



# Modeling sorption and biodegradation of phenanthrene in mangrove sediment slurry

Jian Lin Chen<sup>a</sup>, Ming Hung Wong<sup>b</sup>, Yuk Shan Wong<sup>c</sup>, Nora Fung Yee Tam<sup>a,\*</sup>

<sup>a</sup> Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

<sup>b</sup> Croucher Institute of Environmental Sciences, Hong Kong Baptist University, Kowloon, Hong Kong

<sup>c</sup> Department of Biology, Hong Kong University of Science and Technology, Clearwater Bay, Kowloon, Hong Kong

## ARTICLE INFO

### Article history:

Received 28 November 2010

Received in revised form 1 March 2011

Accepted 16 March 2011

Available online 23 March 2011

### Keywords:

Bioremediation

Biodegradation

Sorption

PAH

The first order rate model

## ABSTRACT

A mathematical model, combining both sorption and biodegradation process, was developed to predict the biodegradation of phenanthrene by *Sphingomonas* sp. in different sediment slurries. The model includes two sorption parameters,  $\alpha$  (the partition coefficient) and  $1/K$  (the diffusion resistance); a kinetic parameter  $k$  (the first order rate constant); and a sediment parameter,  $A_v$  (the specific sediment surface area in unit volume of slurry). These parameters were evaluated and verified in three types of sediment slurry systems (namely sandy clay loam Ho Chung sediment with fastest degradation, sandy Kei Ling Ha sediment with medium degradation, and clay Mai Po sediment with slowest degradation) at different initial phenanthrene concentrations. High  $R^2$  values, ranging from 0.935 to 0.969, were obtained. Based on this integrated sorption–biodegradation model, the phenanthrene biodegradation in any sediment slurry could be predicted as long as the parameters of the specific sediment surface area in unit volume of slurry, total organic carbon and clay content were measured.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) with toxic, mutagenic and carcinogenic properties derived from natural sources and human inputs occur widely in coastal environments and also are accumulated in sediment because of their strong hydrophobicity [1]. With the discovery of a wide variety of microorganisms which have the ability to degrade PAHs [2], bioremediation, a technology that utilizes microorganisms to reduce environmental contaminants, has become a popular and effective remediation technique [3,4]. However, the heterogeneity of soil/sediment has been known to exert a significant influence on the efficiency and effectiveness of bioremediation in various sites [5], probably due to its effects on the sorption and desorption patterns associated with hydrophobic organic contaminants [6]. The organic compartments and the clay content in the sediment were proved to be the two dominant factors which would affect the sorption behavior of PAHs in the sediment/soil–water system [7,8]. But when the PAH in the aqueous phase is degraded or used up by the microorganisms, further biodegradation and continuous growth of the PAH-degrading microorganisms require the transfer of PAH mass from the interior of a non-aqueous phase to a location accessible to microbial

cells, such as the aqueous phase. This means that the rate of transfer of PAHs from the non-aqueous phase(s) determines the overall biodegradation. Wick et al. [9] summarized that limited bioavailability occurred when the capacity of the microbial biomass to consume a substrate exceeded the capacity of its environment to deliver the substrate. Sorption behavior significantly controls the bioavailability of PAHs.

To model the biodegradation process, a non-linear model, namely the Monod equation, is commonly used to describe the kinetics of biodegradation of organic compounds such as PAHs [10–12]. Based on the Monod equation, some other models were also developed for the PAH biodegradation process [11,13]. A complicated model, including the microbial biodegradation activity of the PAHs in the aqueous phase and PAHs sorption kinetics with respect to the organic carbon content, was developed by Artola-Garicano et al. [14]. However, none of these models simultaneously consider parameters such as the types of sediment, the dynamic sorption behavior, etc.

Phenanthrene (Phe), a toxic three-ring PAH, is often accumulated at a relatively high concentration in sediment and has been widely used as the model substrate in degradation studies. The concentrations of Phe have been reported ranging from a few  $\mu\text{g g}^{-1}$ , in low-level contaminated sediment, to a few hundred  $\mu\text{g g}^{-1}$  in the sediment near industrial sites [15] and have reached as high as  $1500 \mu\text{g g}^{-1}$  in some of the seriously contaminated sediment [16]. The present study aims to develop an integrated model including

\* Corresponding author. Tel.: +852 2788 7793; fax: +852 2788 7406.

E-mail address: [bhntam@cityu.edu.hk](mailto:bhntam@cityu.edu.hk) (N.F.Y. Tam).

the parameters of the specific sediment surface area of sediment slurry, dynamic sorption behavior and biodegradation kinetics for predicting the biodegradation process of Phe in the mangrove sediment slurry with the inoculation of *Sphingomonas* sp.

## 2. Materials and methods

### 2.1. Chemicals and phenanthrene degrader

Standards of Phe (96%) were purchased from Sigma Chemicals, USA. The stock solution of Phe was prepared by dissolving an appropriate amount of the standard in acetone, with a final concentration of 5000 mg L<sup>-1</sup>. The solutions were kept in a brown bottle at 4 °C and wrapped with aluminum folds to avoid any light exposure prior to use. Ethyl acetate (A.R.), acetone (99.5%) and dichloromethane (A.R.) were bought from Lab Scan Asia Co. Ltd. (Thailand) and were distilled before use. Methanol (G.R.) was bought from Merck KGaA Co. Ltd. (Germany). The stock culture of *Sphingomonas* sp., a PAH-degrading bacterial strain, enriched and isolated from surface mangrove sediment with ability to degrade PAHs [17], was used in the present study. The stock bacterial culture kept in 80% autoclaved glycerol under -80 °C was sub-cultured in nutrient broth and was harvested when reaching the exponential phase (around 3 days). The harvested cells were centrifuged and washed twice, re-suspended and used as the inoculum.

