



## Competitive sorption of lead and cadmium onto sediments

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### ABSTRACT

Single- and bi-solute competitive sorptions of Pb and Cd onto sediments were investigated. In single-solute sorption, Khan model was fitting better than the other models such as Freundlich, Langmuir, Dubinin–Radushkevich, Sips, Redlich–Peterson and Kargi–Ozmihi models. In bi-solute sorption, competition between the solutes reduced the sorbed amount of each solute compared with that in the single-solute system. Langmuir model parameters for single-solute ( $q_{mL}$  and  $b_L$ ) and bi-solute ( $q_{mL}^*$  and  $b_L^*$ ) competitive sorptions were compared. Sediment with higher pH, CEC and BET surface area had higher maximum sorption capacity ( $q_{mL}$ ). In all sediments, maximum sorption capacity ( $q_{mL}$ ) of Pb was higher than that of Cd, and the presence of both metals reduced the tendency to be sorbed although Cd sorption was more affected than Pb. The  $b_L^*$  values of Pb decreased while those of Cd increased indicating that competition for sorption sites promotes the retention of Cd on more specific sorption sites. The competitive Langmuir model (CLM) and ideal adsorbed solution theory (IAST) coupled to the single-solute sorption models predicted Pb sorption in bi-solute competitive sorption favorably but not Cd sorption.

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### 1. Introduction

Lead and cadmium from anthropogenic sources have been one of the most significant problems because of their toxicity, persistence, and non-biodegradable nature [1]. These metals are particularly toxic to higher animals, producing kidney and blood diseases among other health disorders [2]. Lead and cadmium can be sorbed onto sediments and released again under certain conditions. Therefore, sediments have become the main sink and source of heavy metals like Pb and Cd in river and marine environment. The physico-chemical characteristics of the sediments, such as the amount of organic and inorganic matter, redox potential, pH, and oxygen, affect the mobility of sediment-bound metals [3].

Heavy metals such as Pb and Cd in aquatic systems are easily sorbed on sediments. The metal sorption depends on the sediment characteristics, characteristics of involved metals, and their competition for sorption sites on sediments, which are affected by pH. Christensen [4] reported that the sorption capacity of soils and sediments for Cd increased two to three times for a pH increase of one unit and the sorption for Cd was predominant process at pH 6. The sorption intensity and capacity of sediments for metals are also affected by a variety of sediments substrates such as clay, metal oxides, and organic compounds while the composition and

structure of natural sediments are extremely site-specific [5]. The heavy metals are distributed among the different components of sediments in real environments and variations in the chemical composition of sediments may further affect the partitioning of metals into sorbent [6]. In several studies, Pb, Cu and Cr are more strongly retained in soils and minerals than Zn, Ni and Cd in competitive sorption conditions [7–13]. For sediments, however, little information for competitive sorption is available [14]. Although some researchers reported that Pb sorption onto sediments was higher than Cd under the competitive conditions [3,15–17], further studies are needed to provide more valuable information on competitive sorption mechanisms in sediments.

The competitive sorption model can simulate the sorption process of metals at particle surfaces if sorption is the major process under unsaturated condition [18]. The ideal adsorbed solution theory (IAST) has the advantages that no mixture data are required and no restriction exists for the type of pure-component isotherm equation [19], but IAST can make erroneous predictions caused by a large difference in molecular size and adsorbent heterogeneity [20]. To overcome this drawback, many studies on IAST have been carried out [10,21–25]. Although several thermodynamic competitive sorption models such as ideal adsorbed solution theory (IAST) and competitive Langmuir model (CLM) have been used for understanding and predicting competitive sorption of multi-solutes, little information is currently available for sediments.

In this paper, single- and bi-solute sorption experiments of Pb and Cd onto natural sediments with different characteristics were carried out in a batch-type adsorber. Single-solute sorption data were analyzed using several sorption models: Freundlich,

