

Modeling on the Sorption Kinetics of Lead and Cadmium onto Natural Sediments

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In this study, sorption kinetics of lead (Pb) and cadmium (Cd) onto coastal sediments were investigated at pH 5.5 using laboratory batch adsorbers. Four different models: one-site mass transfer model (OSMTM), pseudo-first-order kinetic model (PFOKM), pseudo-second-order kinetic model (PSOKM) and two compartment first-order kinetic model (TCFOKM) were used to analyze the sorption kinetics. As expected from the number of model parameters involved, the three-parameter TCFOKM was better than the two-parameter OSMTM, PFOKM and PSOKM in describing sorption kinetics of Pb and Cd onto sediments. Most sorption of Pb and Cd was rapidly completed within the first three hours, followed by slow sorption in the subsequent period of sorption. All models predicted that the sorbed amount at the apparent sorption ($q_{e,s}$) equilibria increased as the CEC and surface area of the sediments increased, regardless of initial spiking concentration (C_0) and heavy metal and the sediment type. The sorption rate constant (k_s , hr^{-1}) in OSMTM also increased as the CEC and BET surface area increased. The rate constant of pseudo-first-order sorption ($k_{p1,s}$, hr^{-1}) in PFOKM were not correlated with sediment characteristics. The results of PSOKM analysis showed that the rate constant of pseudo-second-order sorption ($k_{p2,s}$, $\text{g mmol}^{-1} \text{hr}^{-1}$) and the initial sorption rate ($v_{o,s}$, $\text{mg g}^{-1} \text{hr}^{-1}$) were not correlated with sediment characteristics. The fast sorption fraction ($f_{1,s}$) in TCFOKM increased as CEC and BET surface increased regardless of initial aqueous phase concentrations. The sorption rate constant of fast fraction ($k_{1,s}=10^{0.1}-10^{1.0} \text{hr}^{-1}$) was much greater than that of slow sorption fraction ($k_{2,s}=10^{-2}-10^{-4} \text{hr}^{-1}$) respectively.

Key words : aging, sorption, kinetics, sediment, heavy metal, Pb, Cd, model

INTRODUCTION

The fate of heavy metals in sediments has become a growing concern since a large quantities of heavy metals is being accumulated in sedi-

ments. Therefore, it is highly important how the heavy metals will be fixed and released and the rates of fixation and release are directly related to the bioavailability. It is generally accepted that the most important phenomena that controls the bioavailability of heavy metals in sedi-

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ments are adsorption and desorption processes. Recent studies revealed that aging or sequestration process is involved in the fate and transport of heavy metals in contaminated soils and sediments (Scheidegger 1996; Ford *et al.*, 1999, 2001; Koschinsky *et al.*, 2001; Martinez *et al.*, 2003; Mustafa *et al.*, 2006).

Sorption and desorption of metals onto sediments is a slow process and equilibrium between sediment and solutions may not be attained. The bioavailability of metals may be limited by rate of desorption rate of metal from sediment to the supernatant aqueous solutions (Redeker *et al.*, 2004). Therefore, it is important to quantitatively calculate metal release rates under different conditions to make better risk assessments. There have been extensive studies of metal sorption and desorption in soils (Dang *et al.*, 1994; McLaren *et al.*, 1998; Selim *et al.*, 1999; Rupa *et al.*, 2000; Strawn and Sparks, 2000; Li *et al.*, 2001; Shi *et al.*, 2005), but few studies have focused on the sorption and desorption kinetics of heavy metals in sediments (Koschinsky *et al.*, 2001; Ciffroy *et al.*, 2001; Millward and Liu, 2003; Liu *et al.*, 2003; Garnier *et al.*, 2006). It is essential to systematically study sorption kinetics to understand the kinetics of trace metal sorption onto sediments rather than to depend only on equilibrium assumptions.

Sparks (1989) has summarized kinetics models used to describe metal sorption and desorption kinetics. Kinetics of Zn desorption from soils was described by parabolic diffusion, two-constant rate, and Elovich equations (Kuo and Mikkelsen, 1980; Dang *et al.*, 1994; Rupa *et al.*, 2000). However, the rate constants in these models were not constant but changed with experimental conditions. Some researchers developed models based on a mass balance of flow systems to describe sorption and desorption kinetics (Skopp and McCallister, 1986; Bartal *et al.*, 1990; Selim, 1992). The two-site model has been widely used to describe nonequilibrium reactions in soil systems (Selim and Amacher, 1988; Connaughton *et al.*, 1993; Selim *et al.*, 1999). However, most of previous kinetics models are limited to metal desorption from soils (Shi *et al.*, 2005; Mustafa *et al.*, 2006).

In this work, sorption experiments were carried out in a batch-type adsorber using coastal sediments as sorbent and Pb and Cd used as sorbates. Sorption kinetics were analyzed using

one-site mass transfer model (OSMTM), pseudo-first-order kinetic model (PFOKM), pseudo-second-order kinetic model (PSOKM), and two-compartment first-order kinetic model (TCFOKM). The objective of this study is to examine sorption kinetics of heavy metals (Pb and Cd) onto coastal sediments accounting the effect of initial concentration.

MATERIALS AND METHODS

1. Sediments

Three sediment samples were collected from the surface layer (0-20 cm) of coastal sediments in Buan (Sediment A) and Suncheon, Korea (Sediment B and C). The sediment samples were air-dried and passed through a 200-mesh sieve, homogenized and stored in a plastic bottle until use. Some basic physicochemical properties of the sediments are listed in Table 1. Sediment pH was measured using a pH meter (Orion 290A) at sediment to solution ratio of 1 : 2.5 (w/v) in deionized water (Yang *et al.*, 2004). Organic carbon content was determined by an elemental analyzer (Fisons, EA 1110/EA1108) after removal of inorganic carbon (Nelson and Sommers, 1996). Cation exchange capacity (CEC) was determined by the sodium acetate method (EPA Method 9081, Sumner and Miller, 1996; US EPA, 2003). The mineralogical compositions of the sediments were identified by X-ray powder diffraction (Table 1). The background concentrations of Pb and Cd in the sediment were measured by microwave acid digestion (EPA Method 3051, US EPA, 2003). Sediment samples (1.0 g) were digested with *aqua regia* (EPA Method 3051, US EPA, 2003; 2 mL of HNO₃ (65%), and 6 mL of HCl (37%)) in a microwave acid digestion system (MARS 5, CEM Corp., Matthews, NC, USA) for 31 min and diluted to 10 mL with deionized water (digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent, 8 min). This procedure was preferred because it is more accurate with respect to both time and recovery values. The recovery values were nearly quantitative (>95%) for the above digestion method. A blank digestion was carried out in the same way. The concentrations of extracted Pb and Cd were determined by ICP-OES (Perkin Elmer Co., 2100DV).