### 2.2. Mangrove sediment

The surface sediment (0–2 cm) was collected from Ho Chung (HC), Kei Ling Ha (KLH) and Mai Po (MP) mangrove swamps in Hong Kong. The sample was passed through a 2 mm sieve immediately after collection and kept moist at 4 °C before the experiment. A portion of the sample was air-dried and others were freeze-dried. The dried samples were kept in sealed bags and stored in a desiccator. The soil texture was analyzed by the dry sieving technique (Pipette method) following the standard method described by Gee and Bauder [18]. TOC was determined using wet oxidation–redox titration method [19]. The specific surface area of the sediment was determined by the ethylene glycol monoethyl ether (EGME) method [20]. The 16 PAHs in the sediment were extracted and analyzed according to Tam et al. [21].

### 2.3. Dynamic sorption and biodegradation experiment

For each mangrove sediment type, the biodegradation experiment was conducted under high and low initial Phe concentrations, each in triplicate. An appropriate amount of stock Phe solution was added to 250 mL conical flask to yield the designed initial concentrations. The acetone in each flask was allowed to evaporate. Then the sediment slurry was prepared by mixing 100 g sieved sediment with 100 mL distilled water in the 250 mL conical flask. Before inoculating the degrader, 5 mL slurry was sampled from each reactor to determine the precise initial concentrations, which were 37.5 and 105 mg L<sup>-1</sup> slurry. The final sediment densities in unit slurry volume of three types of sediment–slurry were 0.609, 0.505 and 0.348 g mL<sup>-1</sup> for KLH, HC and MP, respectively. *Sphingomonas* sp. was inoculated at a density of 10<sup>6</sup> MPN g<sup>-1</sup> sediment. Then the biodegradation experiment was carried out under pH 6.8 and all flasks were shaken at 180 rpm in dark at 24 ± 2 °C. A 5 mL of slurry sample was collected from each flask at each of the following time intervals: 1-, 7-, 15-, 30- and 48-h. The sterilized sediment slurry (by autoclaving the sediment slurry at 121 °C and 0.1 MPa pressure for 20 min to prevent any microbial activity) without the inoculation of *Sphingomonas* sp. was also prepared as the control to monitor the abiotic loss of Phe during the study. Phe concentrations in the

aqueous and sediment phases of samples were analyzed according to Chen et al. [6]. Although the initial Phe concentration chosen was higher than the normal environmentally relevant value, it was required because of detection limit for GC–FID analysis without highly concentrating Phe in the aqueous phase, in which Phe has very low solubility. Besides, based on the result of our previous studies, the initial Phe concentration (ranging from 5 to 55 mg L<sup>-1</sup>) was found having no effect on the degradation speed [22] and the dynamic sorption behavior [6]. In the present study, the lower concentration, 37.5 mg L<sup>-1</sup> (between 5 and 55 mg L<sup>-1</sup>), was used to study the effect of initial Phe concentration on the partition coefficient and the biodegradation speed during the biodegradation by comparing with the higher initial Phe concentration, 105 mg L<sup>-1</sup>.

### 2.4. Integrated sorption–biodegradation model

To model the Phe sorption behavior and biodegradation process in the mangrove sediment slurry with the inoculation of *Sphingomonas* sp., three assumptions were made:

- i. A steady thin membrane was present between the sediment and aqueous phases, and Phe would diffuse from the sediment to the aqueous phase (through this membrane) without any accumulation in the membrane;
- ii. only Phe dissolved in the aqueous phase could be degraded by microorganisms; and
- iii. Phe was homogenous in the aqueous phase as the reactor was well shaken.

The sorption and transfer of Phe in the sediment slurry were sketched in Fig. 1.

According to Fick's first law:

$$J = -D \frac{\partial C}{\partial x} \quad (1)$$

where  $J$  (mg m<sup>-2</sup> s<sup>-1</sup>) is the diffusion flux,  $D$  (m<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient and  $\partial C/\partial x$  is the gradient of concentration, in the present study, assuming that the gradient of concentration is linear, the flux of Phe through the steady thin membrane was:

$$J = D \frac{\Delta C}{\Delta x} \quad (2)$$

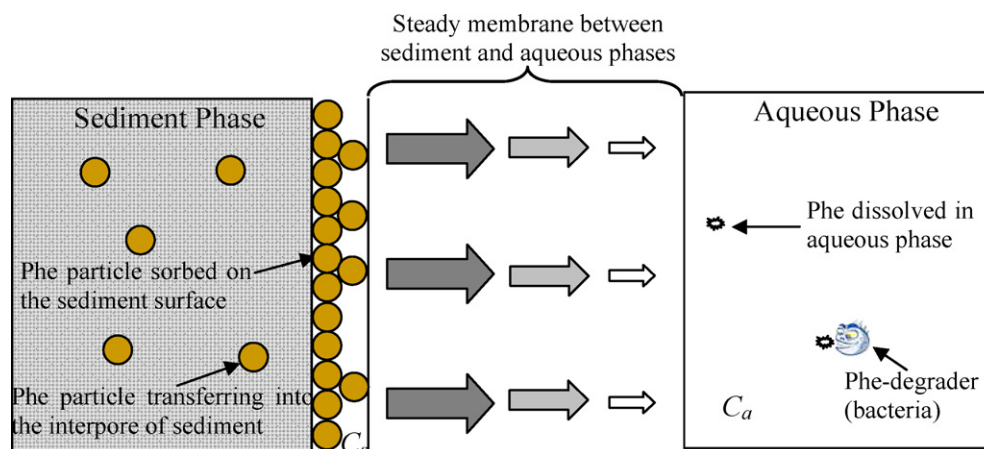
where  $\Delta C$  is the difference between the PAH concentrations in the sediment phase,  $C_s$  (mg m<sup>-3</sup> slurry), and the aqueous phase,  $C_a$  (mg m<sup>-3</sup> slurry), and  $\Delta x$  is the thickness of the membrane. By introducing the parameter  $1/K$  (s m<sup>-1</sup>), which is equal to  $\Delta x/D$  and could be interpreted as the diffusion resistance of the steady thin membrane, the Eq. (2) could be expressed as:

$$J = \frac{C_s - C_a}{1/K} \quad (3)$$

According to the assumptions that there was no Phe accumulated in the membrane and only Phe dissolved in the aqueous phase could be degraded by microorganisms, the Phe diffused to the aqueous phase were either degraded ( $C_d$ ) or accumulated in the aqueous phase ( $C_{a-a}$ ). Thus, the flux of Phe through the steady thin membrane in a short time  $dt$  could also be expressed as:

$$J = \frac{dC_d + dC_{a-a}}{A_V dt} \quad (4)$$

where  $A_V$  (m<sup>2</sup> m<sup>-3</sup>) is the specific sediment surface area in unit volume of slurry, which is the ratio of the specific surface area of sediment to the volume of slurry. According to our previous study on the dynamic sorption behavior of Phe onto different sediment during the biodegradation process with inoculation of *Sphingomonas* sp., Phe concentration in the aqueous phase decreased



