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Effects of nonaqueous phase liquids on the washing of soil in the presence of nonionic surfactants

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Abstract

The removal of malathion from soil by surfactant washing was investigated under various physical–chemical states of the malathion. Three distinctive phases (without nonaqueous phase liquids (NAPL), with NAPL, and the transitional zone of NAPL) were found to be important for a better understanding of the washing process. When there is no NAPL in the system, the washing process is less dependent on the surfactant dose if the applied surfactant concentration is above the critical micelle concentration. The existence of a sorption site boundary, which for the determination of different washing mechanisms, was identified. In the presence of NAPL, the washing performance is generally independent of the organic content (f_{oc}) of the soils but is dominated by the concentration of the surfactant used, due to the lesser resistance for mass transfer in NAPL. If the formation of NAPL is marginal, a two-stage washing pattern is observed, which has been quantified by the term 'unit extraction'. For this two-stage system, a mathematical model was derived based on the observed initial unit extraction and final extraction capacity, which eventually resulted in a practical design equation with the use of primary parameters such as f_{oc} and surfactant dose.

Keywords: Soil sorption; NAPL; Solibilization; Malathion; Brij 35; Mathematical model

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1. Introduction

Because of the spillage of solvents, pesticides, or degreasing agents by industries, the removal of organic contaminants in soil or groundwater has been an environmental concern for decades (Pankow and Cherry, 1996). The in situ pump-and-treat method has been viewed as a convenient and economical way of washing soil (Underwood et al., 1995; Nyer, 1992). Sparingly soluble organic liquids that are dumped or accidentally released to the subsurface as nonaqueous phase liquids (NAPL) reside in a separate phase that is difficult to recover (Hatfield et al., 1992; Mackay and Cherry, 1989). USEPA (1993) has estimated that 60% of the Superfund sites have a medium-to-high possibility of containing dense NAPLs (DNAPLs) that are expected to sink beneath the water table (MacDonald and Kavanaugh, 1994). According to Robert and Cherry (1994), the presence of sparingly soluble NAPLs in soils and aquifers severely limits the effectiveness of the conventional pump-and-treat method. Soil and aquifer remediation requires a clear understanding of the physical–chemical state of the organic contaminants, including the existence of NAPLs. When NAPLs are

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present, surfactants are commonly employed at concentrations above the critical micelle concentration to enhance the solubility of organic matter in an aqueous phase used for washing soil (Reddi and Inyang, 2000; Raghavan et al., 1991). The micelles formed by surfactants have a hydrophobic interior that solubilizes the organic contaminants.

There have been numerous efforts to quantify the sorption of organic contaminants in soil (Schwarzenbach, 2003). Mechanisms that have been identified as causing sorption to soil include van der Waals forces, hydrogen bonding, dipole–dipole interactions, ion exchange, and covalent bonding mechanisms, depending on the nature of the organic contaminant and the type of soil. The presence of surfactants can alter the properties of the surfaces of soil particles and result in the removal of surfactants from the solution (Liu et al., 1992).

Although, there have been a very large number of studies on the relationship between organic pollutants and soil, comprehensive investigations and comparisons of the soil-washing characteristics of surfactants in cases of low, medium and heavy pollution are limited. The degradation of low-level organophosphate pesticides (parathion and azinphosmethyl), for example, can be observed as occurring within a scale of days or weeks. However, the decay rate for contaminants that have accumulated for years or that have accidentally spilled and formed NAPL is seriously retarded (Wolf et al., 1973). In the presence of an NAPL pool, which is treated to be immiscible in the aqueous phase, the NAPL would then accumulate in the aquifer, making the conventional remediation process more ineffective. Therefore, a clear study of such a system with or without the presence of NAPL would be beneficial for the improvement of soil-washing technology. The distribution of pollutants between the water and NAPL phases has been studied by Cowell et al. (2000). They have pointed out the importance of understanding the partitioning of pollutants in the Water/NAPL phases ahead of the application of remediation technology. They have also argued that surfactant partitioning is strongly correlated to the surfactant mixture polydispersity, surfactant hydrophobicity, and the NAPL/water interfacial tension. Dulfer et al. (1995) have suggested that above the cmc, the solubility of excessive amounts of PCBs in surfactant SDS is directly proportional to the concentration of surfactants. Butler and Hayes (1998) have conducted a study involving the mixing of surfactant and two pollutants, haxane and 1,2-DCB. The study showed that the solubility of pollutants in an aqueous phase depends very much on the dosage of the surfactant. McCray et al. (2001) and Shiau et al. (1996) have investigated the solubilization of NAPL mixtures with surfactants, while Backhaus et al. (2001) and Zheng and Obbard (2002) have demonstrated that the sorption of surfactants occurs in the presence of organic pollutants, complicating the surfactant-aided soil-washing process.

