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Modelling the role of surfactant and biodegradation in the remediation of aquifers with non-aqueous phase contaminants

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Abstract

The strong sorption of hydrophobic contaminants poses a serious challenge to the development of remediation technologies. Their low solubilities in water limit the applicability of treatment technologies such as pump-and-treat. Their dissolution by surfactants is a promising approach for circumventing this difficulty. The solubilized contaminant is subsequently irrigated onto a vegetated zone and mineralized. A two-zone model is developed for a system in which the contaminant is flushed from the aquifer with an aqueous surfactant solution and applied to vegetated soil. The model takes into account dissolution, sorption and biodegradation of the contaminant in the aquifer zone under the assumption that local equilibria prevail. It also takes into account sorption, mineralization and plant uptake in the rhizosphere zone assuming that mineralization obeys Monod kinetics. Model simulation was performed to determine the effects of surfactant and oxygen concentrations in enhancing contaminant removal from the aquifer and to evaluate the number of flushings required to reduce the concentrations of contaminant to desired levels. The results indicate that surfactant appreciably reduces the number of flushings by increasing the solubilization of contaminant. Increasing oxygen concentration enhances contaminant degradation. The model predicts an optimistic outcome because of the assumptions imposed; it is expected that the actual number of flushings will be larger than predicted. © 1997 Elsevier Science B.V.

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1. Introduction

In bioremediating soil, a major limiting factor is the mass transfer of non-aqueous phase (NAP) contaminants from the organic phase to the aqueous phase [1–3]; consequently, increasing the solubility of such contaminants is of utmost concern. Present technologies, e.g. pump-and-treat systems, are often ineffective for aquifer restoration, especially for sparingly soluble contaminants [4]; this has led to an interest in developing new efficient technologies [5]. Considerable work has been reported [1–49], and treatment costs have been significantly reduced [5,25,33].

Surfactant addition has been investigated as an innovative technique for decreasing interfacial tension between the NAP and water, and for enhancing aqueous-phase solubility; the NAP contaminants can be solubilized through incorporation of contaminant molecules into micelles of surfactants [6,7]. Several researchers have assessed the potential for surfactants to enhance the bioremediation of contaminated soils [8–13]. Part of the EPAs superfund innovative technology evaluation (SITE) remediation research has been directed at in situ flushing of contaminated soil with aqueous surfactant solutions [14]. This method has been successfully demonstrated in pilotscale and field studies; the results of these studies indicate that the method is effective for removing NAP compounds.

Surfactants are amphipathic molecules consisting of a hydrophillic polar head group and a hydrophobic nonpolar tail group [15]. When a surfactant is added to the aqueous phase, its molecules tend to form clusters called micelles which are transient aggregates of 50–200 surfactant molecules in solution. Micelle formation occurs above a critical concentration of about 0.1–10 mM of surfactant monomers, referred to as the critical micelle concentration (CMC), which is different for every surfactant [16]. Usually, in soil-water systems, the surfactant dose required to achieve significantly enhanced PAH solubility is considerably more than the reported value of the surfactant-water CMC. In soil-water systems, the concentration of surfactant required to form micelles may be much higher than the CMC because of sorption of the surfactant to soil.

The organic interior of micelles acts as an organic pseudophase into which organic contaminants can be partitioned. This phenomenon can greatly enhance the total concentration of the contaminant in solution above its aqueous solubility limit and is referred to as solubilization [16–22]. The solubility of a hydrophobic solute in surfactant micelles has been found to be several orders of magnitude larger than its aqueous solubility in the absence of surfactants [22]. The extent to which a solute will concentrate in a micelle can be related to the octanol–water partition coefficient (K_{ow}) of the solute [17,19,20]. In general, the larger the K_{ow} of a solute, the greater its tendency to concentrate inside the micelle; due to their large K_{ow}, PAHs can be solubilized in the micelles to a great extent, and, therefore, washing of PAHs with surfactant solution is a suitable and promising technique.

There are two mechanisms by which surfactants can enhance the removal of organic compounds in soils [18,21]. The first and most important mechanism involves solubilization of contaminants in surfactant micelles. The second mechanism involves the mobilization of the contaminants from the soil; this depends on the tendency of

surfactants to reduce the interfacial tensions and capillary forces trapping the contaminant in the soil [16].

Tiehm [23] has demonstrated that the degradation of the compounds, pyrene and anthracene, can be enhanced by the presence of non-toxic surfactants. The solubilization of anthracene, phenanthrene and pyrene was evaluated in soil-water systems with several nonionic and anionic surfactants. The most effective surfactants were nonionic octyl- and nonyl-phenylethoxylates with 9–12 ethoxylate units [24].

Phytoremediation may be extended to deep-contaminated sites and sites with deep pools of non-aqueous phase (NAP) liquids; the groundwater contaminants in such sites or collected leachate pond effluent may be treated by pumping and drip irrigation on plantations of trees [25]. Degradation of toxic organic compounds in the root zone has the added advantage of avoiding the need for transferring contaminants from one place to another.

The objectives of this work are to develop a model for a remediation scheme involving both in situ (surfactant flushing and biodegradation) and on-site (phytoremediation) treatment and investigate the feasibility of removing NAP contaminants, such as PAHs, in an aquifer, and to evaluate the effects of surfactant and oxygen concentrations in the flushing solution through simulation based on the model developed and with realistic values of the parameters.

2. Model development

Fig. 1 sketches the remediation system consisting of the saturated aquifer and unsaturated rhizosphere zones. The former, contaminated with a NAP compound, comprises the aqueous phase, the NAP, and the soil solids. In conventional pump-and-treat systems, water is pumped through the aquifer to solubilize the contaminant. In the present work, a surfactant solution is flushed through the aquifer contaminated with a NAP compound. Microorganisms present in the aquifer degrade a portion of the solubilized contaminant and surfactant. After solubilization, the solution is irrigated onto a vegetated zone where the contaminant is allowed to mineralize. The mineralization activity is assumed to take place in the first 30 cm of the soil. The vegetated zone is unsaturated; therefore, it comprises air, the aqueous phase, roots and soil solids.

The following simplifying assumptions are imposed to derive the present mathematical model.

1. The soil in the aquifer is a homogeneous mixture of sand and silt with a sufficiently large permeability to allow surfactant solution to be flushed through the contaminated zone and be recovered.
2. All the NAP is in contact with the surfactant solution; however, no mobilization of the NAP occurs due to flushing in the aquifer; only the solubilized contaminant is flushed out. Ganeshalingam et al. [26] conducted experiments involving surfactant flushings through a soil column contaminated with PAHs and concluded that compared to the reduction in surface forces trapping the PAHs in the sand, micellar solubilization of the PAHs is the dominant mechanism in enhancing their removal.