**Fig. 1.** Sketch map showing the sorption and transfer of Phe in sediment slurry.  $C_s$ : Phe concentration in the sediment phase.  $C_a$ : Phe concentration in the aqueous phase.

along the biodegradation experiment [6]. That means there was no Phe accumulated in the aqueous phase ( $dC_{a-a} = 0$ ), and all of the Phe diffused from the sediment phase to the aqueous phase is equal to the change of total Phe concentration in the sediment–slurry system. Therefore, Eq. (4) could be expressed as:

$$J = \frac{dC_d}{A_v dt} = -\frac{1}{A_v} \frac{dC}{dt} \quad (5)$$

where  $C$  ( $\text{mg m}^{-3}$  slurry) is the total Phe concentration in the slurry. Combining Eqs. (3) and (5), the following equation can be obtained:

$$\frac{C_s - C_a}{1/K} = -\frac{1}{A_v} \frac{dC}{dt} \quad (6)$$

Previous study have proved that the first order rate model ( $C = C_0 e^{-kt}$ , where  $k$  is the first order rate constant,  $C$  is the concentration at time  $t$ ,  $C_0$  is the initial concentration) could be used to describe the Phe biodegradation process [22]. Then Eq. (5) could be converted to:

$$\frac{C_s - C_a}{1/K} = \frac{k}{A_v} C_0 e^{-kt} \quad (7)$$

As the linear model ( $C_s = \alpha C_a$ , where  $\alpha$  is the partition coefficient of Phe between the sediment and aqueous phases) could be used to describe the sorption behavior of Phe during the biodegradation process [6], Eq. (7) could then be written as:

$$C_s = \frac{\alpha k}{A_v K(\alpha - 1)} C_0 e^{-kt} \quad (8)$$

In a very short time  $dt$ , the change of total Phe concentration in the sediment–slurry system was almost equal to that in the sediment

phase ( $dC \approx dC_s$ ). Then, Eq. (8) could be expressed as:

$$-\frac{dC}{dt} = \frac{\alpha k^2}{A_v K(\alpha - 1)} C_0 e^{-kt} \quad (9)$$

### 3. Results

#### 3.1. General properties of mangrove sediment

The sediment properties were summarized in Table 1. The highest TOC content was recorded in the sediment collected from MP, followed by that from HC, and KLH had the lowest TOC. According to the soil texture triangle, it was found that KLH sediment was sandy with a small specific surface area of  $5.42 \times 10^6 \text{ m}^2 \text{ m}^{-3}$  slurry, HC sediment was sandy clay loam with a specific surface area of  $8.43 \times 10^6 \text{ m}^2 \text{ m}^{-3}$  slurry, and MP sediment was clay with a very large specific surface area of  $14.82 \times 10^6 \text{ m}^2 \text{ m}^{-3}$  slurry.

#### 3.2. Dynamic sorption and Phe biodegradation

The changes of Phe concentrations in the sterilized sediment slurry were minimal (0.5–0.9%), indicating that abiotic loss of Phe in the present study was negligible. The partition coefficient ( $\alpha$ ) was evaluated by fitting the different Phe concentration in the aqueous and sediment phases to the linear sorption model ( $C_s = \alpha C_a$ ). The results were summarized in Table 2. The partition coefficient of Phe in three types of sediment slurry was obtained as  $\alpha(\text{HC}) > \alpha(\text{KLH}) > \alpha(\text{MP})$ . All of the biodegradation data (total Phe concentration against time) were fitted to the Eq. (9) to evaluate the diffusion resistance ( $1/K$ ) and the first order rate constant ( $k$ ). The results were shown in Fig. 2 and summarized in Table 2. The diffusion resistance was found  $1/K(\text{MP}) > 1/K(\text{KLH}) > 1/K(\text{HC})$  and the

**Table 1**  
General properties of the sediment.

Properties	Sediment			
		HC	KLH	MP
Texture (%)	Sand	55.71 ± 8.28 <sup>a</sup>	88.98 ± 5.51 <sup>b</sup>	0.85 ± 0.16 <sup>c</sup>
	Silt	23.77 ± 2.68 <sup>a</sup>	4.00 ± 0.12 <sup>b</sup>	47.15 ± 1.70 <sup>c</sup>
	Clay	20.52 ± 3.73 <sup>a</sup>	7.02 ± 0.77 <sup>b</sup>	62.08 ± 0.64 <sup>c</sup>
Total organic carbon (%)	TOC	2.20 ± 0.07 <sup>a</sup>	0.33 ± 0.05 <sup>b</sup>	3.10 ± 0.12 <sup>a</sup>
	16 PAHs	222.7 ± 53.9 <sup>a</sup>	142.2 ± 10.5 <sup>b</sup>	510.4 ± 94.5 <sup>c</sup>
Concentration of PAHs ( $\text{ng g}^{-1}$ air-dried sediment)	Phe	28.13 ± 5.11 <sup>a</sup>	23.44 ± 5.55 <sup>a</sup>	50.66 ± 15.81 <sup>b</sup>
Specific sediment surface area in unit volume of slurry ( $10^6 \text{ m}^2 \text{ m}^{-3}$ )	$A_v$	8.43 ± 0.96 <sup>a</sup>	5.42 ± 0.73 <sup>b</sup>	14.82 ± 1.22 <sup>c</sup>

HC, Ho Chung; KLH, Kei Ling Ha; MP, Mai Po.