Malathion is a widely used organophosphate pesticide in agriculture (WHO/FAO, 1977) and for controlling mosquito-born diseases (Mccarroll et al., 2000). It can cause disruption of the nervous system, and humans exposed to the chemical may experience breathing problems, headache, nausea, dizziness or even become fatally poisoned if exposed to high quantities (Abou-Donia, 1992). The presence of pesticides in abandoned landfill sites, for example, poses a threat to the quality of water and to the environment, the extent of which is not yet known. These sites, often located in rural areas, were historically subjected to little or no regulation in their use or maintenance, and it is often not known what kinds of hazardous materials may have been discarded at the site. Depending upon their concentration, the contaminants may or may not have been dissolved in the water contained in the soil; thus, they may be transported in the soil either in an aqueous (dissolved) phase solution with soil water or as an NAPL (Flerchinger et al., 1997).

In this study, we have examined the soil-washing performances of different types of soils by various doses of surfactants in the presence of very low (no NAPL) to very high (with NAPL) levels of a probe compound malathion. In addition, a mathematical model has been established to generalize the behavior of the soil-washing process, so as to assist the process prediction of soil-washing for engineering applications.

2. Materials and methods

2.1. Chemicals

The malathion (99%, *o*,*o*-dimethyl-*S*-(1,2-dicarbethoxyethyl) phosphorodithioate) was purchased from Sima-Aldrich. Its physical properties are shown in Table 1. A non-ionic surfactant, Brij 35 (polyoxyethylene (23) lauryl alcohol) from Warenzeichen der ICI America Inc. was used in the soil washing process. Brij 35 with a formula of $C_{12}H_{25}(OCH_2CH_2)_{23}OH$ has a

Table 1
Physical properties of malathion (Chu and Chan, 2000)

Chemical	MW	Water solubility (mmol/L)	Melting point (°C)	K_{oc} (mL/g)	K_{ow}
Malathion	330.36	0.40	2.85	1800	776

formula weight of 1220. All of the chemicals in this study were used without further purification.

2.2. Soil

Soil samples were collected from four different clean locations within the territory of Hong Kong. The samples were taken from the upper 15 cm of the soil. Plant and root materials were removed using a 2 mm British Standard Test Sieve. Moisture was removed from the soil by drying the soil at 100 °C for 3 days. The dry samples were further put through a 69 μm British Standard Test Sieve, where soil particles smaller than 69 μm (classified as clay, which has the highest organic content in soil) were collected for the tests.

The organic content of the treated soil, equivalent to the organic carbon, was determined using the Shimadzu Total Organic Carbon Analyser (model TOC-5000A). A small amount of the sample was placed in a combustion furnace containing an oxidation catalyst and heated to 1000 °C. The amount of CO_2 generated from the combustion was measured and the response was compared with the calibration curve by analyzing known carbon standard solutions. The inorganic carbon content was determined by acidifying the soil with a 5% hydrochloric acid solution at 250 °C, from which the quantity of CO_2 released by carbonate species could be measured. The total organic carbon (TOC) in each soil sample was, therefore, calculated by subtracting the total inorganic carbon (TIC) from the total carbon (TC). The fractional organic carbon (f_{oc}) is expressed as a percentage of organic carbon in the dry soil. Some of the soil properties are listed in Table 2.

2.3. Surface tension test

The critical micelle concentrations in various soil and/or surfactant systems were measured using the surface tension technique. Samples with different surfactant concentrations ([Brij]) and f_{oc} levels were mixed for 24 h in a rotary shaker. After centrifugation at 4000 rpm for 30 min, the surface tension of the supernatant was measured by the tensiometer (Fisher Surface Tensiomat Model 21) consisting of a Du Nouy platinum–iridium ring suspended in the surfactant solution by a torsion balance. All of the samples were measured in duplicate.

