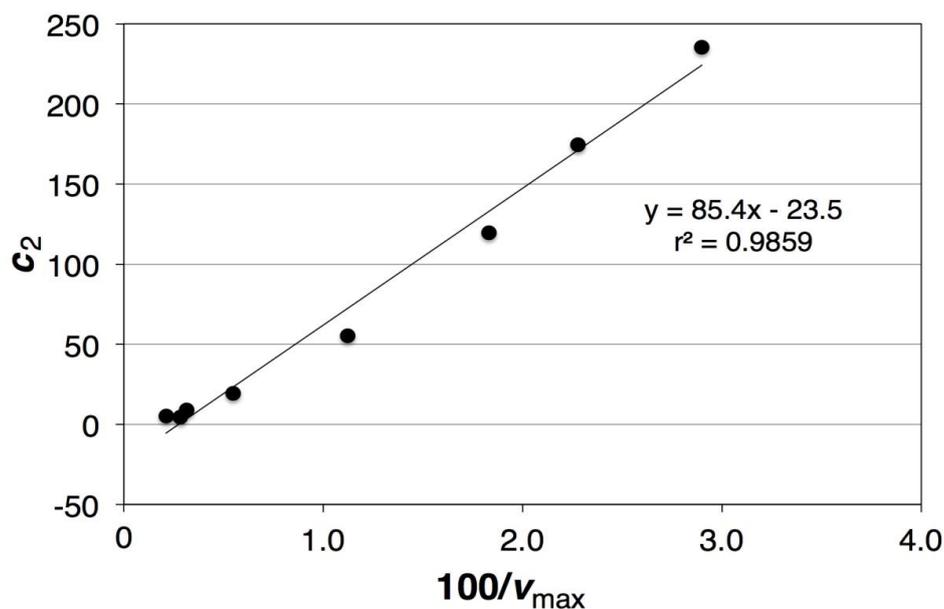


Figure 3.6 Plot of c_2 versus $1/v_{\max}$ for the systems given in Table 3.1. The linearity of this plot confirms high extent of correlation between the parameter c_2 and the reciprocal of the maximum pick-up efficiency.

3.4.2 The correlation of experimental and modelled oil removal efficiency parameters

As described throughout this thesis, experimentally, the efficiency of oil removal from a feather substrate was assessed *via* a number of separate, as well as composite, parameters. These parameters were: $P_0\%$ - which is a measure of the optimum oil removal that was finally achieved (where the characteristic removal isotherm reaches a horizontal plateau); N_{90} , N_{95} or N_{99} - representing the effective number of treatments where 90%, 95% or 99% oil removal is achieved (measuring, to some extent, the initial phase or the ‘acceleration’ of removal) and the ratio $P_0\%/N_{90,95,99}$ - which was used to represent an ‘overall’ efficiency parameter that incorporates both the final removal and the initial phase of removal. The ‘initial’ removal (which is of special relevance for a quick clean) may also be represented by $P\%$ at the arbitrary values of $N = 1, 2$ or 3 .

It was of interest to ascertain how efficiency parameters derived from the mathematical modeling described herein (particularly the parameter c_2), relate to these experimentally derived efficiency parameters. Therefore, the values of c_2 that are derived for the series of Diesel/JCO mixtures described above have been correlated against the other experimental

parameters as follows. For reference, the eight experimental isotherms employed for benchmarking, the mathematically generated isotherms and the superimposed experimental/mathematically generated isotherms are shown in Figures 3.7, 3.8 and 3.9 respectively. The individual mathematical best fits are represented in Appendix 3.2.

In relation to the parameters N_{90} , N_{95} or N_{99} , their evaluation from the experimental data is sometimes complicated by an irregular curve profile due to experimental error. This may be overcome by using the N_{90} , N_{95} or N_{99} values obtained from the mathematically modeled curves. This may be justified by the observation based on the above experiments that there is an excellent correlation between the N_{90} , N_{95} or N_{99} experimental values and the N_{90} , N_{95} or N_{99} values derived from the modeled curves¹². For wider investigations where these parameters are used, this is a potentially very useful application of the mathematical modeling.

¹² These relationships are varying in Figure 3.15, 3.16 and 3.17.

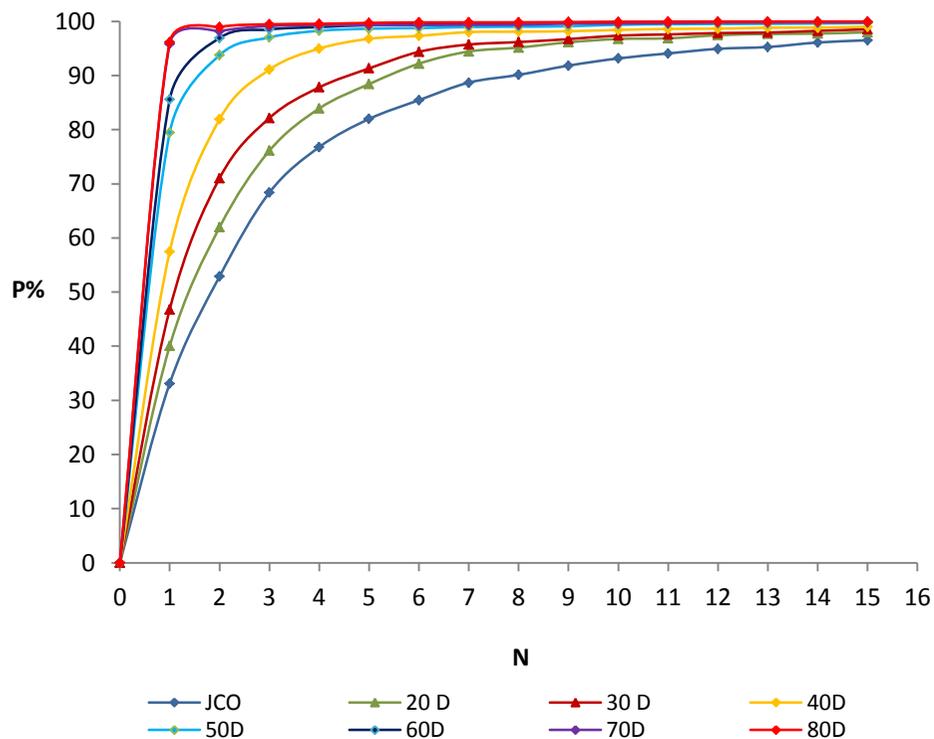


Figure 3.7 Comparisons between the percentage removal, P%, of Jasmine Crude Oil (JCO) and series of JCO/Diesel mixtures from duck feathers as a function of the number of treatments, N, at 22 °C. The raw data are provided in Table 6 in Appendix 3.1

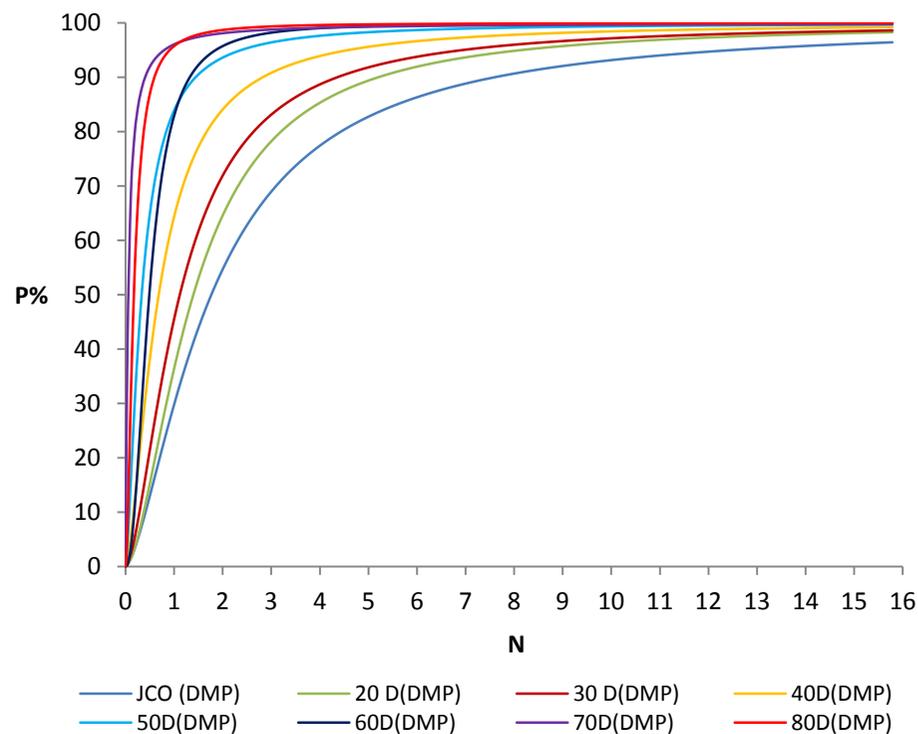


Figure 3.8 Comparisons between the percentage removal, P%, of Jasmine Crude Oil (JCO) and series of JCO/Diesel mixtures, analyzed with the Data Modeling Program (DMP) (mathematically generated isotherms) from duck feathers as a function of the number of treatments, N, at 22 °C. The raw data are provided in Table 7 in Appendix 3.1

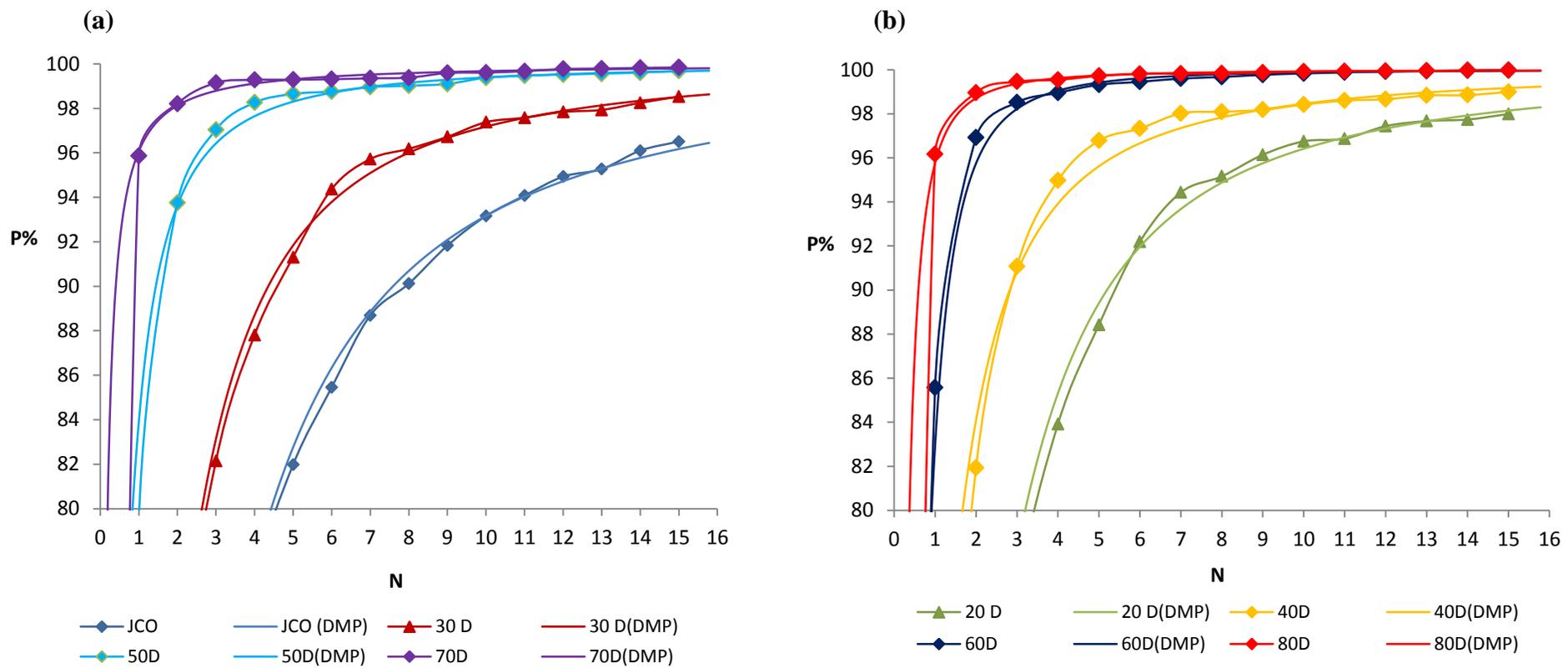


Figure 3.9 (a) and (b) Graphical representation of the fit between the experimental data of Figure 3.7 and the mathematically generated isotherms of Figure 3.8. The raw data are provided in Table 8 in Appendix 3.1.

3.4.2.1 P₀% Correlation with c₂

Figure 3.10 shows the correlation between P₀% and the parameter c₂. Overall, there appears to be a good correlation between these parameters, suggesting that c₂ carries information relating to the final removal efficiency, at least for values of P₀% that are less than approximately 99.69%.

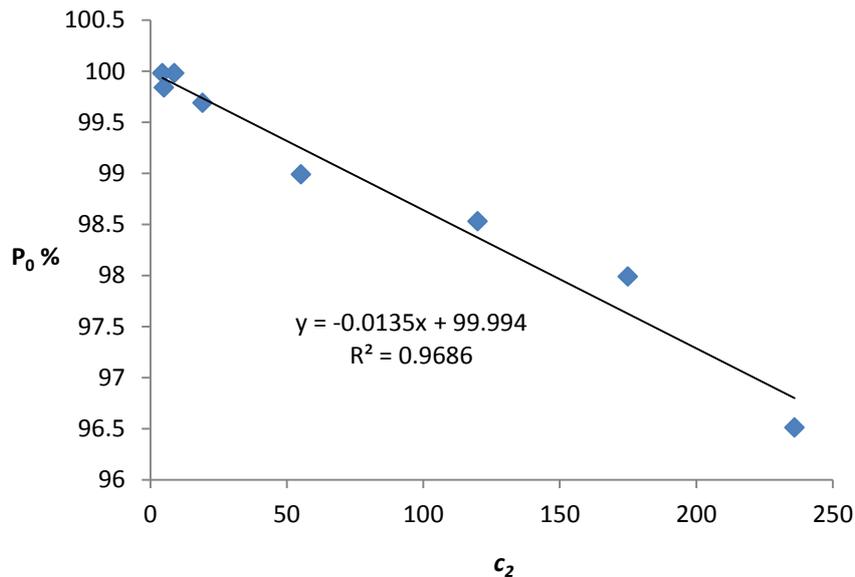


Figure 3.10 Plot of correlation between P₀% and c₂ for 100% JCO and the seven blends of diesel and JCO tested. The data are presented in Table 9 in Appendix 3.1.

3.4.2.2 N₉₀, N₉₅ or N₉₉ Correlation with c₂

Figures 3.11, 3.12 and 3.13 show an excellent correlation between these N₉₀, N₉₅, N₉₉ and c₂, suggesting that the latter parameter is also a good representation of the overall removal efficiency, including the initial stage of removal. In this regard, c₂ also correlates very well with the experimental parameters that are used to represent the ‘initial’ removal such as 1/P% at N = 2, Figure 3.14.

The initial removal is important to optimize for the quick clean approach that has been developed within this project.

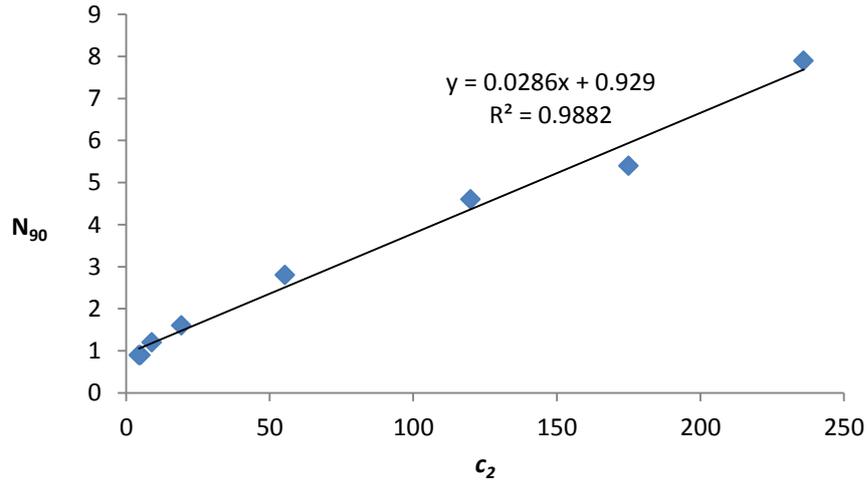


Figure 3.11 Plot of correlation between $N_{95}\%$ and c_2 for 100% JCO and the seven blends of diesel and JCO tested. The raw data are provided in Table 10 in Appendix 3.1.

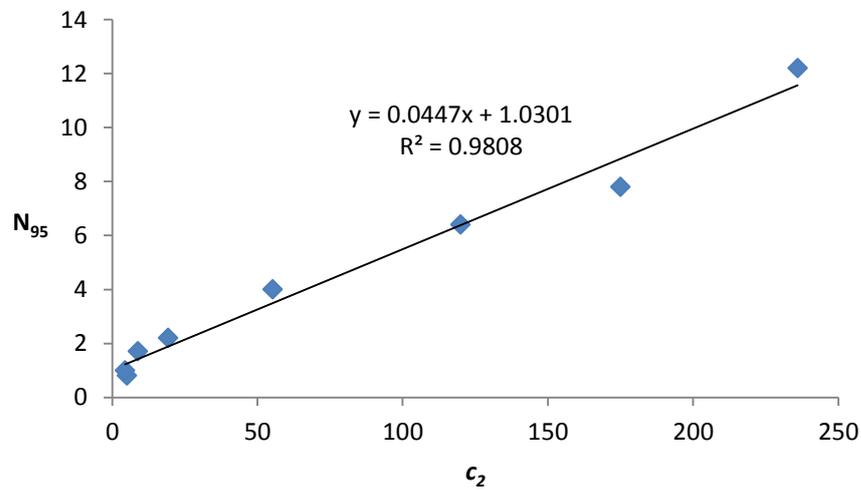


Figure 3.12 Plot of correlation between $N_{90}\%$ and c_2 for 100% JCO and the seven blends of diesel and JCO tested. The raw data are provided in Table 11 in Appendix 3.1.

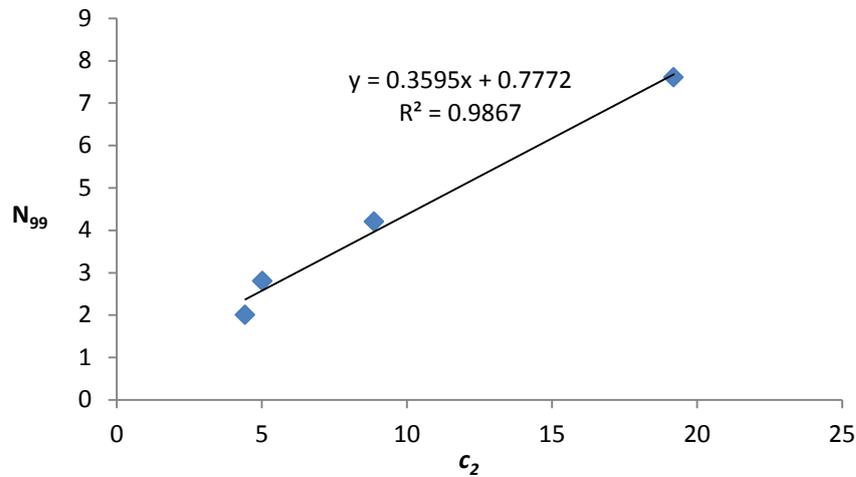


Figure 3.13 Plot of correlation between $N_{99}\%$ and c_2 for 100% JCO and the seven blends of diesel and JCO tested. The raw data are provided in Table 12 in Appendix 3.1.

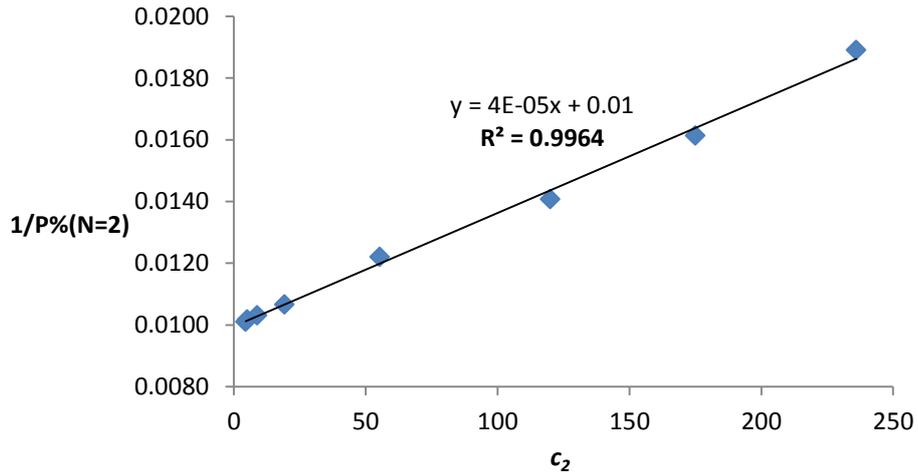


Figure 3.14 Plot of correlation between $1/P\%$ ($N = 2$) and c_2 for 100% JCO and the seven blends of diesel and JCO tested. The raw data are provided in Table 13 in Appendix 3.1.

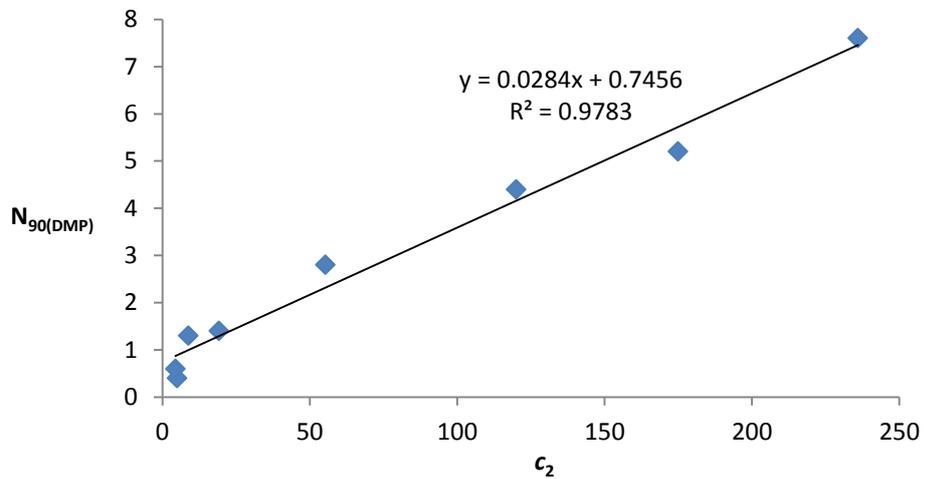


Figure 3.15 Plot of correlation between $N_{90(DMP)}$ and c_2 for 100% JCO and the seven blends of diesel and JCO tested. The raw data are provided in Table 14 in Appendix 3.1.

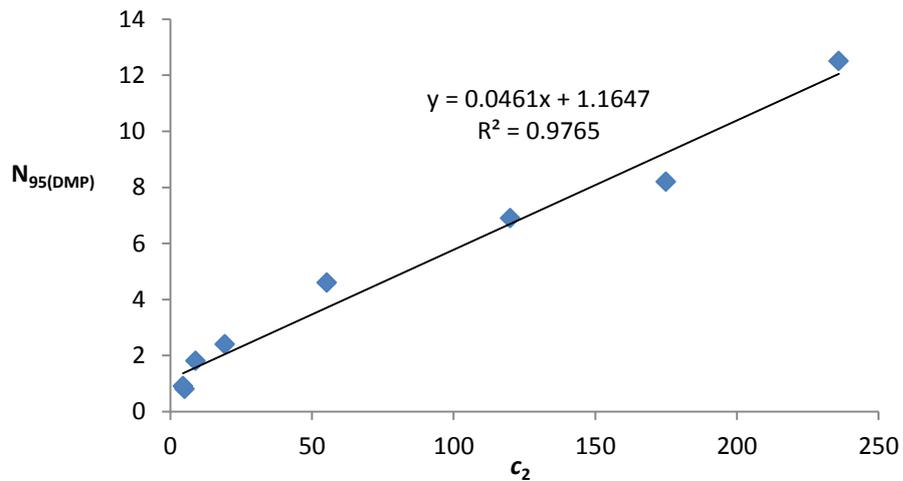


Figure 3.16 Plot of correlation between $N_{95(DMP)}$ and c_2 for 100% JCO and the seven blends of diesel and JCO tested. The raw data are provided in Table 15 in Appendix 3.1.

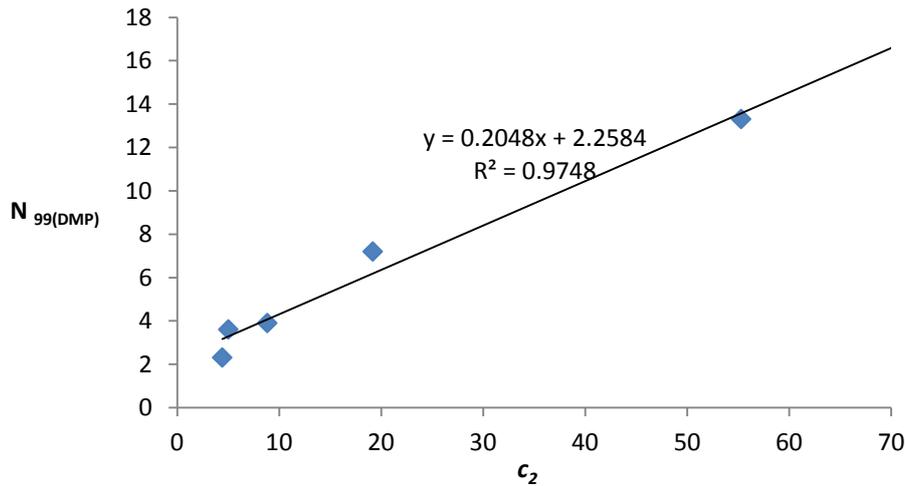


Figure 3.17 Plot of correlation between $N_{99(DMP)}$ and c_2 for 100% JCO and the seven blends of diesel and JCO tested. The raw data are provided in Table 16 in Appendix 3.1.

3.5 Conclusions

Two approaches to mathematically modeling the sequential contaminant pick-up from a given substrate with magnetic particles have been explored and allowance has been made within the models to accommodate departure from idealized behavior. Acceptable fits of the experimental data representing the extremes in expected system behaviors were only obtained using the non-ideal hyperbolic model. This suggests that the non-ideal hyperbolic model may be generally applicable to these systems. The application of the mathematical model to the experimentally obtained pick-up data enables the entire data set to be used in the evaluation of the pick-up efficiency of the system. This has obvious benefits for the routine study and comparison of different systems. It was found that the c_2 fitting parameter in the non-ideal hyperbolic model was highly correlated with the, initial, final and overall pick-up efficiency of these systems that comprise a single contaminant pair. However, other more complex, multi-contaminant systems were not explored in the current work and may not be described adequately by the proposed model. This is an area for future research.

3.6 References

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Chapter 4: The development and exploitation of an assay based on MPT for the quantification of relative pre-treatment agent (PTA) efficacy

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4.9.6 Penguin feather clusters at N_{90} and N_{95}

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Chapter 4: The development and exploitation of an assay based on MPT for the quantification of relative pre-treatment agent (PTA) efficacy

4.1 Introduction

As indicated elsewhere in this thesis, acute and chronic exposure of wildlife and ecosystems to oil contamination is a matter of worldwide concern (Wiener and Parker 1995, Peterson *et al.* 2003). When human intervention is possible, it is important that remedial operations strive to achieve *the highest overall efficiency*. In the case of wildlife remediation, it is important to optimize the survival, the subsequent health and the reproductive success of the released animals (Welte and Frink 1991; Massey *et al.* 2006; Barros *et al.* 2014). In the case of site remediation, it is important to minimize further environmental damage (Welte and Frink 1991; Camphuysen and Hubeck 2001; Rogowska and Namieśnik 2010).

The application of MPT to the problem of contaminant removal, both from wildlife and from environmental domains such as rocky foreshore, and the potential advantages of this technique over the more traditional detergent-based methods, has been described in detail elsewhere in this thesis. Thus experiments on whole bird models have confirmed the effectiveness of this dry cleaning technique for removing contaminants from the plumage of both duck and penguin (Orbell *et al.* 2004) (these being widely different feather types). Recent results by Orbell group have also shown the technique to be equally applicable to contaminated fur and rock surfaces - as described in Chapter 5.

Environmental remediators, employing traditional detergent-based methods, often use PTAs to enhance the removal of contamination (usually oil) from a variety of matrices and, in this regard, various substances and formulations of substances as PTAs have been trialled by groups worldwide. Unfortunately, it has been impossible to *quantify* their effectiveness since, when such traditional cleansing methods are used; everything is washed away in the process. Consequently, the effectiveness of such PTA candidates is currently only *qualitative* and PTAs that are considered to be superior for particular applications tend to be communicated anecdotally, based on subjective assessments. Therefore, there is a need for a method

whereby the effectiveness of existing PTAs (and PTA candidates) may be *quantified* with respect to their relative abilities to enhance the removal of different contaminants from plumage, fur or from substrates such as rock surfaces (either by traditional detergent-based techniques or by other methods such as magnetic cleansing). In relation to this problem, this program to investigate the application of MPT to wildlife rehabilitation and environmental remediation has led to the development of such a method as a ‘spin-off’. More specifically, a gravimetric methodology based on MPT that can be employed to *quantitatively* assay for the relative effectiveness of various PTAs. Preliminary investigations have demonstrated that there is considerable scope for the improvement of existing PTAs and for the tailoring of these agents to specific applications. To the best of this researcher’s knowledge, the invention of this assay represents the first time that it has been possible to quantify the relative ability of PTAs to enhance the removal of a given substance from a given substrate. Therefore, recent international progress in this field of research, apart from being alluded to in a publication from the Orbell group (Orbell *et al.*, 2006), has not yet appeared in the international refereed literature.

By further developing and consolidating this assay, the work presented in this thesis aims to place the assessment and development of PTAs, for use by environmental remediators in general, *onto a more scientific and quantitative basis*. As such data becomes available, this knowledge will contribute to the overall improvement of environmental rehabilitation techniques and hence to better environmental outcomes.

The work presented in this chapter has been aimed at the further development of this assay. This includes refining the methodology and equipment to a point whereby this assay may be performed routinely in the laboratory for all three substrate types (feathers, fur and rock). In this regard, quantitative assays (in replicate) have been carried out for a range of different contaminants and substrates (feathers, fur and rock), in order to quantify the relative effectiveness of a wide range of potential PTAs. Other issues that have been under consideration include, whether recommendations gleaned from assays based on MPT carry over with fidelity to detergent-based methods, the effect of temperature on PTA effectiveness, the systematic investigation of the importance of the “point of PTA application” during a treatment process and to employ this assay, for given contaminants and substrate types, to the screening of selected formulations of PTA candidates (blends) and to

investigate the possibility of rationally developing optimized formulations for specific applications.

4.2 Background to the MPT assay

The gravimetric assay, based on MPT, for *quantifying* the relative ability of different PTAs to enhance the removal of oil from a given substrate is based upon experimental techniques and protocols that are well-established within our research group (Ngeh 2002; Dao 2007) and that have been published in the international literature (Orbell *et al.* 1997, 1999, 2004, 2005, 2006(a), 2006(b), 2007; Dao *et al.* 2006). The assay, described below with respect to the removal of oil from feathers, but which is equally applicable to fur and rock surfaces, is outlined in this section in order to demonstrate the conceptual framework, the basic design and methods involved - and to demonstrate that these are adequately developed, well integrated and appropriate to the aims of this project.

The assay itself is based on the discovery by the Orbell group (Orbell *et al.* 1997) of the ability of iron powder to efficiently sequester a variety of contaminants, including oils and oil/seawater emulsions, from various substrates. Since the iron powder is magnetic, this allows the oil-laden powder to be harvested magnetically, simultaneously removing both the cleansing agent and the contaminant from a given substrate. This process may be followed gravimetrically *with a consistent and demonstrable high degree of accuracy and reproducibility*. Thus, characteristic plots showing the “magnetic removal” of oil from a feather cluster and from a rock surface are shown below in Figure 4.1 (a) and (b) respectively. The error bars shown represent 95% confidence intervals for replicate measurements.

