

Adsorption Kinetics of Lead and Zinc Ions by Coffee Residues

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Abstract

Untreated coffee residues (UCRs) were used to remove heavy metal ions from aqueous solutions. The effects of solution pH, heavy metal ions, and UCR concentrations on heavy metal ion removal by UCRs were determined. The removal percentage for heavy metal ions increased as pH and UCR doses increased; conversely, it decreased as the concentration of heavy metal ions increased. This study employed the pseudo first- and second-order kinetics models, the intraparticle diffusion model, and the Bangham model to simulate adsorption kinetics of Pb²⁺ and Zn²⁺ onto UCRs. Simulation results indicate that adsorption kinetics fit well with the pseudo second-order model. After reaction for 180 min at [adsorbate] = 20 mg/L, [UCRs] = 2 g/L, and pH 5, the adsorption percentage of Pb²⁺ and Zn²⁺ was 96% and 44%, respectively; moreover, the adsorption density of Pb²⁺ and Zn²⁺ onto UCRs was 9.7 and 4.4 mg/g (4.7×10^{-2} and 6.8×10^{-2} mmol/g), respectively. The adsorption of Pb²⁺ and Zn²⁺ onto UCRs is controlled mainly by surface diffusion.

Keywords: adsorption, coffee residues, kinetics

Introduction

Mining, electroplating, and metal processing are the main sources of heavy metal contamination. Metals such as lead, arsenic, chromium, mercury, copper, and zinc have been characterized as hazardous heavy metals. Due to their hazardous effects, persistency, and tendency to accumulate, effective removal of heavy metal ions from wastewater is an important issue.

Various agricultural by-products have been used to remove heavy metals from solutions. Using waste materials as low-cost adsorbents is attractive as it reduces costs for their disposal. Several studies have employed low-cost adsorbents such as orange peels [1], coffee husks [2], cof-

fee residues/clay [3], coffee grounds [4, 5], sugar beet pulp [6], tea leaves [4, 7], rice hulls [8], γ -Al₂O₃ [9], Fe(OH)₃ [10], and black gram husks [11] to remove Zn²⁺ from aquatic solutions. Additionally, Pb²⁺ has been removed from solutions by coffee residues/clay [3], coffee grounds [4, 5, 12], sugar beet pulp [6], tea leaves [4, 7, 13], rice husk ash [14], grape stalks [15], treated human hair [16], and black gram husks [11]. The adsorption kinetics of Cu²⁺ [2, 17], Ni²⁺ [17], Cd²⁺ [2, 18], Pb²⁺ [12], Zn²⁺ [2], and Cr⁶⁺ [2] were reported for adsorption onto coffee residues. However, only pseudo first- and second-order models were tested for adsorption kinetics in these investigations. Generally, an adsorption process can be characterized as three stages:

- (i) external diffusion or boundary-layer diffusion,
- (ii) intraparticle mass diffusion,
- (iii) adsorption on interior sites.

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Table 1. Kinetic parameters for the removal of Pb²⁺ and Zn²⁺ by UCRs (T = 25°C).