Table 2
Some physical properties of soil samples collected within the territory of HK

Sample locations	f_{oc} (%)	pH	Conductivity (μS)	NO_3^- (ppm)
1. Fei Ngo Shan	0.15	5.01	40.2	1.1
2. Fanling	0.64	6.44	35.5	1.1
3. Sai Kung	1.41	5.97	24.9	1.5
4. Nai Chung	2.10	2.84	468	3.2

2.4. Partitioning between the soil and aqueous phase

The distribution of malathion at different concentrations of surfactant was determined by a series of batch experiments. The ratio of soil to the liquid phase was set at 1:20 (w/v) and malathion was spiked into teflon tubes. The capped samples containing 0.5 g of soil and 10 mL of surfactant solution were shaken by a 40 rpm rotary shaker at 20 °C for 24 h. All of the samples were centrifuged at 4000 rpm for 30 min prior to the analysis. Malathion in the supernatant was quantified by HPLC, which consists of a pump (Finnigan MAT SCM 1000), UV lamps (UV 6000LP), an autosampler (Finnigan MAT AS 3000), and an electronic integrator. The chromatographic separations were performed on a stainless-steel Restek column (a 5 μm, 4.6 mm ID × 250 mm pinnacle octyl amine column), and the elution solvent was a mixture of acetonitrile–water (60:40 v/v) with a flow of 1.2 mL/min for a total run time of 10 min. Strongest UV absorption of malathion was observed at 198 nm and, therefore, was selected as the detection wavelength in HPLC. The probe malathion remaining in the soil phase can be calculated from a simple mass balance.

3. Results and discussion

3.1. Solubilization of the surfactant Brij 35

The surface tension of the aqueous phases in the presence of soil with different f_{oc} and surfactant doses is shown in Fig. 1. In general, the surface tension curve has two linear segments for each dose of surfactant. The breakpoint between the two segments indicates the value of cmc in the presence of soils. The cmc increases with the f_{oc} of the soil in a linear relationship with an r^2 of 0.9988, as shown in Fig. 2:

$$\mathrm{cmc}_{\mathrm{obs}} = 0.103 + 0.235 f_{oc}, \tag{1}$$

where the $\mathrm{cmc}_{\mathrm{obs}}$ is the observed critical micelle concentration (mmol/L), f_{oc} is the percentage of the organic content in the soil (%) and the intercept 0.103 mmol/L is the cmc of Brij 35 in pure water. The good linear correlation of cmc with f_{oc} indicates that the organic content in the soil is the critical parameter that determines the loss of surfactants to the soil due to adsorption.

The data in Fig. 1 can also be used to calculate the fraction of the surfactant adsorbed to the soil. A given amount of surfactant in a solution reduces the interfacial tension up to the cmc, and the interfacial reduction in the presence of the soils indicates how much surfactant

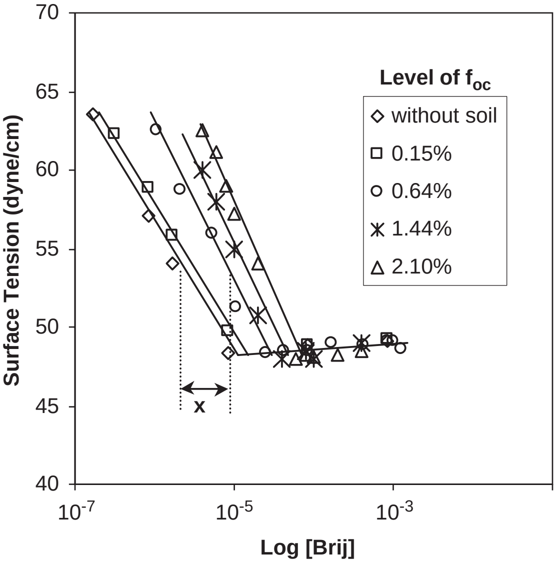

Fig. 1. Change of surface tension at different surfactant doses (Brij 35) and f_{oc} levels.