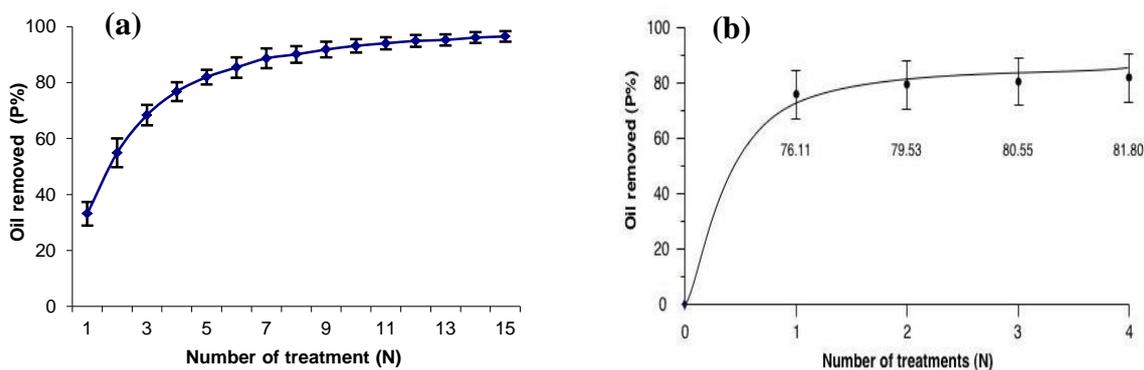


Figure 4.1 Characteristic plots for the removal of oil contamination from (a) feather clusters and (b) rock surface (Orbell *et al.* 2007). The error bars shown represent 95% confidence intervals for replicate measurements. Full data sets are given in Appendix 2.1 (Table 3) for (a).

It has also been demonstrated previously (Orbell *et al.* 2006; Ngeh 2002; Dao 2007) that the magnetic removal of a contaminant from feathers, in particular, was generally improved by the application of a suitable PTA, usually commencing part of the way through the magnetic cleansing process, Figure 4.2.

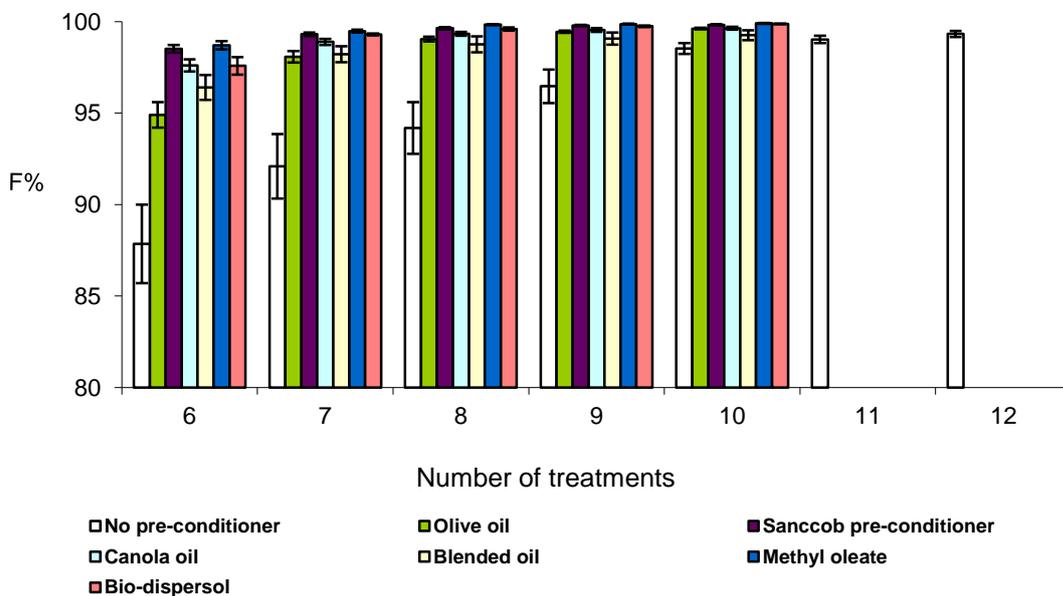


Figure 4.2 Comparison, with and without the use of PTAs, of the percentage removal of weathered bunker oil from duck feathers, $F\%$ ¹³, as a function of the number of treatments, N. Error bars represent the SEs for five replicates. From Dao 2007.

¹³ $F\%$ was used in a previous study and is equivalent to $P\%$ used in the current study.

It can be seen from Figure 4.2 that, for a given contaminant and feather type, the use of a PTA in this way ‘accelerated’ the removal (in terms of the number of treatments required to achieve a defined % removal) and that the optimum removal was generally enhanced. It has also been demonstrated that the use of a pre-conditioner in conjunction with magnetic cleansing consistently removed discolouration from contaminated feathers, Dao 2007.

Experiments of this kind have led to the development of a general assay for quantifying relative PTA effectiveness (for a given substrate and a given contaminant), which is outlined, for the case of feathers, as follows:

4.3 The assay method

For a given feather type, a number of individual feathers (usually, but not limited to, four or five) are tied together to form a cluster and then weighed, f_1 . The feather cluster is then completely immersed in the contaminant to achieve saturation. The cluster is removed and allowed to drain for 10 min prior to being re-weighed, f_2 , on a tared Petri dish. The cluster is then removed from the dish and the residual quantity of contaminant, r , recorded. Hence, the weight of the contaminant-laden feathers, f_3 , for further experimentation is given by the equation: $f_3 = f_2 - r$. The contaminated feathers are then completely covered with iron powder in order for absorption and/or adsorption of the contaminant to occur. This takes only a few seconds. The contaminant-laden magnetic particles are then harvested from the feathers using a magnetic tester, see Section 2.3.1.1. This device, which may be switched on and off mechanically, has been found to be the most suitable for such experiments where a large number of experimental measurements need to be made. The stripped feather cluster is then weighed, f_4 . The percentage removal of the contaminant, P%, is calculated using the equation: $P\% = [(f_3 - f_4)/(f_3 - f_1)] \times 100\%$. This represents the first treatment, $N = 1$. The feather cluster is again completely covered with iron powder and the above magnetic harvesting procedure is repeated. The stripped feather cluster is weighed and a P% value is calculated for $N=2$. This procedure is repeated until a constant (optimal) value of P% is achieved. This is ascertained by plotting P% versus N to obtain the usual removal isotherm, Figure 4.1. Usually 10 - 12 treatments are required for an optimum removal (plateau) to be achieved. After having characterized the magnetic cleansing for a particular feather type and contaminant (using a standard iron powder), the procedure is repeated for another feather

cluster. In this case, part of the way through the treatment process (usually at $N=3 - 6$), the cluster is completely immersed in a candidate pre-conditioning agent and the procedure is resumed. For one or more pre-conditioners, these data may be represented as shown previously in Figure 4.2.

For a given feather type and a given contaminant, the key to quantifying the relative efficacy of different pre-conditioners is based on the fact that a given pre-conditioner is associated with a characteristic “effective number of treatments” required to achieve a defined percentage removal (e.g. 99%) of contaminant (plus pre-conditioner). The effective number of treatments (an efficacy parameter) may then be defined as N_{99} - although this parameter may be defined in other ways, e.g. N_{95} , as appropriate for other types of feather, contaminant and PTA. Relative values of N_{99} (for example) may be visualized in a plot such as Figure 4.3, where they may be read-off from the intercepts (red arrows) for 99% (in this case) horizontal axis (yellow arrow), see Table 4.1 for the intercept values.

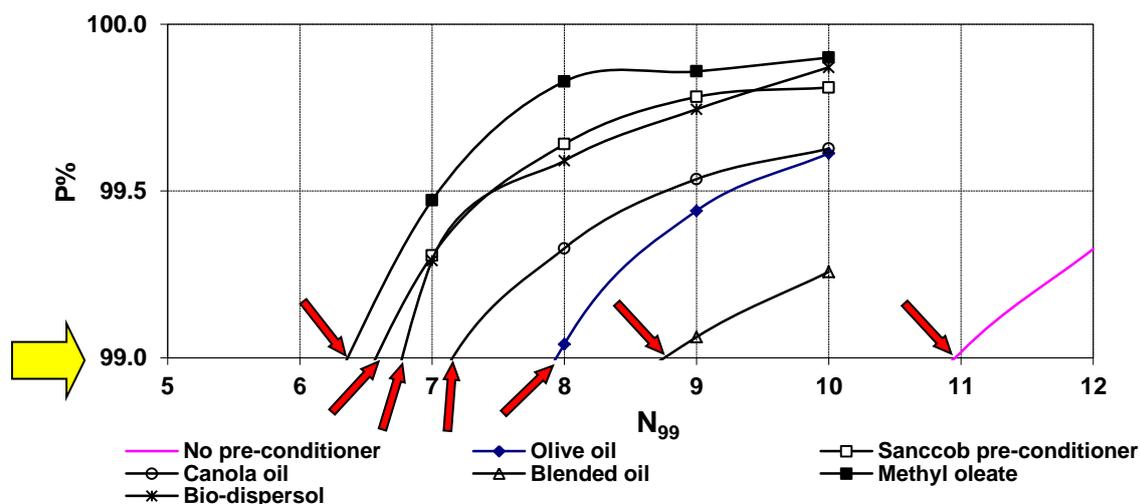


Figure 4.3 The PTA assisted magnetic removal of bunker oil from duck feathers. Relative values of N_{99} for the six PTAs tested, compared to the value in the absence of a PTA, are given by the intercepts on the horizontal axis, shown as red arrows. These values are tabulated in Table 4.1 below. Adapted from Dao, 2007.

Table 4.1 Relative N_{99} values for the removal of bunker oil from duck feather clusters at ambient temperature for seven different PTAs.

PTA	CO	BIO	OO	Blended	Saccob	MO	NPTA
N_{99}	7.2	6.8	7.9	8.8	6.6	6.4	10.9

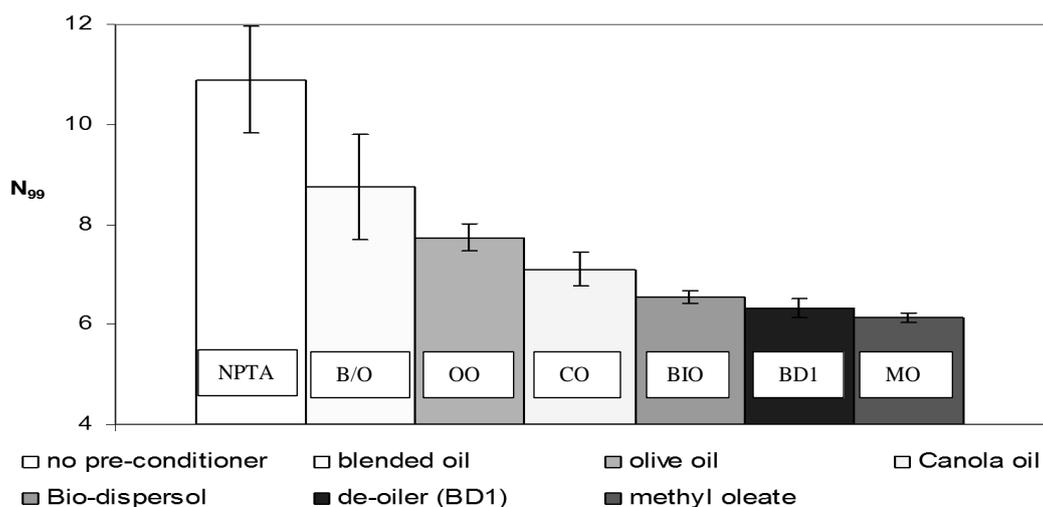


Figure 4.4 Relative average values of N_{99} for six pre-conditioners compared to the average N_{99} value in the absence of a pre-conditioner. Error bars represent the SE for five replicates. Note that MO is better than $BD1 > BIO > CO > OO > BO > NPC$ – for this scenario, i.e. the MPT removal of weathered bunker oil from duck feathers. Adapted from Dao, 2007.

The N_{99} values may also be more conveniently compared as shown in Figure 4.4. Since all experiments may be performed in replicate, it is also possible to indicate confidence intervals for a statistical comparison of the N_{99} data. *The lower the number of effective treatments required to achieve a defined removal criteria, e.g. 99%, the more efficient the pre-conditioner is deemed to be.* Therefore, the effective number of treatments required to achieve a defined removal, represents a quantitative measure of a pre-conditioner's relative efficacy for a given feather type and a given contaminant (using a standard iron powder).

4.4 The general utility of the method

The traditional technique for the cleansing of oiled wildlife is based on the use of dilute surfactant (detergent) solutions (usually 2 - 5% v/v). Over time, this technique has been highly refined with many successful outcomes at rehabilitation facilities worldwide (Barros *et al.* 2014) - and is currently used, almost exclusively, to cleanse oiled wildlife. In this regard, a number of studies have been reported that systematically optimize related materials and protocols. For example, methods have been developed to subjectively evaluate surfactant efficacy for the removal of petrochemicals from contaminated feathers (Brydnza *et al.* 1991 & 1995; Miller *et al.* 2003 & 2006). In some circumstances, the contaminant is resistant to

removal by detergent alone and an additional step of applying a suitable “pre-treatment” agent is required (Tegtmeier & Miller 2007). The choice of a pre-treatment agent (PTA) for a given contaminant and feather type, as well as the method of application, are important considerations - since an additional contaminant is being added to the oiled feathers that also needs to be removed. Indeed, there is anecdotal evidence (personal communication with wildlife rehabilitators at the Phillip Island Nature Parks and elsewhere) to suggest that, under some circumstances, the inappropriate use of a PTA can actually exacerbate the problem.

A wide range of potential PTA candidates are possible and include substances such as olive oil, vegetable oil, methyl oleate and methyl soyate. A comprehensive literature review reveals that there has only been one investigation that evaluates a range of PTA candidates for their ability to facilitate the detergent removal of contaminants from feathers (Tegtmeier and Miller 2007). As is acknowledged by these workers, such experiments are, by their very nature, difficult to carry out and rely on subjective or semi-quantitative evaluations.

As mentioned previously, for more than a decade, the development of MPT for environmental remediation and wildlife rehabilitation has been an active area of collaboration between Victoria University and the Phillip Island Research Department, Victoria, Australia (Orbell *et al.* 1999, 2004, 2006; Bigger *et al.* 2010). This approach to the cleansing of oiled wildlife (“magnetic cleansing”) involves the application of contaminant-sequestering magnetic particles to an affected animal, followed by subsequent magnetic harvesting - to simultaneously remove both contaminant and cleansing agent. This is effectively a dry cleansing process that may offer some advantages over, or be complementary to, traditional detergent-based methods. An additional advantage of the magnetic cleansing technique, especially for research purposes, is that it allows the removal of a given contaminant, or a contaminant/PTA mixture, from a given substrate (feathers, fur or rock surface) to be accurately and reproducibly *quantified*, Figure 4.4. This is very difficult, if not impossible, to achieve using detergent-based removal techniques due to the lack of control over the cleansing agent. Furthermore, the MPT process may be mathematically modeled (Bigger *et al.* 2010, 2013) which allows for the possibility of investigating the physical basis of removal and for more accurately assessing relative removal efficacies. Such modeling has also been explored further in this thesis and is the subject of Chapter 3.

It is worth reiterating that, as with detergent-based methods, the magnetic removal of a contaminant from feathers is found to be generally improved by applying a suitable PTA, Figure 4.2. Notably, it is found that different PTAs vary in their effectiveness for a given contaminant and feather type. This variance is usually statistically significant and is suggestive of a means for conveniently quantifying relative PTA efficacy. Thus based on the observation that different PTAs ‘accelerate’ the removal process to different extents with respect to the removal isotherm, it was seen previously that an assay may be devised whereby an arbitrary “effective number of treatments”, N_{99} for example, may be defined that denotes the effective number of treatments whereby 99% contaminant removal is achieved, Figs. 4.3 & 4.4.

An important consideration for this work, if the assay is to be used to make recommendations to the rehabilitation community, is the extent to which the relative PTA efficacies - as determined by the MPT assay, carry over with fidelity to PTA-assisted detergent-based methods.

Intuitively, one would expect this to be the case since the forces between the substrate, the contaminant and the PTA are the same irrespective of the removal method. Thus, experiments have been designed and conducted herein in order to test this notion for eight different PTAs. Thus, parallel, semi-quantitative detergent-based and fully quantitative MPT-based experiments have been conducted and compared for the PTA assisted removal of a representative contaminant (a Bunker Oil) from feather clusters (Mallard Duck, *Anas platyrhynchos*).

4.5 Some sundry preliminary experiments

4.5.1 Reproducibility check

Previous studies have indicated that the removal of contaminants from duck feather clusters utilizing MPT is highly reproducible. Therefore, before conducting experiments in a new laboratory and with a new researcher (KM), a reproducibility check on previous five-fold replicate experiments (Dao 2007) for the removal of a BO1 from Mallard Duck (*Anas platyrhynchos*) clusters (consisting of 4 individual breast feathers), using a new magnetic

tester, was conducted. The removal experiments were compared at an ambient temperature of 22 °C. BO1 (viscosity, 180 cSt at 40°C) was supplied by IBS Australia; spongy annealed superfine grade iron powder (Grade MH300.29) was supplied by Hoganas AB, Sweden. An established methodology, as described in Section 2.6.2.2, was used in this experiment. The results are displayed in Figure 4.5 - and show remarkable reproducibility.

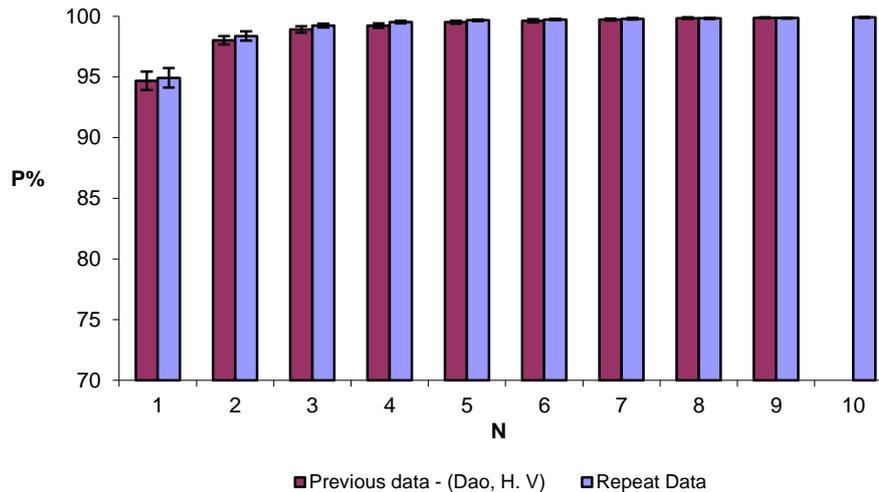


Figure 4.5 Reproducibility check for the percentage removal of bunker oil from duck feather clusters using magnetic Tester at 22°C. The error bars represent 95% confidence intervals for five replicates. Full data sets are given in Appendix 4.1 (Table 1, 2 and 3).

4.5.2 The magnetic tester versus the ‘wand’ for laboratory experimentation

Since two magnetic harvesting devices are available, i.e. the magnetic tester and the ‘wand’ (see Section 2.3.1.1 and 2.3.1.4), an experiment was conducted to determine the effect on experimental outcomes of using one over the other. Therefore, the removal of Arab Medium Crude Oil, AMCO, (viscosity, 50.1 cSt at 22°C - obtained from Exxon/Mobil oil Pty. Ltd, Australia) from duck feather clusters was compared, using both devices. The results that are displayed in Figure 4.6 show that there was a significant difference with respect to the initial removal efficacy between the two magnetic devices but the final removals (N=6 onwards) were identical within experimental error.

These are also important observations from the “quick clean” point of view, Chapter 2, since it demonstrates a dependency of the initial removal (in fact up to N=6) on the magnetic field

strength – and perhaps also upon the surface area of the magnetic device. In fact, the magnetic field strength of the wand (at ~ 10,000 Gauss) is more than three times that of the magnetic tester (at ~ 3,000 Gauss). Although the wand is essentially a “one-handed” device and the magnetic tester a “two-handed” device, the magnetic tester is, from experience, more manageable *in a laboratory setting*. This is, perhaps, to be expected since the wand was specifically designed for field work. However, these results do suggest that care should be taken when translating laboratory data to the field, especially with respect to initial removal.

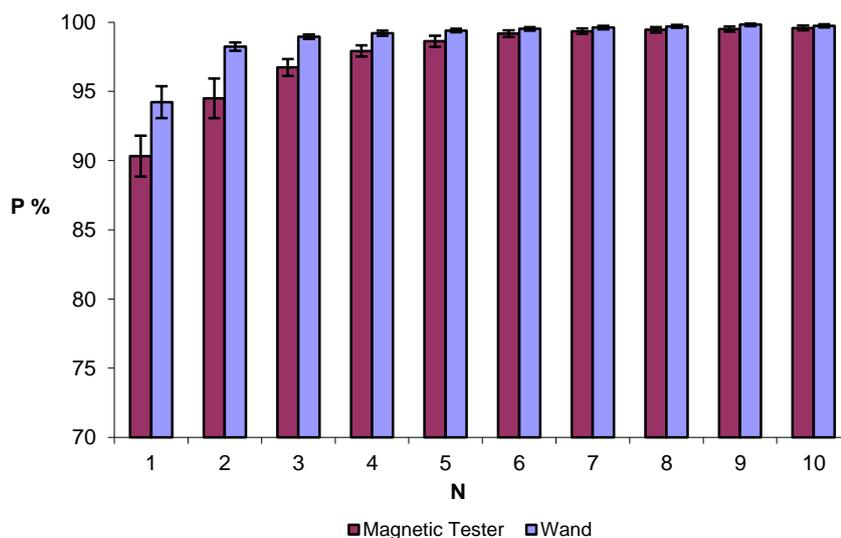


Figure 4.6 Comparison between using a magnetic tester and a wand for the removal of AMCO from duck feathers as a function of the number of treatments. Error bars represent the SE for five replicates. Full data sets are given in Appendix 4.1 (Table 4, 5 and 6).

4.6 Benchmarking the MPT assay for PTA efficacy to PTA assisted detergent-based experiments

As alluded to previously, as an important proof of principle, it is necessary to establish whether the relative quantitative efficacies of PTAs in assisting contaminant removal, as determined by the MPT assay, carry over with fidelity to analogous PTA assisted detergent-based removals, for the same oil and feather types.

Establishing this principle will enable recommendations, based on the MPT assay alone, to be confidently made to the wildlife rehabilitation community on the correct choice of a PTA for detergent-based methods - for a given oil and feather type.

Therefore, controlled *detergent-based* experiments have been designed and conducted whereby a quantification (albeit subjective and semi-quantitative) of the efficacy of a range of PTAs to assist in the removal of a representative grade of oil (here Bunker Oil 1, BO1) from duck feathers, may be determined. These data have been subsequently compared to the quantitative efficacy parameters derived from the analogous MPT assays.

4.6.1 Materials

The contaminant, Bunker Oil 1 (BO1, viscosity, 180 cSt at 40 °C) was obtained from IBS, Australia. Feathers used were those of the Mallard Duck (*Anas Platyrhychos*). The eight PTAs trialled were: Methyl Oleate (MO), Methyl Soyate (MS), Olive Oil (OO), Ethyl Oleate (EO), Isopropyl Oleate (IO), Bio-dispersol (BIO), Canola Oil (CO) and De-oiler (BD1), and were selected based on availability and the fact that they are commonly used by wildlife rehabilitators worldwide. The pre-treatment agents were obtained from VicChem Ltd., and local supermarkets. The South African Foundation for the Conservation of Coastal Birds (SANCCOB) kindly supplied the BD1. The PTAs used in these experiments and their sources are listed in Table 4.2. The detergent employed was Divopluse V2[®] (obtained from Johnson Diversy, NSW, Australia). This is a detergent that is increasingly being preferred by rehabilitators.

Table 4.2 The various PTAs used in these experiments

Pre-treatment Agent (PTA)	Source
Methyl Oleate (MO)	Vic-Chem Ltd., Australia
Bio-disperso (BIO)	Vic-Chem Ltd., Australia
Ethyl Oleate (EO)	Vic-Chem Ltd., Australia
Isopropyl Oleate (IO)	Vic-Chem Ltd., Australia
Methyl Soyate (MS)	Just Fuel, 2 Western Ave, Sunshine, Victoria, Australia
De-oiler (BD1)	The South African Foundation for the Conservation of Coastal Bird (SANCCOB)
Olive Oil (OO)	Local supermarket
Canola Oil (CO)	Local supermarket

4.6.2 Method

4.6.2.1 MPT assay

Using a standard method, as described previously in Section 4.3, the MPT assays were carried out by generating isotherms for the removal of BO1 from duck feather clusters without and with the application, at the sixth treatment, of the eight PTAs. Thus nine isotherms in total were generated. These are shown as comparative histograms in Figure 4.7 and the corresponding assay scheme is shown in Figure 4.8 - from which the $P_0\%$, N_{95} , N_{99} , $P_0\%/N_{95}$ and $P_0\%/N_{99}$ parameters have been determined, Table 4.2.

4.6.2.2 Detergent assays

Nine single duck feathers were used in this study that were individually immersed in the BO1 contaminant and then left to drain for 10 minutes at 22 °C, prior to experimentation, Figure 4.9. The nine individual saturated feathers were then carefully immersed a 5% detergent solution, thermostated to ambient temperature (22 °C). Each feather was left for 15 seconds to soak and then slowly and consistently moved back and forth for 45 seconds, removed, and allowed to drain for 10 seconds.

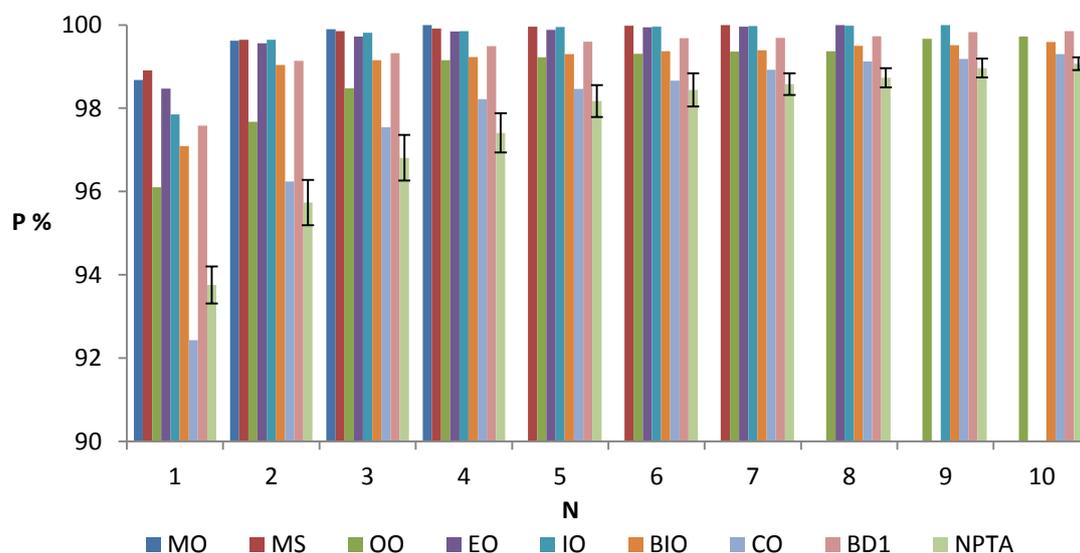


Figure 4.7 A comparison of the percentage removal, $P\%$, of Bunker Oil (BO1) from duck feather clusters versus number of treatments, N , with and without the use of various pre-treatment agents. Error bars represent the SE for five replicates. The full data sets are given in Appendix 4.1 (Table 7 (a), (b) and (c)).

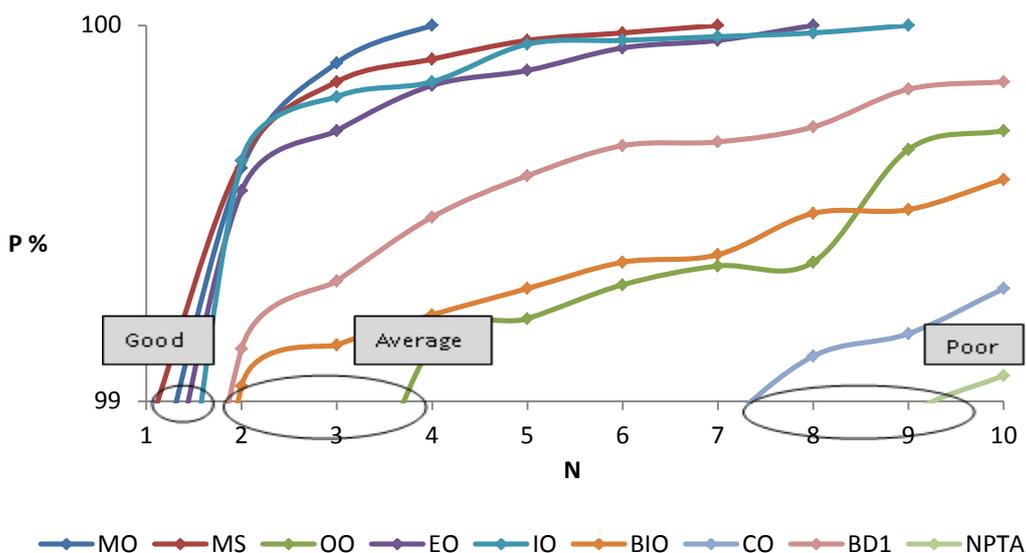


Figure 4.8 Assay scheme for the PTA-assisted removal of BO1 from duck feather clusters. The N_{99} values are calculated from the intercepts of the curves with the horizontal axis, as shown. Note that the relative efficacies may also be qualitatively characterized as “good”, “average” or “poor”. Full data sets are given in Appendix 4.1 (Table 8).

Each feather was then immersed in deionized water and moved back and forth continually for 15 seconds. After this rinsing process, the feathers were allowed to drain for approximately 1 min. This washing was repeated up to the 5th treatment and, at the 6th treatment, each (still-contaminated) feather was immersed into each of the PTAs for 30 sec and then suspended for 5 mins to drain. One feather was used as a control (not immersed in a PTA). This process was repeated up to 14 times (treatments) with an evaluation of oil coverage at each stage – this evaluation process is described below. All of the above procedures were carried out at an ambient temperature of 22°C.

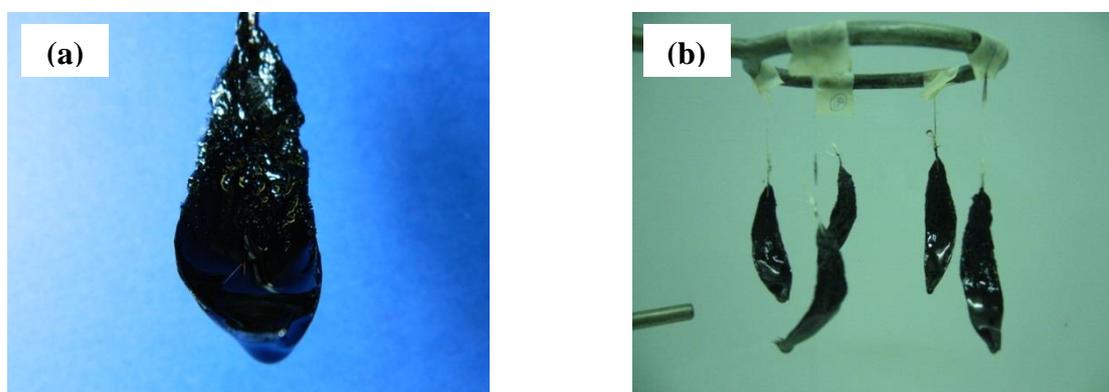


Figure 4.9 (a) Single feather saturated with BO1 being allowed to drain (b) BO1-saturated feathers being left to drain prior to detergent (and PTA-assisted) cleansing.

4.6.3 Ranking the detergent cleansed feathers – the Relative Semi-Quantitative Assessment (RSQA) parameter

A panel of three persons was recruited to subjectively assess the condition of each of the cleansed feathers after each treatment - throughout the 14 treatment process. A score was assigned to each feather based on a Likert scale of 1 to 5, with fractional scores allowed (Likert 1932). Thus, a fully oil-saturated feather is scored 5, a clean feather is scored 1 and a feather estimated to be half-oiled is scored 3. These scores were then averaged and plotted against the treatment number as represented schematically in Figure 4.10 (idealized plot).

The actual (non-idealized) detergent cleansing plots thus generated are shown in Figure 4.11. From these plots it can be seen that the different PTAs can be seen to have very different effects on the oil removal efficacies, as expressed by the relative decline rates of the curves and the relative final scores at the end of the process (N = 14).