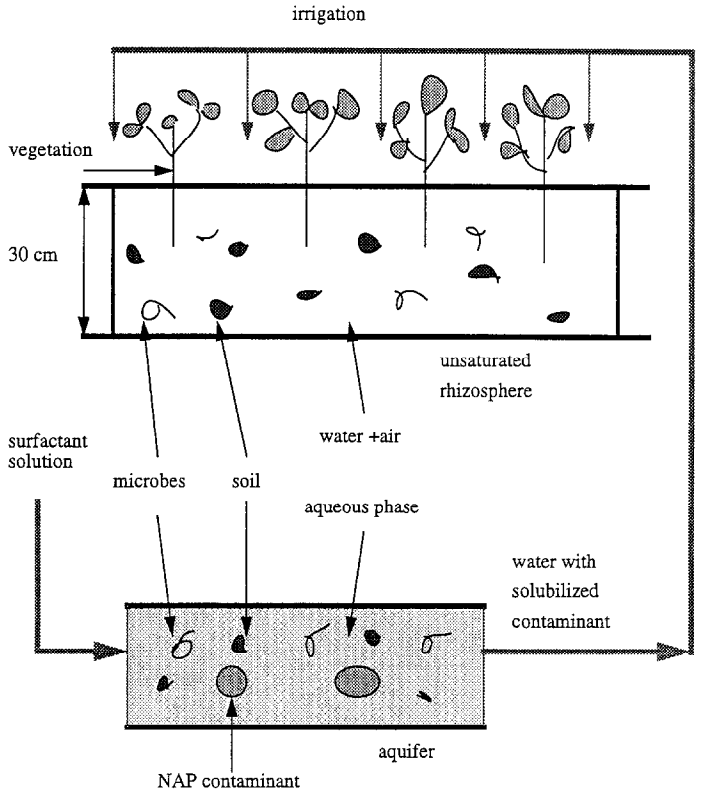

Fig. 1. Schematic representation of the remediation system (not to scale): volume of the aquifer = 10 m^3; volume of the rhizosphere = 1000 m^3.

3. Oxygen entering the aquifer is completely consumed for biodegradation of both the contaminant and surfactant. This assumption is based on a low flow rate of the flushing solution in the aquifer.
4. The contaminant incorporated into the surfactant micelles is accessible to the microorganisms. In micellar solubilization, the dominant factors governing the exit and re-entry rates of solubilizates are largely unknown; however, the reported exit rates for naphthalene, anthracene and pyrene are considerably higher than the microbial mineralization rates [27]. In a study by Tiehm [23], non-toxic surfactants enhanced the degradation of phenanthrene, anthracene and pyrene; the growth of mixed cultures was exponential. Liu et al. [28] have shown that naphthalene solubilized by micelles of Brij 30 or Trition X-100 in liquid media is bioavailable and degradable by the mixed culture of bacteria.
5. The amount of surfactant adsorbed or dissolved in the NAP contaminant is small and can be neglected.
6. Only one contaminant is present in the aquifer, i.e., the model derived is applicable only for single component systems.

7. The aqueous-phase concentrations of the material species are uniform in both the aquifer and rhizosphere.
8. Oxygen and other nutrients such as nitrogen, sulphur and phosphorus are sufficient for the microorganisms in the rhizosphere.
9. The rate of irrigation is equal to the evapotranspiration rate in the vegetated soil so that all of the water applied to the rhizosphere is lost, thus ensuring the constancy of the water phase volume fraction in the rhizosphere.
10. The surfactant is biodegradable and is not inhibitory to the microbial population.

The model consists of two parts: the flushing model for the aquifer and the rhizosphere-biodegradation model.

2.1. Flushing model for the aquifer

An equilibrium flushing model has been developed by Gandhi et al. [29]. The model assumes that the transport in the aquifer is such that phase and chemical equilibria prevail within the zone where flushing is applied. This includes sorption to solid surfaces, dissolution of the NAP and biochemical oxidation; biodegradation is limited by the amount of oxygen supplied with each flushing. The model has been extended here to include the effects of surfactant on the flushing process.

2.1.1. First flushing

Initially, the total concentration of the contaminant in the aquifer is the sum of the contaminant present in the aqueous phase, adsorbed to soil organic matter, and existing in the NAP; hence,

$$C_T = C_W \varepsilon_{W,1} + K_d C_W \rho_B + \rho_N \varepsilon_{N,1} \tag{1}$$

In this expression, C_T is an indicator of the average value that might be obtained when several core samples, saturated with the NAP–water mixture, are extracted and analyzed for the total contaminant concentration. The numeric subscript for the porosity, ε, denotes the number of flushing cycles. The number of flushings is an indicator of the amount of water pumped out of the aquifer calculated in multiples of the aqueous phase void volume in the saturated zone. The porosity values for the first flushing are the initial values. As long as the NAP is present, the concentration of the contaminant in the aqueous phase, C_W, equals its solubility in water, C_{sat}; when surfactant is also present, the solubility increases to C_W^*. In the first flushing, the aqueous phase saturated with the contaminant is flushed out through extraction wells. Thus, the mass fraction of the contaminant removed from the aquifer is given by

$$MF_{O,1} = \frac{C_W \varepsilon_{W,1}}{C_W \varepsilon_{W,1} + K_d C_W \rho_B + \rho_N \varepsilon_{N,1}} \tag{2}$$

The mass fraction remaining is

$$MF_{R,1} = 1 - MF_{O,1} \tag{3}$$

2.1.2. Second flushing

2.1.2.1. Contaminant. In the second flushing, the surfactant solution is pumped into the aquifer. Fig. 2 shows the incorporation of the contaminant into the surfactant micelles; this results in a high concentration of the contaminant in the micelles and a low concentration of the contaminant adsorbed to soil [24]. Kile and Chiou [30] have proposed a two-phase separation model for solute behaviour, expressing the enhanced solubility as C_W^*/C_W (the ratio of the apparent solubility to the true aqueous solubility) where C_W^* is the solubility of the contaminant in the aqueous phase in the presence of the surfactant. This is an adaptation of the pseudophase-micelle model of Shinoda and Hutchinson [31]. As a result of contaminant partitioning from the soil phase to the aqueous (micelle) phase, the equilibrium partition coefficient for adsorption of contaminant to soil, $K_{d,surf}$, decreases; $K_{d,surf}$ is defined as the contaminant adsorbed to a unit mass of soil in the presence of surfactant divided by the contaminant concentration in solution (C_W^*).

Oxygen is made available to the microbes for degrading the contaminant and surfactant. Adequate quantities of all other nutrients necessary for the growth of microbes are assumed to be present. Biodegradation decreases the aqueous concentration of contaminant and causes further dissolution of the NAP; as long as NAP is present, this process continues until oxygen is completely consumed. The saturated aqueous phase is transported out of the aquifer through extraction wells. The decrease in the contaminant concentration attributable to biodegradation is calculated from the stoichiometry of mineralization. The NAP entities shrink due to the transfer of contaminant to the aqueous phase. Thus, the mass balance for the contaminant after the second flushing is as follows:

$$K_d C_W \rho_B + \rho_N \varepsilon_{N,1} = K_{d,surf} C_W^* \rho_B + \rho_N \varepsilon_{N,2} + C_W^* \varepsilon_{W,2} + (S_O f/Y)\varepsilon_{W,1} \qquad (4)$$

The left-hand side of this equation represents the total amount of contaminant present after the first flushing, and the right-hand side, the distribution of the contaminant after

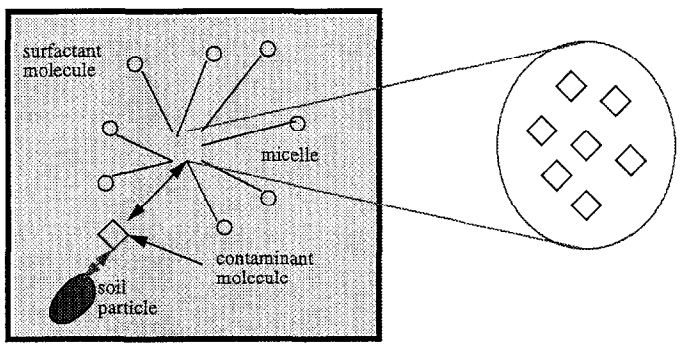

Fig. 2. Mechanism of the increase in the contaminant concentration in the aqueous phase due to the incorporation of the molecules of contaminant within the interior of the hydrophobic micelle.

the second flushing. Moreover, the volume fraction changes due to the dissolution of a portion of the contaminant from the NAP, i.e., $\varepsilon_{N,2} < \varepsilon_{N,1}$ and $\varepsilon_{W,2} > \varepsilon_{W,1}$.