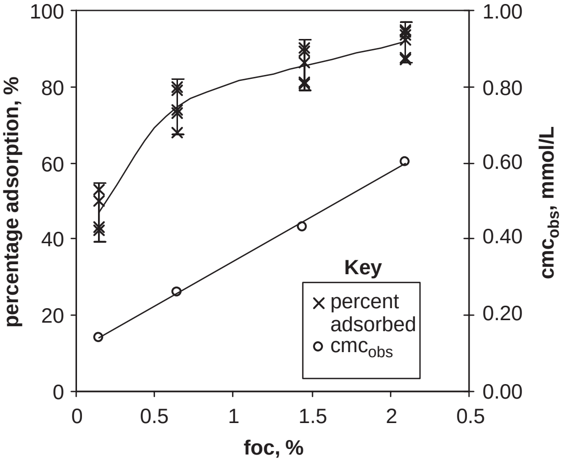

Fig. 2. (Top) The loss of surfactant to soil at different f_{oc} levels as the surfactant doses were below cmc_{obs}. (Bottom) The cmc_{obs} at various f_{oc} levels.

remains in the solution and the remaining surfactant that must be adsorbed. At any arbitrary surface tension, the amount of surfactant in an aqueous phase can theoretically be calculated for each f_{oc} level due to the linear characteristic. The mole number of the surfactant being adsorbed per unit volume of solution is the horizontal difference in the concentration of surfactants between the selected tension line with soil and the line without soil (i.e., surfactant only) (Chu and So, 2001): for example, the amount of surfactant sorbed to the soil with 0.64% f_{oc} is marked as 'x' in Fig. 1. As the surfactant dosages were below the cmc_{obs}, the percentage loss of surfactant to soil was calculable and the results are shown in Fig. 2. In general, the higher the f_{oc} of the soil, the higher the loss of surfactant. The average loss increased from 45% to 92% as the f_{oc} increased from 0.64% to 2.1%, respectively. It was found that as the surfactant doses were lower than the cmc_{obs}, the variation in the percentage loss at each specific f_{oc} was limited to within 10% of the tested f_{oc} ranges from 0.15% to 2.10%. These data reflect that only a small portion of surfactant monomer remains in the aqueous phase to perform as a solubilizing agent in the soil-washing process when the dose of surfactant is lower than cmc_{obs}. However, it was suggested that as the surface tension was lower than that at the cmc_{obs} (i.e., as the surfactant dose is higher than cmc_{obs}), the sorption sites in soil were likely to have been saturated by surfactant and further loss due to the surfactant increment was minimal (Liu et al., 1992). It is known that surfactant micelles have a better soil-washing capability than surfactant monomers (Chu and Chan, 2003). To achieve a better washing performance in a general application, the f_{oc} of the soil should be recognized first and the minimum surfactant level (Brij 35 in this case) required in the soil-washing system would be theoretically equivalent to the corresponding cmc_{obs} of the soil. To facilitate this, a useful correlation between the cmc_{obs} and f_{oc} of different soils has also been included in Fig. 2.

3.2. Soil-washing in different doses of malathion

The surfactant-aided soil-washing performance at equilibrium under a wide range of concentrations of malathion ([Mal]) was investigated and it was discovered that the level of [Mal] is one of the crucial factors in determining the washing performance. According to the results, different washing patterns were observed at various initial levels of malathion ($[\text{Mal}]_0$), which could be categorized by three phases for discussion: (1) no formation of NAPL in the soil-aqueous system, (2) NAPL is present within the soil-aqueous system, and (3) the transition area where the existence of NAPL is uncertain.

3.2.1. Phase I: no NAPL formation

The soil-washing system without NAPL was simulated by adjusting the initial dose, $[\text{Mal}]_0$, below the water solubility level of 0.40 mmol/L. Several initial doses were tested at surfactant levels significantly above the cmc_{obs} in the 0.64% f_{oc} soil. Fig. 3 shows that the percentage of malathion extracted to the liquid phase was independent of surfactant doses.

The observation could be explained by the equilibrium of malathion among water, surfactant micelles, and soil organic matter. We are assuming that the total

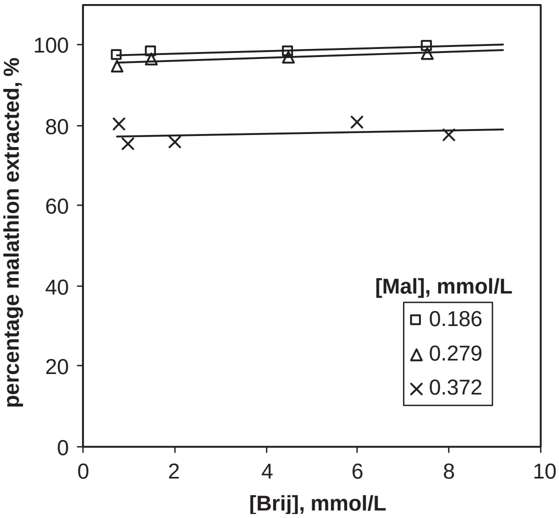

Fig. 3. Percentage of malathion extracted at different surfactant doses without NAPL.