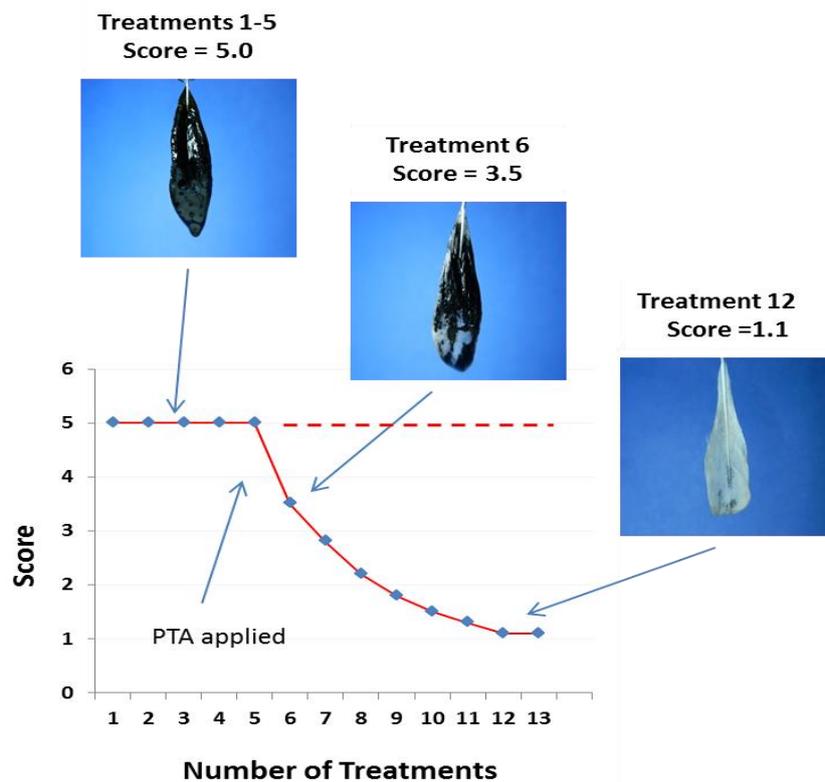


Figure 4.10 Idealized PTA-assisted detergent cleansing plot for a single duck feather contaminated with BO1. Selected Likert rankings for feathers at different stages of cleansing are also shown. Note that the PTA is applied at treatment 6.

4.6.3.1 PTA efficacy parameters

In order to best represent the overall efficacy (incorporating both the final removal and the removal rate) it was decided to use the ratio of either $P_0\%/N_{95}$ or $P_0\%/N_{99}$ as derived from the data presented in Figure 4.8. For the detergent-based experiments, it was decided to compute the average rate of decline for each of the curves in Figure 4.11. This is referred to as the Relative Semi-Quantitative Assessment (RSQA) parameter. A comparison of all of these parameters is given in Table 4.3.

Table 4.3 Comparison of removal of BO1 from duck feather clusters using MPT and detergent washing

PTA	P %	N ₉₅	N ₉₉	P ₀ %/N ₉₅	P ₀ %/N ₉₉	RSQA
MO	99.99	5.30	6.20	18.87	16.13	1.62
MS	99.99	5.40	6.10	18.52	16.39	1.97
OO	99.72	5.75	8.80	17.34	11.33	0.74
EO	99.99	5.20	6.30	19.23	15.87	1.63
IO	99.99	5.50	6.50	18.18	15.38	1.31
BIO	99.59	5.40	6.90	18.44	14.43	1.30
CO	99.30	6.60	12.30	15.05	8.07	0.33
BD1	99.85	5.75	6.80	17.37	14.68	0.97
NPTA	99.32	6.50	14.25	15.24	6.95	0.00

4.6.3.2 The correlation of the $P_0\%/N_{95}$, $P_0\%/N_{99}$ (MPT-based) parameters with the RSQA (detergent-based) parameters

Figures 4.12 (a) and (b) show the correlation plots for $P_0\%/N_{95}$ versus RSQA and $P_0\%/N_{99}$ versus RSQA. Both plots show a high degree of correlation, *confirming the important proof-of-principle hypothesis that the PTA efficacy parameters, as determined by the MPT assay, do carry over with fidelity to the relative efficacy of the same PTAs when used for the removal of contamination using detergent.*

A particularly important observation is that a small (but statistically significant) signal in the MPT assay is significantly amplified in the detergent-based test, Table 4.3, Figure 4.11.

These outcomes enable PTA recommendations based on the MPT assay to be confidently made to rehabilitators who overwhelmingly use detergent-based techniques.

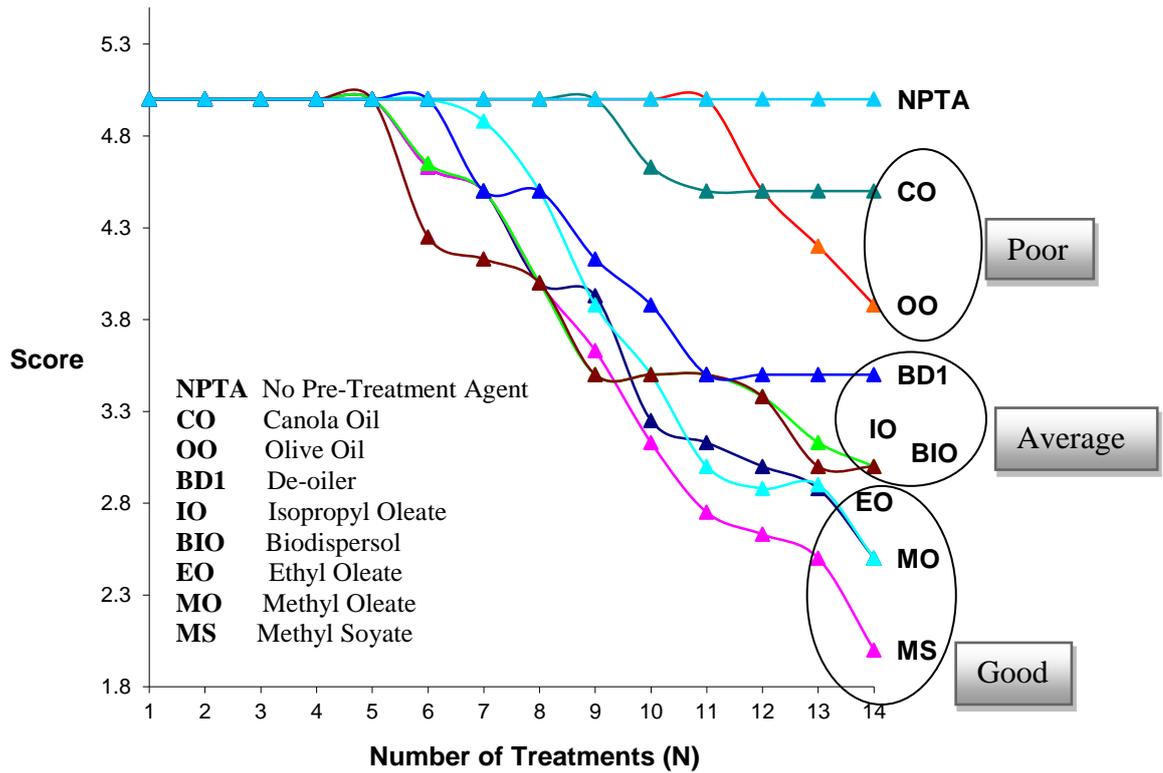
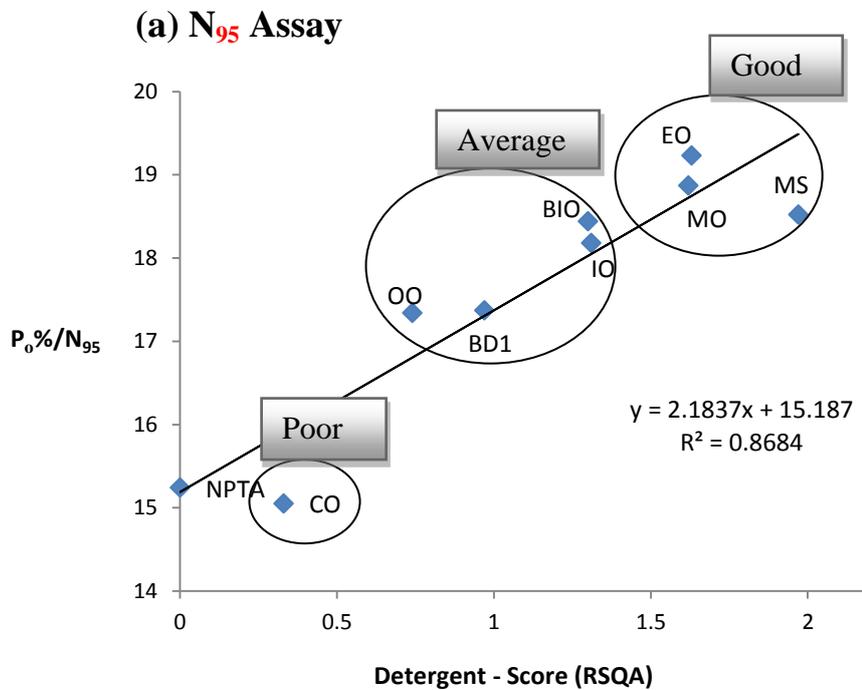


Figure 4.11 PTA-assisted cleansing plots representing the application of eight different PTAs at treatment 6. Full data sets are provided in Appendix 4.1 (Table 9 and 10).



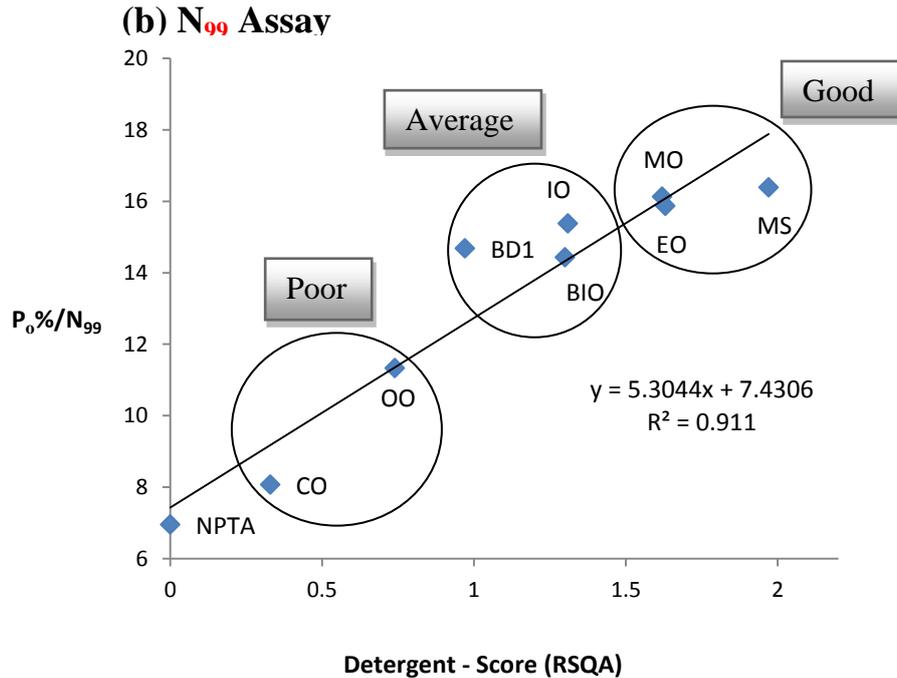


Figure 4.12 (a) Correlation of P₀%/N₉₅ versus RSQA **(b)** Correlation of P₀%/ N₉₉ versus RSQA. Full data sets are provided in Appendix 4.1 (Table 11 and 12).

4.6.3.3 Qualitative considerations

It may also be observed from both the MPT and the detergent experiments, Figures 4.11 and 4.12, that the PTAs may be grouped into *qualitative* efficacy categories, i.e. Good, Average or Poor. Thus from the detergent-based experiment the qualitative results may be displayed as follows

- 6th Evaluation: BIO>MO=MS>IO>OO=EO=CO=BD1=NPTA
- 7th Evaluation: BIO>MO=MS=IO=BD1>EO>OO=CO=NPTA
- 8th Evaluation: MO=MS=IO=BIO>EO=BD1>OO=CO=NPTA
- 9th Evaluation: IO=BIO>MS>EO>MO>BD1>OO=CO=NPTA
- 10th Evaluation: MS>MO>EO=IO=BIO>BD1>CO>OO=NPTA
- 11th Evaluation: MS>EO>MO>IO=BIO=BD1>CO>OO=NPTA
- 12th Evaluation : MS>EO>MO>IO=BIO>BD1>OO=CO>NPTA
- 13th Evaluation : MS>MO>EO>BIO>IO>BD1>OO>CO>NPTA
- 14th Evaluation: MS>MO=EO>IO=BIO>BD1>OO>CO>NPTA

Notably, the 14th evaluation was found to compare very favourably with the *quantitative* ranking from the MPT assay, i.e.

$$MS>MO>EO>IO>BD1>BIO>OO>CO>NPTA$$

4.7 The intrinsic removal characteristics of the PTAs

As discussed previously, environmental remediators often use PTAs to enhance oil removal from a variety of matrices - and various PTA substances and formulations have been trialled worldwide (Bakner *et al.* 1977; Randall *et al.* 1980; Bryndza *et al.* 1991; Hill 1999; OWCN 1999, 2003; Lamy *et al.* 2001; USFWS 2002; Walraven 1992, 2004; Gregory, 2006). Of course, it is also essential to remove the PTAs themselves (usually as a PTA/contaminant blend) during the cleansing process (USFWS 2002) - since applying PTAs represents adding an additional contaminant. For this reason, and also since variety of PTAs used here represents a wide range of formulations, we were interested in assessing the relative removal efficacies of the PTA candidates themselves, as well as a variety of their 50:50 blends. No previous work has been conducted on quantifying the effect of blending on removal efficacy.

4.7.1 Materials and method

Iron powder (Grade MH 300.29) was supplied by Höganäs AB, Sweden, and was described by the manufacturer as “spongy annealed superfine”. The feathers of the clusters used in this study were the breast/contour feathers of the Mallard Duck (*Anas platyrhynchos*). Nine types of PTA were used, namely: Methyl Oleate (MO), Methyl Soyate (MS), Vegetable Oil (VO), Olive Oil (OO), Ethyl Oleate (EO), Isopropyl Oleate (IO), Bio-dispersol (BIO), Canola Oil (CO) and De-oiler (BD1), Table 4.2. The various 50:50 blends (seven) that were also characterized are listed in Table 4.4.

Each duck feather cluster was prepared by tying four feathers together at the base with cotton thread and immersed in each PTA, or PTA blend, in turn in order to achieve saturation. After draining, removal isotherms were determined by the usual method, as described previously. The overall assay scheme(s), for all the data, for determining the N_{99} values (N_{95} is determined in an analogous way) is shown in Figure 4.13. All nine individual PTAs were thus characterized plus the seven selected PTA blends; i.e. sixteen individual isotherms in total, each in five-fold replicate. The relevant efficacy parameters for these experiments are summarized in Table 4.4. The isotherms for the seven blends, and their relevant efficacy parameters, have also been separately compared with those of their respective components. A representative example for VO, OO and OO:VO (50:50), is shown in Figures 4.14, 4.15 and

Table 4.5. In order to effectively compare the parameters for individual PTAs with their 50:50 blends, the data of Table 4.4 data has been organized into a series of smaller Tables, i.e. 4.5 to 4.11. The full data for all blends are provided in Appendix 4.2.

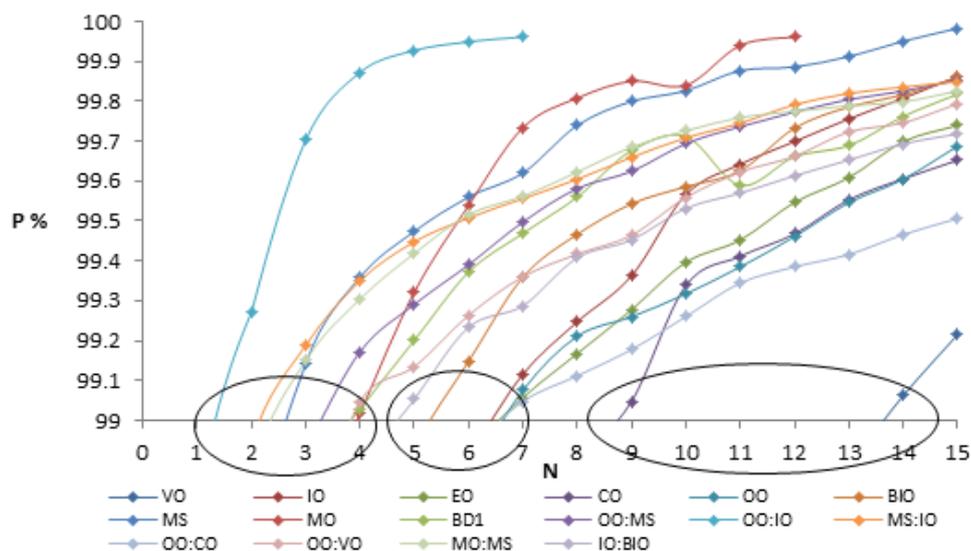


Figure 4.13 Assay scheme for the determination of the N_{99} parameters for the removal of PTAs and their 50:50 blends from duck feather clusters; see Table 4.4 for listing of removal and efficacy parameters. From left to right the circles represent Good (≤ 4.0); Average (4.0 – 7.0); Poor (≥ 7.0). Full data sets are given in Appendix 4.2 (Table 1 (a) and (b)).

Table 4.4 Tabulation of relative efficacy parameters for the intrinsic removal from duck feather clusters of PTAs and various 50:50 PTA blends. The qualitative descriptors of relative efficacy of intrinsic removal are: P=Poor; A=Average; G=Good, see Figure 4.13.

Descriptor	PTA & BPTA	N=1	N=2	$P_0\%$	N_{95}	N_{99}
G	BD1	97.6	98.5	99.8	1.0	4.0
A	BIO	95.4	97.3	99.9	1.0	5.2
P	CO	91.4	94.9	99.7	2.1	8.8
A	EO	94.4	96.4	99.7	1.2	6.6
A	IO	95.0	97.0	99.9	1.0	6.4
G	MO	96.7	98.1	99.9	1.0	4.0
G	MS	97.0	98.6	99.9	1.0	2.7
A	OO	91.4	94.6	99.7	2.2	6.6
P	VO	84.5	89.0	99.2	5.0	13.7
P+G=G	OO:MS	97.9	98.7	99.9	1.0	3.2
P+A=G	OO:IO	98.7	99.3	99.9	0.9	1.3
G+A=G	MS:IO	98.3	98.9	99.9	1.0	2.2
A+P=A	OO:CO	96.9	98.0	99.5	1.0	6.6
P+P=G	OO:VO	97.4	98.4	99.8	1.0	3.9
G+G=G	MO:MS	98.2	98.9	99.8	1.0	2.3
A+A=A	IO:BIO	97.5	98.3	99.7	1.0	4.8

Thus, individual pairs and pair blends have been separated to assist in analysis and discussion. For example, a comparison of the relevant data for OO, VO and the blend OO:VO is shown graphically in Figures 4.14 & 4.15 and summarized in Table 4.5.

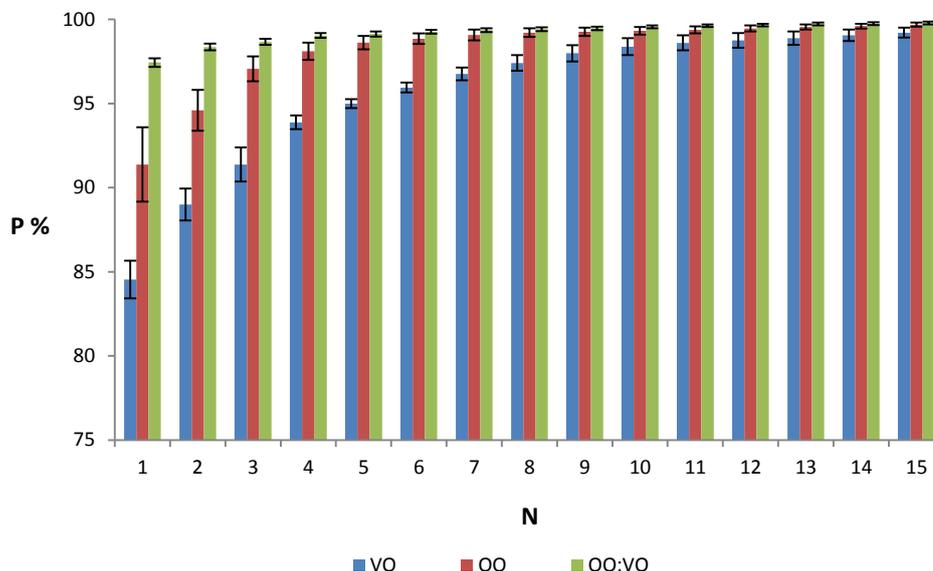


Figure 4.14 Removal, P%, of individual pre-treatment agents OO and VO, and their 50:50 (OO:VO) blend from duck feather clusters as a function of the number of treatments, N, using MH300.29 at 22°C. Error bars represent the SEs for five replicates. The full data sets are given in Appendix 4.2 (Table 2, 3 and 4).

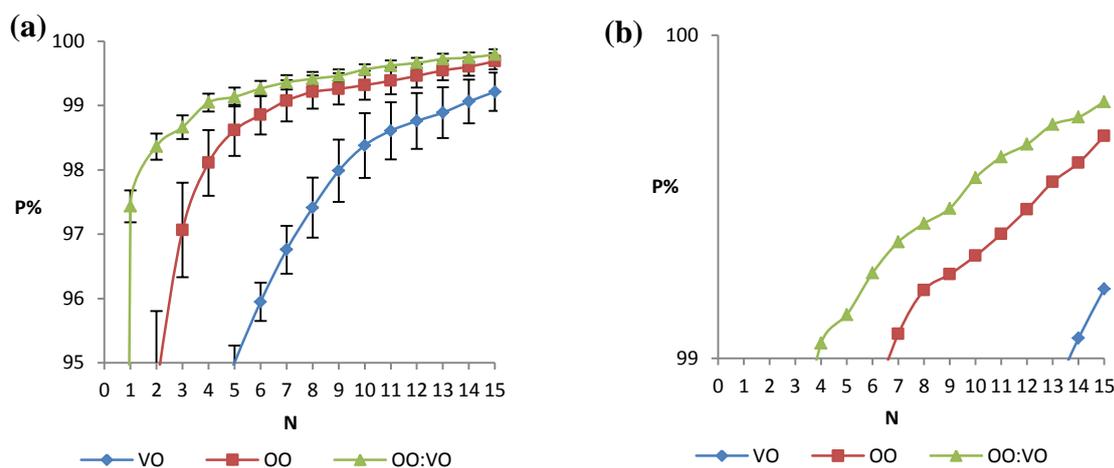


Figure 4.15 (a) N₉₅ assay scheme for the comparison of removal efficacies for VO, OO and OO:VO (50:50) **(b)** corresponding N₉₉ assay scheme. Here, the error bars (SEs for five replicated) have been removed for clarity.

Table 4.5 Relative removal parameters for VO, OO and OO:VO (50:50) from duck feather clusters at 22°C

PTA or BPTA	N=1	N=2	P ₀ %	N ₉₅	N ₉₉
VO (P)	84.5 ±1	89.0 ±1.0	99.2 ±0.3	5.0	13.7
OO (A)	91.4 ±2	94.6 ±1.0	99.7 ±0.1	2.2	6.6
OO:VO (G)	97.4 ±0.3	98.4 ±0.2	99.8 ±0.1	1.0	3.9

The remaining six such tables are listed as follows, i.e. Tables 4.6 to 4.11. The relevant graphs are provided in Appendix 4.2.

Table 4.6 Relative removal parameters for OO, MS and OO:MS (50:50) from duck feather clusters at 22°C

PTA or BPTA	N=1	N=2	P ₀ %	N ₉₅	N ₉₉
OO (A)	91.4 ±22	94.6 ±1	99.7 ±0.1	2.2	6.6
MS (G)	97.0 ±0.6	98.6 ±0.3	99.9 ±0.01	1.0	2.7
OO:MS (G)	97.9 ±0.2	98.7 ±0.2	99.95 ±0.1	1.0	3.2

Table 4.7 Relative removal parameters for OO, IO and OO:IO (50:50) from duck feather clusters at 22°C

PTA or BPTA	N=1	N=2	P ₀ %	N ₉₅	N ₉₉
OO (A)	91.4 ±2	94.6 ±1	99.7 ±0.1	2.2	6.6
IO (A)	94.9 ±1	97.0 ±0.4	99.9 ±0.04	1.0	6.4
OO:IO (G)	98.7 ±0.2	99.3 ±0.1	99.9 ±0.03	1.0	1.3

Table 4.8 Relative removal parameters for IO, MS and MS:IO (50:50) from duck feather clusters at 22°C

PTA or BPTA	N=1	N=2	P ₀ %	N ₉₅	N ₉₉
MS (G)	97.0 ±0.6	98.6 ±0.3	99.9 ±0.01	1.0	2.7
IO(A)	95.0 ±0.1	97.0 ±0.4	99.9 ±0.04	1.0	6.4
MS:IO (G)	98.3 ±0.2	98.9 ±0.1	99.9 ±0.1	1.0	2.2

Table 4.9 Relative removal parameters for OO, CO and OO:CO (50:50) from duck feather clusters at 22°C

PTA or BPTA	N=1	N=2	P ₀ %	N ₉₅	N ₉₉
OO (A)	91.4 ±2	94.59 ±1.2	99.7 ±0.1	2.1	6.6
CO (P)	91.4 ±0.8	94.88 ±1	99.7 ±0.2	2.2	8.8
OO:CO (A)	96.9 ±0.2	98.02 ±0.2	99.5 ±0.2	1.0	6.6

Table 4.10 Relative removal parameters for MO, MS and MO:MS (50:50) from duck feather clusters at 22°C

PTA or BPTA	N=1	N=2	P ₀ %	N ₉₅	N ₉₉
MO (G)	96.7 ±0.8	98.1 ±0.3	99.9 ±0.02	1.0	4.0
MS (G)	97.0 ±0.6	98.6 ±0.3	99.9 ±0.01	1.0	2.7
MO:MS (G)	98.2 ±0.2	98.9 ±0.2	99.8 ±0.03	1.0	2.3

Table 4.11 Relative removal parameters for IO, BIO and IO:BIO (50:50) from duck feather clusters at 22°C

PTA or BPTA	N=1	N=2	P ₀ %	N ₉₅	N ₉₉
IO (A)	94.9 ±0.6	97.0 ±0.4	99.9 ±0.1	1.0	6.4
BIO (A)	95.4 ±0.3	97.3 ±0.2	99.9 ±0.1	1.0	5.2
IO:BIO (A)	97.5 ±0.1	98.3 ±0.1	99.7 ±0.1	1.0	4.8

The PTAs are categorized into either Poor, Average or Good, see Figure 4.13, in order to facilitate a discussion of the relative removal efficacies as documented in the Tables above. Thus, an examination of the data presented in Tables 4.5 to 4.11, enables the following comments to be made.

Firstly, all individual PTAs and their blends achieve > 99%, and sometime 100% final removal - within experimental error. The blends performed better than the individual components with respect to initial removal. For example at N=1 the individual component removals range from 84.5 – 97.6% and the blend removals range from 96.9 to 98.7%. At N=2, the individual component removals range from 89.9 to 98.6% and the blend removals range from 98.0 to 99.3%. Overall, with one exception, Table 4.6, the blends show better removal efficacies than the individual components, as evidenced by the N₉₉ values. This effect can be quite dramatic, as in the case of the blending of the two “poor” performers VO and OO. The 50:50 OO:VO blend then becomes a “good” performer. This is clearly illustrated, especially with respect to initial removals, in Figure 4.14. Specific comments are as follows:

- As can be observed from Table 4.5, with respect to initial removal (at N=1 and N=2), the blended OO:VO is significantly more efficient than either component, as is evidenced by the relative N₉₅ and N₉₉ values. The final removals, as indicated by P₀%, are essentially equivalent.

- From Table 4.6, with respect to initial removal (at N=1 and N=2), the blended OO:MS is essentially equivalent to the individual component MS but significantly better than the individual component OO. The final removals are essentially equivalent.
- From Table 4.7, with respect to initial removal (at N=1 and N=2), the removal of the OO:IO blend, as reflected by N₉₅ and especially N₉₉, is better than both PTAs individually. All final removals are comparable.
- From Table 4.8, the removal of the MS:IO blend is comparable to the removal efficacy of MS and slightly better than IO. The final removals are all comparable.
- From Table 4.9, all the parameters show that the MO:MS blend is less than but roughly equivalent to the individual components with respect to initial and final removal efficacy. All final removals are comparable.
- From Table 4.10, again we see that the OO:CO blend is less than, but roughly equivalent to, the individual PTAs with respect to initial removal and this is also reflected in the N₉₅ and N₉₉ values. The final removals are comparable.
- From Table 4.11, the N₉₉ values suggest an improvement for the blend and the initial removals are also significantly better for the blend. Again, the final removals are equivalent.

From the above analysis of the data, it is apparent that blending enhanced the efficacy of removal, especially the initial removal, Table 4.12. The proportion of PTAs in the “Good” category dramatically increases for the blends of the same PTAs whereas the proportion of the blends in the “Average” and “Poor” categories dramatically decrease. Notably, none of the BPTAs are categorized as being “Poor”.

Table 4.12 Comparison of qualitative efficacy descriptors for the PTAs and their blends.

Category	PTA	BPTA
Good - G	33%	71%
Average - A	45%	29%
Poor - P	22%	0%

In terms of the N_{99} values, the order of PTA removal efficacy is:

MS (G) > MO (G) > BD1 (G) > BIO (A) > IO (A) > OO (A) > EO (A) > CO (CO) > VO (P)

In terms of the N_{99} values, the order of BPTA removal efficacy is:

OO:IO (A+A=G) > MS:IO (G+A=G) > MO:MS (G+G=G) > OO:MS (A+G=G) > OO:VO (P+A =G) > IO:BIO (A+A = A) > OO:CO (A+P=A)

Overall, for the PTAs and the BPTAs the order is:

MS:IO \geq MS \geq MO \geq IO \geq OO:MS \geq BIO \geq OO:IO > MO:MS \geq OO:VO \geq BD1 > IO:BIO \geq EO \geq OO \geq CO > OO:CO > VO

Specifically, the blends OO:VO (P+A=G); OO:IO ;OO:CO and IO:BIO are clearly enhancing (synergistic) with respect to the initial removal. The blends OO:MS; MS:IO and MO:MS have a lesser enhancement effect. The final removals are essentially the same in all cases. It is perhaps not surprising that blending the PTAs can have a significant effect on the initial removal since the chemical composition of the overall contaminant is being altered. The fact that an improvement is usually observed is probably related to the greater diversity of chemical components in the mixture. This could be an important pointer for the improvement of PTA formulations. These experiments show how the MPT assay method may systematically explore this phenomenon and opens the possibility for optimizing mixtures for their most efficient initial removal. These results also suggest that more controlled experiments, for which the chemical compositions of the mixture are well-defined, could yield even more insight. This could assist in the analysis of such removal phenomena from a molecular perspective.

4.8 Application of the MPT assay to the removal of Bunker Oil 2 (BO2) from duck feather clusters - assisted by Pre-Treatment Agents (PTA) and by Blended Pre-Treatment Agents (BPTA)

The removal of a moderate viscosity bunker oil, Bunker Oil 2 (BO2), from clusters of duck breast feathers has been characterized with and without the application, part-way through the treatment at N=6, of seven PTAs and seven 50:50 blended pairs of these PTAs, i.e. the BPTAs. Thus isotherms for the removal of BO2 without PTA or BPTA (NPTA), and the PTA and BPTA-assisted BO2 removal isotherms using olive oil (OO), vegetable oil (VO), canola oil (CO), methyl soyate (MS), isopropyl oleate (IO), methyl oleate (MO), bio-dispersol (BIO), and the 50:50 IO:BIO, MS:IO, MO:MS, OO:IO, OO:MS, OO:CO and OO:VO BPTAs, were determined by standard methods as described previously.

4.8.1 Materials and methods

The materials and method are the same as those described in Section 4.7.1 except for the fact that the experiments were carried out using Bunker Oil 2 (BO2) (viscosity, 222 cSt at 22°C) as a contaminant - supplied by IBS Australia. All PTAs were sourced as shown in Table 4.2.

