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Effect of sorbent concentration on Pb(II) sorption on Mg-Al-EDTA layered double hydroxides

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The sorption of Pb(II) on a Mg-Al-EDTA layered double hydroxide (LDH) sample was investigated at different sorbent concentrations and the sorbent concentration effect (C_s-effect) was observed. The sorption isotherm and kinetic process at a given C_s value can be adequately described by the classic Freundlich model and a pseudo-second-order kinetic equation. However, the classic Freundlich model cannot describe the C_s-effect observed in the studied sorption system. We believe that the C_s-effect can be attributed to the deviation of the real sorption system from an ideal one. It was confirmed that the surface component activity (SCA) model can adequately describe the C_s-effect observed in sorption experiments.

Key words: Pb(II), LDH, Sorbent concentration effect, Surface component activity model.

INTRODUCTION

Pb(II) is a common heavy metal pollutant resulting from both natural and anthropogenic sources. Sorption is the primary technology considered for the treatment of wastewater containing Pb(II) because of its simplicity, low cost, high efficiency and wide adaptability. The layered double hydroxides (LDHs) are a kind of potential sewage treatment agent. From both theoretical and practical aspects, it is essential to understand the sorption process behavior of Pb(II) on LDHs.

The sorbent concentration (C_s) used in the sorption treatment process of wastewater is an important factor influencing the removal efficiency of pollutants from aqueous solutions [1–4]. It has been observed that the pollutant-removal efficiency increases with increasing C_s for a given initial pollutant concentration; however, the sorption capacity of the sorbent decreases [1–4]. This phenomenon is known as the C_s-effect [5–7] and has been observed in numerous laboratories in various solid-liquid systems during sorption equilibrium studies [7–12].

Recently, we developed a surface component activity (SCA) model [13–15] in which the activity coefficient of the solid surface component sorption sites was assumed to be a function of C_s rather than unity because of the deviations in the behavior of a real sorption system from that of an ideal one.

In this study, Mg_2Al-EDTA-LDH was synthesized and the sorption of Pb(II) on this LDH in aqueous solutions was examined at various C_s values. The C_s-effect was studied. Special emphasis was placed on the applicability of the SCA model in describing sorption equilibria and kinetics with the C_s-effect.

MATERIALS AND METHODS

Materials

All chemicals used in this work were of analytical grade. Ultra-pure water was used in all cases.

Mg_2Al-EDTA LDH with a Mg^{2+}/Al^{3+} molar ratio of 2:1 was prepared by co-precipitation. An aqueous solution containing 0.1 mol $Mg(NO_3)_2 \cdot 6H_2O$ and 0.1 mol $Al(NO_3)_3 \cdot 9H_2O$ was dropwise added to distilled water while the solution was stirred. During the synthesis, the temperature was maintained at 65°C and pH at 11-12 by the simultaneous addition of EDTA-Na_2 ammonia solution with EDTA-Na_2/Al molar ratio equal to 1. The reaction mixture was aged in the mother solution at room temperature and then filtered, washed with deionized water until the pH was neutral. The filter cake was further hydrothermally treated at 80°C for 24 h. The sol was dried, triturated and sieved to collect the particles of <74 μm in diameter. Mg_2Al-EDTA LDH was characterized by XRD (Fig. 1).

Sorption experiments

Kinetic experiments of the sorption of Pb(II) on Mg_2Al-EDTA LDH sample were carried out by the following steps. A known mass of Mg_2Al-EDTA LDH sample was dispersed in 250 mL of $Pb(NO_3)_2$ solution. The suspension was stirred at a constant

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speed and maintained at 25±0.2 ℃. Aliquots (5 mL) of the suspension were withdrawn at predetermined time intervals (t) and filtered through a 0.45 μm syringe filter. The remaining Pb(II) concentration of the filtrate was determined by atomic absorption spectrometry (TAS-990, Beijing Purkinje General Instrument Co., Ltd.). The sorbed amount Γ_t was calculated by the following equation:

$$\Gamma_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

where C_0 (mg/L) and C_t (mg/L) are the initial and the remaining concentration, respectively, V (mL) is the volume of the suspension and m (g) is the mass of the LDH sample.

Sorption isotherms of Pb(II) on Mg_2Al-EDTA LDH sample were obtained by the batch equilibration technique [16-18]. Solutions Pb(II) with various concentrations (0-1000 mg/L) of were prepared in 0.01 mol/L $NaNO_3$ with $Pb(NO_3)_2$, and the pH values of the solutions were adjusted to 5.0. Known masses of LDH samples were mixed with Pb(II) solutions of various initial concentrations in polyethylene centrifugal tubes. The centrifugal tubes were put into a thermostated water bath shaker at 25±0.2°C for 24 h. Then the suspensions were centrifuged at a speed of 4000 r/min. The Pb(II) equilibrium concentrations in the supernatants were determined by flame atomic absorption spectrometry. The equilibrium sorbped amounts were calculated using the following equation:

$$\Gamma_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

where C_e (mg/L) is the remaining (equilibrium) concentration.