number of adsorption sites in soil is constant and that these sites can be divided into two individual parts, one for the surfactant and the other for the malathion. Because the sorption (or loss) of surfactant to the soil is a constant, if cmc_{obs} is reached as indicated before, the sites available for the adsorption of malathion is likely to be close to a constant. As the $[Mal]_0$ level is much lower than the solubility, the malathion molecules will partition between the sorption sites and the liquid phase, where the involvement of surfactant in the transfer of malathion is insignificant. However, as the $[Mal]_0$ level increases and approaches solubility, a competition for sorption sites is likely to be observed. Since the surfactants (to be a soil-washing agent) presumably have a good affinity to the sites, it is rational to assume that most of the adsorbed malathion will be washed out if the ratio of $[Brij]/[Mal]_0$ is high. However, as the ratio reduced, both surfactant and malathion compete for the adsorption sites on the soil, which causes a reduction of extraction performance. To verify this, the extraction performance of malathion at various initial concentrations at a constant surfactant concentration was investigated, and the results are shown in Fig. 4(a). The extraction efficiencies of malathion were maintained at around 95% for those low $[Mal]_0$ levels, but suddenly drops to about 80% as the $[Mal]_0$ dose approaches solubility. Such a gap was in evidence when demonstrating the existence of a boundary where the utmost site limitation was located. Therefore, as the number of malathion molecules is lower than the equivalent site boundary, free partitioning was the main mechanism. Above the boundary, the competition becomes dominant and higher portion of malathion resides in the soil. In addition, the extraction performance was also found to be related to the soil's f_{oc}: the higher the f_{oc}, the lower the extraction percentage. This verifies the existence of the boundary of the site limitation, and shows that the capacity of the site is proportional to the f_{oc}, as seen in Fig. 4(b).

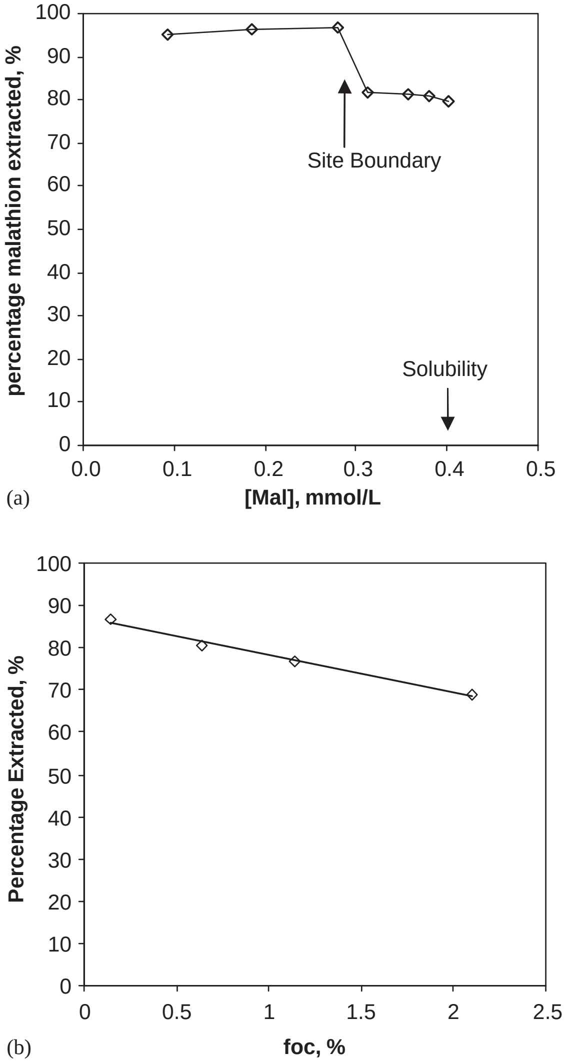

Fig. 4. (a) Percentage of malathion extracted at different initial dosages without NAPL, where f_{oc} and [Brij] are 0.64% and 0.8 mmol/L, respectively. (b) Malathion extraction in soil with different f_{oc}, where the [Mal] was 0.37 mmol/L (slightly below its solubility).