4.8.2 Results and discussion

The full data and the individual isotherms are given in Appendix 4.3. Relevant nested sections of these isotherms are shown in Figure 4.16. Since the addition of a PTA/BPTA is effectively adding a further contaminant(s), a dip is often observed in the curve(s) at the point at which the PTA is added (here at N=6). The extent of this dip carries information on the nature of the interaction of the PTA with the contaminant and the resulting interaction of the mixture with the substrate. A complete analysis of this phenomenon would be desirable but is outside of the scope of this thesis.

The assay scheme derived from these nested curves is depicted in Figure 4.17. All relevant efficacy parameters are provided in Table 4.13. It may be noted from this data that all PTAs and BPTAs confer a removal advantage over no PTA (NPTA), for which $P_o\%/N_{95} = 12.6$, except for OO:VO, for which $P_o\%/N_{95} = 10.8$. Given the amplification effect noted

previously for this assay, see Section 4.6.3.2, this particular blend would be considered as being detrimental for detergent-based cleansing of an oil of this type.

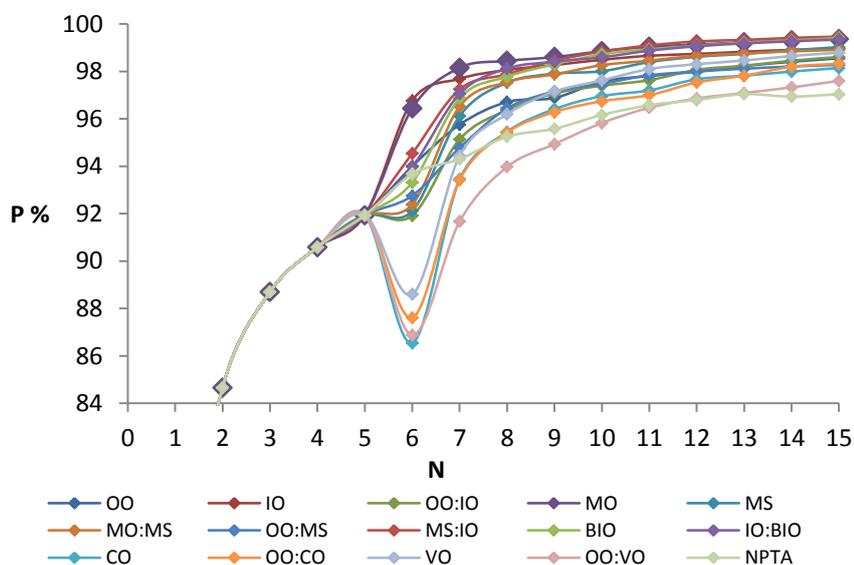


Figure 4.16 Comparison between the percentage removal, P%, of BO₂ from duck feather clusters as a function of the number of treatment, N, using PTA, BPTA and NPTA. Error bars, SEs for five replicates, have been removed for clarity. Full data sets and the individual profiles are given in Appendix 4.3 (Table 1 to 24).

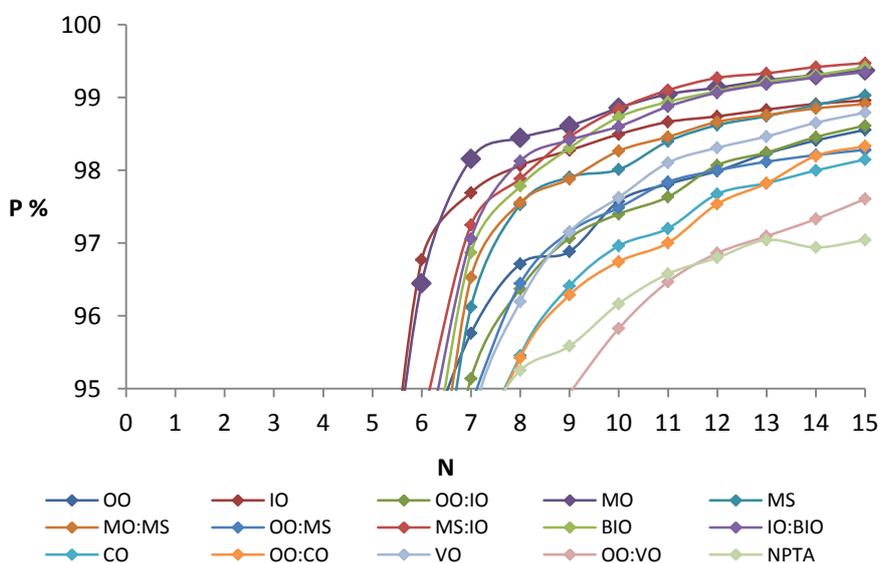


Figure 4.17 Assay scheme for the removal, P%, of BO₂ from duck feather clusters as a function of the number of treatment, N, using NPTA, PTAs, and BPTAs. Error bars, SEs for five replicates, have been removed for clarity. N₉₅ value may be obtained from the intercepts with the horizontal axis. Full data sets and the individual profiles are given in Appendix 4.3 (Table 1 to 24).

Table 4.13 Efficacy parameters for the aassisted MPT removal of BO2 from duck feather clusters using PTAs and BPTAs at N=6. Best PTAs are shaded green, worst are shaded orange.

PTA	P ₀ %	N ₉₅	N ₉₉	P ₀ %/N ₉₅
BIO	99.4	6.4	11.4	15.5
CO	98.2	7.7	-	12.8
IO	99.0	5.6	-	17.7
MO	99.4	5.7	10.7	17.4
MS	99.0	6.7	14.8	14.8
OO	98.6	6.5	-	15.2
VO	98.8	7.2	-	13.7
OO:MS	98.3	7.1	-	13.9
OO:IO	98.6	6.9	-	14.3
MS:IO	99.5	6.2	10.5	16.1
OO:CO	98.3	7.7	-	12.8
OO:VO	97.6	9.0	-	10.8
MO:MS	98.9	6.6	-	15.0
IO:BIO	99.4	6.3	11.6	15.8
NPTA	97.0	7.7	-	12.6

The order of preference for PTAs or BPTAs is as follows:

IO ≥ MO > MS:IO ≥ IO:BIO > BIO ≥ OO ≥ MO:MS > MS > OO:IO > OO:MS ≥ VO > CO ≥ NPTA > OO:VO

Based on the efficacy parameters listed in Table 4.13, the best candidates are either IO or MO and the worst candidates are VO and CO. A warning is warranted for the use of a OO:VO blend. Considering the effects of the particular blends on the removal of BO2 compared to their individual components, each blend may be considered in turn.

A section of the three representative superimposed isotherms are shown in Figure 4.18, highlighting the effect of PTA or BPTA addition on the removal of BO2. From these graphs, an enhancement of the final removal is evident for OO, IO and OO:IO, with IO itself being obviously superior. This is reflected in the efficacy parameters that are derived from the assay scheme shown in Figure 4.19 and given in Table 4.14. Thus OO, IO and OO:IO PTAs enhance the final removal compared to no pre-treatment agent (NPTA). It may also be seen that IO is superior to OO and OO:IO and this is reflected in the smaller value of N₉₅ (5.6) for

IO compared to OO (6.5), OO:IO (6.9) and NPTA (7.7). It should be noted here that the blend barely improves upon the efficacies of OO or IO alone.

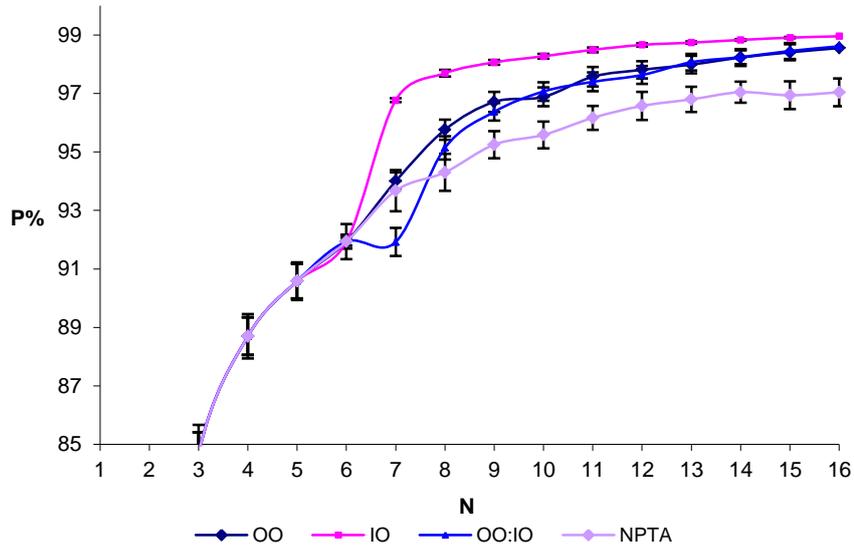


Figure 4.18 Comparison between the percentage removal, P%, of Bunker Oil 2 (BO2) from duck feather clusters as a function of the number of treatments, N, using the PTAs olive oil (OO), isopropyl oleate (IO), 50:50 blended OO:IO, applied at N=6, and with no pre-treatment agent (NPTA). Error bars represent SEs for five replicates. The full data sets are given in Appendix 4.3 (Table 3, 4, 5, 6 and 7).

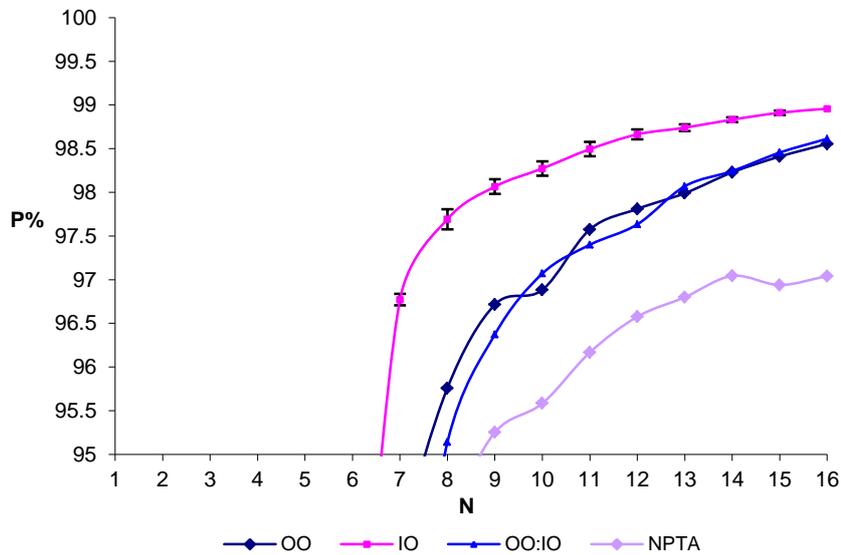


Figure 4.19 Assay scheme for the determination of the N_{95} values for the experiment shown in Figure 4.18.

Table 4.14 Relative N_{95} and N_{99} values for the removal of BO2 from duck feather clusters at 22°C for OO, IO, 50:50 OO:IO and NPTA. Note that N_{95} is the relevant assay parameter here since none of the removals achieve a P% of 99%. The errors are SEs.

PTA or BPTA	P ₀ %	N ₉₅	N ₉₉
OO	98.6 ± 0.3	6.5	-
IO	98.9 ± 0.1	5.6	-
OO:IO	98.6 ± 0.3	6.9	-
NPTA	97.0 ± 0.5	7.7	-

The efficacy parameters for the remaining blends in Table 4.13 are provided in Figure 1 to 6 in Appendix 4.3. This data has been broken down into Tables 4.15 to 4.20 for subsequent analysis and discussion.

Table 4.15 Relative N_{95} and N_{99} values for the removal of BO2 from duck feather clusters at 22°C for MO, MS, 50:50 MO:MS and NPTA. Note that N_{95} is the relevant assay parameter here since none of the removals achieve a P% of 99%. The errors are SEs.

PTA or BPTA	P ₀ %	N ₉₅	N ₉₉
MO	99.4 ± 0.1	5.7	10.7
MS	99.0 ± 0.1	6.7	14.8
MO:MS	98.9 ± 0.1	6.6	-
NPTA	97.0 ± 0.5	7.7	-

Table 4.16 Relative N_{95} and N_{99} values for the removal of BO2 from duck feather clusters at 22°C for MO, MS, 50:50 MO:MS and NPTA. Note that N_{95} is the relevant assay parameter here since none of the removals achieve a P% of 99%. The errors are SEs.

PTA or BPTA	P ₀ %	N ₉₅	N ₉₉
OO	98.6 ± 0.3	6.5	-
MS	99.0 ± 0.1	6.7	14.8
OO:MS	98.3 ± 0.3	7.2	-
NPTA	97.0 ± 0.5	7.7	-

Table 4.17 Relative N_{95} and N_{99} values for the removal of BO2 from duck feather clusters at 22°C for MS, IO, 50:50 MS:IO and NPTA. Note that N_{95} is the relevant assay parameter here since none of the removals achieve a P% of 99%. The errors are SEs.

PTA or BPTA	P ₀ %	N ₉₅	N ₉₉
MS	99.0 ± 0.1	6.7	14.8
IO	99.0 ± 0.1	5.6	-
MS:IO	99.5 ± 0.2	6.2	10.5
NPTA	97.0 ± 0.5	7.7	-

Table 4.18 Relative N_{95} and N_{99} values for the removal of BO2 from duck feather clusters at 22°C for IO, BIO, 50:50 IO:BIO and NPTA. Note that N_{95} is the relevant assay parameter here since none of the removals achieve a P% of 99%. The errors are SEs.

PTA or BPTA	P ₀ %	N ₉₅	N ₉₉
IO	99.0 ± 0.02	5.6	-
BIO	99.0 ± 0.2	6.4	11.4
IO:BIO	99.4 ± 0.1	6.3	11.6
NPTA	97.0 ± 0.5	7.7	-

Table 4.19 Relative N_{95} and N_{99} values for the removal of BO2 from duck feather clusters at 22°C for OO, CO, 50:50 OO:CO and NPTA. Note that N_{95} is the relevant assay parameter here since none of the removals achieve a P% of 99%. The errors are SEs.

PTA or BPTA	P ₀ %	N ₉₅	N ₉₉
OO	98.6 ± 0.3	6.5	-
CO	98.2 ± 0.5	7.7	-
OO:CO	98.3 ± 0.2	7.7	-
NPTA	97.0 ± 0.5	7.7	-

Table 4.20 Relative N_{95} and N_{99} values for the removal of BO2 from duck feather clusters at 22°C for OO, CO, 50:50 OO:CO and NPTA. Note that N_{95} is the relevant assay parameter here since none of the removals achieve a P% of 99%. The errors are SEs.

PTA or BPTA	P ₀ %	N ₉₅	N ₉₉
OO	98.6 ± 0.3	6.5	-
VO	98.8 ± 0.1	7.2	-
OO:VO	97.6 ± 0.1	9.1	-
NPTA	97.0 ± 0.5	7.7	-

Thus, an examination of the data presented in Tables 4.15 to 4.20, enables the following comments to be made.

- From Table 4.15, using MO was seen to be more effective in removing the BO2 than using MS, MO:MS or NPTA. It is also apparent that MS and MO:MS were effectively equivalent in their efficacies suggesting the blend conferred no advantage in this case. However, all PTAs here provided an improvement over NPTA.
- It appears from Table 4.16, that MS was more effective with respect to final contaminant removal than OO, OO:MS or NPTA. It was also apparent that OO:MS was actually

inferior to either of the individual components in this case. Again, however, all PTAs provided an improvement over NPTA.

- From the data in Table 4.17, the MS:IO blend appeared to be slightly better than IO alone but was comparable to MS alone. All PTAs provided an improvement over NPTA.
- From Table 4.18, using IO was seen to be slightly more effective with respect to initial removal than BIO, IO:BIO or NPTA. However, the blend effectively conferred no advantage in this case. However, all PTAs here provided an improvement over NPTA.
- From Table 4.19, using OO was seen to be slightly more effective with respect to initial contaminant removal than CO or OO:CO. It was also apparent that OO, CO and OO:CO were all equivalent in their final removal efficacies and an improvement on NPTA.
- From the data in Table 4.20, OO appeared to be slightly better than VO - and both were significantly better than the blend or OO:VO, suggesting that the blend conferred no advantage in this case. All PTAs provided an improvement over NPTA.

Thus although none of the 50:50 blend can be said to confer significant advantages over the component PTAs, the assay has identified a detrimental blend and provides a ranking of the available PTAs for this type of contaminant and for this type of feather.

4.8.3 The PTA application method

In order to “soften” a contaminant on a feather substrate, it may be tacitly assumed that complete saturation by an appropriate PTA is required. Such an application may be referred to as a “DIPPING” process with respect to experiments conducted on either single feathers or feather clusters. However, it was deemed worthwhile to investigate whether a lighter application of PTA via a “DRIPPING” process could be equally effective, since this might focus on the removal of a layer at a time. Consequently, some preliminary experiments were conducted in order to test the effects on removal efficacy of these two different methods of PTA application.

Therefore three PTA blends¹⁴, MO:MS, OO:CO and OI:BIO, were tested for the efficacy of removal of JCO from duck feather clusters. For each of these blends, the removals for the two different methods of PTA application (i.e. dipping or dripping) were compared from the point of PTA application at N=6, until the final removal.

The materials and methods used in this section were similar to those used previously. Thus the PTAs were blended 50:50 and applied at the 6th treatment using the two different methods: i.e. (i) Dripping method - the blended PTA was dripped carefully onto the contaminated feathers to give a uniform surface coating and left to soak in for more than 30 sec; (ii) Dipping method – the oil contaminated feather cluster was dipped into a 25 mL jar of the blended PTA for 30 sec. Both sets of feather clusters were allowed to drain for 5 minutes before the cleansing process.

A representative curve for the MO:MS blend is shown in Figure 4.20. Typically, from the point of PTA application at N=6, the efficacy of removal for the ‘dripped’ application was found to be lower than that for the ‘dipped’. Similar curves for the other two blends were obtained Appendix 4.4. The P₀% values are compared in Table 4.21. It is noted that the PTA blends conferred no overall advantage for the removal of the JCO from the clusters. Indeed, this is an example of where the application of PTAs can actually make the situation worse.

Table 4.21 Final removals for the blended Pre-Treatment Agent (BPTA)-assisted removal of JCO from duck feather clusters, according to the method of PTA application.

N₇₀	P₀% Dipped	P₀ % Dripped	Δ (dipped P₀ % - Dipped P₀ %)	P₀% NBPTA
MO:MS	92.9 ± 1.5	75.9 ± 1.5	17.0	96.5 ± 0.7
OO:CO	87.9 ± 3.3	67.2 ± 2.2	20.7	96.5 ± 0.7
OI:BIO	91.9 ± 1.2	81.8 ± 2.0	10.1	96.5 ± 0.7

¹⁴ Blends were used here since the N₉₉ values for the blends were better than for the individual components.

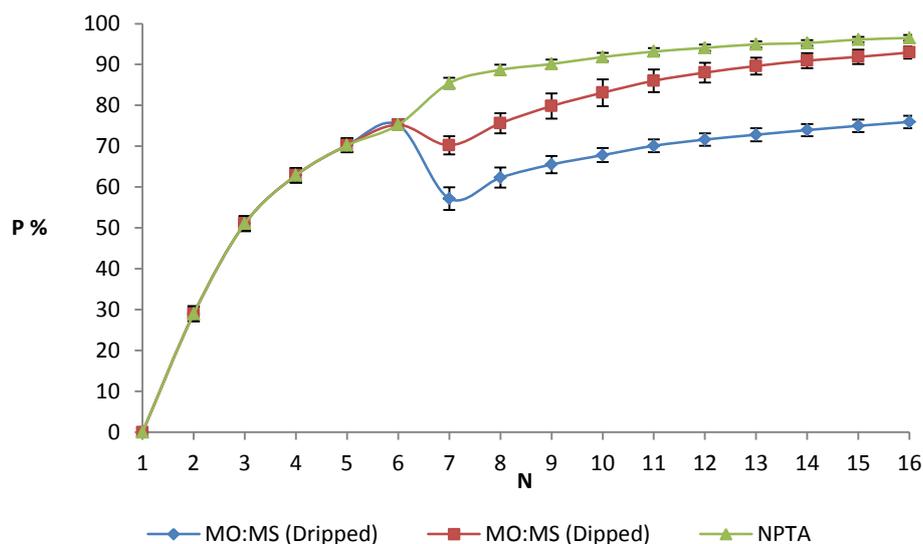


Figure 4.20 Comparison of JCO removal, P%, from duck feather clusters as a function of the number of treatments, N, using BPTAs (50:50) applied at the 6th treatment via two different application methods (by dripping onto feathers and by complete immersion or dipping). All experiments were conducted at 22 °C and iron powder MH300.29 was employed. Error bars represent the SE for five replicates. Individual profiles and full data sets are provided in Appendix 4.4 (Table 1, 2, 3 and 4).

Therefore, it is concluded that the “dipping” process is superior, arguing for as much penetration of the PTA as possible.

4.9 An MPT assessment of removal efficacy with respect to the point of PTA application to a contaminated feather(s)

As mentioned in the introduction to this chapter, anecdotally, the point of application of a PTA agent during a cleansing process is known to affect the efficacy of the removal process (albeit for detergent-based methods). Indeed, in some cases, it is worth reiterating that the application of a PTA is reputed to make the situation worse, in so far as the combination of some PTAs with some contaminants actually results in a more intractable problem. We have also found this to be reflected in our investigations involving the use of MPTs to remove contaminants with the assistance of PTAs, whereby application at the very beginning (N=1) was sometimes found to be not as beneficial as application at a later stage of the process (usually at around N=5 or 6). This is probably related to the composition of the contaminant changing throughout the removal process. The ability of the MPT method to accurately quantify contaminant removal (including contaminant plus PTA) throughout the course of a number of treatments, combined with the fact that the MPT assay results for removal efficacy

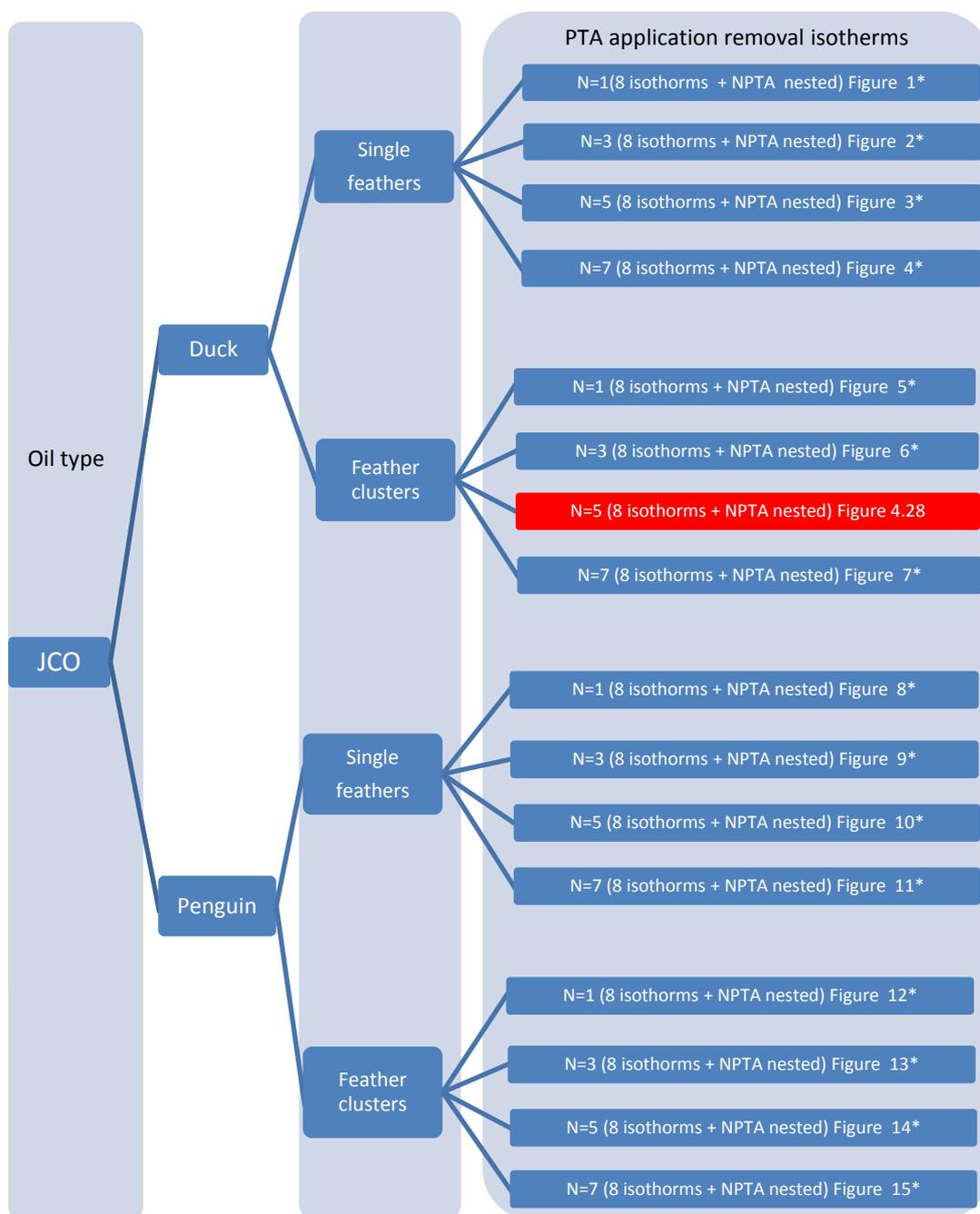
have been demonstrated to reflect, with fidelity, the outcomes for detergent-based methods, see Section 4.6, enabled this “point of PTA application” phenomenon to be systematically investigated in a quantitative manner. Therefore, the following series of MPT experiments were conducted. For both single duck feathers and duck feather clusters and single penguin feathers and penguin feather clusters, the magnetic removal of high viscosity Jasmine Crude Oil (JCO) with NH300.29 particles, employing eight different types of PTA, was quantitatively assessed in terms of the point of treatment (i.e. the value of N) at which a particular PTA was applied. The decision to compare single feathers with feather clusters was motivated by a desire to improve the efficiency of the assay (i.e. to speed up the testing procedure) and to ascertain the effect of the clustering *per se*.

4.9.1 Experimental details and method

The materials and method were the same as those described in Sections 4.5.1 and 4.5.2, except for the fact that the following experiments were carried out using Jasmine Crude Oil (JCO) as a contaminant, and the feathers used were those of the Mallard (domestic) Duck (*Anas platyrhynchos*) and Little Penguin (*Anas platyrhynchos*). The eight types of PTA used in these experiments were as previously described, Table 4.2.

The JCO is tarry at ambient temperature ($\sim 22^\circ\text{C}$) and has a viscosity of 682 cSt at 50°C . A single feather or a feather cluster (4 \times) (duck or penguin) was contaminated with JCO as described previously in Section 2.6.2.2. The oiled feather(s) was then immersed into the PTA for 30 seconds at different stages of the magnetic cleansing process (i.e. at N=1, N=3, N=5, N=7) in order to soften the contaminant. Excess contaminant and PTA were allowed to drain off before the removal process commenced or resumed. Standard removal isotherms were then generated corresponding to the application of each PTA at treatments N=1, N=3, N=5 and N=7, for which $P_o\%$, N_{90} , N_{95} or N_{99} , or $P_o\%/N_x$ ($x = 90$ or 95) parameters were calculated and compared. The magnetic harvesting process was continued until the maximum removal was achieved - until $P_o\%$, was achieved for each isotherm. The overall experimental procedure is depicted in Scheme 4.1. Thus for each feather type (duck and penguin), two parallel sets of 36 experiments (isotherms) were carried out¹⁵, one set using single feathers and the other using feather clusters.

¹⁵ Each set of 8 nested isotherms also included a control isotherm for removal with no pre-treatment agent (NPTA) - the same in each case.



Scheme 4.1 Experiments plan for the removal of JCO from duck and penguin feathers. The * indicates that the figures are provided in Appendix 4.5 and the red highlighted entry denotes the representative example given in the text, as follows.

4.9.2 Results and discussion

To clarify how these experiments have been conducted and how the data may be interpreted, one representative example has been drawn from Scheme 4.1 (highlighted red), where the relative effect of eight PTA treatments, applied at N=5, on the magnetic removal of JCO from

duck feather clusters, compared to no pre-treatment agent (NPTA), are shown as nine nested isotherms, Figure 4.21, and the assay schemes for the evaluation of the N_{90} , N_{95} and the $P_0\%$ values are shown in Figures 4.22 (a) and (b), respectively. A summary of the relevant data for this representative example is presented as a matrix, Table 4.22.

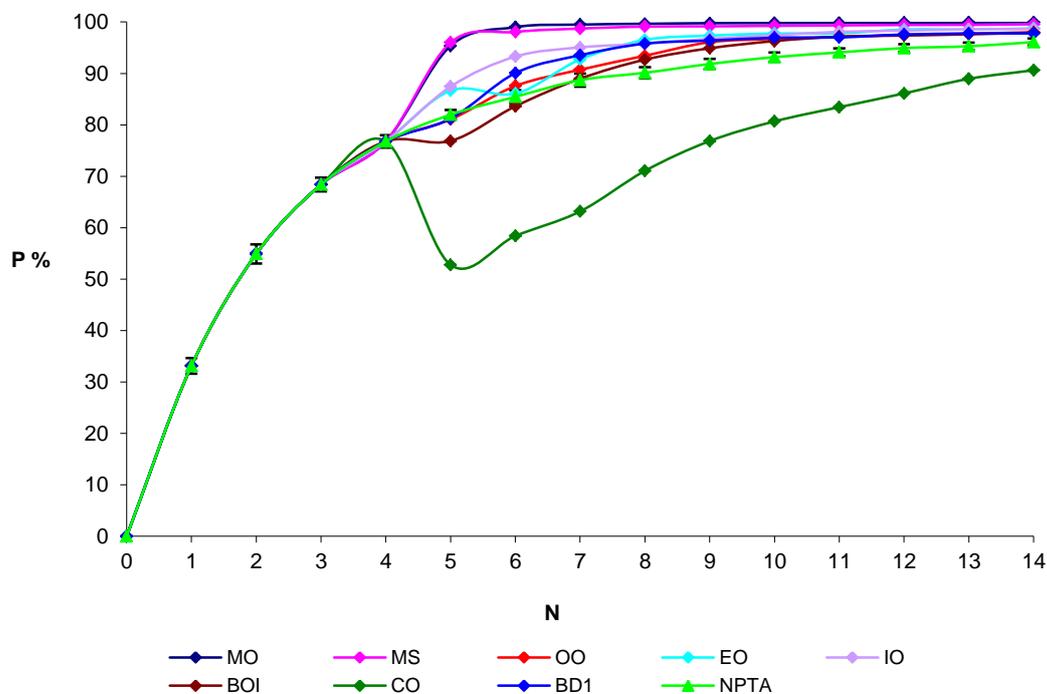


Figure 4.21 Percentage removal, P%, of Jasmine Crude Oil (JCO) from duck feather clusters with eight different PTAs, each used at the fifth treatment, compared to no pre-treatment agent (NPTA). Up to $N=5$ each point on the curve represent the average of 13 replicates, and after $N=5$, each point for the NPTA curve represent 5 replicates. Post $N=5$, all data points bar NPTA are single measurements. For the replicates the error bars represent SE and demonstrate the high reproducibility of the MPT method. The full data is provided in Appendix 4.5 (Table 1 and 2).

It is clear from Figure 4.21 and Figure 4.22 (a) and (b) that different PTAs applied at $N=5$ can have dramatically different outcomes, both with respect to boosting or inhibiting the removal process, reflected in N_{90} , N_{95} and with respect to the final removal $P_0\%$. The parameter $P_0\%/N_{90 \text{ or } 95}$ attempts to capture the overall efficacy.