Air, pure oxygen or hydrogen peroxide can be supplied to the aqueous surfactant solution pumped into the aquifer; in the numerical simulation, the concentration of oxygen is assumed to be 8 $mg\,l^{-1}$, 40 $mg\,l^{-1}$ or 100 $mg\,l^{-1}$. At a concentration of 100 $mg\,l^{-1}$, some authors have suggested that H_2O_2 may not be fully utilized [32,33] while others have reported microbial toxicity [34].

Since both the contaminant and surfactant are assumed to be simultaneously biodegraded, the fraction, f, is defined to indicate the proportion of oxygen utilized for the oxidation of contaminant. Knaebel et al. [35] showed that linear alcohol ethoxylate and linear alkyl benzene sulphonate surfactants were degraded by natural soil microorganisms. Brij 30, an alkyl ethoxylate nonionic surfactant, was found to be biodegraded along with naphthalene [28].

The stoichiometric coefficient, Y, is the mass of oxygen required for mineralizing a unit mass of contaminant. For example, complete mineralization of pyrene can be considered to proceed as follows:

$$C_{16}H_{10} + 18.5O_2 \rightarrow 16CO_2 + 5H_2O$$

which yields the stoichiometric coefficient, $Y = 592/202 = 2.93$ (g oxygen)(g pyrene)$^{-1}$. This procedure for calculating the amount of biodegradation implies that the substrate is freely available whereas oxygen transport is the limiting process in bioremediation.

For the i-th flushing, the total porosity is the sum of volume fractions of the NAP and the water phase, i.e.,

$$\varepsilon_T = \varepsilon_{N,i} + \varepsilon_{W,i} \tag{5}$$

By substituting $i = 1$ and 2 into this equation and combining the resultant expressions with Eq. (4), the new volume fraction of the aqueous phase is obtained as

$$\varepsilon_{W,2} = \varepsilon_{W,1} \frac{[1 + (S_O f/Y\rho_N)]}{[1 - (C_W^*/\rho_N)]} + \frac{[K_{d,surf} C_W^* - K_d C_W]\,\rho_B}{[1 - (C_W^*/\rho_N)]\,\rho_N} \tag{6}$$

The amount of contaminant adsorbed to soil in the presence of surfactant ($K_{d,surf} C_W^* \rho_B$) is different to that in the absence of surfactant ($K_d C_W \rho_B$). This causes the water-phase porosity to vary as indicated by the second term in the right-hand side of Eq. (6). Since the surfactant continues to enter, this term vanishes with the third flushing and for $i \geq 3$.

The fraction of the contaminant removed in the second flushing equals the sum of the amount of contaminant present in the surfactant solution and the amount biodegraded divided by the total amount present after the first flushing, i.e.,

$$MF_{O,2} = \frac{C_W^* \varepsilon_{W,2} + (S_O f/Y)\,\varepsilon_{W,1}}{K_d C_W \rho_B + \rho_N \varepsilon_{N,1}} \tag{7}$$

Thus, the mass fraction of the contaminant remaining in the aquifer after the second flushing is

$$MF_{R,2} = (1 - MF_{O,2})\,MF_{R,1} \tag{8}$$

2.1.2.2. Surfactant. As mentioned earlier, the surfactant is present in the aquifer from the second flushing onwards. A portion of the total surfactant entering is adsorbed to soil, another portion is biodegraded, and the remainder leaves the aquifer. The mass balance for the surfactant is

$$\varepsilon_{W,1}C_{u,a} = K_u C_{u,2}\,\rho_B + \left[S_O(1-f)/Y'\right]\varepsilon_{W,1} + \varepsilon_{W,2}C_{u,2} \tag{9}$$

The concentration of the surfactant in the solution exiting the aquifer is obtained from the above equation as

$$C_{u,2} = \frac{\varepsilon_{W,1}C_{u,a} - \left[S_O(1-f)/Y'\right]\varepsilon_{W,1}}{\varepsilon_{W,2} + K_u\,\rho_B} \tag{10}$$

2.1.3. Third flushing

2.1.3.1. Contaminant. The amount of contaminant adsorbed to soil after the third flushing remains the same as that of the second flushing. Therefore, the second term of Eq. (6) vanishes and the resulting aqueous phase volume fraction is

$$\varepsilon_{W,3} = \varepsilon_{W,2}\frac{\left[1 + (S_O\,f/Y\rho_N)\right]}{\left[1 - (C_W^*/\rho_N)\right]} \tag{11}$$

The mass fraction of the contaminant removed in the third flushing is

$$MF_{O,3} = \frac{C_W^*\varepsilon_{W,3} + (S_O\,f/Y)\,\varepsilon_{W,2}}{K_{d,surf}C_W^*\rho_B + \rho_N\varepsilon_{N,2}} \tag{12}$$

The mass fraction of the contaminant remaining in the aquifer after the third flushing is

$$MF_{R,3} = (1 - MF_{O,3})\,MF_{R,2} \tag{13}$$

2.1.3.2. Surfactant. According to the assumption of sorption equilibrium, the amount of surfactant adsorbed to soil depends on the aqueous-phase concentration of the surfactant in the aquifer. The mass balance for the surfactant after the third flushing is as follows:

$$\varepsilon_{W,2}C_{u,a} + K_u C_{u,2}\,\rho_B = \varepsilon_{W,3}C_{u,3} + \left[S_O(1-f)/Y'\right]\varepsilon_{W,2} + K_u C_{u,3}\,\rho_B \tag{14}$$

The exit concentration can be obtained from the above equation as

$$C_{u,3} = \frac{\varepsilon_{W,2}C_{u,a} + K_u C_{u,2}\,\rho_B - \left[S_O(1-f)/Y'\right]\varepsilon_{W,2}}{\varepsilon_{W,3} + K_u\,\rho_B} \tag{15}$$

2.1.4. Flushings when NAP is present (3 < Q)

2.1.4.1. Contaminant. The above treatment for the third flushing is easily extended to subsequent flushings until the NAP disappears at the Q-th flushing. The NAP volume

fraction, therefore, becomes zero, and the aqueous-phase volume fraction equals the total porosity in the Q-th flushing, i.e.,

$$\varepsilon_{N,Q} = 0 \text{ and } \varepsilon_{W,Q} = \varepsilon_T \tag{16}$$

The general equations for the P-th flushing between the third and Q-th are: for the aqueous-phase volume fraction,

$$\varepsilon_{W,P} = \varepsilon_{W,P-1} \frac{[1 + (S_O f/Y\rho_N)]}{[1 - (C^*_W/\rho_N)]} \tag{17}$$

for the NAP volume fraction,

$$\varepsilon_{N,P} = \varepsilon_T - \varepsilon_{W,P} \tag{18}$$

for the fraction of the contaminant removed,

$$MF_{O,P} = \frac{C^*_W \varepsilon_{W,P} + (S_O f/Y)\varepsilon_{W,P-1}}{K_{d,surf} C^*_W \rho_B + \rho_N \varepsilon_{N,P-1}} \tag{19}$$

and for the mass fraction of the contaminant remaining in the aquifer,

$$MF_{R,P} = (1 - MF_{O,P}) MF_{R,P-1} \tag{20}$$

2.1.4.2. Surfactant. The general equation for the exit concentration of the surfactant is

$$C_{u,P} = \frac{\varepsilon_{W,P-1} C_{u,a} + K_u C_{u,P-1} \rho_B - [S_O(1-f)/Y']\varepsilon_{W,P-1}}{\varepsilon_{W,P} + K_u \rho_B} \tag{21}$$

2.1.5. Q-th flushing

Biodegradation and flushing reduce the volume of the NAP continuously until it disappears in the Q-th flushing. After the disappearance of the NAP, the concentration of the contaminant in the aqueous solution decreases; this is governed by the mass balance for the Q-th flushing.