3.2.2. *Phase II: NAPL presence*

When the level of organic pollutants is much higher than their aqueous solubility, NAPLs are likely to be present. To simulate the conditions when an NAPL is present, the $[Mal]_0$ dosage was set at five times the solubility of water. Under these circumstances, the

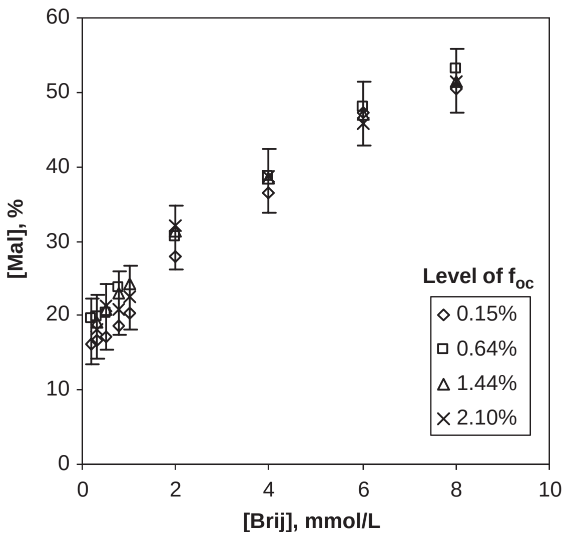

Fig. 5. Soil washing efficiency at different f_{oc} levels in the presence of malathion with NAPL, where the $[\mathrm{Mal}]_0 = 1.86\,\mathrm{mmol/L}$ and error bar is within 10%.

distribution of malathion in the subsurface includes the NAPL and surfactant micellar phases, along with the dissolved and soil adsorbed components. The washing efficiencies at high concentrations of malathion as a function of surfactant doses are shown in Fig. 5. It was interesting to note that the extractions of malathion in the presence of NAPL at any fixed surfactant concentration were similar regardless of the different f_{oc} levels of soils that we used, and that the washing efficiencies increased linearly with the surfactant dose.

The observation implies that the washing performance of malathion in soil present as an NAPL is generally independent of the organic content (f_{oc}) of soils, and that the sole parameter for determining the soil-washing performance is the concentration of the surfactant. This can be explained by a simple 'resistance' theory analogous to the flow of current in two power lines with different resistances, where a high current will be observed in the low resistance line. In the soil-washing system, the malathion molecules are adsorbed (or locked) in the soil structure, while the malathion present as an NAPL is free to partition in the water solution. Apparently, in the latter case less resistance is encountered for mass transfer (i.e., from NAPL to surfactant micelles), and the former becomes a stagnate pool with insignificant contribution or remains intact for the mass transfer. In addition, compared to the extraction percentage from phase I (with lower dosages of $[\mathrm{Mal}]_0$), the removal percentage at a high malathion level is greatly reduced. However, the extraction performance is linearly increased when the surfactant is introduced to the system, and up to 50% of the original malathion can be washed into the liquid phase within the test ranges of the surfactant. Therefore, in a practical surfactant-aided soil-washing process, it is possible to clean out the NAPL by means of either multi-extraction with lower surfactant doses or single-extraction with a higher surfactant dose. As the intercept of y-axis is greater than zero (Fig. 5), it is expected that multiple extraction should be more effective.

3.2.3. Phase III: Transitional area of forming NAPL

As previously indicated, the soil washing mechanisms at relatively high- and low-malathion concentrations were completely different, which triggered an interesting but critical issue—what if the malathion dose is in a marginal condition in between the soluble form and the NAPL? Considering that 50% of malathion can be removed in the washing system and the possible adsorption of malathion in the soil, the soil-washing process was conducted by using an initial $[\mathrm{Mal}]_0$ at twice its solubility (i.e., 0.80 mmol/L). The experimental results of the extraction of malathion at various surfactant and f_{oc} levels are shown in Fig. 6. It is surprising to see that the extraction of malathion can be divided into two distinctive stages: the extraction performance increased rapidly with the increment of surfactant concentration, followed by a stabilizing stage, where the final extraction capacities depend upon the f_{oc} levels.