Pseudo first-order model	q _{e, exp} (mg/g)	k ₁ (1/min)	q _{e, cal} (mg/g)	R ²
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	9.7	6.7×10 ⁻³	5.3	0.977
	(4.7×10 ⁻²)		(2.6×10 ⁻²)	
[Pb ²⁺] = 80 mg/L, [UCRs] = 2 g/L, pH = 5	25.5	1.9×10 ⁻²	22.8	0.994
	(1.2×10 ⁻¹)		(1.1×10 ⁻¹)	
[Pb ²⁺] = 20 mg/L, [UCRs] = 1 g/L, pH = 5	13.3	1.3×10 ⁻²	10.4	0.997
	(6.4×10 ⁻²)		(5.0×10 ⁻²)	
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 3	6.9	1.6×10 ⁻²	6.0	0.999
	(3.3×10 ⁻²)		(2.9×10 ⁻²)	
[Zn ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	4.4	1.8×10 ⁻²	3.9	0.949
	(6.8×10 ⁻²)		(6.0×10 ⁻²)	
Pseudo second-order model	q _{e, exp} (mg/g)	k ₂ (g/mg.min)	q _{e, cal} (mg/g)	R ²
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	9.7	9.7×10 ⁻³	9.5	0.990
	(4.7×10 ⁻²)		(4.6×10 ⁻²)	
[Pb ²⁺] = 80 mg/L, [UCRs] = 2 g/L, pH = 5	25.5	9.5×10 ⁻⁴	26.3	0.993
	(1.2×10 ⁻¹)		(1.3×10 ⁻¹)	
[Pb ²⁺] = 20 mg/L, [UCRs] = 1 g/L, pH = 5	13.3	1.0×10 ⁻²	12.0	0.994
	(6.4×10 ⁻²)		(5.8×10 ⁻²)	
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 3	6.9	1.1×10 ⁻²	6.8	0.997
	(3.3×10 ⁻²)		(3.3×10 ⁻²)	
[Zn ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	4.4	2.1×10 ⁻²	4.6	0.999
	(6.8×10 ⁻²)		(7.0×10 ⁻²)	
Intraparticle diffusion model	k _i (mg/g.min ^{0.5})		C (mg/g)	R ²
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	1.44		5.35	0.926
[Pb ²⁺] = 80 mg/L, [UCRs] = 2 g/L, pH = 5	14.2		-5.70	0.973
[Pb ²⁺] = 20 mg/L, [UCRs] = 1 g/L, pH = 5	2.97		4.79	0.989
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 3	3.25		-0.38	0.992
[Zn ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	1.60		0.87	0.980
Bangham model	α		k ₀ (l/(mg.l))	R ²
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	0.17		7.8×10 ⁻²	0.924
[Pb ²⁺] = 80 mg/L, [UCRs] = 2 g/L, pH = 5	0.43		1.1×10 ⁻²	0.962
[Pb ²⁺] = 20 mg/L, [UCRs] = 1 g/L, pH = 5	0.29		1.9×10 ⁻²	0.922
[Pb ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 3	0.32		2.0×10 ⁻²	0.995
[Zn ²⁺] = 20 mg/L, [UCRs] = 2 g/L, pH = 5	0.27		1.5×10 ⁻²	0.951

(): value in mmol/g

However, pseudo first- and second-order models cannot apply to fit the experimental results to examine the mechanism of adsorption of heavy metals onto adsorbents. Moreover, no study has clearly provided kinetics model analyses of adsorption of Pb²⁺ and Zn²⁺ onto untreated coffee residues (UCRs). Hence, this work applied pseudo first- and second-order models, the intraparticle diffusion model,

and the Bangham model to simulate the adsorption kinetics of Pb²⁺ and Zn²⁺ onto UCRs. Study objectives were:

- (i) to assess the effectiveness of Pb²⁺ and Zn²⁺ removal while varying solution pH, heavy metal ion concentrations, and UCRs concentrations;
- (ii) to provide parameters and adsorption-controlled mechanism for adsorption kinetics of Pb²⁺ and Zn²⁺ onto UCRs.

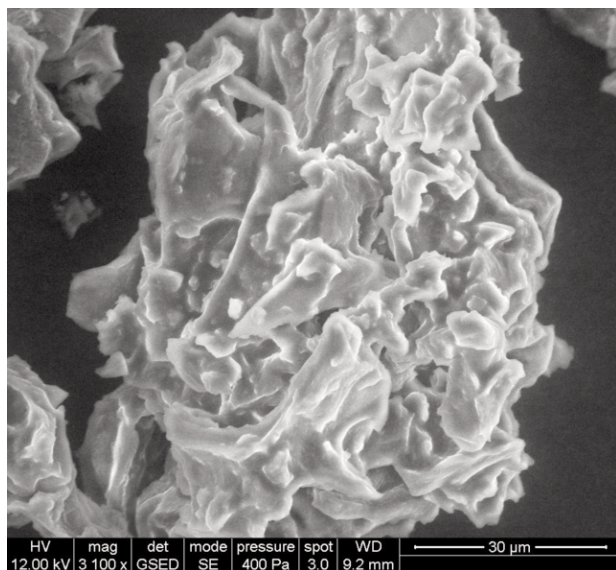


Fig. 1. SEM micrograph of UCRs.