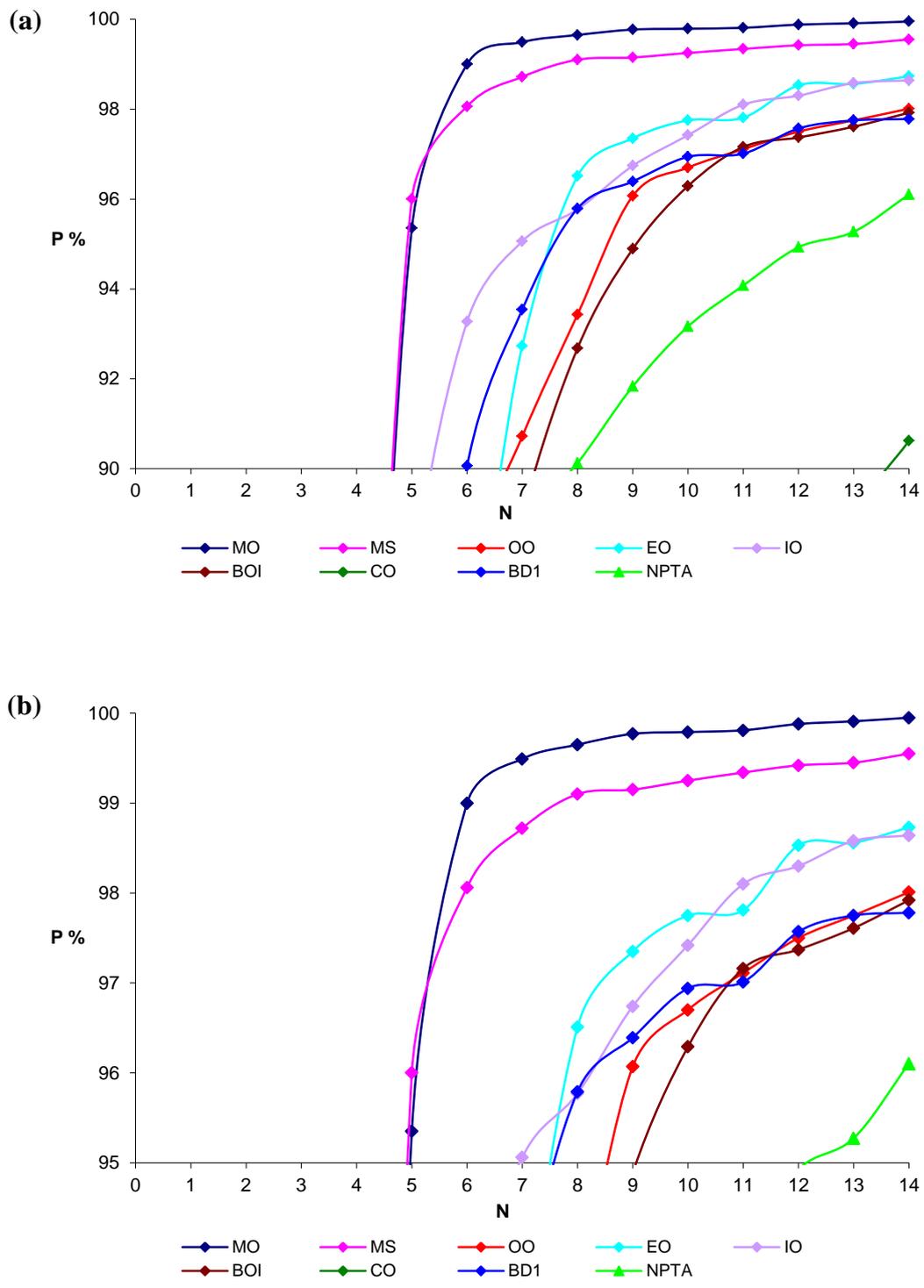


Figure 4.22 N_{90} assay scheme for the PTA assisted removal (at $N=5$) of Jasmine Crude Oil (JCO) from duck feather clusters **(b)** N_{95} assay scheme for the PTA assisted removal of Jasmine Crude Oil (JCO) from duck feather clusters.

Table 4.22 Matrix of the relevant efficacy parameters for the PTA-assisted (applied at N=5) removal of JCO from duck feather clusters. The # entry means that the PTA is applied but 95% removal (for N₉₅) is not achieved. Note: the lower N_{90/95} values and the higher the P₀%/N_{90/95} values, the better the immediate removal after the application of PTA. Obviously, the higher P₀%, the better the final removal.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
P ₀ % (N=5)	99.9	99.6	98.0	98.7	98.6	97.9	90.6	97.8	96.1
N ₉₀ (N=5)	4.7	4.7	6.8	6.6	5.4	7.2	13.6	6.0	8.0
P ₀ %/N ₉₀ (N=5)	21.3	21.2	14.1	15.0	18.3	13.6	6.7	16.3	12.0
N ₉₅ (N=5)	5	5	8.6	7.5	7	9.1	#	7.6	12.2
P ₀ %/N ₉₅ (N=5)	20.0	19.9	11.4	13.2	14.1	10.8	#	12.9	7.9

P₀% (N=5) MO>MS>EO~IO>OO>BIO>BD1>NPTA>CO

P₀%/N₉₀ (N=5) MO~MS>IO>BD1>EO>OO>BIO>NPTA>CO

P₀%/N₉₅ (N=5) MO~MS>IO>EO>BD1>OO>BIO>NPTA>CO

From the above data, with respect to the removal of JCO, it is apparent, by comparing the relative values of P₀%/N₉₀ (blue row) and P₀%/N₉₅ (green row), and the inequalities below the table, that the application of seven of the eight PTAs at N=5 conferred an overall advantage compared to no PTA (NPTA) at all; with MO and MS being the most effective (at **21.3/21.2** and **20.0/19.9**, respectively). However, it should be noted that CO applied at N=5 actually hindered removal compared to NPTA (**6.7/12.0** and **#/7.9** respectively and **90.6%/96.1%** respectively). This is consistent with anecdotal evidence, *vide supra*, that suggests that sometimes a PTA can make the problem of removal worse¹⁶. The dramatic effect in this case with respect to CO can be anticipated by the depression of the CO isotherm in Figure 4.21 above. The complex chemistry of CO mixing with JCO at N=5 to make it more resistant to removal, although fascinating, was beyond the scope of this thesis but will be explored further within the group in the future. MO and MS applied at N=5 were also clear favourites for achieving a final removal approaching 100%. This representative example demonstrates how, based on carefully designed experimental PTA assays; recommendations may be made to wildlife rehabilitators on PTA choice and choice of application point.

The full set of relevant parameters extracted from all of the isotherms shown in Scheme 4.1, are given in Table 4.23 - 4.27 (duck feathers - single and clusters) and Tables 4.28 - 4.32

¹⁶ It is important to note here that this kind of analysis not only points to the preferred PTAs and points of application but also to detrimental PTAs and points of application.

(penguin feathers - single and clusters). Note that: PTA treatments at N=1 to 4 are expected to carry more information on the initial removal and PTA treatments at N=5 to 7 are expected to carry more information on the final removal. Therefore, N_{90} , N_{95} , tend to be more relevant to N=1 to 4 and $P_o\%$ tend to be more relevant to N= 5 to 7. $P_o\%/N_{90}$ and $P_o\%/N_{95}$ provide information on the overall efficacy. Individual isotherms and associated data described in Scheme 4.1 are given in Appendix 4.5.

4.9.3 Single duck feathers at N_{90} and N_{95}

All the relevant parameters for assessing PTA efficacy for eight PTAs applied at N=1, 3, 5 & 7 in relation to the removal of JCO from single duck feathers and duck feather clusters at N_{90} and N_{95} are tabulated in Tables 4.23 – 4.26 as follows.

Table 4.23 Matrix of the relative efficacy parameters (w.r.t. N_{90}) for the PTA-assisted removal of JCO from SINGLE DUCK FEATHERS at N=1, 3, 5 & 7. The * entries indicate that 90% removal was achieved before the application of the PTA. In these cases the relevant parameter is $P_o\%$.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N_{90} (N=1)	6.3	3.3	4.1	3.7	2.9	3.3	4.4	6.1	6.9
$P_o\%$ (N=1)	98.0	99.0	98.6	99.0	99.6	99.3	98.7	98.1	95.3
$P_o\%/N_{90}$ (N=1)	15.6	30.0	24.0	26.8	34.4	30.1	22.4	16.1	13.8
N_{90} (N=3)	3.5	3.7	4.6	4.5	4.1	4.1	4.0	5.6	6.9
$P_o\%$ (N=3)	99.6	99.1	98.5	98.7	99.3	99.2	98.3	98.9	95.3
$P_o\%/N_{90}$ (N=3)	28.5	26.8	21.4	21.9	24.2	24.2	24.6	17.7	13.8
N_{90} (N=5)	*	*	5.1	*	*	6.6	7.6	*	6.9
$P_o\%$ (N=5)	99.9	99.9	99.4	99.9	99.9	96.8	97.8	99.8	95.3
$P_o\%/N_{90}$ (N=5)	*	*	19.5	*	*	14.7	12.9	*	13.8
N_{90} (N=7)	*	7.3	*	*	*	*	*	*	6.9
$P_o\%$ (N=7)	99.9	97.8	99.9	99.9	99.7	99.0	99.4	99.9	95.3
$P_o\%/N_{90}$ (N=7)	*	13.4	*	*	*	*	*	*	13.8

From this matrix, it is clearly apparent that different PTAs applied at different stages into the removal give dramatically different outcomes, especially with respect to initial removals, as reflected in the N_{90} and $P_o\%/N_{90}$ parameters.. With respect to final removals, as reflected by the $P_o\%$ values, it may be seen that the application of any PTA at any point improved the final removal, with some approaching 100% (highlighted in yellow). All things considered,

the preferred applications to favour both initial and final removals are IO at N=1 and MO at N=3 (yellow highlight). More detrimental situations are highlighted in green. This includes NPTA and perhaps the application of MS at N=7 and CO at N=5. For applications at N=1 and 3, the actual preferred orders of PTAs are:

P₀%/N₉₀ (N=1) IO>BIO~MS>EO>OO>>CO>BD1>MO>NPTA

P₀%/N₉₀ (N=3) MO>MS>CO~IO~BIO>EO~OO>BD1>NPTA

Thus overall, for the PTA-assisted removal of JCO from single duck feathers, IO applied at N=1 was the best followed by MO applied at N=3 with respect to both initial and final removal. CO applied at N=5 and MS applied at N=7 were not recommended, especially with respect to initial removal. It is notable that the relative beneficial effects of MO were reversed between treatments N=1 and N=3.

Table 4.24 Matrix of the relative efficacy parameters (w.r.t. N₉₅) for the PTA-assisted removal of JCO from SINGLE DUCK FEATHERS at N=1, 3, 5, 7. The * entry indicates that 95% removal has been achieved before the application of the PTA.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N ₉₅ (N=1)	8.4	4.3	6	4.7	3.7	4.2	5.4	8.7	13.4
P ₀ % (N=1)	98.0	99.0	98.6	99	99.6	99.3	98.7	98.1	95.3
P ₀ %/N ₉₅ (N=1)	11.7	23.0	16.4	21.1	26.9	23.6	18.3	11.3	7.1
N ₉₅ (N=3)	4.8	4.4	7.5	5.3	5	4.9	5.8	7.9	13.4
P ₀ % (N=3)	99.6	99.1	98.5	98.7	99.3	99.2	98.3	98.9	95.3
P ₀ %/N ₉₅ (N=3)	20.8	22.5	13.1	18.6	19.9	20.2	16.9	12.5	7.1
N ₉₅ (N=5)	*	*	5.8	5	*	8.5	9	5.3	13.4
P ₀ % (N=5)	99.9	99.9	99.4	99.9	99.9	96.8	97.8	99.8	95.3
P ₀ %/N ₉₅ (N=5)	*	*	17.1	20.0	*	11.4	10.9	18.8	7.1
N ₉₅ (N=7)	*	8.7	7.3	*	7	7.9	7.1	*	13.4
P ₀ % (N=7)	99.9	97.8	99.9	99.9	99.7	99.0	99.4	99.9	95.3
P ₀ %/N ₉₅ (N=7)	*	11.2	13.7	*	14.2	12.5	14.0	*	7.1

As expected, the outcomes for the N₉₅ matrix above reflected those for the N₉₀ matrix. Thus IO at N=1 and MO at N=3 were preferred to enhance both initial and overall removals – yellow highlight. The more detrimental applications were, as in the N₉₀ assay – green highlight. Again, with respect to final removals it may be seen that the application of any PTA at any point improved the final removal, with some approaching 100%. Applications

Table 4.25 Matrix of the relative efficacy parameters (w.r.t. N_{90}) for the PTA-assisted removal of JCO from DUCK FEATHER CLUSTERS at $N=1, 3, 5, 7$. The # entry means that the PTA is applied but 90% removal is not achieved. The * entry indicates that 90% removal has been achieved before the application of the PTA.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N_{90} (N=1)	5.40	4.5	6.6	7.6	6.1	7.1	6.0	9.5	8.0
$P_o\%$ (N=1)	98.5	98.7	98.3	97.6	98.1	98.3	97.9	96.7	96.1
$P_o\%/N_{90}$ (N=1)	18.2	21.9	14.9	12.8	16.1	13.8	16.3	10.2	12
N_{90} (N=3)	4.60	8.2	6.7	6.3	7.5	4.4	5.5	3.8	8.0
$P_o\%$ (N=3)	98.5	98.0	96.5	97.8	97.3	98.9	97.9	99.7	96.1
$P_o\%/N_{90}$ (N=3)	21.4	12.0	14.4	15.5	13.0	22.5	17.8	26.2	12.0
N_{90} (N=5)	*	*	6.8	6.6	5.4	7.2	13.6	6.0	8.0
$P_o\%$ (N=5)	99.9	99.6	98.0	98.7	98.6	97.9	90.6	97.8	96.1
$P_o\%/N_{90}$ (N=5)	*	*	14.1	15.0	18.3	13.6	6.7	16.3	12.0
N_{90} (N=7)	#	8.7	7.8	#	*	7.6	7.9	*	8.0
$P_o\%$ (N=7)	84.8	97.6	97.5	88.5	99.4	98.3	98.7	99.2	96.1
$P_o\%/N_{90}$ (N=7)	#	11.2	12.5	#	*	13.0	12.7	*	12.0

However, the application of MO and EO at $N=7$ compromised the final removal and CO at $N=5$ compromised the initial and final removals – green highlights. Thus the preferred PTAs and points of application are highlighted in yellow and those that are potentially detrimental are highlighted in green. For applications at $N=1$ and 3, the preferred order of PTAs is:

$P_o\%/N_{90}$ (N=1) MS>MO>CO>IO>OO>BIO>EO>BD1>NPTA

$P_o\%/N_{90}$ (N=3) BD1>BIO>MO>CO>EO>OO>IO>MS>NPTA

An analysis of the matrix shown in Table 4.26, again representing feather clusters, also demonstrated that that different PTAs applied at different stages in the removal gave dramatically different outcomes, especially with respect to initial removals. As expected, the best performers with respect to initial removal are reflective of the N_{90} values, namely BD1 at $N=3$ and MS at $N=1$. It should also be noted that MO and MS applied at $N=5$ gave superior outcomes with small values of N_{95} (both at 5.0) and large values of $P_o\%/N_{95}$ (20.0 and 19.9 respectively) and $P_o\%$ (99.9% and 99.6% respectively). With respect to final removals it may be seen that the application of any PTA at any point generally improved the final removal, with MO at $N=5$ approaching 100%. However, the application of MO and EO at $N=7$ and CO at $N=5$, again, compromised the final removal. Thus the preferred PTAs and points of

application are highlighted in yellow and those that are potentially detrimental are highlighted in green.

Table 4.26 Matrix of the relative efficacy parameters (w.r.t. N_{95}) for the PTA-assisted removal of JCO from DUCK FEATHER CLUSTERS at $N=1, 3, 5, 7$. The # entry means that the PTA is applied but 95% removal is not achieved.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N_{95} (N=1)	7.3	6.1	8.6	9.3	9.1	9	8	11.1	12.2
$P_o\%$ (N=1)	98.5	98.7	98.3	97.6	98.1	98.3	97.9	96.7	96.1
$P_o\%/N_{95}$ (N=1)	13.5	16.2	11.4	10.5	10.8	10.9	12.2	8.7	7.9
N_{95} (N=3)	6.6	10.5	9.7	7.8	10.1	5.6	7.5	5.1	12.2
$P_o\%$ (N=3)	98.5	98	96.5	97.8	97.3	98.9	97.9	99.7	96.1
$P_o\%/N_{95}$ (N=3)	14.9	9.3	9.9	12.5	9.6	17.7	13.1	19.5	7.9
N_{95} (N=5)	5.0	5.0	8.6	7.5	7	9.1	#	7.6	12.2
$P_o\%$ (N=5)	99.9	99.6	98	98.7	98.6	97.9	90.6	97.8	96.1
$P_o\%/N_{95}$ (N=5)	20.0	19.9	11.4	13.2	14.1	10.8	#	12.9	7.9
N_{95} (N=7)	#	10.2	9.9	#	7.4	9.2	9.2	7.3	12.2
$P_o\%$ (N=7)	84.8	97.6	97.5	88.5	99.4	98.3	98.7	99.2	96.1
$P_o\%/N_{95}$ (N=7)	#	9.6	9.8	#	13.4	10.6	10.7	13.6	7.9

For applications at $N=1$ and 3 , the preferred order of PTAs for the N_{95} assay may be compared with the N_{90} assay as follows:

$P_o\%/N_{95}$ (N=1) MS>MO>CO>OO>IO~BIO>EO>BD1>NPTA
 $P_o\%/N_{90}$ (N=1) MS>MO>CO>IO>OO>BIO>EO>BD1>NPTA
Best Worst
 $P_o\%/N_{95}$ (N=3) BD1>BIO>MO>CO>EO>OO>IO>MS>NPTA
 $P_o\%/N_{90}$ (N=3) BD1>BIO>MO>CO>EO>OO>IO>MS>NPTA

As expected, as with the single feathers, there is a good correspondance between the N_{90} (shown in red) and the N_{95} assays (shown in black), especially with respect to a qualitative comparison as to what is the best and the worst (*vide supra*). Again, note that what was one of the worst at $N=1$ (e.g. BD1) was the best at $N=3$! This illustrates once more the importance of the point of application of the PTA. At the qualitative level, the above experiments allow the assays based on single feathers to be compared to those based on clusters, Table 4.27.

Table 4.27 A qualitative comparison of PTA removal efficacy for the single duck feather assay compared to the duck feather cluster assay. The blue colours signify a correspondance between single feathers and feather clusters.

Substrate	Best three PTAs	Worst three PTAs
Single feather	N=1; IO>BIO>MS N=3; MO>MS>BIO	N=1; BD1<MO<OO N=3; BD1<OO<CO
Feather cluster	N=1; MS>MO>CO N=3; BD1>BIO>MO	N=1; BD1<EO<BIO N=3; MS<IO<OO

From Table 4.27 it may be seen that whilst there was some correspondance between single feathers and clusters, there were also differences. Such differences reflect the importance of feather-feather interaction in relation to magnetic cleansing¹⁷. A more detailed examination of this phenomenon is beyond the scope of this thesis.

4.9.5 Single penguin feathers at N₉₀ and N₉₅

All the relevant parameters for assessing PTA efficacy for eight PTAs applied at N=1, 3, 5 & 7 in relation to the removal of JCO from single penguin feathers and penguin feather clusters at N₉₀ and N₉₅ are tabulated in Tables 4.28 – 4.32 as follows.

This matrix depicted in Table 4.28 demonstrates that for, single penguin feathers, initial and overall removal was not advantaged by any PTAs, at any point of application, since all P₀%/N₉₀ values were considerably less than the value of 66.1 for NPTA (highlighted in yellow). It is interesting to note how certain applications actually hindered initial removal, as indicated by the relatively low values of P₀%/N₉₀ (highlighted in green). For example, it would not be advisable to apply OO at N=3 or CO at N=1, 3 or 5 (especially), either from an initial and/or final removal perspective.

¹⁷ It is surmised that this effect may be more significant for magnetic cleansing than for detergent-based cleansing.

Table 4.28 Matrix of the relative efficacy parameters (w.r.t. N_{90}) for the PTA-assisted removal of JCO from SINGLE PENGUIN FEATHERS at N=1, 3, 5, 7. The * entry indicates that 90% removal has been achieved before the application of the PTA.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N_{90} (N=1)	3.3	2.8	5.0	2.3	4.0	4.6	4.5	3.8	5.2
$P_o\%$ (N=1)	99.0	99.4	99.0	99.0	99.4	99.0	97.2	99.2	99.1
$P_o\%/N_{90}$ (N=1)	30	35.5	19.8	43.0	24.9	21.5	21.6	26.1	66.1
N_{90} (N=3)	3.4	*	6.3	4.3	*	*	4.3	*	5.2
$P_o\%$ (N=3)	99.4	99.6	97.1	99.6	99.9	99.2	97.8	99.9	99.1
$P_o\%/N_{90}$ (N=3)	29.2	*	15.4	23.2	*	*	22.2	*	66.1
N_{90} (N=5)	*	*	*	*	*	*	7.5	*	5.2
$P_o\%$ (N=5)	99.9	98.0	99.7	99.1	99.7	97.4	95.0	99.3	99.1
$P_o\%/N_{90}$ (N=5)	*	*	*	*	*	*	12.5	*	66.1
N_{90} (N=7)	*	*	*	*	*	7.8	*	7.3	5.2
$P_o\%$ (N=7)	99.9	99.9	98.4	99.1	99.1	99.9	99.9	99.9	99.1
$P_o\%/N_{90}$ (N=7)	*	*	*	*	*	12.8	*	13.7	66.1

However, it should be noted that the application of a number of PTAs at various points can boost the final removal - in some cases to a value approaching 100% (also highlighted in yellow). Thus the following applications were seen to boost the final removal: MO at N=3, 5 or 7 (the latter two especially), MS at N=1, 3 or 7 (especially), IO at 1, 3 (especially) or 5, BIO at N=7 (especially), CO at N=7, BD1 at 3 (especially), 5 or 7 (especially). Contraindications in relation to the final removal were for OO at N=3, BIO at N=5 and for CO at N=1, 3 or 5 (especially).

Thus the N_{90} ordering for single penguin feathers at N=1 was:

$P_o\%/N_{90}$ (N=1): NPTA>EO>MS>MO>BD1>IO>CO~BIO>OO

Notably, the comparative ordering for single duck feathers was:

$P_o\%/N_{90}$ (N=1): IO>BIO~MS>EO>OO>>CO>BD1>MO>NPTA

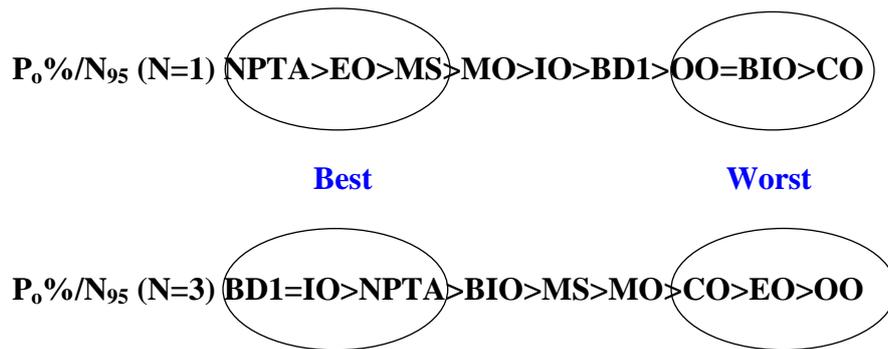
It can be seen that these comparative orderings were quite different - demonstrating that different feathers responded very differently to the different PTAs and their points of application. This was not unexpected since it has been previously demonstrated within the

group that different feather types (even breast versus back feathers of the same species) display different removal isotherms - even without PTAs (Ngeh, 2002).

Table 4.29 Matrix of the relative efficacy parameters (w.r.t. N_{95}) for the PTA-assisted removal of JCO from SINGLE PENGUIN FEATHERS at $N=1, 3, 5, 7$. The * entry indicates that 95% removal has been achieved before the application of the PTA.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N_{95} (N=1)	4.1	3.8	6.3	2.8	4.9	6.3	9.4	5.9	6.4
$P_0\%$ (N=1)	99.0	99.4	99.0	99.0	99.4	99.0	97.2	99.2	99.1
$P_0\%/N_{95}$ (N=1)	24.1	26.2	15.7	35.4	20.3	15.7	10.3	16.8	43.1
N_{95} (N=3)	4.8	3.7	9.7	6.7	*	3.5	6.4	*	6.4
$P_0\%$ (N=3)	99.4	99.6	97.1	99.6	99.9	99.2	97.8	99.9	99.1
$P_0\%/N_{95}$ (N=3)	20.7	26.9	10.0	14.9	*	29.2	15.3	*	43.1
N_{95} (N=5)	*	*	*	*	*	6.5	*	5.4	6.4
$P_0\%$ (N=5)	99.9	98.0	99.7	99.1	99.7	97.4	95.0	99.3	99.1
$P_0\%/N_{95}$ (N=5)	*	*	*	*	*	15.0	*	18.4	43.1
N_{95} (N=7)	*	*	8.6	7.2	7.4	8.8	7.8	8.4	6.4
$P_0\%$ (N=7)	99.9	99.9	98.4	99.1	99.1	99.9	99.9	99.9	99.1
$P_0\%/N_{95}$ (N=7)	*	*	11.4	13.8	13.4	11.4	12.8	11.9	43.1

From this matrix, as with the N_{90} assay, it is apparent that initial removal was not advantaged by any PTAs, at any point of application, since all $P_0\%/N_{95}$ values were considerably less than the value of 43.1 for NPTA (highlighted in yellow). However, as with the N_{90} assay data, the application of a PTA at certain points was seen to enhance the final removal (approaching 100% in some cases – again highlighted in yellow). Notable amongst these was the application of IO or BD1 at $N=3$ and the application of a wide range of PTAs at $N=7$ (all giving a final removal of 99.9%). As with the N_{90} assay, there were some contraindications (highlighted in green). For example, the application of OO was not recommended, with respect to either initial or final removal, at $N=3$ or 7; the application of BIO was not recommended, with respect to either initial or final removal, at $N=5$ and the application of CO, with respect to either initial or final removal, was not recommended at $N=1$ or 3 and was especially not recommended, with respect to the final removal for $N=5$. Thus the N_{95} ordering for single penguin feathers was:



Note that, as in the case of duck feathers and as expected, there was a close correspondence between the N_{90} and N_{95} outcomes, *vide supra*.

4.9.6 Penguin feather clusters at N_{90} and N_{95}

An analysis of the matrix shown in Table 4.30 shows that, as with single feathers, from this matrix representing penguin feather clusters, it was again apparent that different PTAs applied at different stages in the removal gave dramatically different outcomes, especially with respect to initial removals. It was also apparent that initial removal was not advantaged by any PTAs, at any points of application, since all $P_0\%/N_{90}$ values were considerably less than the value of 39.7 for NPTA (highlighted in yellow). With respect to the final removal, it may be seen that MO and MS applied at $N=5$ boosted the final removal to values approaching 100% - yellow highlights. Contraindications were OO, EO and IO applied at $N=1$; CO (especially) and BD1 applied at $N=3$; CO applied at $N=5$ and BIO and CO applied at $N=7$ - green highlights. The N_{90} orderings for $N=1$ and 3 were:

$P_0\%/N_{90}$ (N=1): NPTA>BD1>CO>BIO>EO>MO>MS>OO>IO

$P_0\%/N_{90}$ (N=3): MS>NPTA>BIO>EO>MO>IO>BD1>CO>OO

Not only were these very different from each other (again emphasizing the importance of the point of application) but they were also very different from the analogous data for *duck* clusters (shown below in red below), illustrating that different feather types responded very differently.

$P_0\%/N_{90}$ (N=1): MS>MO>CO>IO>OO>BIO>EO>BD1>NPTA

$P_0\%/N_{90}$ (N=3): BD1>BIO>MO>CO>EO>OO>IO>MS>NPTA

Table 4.30 Matrix of the relative efficacy parameters (w.r.t. N_{90}) for the PTA-assisted removal of JCO from PENGUIN FEATHER CLUSTERS at $N=1, 3, 5, 7$. The * entry indicates that 90% removal has been achieved before the application of the PTA.

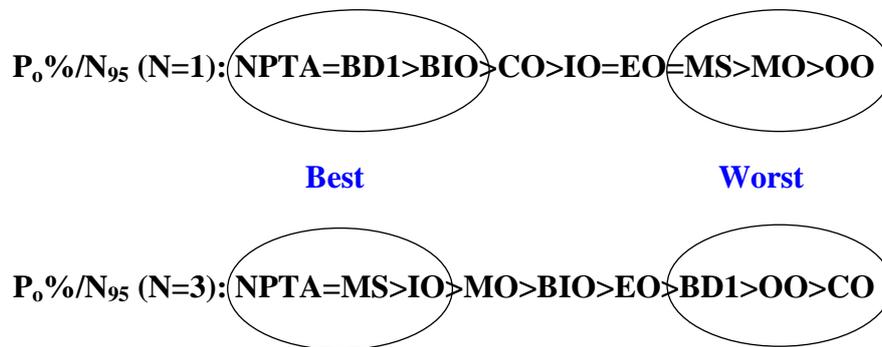
	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N_{90} (N=1)	5.9	6.2	7.1	5.1	8.6	4.6	3.9	2.8	5.5
$P_o\%$ (N=1)	98.0	98.0	97.0	97.2	97.0	99.0	98.0	99.1	99.3
$P_o\%/N_{90}$ (N=1)	16.6	15.8	13.7	19.1	11.3	21.5	25.1	35.4	39.7
N_{90} (N=3)	4.2	*	7.8	4.0	4.4	3.1	6.0	5.8	5.5
$P_o\%$ (N=3)	99.0	99.3	98.0	99.0	98.2	98.4	96.0	97.0	99.3
$P_o\%/N_{90}$ (N=3)	23.6	*	12.6	24.8	22.3	31.7	16	16.7	39.7
N_{90} (N=5)	*	*	*	*	*	*	5.8	5.6	5.5
$P_o\%$ (N=5)	99.9	99.8	99.7	99.6	99.4	99.3	97.4	99.0	99.3
$P_o\%/N_{90}$ (N=5)	*	*	*	*	*	*	16.8	18.3	39.7
N_{90} (N=7)	*	*	*	*	*	8.4	7.8	*	5.5
$P_o\%$ (N=7)	99.0	98.0	99.3	99.0	99.1	97.0	97.2	99.5	99.3
$P_o\%/N_{90}$ (N=7)	*	*	*	*	*	11.6	12.5	*	39.7

The same analysis at N_{95} for penguin feather clusters, Table 4.31 below, led to the same conclusions with different PTAs applied at different stages giving dramatically different outcomes. Unlike duck feathers, the application of PTAs at any point did not confer an advantage with respect to the initial removal, since all $P_o\%/N_{95}$ values were considerably less than the value of 26.1 for NPTA (highlighted in yellow). Application of MO or MS at $N=5$ boosts the final removal to approaching 100%. As with the N_{90} assay, contraindications were application of OO, EO or IO at $N=1$; CO (especially) or BD1 at $N=3$; CO at $N=5$ and BIO or CO at $N=7$.

Table 4.31 Matrix of the relative efficacy parameters (w.r.t. N_{95}) for the PTA-assisted removal of JCO from PENGUIN FEATHER CLUSTERS at $N=1, 3, 5, 7$. The * entry indicates that 95% removal has been achieved before the application of the PTA.

	MO	MS	OO	EO	IO	BIO	CO	BD1	NPTA
N_{95} (N=1)	9.3	8.9	10.2	8.8	11.7	5.9	5.8	3.8	6.5
$P_0\%$ (N=1)	98.0	98.0	97.0	97.2	97.0	99.0	98.0	99.1	99.3
$P_0\%/N_{95}$ (N=1)	10.5	11.0	9.5	11.0	11.1	17.1	16.9	26.1	26.1
N_{95} (N=3)	4.9	3.8	10.5	6.1	6.2	5.3	12.4	9.5	6.5
$P_0\%$ (N=3)	99.0	99.3	98.0	99.0	98.2	98.4	96.0	97.0	99.3
$P_0\%/N_{95}$ (N=3)	20.6	26.1	9.3	16.2	22.3	18.6	7.7	10.2	26.1
N_{95} (N=5)	*	*	*	*	*	*	8.9	7.2	6.5
$P_0\%$ (N=5)	99.9	99.8	99.7	99.6	99.4	99.3	97.4	99.0	99.3
$P_0\%/N_{95}$ (N=5)	*	*	*	*	*	*	10.9	13.8	26.1
N_{95} (N=7)	7.5	8.5	7.5	7.7	*	11.2	10.3	*	6.5
$P_0\%$ (N=7)	99.0	98.0	99.3	99.0	99.1	97.0	97.2	99.5	99.3
$P_0\%/N_{95}$ (N=7)	13.2	11.5	12.9	12.9	*	8.7	9.4	*	26.1

The N_{95} orderings for $N=1$ and $N=3$ were:



Again these were very different from the analogous data for *duck* clusters (shown below in red below), illustrating that different feather types responded very differently.

$P_0\%/N_{95}$ (N=1): MS > MO > CO > OO > IO ~ BIO > EO > BD1 > NPTA

$P_0\%/N_{95}$ (N=3): BD1 > BIO > MO > CO > EO > OO > IO > MS > NPTA

Table 4.32 A qualitative comparison of PTA removal efficacy for the single penguin feather assay compared to the penguin feather cluster assay. The blue colours signify a correspondance between single feathers and feather clusters.