2. Chemicals

Lead and cadmium solutions were prepared using Pb (NO₃)₂ (Sigma-Aldrich Co., < 98%) and Cd (NO₃)₂ (Kanto Chemical Co., < 98%) and the background solution consisted of a mixture of NaNO₃ (Kanto Chemical Co., < 98%) and MES (2-[N-morpholino]ethanesulfonic acid) hydrate, Sigma-Aldrich Co., 99.5%) buffer. The effect of carbon dioxide was eliminated by minimizing the head space of the vials.

3. Sorption kinetics

Sorption kinetic studies were conducted in batch mode using 50 mL polycarbonate vials (Nalgene Co.). To investigate the effect of the initial concentrations of the heavy metals, the initial concentrations were adjusted to 0.49 and 4.63 mmol L⁻¹ for Pb and 0.83 and 9.20 mmol L⁻¹ for Cd, respectively. The pH values of the sediments were controlled at 5.5 by using 0.05 M MES buffer solution (heavy metal free) before all experiments. The vials containing 1.0 g of sediment each were filled with chemical stock solutions minimizing headspace and then mixed at 10 rpm in a tumbler at 20°C. The exact amount of the stock solution added was determined gravimetrically. The pH values of the heavy metal solutions were maintained at 5.5 using 0.05 M MES buffer and 0.01 M NaNO₃ was added as a background electrolyte. Variation in pH was less than ±0.05 units. Experiments with this buffer in solutions of heavy metal confirmed the results of others (Baeyens and Bradbury, 1997; Strawn and Sparks, 2000); no detectable complexation reactions occur between heavy metals and the MES buffer.

After predetermined time intervals (15 min to 48 hrs), the vials were collected and centrifuged at 2,800 rpm for 20 minutes. The supernatant was then filtered through a 0.2 µm syringe filter (Whatman, cellulose nitrate membrane filter, φ= 25 mm). The aqueous phase equilibrium concentrations of Pb and Cd were determined by ICP-OES (PerkinElmer, 2100DV). The solid phase equilibrium concentrations were calculated by assuming all concentration changes in solution phase result from sorption onto the solid phase. All experiments were run in duplicate. The equilibrium pH was determined by a pH meter (Orion 290A).

SORPTION KINETIC MODELS

1. One-Site Mass Transfer Model (OSMTM)

One-site mass transfer model (OSMTM) for sorption rate was proposed by Nzengung *et al.* (1997). In OSMTM, sorption rate was represented as a first-order function of the concentration difference between the solution and sorbed phases under the assumption of the linear sorption equilibrium. The OSMTM is defined as:

$$\frac{C(t)}{C_0} = \frac{C_e}{C_0} + \left(1 - \frac{C_e}{C_0}\right) \exp\left[\left(-\frac{C_0}{C_e} k_s\right) t\right] \quad (1)$$

where $C(t)$ and C_0 denote the solute concentrations in the solution (mg L⁻¹) at time t (hr) and at time 0, respectively, C_e is the equilibrium concentration in the solution phase and k_s is the mass transfer coefficient (hr⁻¹) for sorption between the solution and solid phase. Values of C_e and k_s were estimated by curve-fitting Eq. (1) to the sorption kinetic data.

2. Pseudo-First-Order Kinetic Model (PFOKM)

The Lagergren pseudo-first-order kinetic model has been widely used to predict sorption kinetics (Ho and McKay, 2000):

$$\frac{dq(t)}{dt} = k_{p1,s}(q_{e,s} - q(t)) \text{ with } q=0 \text{ at } t=0 \quad (2)$$

where $k_{p1,s}$ is the rate constant of pseudo-first-order sorption (1 hr⁻¹) and $q_{e,s}$ is the sorption equilibrium concentration in the solid phase, respectively. Integrating Eq. (2) gives:

$$q(t) = q_{e,s}(1 - e^{-k_{p1,s}t}) \quad (3)$$

Using the mass balance, $W(q - q_0) = V(C_0 - C)$, following equation is obtained:

$$\frac{C(t)}{C_0} = 1 - \frac{q_{e,s}}{C_0} \cdot \frac{W}{V} (1 - e^{-k_{p1,s}t}) \quad (4)$$

Values of $q_{e,s}$ and $k_{p1,s}$ were estimated by curve-fitting Eq. (4) to sorption kinetic data.

3. Pseudo-Second-Order Model (PSOKM)

The pseudo-second-order equation based on sorption equilibrium capacity is expressed as (Ho and McKay, 2000):

$$\frac{dq(t)}{dt} = k_{p2,s}(q_{e,s} - q(t))^2 \text{ with } q=0 \text{ at } t=0 \quad (5)$$

where $k_{p2,s}$ is the rate constant of pseudo-second-order sorption ($\text{g mg}^{-1} \text{hr}^{-1}$). Integrating Eq. (5) yields:

$$q(t) = \frac{t}{1/(k_{p2,s}q_{e,s}^2) + t/q_{e,s}} \quad (6)$$

Using the mass balance, $W(q - q_0) = V(C_0 - C)$, following equation is obtained:

$$\frac{C(t)}{C_0} = 1 - \frac{1}{C_0} \cdot \frac{(W/V) \cdot t}{1/(k_{p2,s}q_{e,s}^2) + t/q_{e,s}} \quad (7)$$

Values of $q_{e,s}$ and $k_{p2,s}$ were estimated by curve-fitting Eq. (7) to sorption kinetic data.