Materials and Methods

Materials

The UCRs were obtained from a local manufacturer after steam extraction from coffee grounds for the manufacture of instant coffee. The UCRs were dried at 50°C for 48 h and then passed through a 100-mesh sieve. The $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, HNO_3 , and NaOH were purchased from Merck. Solution pH was adjusted by adding HNO_3 and NaOH . All compounds were used as received and all solutions were prepared using Milli-Q deionized water and reagent-grade chemicals.

Experimental Methods

The morphology of UCRs was examined by scanning electron microscopy (SEM) (JEOL JSM-6500F, Japan), the specific surface area was determined by the BET method with a surface area analyzer (ASAP 2010; Micromeritics, USA), and surface potential was assessed by a Zeta-Meter 3.0 (Zeta-Meter, Inc., USA).

All adsorption experiments were conducted in a closed 250 mL pyramidal glass bottle. Adsorption was determined over 3 h at 25°C. Initial pH was 5.0 in all adsorption experiments, except for experiments assessing the effect of pH. In total, 0.4 g UCRs were placed in a bottle containing 200 mL heavy metal solution at 20 mg/L, and the bottle was then shaken at 100 rpm. The effect of heavy metal concentration on heavy metal removal by UCRs was investigated by using heavy metal concentrations of 20 and 80 mg/L at $[\text{UCRs}] = 2 \text{ g/L}$. The effect of UCR dosage on heavy metal removal was studied at UCR concentrations of 1 and 2 g/L at $[\text{heavy metal}] = 20 \text{ mg/L}$. The effect of pH on heavy metal removal by UCRs was studied with initial pH values of 3 and 5 at $[\text{heavy metal}] = 20 \text{ mg/L}$ and $[\text{UCRs}] = 2 \text{ g/L}$. Suspended particles were separated by filtration through a 0.22 μm filter (Millipore). Heavy metal concentrations

before and after adsorption were measured by an atomic absorption spectrophotometer (Perkin Elmer 3300, USA). All adsorption experiments were performed in triplicate and means are reported.

Results and Discussion

Surface Properties of UCRs

Fig. 1 presents an SEM micrograph of UCRs, shows a surface morphology comprised of plates, likely with a small specific surface area. The specific surface area of UCRs was 0.19 m^2/g . This experimental result was similar to those obtained by Boonamnuyvitaya et al. [3] and Kyzas et al. [19], both of whom also reported that the surface area of UCRs was small. The surface potential of UCRs at pH 3 and 5 was 21 and -25 mV, respectively. These surface potentials were the same as those acquired by Franca et al. [20] and Kyzas et al. [19]. The pH_{zpc} of UCRs was 3.9. At $[\text{adsorbate}] = 20 \text{ mg/L}$, Pb^{2+} and Zn^{2+} precipitated to $\text{Pb}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ at pH 8.9 and 7.1, respectively. Accordingly, $\text{Pb}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ were not formed.