Substrate	Best three PTAs	Worst three PTAs
Single feather	N=1; NPTA >EO>MS N=3; BD1 =IO> NPTA	N=1; OO =BIO> CO N=3; CO >EO> OO
Feather cluster	N=1; NPTA = BD1 >BIO N=3; NPTA =MS>IO	N=1; MS>MO> OO N=3; BD1 > OO > CO

As in Table 4.27 that relates to duck feathers, from Table 4.32 it may also be seen that, for penguin feathers, whilst there was some correspondance between single feathers and clusters, there were also differences. Again, such differences reflected the importance of feather-feather interaction in relation to magnetic cleansing. A more detailed examination of this phenomenon was beyond the scope of this thesis.

Due to the observed lack of an exact correspondance between single and cluster assays it was decided that, even though more time consuming, the cluster assays should be the ones on which efficacy assays should be based - since these more realistically reflect real plumage.

The extent of this lack of correlation between tests performed on single feathers versus feather clusters has also been confirmed in a separate series of experiments whereby the removal of a moderate viscosity bunker oil (BO1) from single duck feathers has been compared to removal from feather clusters. The correlation coefficients between the N₉₅ and N₉₉ parameters for single duck feathers and duck feather clusters are 0.0522 and 0.6293 respectively. The detailed data and assay schemes are given in Figure 1 to 17 and Table 1 to 19 in Appendix 4.5. This provides further support for the decision to employ clusters rather than single feathers in the assay.

4.10 Conclusions

This chapter involved the development and application of an assay based on MPT for the quantification of relative PTA efficacy. Experiments were designed and conducted in order

to establish the important proof of principle that conclusions based on the MPT assay may be carried over with fidelity to detergent-based methods of cleansing. The establishment of this principle is an important advance and paves the way for the systematic establishment of a database that wildlife rehabilitators may refer to for choosing the most appropriate PTA for a particular contaminant and bird type. The further development of such a database is an important topic for future research. Importantly, it allows contra-indications to be established and supports the anecdotal evidence that some PTAs applied at the wrong stage of the treatment can actually make matters worse. An interesting, and most fortunate, aspect of these experiments is the fact that small but statistically significant signals gleaned from the MPT assays are greatly magnified (by at least seven-fold) when translated to the analogous detergent-based method.

Using our established methods, the intrinsic removal characteristics of a wide range of PTAs themselves were examined and the effects of blending PTAs on removal efficacies was investigated. These studies turned up a number of surprises, *vide supra*, including the observation that the combination of two ‘poor’ PTAs can actually produce a ‘good’ PTA. The explanation for such effects, although intriguing is complex and has been reserved for future studies.

The MPT assay was exhaustively applied to assess the removal efficacy with respect to the point of PTA application. These investigations were conducted with respect to the removal of viscous JCO from both duck and penguin feathers, assisted by eight different PTAs. Such studies result in matrices of efficacy parameters that may be used to recommend the best PTA and the best point of application for a given contaminant and feather type. Information may be gleaned with respect to initial removal (for a quick clean), for the final removal and/or for the overall efficacy. In an attempt to make the assay as efficient as possible, assays were conducted on both single feathers and feather clusters. Based on these outcomes, it was decided that the assay should appropriately be conducted on feather clusters. There were major differences observed between the recommendations made for duck feathers as compared to penguin feathers, indicating that there is a unique response for each feather type.

4.11 References

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Chapter 5: The magnetic removal of oil contamination from fur and rock substrates – effect of PTAs

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Chapter 5: The magnetic removal of oil contamination from fur and rock substrates – effect of PTAs

5.1 Introduction

Oil spills have deleterious effects on the environment generally and wildlife specifically, including birds and mammals. Whilst there has been many studies on the effect of oil spills at on birds (Camphuysen and Heubeck 2001; Massey 2006; Barron 2012) and, there are fewer such reported studies on mammals (Geraci and Aubin 1988. Garrot *et al.* 1993, Hoover-Miller *et al.* 200; Jessup *et al.* 2012). However, oil spills also come from land-based sources such as pipelines (Owens and Henshaw 2002) and storage facilities (Fisher *et al.* 1992). Leakage from pipelines, in particular, is a considerable source of oil pollution on land (Etkin 1999). For example, the Isiokpo oil pipeline leakage, which happened in Nigeria in 1997, released 12,000 barrels of crude oil and affected a large area (Osuji *et al.* 2005). In Russia, where crude oil is transported for thousands of kilometres overland via pipelines, oil leakage is not uncommon (ESMAP 2003). For instance, the Kharyaga Usink pipeline oil spill, which occurred in Russia in 1995, discharged 104,420 tonnes of oil and contaminated a large area (Etkin 1999). It is estimated that around 15-20 million tonnes of oil are lost through pipeline accidents annually in Russia (Pelley 2001). This causes considerable environmental damage, including effects upon terrestrial wildlife. In Australia, oil is also transported by an extensive network of pipelines. This sometimes results in oil leakage that affects the environment, such as an oil pipeline spill in Brisbane in 2003 (Ames 2004). Also, there are concerns with respect to the possible impact of oil and gas development projects on Barrow Island, Western Australia, especially with respect to local land mammals, including threatened species such as golden bandicoots (*Isoodon auratus*) and the black-footed rock wallaby (*Petrogale lateralis*) (CCWAI 2007). In another part of the globe, Alaska, there are growing concerns over the effect on the environment of oil and gas development, especially on Arctic animals such as porcupine caribou (*Rangifer tarandus*), polar bears (*Ursus maritimus*), foxes (*Alopex lagopus*) and muskoxen (*Ovibos moschatus*) (Pelley 2001; NRC 2003). Many such incidents would be expected to occur in extremely remote locations and it is likely that the impact of such oil pollution on land mammals could be overlooked or considered to be too difficult to address from a wildlife rescue/rehabilitation perspective.

There are a number of ways in which an animal can be affected by oil contamination. Apart from toxicity, oil reduces heat insulation and the water proofing ability of mammals, leading to water penetration (Davis *et al.* 1988; Gregory 2006). Thus, contamination has to be removed from feathers or fur as part of the rehabilitation process. Conventional techniques for cleaning oiled wildlife involve the use of warm water and detergent (Davis *et al.* 1988; Hill 1999; USFWS 2002; OWCN 2003; IPIECA 2004, Parsons and Underhill 2005; Gregory 2006). Sometimes, pre-treatment agents also need to be employed (Jessup *et al.* 2012). Although these techniques have improved a lot and acquired a considerable degree of success (Newman *et al.* 2003; Parsons and Underhill 2005; Gregory 2006), they are time-consuming and labour intensive. In particular, in remote areas, such as in Australian deserts, the Alaskan wilderness or in Antarctica, the logistics for the rescue of oiled land mammals using the detergent and warm water method is problematic. Therefore, the development of improved and more portable technology for the removal of contamination from wildlife is urgently required. A new technique based on oil absorbing magnetic particle technology has been developed (Orbell *et al.* 1999) and has shown to be effective at removing fresh, tarry and weathered oil from feathers and plumage (Orbell *et al.* 2004, 2005; Dao *et al.* 2006). In light of the above discussion, it is appropriate to consider whether this technology also has a role in the removal of oil from mammalian fur. In this regard, an investigation into the use of magnetic particles into the cleaning of oil from mammalian fur has been conducted as part of this project.

The remediation of contaminated shoreline (foreshore) is also an important environmental issue (Wang and Fingas, 1999) and is, perhaps, an even more complex problem than the removal of oil from wildlife – since the contaminated surfaces are less well defined and the effects of weather make the event highly unpredictable. Thus it may take days for the contaminant to reach the shoreline under the influence of waves, wind and current. This is often exacerbated due to the oil becoming thickened, emulsified and weathered (Pereira and Mudge 2004; Orbell *et al.* 2007).

There have been numerous events, such as, the grounding of the Exxon Valdez in Prince William Sound in 1989, which resulted in the contamination of 1750 km of Alaskan Shoreline (Tumeo *et al.* 1994) and the killing of 3,000 - 6,000 sea otters (*Enhydra lutris*) (Jessup *et al.* 2012) and more than 30,000 birds (Piatt *et al.* 1990). The prestige oil tanker spill

of Spain and France in winter (November) of 2002, also affected 1,900 km of shoreline (Fernández-Álvarez *et al.* 2007) and resulted in the contamination of around 115,000 - 230,000 birds and animals (Zuberogoitia *et al.* 2006). Some animal species that live by the coast and cannot fly, such as penguins, are much more vulnerable to spilled oil on foreshore (Crawford *et al.* 2000) as they are likely to walk directly through the contaminated foreshore. Therefore, shoreline clean-up is essential to the process of restoration of habitats and the environment (Orbell *et al.* 2007).

In general, shoreline clean-up methods are dependent on the nature of a contaminant, the condition of the shoreline and the nature of the habitat. The methods that are commonly employed to remove oil from shoreline include natural processes such as oxidation, evaporation and bioremediation using microorganisms. Such methods are considered environmentally friendly, although the degradation process may take several years to complete (Venosa and Zhu 2003; Prince *et al.* 2003; EPA, 2004). Physical methods include shore washing with high-pressure water. Sometimes, this requires the water to be hot or the prior application of pre-treatment agents to remove weathered or sticky contaminants from substrates such as rock. Specific technology has been developed to assist with particular problems such as the localized oiling of rocks, Figure 5.1, and labour intensive cleaning using shovels, buckets and towels is not uncommon (Tumeo *et al.* 1994; Crawford *et al.* 2000; Fernández-Álvarez *et al.* 2007).



Figure 5.1 Rock cleaning (Source: Calendar 2013 – www.lamor.com)

Occasionally, highly aggressive methods are called for such as raking and bulldozing to remove oil that has soaked into pebbles and sand. However, these techniques generate a large amount of waste that is difficult to dispose of (Mateo *et al.* 2005). Organic solvents (with or without surfactant) have also been used to remove oil from shoreline whereby the mixture of oil and chemicals are collected with a skimmer. However, the chemicals that are used in this method can in themselves pose a hazard to the environment (Walker *et al.* 1999; Pereira and Mudge 2004).

Such oil clean-up operations are obviously very time consuming and expensive (Pereira and Mudge 2004). Indeed, shoreline clean-up operations may constitute 80 - 90% of the total clean-up costs (Etkin, 1998 and 2005). In the context of the above discussion, the development and trialling of new technologies and methods is desirable. It is also appropriate to consider whether this technology also has a role in the removal of oil from rock surfaces and in this regard, an investigation into the use of magnetic particles into the cleaning of oil from rock surfaces has also been carried out as part of this project.

Specific aims in this chapter are:

- To extend the MPT technology to a variety of substrates such as fur and rock and to investigate its potential for such applications. Specifically, the removal of oil contamination from two different types of mammalian fur will be examined and the effect of different fur microstructures in relation to the penetration of the contaminant through the fur and onto the skin will be elucidated.
- For fur, the effect of PTA application at various treatment stages will also be examined and compared to the outcomes for feather substrates.
- For oil removal from a rock surface, previous published studies carried out by the Orbell group (Orbell *et al.* 2006) will be extended to investigate the problem of oil penetration into porous rock material and the use of various PTAs to enhance the removal in such circumstances will be investigated.
- The possibility of quantifying the extent of oil penetration into porous rock by the MPT method will be examined.

5.2 Removal of oil contamination from rabbit and seal fur

5.2.1 Materials and method

Materials

Three types of contaminant, of varying viscosities, were used in these experiments: namely, thick/tarry ‘Jasmine Crude Oil’ (JCO) (kinematic viscosity of 682 cSt at 50°C), supplied by Leeder Consulting, Victoria, Australia; Mobil Super XHP 20W-50 Engine Oil (EO) (kinematic viscosity of 168 cSt at 40°C), supplied by Valvoline Pty. Ltd., and Diesel Fuel Oil (DFO) (kinematic viscosity of 3 cSt at 40°C), obtained from a local service station. Fur pelt was taken from the European Rabbit (*Oryctolagus cuniculus*) – a common introduced terrestrial mammal in Australia; kindly supplied by Glenn McNeill, (Local Abattoir), Geelong, and the Australian Fur Seal (*Arctocephalus pusillus doriferus*) which was obtained from the Melbourne Museum, Carlton, Victoria, Australia. Due to its limited availability, experiments were conducted on recycling of the seal pelt, with a view to reuse, in controlled oil removal experiments, as described in Section 5.3.1. Three types of pre-treatment agents were employed in these experiments, i.e. methyl oleate (MO), supplied by Victorian Chemical Co. Pty. Ltd., methyl soyate (MS), supplied by Just Fuel, 2 Western Avenue, Sunshine, Victoria, Australia and “De-oiler (BD1)”, which was kindly provided by the South African Foundation for the Conservation of Coastal Birds (SANCCOB).

The oil sequestering magnetic particles (iron powder) used, were grade MH 300.29, supplied by Hoganas AB, Sweden. These particles are described as ‘spongy annealed superfine’ by the manufacturer and have been shown in previous experiments to be the optimum grade for the removal of contamination from feathers (Dao *et al.* 2006). It was assumed that this optimum removal would be carried over to other substrates such as fur and rock – although this has yet to be definitively established.

Method

Existing gravimetric methods, developed for assessing the magnetic removal of oil from a particular substrate; e.g. feather clusters (Orbell *et al.* 1999), feather plumage (Orbell *et al.* 2004) and rock (Orbell *et al.* 2006) were adapted for the gravimetric assessment of oil removal from fur pelt. Thus, the rabbit/seal pelt was cut into 4 × 4 cm² squares and the

weight of a given fur patch in a tared petri-dish was recorded as f_1 . The contaminant was then applied to the fur-side of the sample as a patch. The oil laden fur sample was re-weighed as f_2 . Any excess oil (run-off) that remained in the petri-dish was recorded as r , after the patch was removed to another petri-dish for further experimentation. The adjusted weight of the oil-laden patch, f_3 , is thus:

The weight of the oil-laden patch (f_3) = weight of patch plus oil (f_2) – any oil residue left in petri-dish (r).

The oil-laden fur sample was carefully placed into another petri-dish and the iron powder was applied to cover the contaminated patch and left for 2 to 3 minutes to ensure maximum adsorption. The oil-laden iron powder was then harvested magnetically, using a “magnetic tester” device, which was obtained from Alpha Magnetics, Victoria, Australia. This device allows the magnetic field to be switched on and off mechanically simply by moving the plunger in and out.

Two methods of magnetic harvesting were tested whereby (i) the magnetic probe only superficially contacted the contaminated surface (this is referred to as “non-massaged”) and (ii) where the magnetic probe was massaged into the body of the fur (referred to as “massaged”). The sample was then re-weighed, f_4 . The percentage removal by weight, $P\%$, of contaminant was calculated as follows:

$$P (\%) = [(f_3 - f_4)/(f_3 - f_1)] \times 100 \%$$

The procedure was then repeated for subsequent removals until a constant removal was achieved. For the experiments with pre-treatment agents, the agent was dripped on to the oil contaminated area of the sample and the previously described procedural steps were repeated until the highest removal was achieved.

5.2.2 Characterisation and comparison of rabbit and seal fur micro-structure

Given that two different fur types were used in these experiments, the characteristics of their respective micro-structures were examined and compared utilizing Scanning Electron

Microscopy (SEM), Figures 5.2 – 5.5. Differences in microstructure were expected to affect the relative efficacies of contaminant removal. More specifically, for these two fur types, the elements of hair length and hair width have been compared both qualitatively and quantitatively. As can be seen in Figures 5.2 - 5.5, the microstructures of the rabbit fur and seal fur used in these experiments exhibit significant differences that were expected to be reflected in the oil removal characteristics. Estimated average widths and lengths of rabbit and seal fur sampled from the material available are presented in Table 5.1. It can be seen that, although both furs were of a similar “broad petal” type, (Brunner and Coman 1974), there was a considerable difference between their width to length ratios, with the seal hairs being relatively shorter and broader and the rabbit hairs being narrower and longer (and more intertwined).

Table 5.1 Average width and length of rabbit and seal fur (μm) – taken from electron micrographs. Errors represent the SE in the mean for replicate measurements. The raw data are given Table 1 in Appendix 5.

Fur type	Average width (μm)	Average length (μm)	Length/width (μm)
Rabbit fur	15.80 ± 1.15	39200 ± 1600	2481 ± 280
Seal Fur	37.00 ± 2.90	13700 ± 300	370 ± 37

Rabbit Fur

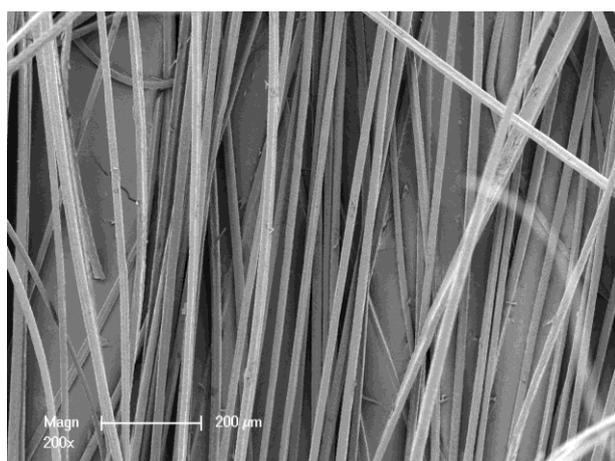


Figure 5.2 Scanning electronic microscopy of rabbit fur. (Magnification 200 \times)

Seal Fur

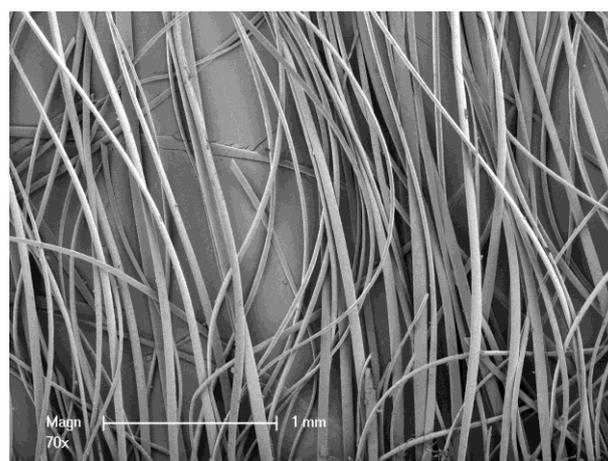


Figure 5.3 Scanning electronic microscopy of seal fur. (Magnification 70 \times)

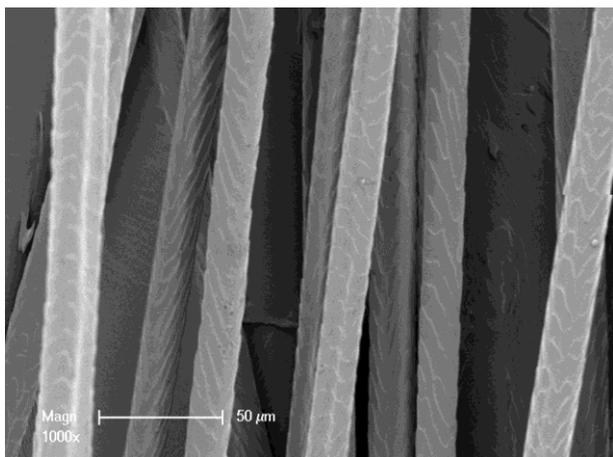


Figure 5.4 Scanning electronic microscopy of rabbit fur (Magnification 1000×)

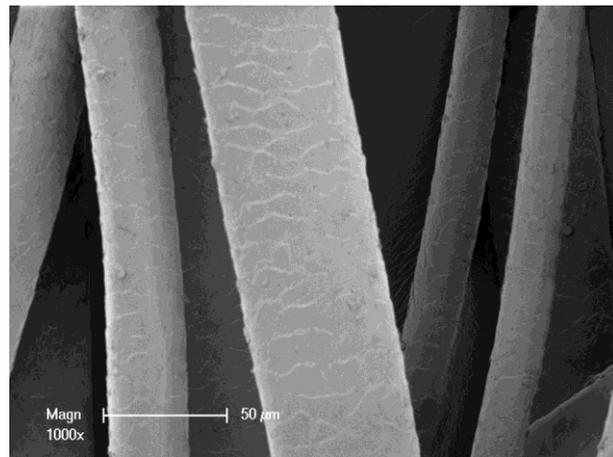
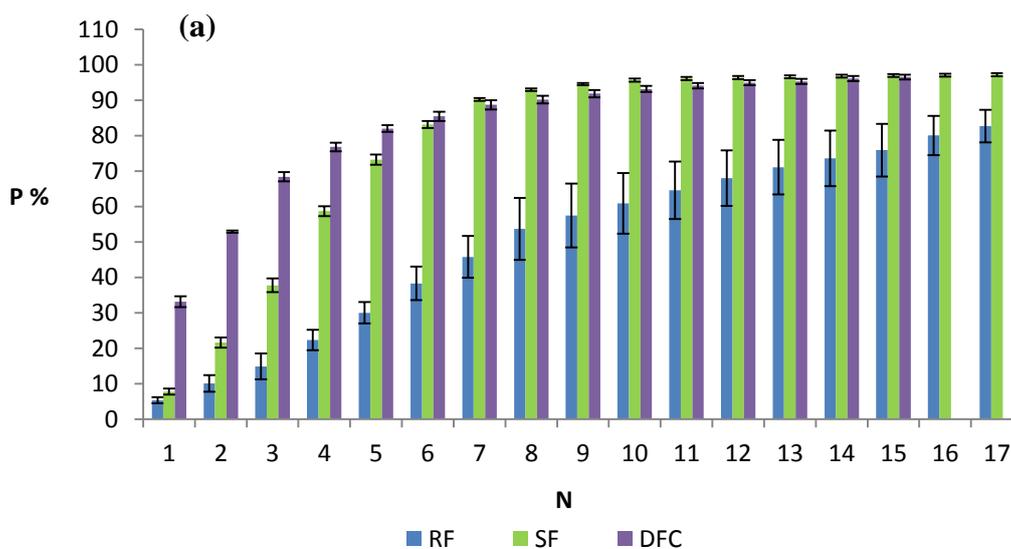


Figure 5.5 Scanning electronic microscopy of seal fur (Magnification 1000×)

5.2.3 Removal of JCO, ENO and DFO from rabbit pelt and seal pelt – comparison with removal from feathers

5.2.3.1 Jasmine Crude Oil (JCO)

Following the method described in Section 5.2.1, the magnetic removal of JCO from rabbit and seal fur (pelt) may be compared and benchmarked against the removal from duck feather clusters, Figures 5.6 (a) and (b).



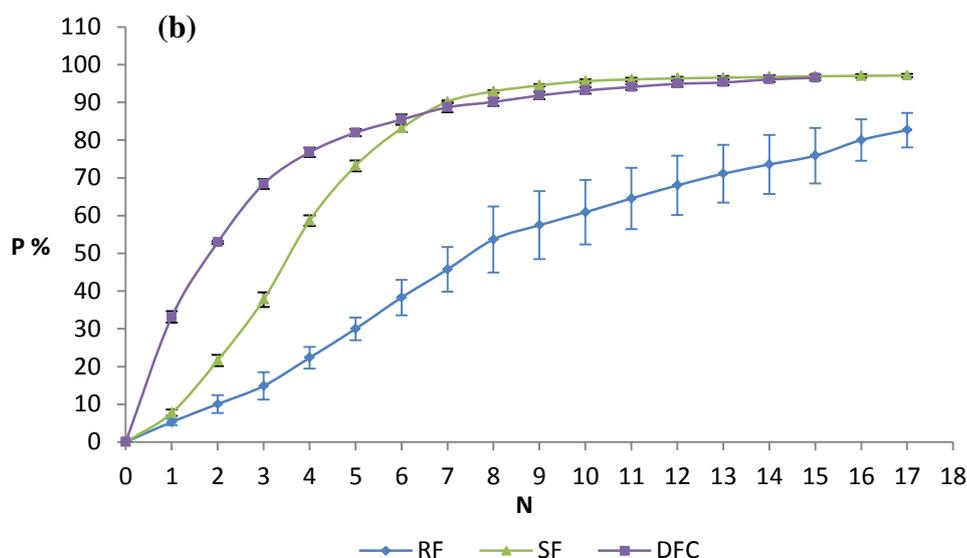


Figure 5.6 (a) Comparative histograms and (b) comparative isotherms for the percentage removal, P%, of Jasmine Crude Oil (JCO) from the substrates: rabbit fur (RF), seal fur (SF) and duck feather clusters (DFC), as a function of the number of treatments, N, at 22°C. The error bars for the experimental isotherms represent the SEs for five replicates. The data are provided in Table 2 and the individual data profiles are given in Tables 3, 4 and 5 in Appendix 5.

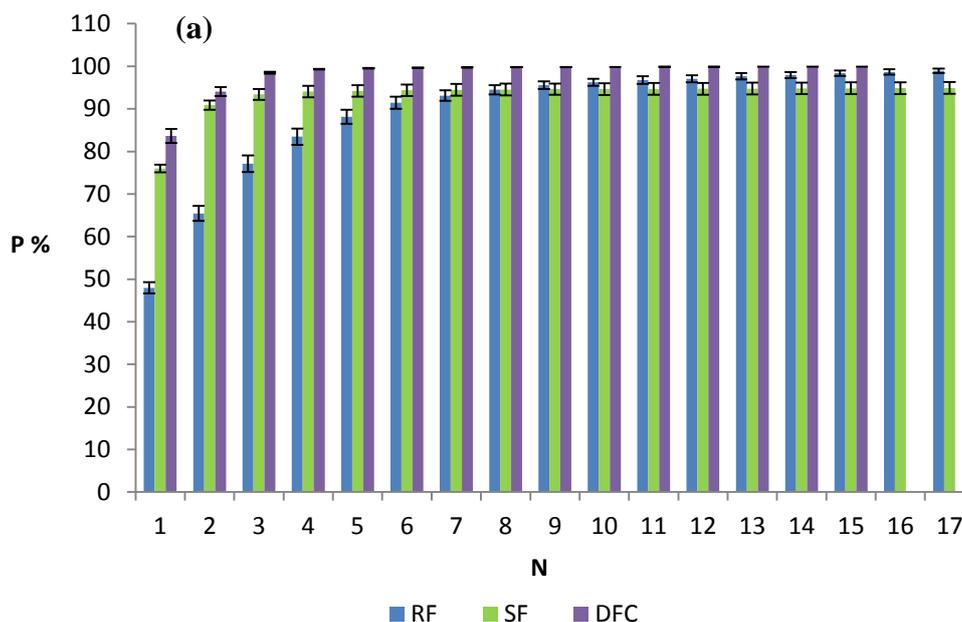
As can be seen from Figures 5.6 (a) and (b), there was a considerable variation in JCO removal between the different substrates. In particular, it can be noted that the removal of this type of highly viscous oil from the rabbit fur was considerably more problematic than for the seal fur. This can be attributed to the longer and finer nature of the rabbit fur, Table 5.1. In terms of the final removal, $P_0\%$, seal fur and duck feather clusters all eventually plateau in the high 90s, Table 5.2. The optimum rabbit fur removal achieved only in the low 80s, at best, and the difficulty in removal was also reflected in the relatively high SE values. These results suggest that for a contaminant and substrate of this type, a suitable pre-treatment agent might be appropriate. This is discussed in more detail later. In terms of using this technology for a “quick clean” the initial removals are of relevance. The “initial” removals at treatments 1, 2 and 3, Figure 5.6, were found to be very low for the rabbit fur and were lower for the seal fur than for the feather clusters. This suggests, that for this oil type and for the species examined here, a quick clean would be more effective for birds than for mammals. From the data presented in Table 5.2, it can be seen that, overall, the removal from seal fur was the most effective (as reflected in the relative $P_0\%/N_{90}$ and $P_0\%/N_{95}$ values), although the initial removal was clearly more effective for feathers; see Chapter 4 for the definition of these efficacy parameters.

Table 5.2 Removal of jasmine crude oil (JCO) from rabbit fur (RF), seal fur (SF) and duck feather clusters (DFC). The # entry means that the final removal ($P_0\%$) does not reached N_{90} , N_{95} or N_{99} .

Substrate	$P_0\%$	N_{90}	N_{95}	N_{99}	$P_0\%/N_{90}$	$P_0\%/N_{95}$	$P_0\%/N_{99}$
RF	82.7	#	#	#	-	-	-
SF	97.1	7.0	9.4	#	13.9	10.3	-
DFC	96.5	8.0	12.2	#	12.1	7.91	-

5.2.3.2 Engine Oil (ENO)

Following the method described in Section 5.2.1, the magnetic removal of ENO from rabbit and seal fur (pelt) may also be compared and benchmarked against the removal from duck feather clusters, Figures 5.7 (a) and (b).



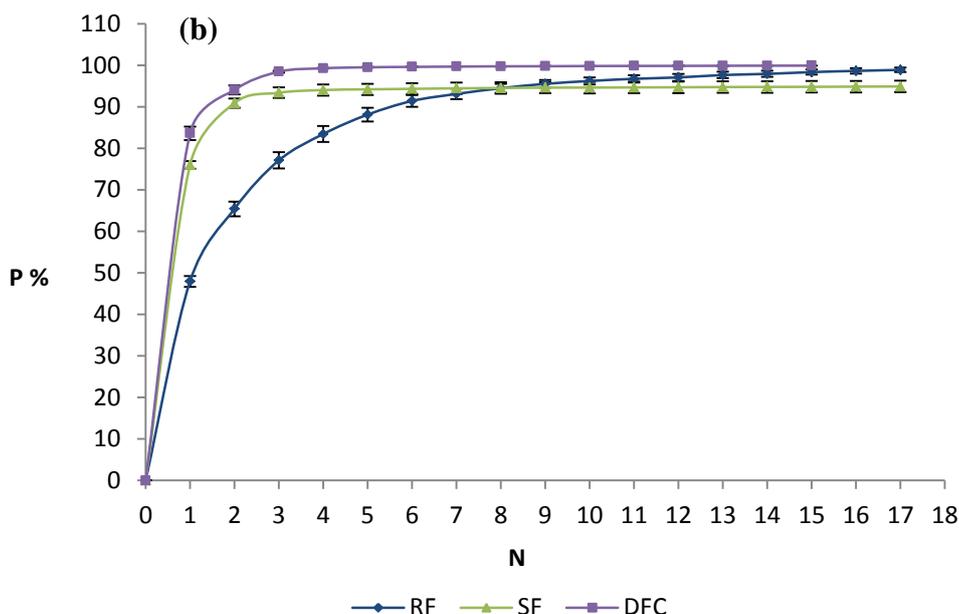


Figure 5.7 (a) Comparative histograms and **(b)** comparative isotherms for the percentage removal, P%, of Engine Oil (ENO) from the substrates: rabbit fur (RF), seal fur (SF) and duck feather clusters (DFC) as a function of the number of treatments, N, at 22°C. Error bars represent the SE for five replicates. The data are provided in Table 6 and the individual data profiles are given in Tables 7, 8 and 9 in Appendix 5.

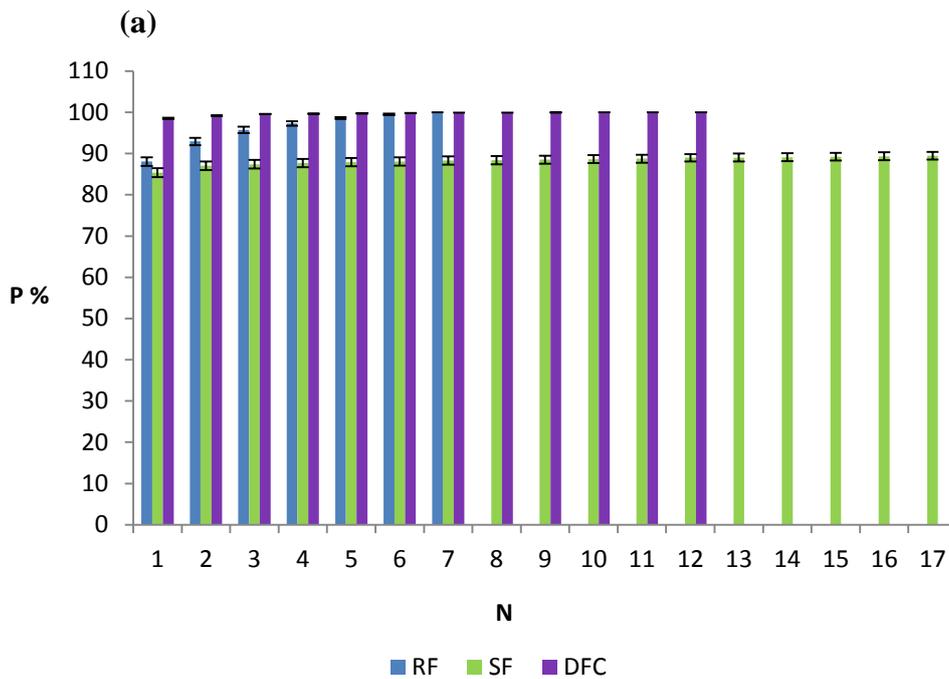
It can be seen in Figure 5.7, that for ENO removal, the main variation prior to the plateaus again appears to be for rabbit fur, with removals from the two other substrates being approximately equivalent. However, for this medium viscosity oil type, the final removals were higher than for JCO for rabbit fur and duck feather clusters but the final removal for seal fur was actually lower than for JCO. This apparent anomaly can be explained by the fact that the seal fur allows more of this relatively lighter oil to penetrate to the pelt surface. This was an important observation and relates the density of the fur to the potential for skin absorption. With respect to initial removal, as with JCO, both seal fur and feathers were found to be superior to rabbit fur. From the data presented in Table 5.3, it can be seen that, overall, the relative efficiencies of removal (as shown by the $P_0\%/N_{90}$ values) are in the order of $DFC > SF > RF$. Notable, in this case the removal isotherm for RF followed a more typical trajectory and the SE values are small.