The constant $k_{p2,s}$ is used to calculate the initial sorption ($v_{0,s}$, $\text{mmol g}^{-1} \text{hr}^{-1}$) at $t \rightarrow 0$, as follows:

$$v_{0,s} = k_{p2,s}q_{e,s}^2 \quad (8)$$

4. Two Compartment First-Order Kinetic Model (TCFOKM)

The overall sorption in two compartment first-order kinetic model (TCFOKM) was assumed to consist of the sum of the two first-order sorption rates in the fast and slow compartments (Cornellison *et al.*, 1997a, b; Opdyke and Loehr, 1999):

$$\frac{C(t)}{C_0} = f_{1,s}e^{-k_{1,s}t} + (1 - f_{1,s})e^{-k_{2,s}t} \quad (9)$$

where $f_{1,s}$ and $f_{2,s} = 1 - f_{1,s}$ are the fast and slow sorption fractions, respectively, and $k_{1,s}$ and $k_{2,s}$ are the sorption rate constants in the fast and slow compartments (hr^{-1}), respectively. Values of the three model parameters, $f_{1,s}$, $k_{1,s}$ and $k_{2,s}$,

were determined by curve-fitting to the sorption kinetic data.

All model parameters were estimated by using a commercial software package, TableCurve 2D[®] (Version 5.0, SPSS, Inc.).

RESULTS AND DISCUSSION

1. Sediment characteristics

The physicochemical characteristics were summarized in Table 1. In all sediments, quartz was the dominating (43-52%) mineral followed by muscovite (23-38%), albite (13-22%) and kaolinite (3%). The organic carbon content was in the order of Sediment A (0.88 wt%) > Sediment B (0.76 wt%) > Sediment C (0.38 wt%). The cationic capacity (CEC) was in the order of Sediment B (35.9 meq/100 g) > Sediment A (33.3 meq/100 g) > Sediment C (18.0 meq/100 g).

2. Sorption kinetics

Sorption of Pb and Cd onto natural sediments over time was investigated. The two-parameter OSMTM, PFOKM and PSOKM and three-parameter TCFOKM were fitted to the sorption kinetic data (Figs. 1-2). OSMTM is based on the assumption that sorption domain in sorbent is homogeneous. In PFOKM, sorption is a pseudo-chemical reaction process and the adsorption rate can be determined by the first-order dependence on the difference in the equilibrium concentration (q_e) and concentration at time t ($q(t)$) in the solid phase (i.e., driving force). PSOKM is based on the

Table 1. The physicochemical characteristics of the coastal sediments used.

Analysis items		Sediment		
		A	B	C
Location	The north latitude	35° 82'12"	34° 82'52"	34° 87'39"
	The east longitude	126° 65'63"	127° 40'74"	127° 35'74"
pH		8.0	7.9	7.8
Organic carbon (weight %)		0.88	0.76	0.38
CEC (meq/100 g)		33.3	35.9	18.0
Surface Area ($\text{m}^2 \text{g}^{-1}$)		25.8	36.1	13.3
Indigenous heavy metal content (mg kg^{-1})		Pb=33.8	Pb=19.0	Pb=10.0
		Cd=0.0	Cd=0.0	Cd=0.0
Mineral content	Quartz (%)	47	43	52
	Muscovite (%)	36	38	23
	Albite (%)	13	16	22
	Kaolinite (%)	3	3	3

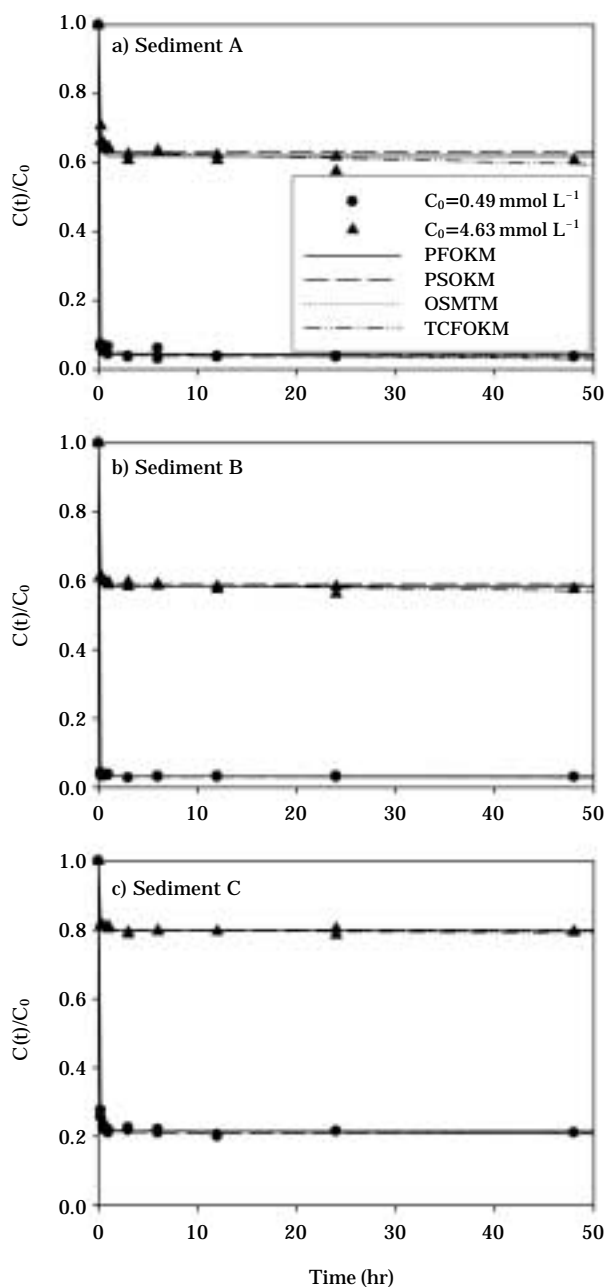


Fig. 1. Sorption kinetics of Pb onto sediments at different initial concentrations ($C_0=0.49 \text{ mmol L}^{-1}$ and 4.63 mmol L^{-1} ; pH=5.5).