Phe, phenanthrene.

The mean ± standard deviation of triplicates are shown, and the values in the same row followed by different letters in the superscript position indicate they were significantly different according to one-way ANOVA at  $p \leq 0.05$ .

**Table 2**  
Parameters of the integrated sorption-biodegradation model (Eq. (9)).

Parameter	Sediment					
	HC		KLH		MP	
	37.5 (mg L <sup>-1</sup> )	105 (mg L <sup>-1</sup> )	37.5 (mg L <sup>-1</sup> )	105 (mg L <sup>-1</sup> )	37.5 (mg L <sup>-1</sup> )	105 (mg L <sup>-1</sup> )
$k$ (h <sup>-1</sup> )	0.0962	0.0956	0.0471	0.0472	0.0293	0.0287
$\alpha$	105.09	105.46	99.53	99.01	93.41	92.88
$1/K$ ( $\times 10^{11}$ s m <sup>-1</sup> )	3.12	3.14	4.10	4.09	18.01	18.39

Same legends as those in Table 1.

$\alpha$ , partition coefficient of Phe between the sediment and aqueous phases.

$k$ , first rate order model constant.

$1/K$ , diffusion resistance.

first order rate constant was obtained as  $k(\text{HC}) > k(\text{KLH}) > k(\text{MP})$ . It also can be seen that the first order rate constants ( $k$ ) in the same sediment slurry were similar under different initial concentration, suggesting initial concentration has no effect on the biodegradation speed. This result is comparable to the finding in our previous study [22]. The largest  $k$  value around  $0.096 \text{ h}^{-1}$  was found in HC sediment slurry and this value was even larger than the value which the biodegradation of Phe has been reported [23–26]. Conversely, the lower  $k$  value around  $0.029$  and  $0.047 \text{ h}^{-1}$  were obtained in MP and KLH sediment slurry, respectively, suggesting the slower biodegradation rate in these two types of sediment slurry but also even faster than the reported biodegradation rate mentioned above. These results indicated that the inoculated PAH-degrader, *Sphingomonas* sp., adapted sediment slurry conditions and maintained its degradation ability well.

### 3.3. Integrated model for sorption and biodegradation

Table 2 showed that the HC sediment slurry had the lowest diffusion resistance ( $1/K = 3.13 \times 10^{11} \text{ s m}^{-1}$ ) and the highest partition coefficient ( $\alpha = 105.22$ ), suggesting that more Phe would be dissolved in the aqueous phase and became available, leading to the fastest biodegradation rate. However, it was found that the MP sediment slurry had the largest diffusion resistances ( $1/K = 18.20 \times 10^{11} \text{ s m}^{-1}$ ) but the lowest partition coefficient (93.14) leading to the slowest biodegradation rate in this type of sediment slurry.

The predicted Phe biodegradation curves by the integrated sorption-biodegradation model (Eq. (9)) in different sediment slurry are shown in Fig. 2. The high  $R^2$  values suggested that the integrated sorption-biodegradation model could be used to predict the Phe biodegradation process in three types of mangrove sediment slurries with the inoculation of *Sphingomonas* sp.

## 4. Discussion

### 4.1. Sorption of PAHs onto sediment

One of the important factors affecting the fate and transport of organic contaminants in aquatic environments is the sorption onto sediment. Sorption can occur by partitioning into organic matter or onto mineral surfaces in sediment. The partitioning behavior (adsorption and desorption processes) of PAHs between soil and water can be regarded as a distribution of chemicals in a classical two-phase system of immiscible fluids [27]. The sorption equilibrium between the soil and the aqueous phase is therefore present. The mobility and fate of PAHs in soil/sediment is often predicted by the soil:water ( $K_d$ ) or soil organic matter:water ( $K_{oc}$ ) partitioning coefficients [28]. One assumption of such calculation is that the partitioning behavior will remain unchanged regardless of the source of PAHs and what determine the rate and extent of the release of PAHs is the soil parameter alone.

The partitioning behavior of PAHs would be influenced by many factors, such as dissolved organic matter, clay minerals, soil organic matter, etc. For the dissolved organic matter like humic and fulvic acids, it is well known that they can enhance the water solubility and subsequent desorption of several PAHs [29]. However, dissolved organic matter can also reduce the mobility of PAHs due to co-sorption or cumulative sorption [30,31]. In the study of the sorption phenomena of pyrene and Phe in single and binary solute systems, it was found that co-sorption with dissolved organic matter complexes occurred thereby reducing the desorption amount [8]. Moreover, Hwang and Cutright [8] also found that PAH desorption from the soil containing only organic matter was easier than that from the bulk soil containing clay minerals. The fraction of PAH bound onto soil organic matter surfaces was easily desorbed due to relatively weak binding forces, while the desorption-resistant fraction was attributed to the PAH binding to the clay minerals [32]. The composition of soil/sediment in a given medium is very important in PAH bioremediation. Understanding or estimating the reversibly sorbed fraction of PAHs in sediment could determine the amount of PAHs that is freely desorbed relative to its total concentration.