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## Nomenclature

|                      |   |
|----------------------|---|
| $b_K$                | Khan model constant (L/mmol)  |
| $b_L$                | Langmuir model constant (L/mmol)  |
| $b_{L,i}$            | Langmuir model constant for solute $i$ (L/mmol)   |
| $b_R$                | Redlich–Peterson model constant (L/mmol) <sup><math>N_R</math></sup>  |
| $b_S$                | Sips model constant (L/mmol)  |
| $C$                  | aqueous-phase equilibrium concentration (mmol/L)  |
| $C_{m,i}$            | aqueous-phase equilibrium concentration of a solute $i$ in a mixture (mmol/L)                                   |
| $C_i^*$              | equilibrium concentration of a solute $i$ sorbed singly at the same condition as a mixture (mmol/L)             |
| CLM                  | competitive Langmuir model  |
| $E$                  | mean free energy (J/mol) in Dubinin–Radushkevich model  |
| IAST                 | ideal adsorbed solution theory  |
| $K_F$                | Freundlich sorption coefficient (mmol/g)/(mmol/L) <sup><math>N_F</math></sup>                                   |
| $K_G$                | Kargi–Ozmihiç saturation constant (mmol/L)  |
| $N$                  | total number of solutes in a mixture  |
| $N_F$                | exponent in Freundlich model  |
| $N_G$                | exponent in Kargi–Ozmihiç model   |
| $N_K$                | exponent in Khan model  |
| $N_R$                | exponent in Redlich–Peterson model  |
| $N_S$                | exponent in Sips model  |
| $q$                  | solid-phase equilibrium concentration (mmol/g)  |
| $q_i^*$              | solid-phase equilibrium concentration of a solute $i$ sorbed singly at the same condition as a mixture (mmol/L) |
| $q_{m,i}$            | solid-phase equilibrium concentration of a solute $i$ in an sorbent (mmol/g)                                    |
| $q_{mD}$             | maximum sorption capacity in Dubinin–Radushkevich model (mmol/g)  |
| $q_{mG}$             | maximum sorption capacity in Kargi–Ozmihiç model (mmol/g)   |
| $q_{mK}$             | maximum sorption capacity in Khan model (mmol/g)  |
| $q_{mL}$             | maximum sorption capacity in Langmuir model (mmol/g)  |
| $q_{mL,i}$           | maximum sorption capacity for solute $i$ in Langmuir model (mmol/g)   |
| $q_{mR}$             | maximum sorption capacity in Redlich–Peterson model (mmol/g)  |
| $q_{mS}$             | maximum sorption capacity in Sips model (mmol/g)  |
| $q_T$                | total sorbed concentration of all solute in the mixture (mmol/g)  |
| $R$                  | gas constant, 8.314 (J/mole/K)  |
| SSE                  | sum of square errors  |
| $T$                  | absolute temperature (K)  |
| $V$                  | solution volume (L)   |
| $W$                  | sorbent weight (g)  |
| $z_i$                | mole fraction of solute $i$ in the sorbed phase   |
| <i>Greek letters</i> |   |
| $\beta$              | Dubinin–Radushkevich model parameter (mol <sup>2</sup> /J <sup>2</sup> )  |
| $\varepsilon$        | Polanyi potential (J/mol)   |

Langmuir, Dubinin–Radushkevich, Sips, Redlich–Peterson, Kargi–Ozmihiç and Khan models. Langmuir model parameters for single- ( $q_{mL}$  and  $b_L$ ) and bi-solute ( $q_{mL}^*$  and  $b_L^*$ ) competitive sorptions were compared to analyze the effect of competition. Bi-solute competitive sorption data were compared with the predictions from the competitive Langmuir model (CLM) and the ideal adsorbed solution theory (IAST) coupled to the single-solute sorption models.

## 2. Materials and methods

### 2.1. Materials

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. Organic carbon content was determined by an elemental analyzer (Fisons, EA 1110/EA1108) after removal of inorganic carbon. Cation exchange capacity (CEC) was determined by the Sodium Acetate Method (U.S. EPA Method 9081) [26]. The mineralogical compositions of the sediments were identified by an X-ray diffractometer (Rigaku, D/Max-IC) (Fig. 1 and Table 1). The background concentrations of Pb and Cd in the sediment were measured by microwave acid digestion (U.S. EPA Method 3051) [27]. Sediment samples (1.0 g) were digested with 2 mL of HNO<sub>3</sub> (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 digest was carried out in the same way. The concentrations of extracted Pb and Cd were determined by ICP-OES (Perkin Elmer Co., 2100DV).

Lead and cadmium solutions were prepared using Pb(NO<sub>3</sub>)<sub>2</sub> (Aldrich Chemical Co., <98%) and Cd(NO<sub>3</sub>)<sub>2</sub> (Kanto Chemical Co., <98%) and the background solution consisted of a mixture of NaNO<sub>3</sub> (Kanto Chemical Co., <98%) and MES (2-[N-morpholino]ethanesulfonic acid hydrate, Aldrich Chemical Co., 99.5%) buffer. The effect of carbon dioxide was eliminated by minimizing the head space of the vials. Brunauer–Emmett–Teller (BET) surface area was determined by specific surface area analyzer (Micromeritics, ASAP-2010). Point of zero charge of sediment was determined by potentiometric titration.

### 2.2. Single- and bi-solute sorption of Pb and Cd onto the sediments

Single-solute sorption experiments were conducted at 25 °C in 50 mL polycarbonate vials (Nalgene Co.). 1.0 g of sediment was transferred into the vial before the addition of heavy metal solutions. To investigate the effect of pH on sorption, pH values of the sediments were adjusted to 2–10 with HNO<sub>3</sub> and NaOH. The vials containing 1.0 g of the sediment each were filled with approximately 50 mL of 2 mM of Pb and Cd solutions at varying pH values. Other than the pH edge experiment, two different pHs (available under natural conditions) were tested because aqueous pH can affect metal sorption. The pH values of the sediments were adjusted to 4.5 or 5.5 by using MES buffer solution (heavy metal free) before all experiments. The vials containing 1.0 g of the sediment each were filled with approximately 50 mL of chemical stock solutions minimizing headspace and then mixed at 10 rpm in a tumbler at 25 °C. The exact amount of the stock solution added was determined gravimetrically. To obtain sorption isotherms, six different initial concentrations of each heavy metal (Pb: 0.24, 1.45, 2.89, 4.34, 5.79 and 7.72 mM; Cd: 0.44, 3.56, 7.12, 10.68, 14.23 and 17.79 mM) were used. The pH values of the heavy metal solutions were also controlled at 4.5 or 5.5 using 0.05 M MES buffer and 0.01 M NaNO<sub>3</sub> was added as a background electrolyte. Variation in pH was less than ± 0.05 units. Experiments with this buffer in solutions of

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