assumption that sorption occurs mainly due to chemisorption and that the adsorption rate can be determined by the second-order dependence on the difference in the equilibrium concentration (q_e) and concentration at time t ($q(t)$) in the solid phase. In TCFOKM, sorption domain is divided into two regions: fast and slow compart-

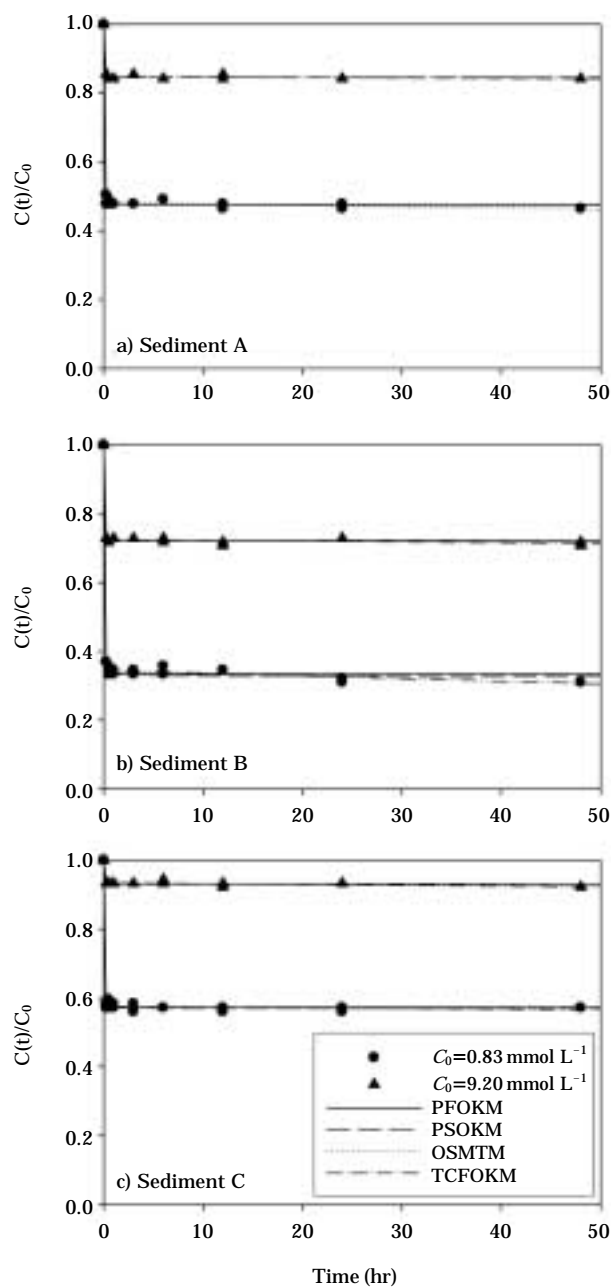


Fig. 2. Sorption kinetics of Cd onto sediments at different initial concentrations ($C_0=0.83 \text{ mmol L}^{-1}$ and 9.20 mmol L^{-1} ; pH=5.5).

ments. All sorption kinetic models well fitted to the sorption kinetic data (Figs. 1 and 2). The model parameters of OSMTM, PFOKM, PSOKM and TCFOKM determined from the nonlinear curve fitting are listed in Tables 2-5, respectively.

As shown in Figs. 1 and 2, a substantial portion

Table 2. One-site mass transfer model (OSMTM) parameters for sorption of Pb and Cd at different initial concentrations ($C_0=0.49$ and 4.63 mmol L^{-1} for Pb and $C_0=0.83$ and 9.20 mmol L^{-1} for Cd). Number in the parenthesis indicates standard deviation in 95% confidence interval.

Solute	Sediment	$C_0 (\text{mmol L}^{-1})$	$C_e (\text{mmol L}^{-1})$	$k_s (\text{hr}^{-1})$	R^2	SSE	$t_{eq,s} (\text{hr})$	q/q_0 at $t=1 \text{ hr}$
Pb	A	0.49	0.0209 ± 0.0015	0.6206 ± 0.0870	0.9976	0.0021	1.3	0.948
	B		0.0154 ± 0.0004	0.6175 ± 0.0480	0.9998	0.0001	1.0	0.969
	C		0.1046 ± 0.0011	2.3232 ± 0.1174	0.9981	0.0011	1.7	0.784
	A	4.63	2.8670 ± 0.0257	4.1425 ± 0.5129	0.9588	0.0059	2.7	0.380
	B		2.9041 ± 0.0118	6.2419 ± 0.5869	0.9919	0.0013	1.7	0.415
	C		3.6909 ± 0.0098	8.0036 ± 1.1471	0.9767	0.0009	1.7	0.202
Cd	A	0.83	0.3960 ± 0.0021	6.7912 ± 1.0152	0.9923	0.0013	1.3	0.523
	B		0.2770 ± 0.0034	3.8835 ± 0.4427	0.9917	0.0035	1.6	0.666
	C		0.4750 ± 0.0021	9.9941 ± 3.0244	0.9923	0.0013	1.1	0.428
	A	9.20	7.7740 ± 0.0121	9.5578 ± 1.3589	0.9845	0.0004	1.6	0.155
	B		6.6380 ± 0.0185	10.753 ± 2.4449	0.9886	0.0008	1.2	0.278
	C		8.5652 ± 0.0132	13.949 ± 9.3122	0.9113	0.0004	1.1	0.069

$t_{eq,d}$ =equilibration time for sorption (hr)

of Pb and Cd was sorbed within the first 3 hours, followed by a slow sorption over 48 hours of sorption period. All models predicted that the sorbed amount ($q_{e,s}$) at the apparent sorption equilibria increased as the CEC and surface area of the sediments increased (i.e., Sediment B > Sediment A > Sediment C), regardless of initial spiking concentration (C_0) and heavy metal and the sediment type. The sediment with a higher CEC and surface area had a higher sorbed amount.