Effects of Heavy Metal Concentration, UCRs Dosage, and Solution pH on Adsorption

Fig. 2 presents the effects of Pb^{2+} concentration, UCR dosage, and solution pH on adsorption of Pb^{2+} by UCRs. Fig. 3 shows the effects of the Zn^{2+} concentration, UCR dosage, and solution pH on adsorption of Zn^{2+} by UCRs. After reaction for 180 min at $[\text{heavy metal}] = 20 \text{ mg/L}$, $[\text{UCRs}] = 2 \text{ g/L}$, and pH 5, the adsorption percentage of Pb^{2+} and Zn^{2+} was 96% and 44%, respectively; moreover, the adsorption density of Pb^{2+} and Zn^{2+} onto UCRs was 9.7 and 4.4 mg/g (4.7×10^{-2} and $6.8 \times 10^{-2} \text{ mmol/g}$), respectively. Both removal percentages for Pb^{2+} and Zn^{2+} increased as pH and UCR dose increased; conversely, they decreased as the Pb^{2+} and Zn^{2+} concentrations increased. Increasing the UCR dosage increased heavy metal adsorption. These experimental results were expected because as the UCR dose increased, the number of adsorption sites increased and the amount of adsorbate attached increased. At pH 5 the surface charge of UCRs was negative; conversely, it was positive at pH 3. Hence, the heavy metal removal percentage at pH 3 was lower than that at pH 5 because of electrical repulsion between cations and the positively charged surfaces of UCRs. Adsorption rate was rapid in the first 40 min of the reaction and then slowed; that is, the surface sites of UCRs were initially vacant and the heavy metal concentration gradient was relatively high. This rapid adsorption may be characterized as passive uptake through physical adsorption or adsorbent surface ion exchange [1, 21]. The amount of heavy metal adsorbed per unit mass of UCRs ($q_{\text{e, exp}}$) increased as pH and the heavy metal concentration increased; conversely, it decreased as UCR dosage increased (Table 1). This decrease in unit adsorption as the adsorbent dose increases was due to a large number of

adsorption sites remaining unsaturated during the adsorption process. Several studies have also shown that unit adsorption capacity decreased as adsorbent dosage increased [22-24]. This study found that the adsorption percentage and adsorption density ($q_{e, \text{exp}}$) of Pb^{2+} was higher than that of Zn^{2+} under the same experimental conditions, suggesting that the affinity of Pb^{2+} for UCRs exceeded that of Zn^{2+} .

Analyses of Adsorption Kinetics

Adsorption kinetics, which indicates the adsorption rate, is an important characteristic of adsorbents. The pseu-

do first- and second-order models, the intraparticle diffusion model, and the Bangham model were adopted to test experimental data and thereby elucidate the kinetics of the adsorption process. The pseudo first-order model can be expressed as:

$$\ln(q_e - q) = \ln(q_e) - k_1 t \quad (1)$$

...where q_e and q are the amounts of heavy metals adsorbed onto UCRs at equilibrium and at various times t (mg/g), respectively, and k_1 is the rate constant of the pseudo first-order model of adsorption (1/min) [25]. The values of q_e

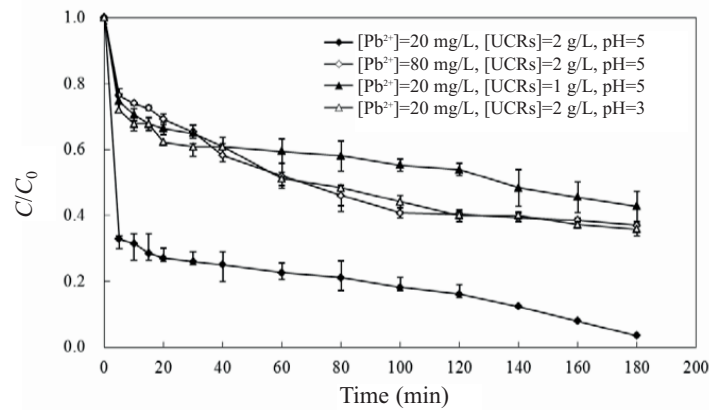


Fig. 2. Removal of Pb^{2+} according to Pb^{2+} concentration, UCR dose, and solution pH.

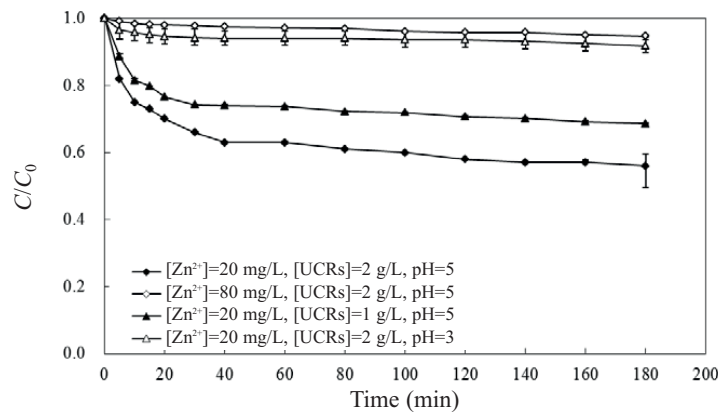


Fig. 3. Removal of Zn^{2+} according to Zn^{2+} concentration, UCR dose, and solution pH.