Table 5.3 Assisted removal of engine oil (ENO) from rabbit fur (RF), seal fur (SF) and duck feather clusters (DFC). The # entry means that the final removal ($P_0\%$) does not reached N_{90} , N_{95} or N_{99} .

Substrate	$P_0\%$	N_{90}	N_{95}	N_{99}	$P_0\%/N_{90}$	$P_0\%/N_{95}$	$P_0\%/N_{99}$
RF	98.9	5.6	8.5	#	17.7	11.6	-
SF	94.9	1.9	#	#	50.0	-	-
DFC	99.9	1.4	2.2	3.3	71.4	45.4	30.3

5.2.3.3 Diesel Fuel Oil (DFO)

Following the method described in Section 5.2.1, the magnetic removal of DFO from rabbit and seal fur (pelt) may also be compared and benchmarked against the removal from duck feather clusters, Figures 5.8 (a) and (b).



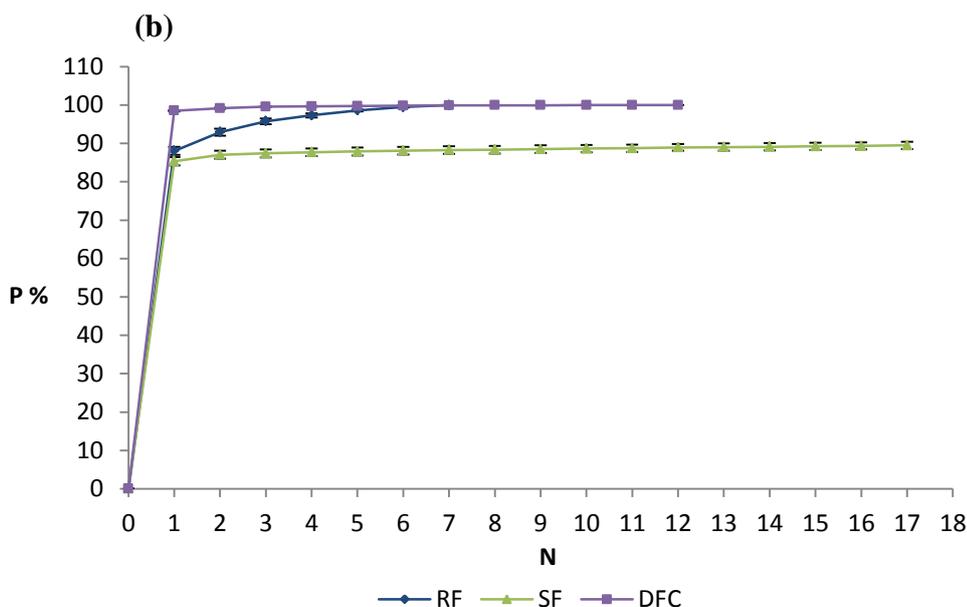


Figure 5.8 (a) Comparative histograms and **(b)** comparative isotherms of the percentage removal, P%, of diesel fuel oil (DFO) from different substrates: rabbit fur (RF), seal fur (SF) and duck feather clusters (DFC) as a function of the number of treatments, N. Error bars represent the SE for five replicates. The data are provided in Table 10 and the individual data profiles are given in Tables 11, 12 and 13 in Appendix 5.

Not unexpectedly, for this low viscosity contaminant, the initial removal was high for all substrates. The final removals for RF and DFC were also high, Table 5.4. However, as for medium viscosity ENO, the final removal, $P_o\%$, from the seal fur can be seen to be inhibited which may also be attributed to the permeability of the DFO through the fur structure and onto the pelt surface (skin), Table 5.4.

Table 5.4 Assisted removal of diesel oil from rabbit fur (RF), seal fur (SF) and duck feather clusters (DFC). The # entry means that the final removal ($P_o\%$) does not reached N_{90} , N_{95} or N_{99} .

Substrate	$P_o\%$	N_{90}	N_{95}	N_{99}	$P_o\%/N_{90}$	$P_o\%/N_{95}$	$P_o\%/N_{99}$
RF	98.9	1.2	2.7	5.4	82.4	36.6	18.3
SF	89.5	#	#	#	-	-	-
DFC	99.9	0.9	1.0	1.2	111.0	105.2	83.3

A comparison of the final removal values, $P_o\%$, for the three different oils from the three different substrates is represented in Figures 5.9 (a) and (b).

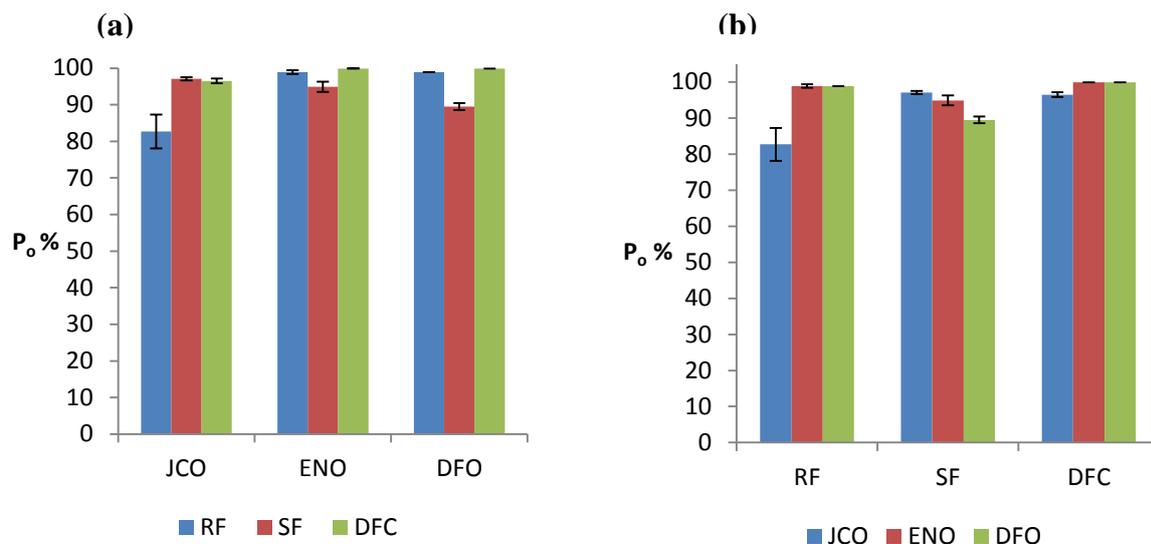


Figure 5.9 (a) Comparison of the final removal values, P_o %, for each oil type with respect to substrate and (b) for each substrate with respect to oil type. Error bars represent SE for five replicates. The full data are presented in Table 14 and 15 in Appendix 5.

From Figure 5.9 (a), the final removal of JCO was seen to be more problematic for RF than for SF or DFC. This reflects the tangled nature of the rabbit fur. The final removals for RF and DFC, for both ENO and DFO, were approximately equivalent but these values were depressed for SF due to the more open nature of this fur, allowing the less viscous oils to penetrate and absorb onto the skin of the pelt.

From Figure 5.9 (b), the effect of the less viscous oils, ENO and DFO, in penetrating SF and absorbing onto the pelt skin, can also be seen by the fact that the final removal values for these oils with respect to SF were actually lower than the final removal for the highly viscous JCO. For RF and DFC, where such penetration was minimal, the final removal values for ENO and DFO were higher than those for JCO, as expected.

A comparison of the above data from the perspective of the removal of different oils from the same substrate (as opposed to the removal of the same oil from different substrates, *vide supra*) is represented by Figures 5.10 to 5.12.

5.2.3.4 Rabbit Fur (RF)

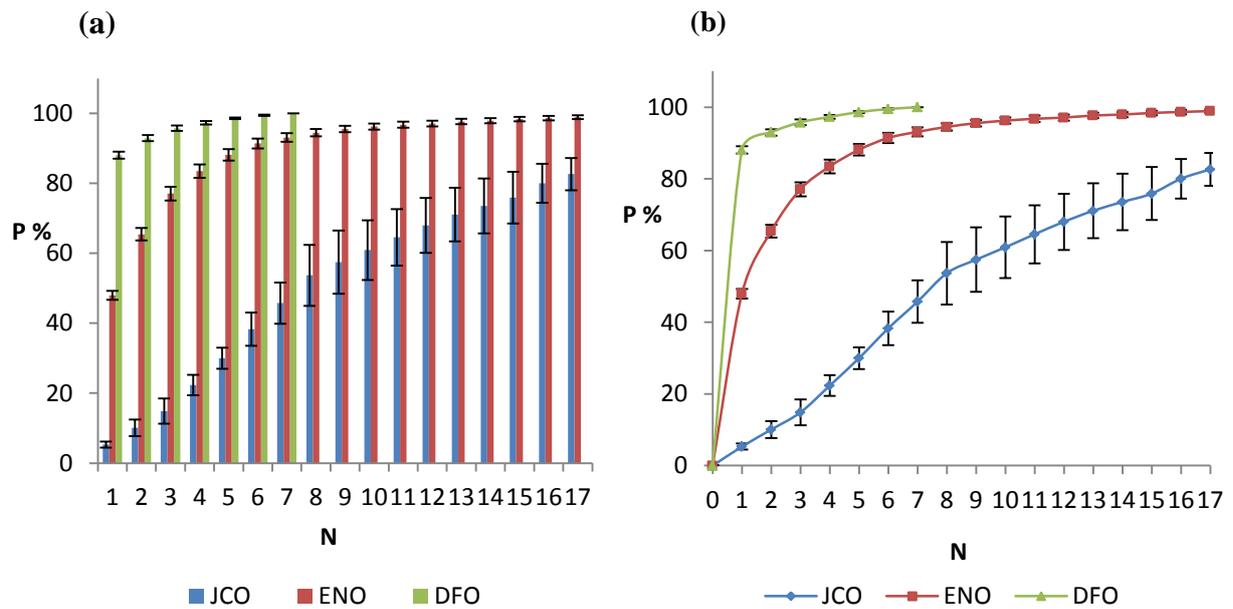


Figure 5.10 (a) Histogram and (b) curve comparisons of three different contaminant (JCO, ENO and DFO) removal, P%, from rabbit fur (RF) as a function of the number of treatments, N. Error bars represent the SE for five replicates. The data are provided in Table 16 in Appendix 5.

5.2.3.5 Seal Fur (SF)

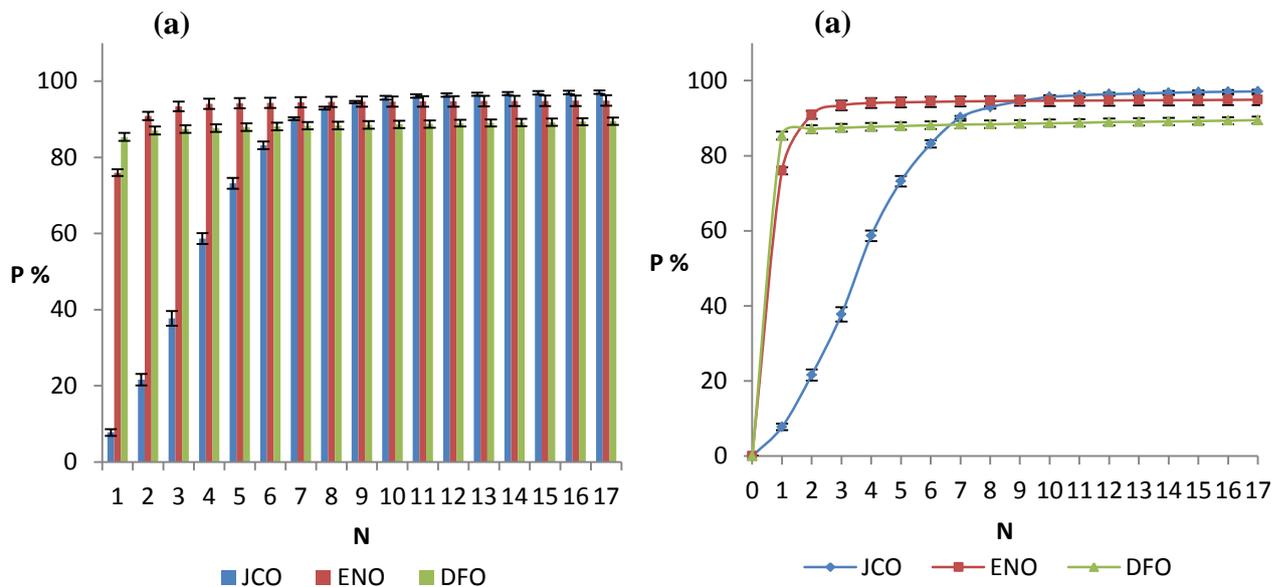


Figure 5.11 (a) Histogram and (b) curve comparisons of three different contaminant (JCO, ENO and DFO) removal, P%, from seal fur (SF) as a function of the number of treatments, N. Error bars represent the SE for five replicates. The data are provided in Table 17 in Appendix 5.

5.2.3.6 Duck Feather Clusters (DFC)

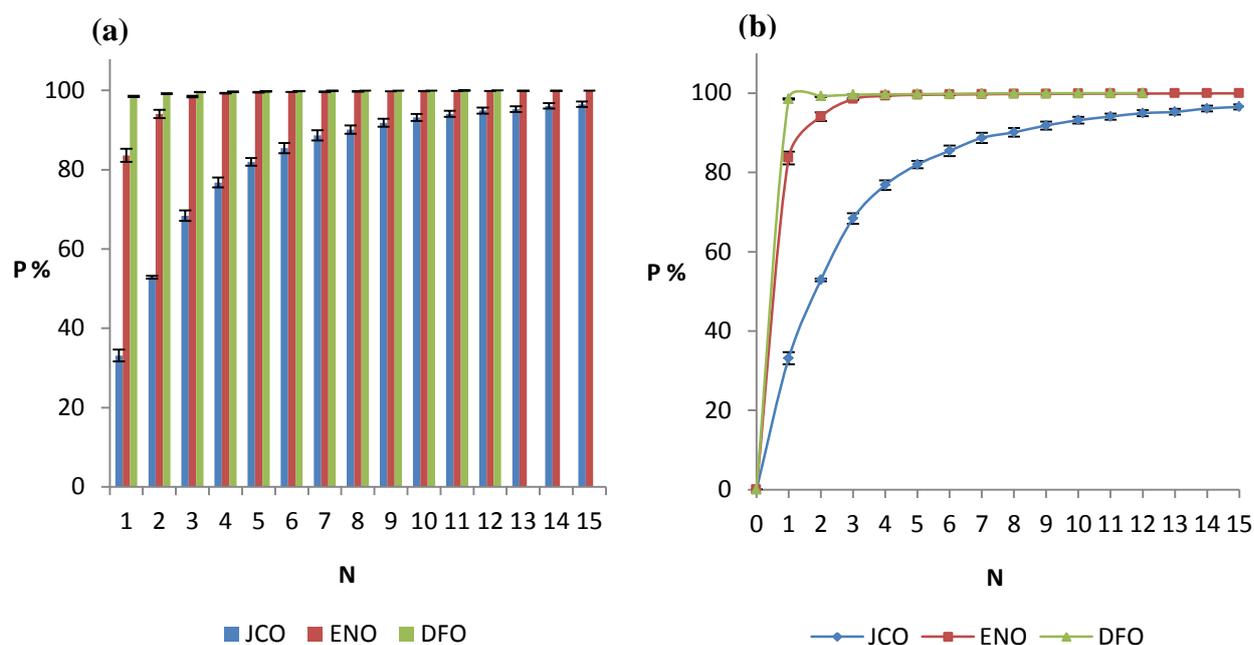


Figure 5.12 (a) Histogram and (b) curve comparisons of three different contaminants (JCO, ENO and DFO) removal, P%, from duck feather clusters (DFC) as a function of the number of treatment, N, Error bars represent the SE for five replicates. The data are provided in Table 18 in Appendix 5.

5.2.4 The recycling of seal pelt substrate samples

The purpose of these experiments was to assess the re-use of the seal pelt, since this material was difficult to acquire. Thus, used seal pelts were washed clean with detergent and compared with original seal pelt with respect to oil removal experiments (the washing process is described below). Two different methods were also applied when handling the magnetic tester, i.e. where the pelt was actually ‘massaged’ with the tester and where the tester was not allowed to touch the pelt (the non-massage technique). These two methods have also been assessed.

5.2.4.1 The re-cycling ‘washing’ process

Used seal pelt (4cm × 4cm), which was previously cleansed of oil using MPT, was dipped in 6% ‘Divoplus V2’ dishwashing solution and warmed to 38° - 40°C for two minutes. The used pelt was then cleaned by finger-rubbing the surface for one minute. The process was repeated three times followed by rinsing in warm deionized water (40° - 45°C) until it was considered clean. This recycled seal pelt was hung to dry in air and then dried in an oven at 40°C.

5.2.4.2 A comparison of contaminant removal from non-washed (original) and washed (recycled) seal fur using the ‘massage’ and non-massage’ techniques

Oil removal experiments on original and recycled SF were conducted using both the ‘massage’ and the ‘non-massage’ techniques under identical conditions. The contaminant used in these experiments was JCO (viscosity of 658 cSt at 50°C). Comparative data for the removal of JCO from original and recycled seal fur using both of these techniques are presented in Figure 5.13.

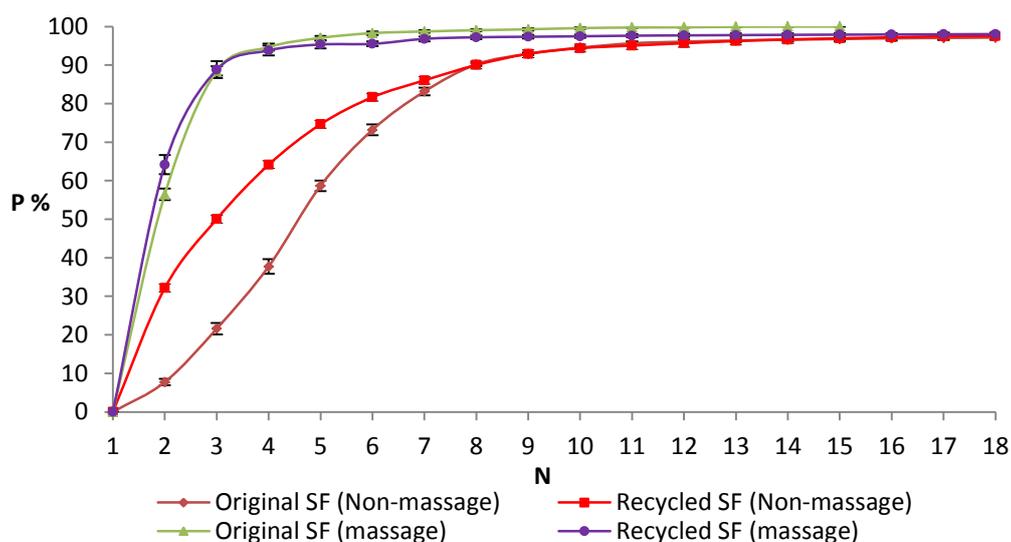


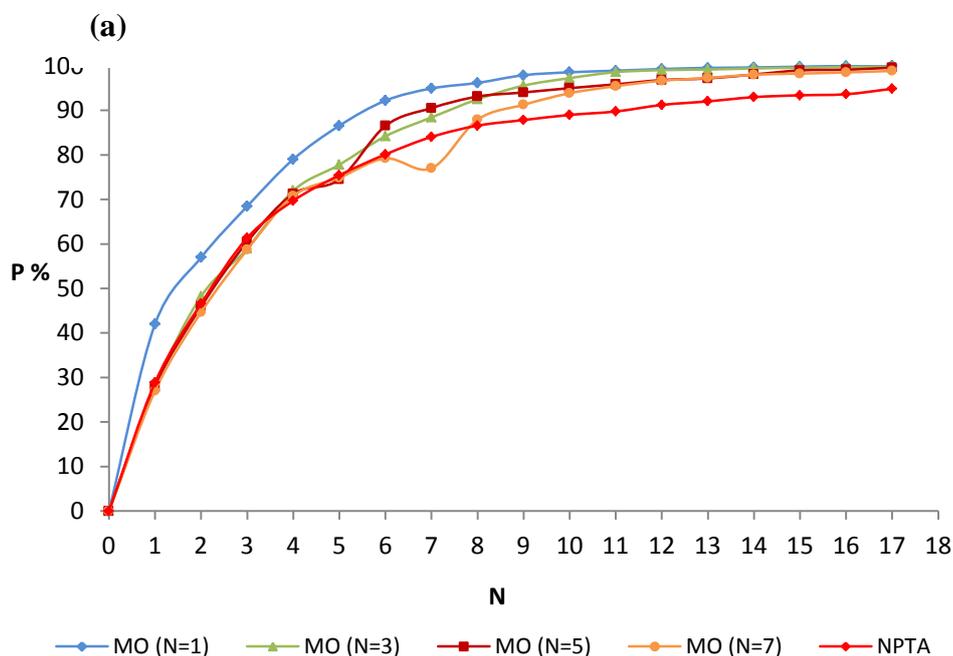
Figure 5.13 Comparison of the removal jasmine crude oil (JCO) from original and recycled seal fur (SF), using different techniques (massage and non-massage). P% is plotted as a function of the number of treatment, N. Error bars represents the SE for five replicates. The full data sets are given in Table 19 and the individual data profiles are given in Table 20, 21, 22 and 23 in Appendix 5.

From Figure 5.13, it can be seen that for the non-massage technique the initial removal for the original fur was less than that for the recycled fur (e.g. 21.6% at N=2 compared to 50.0%) - although the final removals (~ 98%) were essentially identical. This suggests that there was less penetration of the oil for the recycled fur, which could be due to the fibres being more disrupted and entangled. It can also be seen that for the massage technique the removal isotherms for the original and recycled furs were essentially identical, with removals of 88.5% and 88.8% at the respective second treatments, N=2. The maximum removal for original seal pelt was ~ 100% at the 14th treatment, slightly lower than the 98% obtained for the recycled seal pelt at the final treatment.

Therefore, the massage technique was clearly preferred for experimental purposes. It may also be concluded that, provided the appropriate removal technique was employed, i.e. the massage technique, *the seal pelt may be recycled for subsequent experiments*. These results also demonstrated the sensitivity of the MPT technique in general for delineating subtle removal effects.

5.2.4.3 The application of PTA at four different treatment stages for JCO removal from rabbit fur (pelt)

The application of three different PTAs, namely methyl oleate (MO), methyl soyate (MS) and de-oiler (BD1) to JCO contaminated rabbit fur pelt (original, i.e. not recycled) at four different stages of treatment (N = 1, 3, 5 and 7) was assessed with respect to MPT removal of the JCO contaminant. The ‘massage’ magnetic harvesting technique was used based on previous experiments (see above) - and for all subsequent experiments. Therefore, three sets of nested isotherms were generated as shown in Figures 5.14 (a) to (c).



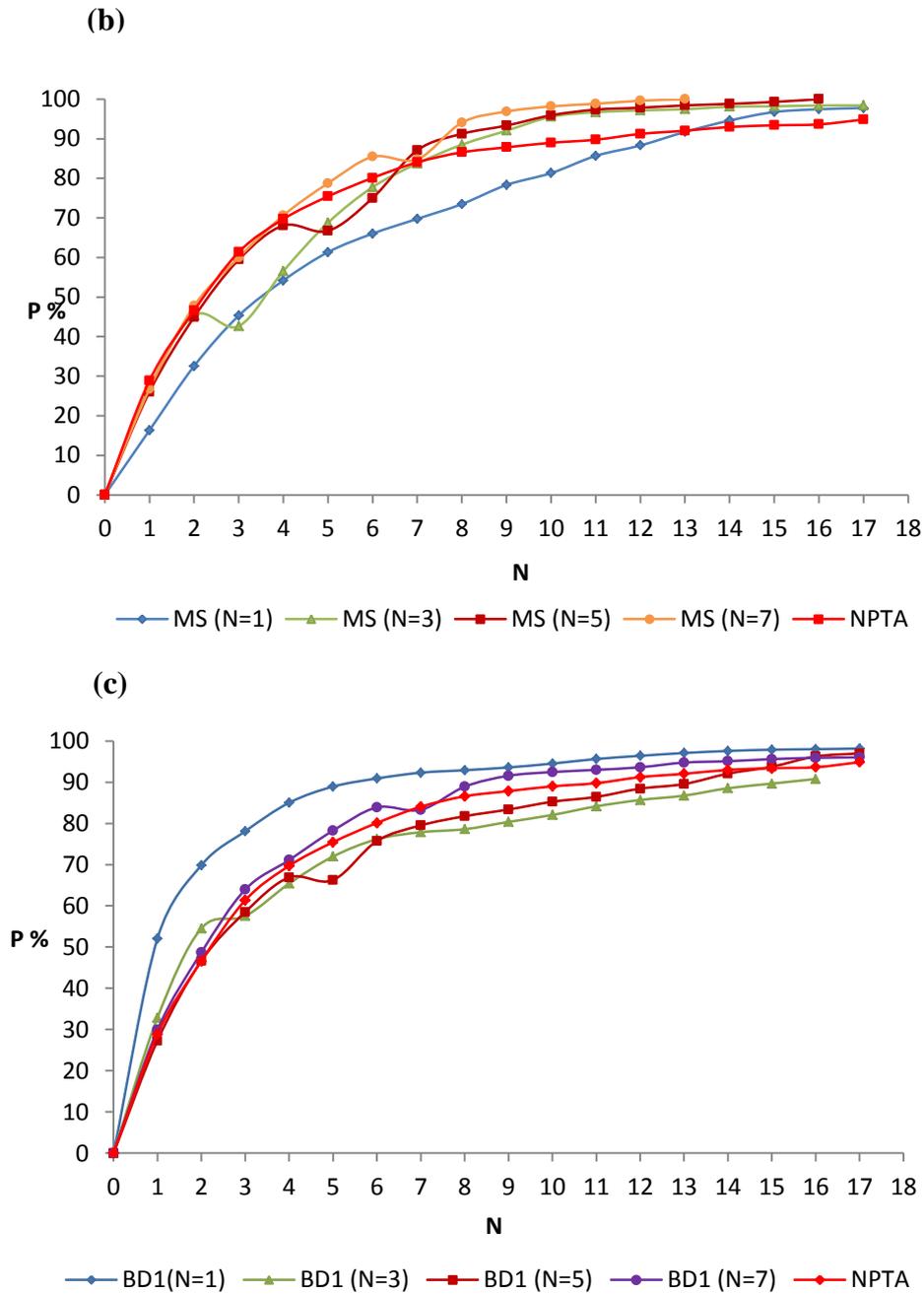


Figure 5.14 (a) Stage-dependent ($N = 1, 3, 5, 7$ and NPTA) MO-assisted removal of JCO from rabbit pelt (b) Stage-dependent ($N = 1, 3, 5, 7$ and NPTA) MS-assisted removal of JCO from rabbit pelt (c) Stage-dependent ($N = 1, 3, 5, 7$ and NPTA) BD1-assisted removal of JCO from rabbit pelt. Complete data sets and comparative histograms are provided in Tables 24, 25 and 26; Figures 1(a) to (c) of Appendix 5.

Based on Figures 5.14 (a) to (c), the efficacy parameters, $P_o\%$ (final removal achieved), N_{90} ('acceleration' towards final removal) and $P_o\%/N_{90}$ (overall efficacy) are tabulated in Tables 5.5 to 5.7.

Table 5.5 The effect of PTA application at different stages of treatment on the final removal, $P_o\%$, of JCO from rabbit fur (pelt).

PTA	N=1	N=3	N=5	N=7	NPTA	Plots
MO	99.9	99.8	99.6	98.9	94.9	Fig. 5.15 (a)
MS	97.8	98.4	99.9	99.9	94.9	Fig. 5.15 (b)
BD1	98.2	90.8	96.9	96.0	94.9	Fig. 5.15 (c)

Table 5.6 The effect of PTA application at different stages of treatment on the efficacy parameter N_{90} , for the removal of JCO from rabbit fur (pelt).

PTA	N=1	N=3	N=5	N=7	NPTA	Plots
MO	5.5	7.4	6.3	8.5	11.3	Fig. 5.15 (a)
MS	12.5	8.4	7.6	4.9	11.3	Fig. 5.15 (b)
BD1	5.5	15.4	13.2	8.3	11.3	Fig. 5.15 (c)

Table 5.7 The effect of PTA application at different stages of treatment on the efficacy parameter, $P_o\%/N_{90}$, for the removal of JCO from rabbit fur (pelt).

PTA	N=1	N=3	N=5	N=7	NPTA	Plots
MO	18.2	13.5	15.8	11.6	8.4	Fig. 5.15 (a)
MS	7.8	11.7	13.2	20.4	8.4	Fig. 5.15 (b)
BD1	17.9	5.9	7.4	11.6	8.4	Fig. 5.15 (c)

It can be concluded from these assays that:

The use of any of the PTAs at any treatment stage, for the removal of JCO from rabbit fur (pelt), was generally better than no PTA being used at all. However, there was an important exception, namely the use of BD1 at N=3, see pink boxes highlighted in the above Tables and below.

An important observation from this data is that, as with feathers (see Chapter 4), different PTAs applied at different stages of treatment result in different removal efficacies. This reinforces the suggestion that such data can be used to make recommendations to rehabilitators with respect to what PTA to use (or not to use) for a given contaminant and a given substrate – and, importantly, at which stage of the treatment the PTA should be applied.

For example, for the specific JCO contaminant, for the PTAs (MO, MS and BD1) and for the specific substrate (rabbit fur – pelt) employed here, the following general recommendations can be made.

- Except for BD1 applied at N = 3 or 5 and MS applied at N = 1, any of the PTAs applied at any stage is better than none being used.
- For application at N = 1, MO>BD1>NPTA>MS.
- For application at N = 3, MO>MS>NPTA>BD1.
- For application at N = 5, MO>MS>NPTA>BD1.
- For application at N = 7, MS>MO>BD1>NPTA.
- The best recommended treatments overall are MO or BD1 at N = 1 or MS at N = 7.
- Note, applying MS at N = 1 and BD1 at N = 3 and 5 compromises removal.
- The P₀%, N₉₀ and P%/N₉₀ parameters generally all reflect the above conclusions.

Thus specific recommendations are: to apply MO at Treatment 1 or MS at treatments 5 or 7 (see green highlighted boxes in the tables) and do **NOT** apply BD1 at Treatment 3. Such recommendations reflect what might be made to wildlife rehabilitators, cleansing mammalian fur, based on an established database. Note that previous work in this thesis (Chapter 4) has shown that such MPT assay results are transferable to detergent-based methods of cleansing - at least for feathers. Further research could involve establishing this important principle for fur substrates, although it may be tacitly assumed that this would be the case since the physical interactions involved would be the same.

5.2.4.4 The application of PTA at each individual treatment stage for JCO removal from rabbit fur (pelt)

The fact that the oil removal characteristics depend upon the point of PTA application, and that the specific characteristics are PTA dependent, originate from the fact that the contaminant composition changes as the PTA blends with the contaminant and also inherently as the MPT removal progresses. With regards to the latter, previous work suggests that the more volatile, less viscous components are removed first (Dao, 2007). In this regard it is informative to examine the isotherms of the above section with respect to each individual point of application, Figures 5.15 – 5.18.