As summarized in Table 2, the time required to reach apparent sorption equilibria (equilibration time, $t_{eq,s}$) were observed within 1-3 hours. In other words, a substantial portion of the solute was sorbed within 1 to 3 hours, followed by a slow sorption over 48 hours of sorption period. At the apparent equilibrium, the sorbed amount of Pb was in the order of Sediment B (96.9% at $C_0=0.49 \text{ mmol L}^{-1}$ and 41.5% at $C_0=4.63 \text{ mmol L}^{-1}$) > Sediment A (94.8% at $C_0=0.49 \text{ mmol L}^{-1}$ and 38.0% at $C_0=4.63 \text{ mmol L}^{-1}$) > Sediment C (78.4% at $C_0=0.49 \text{ mmol L}^{-1}$ and 20.2% at $C_0=4.63 \text{ mmol L}^{-1}$) as indicated by the C_e values. The sorbed amount of Cd at the apparent equilibrium was also in the same order: Sediment B (66.6% at $C_0=0.83 \text{ mmol L}^{-1}$ and 27.8% at $C_0=9.20 \text{ mmol L}^{-1}$) > Sediment A (52.3% at $C_0=0.83 \text{ mmol L}^{-1}$ and 15.5% at $C_0=9.20 \text{ mmol L}^{-1}$) > Sediment C (42.8% at $C_0=0.83 \text{ mmol L}^{-1}$ and 6.86% at $C_0=9.20 \text{ mmol L}^{-1}$). Again this order was consistent with the CEC and surface area of the sediment, but not with the organic carbon content (f_{oc}). The results of OSMTM analysis (Table 2) showed

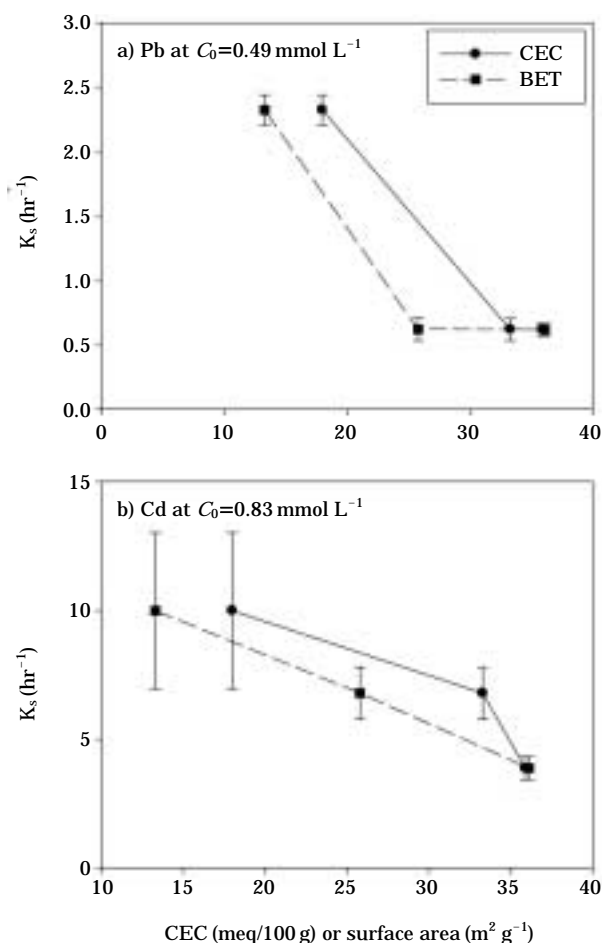


Fig. 3. The relationship between sorption rate constant (k_s) of OSMTM and CEC or surface area of the sediments at low concentrations (Pb= 0.49 mmol L^{-1} and Cd= 0.83 mmol L^{-1}).

Table 3. Pseudo-first-order kinetic model (PFOKM) parameters for sorption of Pb and Cd at different initial concentrations ($C_0=0.49$ and 4.63 mmol L^{-1} for Pb and $C_0=0.83$ and 9.20 mmol L^{-1} for Cd). Number in the parenthesis indicates standard deviation in 95% confidence interval.

Solute	Sediment	$C_0 (\text{mmol L}^{-1})$	$q_{e,s} (\text{mmol g}^{-1})$	$k_{p1,s} (\text{hr}^{-1})$	R^2	SSE
Pb	A	0.49	0.0193 ± 0.0001	14.437 ± 1.3766	0.9976	0.0021
	B		0.0196 ± 0.0000	19.551 ± 1.2648	0.9998	0.0001
	C		0.0159 ± 0.0000	10.813 ± 0.4914	0.9981	0.0011
	A	4.63	0.0731 ± 0.0011	6.6827 ± 0.8011	0.9588	0.0059
	B		0.0800 ± 0.0005	10.675 ± 0.9852	0.9919	0.0013
	C		0.0389 ± 0.0004	10.029 ± 1.4270	0.9767	0.0009
Cd	A	0.83	0.0179 ± 0.0001	14.236 ± 2.097	0.9938	0.0016
	B		0.0229 ± 0.0001	11.635 ± 1.2660	0.9917	0.0035
	C		0.0147 ± 0.0001	17.465 ± 5.2572	0.9923	0.0013
	A	9.20	0.0590 ± 0.0005	11.306 ± 1.6008	0.9845	0.0004
	B		0.1043 ± 0.0008	14.896 ± 3.3718	0.9886	0.0008
	C		0.0263 ± 0.0006	14.976 ± 9.9895	0.9113	0.0004

Table 4. Pseudo-second-order kinetic model (PSOKM) parameters for sorption of Pb and Cd at different initial concentrations ($C_0=0.49$ and 4.63 mmol L^{-1} for Pb and $C_0=0.83$ and 9.20 mmol L^{-1} for Cd). Number in the parenthesis indicates standard deviation in 95% confidence interval.