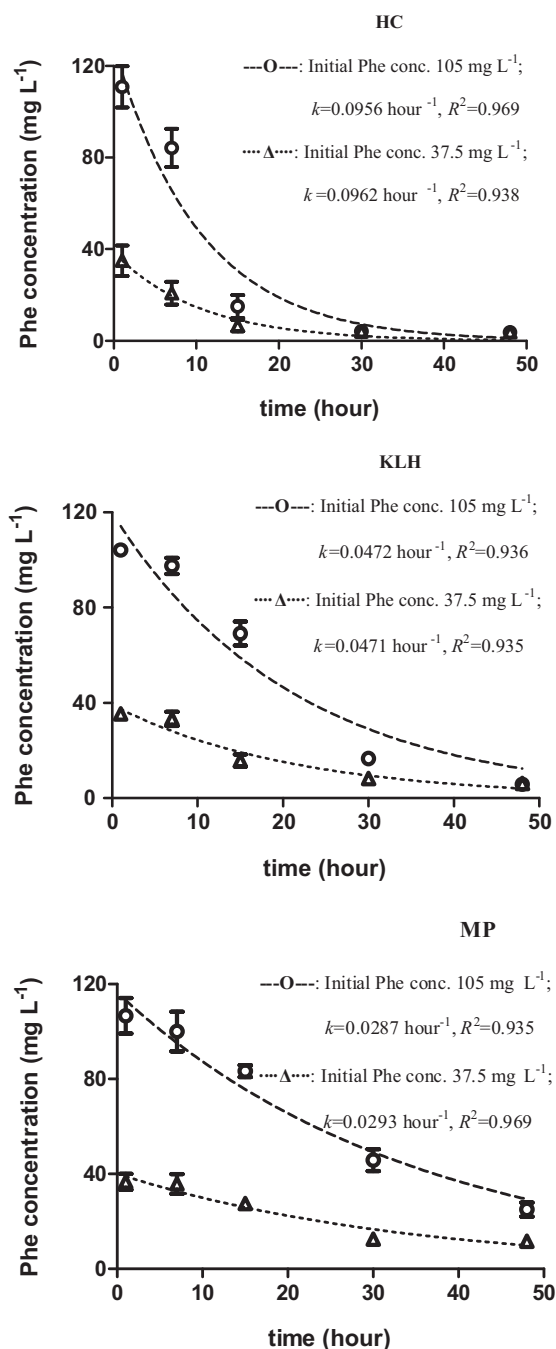
The linear model [33,34], the Freundlich adsorption isotherm [8,35] and the Langmuir adsorption isotherm [36,37] were strongly recommended to describe the static sorption behavior of PAHs onto soil/sediment. Although all of them were capable of adequately describing the equilibrium data, the application varied according to the soil types, environmental conditions (pH, temperature) and amendments (surfactant, oil, etc.) [7,33,38–40]. However, when the PAH in the aqueous phase is degraded or used up by the microorganisms, it was found that the linear model was more suitable to describe this PAH partitioning behavior between the aqueous and sediment phase during biodegradation process [6].

### 4.2. Kinetics of PAHs biodegradation

The kinetics for modeling the bioremediation of contaminated soil can be extremely complicated. Many models based on kinetics are developed to describe the biodegradation of PAHs or together with sorption behavior. For the biodegradation in soil–water systems, a widely applied rate model is the two-compartment model [41]. However, because many of the coefficients in two-compartment model are difficult to evaluate through independent experiments, they have to be obtained simultaneously by fitting parameters [42,43]. Thus, the two-compartment model is fundamentally empirical and appropriate model parameters are likely to vary with experimental conditions such as soil/water ratio, soil particle size, and number of microorganisms. Other recent bioremediation studies have indicated that a first-order reaction, such as the well-known Michaelis–Menton kinetic model, could adequately represent the PAH degradation kinetics [24,44,45].

More recently developed rate models tend to explicitly recognize the unavailability of the sorbed phase contaminants by considering that biodegradation comprises two separate and





**Fig. 2.** Changes of residual Phe concentrations in sediment slurry with time and the curves fitted to the integrated sorption–biodegradation model showing the rates of degradation in the inoculated system at different initial concentration: dotted line 37.5 mg L<sup>-1</sup>, dash line 105 mg L<sup>-1</sup>; mean and standard deviation of three replicates are shown.

sequential steps, a mass transfer step followed by a biodegradation step. In this way, characteristics of the extent and rate of sorption process could be specifically included in the mathematical simulation of the overall behavior [42,43,46–49]. Unfortunately, previous studies on the kinetics of PAHs biodegradation and sorption were not that comprehensive. Although Mulder et al. [50] developed mass-transfer and biodegradation models for three theoretical physical states of PAHs in soil, the application of these models was restricted to single type of soil.

The sequestration of sorbed chemicals in soil/sediment with time presents a source of uncertainty in the modeling and their

application in *in situ* bioremediation [51]. For many experimental studies on biodegradation, the contact time between soil and organic compounds was relatively short (days to weeks). Sequestration effects such as those described in previous paragraphs have not been evaluated. Appropriate quantitative models describing the effect of aging or sequestration on the rate and extent of biodegradation are also not available. Development of mathematical models that could comprehensively simulate sorption behavior, treatment time to site closure point, and treatment extent for bioremediation on site will be useful.

#### 4.3. Integrated model for sorption and biodegradation

Because the naturally occurring particles contain pores of different sizes, many of which are smaller than the sizes of microorganisms, bacteria will be physically excluded from most of the intra-particle pores of these grains [52]. The microorganisms unable to enter into the pore space of the particle may be uniformly distributed through the outer solution and consume the PAHs dissolved in the liquid phase. The PAHs within the particle can then be desorbed from the solid phase into the pore water phase, diffused out of the soil particle and finally biodegraded in the bulk liquid phase. Although there are studies reporting that microbes could utilize the sorbed PAHs directly [34,53], most works conclude that bacterial attachment does not occur on the surface of the solid phase, and there is no direct uptake of substrate from the solid phase. Substrate dissolution to the aqueous phase is still essential to make the solid-associated hydrophobic organic compounds bioavailable to the degrading microbes. The mass transfer of PAHs from the sorbed or non-aqueous liquid phases to the aqueous phase thus controls the overall rates of biodegradation [9,49,54]. The degree of such mass transfer is an important consideration.