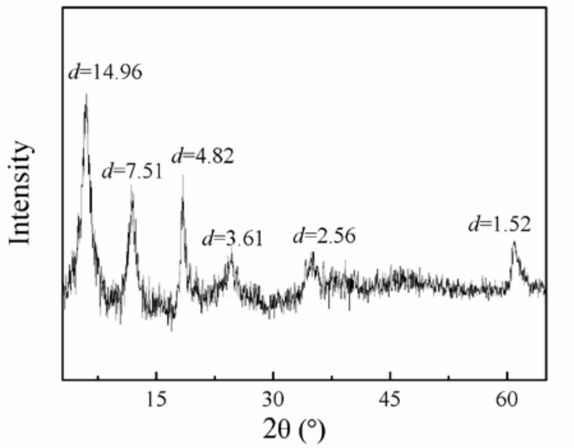

Fig. 1. XRD pattern of the Mg_2Al-EDTA LDH sample

RESULTS AND DISCUSSION

Sorption isotherms

Fig. 2(a) shows the sorption isotherms of Pb(II) on Mg_2Al-EDTA LDH at different LDH concentrations. As can be seen, the sorption isotherms decline significantly as the sorbent concentrations increase. This phenomenon accords with the law which is described by a C_s-effect.

Classical Freundlich equation is represented as:

$$\Gamma_e = K_F C_e^{n_F} \qquad (3)$$

where Γ_e is equilibrium sorption amount, C_e is equilibrium concentration, K_F and n_F are Freundlich constants [19].

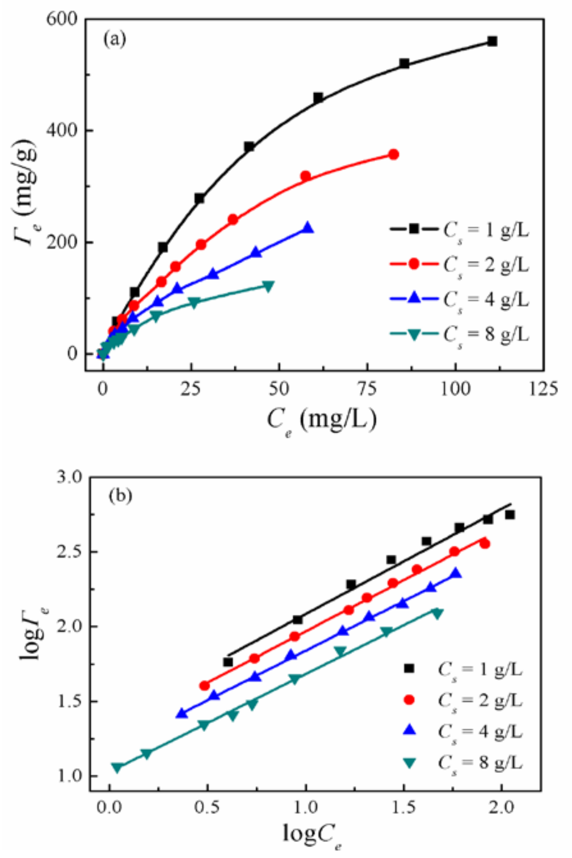

Fig.2. Sorption isotherms (a) and linear correlation plots for the classical Freundlich equation (b) at different sorbent concentrations

Table 1. Parameters of the classical Freundlich equation at different sorbent concentrations

C_s (g/L)	n_F	K_F	R^2
1.0	0.704	24.02	0.980
2.0	0.685	19.24	0.996
4.0	0.663	15.03	0.999
8.0	0.651	10.71	0.995

The sorption data of Pb(II) on Mg_2Al-EDTA LDH were fitted with the Freundlich equation (see Fig.2(b)). It was found that the Freundlich equation can adequately describe the sorption equilibrium for a given C_s value, and all correlation coefficients (R^2) were greater than 0.98. The fitted Freundlich parameters, K_F and n_F, for various C_s values are presented in Table 1. The dependence of the Freundlich parameters on C_s showed that the classical Freundlich model cannot predict the C_s-effect.