(Mass present at the beginning of flushing) = (Mass remaining at the end of flushing) + (Mass flushed out) + (Mass biodegraded),

$$K_{d,surf} C^*_{W,Q-1} \rho_B + \rho_N \varepsilon_{N,Q-1} = K_{d,surf} C^*_{W,Q} \rho_B + C^*_{W,Q} \varepsilon_T + (S_O f/Y)\varepsilon_{W,Q-1} \tag{22}$$

The subscript, Q, is appended to the aqueous-phase concentration of the contaminant to denote that the value varies from flushing to flushing. Solving Eq. (22) for $C^*_{W,Q}$ yields

$$C^*_{W,Q} = \frac{K_{d,surf} C^*_{W,Q-1} \rho_B + \rho_N \varepsilon_{N,Q-1} - (S_O f/Y)\varepsilon_{W,Q-1}}{K_{d,surf} \rho_B + \varepsilon_T} \tag{23}$$

Hence,

$$MF_{O,Q} = \frac{C^*_{W,Q}\varepsilon_T + (S_O f/Y)\varepsilon_{W,Q-1}}{K_{d,surf}C^*_{W,Q-1}\rho_B + \rho_N\varepsilon_{N,Q-1}} \tag{24}$$

and

$$MF_{R,Q} = (1 - MF_{O,Q})MF_{R,Q-1} \tag{25}$$

2.1.6. Flushings after disappearance of NAP (Z > Q)

2.1.6.1. Contaminant. The equations for this case are similar to those presented above; however, the NAP term, ε_N, is absent. Thus, the aqueous-phase concentration is

$$C^*_{W,Z} = \frac{K_{d,surf}C^*_{W,Z-1}\rho_B - (S_O f/Y)\varepsilon_T}{K_{d,surf}\rho_B + \varepsilon_T} \tag{26}$$

the mass fraction removed is

$$MF_{O,Z} = \frac{C^*_{W,Z}\varepsilon_T + (S_O f/Y)\varepsilon_T}{K_{d,surf}C^*_{W,Z-1}\rho_B} \tag{27}$$

and the mass fraction remaining is

$$MF_{R,Z} = (1 - MF_{O,Z})MF_{R,Z-1} \tag{28}$$

When the contaminant concentration, $C^*_{W,Z}$, reaches the desired value in the aquifer, the flushings are stopped.

2.1.6.2. Surfactant. Potential difficulties in the development of surfactants for soil clean-up include soil clogging for in situ use, separation and treatment of surfactant solutions, and recovery of surfactants for reuse [36]. When it is undesirable for the surfactant to be present in ground-water, its concentration should be reduced. Thus, once the NAP disappears, no surfactant is added to the flushing solution. For the Z-th flushing, the mass balance equation becomes

$$K_u C_{u,Z-1}\rho_B = \varepsilon_T C_{u,Z} + [S_O(1-f)/Y']\varepsilon_T + K_u C_{u,Z}\rho_B \tag{29}$$

and the concentration in the exit stream is

$$C_{u,Z} = \frac{K_u C_{u,Z-1}\rho_B - [S_O(1-f)/Y']\varepsilon_T}{\varepsilon_T + K_u\rho_B} \tag{30}$$

2.2. Rhizosphere-biodegradation model

The solution from the aquifer containing the solubilized contaminant and the surfactant is irrigated onto the vegetated zone (see Fig. 1). The contaminant and surfactant are mineralized in the root zone of the surface soil. The details of the model development are given elsewhere [37]. The resultant mass balances are presented below.

2.2.1.1. Contaminant. The mass balance for the contaminant in the rhizosphere is

$$\frac{d}{dt}\{C(\theta + R_d R_{cf} + \rho K_d)\} = F_R C_{in} - qT_{SCF} C - \frac{\mu_m}{Y_S}(\theta + R_d R_b + \rho K_b) C_b \frac{C}{K_{rsu} + C + C_u + C_r} \quad (31)$$

The first term on the right-hand side of this equation is the mass flow rate of the contaminant entering the rhizosphere, the second term, the rate of contaminant uptake by plants, and the third term, the rate of contaminant biodegradation by the microorganisms.

2.2.1.2. Microbial biomass. The balance for the microbial biomass is

$$\frac{d}{dt}\{C_b(\theta + R_d R_b + \rho K_b)\} = F_R C_{b,in} + \frac{\mu_m (C + C_u + C_r) C_b (\theta + R_d R_b + \rho K_b)}{K_{rsu} + C + C_u + C_r} - k_{ed} C_b (\theta + R_d R_b + \rho K_b) \quad (32)$$

The first term on the right-hand side of this equation is the mass flow rate of biomass entering the rhizosphere from the aquifer, the second term, the microbial growth rate, and the third term, the endogenous decay rate. The microbial growth term reflects the fact that the contaminant, surfactant and root exudates all provide carbon for the degrading microorganisms.

2.2.1.3. Root Exudates. The mass balance for root exudates is

$$\frac{d}{dt}\{C_r(\theta + R_d R_r + \rho K_r)\} = q_r C_{rr} - qT_{SCFr} C_r - \frac{\mu_m}{Y_R}(\theta + R_d R_b + \rho K_b) C_b \frac{C_r}{K_{rsu} + C + C_u + C_r} \quad (33)$$

The first term on the right-hand side of this equation is the rate of secretion from the roots, the second term, the rate of root exudate uptake by plants, and the third term, the rate of biodegradation of root exudates by the microorganisms.

2.2.1.4. Surfactant. The mass balance for surfactant in the rhizosphere is

$$\frac{d}{dt}\{C_u(\theta + R_d R_u + \rho K_u)\} = F_R C_{u,in} - qT_{SCFu} C_u - \frac{\mu_m}{Y_U}(\theta + R_d R_b + \rho K_b) C_b \frac{C_u}{K_{rsu} + C + C_u + C_r} \quad (34)$$

The first term on the right-hand side of this equation is the mass flow rate of surfactant entering the rhizosphere, the second term, the rate of surfactant uptake by plants, and the third term, the rate of biodegradation of surfactant by the microorganisms.

3. Numerical Simulation

For simulation, Eqs. (31)–(34) are solvable numerically by the fourth-order Runge-Kutta method [38]. For demonstration, the volumes of the aquifer and rhizosphere are taken to be 10 m^3 and 1000 m^3, respectively. This ratio depends on the flushing rate for the aquifer. In typical field situations two pore volumes of the solution from the aquifer are flushed each day to the rhizosphere [39].

Pyrene is chosen as the model compound. Simulation is stopped when the aqueous-phase concentration of the contaminant in the aquifer is reduced to 0.1 ppm. This concentration is appropriate because in the presence of surfactant, the contaminant is almost completely removed from the aquifer. However, without surfactant, more than 1% of the initial mass of the contaminant may remain in the aquifer adsorbed to solids.

Tables 1–3 list the values of the constants and initial conditions for the simulation. The concentrations of the material species in the inlet stream to the rhizosphere are presented in Table 4; the values of the parameters for four PAHs, viz., naphthalene, phenanthrene, pyrene and anthracene, are shown in Table 5. The values of sorption coefficients and solubilities are taken from Knox et al. [46].