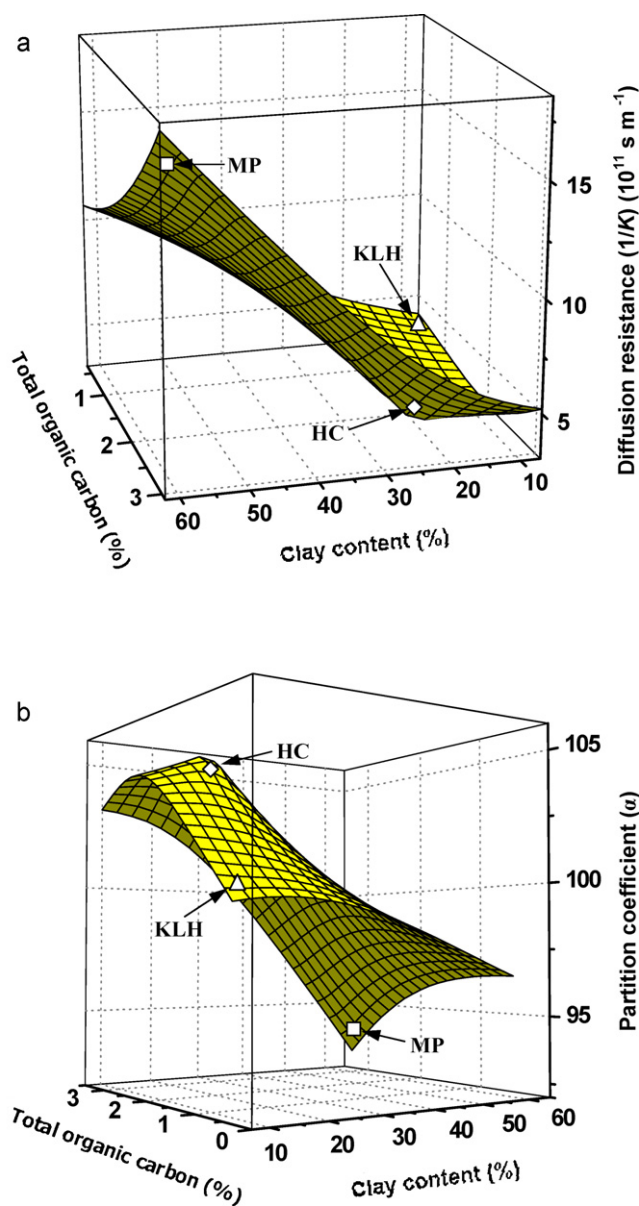
The present integrated sorption–biodegradation model included the parameter of  $1/K$ , the diffusion resistance, and  $\alpha$ , the partition coefficient of PAHs between the sediment and the aqueous phases. These two parameters had opposite effects on the biodegradation process. The larger the  $1/K$ , the slower and more difficult it is for the adsorbed PAHs to be desorbed. Conversely, the smaller the  $\alpha$ , the lower the PAH bioavailability will be. MP sediment, a type of muddy sediment with the highest TOC and clay content, had the highest  $1/K$  but the lowest  $\alpha$  and the lowest biodegradation rate.

Because of their strong hydrophobicity, PAHs are generally associated with solid or non-aqueous phases, such as clay and organic matter in sediment/soil, thus reducing their bioavailability. As the parameters of  $1/K$  and  $\alpha$  were related to the clay content and TOC, the evaluated values of  $1/K$  and  $\alpha$  (Table 2) together with TOC and clay content (Table 1) were plotted on three-dimensional graphs using the software of Origin 8.0 (Microcal Software, Inc., USA). Two predicted surfaces were obtained which could be used to investigate the effect of combined TOC and clay content on these two parameters (Fig. 3). When the clay content and TOC was around 20% and 2%, respectively, the diffusion resistance ( $1/K$ ) dropped to the minimum level, while the partition coefficient ( $\alpha$ ) reached the maximum. These results suggested that the Phe biodegradation could reach the fastest rate under this particular situation.

The first order rate model ( $-dC/dt = C_0 k e^{-kt}$ ) was recommended to describe the biodegradation kinetics of organic contaminants [22,24]. In the present study, an integrated sorption–biodegradation model ( $-dC/dt = (\alpha k^2 / A_v K (\alpha - 1)) C_0 e^{-kt}$ ) was developed. Combining these two models, it could be obtained that

$$\frac{\alpha k}{A_v K (\alpha - 1)} = 1 \quad (10)$$

This means that Phe biodegradation in any sediment slurry could be predicted as long as the parameters of the specific sed-



**Fig. 3.** Three-dimensional plots showing the relationships among clay content, total organic carbon, (a) diffusion resistance ( $1/K$ ) and (b) partition coefficient ( $\alpha$ ) of Phe in sediment slurry (HC: Ho Chung; KLH: Kei Ling Ha; MP: Mai Po) using Origin 8.0 (Microcal Software, Inc., USA).

iment surface area in unit volume of slurry ( $A_v$ ), TOC and clay content were measured. The parameters of diffusion resistance ( $1/K$ ) and partition coefficient ( $\alpha$ ) could be obtained from the graphs in Fig. 3 and the first order rate constant ( $k$ ) could then be calculated from Eq. (10), eliminating the necessity of conducting multiple Phe biodegradation experiments. The integrated model provided a rapid means to assessing the Phe biodegradation potential in different sediment slurry.

### Acknowledgement

The work described in this paper was supported by the Areas of Excellence established under the University Grants Committee of the Hong Kong SAR, China (Project no. AoE/P-04/2004).