5.2.4.4.1 Pre-treatment agents applied at the 1st treatment

A comparison of the percentage removal of JCO from RF using different PTAs at the 1st treatment is presented in Fig. 5.15. This set of nested isotherms is particularly informative in that it clearly demonstrates that different PTAs applied, at the outset, to the JCO contaminated fur results in very different removal profiles for each PTA. Overall it shows that MO applied at this stage gives the superior outcome, *vide supra*.

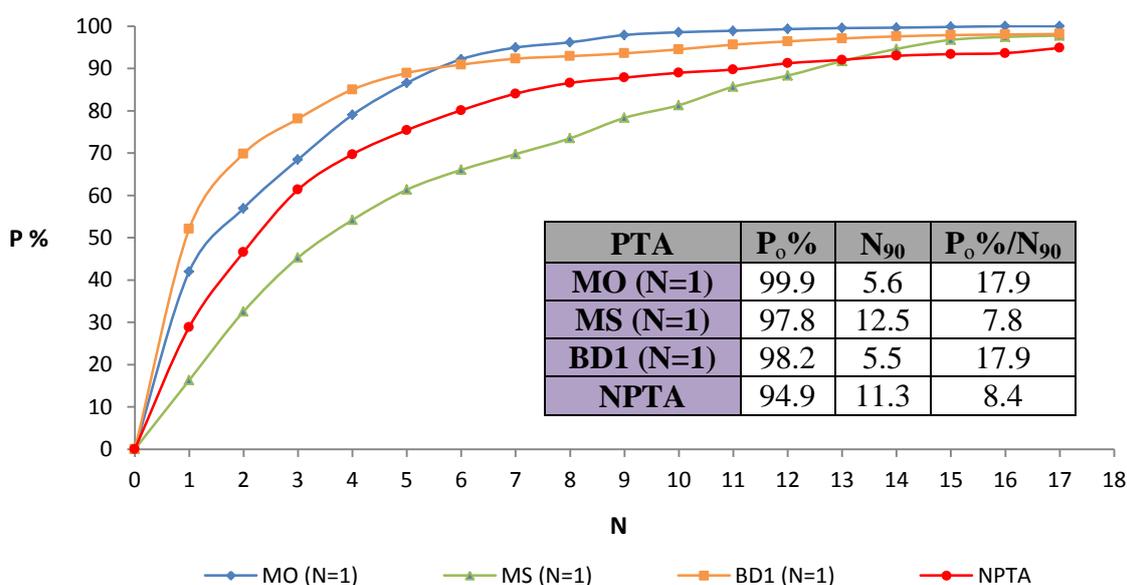


Figure 5.15 Comparison of the PTA-assisted percentage removals, P% of JCO from RF, as a function of the number of treatments, N. PTAs applied at N=1. Methyl oleate (MO); methyl soyate (MS); de-oiler (BD1); No PTA (NPTA). Assay removal parameters are inset and the full data sets are given in Table 27 of Appendix 5. Due to time constraints these isotherms were not performed in replicate.

5.2.4.4.2 Pre-treatment agents applied at the 3rd, 5th and 7th treatments

A comparison of percentage removal of JCO from rabbit fur using different PTAs at the 3rd, 5th and 7th treatments are presented in Figures 5.16 – 5.18. As expected, up to the point of PTA application, the isotherms are effectively identical since the contaminant composition is changing in the same way in each case. At the different points of PTA application, a dip can sometimes be observed in the isotherm. This is due to the additional loading of the PTA onto the substrate. It can again be observed that after the PTA application the profiles of the isotherms were found to be different for each PTA.

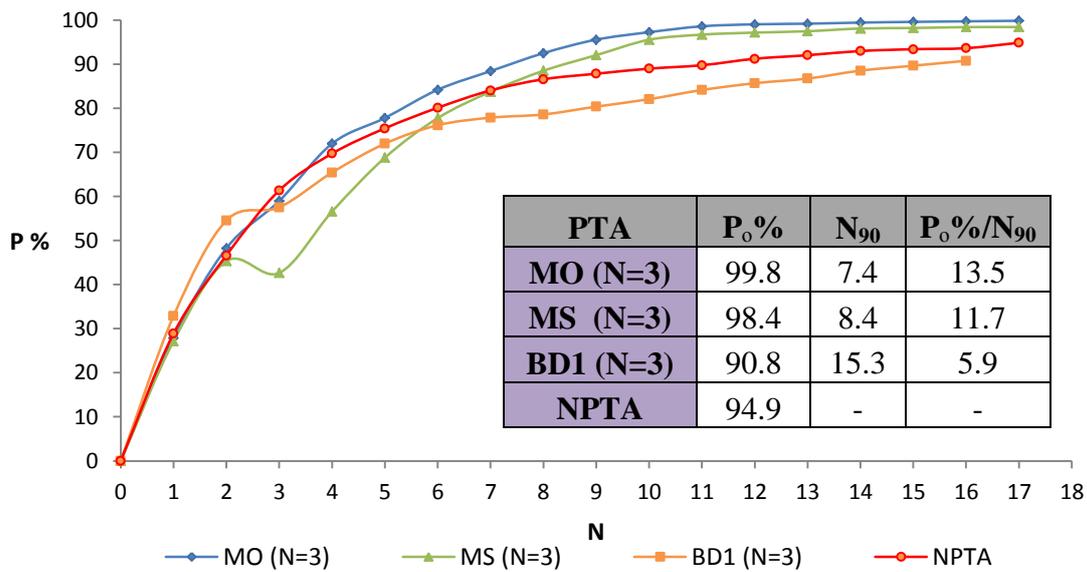


Figure 5.16 Comparison of the PTA-assisted percentage removals, P% of JCO from RF, as a function of the number of treatments, N. PTAs applied at N=3. Methyl oleate (MO); methyl soyate (MS); de-oiler (BD1); No PTA (NPTA). Assay removal parameters are inset and the full data sets are given in Table 28 of Appendix 5. Due to time constraints these isotherms were not performed in replicate.

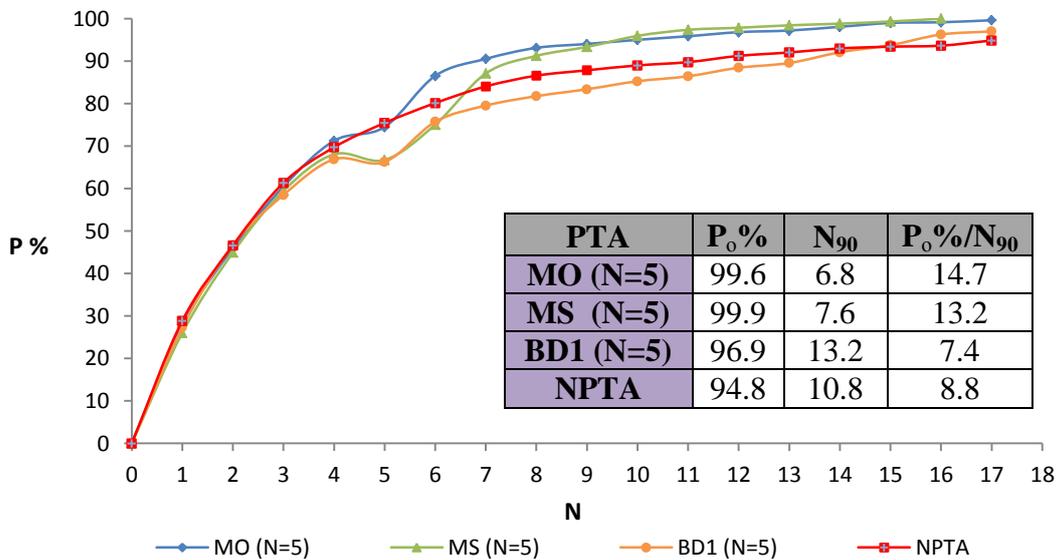


Figure 5.17 Comparison of the PTA-assisted percentage removals, P% of JCO from RF, as a function of the number of treatments, N. PTAs applied at N=5. Methyl oleate (MO); methyl soyate (MS); de-oiler (BD1); No PTA (NPTA). Assay removal parameters are inset and the full data sets are given in Table 29 of Appendix 5. Due to time constraints these isotherms were not performed in replicate.

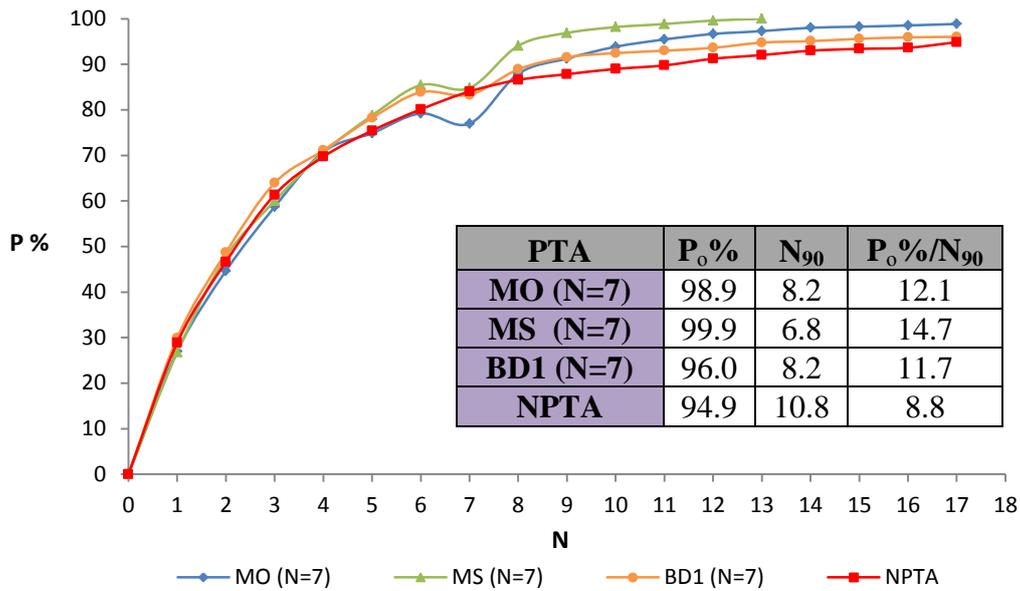


Figure 5.18 Comparison of the PTA-assisted percentage removals, P% of JCO from RF, as a function of the number of treatments, N. PTAs applied at N=7. Methyl oleate (MO); methyl soyate (MS); de-oiler (BD1); No PTA (NPTA). Assay removal parameters are inset and the full data sets are given in Table 30 of Appendix 5. Due to time constraints these isotherms were not performed in replicate.

For the fur studies, following general conclusion can be drawn:

- For the fur studies, the MPT assay may be use just as effectively for fur studies as for feather studies.
- The fur microstructure has been examined and compared both qualitatively and quantitatively. The results exhibit that different fur microstructures give different contaminant removal profiles.
- Some fur types allow less viscous oils to penetrate and absorb onto the skin and this is reflected, and may be assessed, by an analysis of the isotherms.
- Both massage and non-massage techniques were used for this study for contaminant removal and the massage technique is preferred to be the best for contaminant removal from fur substrate.
- Experiments have demonstrated that provided a massage technique is employed that recycled fur may be used for experimentation.

- The role of PTAs for contaminant removal from fur has been studied; the results suggest that, as with feathers, different PTAs applied at different stages of treatment give different removal efficacies. As with feathers, it is also possible to make recommendations to rehabilitators of furry mammals with respect to the preferred PTA for given oil and fur type as well as the recommended point of PTA application.

5.3 Magnetic removal of oil contamination from glass and rock surfaces

5.3.1 Previous work

A previous study of the potential of MPT to remove oil contamination from rock was conducted by the Orbell group and published in 2007 (Orbell *et al.* 2007). This work demonstrated that more than 80% by weight of heavy bunker oil could be removed from a common foreshore rock type (Olivine Basalt) after a single treatment and that a final removal, after three more treatments, of 94% by weight, could be achieved. The failure to achieve 100% could be due to absorption by the substrate and it was suggested that the use of appropriate PTAs could influence the removal profile. This investigation has been continued in this thesis, with a view to further characterizing the absorption problem and to investigate the influence of PTAs on the MPT removal of oil contamination from inorganic (rock) substrates. The study was initiated with removal from a glass surface, which was assumed to be completely non-porous. Studies were then carried out on PTA-assisted contaminant removal from Olivine Basalt that was previously considered to have some porosity to the oil. The Olivine Basalt was used both in its rough form and in a polished (sectioned) form to vary the natural porosity – it was assumed that the naturally rough rock would have many of the pores occluded by other material and that a proportion of these blockages would not be removed by simple washing procedures. Hence it was expected that the polishing (sectioning) process would enhance the natural porosity of the surface.

5.3.2 Materials

Two types of contaminant were used in these experiments: namely, “Bunker Oil 1” (BO1) (kinematic viscosity of 180 cSt at 40°C) supplied by International Bunker Supplies (IBS) Pty. Ltd., Australia, and Mobil Super XHP 20W-50 Engine Oil (ENO) (kinematic viscosity of 168

cSt at 40°C) supplied by Valvoline Pty. Ltd. The glass substrate used was a standard glass Petri dish and the rock substrate was Olivine Basalt, a common type of marine foreshore rock from Williamstown, Victoria, Australia – as used previously. Rock samples were either used as original (rough) and were recycled with a view to reuse by washing with 2% detergent and rinsing with warm water at 40 – 45 °C (Orbell *et al.* 2007); or they were sectioned and polished in order to reveal maximum porosity, Figures 5.19 (a) & (b). Two types of pre-treatment agents were employed in these experiments, methyl oleate (MO), supplied by Victorian Chemical Co. Pty. Ltd. and olive oil (OO), obtained from local supermarket. The oil sequestering magnetic particles (iron powder) used, was grade MH 300.29, supplied by Hoganas AB, Sweden. These particles were described as ‘spongy annealed superfine’ by the manufacturer and have been shown in previous experiments to be the optimum grade for the removal of contamination from feathers and rock (Dao *et al.* 2006; Orbell *et al.* 2007).



Figure 5.19 (a) Olivine Basalt (Rough surface) **(b)** Olivine Basalt (Smooth surface)

5.3.3 The removal of ENO from a smooth, non-porous, inorganic surface

5.3.3.1 Method

A quantity of oil (w_1) was charged onto a tared petri dish. Excess iron powder was applied to the oil and left for at least one minute to ensure that maximum absorption had occurred. The oil-laden particles were then harvested using a magnetic tester¹⁸. The petri dish with residual

¹⁸ The oil laden particles were not “massaged” with the tester since this test is to serve as a non-porous benchmark for removal from rock and such a massage technique would not be employed with a rough rock surface.

oil was then reweighted on the same tared balance, the weight of the residual oil being w_2 . The percentage by weight of oil removed is given by equation 5.11. This procedure was then repeated until a maximum removal of ~ 99% was achieved. The removal isotherm for P% versus the number of treatments is shown in Figure 5.20.

$$P\% = 100 \times (w_1 - w_2) / w_2 \quad (5.11)$$

This experiment demonstrated that almost 100% removal (98.6% at treatment N=12) of this oil type from a smooth nonporous inorganic surface was possible and that the experiment was highly reproducible.

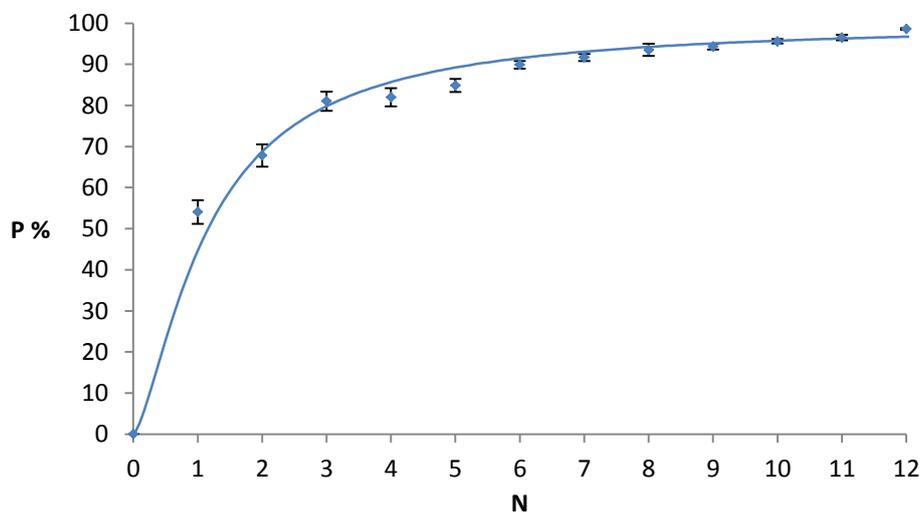


Figure 5.20 The removal of Engine Oil (ENO) from a Petri dish glass surfaces as a function of the number of treatments using MH300.29 powder. Error bars represent the SEs for five replicates. The full data are provided in Table 31 in Appendix 5.

5.3.4 The removal of BO1, ENO and PTA-blended ENO from Olivine Basalt rock

The following experiments were carried out by a previous method (Orbell *et al.* 2007). This method was applied to the removal of the BO1 alone from both rough and smooth (polished) rock, Figure 5.21; MO and OO assisted removal of BO1 from smooth rock, Figure 5.22; MO and OO assisted BO1 removal from rough rock, Figure 5.23, and 5% and 10% MO and OO blended ENO removal from rough rock, Figures 5.24 and 5.25, respectively.

5.3.4.1 Removal of BO1 from smooth and rough (natural) rock surfaces

Two different rock surfaces, smooth and rough, of the same rock type (Olivine Basalt), Figure 5.19 (a.) & (b) were used in these experiment. Figure 5.21 compares the efficiency of oil removal from these two rock surfaces.

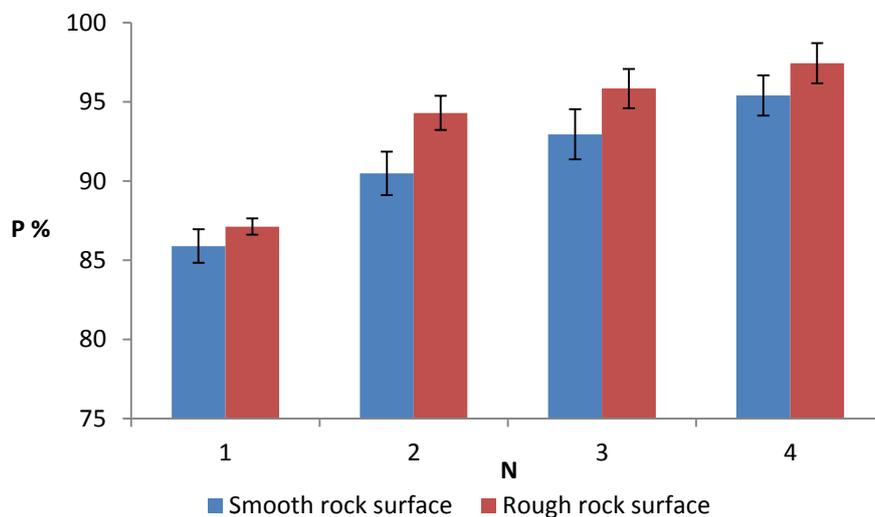


Figure 5.21 Comparison of MPT removal of Bunker Oil 1 (BO1) from smooth and rough Olivine Basalt rock surfaces, P%, as a function of the number of treatment, N. Error bars represent the SE for five replicates. The full data sets are provided in Table 32 and the individual data profiles are given in Table 33 and 34 in Appendix 5.

From Figure 5.21, it can be seen that the removal of the contaminant from the smooth rock surface was lower than for the rough surface, the initial pickup for the smooth rock surface being 85.9% compared to 87.1% for the rough rock surface. After the fourth treatment the final removals for the smooth and rough surfaces were 95.3% and 97.4% respectively. This may appear to be a rather surprising, even counterintuitive, outcome. However, the volcanic rock Olivine Basalt was expected to be porous to some extent and the rough rock was more likely to have pores occluded by debris, some of which cannot be removed by washing alone. On the other hand, the polished (sectioned) rock surface would have the maximum number of pores exposed and hence will be more absorbent of the oil. Depending on the depth of the pores, this would interfere with oil removal. Interestingly, if this was the case, then the data of Figure 5.21 suggests a means for quantifying the degree of pore occlusion of a rock.

5.3.4.2 Removal of oil contaminant from smooth rock surfaces using PTAs

Given that the smooth rock surface should have the maximum quantity of available pores exposed, it was of interest to see whether the use of a PTA could assist in the release of the contaminant from these pores and hence enhance removal. A comparison of the percentage removal of BO1 from a smooth rock surface using MO and OO applied at N=2 is presented in Figure 5.22.

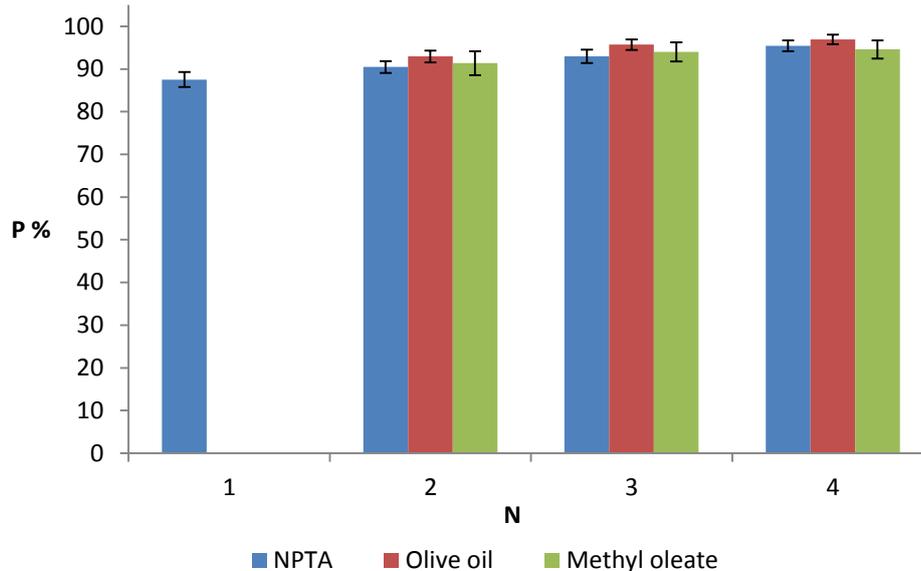


Figure 5.22 Comparison of MPT removal and PTA-assisted MPT removal of BO1 from a smooth Olivine Basalt rock surface, P %, as a function of the number of treatments, N. The PTAs used were Olive Oil (OO) and Methyl Oleate (MO). Error bars represent the SE for five replicates. The full data sets are provided in Table 35 and the individual data profiles are given in Table 33, 36 and 37 in Appendix 5.

It can be seen from Figure 5.22 that OO in particular affects the removal of the BO1 from the rock surface. Indeed, with OO as a PTA, a final removal of 96.9% can be achieved compared to 95.4% for NPTA. It is tempting to suggest that the more viscous OO served to draw the contaminant from the pores to a greater extent than the less viscous MO.

5.3.4.3 Removal of oil contaminant from rough rock surfaces using PTAs

With the pores of the rough rock surface more likely to be clogged, it might be expected to see different profiles for the PTA-assisted removals compared to those shown in Figure 5.22. Thus comparisons of the percentage removal of BO1 from a rough rock surface using MO and OO applied at N=2 are presented in Figure 5.23.

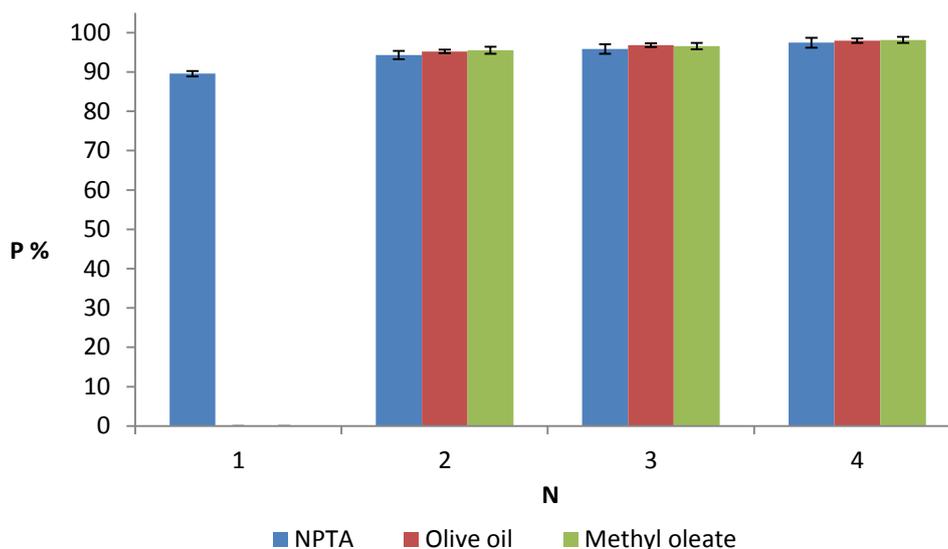


Figure 5.23 Comparison of MPT removal and PTA-assisted MPT removal of BO1 from a rough Olivine Basalt rock surface, P %, as a function of the number of treatments, N. The PTAs used were Olive Oil (OO) and Methyl Oleate (MO). Error bars represent the SE for five replicates. The full data sets are provided in Table 38 and the individual data profiles are given in Table 34, 39 and 40 in Appendix 5.

Although the PTAs appeared to enhance the removal of the contaminant (although not within experimental error – but note that such errors tend to be enhanced for experiments of this type), the effect was not as pronounced as in Figure 5.22, especially with respect to OO. This supports the contention that the OO has a role in extracting the contaminant from the pores. Further experimentation on the role of porosity is warranted that is beyond the scope of this thesis.

5.3.4.4 Removal of OO and MO blended engine oil (ENO) from a rough rock surface

Previous studies with respect to MPT removal of oil from feathers and fur have shown OO and MO to be, in general, the worst and the best of PTAs. In this experiment, these PTAs were blended with ENO at 5 and 10 % v/v.

It can be seen from Figure 5.24 that the removal of engine oil itself from the rough surface was higher than for the ENO blended with OO and MO, at 5 and 10% v/v. The initial pick up of ENO of 87.0% was higher than that of 81.9% for 5% MO and 80.5% for 10% MO. At the final treatment (N=4), removal of ENO of 96.7% was also higher than that of 92.4% for 5% MO and 90.3% for 10% MO. This is consistent with the increasing levels of MO decreasing

the viscosity of the contaminant allowing it to more easily absorb into the available pores of the rough rock, in this case.

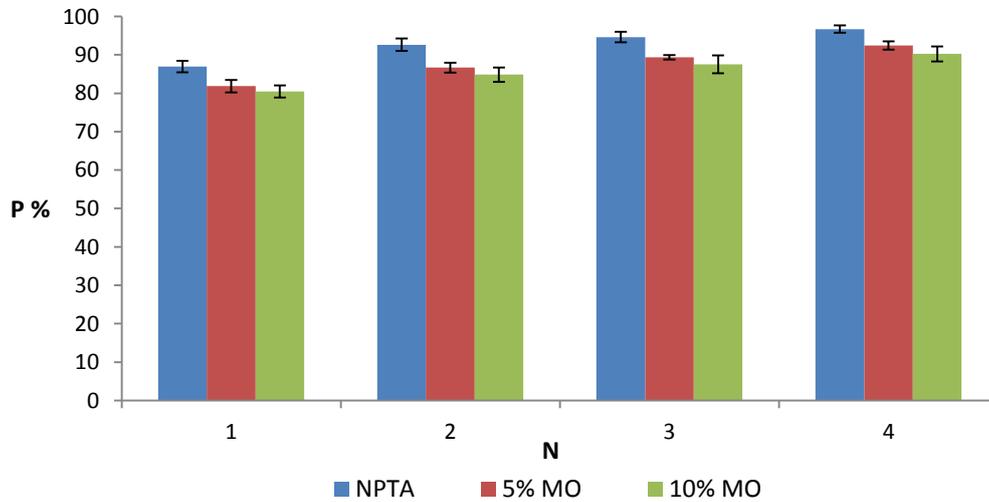


Figure 5.24 Comparison of MPT removal of ENO mixed with 5% and 10% of MO from rough Olivine Basalt rock surface, P%, as a function of the number of treatment; N. Error bars represent the SE for five replicates. The full data sets are provided in Table 41 and the individual data profiles are given in Table 42, 43 and 44 in Appendix 5.

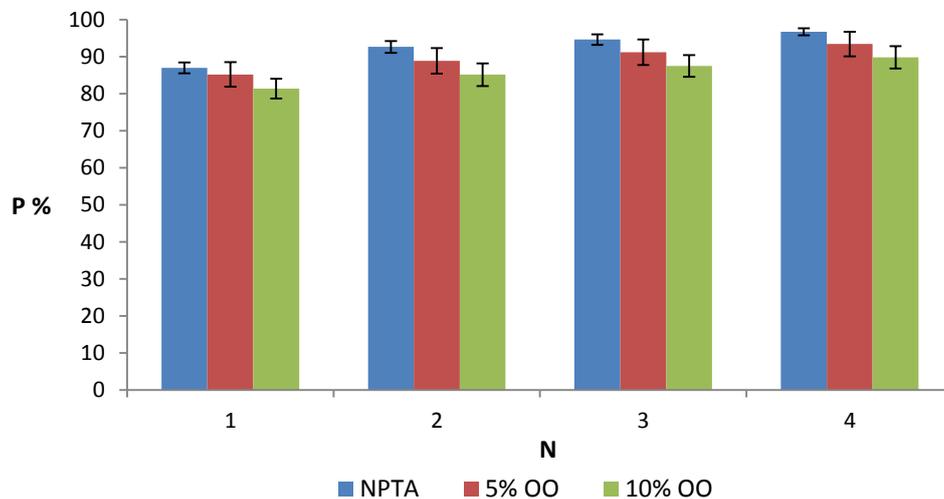


Figure 5.25 Comparison of MPT removal of ENO mixed with 5% and 10% of OO from rough Olivine Basalt rock surface, P%, as a function of the number of treatment; N. Error bars represent the SE for five replicates. The full data sets are provided in Table 45 and the individual data profiles are given in Table 42, 46 and 47 in Appendix 5.

It can be seen from Figure 5.25 that the initial pick up of ENO of 87.0% was also higher than that of 85.2% for 5% OO and 81.4% for 10% OO. At the final treatment (N=4), removal of

ENO of 96.7% was also higher than that of 93.4 % for 5% OO and 89.8% for 10% OO. This is a similar trend to that observed in Figure 5.24, i.e. as the percentage of PTA increases (5% to 10%) the efficiency of removal becomes less.

For the rock surfaces studies, following general conclusion can be drawn:

- For smooth, non-porous, inorganic surfaces, it is possible to achieved 100% removal of JCO with high reproducibility. This suggests that removals of less than 100% from inorganic surfaces could be due to surface roughness and/or porosity.
- The effects of the different physical characteristics of the rock surface on the pick-up of oil have been examined. The results confirm that different characteristics on the surface (pores) give different contaminant removals.
- The use of PTAs for contaminant removal from different (smooth and rough) rock surfaces has been studied and compared with NPTA. The results suggest that the application of different PTAs results in different removal efficacies.
- The degree of oil absorption into a porous rock surface has been shown to be related to the viscosity of the contaminant. In this regard, the ability of a PTA to alter the viscosity of the contaminant may be exploited to enhance the removal from a porous surface. Indeed, these results suggest that MPT might be useful for assessing rock porosity with respect to different potential contaminants. This is an obvious direction for future research.

5.4 Conclusions

This chapter has explored the application of magnetic particle technology (MPT) to the removal of oil contamination from a variety of different substrates; including mammalian fur (rabbit and seal) - and this has been referenced to MPT removal from feathers.

With respect to removal from mammalian fur, it has been demonstrated that different fur microstructures have a profound effect on relative removal efficacies for a range of contaminants of different viscosities. In particular, since fur *pelt* was employed, it has been possible to discern the relationship between the fur structure, the oil viscosity and the extent of absorption onto the skin.

Experimental procedures have been refined and the role of PTAs has also been investigated with respect to the assay developed in Chapter 4 and the point of PTA application. In this regard, it is also possible to make recommendations to rehabilitators of furry animals, with respect to a given type of contaminant and animal, on preferred PTAs and recommended points of application. As with the application of the assay to feathers, it is also possible to suggest contra-indications.

The magnetic cleansing of rock surfaces has also been investigated from the point of view of establishing the effects of the absorption of the oil contaminant into the rock pores. It has been demonstrated that the use of various PTAs can affect and possibly ameliorate this absorption process.

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