The initial NAP fraction is considered to be 0.5%, which corresponds to 1% saturation of the void volume since the total porosity of the aquifer is assumed to be 0.5. The aqueous phase is assumed to be saturated with contaminant and in equilibrium with contaminant adsorbed to the soil. Typically, a surfactant concentration between 1 and 10 $g\,l^{-1}$ is necessary to achieve significant solubilization of PAH compounds [23,24,26]. In

Table 1
Values of the parameters for pyrene [a]

Parameter	Value
C_{sat}	$0.135\ mg\,l^{-1}$
μ_m	$5.0\ day^{-1}$
K_{rsu}	$10\ mg\,l^{-1}$
R_{cf}	251.6
K_d	$1.937\times10^{-3}\ l\,mg^{-1}$
$\log K_{oc}$	4.81
ρ_N	$1.271\times10^{6}\ mg\,l^{-1}$
T_{SCF}	8.795×10^{-3}
$\log K_{ow}$	5.09
k_{cd}	$0.05\ day^{-1}$
Y	2.93
Y_S	0.5

[a] Values taken from Briggs et al. [45], Knox et al. [46], Santharam [48] and Santharam et al. [37].

Table 2
Values of the parameters for surfactant and aquifer [a,b]

Parameter	Value
$C_{u,a}$	$10\ g\,l^{-1}$
Y'	1.0
K_u	$1.0\times10^{-6}\ l\,mg^{-1}$
ε_T	0.5
ρ_B	$1.4\times10^{6}\ mg\,l^{-1}$
f_{oc}	0.03

[a] The initial conditions: $\varepsilon_w = 0.495$, $\varepsilon_N = 0.005$ and $C_u = 0$.
[b] Values taken from Knox et al. [46] and Santharam [48].

Table 3
Values of the constants used in the rhizosphere [a,b]

Parameter	Value	Parameter	Value
R_d	0.01	θ	0.25
R_b	100	q	$0.01\ day^{-1}$
R_r	100	$q_r C_{rr}$	2.4 mg/L day
R_u	100	T_{SCFr}	0.75
ρ	$1.4\times10^{6}\ mg\,l^{-1}$	T_{SCFu}	0.75
K_b	$1.0\times10^{-5}\ l\,mg^{-1}$	Y_S	0.5
K_r	$1.0\times10^{-5}\ l\,mg^{-1}$	Y_R	0.5
F_R	$0.01\ day^{-1}$	Y_U	0.5

[a] The initial conditions: $C = 0$, $C_b = 10\ mg\,l^{-1}$, $C_r = 10\ mg\,l^{-1}$ and $C_u = 0$.
[b] Values taken from Tracy et al. [47] and Santharam et al. [37].

Table 4
Inlet flow conditions for the rhizosphere

C_{in}	$C_w\ i = 1$ $C_w^*\ 1 < i < Q$ $C_{w,Z}^*\ i \geq Q$
$C_{b,in}$	$0.1\ mg\,l^{-1}$
$C_{r,in}$	$10.0\ mg\,l^{-1}$
$C_{u,in}$	$C_{u,i}$

Table 5
Values of the parameters for the four PAHs [a]

Contaminant	ρ_N ($\times10^{6}\ mg\,l^{-1}$)	K_{oc} ($\times10^{-3}\ l\,mg^{-1}$)	C_{sat} ($mg\,l^{-1}$)	Y
Naphthalene	1.145	1.288	30	1.75
Phenanthrene	1.179	23	1	2.96
Pyrene	1.271	64.57	0.135	2.93
Anthracene	1.26	18.62	0.075	2.97

[a] Values taken from Knox et al. [46].

Table 5, the flow rate from the aquifer, F_R, equals the evapotranspiration rate, q. The soil-water content in the rhizosphere is assumed to be 0.25 because it is unsaturated.

The results of several studies [23,40–42] indicate that the presence of nonionic surfactant micelles in aqueous solution leads to effective removal of sorbed PAHs from soil through solubilization. With a surfactant dose of 1% by volume, corresponding to a concentration of approximately 10 $g l^{-1}$ for three surfactants, Igepal CA-720, Trition X-100 and Hyonic NP-90, 70–90% solubilization of the PAHs, phenanthrene, anthracene and pyrene, was achieved [23]. The solubility of the total pyrene was increased from 0.6% to 80% (about 130 times) by the surfactant Trition X-100 at a concentration of 10.8 $g l^{-1}$. The value of $K_{d,surf}$, the partition coefficient for pyrene in the presence of surfactant, was determined experimentally [23] for a range of surfactant concentrations. A model developed by Edwards et al. [43] to calculate $K_{d,surf}$ fits the experimental data well. The above studies indicate that the value of $K_{d,surf}$ for pyrene can be 0.015–15.5 times K_d, the partition coefficient in the absence of the surfactant depending on the surfactant concentration.

The increase in the partition coefficient has been encountered in certain circumstances and is attributed to the contribution of the adsorbed surfactant on soil to the organic carbon. This aspect has been neglected in our model since it is assumed that a surfactant concentration of 10 $g l^{-1}$ enhances the solubility of pyrene 100 times. Above CMC, the solubilization effect usually increases linearly with the surfactant concentration [17,30]. For example, the surfactant employed in the simulation can increase the solubilization 10 times at a concentration of 1 $g l^{-1}$. For the numerical simulation, the values of $K_{d,surf}/K_d$ corresponding to $C_W^*/C_W = 1$, 10, 50 and 100 are assumed to be 1, 0.01, 0.005 and 0.001, respectively.

4. Results and discussion

Table 6 gives the number of flushings required for remediating the sites contaminated by selected PAHs for four values of surfactant concentration and three values of inlet oxygen concentration; the final concentration of contaminant in the aquifer is 100 ppb. Note that for each contaminant the effect of oxygen concentration is revealed through comparison of the data in a row, and the effect of surfactant concentration, in a column. Since the solubility of naphthalene is relatively high compared to other PAHs, the oxygen concentration does not have as significant an effect as the surfactant concentration. The number of flushings are drastically reduced for naphthalene when solubilization is enhanced 100 fold by surfactant. When both oxygen and surfactant are absent, the number of flushings is 1005. This is reduced to 11 without oxygen at a surfactant concentration of 10 $g l^{-1}$, and to 309 at an oxygen concentration of 40 $mg l^{-1}$ without surfactant. For anthracene, the number of flushings exceeds 15 000 when both oxygen and surfactant are absent. This number is reduced to 1713 without oxygen at a surfactant concentration of 10 $g l^{-1}$, and to 937 at an oxygen concentration of 40 $mg l^{-1}$ without surfactant. The specifications of oxygen and surfactant concentrations for optimal operating conditions are dictated by economy.

Table 6
Number of flushings required for remediating sites contaminated by selected PAHs for four values of the surfactant concentration, and three values of the inlet oxygen concentration

Inlet oxygen level ($mg\,l^{-1}$)		0 [a]	8	40
Contaminant	C_W^*/C_W	Number of flushings		
Naphthalene	1 [b]	1005	552	309
	10	62	56	52
	50	20	16	15
	100	11	9	8
Phenanthrene	1	d	3740	942
	10	1453	1241	831
	50	331	297	257
	100	154	145	135
Pyrene	1	d	4526	942
	10	10100	4985	1654
	50	2092	1691	1001
	100	1026	919	668
Anthracene	1	d	4575 [c]	937 [c]
	10	d	6098	1709
	50	3432	2514	1221
	100	1713	1448	899

[a] An inlet oxygen concentration of zero corresponding to the case without biodegradation.
[b] $C_W^*/C_W = 1$ corresponding to the case of no surfactant.
[c] Number of flushings required for the disappearance of the NAP.
[d] More than 15000 flushings required.
Note: The initial NAP saturation is 1%; the volumes of the aquifer and the rhizosphere are 10 m^3 and 1000 m^3, respectively, and the final concentration of the contaminant in the aquifer is 100 ppb.