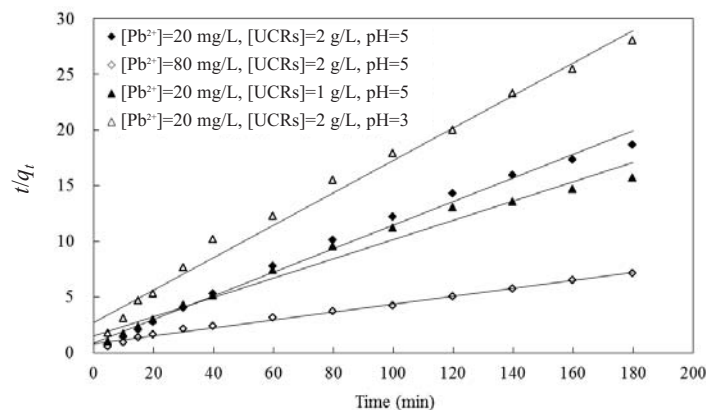


Fig. 4. Pseudo second-order adsorption kinetic plots of Pb^{2+} onto UCRs.

Table 2. Calculations of the sum of the absolute errors for different models ([UCRs] = 2 g/L, [adsorbate] = 20 mg/L and pH = 5).

SAE	Pb ²⁺	Zn ²⁺
Pseudo first-order model	3.89	1.78
Pseudo second-order model	0.44	1.38
Intraparticle diffusion model	74.94	45.39
Bangham model	4.50	5.35

and k_1 can be derived from the intercept and slope of the linear plot of $\ln(q_e - q)$ versus t , respectively. The pseudo second-order model is:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

...where q_e and q are the amounts of heavy metals adsorbed onto UCRs at equilibrium and at various times t (mg/g), respectively, and k_2 is the rate constant of the pseudo second-order model for adsorption (g/mg·min) [26, 27]. The slope and intercept of the linear plot of t/q as a function of t yielded the values of q_e and k_2 , respectively. The adsorption process on porous adsorbents generally has four sequential stages: bulk diffusion, film diffusion, intraparticle diffusion, and adsorption of the adsorbate onto the surface of the adsorbent. Typically, bulk diffusion and adsorption are assumed to be rapid and, therefore, not rate determining. Since neither the pseudo first-order nor the second-order model can identify the diffusion mechanism, kinetic results were analyzed using the intraparticle diffusion model to elucidate the diffusion mechanism. For the intraparticle diffusion model, film diffusion was negligible and intraparticle diffusion was the only rate-controlling step. The intraparticle diffusion model is expressed as:

$$q = k_i t^{1/2} + C \tag{3}$$

...where C is the intercept and k_i is the intraparticle diffusion rate constant (mg/g·min^{0.5}), which can be determined from

the slope of the linear plot of q versus $t^{1/2}$ [25]. Kinetic data were further utilized in this adsorption system based on the Bangham model [25]:

$$\log \log \left(\frac{C_0}{C_0 - qm} \right) = \log \left(\frac{k_0 m}{2.303V} \right) + \alpha \log(t) \tag{4}$$

...where q and t are defined in the pseudo first-order model, C_0 is the initial heavy metal concentration in the solution (mg/L), V is solution volume (mL), m is the mass of UCRs per liter of solution (g/L), and k_0 and α are constants.

The validity of these models was assessed by calculating the sum of absolute errors (SAE) using Eq. (5):

$$SAE = \sum_{i=1}^N |q_{e,cal} - q_{e,means}|_i \tag{5}$$

...where subscripts “means” and “cal” denote experimental and calculated values, and N is the number of data points.