Solute	Sediment	$C_0 (\text{mmol L}^{-1})$	$q_{e,s} (\text{mmol g}^{-1})$	$k_{p2,s} (\text{g mmol}^{-1} \text{hr}^{-1})$	$v_{o,s} (\text{mmol g}^{-1} \text{hr}^{-1})$	R^2	SSE
Pb	A	0.49	0.0194 ± 0.0001	$5,705.2 \pm 1,226.2$	2.15	0.9981	0.0011
	B		0.0196 ± 0.0000	$22,913 \pm 5432.6$	8.80	0.9999	0.0001
	C		0.0160 ± 0.0001	$3,588.3 \pm 481.34$	0.92	0.9981	0.0011
	A	4.63	0.0747 ± 0.0010	222.76 ± 42.07	1.24	0.9742	0.0037
	B		0.0805 ± 0.0004	579.68 ± 101.98	3.76	0.9953	0.0008
	C		0.0395 ± 0.0004	857.57 ± 193.39	1.34	0.9869	0.0005
Cd	A	0.83	0.0180 ± 0.0001	$6,310.0 \pm 2,687.3$	2.05	0.9945	0.0014
	B		0.0230 ± 0.0002	$2,787.8 \pm 798.36$	1.48	0.9929	0.0030
	C		0.0148 ± 0.0001	$9,342.0 \pm 5,213.7$	2.04	0.9935	0.0011
	A	9.20	0.0592 ± 0.0006	$1,479.9 \pm 915.95$	5.18	0.9814	0.0004
	B		0.1064 ± 0.0009	$1,601.2 \pm 1,459.6$	18.13	0.9885	0.0008
	C		0.0265 ± 0.0006	$3,211.6 \pm 4,320.1$	2.25	0.9138	0.0004

that the mass transfer coefficient for sorption (k_s) was in the order of Sediment C > Sediment A > Sediment B, and reversely correlated to the increase in CEC and surface area (Fig. 3).

OSMTM fitted well to the sorption kinetic data ($0.91 < R^2 < 1.0$).

The results of PFOKM analysis of sorption kinetics were depicted in Figures 1 (Pb) and 2 (Cd), respectively, and the model parameters were summarized in Table 3. In terms of R^2 values, PFOKM (Table 3) was nearly the same goodness-of-fit as OSMTM (Table 2). Although PFOKM was fitting well to the sorption kinetic data ($0.91 < R^2 < 1.0$), the rate constant of pseudo-first-order sorption ($k_{p1,s}$) of Pb increased with CEC

and surface area of the sediment, while that of Cd decreased. This indicates that the applicability of PFOKM in sorption kinetics of Pb and Cd onto sediments is limited.

The PSOKM was fitted to the sorption kinetic data (Figs. 1 and 2) and the model parameters were listed in Table 4. Comparison of R^2 values showed that PSOKM (Table 4) was slightly better or nearly the same goodness-of-fit as OSMTM (Table 2) and PFOKM (Table 3).

Although PSOKM fitted well to the sorption kinetic data ($0.91 < R^2 < 1.0$), the model parameter ($k_{p2,s}$, $\text{g mmol}^{-1} \text{hr}^{-1}$) and the initial sorption rate ($v_{o,s}$, $\text{mmol g}^{-1} \text{hr}^{-1}$) were not correlated with CEC and surface area (figure not shown). This

Table 5. Two compartment first-order kinetic model (TCFOKM) parameters for sorption of Pb and Cd at different initial concentrations ($C_0=0.49$ and 4.63 mmol L⁻¹ for Pb and $C_0=0.83$ and 9.20 mmol L⁻¹ for Cd). Number in the parenthesis indicates standard deviation in 95% confidence interval.

Solute	Sediment	C_0 (mmol L ⁻¹)	Fast compartment		Slow compartment		R^2	SSE
			$f_{1,s}$	$k_{1,s}$ (hr ⁻¹)	$f_{2,s}=1-f_{1,s}$	$k_{2,s}$ (hr ⁻¹)		
Pb	A	0.49	0.9515 ± 0.0040	15.427 ± 1.7122	0.0495	0.0097 ± 0.0052	0.9981	0.0016
	B		0.9676 ± 0.0011	79.993 ± 1.4669	0.0324	0.0018 ± 0.0017	0.9999	0.0001
	C		0.7825 ± 0.0030	11.031 ± 0.5340	0.2175	0.0009 ± 0.0007	0.9983	0.0010
	A	4.63	0.3692 ± 0.0065	7.4460 ± 0.9433	0.6308	0.0012 ± 0.0005	0.9706	0.0042
	B		0.4096 ± 0.0027	11.629 ± 1.0467	0.5904	0.0007 ± 0.0002	0.9953	0.0008
	C		0.1993 ± 0.0027	10.879 ± 1.8136	0.8007	0.0002 ± 0.0002	0.9798	0.0008
Cd	A	0.83	0.5175 ± 0.0031	16.114 ± 2.9898	0.4825	0.0008 ± 0.0003	0.9960	0.0010
	B		0.6552 ± 0.0035	13.145 ± 1.2618	0.3448	0.0024 ± 0.0005	0.9968	0.0013
	C		0.4256 ± 0.0033	19.600 ± 9.3996	0.5744	0.0003 ± 0.0003	0.9928	0.0012
	A	9.20	0.1536 ± 0.0017	11.781 ± 1.9134	0.8464	0.0001 ± 0.0001	0.9854	0.0003
	B		0.2755 ± 0.0025	16.844 ± 5.4639	0.7245	0.0003 ± 0.0002	0.9905	0.0007
	C		0.0655 ± 0.0015	$1,376 \pm 1.6712$	0.9345	0.0002 ± 0.0001	0.9478	0.0003

indicates that the applicability of PSOKM in sorption kinetics of Pb and Cd onto sediments is also limited.

The results of TCFOKM analysis for sorption kinetics were shown in Figures 1 and 2 and the model parameters are summarized in Table 5. As shown in Figure 1, the fast sorption fraction ($f_{1,s}$) of Pb was greater than the slow sorption fraction ($f_{2,s}$) at lower initial concentration ($C_0=0.49$), but $f_{2,s}$ was greater than $f_{1,s}$ at higher initial concentration ($C_0=4.63$). This tendency was same for Cd as shown in Figure 2. The slow sorption fraction ($f_{2,s}$) of Cd was greater than the slow fraction $f_{1,s}$, except Pb sorption onto sediments A and B at $C_0=0.83$. In all sediments, the sorption rate constant of fast sorption compartment ($k_{1,s}$) was order of magnitude greater than that of slow sorption compartment ($k_{2,s}$), regardless of the initial spiking concentrations. Comparison of R^2 values (Table 2-5) shows that three-parameter TCFOKM fitted the data better than two-parameter OSMTM, PFOKM and PSOKM for sorption as expected from the number of fitting parameters involved in each model (i.e., three vs. two). For both heavy metals, the fast sorption fraction ($f_{1,s}$) decreased, while the slow sorption fraction ($f_{2,s}$) increased in the order of Sediment B > Sediment A > Sediment C, regardless of initial spiking concentrations and metal type. The order of decrease in $f_{1,s}$ was consistent with CEC surface area. The firstorder rate constant in the fast fraction ($k_{1,s}$) increased with CEC and surface area for Pb at $C_0=0.49$ mmol L⁻¹ but no consi-