Under four sets of conditions in Table 6, the contaminant is not completely removed, even after 15000 flushings. Without surfactant or oxygen, 2.7% of the mass of phenanthrene remains after 15000 flushings. The surfactant reduces the number of flushings drastically; a surfactant concentration of $C_{u,a} = 10\ g\,l^{-1}$ ($C_W^*/C_W = 100$) reduces the number of flushings to 154. Moreover, biodegradation plays an important role when surfactant is absent. Increasing the oxygen concentration reduces the number of flushings, but not significantly at high surfactant concentrations.

With pyrene as the contaminant, and without biodegradation and surfactant, 85% of the mass remains after 15000 flushings. Without biodegradation, for the cases of no surfactant and $C_{u,a} = 1\ g\,l^{-1}$, 91% and 12% of anthracene remain, respectively, in the aquifer after 15000 flushings. The number of flushings without surfactant in Table 6 also indicates the point at which NAP disappears because of the low solubility of anthracene; for the oxygen concentration of 8 and 40 $mg\,l^{-1}$, the mass fractions of anthracene remaining are 0.94% and 0.82%, respectively. With pyrene or anthracene as contaminant, the number of flushings increases when the surfactant concentration is increased from 0 to 1 $g\,l^{-1}$. This is due to competition: half of the inlet oxygen is

consumed for surfactant degradation whereas all of the inlet oxygen is consumed for the mineralization of the contaminant when no surfactant exists. This inefficiency is overcome if $C_W^*/C_W = 100$ ($C_{u,a} = 10\ g\,l^{-1}$) and the increased solubilization dominates over the effect of oxygen concentration. For pyrene, when the surfactant concentration is increased to 1 $g\,l^{-1}$ at an oxygen concentration of 8 $mg\,l^{-1}$, the number of flushings increases due to competition of the surfactant for oxygen. However, at the stopping point of 0.1 ppm in the aqueous phase, 0.036% of the mass remains whereas 3.97% remains in the case of no surfactant.

Fig. 3 is a plot of the simulated values of the mass fraction of pyrene remaining in the aquifer versus the number of flushings for three different initial NAP saturations, viz., 0.5%, 1% and 2%. The inlet oxygen concentration is 40 $mg\,l^{-1}$, half of which is consumed for the mineralization of pyrene ($f = 0.5$). The ratio of the aqueous-phase concentration of pyrene in the presence of surfactant to that in its absence is 100. Since local equilibrium is assumed, the amount of contaminant flushed out of the aquifer and biodegraded in the aquifer is constant in each flushing until the NAP disappears, and thus the plots are linear. Only a few more flushings were required after the disappearance of the NAP, and, therefore, the tailing is not manifested in these curves. Note that 353 flushings are required to remove all pyrene from the aquifer for 0.5% saturation, 668 flushings for 1% saturation, and 1303 flushings for 2% saturation, implying a linear dependence on the initial NAP saturation.

The results shown in Figs. 4–8 correspond to 1% initial NAP saturation for pyrene, which is equivalent to 63.55 kg in the aquifer volume considered. In Fig. 4, the mass fraction of pyrene remaining, the fraction biodegraded in the aquifer, and the fraction flushed from the aquifer are plotted against the number of flushings. The oxygen

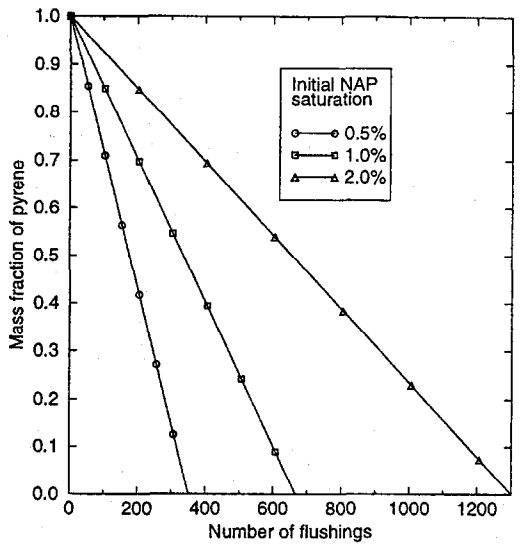

Fig. 3. Effect of the initial NAP saturation in the aquifer on the number of flushings to remove pyrene: $S_o = 40\ mg\,l^{-1}$, $f = 0.5$ and $C_W^*/C_W = 100$.

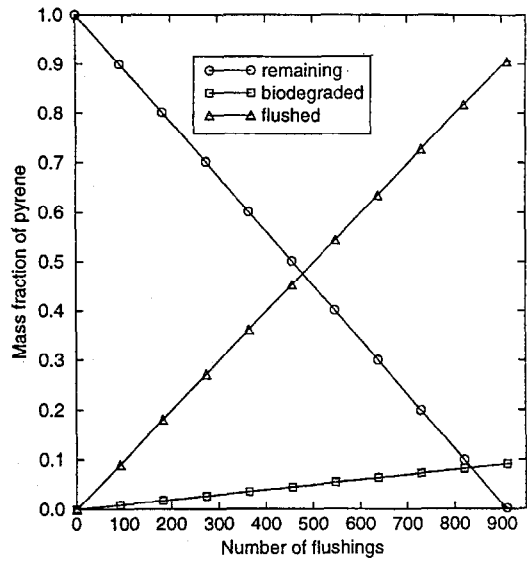

Fig. 4. Mass fractions of pyrene remaining in the aquifer, biodegraded in the aquifer, and flushed from the aquifer: $S_o = 8\ \mathrm{mg\,l^{-1}}$, $f = 0.5$ and $C_W^*/C_W = 100$.

concentration of 8 $\mathrm{mg\,l^{-1}}$ corresponds to the aqueous solubility of oxygen in air. Note that only 12% of the pyrene is biodegraded and the remaining 88% is flushed out. To remove all pyrene from the aquifer, 919 flushings are required. In this case, the number

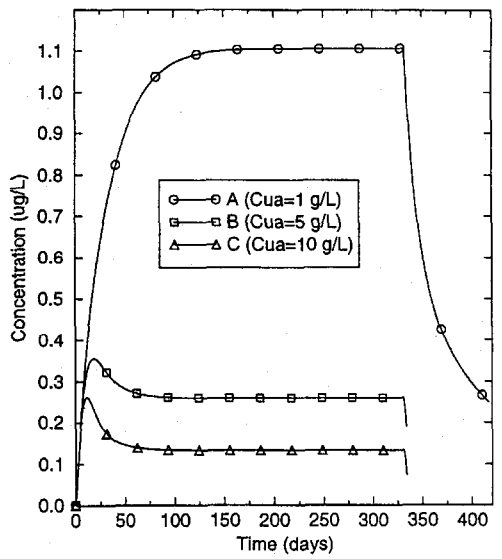

Fig. 5. Variation of the aqueous-phase concentration of pyrene in the rhizosphere for three different surfactants entering the aquifer: $S_o = 40\ \mathrm{mg\,l^{-1}}$, $f = 0.5$ and $C_W^*/C_W = 100$.