### References

- [1] P.A. White, L.D. Claxton, Mutagens in contaminated soil: a review, *Mutat. Res./Rev. Mutat. Res.* 567 (2004) 227–345.
- [2] A.L. Juhasz, R. Naidu, Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo a pyrene, *Int. Biodeterior. Biodegrad.* 45 (2000) 57–88.
- [3] X. Li, X. Lin, P. Li, W. Liu, L. Wang, F. Ma, K.S. Chukwuka, Biodegradation of the low concentration of polycyclic aromatic hydrocarbons in soil by microbial consortium during incubation, *J. Hazard. Mater.* 172 (2009) 601–605.
- [4] R.-a. Doong, W.-g. Lei, Solubilization and mineralization of polycyclic aromatic hydrocarbons by *Pseudomonas putida* in the presence of surfactant, *J. Hazard. Mater.* 96 (2003) 15–27.
- [5] J.L. Chen, K.C. Au, Y.S. Wong, N.F.Y. Tam, Using orthogonal design to determine optimal conditions for biodegradation of phenanthrene in mangrove sediment slurry, *J. Hazard. Mater.* 176 (2010) 666–671.
- [6] J.L. Chen, Y.S. Wong, N.F.Y. Tam, Static and dynamic sorption of phenanthrene in mangrove sediment slurry, *J. Hazard. Mater.* 168 (2009) 1422–1429.
- [7] R.G. Luthy, G.R. Aiken, M.L. Brusseau, S.D. Cunningham, P.M. Gschwend, J.J. Pignatello, M. Reinhard, S.J. Traina, W.J. Weber, J.C. Westall, Sequestration of hydrophobic organic contaminants by geosorbents, *Environ. Sci. Technol.* 31 (1997) 3341–3347.
- [8] S.C. Hwang, T.J. Cutright, Impact of clay minerals and DOM on the competitive sorption/desorption of PAHs, *Soil Sediment Contam.* 11 (2002) 269–291.
- [9] L.Y. Wick, T. Colangelo, H. Harms, Kinetics of mass transfer-limited bacterial growth on solid PAHs, *Environ. Sci. Technol.* 35 (2000) 354–361.
- [10] C.D. Knightes, C.A. Peters, Statistical analysis of nonlinear parameter estimation for Monod biodegradation kinetics using bivariate data, *Biotechnol. Bioeng.* 69 (2000) 160–170.
- [11] P. Dimitriou-Christidis, R.L. Autenrieth, Kinetics of biodegradation of binary and ternary mixtures of PAHs, *Biotechnol. Bioeng.* 97 (2007) 788–800.
- [12] L. Liu, J.A. Tindall, M.J. Friedel, W.X. Zhang, Biodegradation of organic chemicals in soil/water microcosms system: model development, *Water Air Soil Pollut.* 178 (2007) 131–143.
- [13] L. Liu, J.A. Tindall, M.J. Friedel, Biodegradation of PAHs and PCBs in soils and sludges, *Water Air Soil Pollut.* 181 (2007) 281–296.
- [14] E. Artola-Garicano, I. Borkent, K. Damen, T. Jager, W.H.J. Vaes, Sorption kinetics and microbial biodegradation activity of hydrophobic chemicals in sewage sludge: model and measurements based on free concentrations, *Environ. Sci. Technol.* 37 (2003) 116–122.
- [15] M. Eriksson, G. Dalhammar, A.K. Borg-Karlson, Biological degradation of selected hydrocarbons in an old PAH/creosote contaminated soil from a gas work site, *Appl. Microbiol. Biotechnol.* 53 (2000) 619–626.
- [16] C.D. Simpson, A.A. Mosi, W.R. Cullen, K.J. Reimer, Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada, *Sci. Total. Environ.* 181 (1996) 265–278.
- [17] C.L. Guo, H.W. Zhou, Y.S. Wong, N.F.Y. Tam, Isolation of PAH-degrading bacteria from mangrove sediments and their biodegradation potential, *Mar. Pollut. Bull.* 51 (2005) 1054–1061.
- [18] G.W. Gee, J.W. Bauder, Particle-size analysis, in: A.L. Page (Ed.), *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*, Agronomy Monograph 9, American Society of Agronomy, Madison, WI, 1986, pp. 383–411.
- [19] H. Tiessen, J.O. Moir, Total and organic carbon, in: M.R. Carter (Ed.), *Soil Sampling and Methods of Analysis*, Lewis, Boca Raton, FL, 1993, pp. 187–199.
- [20] R.S. Dyal, S.B. Hendricks, Total surface area of clays in polar liquids as a characteristic index, *Soil Soc.* 69 (1950) 421–432.
- [21] N.F.Y. Tam, C.L. Guo, W.Y. Yau, Y.S. Wong, Preliminary study on biodegradation of phenanthrene by bacteria isolated from mangrove sediments in Hong Kong, *Mar. Pollut. Bull.* 45 (2002) 316–324.
- [22] J. Chen, M.H. Wong, Y.S. Wong, N.F.Y. Tam, Multi-factors on biodegradation kinetics of polycyclic aromatic hydrocarbons (PAHs) by *Sphingomonas* sp. a bacterial strain isolated from mangrove sediment, *Mar. Pollut. Bull.* 57 (2008) 695–702.
- [23] B. Antizar-Ladislao, J. Lopez-Real, A.J. Beck, Degradation of polycyclic aromatic hydrocarbons (PAHs) in an aged coal tar contaminated soil under in-vessel composting conditions, *Environ. Pollut.* 141 (2006) 459–468.
- [24] H.S. Kim, W.J. Weber, Optimizing contaminant desorption and bioavailability in dense slurry systems. 2. PAH bioavailability and rates of degradation, *Environ. Sci. Technol.* 39 (2005) 2274–2279.
- [25] S. Thiele-Bruhn, G.W. Brummer, Kinetics of polycyclic aromatic hydrocarbon (PAH) degradation in long-term polluted soils during bioremediation, *Plant Soil* 275 (2005) 31–42.
- [26] R. Xu, N.L.A. Lau, K.L. Ng, J.P. Obbard, Application of a slow-release fertilizer for oil bioremediation in beach sediment, *J. Environ. Qual.* 33 (2004) 1210–1216.
- [27] C.T. Chiou, Partition and adsorption on soil and mobility of organic pollutants and pesticides, *Toxic Org. Chem. Porous Media* 73 (1989) 163–175.
- [28] T. Mill, Environmental chemistry-transport processes: partitioning and volatilization, in: G.W. Suter (Ed.), *Ecological Risk Assessment*, Lewis, Boca Raton, FL, USA, 1993, pp. 96–101.
- [29] P. Lassen, L. Carlsen, Solubilization of phenanthrene by humic acids, *Chemosphere* 34 (1997) 817–825.
- [30] A.S. Abdul, T.L. Gibson, D.N. Rai, Use of humic acid solution to remove organic contaminants from hydrogeologic systems, *Environ. Sci. Technol.* 24 (1990) 328–333.