Figs. 4 and 5 show the pseudo second-order adsorption kinetic plots of Pb²⁺ and Zn²⁺ onto UCRs, respectively. Table 1 presents the kinetic parameters for the removal of Pb²⁺ and Zn²⁺ by UCRs and Table 2 lists the sum of absolute errors for different models. For both the Pb²⁺ and Zn²⁺ adsorption processes, the calculated SAE values of the pseudo second-order model were smallest. Additionally, the q value ($q_{e,cal}$) derived from the pseudo second-order model was in agreement with experimental q values ($q_{e,exp}$), suggesting that the pseudo second-order model best represents adsorption kinetics (Table 1). Various researchers also have reported that adsorption kinetics followed the pseudo second-order model [18, 24, 28]. When the regression of q versus $t^{1/2}$ is linear and passes through the origin, intraparticle diffusion is the sole rate-limiting step [25]. Although regression was linear, the plot did not pass through the origin (Table 1), indicating that adsorption merely involved intraparticle diffusion; that is, intraparticle diffusion was not the only rate-controlling step and other kinetic mechanisms controlled the adsorption rate. The double logarithmic plot using the Bangham equation yielded a good linear ($R^2 > 0.92$) for the removal of Pb²⁺ and Zn²⁺ by UCRs, indicating that the diffusion of heavy metal into UCR pores is not the only rate-controlling step [29]. Akkaya et al. [30]

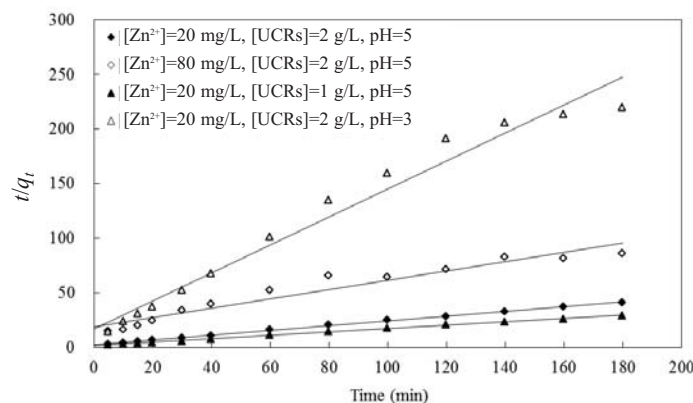


Fig. 5. Pseudo second-order adsorption kinetic plots of Zn²⁺ onto UCRs.

demonstrated that pore diffusion and surface diffusion are simultaneous within an adsorbent particle. Since the BET surface area of UCRs is very small, study results suggest that adsorption kinetics were controlled mainly by surface diffusion.

Comparisons of Pb²⁺ and Zn²⁺

The hydration enthalpy of metal ions can be applied to assess the theoretical affinity of metal ions for adsorbents. Hydration enthalpy corresponds to the energy that permits detachment of water molecules from metal ions and also reflects the ease with which one ion interacts with a ligand located on the surface of UCRs. As the hydration of a metal ion increases, the strength of metal hydration increases, such that the likelihood that the metal ion will interact with a ligand declines [31]. Martin-Dupont et al. [31] indicated the hydration enthalpy of Pb²⁺ and Zn²⁺ was -1481 and -2046 kJ/mol, respectively; accordingly, the theoretical affinity of Pb²⁺ and Zn²⁺ for a ligand follows the order Pb²⁺ > Zn²⁺. The theoretical affinity order is in agreement with experimental results and those of several previous studies [3, 5, 6, 31], which also found that the adsorption affinity of Pb²⁺ was greater than that of Zn²⁺ for biosorbents.

Conclusions

The adsorption kinetics of Pb²⁺ and Zn²⁺ onto UCRs were examined. Metal ions adsorbed per unit mass of UCRs increased as pH and the concentration of metal ions increased; conversely, it decreased as the UCR dosage increased. Based on SAE and adsorption density, the pseudo second-order model best represents adsorption kinetics. The adsorption kinetics are controlled mainly by surface diffusion according to analyses of the intraparticle diffusion model and Bangham model. Maximum adsorption onto UCRs followed the order Pb²⁺ > Zn²⁺, which agreed with theoretical analyses for hydration enthalpy of Pb²⁺ and Zn²⁺.

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