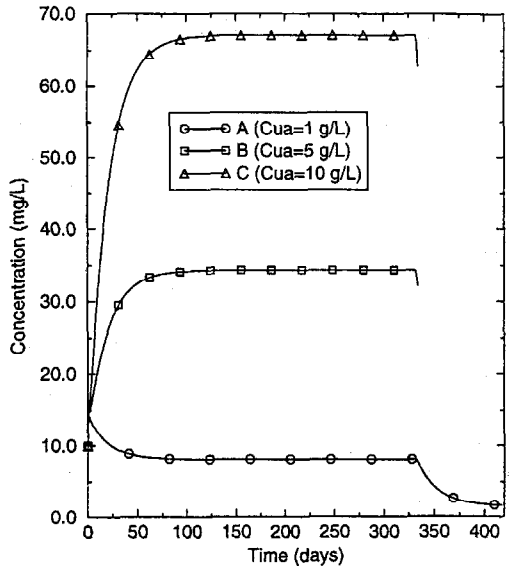

Fig. 6. Variation of the aqueous-phase concentration of microbial biomass during pyrene degradation in the rhizosphere for three different surfactants entering the aquifer: $S_0 = 40\ \mathrm{mg\,l^{-1}}$, $f = 0.5$ and $C_W^* / C_W = 100$.

of flushings, Q, required for the disappearance of the NAP pyrene, is 905, and it takes only 14 additional flushings to attain the contaminant concentration of 0.1 ppm in the aqueous phase; also, the mass remaining at this stage is only 0.002% of the initial

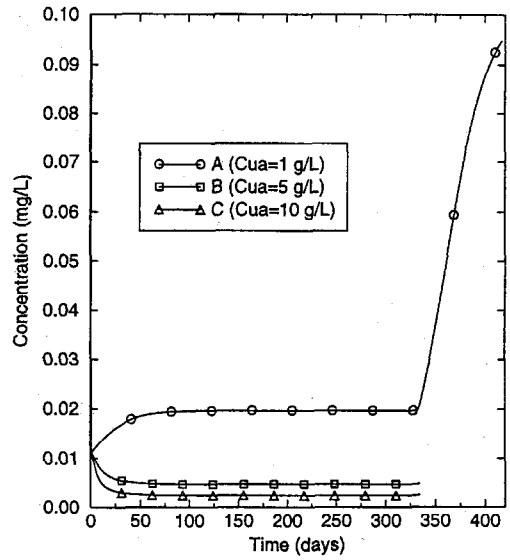

Fig. 7. Variation of the aqueous-phase concentration of root exudates during pyrene degradation in the rhizosphere for three different surfactants entering the aquifer: $S_0 = 40\ \mathrm{mg\,l^{-1}}$, $f = 0.5$ and $C_W^* / C_W = 100$. The initial root exudates concentration is $10\ \mathrm{mg\,l^{-1}}$.

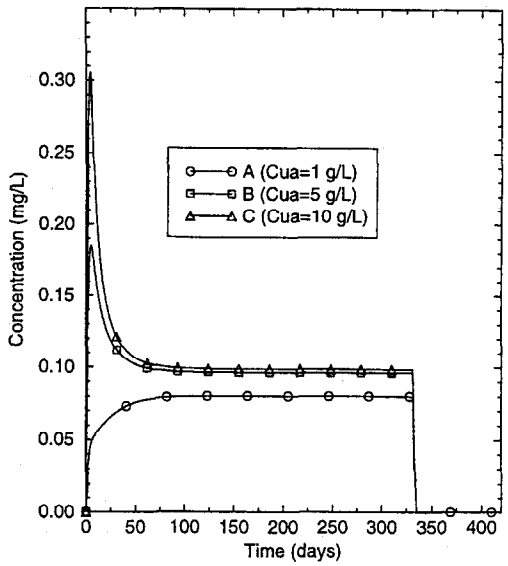

Fig. 8. Variation of the aqueous-phase concentration of surfactant during pyrene degradation in the rhizosphere for three different surfactants entering the aquifer: $S_0 = 40\ \mathrm{mg\,l^{-1}}$, $f = 0.5$ and $C_W^*/C_W = 100$.

amount of pyrene. Thus, when surfactant is present, it is quite reasonable to have a stopping point of 0.1 ppm.

By replacing air with pure oxygen, an increase in the oxygen concentration from 8 to 40 $\mathrm{mg\,l^{-1}}$ reduces the number of flushings from 919 to 668 [48]; the amount of pyrene biodegraded increases three-fold. In this case, the number of flushings, Q, required for the disappearance of the NAP, is 662, and only 6 additional flushings are required to reduce the contaminant concentration from 13.5 ppm to 0.1 ppm.

When surfactant is absent ($C_W^*/C_W = 1$), only a small quantity ($\sim 1\%$) of pyrene is flushed out of the aquifer owing to its low solubility [48]. Without surfactant, the number of flushings is primarily dependent upon the concentration of oxygen. For 40 $\mathrm{mg\,l^{-1}}$ of oxygen, the number of flushings, Q, required for the disappearance of the NAP, is 927, and 15 additional flushings are needed to attain an aqueous-phase pyrene concentration of 0.1 ppm; the mass fraction of pyrene remaining at this stage is 3.97%, which is attributable to adsorption to solid surfaces.

Three cases are compared in Figs. 5–8 for the rhizosphere. It is assumed that three different surfactants, A, B and C, enter at concentrations of 1, 5 and 10 $\mathrm{g\,l^{-1}}$, respectively, each of which has the same effect on the solubilization of pyrene ($C_W^*/C_W = 100$). Studies by Liu et al. [24] have shown that various surfactants solubilize pyrene differently.

Fig. 5 illustrates the variation of aqueous-phase pyrene concentration with time in the rhizosphere. In the case of surfactant A, the concentration of pyrene is larger because the population of microorganisms is lower (see Fig. 6). The concentration of pyrene increases initially and then remains constant at 1.1 ppb; after 334 days, the concentration falls rapidly when the influx of the contaminant and surfactant stops. For cases B and C,

the concentration of the surfactant entering the rhizosphere is higher and therefore the microbial population is larger. The concentrations of the surfactant entering the rhizosphere in cases A, B and C are 0.98 gl^{-1}, 4.98 gl^{-1} and 9.98 gl^{-1}, respectively, and this accounts for the differences in the microbial growth. After about 50 days, however, the concentrations of contaminant (Fig. 5), root exudates (Fig. 7) and surfactant (Fig. 8), approach steady state levels. Consequently, the microbial growth and endogenous decay become equal and the population of microorganisms levels off, also.

Fig. 6 shows the variation of the aqueous-phase microbial concentration with time in the rhizosphere. The concentration, in the range of 1–70 mgl^{-1}, corresponds to bacterial numbers of about 10^7–10^8 g of dry soil. This is of the order found experimentally in PAH contaminated soil [44]. It is interesting that the microbial concentration increases and remains constant at a higher value for cases B and C than for case A, which immediately increases to about 15 mgl^{-1} because of the initial concentration of root exudates and then drops and remains constant (until 334 days) at about 9 mgl^{-1}. Examination of Figs. 5–8 in conjunction with Eq. (32) indicates that when the term, $C + C_u + C_r$, reaches a steady-state value of approximately 0.1 mgl^{-1}, growth and endogenous metabolism are balanced, and nearly constant concentrations are found for a significant period of time. The higher populations of microorganisms for cases B and C result in lower contaminant concentrations. For case A, which has a smaller number of microorganisms, the microbes continue to degrade the contaminant to the desired final concentration even after the flushings are stopped at 334 days. Since there is no inflow of carbon after 334 days, the population decreases and a tailing effect is evident (see Fig. 6). It takes 6 additional flushings (3 days) after the complete solubilization (at $Q = 662$nd flushing) to attain an aqueous phase concentration of 0.1 ppm. Since the surfactant concentration entering the aquifer is zero after the Q-th flushing, its concentration decreases in the inflow to the rhizosphere. For surfactant A, the concentration in the solution entering the rhizosphere decreases from 0.98 mgl^{-1} at the 662nd flushing to 0.197 mgl^{-1} at the 668th flushing. For surfactant B, the concentration decreases from 4.98 mgl^{-1} at the 662nd flushing to 1.066 mgl^{-1} at the 668th flushing. For surfactant C, the concentration decreases from 9.98 mgl^{-1} at the 662nd flushing to 2.15 mgl^{-1} at the 668th flushing. Thus, the concentration of the biomass decreases only slightly due to the decrease in the surfactant concentration.