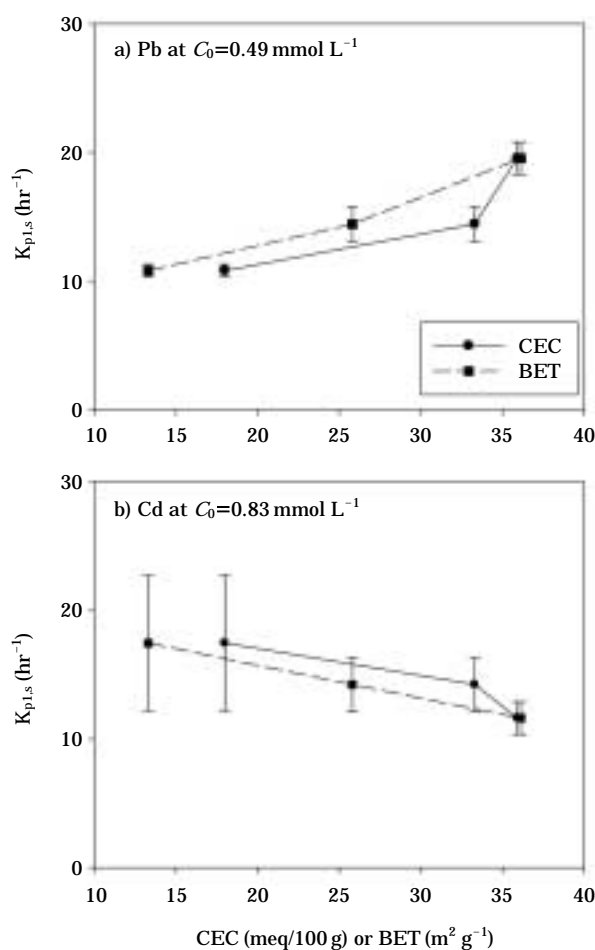


Fig. 4. The relationship between rate constant of pseudo-first-order sorption (k_s) of PFOKM and CEC or surface area of the sediments at low concentrations (Pb=0.49 mmol L⁻¹ and Cd=0.83 mmol L⁻¹).

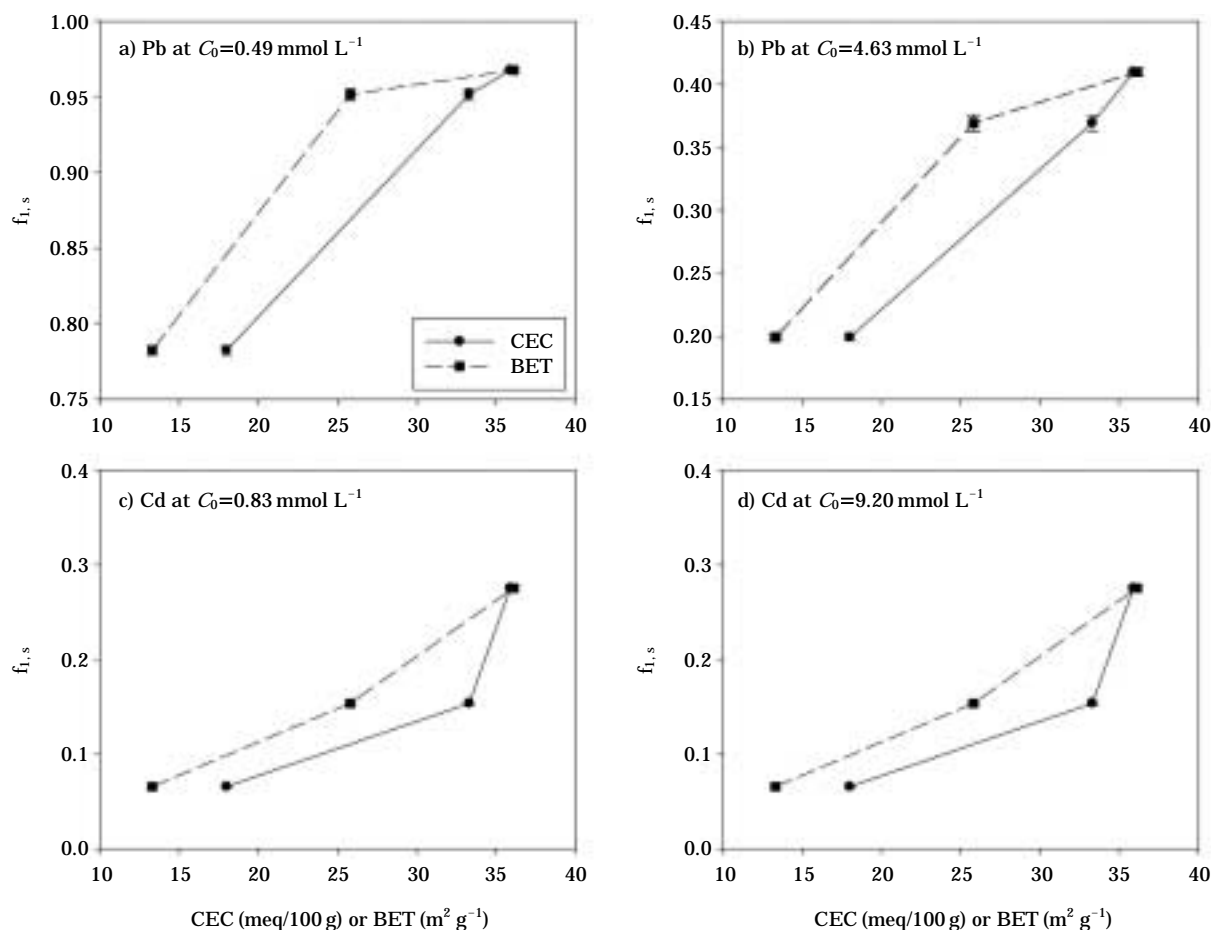


Fig. 5. The relationship between fast sorption fraction ($f_{1,s}$) of TCFOKM and CEC or surface area of the sediments.