- [31] K.U. Totsche, J. Danzer, I.J. Koegel-Knabner, Dissolved organic matter-enhanced retention of polycyclic aromatic hydrocarbons in soil miscible displacement experiments, *J. Environ. Qual.* 26 (1997) 1090–1100.
- [32] S.C. Hwang, T.J. Cutright, Evidence of underestimation in PAH sorption/desorption due to system nonequilibrium and interaction with soil constituents, *J. Environ. Sci. Health Part A: Toxic/Hazard. Subst. Environ. Eng.* 39 (2004) 1147–1162.
- [33] A.P. Khodadoust, L. Lei, J.E. Antia, R. Bagchi, M.T. Suidan, H.H. Tabak, Adsorption of polycyclic aromatic hydrocarbons in aged harbor sediments, *J. Environ. Eng.-ASCE* 131 (2005) 403–409.
- [34] S.H. Woo, J.M. Park, B.E. Rittmann, Evaluation of the interaction between biodegradation and sorption of phenanthrene in soil-slurry systems, *Biotechnol. Bioeng.* 73 (2001) 12–24.
- [35] L.F. Ping, Y.M. Luo, L.H. Wu, W. Qian, J. Song, P. Christie, Phenanthrene adsorption by soils treated with humic substances under different pH and temperature conditions, *Environ. Geochem. Health* 28 (2006) 189–195.
- [36] P. Blanc, A. Saada, P. Baranger, A nonlinear parametric model for phenanthrene sorption, *J. Colloid Interface Sci.* 299 (2006) 14–21.
- [37] O. Braass, C. Tiffert, J. Hohne, X. Luo, B. Niemeyer, Decontamination of polyaromatic hydrocarbons from soil by steam stripping: mathematical modeling of the mass transfer and energy requirement, *Environ. Sci. Technol.* 37 (2003) 5001–5007.
- [38] J.C. Appert-Collin, S. Dridi-Dhaouadi, M.O. Simmonot, M. Sardin, Nonlinear sorption of naphthalene and phenanthrene during saturated transport in natural porous media, *Phys. Chem. Earth Pt. B* 24 (1999) 543–548.
- [39] F. Cheikh, C. Chavarie, J. Chaouki, R.E. Ortega, Multivariable study of phenanthrene adsorption in soil-water systems, *Ing. Hidraul. Mex.* 18 (2003) 21–33.
- [40] C. Forst, K. Schafer, A. Andl, L. Stieglitz, Investigation of sorption of some chlorinated pollutants on soil in oil contaminated systems by static and dynamic methods, *Chemosphere* 29 (1994) 2157–2162.
- [41] L.W. Ma, H.M. Selim, Predicting pesticide transport in mulch-amended soils: a two-compartment model, *Soil Sci. Soc. Am. J.* 69 (2005) 318–327.
- [42] H.H.M. Rijnaarts, A. Bachmann, J.C. Jumelet, A.J.B. Zehnder, Effect of desorption and intraparticle mass transfer on the aerobic biomineralization of  $\alpha$ -hexachlorocyclohexane in a contaminated calcareous soil, *Environ. Sci. Technol.* 24 (1990) 1349–1354.
- [43] W. Zhang, E. Bouwer, L. Wilson, N. Durant, Biotransformation of aromatic hydrocarbons in subsurface biofilms, *Water Sci. Technol.* 31 (1995) 1–14.
- [44] K.H. Baker, D.S. Herson, *Bioremediation*, McGraw-Hill, New York, 1994.
- [45] K.H. Wammer, C.A. Peters, Polycyclic aromatic hydrocarbon biodegradation rates: a structure-based study, *Environ. Sci. Technol.* 39 (2005) 2571–2578.
- [46] J.T. Angley, M.L. Brusseau, W.L. Miller, J.J. Delfino, Nonequilibrium sorption and aerobic biodegradation of dissolved alkylbenzenes during transport in aquifer material: column experiments and evaluation of a coupled-process model, *Environ. Sci. Technol.* 26 (1992) 1404–1410.
- [47] G.Y. Chung, B.J. McCoy, K.M. Scow, Criteria to assess when biodegradation is kinetically limited by intraparticle diffusion and sorption, *Biotechnol. Bioeng.* 41 (1993) 625–632.
- [48] B.B. Dykaar, P.K. Kitanidis, Macrotransport of a biologically reacting solute through porous media, *Water Resour. Res.* 32 (1996) 307–320.
- [49] J.R. Mihelcic, D.R. Lueking, R.J. Mitzell, J.M. Stapleton, Bioavailability of sorbed and separate-phase chemicals, *Biodegradation* 4 (1993) 141–153.
- [50] H. Mulder, A.M. Breure, W.H. Rulkens, Prediction of complete bioremediation periods for PAH soil pollutants in different physical states by mechanistic models, *Chemosphere* 43 (2001) 1085–1094.
- [51] D. Linz, D. Nakles, *Environmental Acceptable Endpoints in Soils*, Maryland American Academy of Environmental Engineers, Annapolis, 1997.
- [52] W.P. Ball, C. Buehler, T.C. Harmon, D.M. Mackay, P.V. Roberts, Characterization of a sandy aquifer material at the grain scale, *J. Contam. Hydrol.* 5 (1990) 253–295.
- [53] T.S. Poeton, H.D. Stensel, S.E. Strand, Biodegradation of polyaromatic hydrocarbons by marine bacteria: effect of solid phase on degradation kinetics, *Water Res.* 33 (1999) 868–880.
- [54] M. Bouchez, D. Blanchet, J.P. Vandecasteele, Degradation of polycyclic aromatic-hydrocarbons by pure strains and by defined strain associations – inhibition phenomena and cometabolism, *Appl. Microbiol. Biotechnol.* 43 (1995) 156–164.