When the performance of malathion extraction is compared with the dose of surfactant, a 'unit extraction' is defined by $\Delta[\mathrm{Mal}]/\Delta[\mathrm{Brij}]$. High unit extractions (1.23–1.69, depending on the f_{oc}) are observed at low

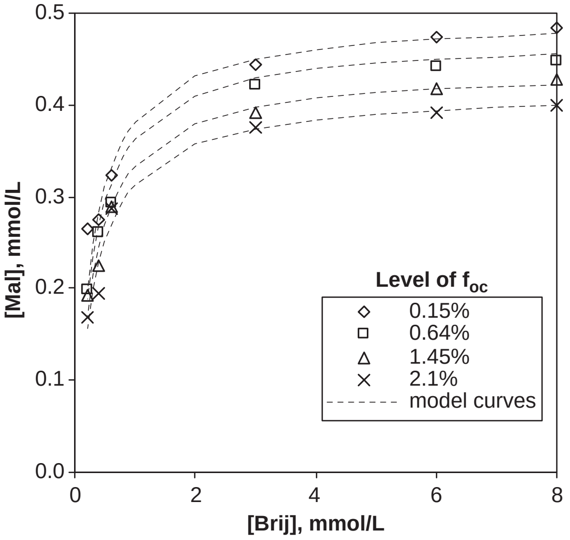

Fig. 6. Soil washing performance at various f_{oc} levels within the NAPL transitional area, where the curves are the modelled trends resulting from Eq. (8).

doses of surfactant, while the unit extraction drops to 0.007 when [Brij] increases from 6 to 8 mmol/L. Although not exactly the same, the recovery of malathion within phase III is a combination of the phases I and II, as discussed in the previous sections. At the initial stage, similar to phase II, as the [Brij] is relatively lower than the requirement, the solubilization of malathion is not obvious, resulting in the formation of NAPLs. The presence of an NAPL pool due to the insolubility of malathion dominates the extraction process. The extraction performance is strongly dependent on the amount of surfactant introduced, which gives a high unit extraction within this range. The extraction of NAPL keeps increasing until the addition of surfactant Brij 35 is adequate to fully solublize the NAPL of malathion. As this point is reached, the malathion trapped in the structure of the soil becomes the main source for the extraction process. Further increases of [Brij] show little improvement on the extraction performance (i.e., there is a very low unit extraction within this range), which is similar to the previous observations in phase I.

To facilitate the prediction of the complicated soil-washing performance in phase III, a mathematical model incorporating these observations is derived to describe the performance of the process within the transitional zone.

$$[\mathrm{Mal}] = \frac{[\mathrm{Brij}]}{a + b[\mathrm{Brij}]}, \tag{2}$$

where [Mal] is the amount of malathion extracted to the aqueous phase (mmol/L), and [Brij] is the surfactant Brij 35 applied to the system (mmol/L).

The a and b are two characteristic constants. By taking the derivation of Eq. (2) with [Brij] and setting [Brij] to zero, the term a can, therefore, be solved as follows:

$$\frac{d[\mathrm{Mal}]}{d[\mathrm{Brij}]} = \frac{1}{a}. \tag{3}$$

The physical meaning of $1/a$ is the slope at the commencement or the unit extraction in the initial stage of extraction. On the other hand, when [Brij] is approaching infinity in Eq. (2), the term a in the denominator can be ignored compared to the term of b[Brij], and $1/b$ can be solved as:

$$[\mathrm{Mal}]_{[\mathrm{Brij}]\to\infty} = \frac{1}{b}. \tag{4}$$

The physical meaning of $1/b$ is the theoretical maximum [Mal] concentration in the liquid phase, or the extraction capacity in the surfactant-aided soil-washing process. Accordingly, the performance and kinetics of the initial extraction stage and stabilizing stage in phase III can be characterized by constants $1/a$ (the initial unit extraction, dimensionless) and $1/b$ (the final extraction capacity, L/mmol), respectively. To solve the character constants, Eq. (2), can therefore be linearized to Eq. (5). By plotting [Brij]/[Mal] versus [Brij], a straight line with intercept a and slope b results

$$\frac{[\mathrm{Brij}]}{[\mathrm{Mal}]} = a + b[\mathrm{Brij}]. \tag{5}$$

Fig. 7 showed the results of plotting [Brij]/[Mal] at various [Brij], where very good linear correlations were observed. The values of constants a and b with respect to different f_{oc} are summarized in Table 3.