The variation of the aqueous-phase concentration of root exudates with time in the rhizosphere is displayed in Fig. 7, where the initial concentration of the root exudates is assumed to be 10 mgl^{-1}. The concentration responds to the population of the microbes. In all these cases, it falls rapidly due to the increase in biomass from growth on root exudates. In case A, the concentration increases at the end of the plateau region when the population of the degrading microbes decreases as the surfactant concentration decreases.

Fig. 8 shows the variation of the aqueous-phase surfactant concentration with time in the rhizosphere. For case A, the concentration increases initially, remains constant, and eventually vanishes. For cases B and C, the concentration initially peaks, implying that the surfactant influx is large. As microbes accumulate, the concentration drops to a constant lower level of about 0.1 mgl^{-1}. The surfactant concentration is negligible in the solution injected into the aquifer after the disappearance of the NAP contaminant in

the aquifer. The concentration in the rhizosphere rapidly disappears after the feeding of surfactant is stopped.

The aquifer model has been extended to mixtures of contaminants by Gandhi et al. [49] for flushing processes without surfactants. It is expected, therefore, that the present model for treatment of a single contaminant under the presence of surfactants can similarly be extended to mixtures of contaminants. Additional information on selecting realistic parameters for the present model is available in Santharam [48]. In fact, such parameters, including those related to sorption, solubilities and kinetics, have been chosen from published literature for numerical examples of the present work [37,45–48]. Nevertheless, the performance of the process in the field is expected to be below the most optimistic result of the present work since diffusion and mass transfer limitations reduce the rate of dissolution of the contaminant. Oxygen consumption for abiological processes in the aquifer and oxygen transfer limitation in the rhizosphere may further reduce the rate as well.

5. Conclusions

Surfactants added to the flushing solution stimulate dissolution of contaminants and substantially accelerate the remediation of NAP contaminated sites. Increasing the oxygen concentration also facilitates the degradation of these contaminants. The time required to remove a NAP contaminant from the aquifer increases linearly with the initial NAP saturation. The relative effect of surfactant and oxygen may be contaminant specific. The dissolved contaminant removed through flushing is readily biodegraded by the increased population of microorganisms in the rhizosphere. The combination of surfactant-enhanced pump-and-treat and vegetation irrigation is a promising and cost-effective scheme for remediation of NAP contaminants. Since the proposed model imposes simplifying assumptions, it tends to predict the optimistic case corresponding to an upper bound of the efficiency of the technology. The number of actual flushings is expected to be larger.

6. Nomenclature

C	aqueous-phase concentration of the contaminant in the rhizosphere ($mg\,l^{-1}$)
C_b	aqueous-phase concentration of microbial biomass in the rhizosphere ($mg\,l^{-1}$)
$C_{b,in}$	microbial biomass concentration in the solution entering the rhizosphere from the aquifer ($mg\,l^{-1}$)
C_r	aqueous-phase concentration of root exudates in the rhizosphere ($mg\,l^{-1}$)
C_{sat}	aqueous-phase solubility of the contaminant ($mg\,l^{-1}$)
C_u	aqueous-phase concentration of surfactant in the rhizosphere ($mg\,l^{-1}$)
$C_{u,in}$	surfactant concentration in the solution entering the rhizosphere from the aquifer ($mg\,l^{-1}$)
$C_{u,a}$	surfactant concentration in the solution injected into the aquifer ($mg\,l^{-1}$)
$C_{u,i}$	surfactant concentration in the solution leaving the aquifer after the i-th flushing ($mg\,l^{-1}$)

C_w aqueous-phase concentration of the contaminant in the aquifer ($mg\,l^{-1}$)

C_w^* aqueous-phase (including micelles) concentration of the contaminant in the aquifer in the presence of surfactant ($mg\,l^{-1}$)

f fraction of the oxygen consumed for the mineralization of the contaminant (dimensionless)

f_{oc} fraction of organic carbon in the soil (dimensionless)

F_R flow rate of the solution entering the rhizosphere from the aquifer (day^{-1})

K_b phase equilibrium partition coefficient for the adsorption of microbial biomass to soil surfaces ($l\,mg^{-1}$)

K_d phase equilibrium partition coefficient for the adsorption of the contaminant to soil surfaces ($l\,mg^{-1}$) $= K_{oc} f_{oc}$

$K_{d,surf}$ phase equilibrium partition coefficient for the adsorption of the contaminant to soil surfaces in the presence of surfactant ($l\,mg^{-1}$)

k_{ed} decay rate constant for microbial biomass (day^{-1})

K_{oc} organic carbon–water partition coefficient ($l\,mg^{-1}$)

K_{ow} octanol–water partition coefficient (dimensionless)

K_r phase equilibrium partition coefficient for the adsorption of root exudates to soil surfaces ($l\,mg^{-1}$)

K_{rsu} saturation constant associated with the organic substrates, viz. root exudates, contaminant and surfactant ($mg\,l^{-1}$)

K_u phase equilibrium partition coefficient for the adsorption of the surfactant to soil surfaces ($l\,mg^{-1}$)

NAP non-aqueous phase

PAH polycyclic aromatic hydrocarbon

q rate of extraction of soil–water by a plant's root system (day^{-1})

$q_r C_{rr}$ root exudate loading factor ($mg/l\,day$)

R_b phase equilibrium parameter associated with the adsorption of microbial biomass to root surfaces (dimensionless)

R_{cf} plant's root concentration factor for the contaminant (dimensionless)

R_d root density in the soil ($l\,l^{-1}$)

R_r phase equilibrium parameter associated with the adsorption of root exudates to root surfaces (dimensionless)

R_u phase equilibrium parameter associated with the adsorption of surfactant to root surfaces (dimensionless)

S_o oxygen concentration in the solution entering the aquifer ($mg\,l^{-1}$)

TSCF plant's transpiration stream concentration factor for contaminant (dimensionless)

$TSCF_r$ plant's transpiration stream concentration factor for root exudates (dimensionless)

$TSCF_u$ plant's transpiration stream concentration factor for surfactant (dimensionless)

Y_S, Y_R observed yield coefficient for microbial growth on contaminant and root exudates, respectively ($mg\,mg^{-1}$)

Y_U observed yield coefficient for microbial growth on surfactant ($mg\,mg^{-1}$)

Y stoichiometric coefficient for the mineralization of the contaminant ($mg\,mg^{-1}$)

Y' stoichiometric coefficient for the mineralization of the surfactant ($mg\,mg^{-1}$)

$\varepsilon_{N,i}$ NAP volume fraction after the i-th flushing ($1l^{-1}$)
ε_T total porosity of the soil in the aquifer ($1l^{-1}$)
$\varepsilon_{W,i}$ aqueous phase volume fraction in the aquifer after the i-th flushing ($1l^{-1}$)
μ_m maximum specific growth rate ($1\,day^{-1}$)
ρ bulk density of the soil in the rhizosphere ($mg\,l^{-1}$)
ρ_B bulk density of the soil in the aquifer ($mg\,l^{-1}$)
ρ_N density of the NAP contaminant ($mg\,l^{-1}$)
θ soil-water content in the rhizosphere ($1l^{-1}$)

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