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# Mathematical Model for the Sequential Pick-Up of Chemical Contaminants by Magnetic Particles

**R E V I S E D   M A N U S C R I P T - Revision #2**

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## Abstract

Two conceivable types of mathematical model, i.e. exponential or hyperbolic, that describe the sequential pick-up of a contaminant from a substrate upon successive treatment with magnetic particles, have been developed and tested.  The models were applied to sets of experimental data spanning extremes of system behavior. Allowance was made within each model to account for departure from ideality. The non-ideal hyperbolic model was identified as being the one that can be better applied to the experimental data.  The successful application of this model to a given data set enables a pick-up efficiency that is based on all of the available experimental data to be accurately determined.  Thus it was found that the pick-up efficiency is highly correlated with one of the fitting parameters introduced to account for non-idealized behavior. The ability to accurately assess removal efficiency in the sequential pick up of chemical contaminants by magnetic particles is essential for the optimization of this technology for practical application in the field, particularly with respect to environmental remediation.

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## Introduction

Magnetic particle technology has well-established and emerging applications across a wide range of discipline areas (Safarikova and Safarik 2001; Orbell *et al*. 2007a). 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 demonstrates 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*. 2006c) as well as the  acute temperature dependency and the thermodynamics of the pickup 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*. 2007b).

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" cleaning process that offers significant advantages, since iron powder is both non-toxic and is 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 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 paper 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 range of *sequential* data 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.

## Theory

### *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 $n$.

***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. In this case the efficiency decreases with the number of treatments suggesting that the removal mechanism is one where successive layers of contaminant are removed upon successive treatments. Each treatment can be considered as a process in which the equilibrium associated with the partitioning of the contaminant between the substrate and the magnetic particles is shifted in such a way that it favors the transfer of the contaminant from the substrate to the particles.

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:

$$\mathrm{d}P_1(n)/\mathrm{d}n = -k_1 P_1(n) \qquad (1)$$

where $P_1(n) = P_\infty - P(n)$ which is the difference between $P_\infty$, 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:

$$P(n) = P_\infty[1 - \exp(-k_1 n)] \qquad (2)$$

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 $v_0 = k_1P_\infty$. 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. Such deviation may be caused by impurities and/or irregularities on the surface of the magnetic particles that may cause disproportionate pick-up upon successive treatments. An adjustment can be achieved by allowing the constant $k_1$ to vary with $n$ in an empirical power law relation. Whence:

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

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:

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

***Hyperbolic Model***

A hyperbolic model can be derived by assuming that the difference between the percentage pick-up after an infinite number of treatments, $P_\infty$, and the function $P(n)$ is inversely proportional to $n$. This difference corresponds to the amount of contaminant that remains on the substrate after the $n$th treatment. Similarly to the exponential case explored above, the removal mechanism in the hyperbolic model is once again consistent with the notion that successive layers of contaminant are removed upon subsequent treatments. Thus in the case of the hyperbolic model:

$$P_\infty - P(n) \propto 1/n \qquad (6)$$

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

$$P(n) = P_\infty - k_2/(n + b) \qquad (7)$$

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) is obtained:

$$P(n) = nP_\infty^2/(nP_\infty + k_2) \qquad (8)$$

The derivative function of equation (8) with respect to $n$ can also be obtained and evaluated at $n = 0$ to produce 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:

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

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

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

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, $v_1'$:

$$v_1' = [\mathrm{d}P(n)/\mathrm{d}n]_{\mathrm{n=1}} = c_2 P_\infty^2(1 - m_2)/(P_\infty + c_2)^2 \qquad (11)$$

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.

## 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 Höganas AB, Sweden, and was described by the manufacturer as "spongy annealed superfine" (Grade MH 300.29). 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 is provided for this although a previous study has indicated that the absorption/adsorption process is 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 re-weighed ($f_4$). 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 1, are generated by plotting $P(n)$ versus $n$.

**Results and Discussion**

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 generates a $P(n)$ versus $n$ isotherm that is 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 is 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 is representative of one with a relatively low efficiency where the function $P(n)$ gradually approaches an asymptotic upper limit of close to 100% after *ca*. $n = 16$ contaminant removal treatments. The second case that was chosen is the isotherm for the removal of an 80:20 Diesel/JCO mixture from the same substrate and under the same experimental conditions. This system exhibits a very high pick-up efficiency where the function $P(n)$ rapidly approaches the asymptotic upper limit after *ca*. $n = 1$ treatment.

Figure 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).

>>>INSERT **Figure 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)) has little effect on the quality of fit of the experimental data. Figure 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 is 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 is 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.

>>>INSERT **Figure 2**

Figure 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 is 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.

>>>INSERT **Figure 3**

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)) produces a comparatively acceptable fit of the experimental data for the two extreme systems that are under investigation. This is apparent in Figure 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) show a considerable improvement on the respective data generated from the ideal hyperbolic model depicted in Figure 3. 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 $r^2_{av}$(ideal hyperbolic model) = 0.579 ± 0.038 and $r^2_{av}$(non-ideal hyperbolic model) = 0.816 ± 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 provides 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.

>>>INSERT **Figure 4**

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 5 that 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 5 at the theoretical point $n$ = 0.04 which is denoted $[dP(n)/dn]_{n=0.4}$ is significantly less that 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.

>>>INSERT **Figure 5**

The hyperbolic model is based on the assumption that the difference between the percentage pick-up after an infinite number of treatments, $P_\infty$, 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 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. In the current system, it is believed 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.