In addition, the values of a and b were also found to be correlated to the f_{oc} of the soils (see Fig. 8), where the linear correlations were shown as follows:

$$1/a = -0.21 f_{\mathrm{oc}} + 1.70, \tag{6}$$

$$b = 1.98 \times 10^5 f_{\mathrm{oc}} + 1.99 \times 10^6. \tag{7}$$

It is noticed that values a and b slowly increase with f_{oc}, implying that the soil washing performance is hindered by the organic content in the soil. This result concurs with those of previous studies conducted by several different researchers (Chu and So, 2001; Gerstle and

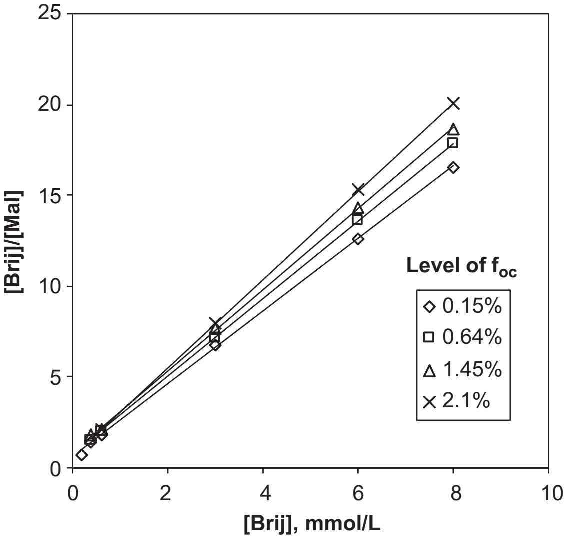

Fig. 7. Linearization of the proposed model by plotting [Brij] vs. [Brij]/[Mal].

Table 3
Values of a and b at different soil f_{oc}

f_{oc}	a	b (mmol)	r^2
0.15	0.59	2.00×10^6	0.9992
0.64	0.66	2.15×10^6	0.9990
1.45	0.68	2.27×10^6	0.9995
2.10	0.81	2.41×10^6	0.9992

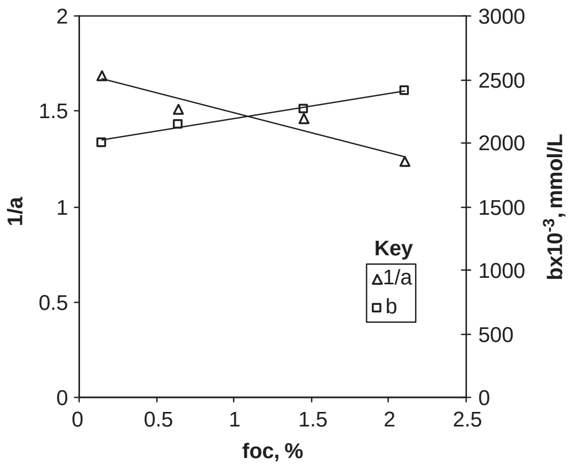

Fig. 8. A plot of coefficients *a* and *b* against levels of f_{oc}.

Mingelgrin, 1984; Karickhoff, 1981). The predictions of the model are successfully compared with the original data in Fig. 6. The results indicate that the two characteristic constants (*a* and *b*) are critical in describing the soil-washing process. The proposed model provides an easy and fast way of predicting the soil-washing process: by measuring the f_{oc} in soil, the initial unit extraction and the final extraction capacity can be calculated through the use of Eqs. (6) and (7). These parameters are useful in helping to predict the partitioning of organic pollutants and in determining the cost-effective concentrations of surfactants. By merging Eqs. (2), (6) and (7), a practical equation can result, where the soil-washing performance can be determined in terms of f_{oc} and the concentration of surfactant

$$[\mathrm{Mal}] = \frac{[\mathrm{Brij}]}{(1.70 - 0.21 f_{oc})^{-1} + (1.98 \times 10^5 f_{oc} + 1.99 \times 10^6)[\mathrm{Brij}]}. \tag{8}$$

4. Conclusion

The surfactant-aided soil-washing process has been used for the remediation of NAPL contaminated soil with success. In this study, the authors successfully use three distinctive phases (without NAPL, with NAPL, and the transitional zone of NAPL) to picture the process and reveal the washing mechanisms behind each phase. The washing process is less dependent on the surfactant dose if there is no NAPL in the system, while the washing performance is generally independent of the soil's f_{oc} in the presence of NAPL. If the existence of NAPL was marginal, a complicated transitional zone was observed and a mathematical model was derived based on the observations by using two newly defined characteristic parameters (initial unit extraction and final extraction capacity), which resulted in a useful equation for the purpose of practical design.

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