stency was found at $C_0 = 4.63$. Different tendency was observed for Cd; $k_{1,s}$ decreased with CEC and BET surface area at $C_0 = 0.49$ mmol L⁻¹ and no consistency was found at $C_0 = 9.20$ mmol L⁻¹. The first-order rate constants in the fast (k_1) and slow (k_2) compartments were found to 10^{0.1}-10^{1.0} hr⁻¹ and 10⁻²-10⁻⁴ hr⁻¹, respectively.

The precision of estimated k_2 is only good when experiments were conducted to near the time of $1/k_2$ (approximately 10,000 hours). An extension of time frame to 10,000 hours would be unrealistic for the sorption of heavy metals in sediments used in this study because most of the fast sorption fraction was sorbed within three hours. Therefore, the precision of k_2 values obtained in this study may be unsatisfactory and only an order of magnitude estimate is useful in interpreting the time frame for the sorption in the slow compartment. However, precision of k_1 in this study would be useful since the time frame in the

fast compartment is 10^{0.1}-10^{1.0} hr (i.e., $1/k_1$).

CONCLUSIONS

One-site mass transfer model (OSMTM), pseudo-first-order kinetic model (PFOKM), pseudo-second order kinetic model (PSOKM) and two compartment first-order kinetic model (TCFOKM) were used to analyze sorption kinetics of Pb and Cd in natural sediments. The PFOKM and PSOKM applicable to desorption kinetics were derived in this work. As expected, the three-parameter TCFOKM was better than two-parameter OSMTM, PFOKM and PSOKM in describing sorption kinetics due to the number of model parameters involved (i.e., three vs. two). Based on the results, following conclusions are reached.

Sorption affinity of Pb was higher than Cd in

all sediments. All models predicted that apparent sorption equilibria were reached within the first 3 hours, followed by a slow sorption over 48 hours of sorption period. At the apparent equilibrium, both the sorbed amount ($q_{e,s}$) of Pb and Cd increased as the CEC and surface area of the sediments increased, regardless of initial spiking concentration (C_0), and heavy metal and the sediment type. The sediment with a higher CEC and surface area had a higher sorbed amount after sorption equilibria, respectively.

The sorption rate constant (k_s) in OSMTM increased as the CEC and surface area increased. The rate constant of pseudo-first-order sorption ($k_{p1,s}$) in PFOKM were not correlated with the sediment characteristics such as CEC and surface area. The rate constant of pseudo-second-order sorption ($k_{p2,s}$) and the initial sorption rate ($v_{0,s}$, $\text{mg g}^{-1} \text{hr}^{-1}$) in PSOKM were also not correlated with the sediment characteristics. The results indicate that PFOKM and PSOKM may not be applicable for modeling sorption kinetics of heavy metals onto sediments. The fast sorption fraction ($f_{1,s}$) in TCFOKM increased as CEC and BET surface increased regardless of initial aqueous phase concentrations. The sorption rate constant of fast fraction ($k_{1,s}=10^{0.1}-10^{1.0} \text{ hr}^{-1}$) was much greater than that of slow sorption fraction ($k_{2,s}=10^{-2}-10^{-4} \text{ hr}^{-1}$) respectively.

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< 국문적요 >

퇴적물에서의 납과 카드뮴의 흡착 동력학 모델링

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본 연구에서는 pH 5.5에서 연안퇴적물내 납과 카드뮴의 흡착 동력학을 실험실규모의 회분식 반응을 이용하여 조사하였다. 4종류의 모델: 단일영역 물질전달모델 (one-site mass transfer model, OSMTM), 겔보기 1차속도모델 (pseudo-first-order kinetic model, PFOKM), 겔보기 2차속도모델 (pseudo-second-order kinetic model, PSOKM)과 두영역 1차속도모델 (two compartment first-order kinetic model, TCFOKM)을 사용하여 흡착속도를 분석하였다. 관련된 모델매개변수의 수에서 기대되듯이 변수가 3개인 TCFOKM이 변수가 2개인 OSMTM, PFOKM, PSOKM 보다 흡착속도를 더 잘 표현할 수 있었다. 납과 카드뮴의 대부분의 흡착은 초기 3시간 이내에 빠르게 완료되었으며, 이후 기간 동안은 느린 흡착이 이루어졌다. 모든 모델에서 겔보기 흡착평형농도 ($q_{e,s}$)는 퇴적물의 양이온 교환능 (CEC)과 표면적이 증가함에 따라 증가하는 것으로 예측되었으며, 이는 초기 중금속 투여 농도와 중금속 및 퇴적물의 형태와 무관하였다. OSMTM에서의 흡착속도 상수 (k_s , hr⁻¹)는 퇴적물의 CEC와 표면적이 증가함에 따라 증가하였다. PFOKM의 겔보기 1차흡착속도상수 ($k_{p1,s}$, hr⁻¹)는 퇴적물의 특성과 관련이 없었다. PSOM 분석결과 겔보기 2차흡착속도상수 ($k_{p2,s}$, g mmol⁻¹ hr⁻¹)와 초기흡착속도 ($v_{0,s}$, mg g⁻¹ hr⁻¹)는 퇴적물의 특성과 연관되지 않았다. TCFOKM의 빠른 흡착영역의 분율 (f_1)은 수용액상의 초기농도와는 무관하게 퇴적물의 CEC와 표면적이 증가함에 따라 증가하였다. 빠른 부분에서의 흡착속도 상수 ($k_{1,s}=10^{0.1}-10^{1.0}$ hr⁻¹)는 느린 부분에서의 흡착속도 상수 ($k_{2,s}=10^{-2}-10^{-4}$ hr⁻¹) 보다 훨씬 더 큰 것으로 나타났다.