Although the nature of the experiments performed in the current work makes it difficult to clearly and unequivocally ascertain the mechanism of the adsorption an insight into the physical chemistry aspects of the process may be achieved by dividing both sides of equation (8) by the constant $P_\infty$ to yield equation (14):

$$P(n)/P_\infty = nP_\infty/(nP_\infty + k_2) \quad (14)$$

The form of this equation bears remarkable resemblance to the Langmuir adsorption isotherm (Langmuir 1918) if one recognizes the $P(n)/P_\infty$ term as being representative of the fraction of the total surface sites on the iron particles that are available to adsorb the contaminant and one invokes the approximation that the cumulative amount of contaminant that is picked up after $n$ treatments is proportional to $n$.

Clearly, in any attempt to map equation (14) to the Langmuir adsorption isotherm model one would also have to assume that the constant $k_2 \approx 1$. The latter assumption is necessary to obtain complete correspondence with the Langmuir model but any departure of $k_2$ from unity in a real system, as in the current study, would presumably reflect the fact that the Langmuir isotherm itself is an idealized case and the implicit assumptions that are made in its derivation are seldom all true (Daniels and Alberty, 1966). Furthermore, the analogous nature of the hyperbolic pick-up model to the Langmuir adsorption isotherm as revealed in equation (14) suggests the adsorption is most likely a physisorption process rather than chemisorption as the former is more commonly associated with a fit to a Langmuir-type adsorption isotherm (Castellan, 1983).

Under some circumstances, the point of inflexion identified in Figure 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 1 along with the regression coefficient $r^2$ pertaining to each analysis. In analyzing the experimental data to produce Table 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*. ±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 1.

>>>INSERT **Table 1**

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 1 indicate that the parameter $c_2$ is large in cases where the system exhibits a relatively low efficiency and vicé vèrsa. This apparent correlation was tested further by plotting the reciprocal of $v_{max}$ as a function of $c_2$ and is shown in Figure 6.

>>>INSERT **Figure 6**

It is clear from Figure 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. Furthermore, the data in Table 1 can be can be used to explore the range of $k_2$ values within the experimental domain. In particular, the calculated value of $k_2$ ranges from 59.8 to 236 across the domain for the removal of 100% JCO where the removal process is seen to be relatively inefficient compared to the 80:20 Diesel/JCO system. In the case of the latter the value of $k_2$ ranges from 0.564 to 4.43 and clearly encompasses the case where $k_2$ =1 corresponding to the idealized Langmuir adsorption isotherm discussed above. From the physical chemistry point of view this may suggest that contaminant removal by a chemisorption process predominates in systems that demonstrate high removal efficiencies and that significant departure form this occurs in systems of low removal efficiency.

The data in Table 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.

**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.

An analogy between the derived mathematical model and the Langmuir adsorption isotherm was identified and found to provide a possible link between the model and the underlying physical chemistry of the removal process. This has suggested that the contaminant removal is akin to chemisorption in systems that demonstrate high removal efficiencies and that deviation from this process occurs in systems where the removal efficiency is low. It is not possible to infer the nature of the latter from the results of the current experiments.

It was found that the $c_2$ fitting parameter in the non-ideal hyperbolic model is highly correlated with the 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.

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**Notation**

| | |
|---|---|
| $b$ | constant used in the hyperbolic pick-up model |
| $c_1$ | proportionality constant allowing for deviation for idealized behaviour in the exponential pick-up model |
| $c_2$ | proportionality constant allowing for deviation for idealized behaviour in the hyperbolic pick-up model |
| $f_1$ | 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 |
| $k_1$ | 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 |
| $n$ | number of treatments issued to a given oil-contaminated system using magnetic particles |
| $P$ | percentage pick-up of contaminant |
| $P(n)$ | cumulative percentage pick-up of contaminant from the system upon treatment $n$ |
| $P_\infty$ | cumulative percentage pick-up after an infinite number of treatments |
| $P_1(n)$ | the difference between $P_\infty$ and $P(n)$ expressed in the exponential pick-up model |
| $r$ | linear regression coefficient |
| $r_1$ | mass of residual contaminant |
| $v_0$ | initial contaminant pick-up efficiency derived from the ideal exponential pick-up model |
| $v_1$ | contaminant pick-up efficiency after one treatment derived from the exponential pick-up model |

| | |
|---|---|
| $v_0'$ | initial contaminant pick-up efficiency derived from the ideal hyperbolic pick-up model |
| $v_1'$ | contaminant pick-up efficiency after one treatment derived from the hyperbolic pick-up model |
| $v_{max}$ | maximum gradient of the $P(n)$ versus $n$ isotherm as fitted by the hyperbolic pick-up model |

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**Table 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 | -0.507 | 34.5 | 0.972 |
| 20 | 175 | -0.671 | 43.9 | 0.967 |
| 30 | 120 | -0.615 | 54.6 | 0.977 |
| 40 | 55.3 | -0.548 | 89.1 | 0.827 |
| 50 | 19.2 | -0.496 | 182 | 0.850 |
| 60 | 8.87 | -0.462 | 317 | 0.655 |
| 70 | 5.03 | -0.122 | 474 | 0.443 |
| 80 | 4.43 | -0.761 | 354 | 0.834 |

**Figure Captions**

**Figure 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 MH 300.29 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)).

**Figure 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).

**Figure 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)).

**Figure 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)).

**Figure 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.

**Figure 6** Plot of $c_2$ versus $1/v_{max}$ for the systems given in Table 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.