Considering the deviation of a real sorption system from an ideal one, we proposed an alternative model, SCA model [13-15]. It suggests that (1) the surface of the sorbent is uniform, that is, all sorption sites are equivalent; (2) all sorption occurs through the same mechanism; (3) at the maximum sorption, only a monolayer is formed; (4) the molecular sizes of solute and solvent are similar; (5) surface component (sorption site or adsorbed solute) activity coefficient is not equal to unity because of the deviation of the real sorption system from an ideal one. A Freundlich-SCA equation can be derived as follows:

$$\Gamma_e = K_S \cdot f^s_{H_2O} \cdot C_e^{n_S} \qquad (4)$$

The coefficients, n_S and K_S, of a given system are independent of sorbent concentration.

The C_s-dependent function of $f^s_{H_2O}$ is in exponential form:

$$f^s_{H_2O} = \exp(-\gamma C_s^{\alpha}) \qquad (5)$$

where γ and α are empirical constants. Then,

$$K_F = K_S \exp(-\gamma C_s^{\alpha}) \qquad (6)$$

Thus, the C_s-dependent function of $f^s_{H_2O}$ can be estimated from the relationship between the experimentally measured K_F values and C_s values.

The change of K_F with C_s for the sorption system was fitted to Eq. (6) using a non-linear least-squares method (Excel Solver) (see Fig. 3), and the best-fit values of the empirical constants, γ and α, are 0.563 and 0.452.

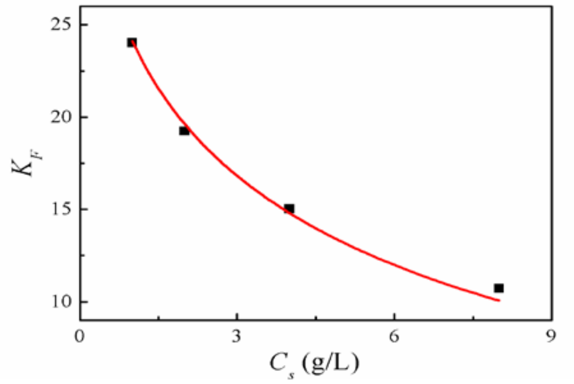

Fig.3. Relationship between K_F and C_s

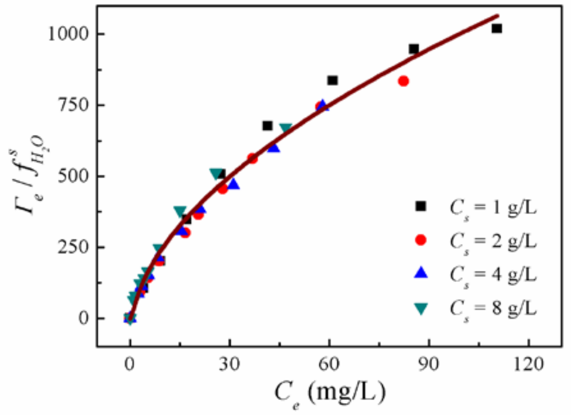

Fig.4. Isotherm plot of the Freundlich-SCA model

Using the simulated γ and α values, the normalized non-linear plot of $\left(\Gamma_e / f^s_{H_2O}\right)$ *vs.* C_e for the studied system was obtained (see Fig. 4). As can be seen, a unique line for various C_s values was obtained. The K_S and n_S values are 52.87 and 0.651. The correlation coefficients (R^2) of the non-linear plot were higher than 0.98, indicating that the Freundlich-SCA equation can adequately describe the C_s-effect observed in the studied system.

Sorption kinetics

Fig. 5 shows the sorption kinetics of Pb(II) on Mg_2Al-EDTA LDH at different LDH concentrations. It is seen that the sorption processes are rapid.

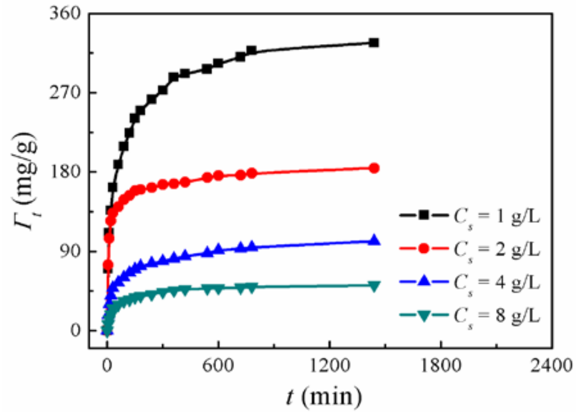

Fig. 5. Sorption kinetics at various sorbent concentrations

The first step involved fast sorption of almost the whole amount of Pb(II) in the solution within a few hours, followed by slower sorption. Pseudo-second-order model can fit the kinetic data for a given C_s value (Fig. 6).

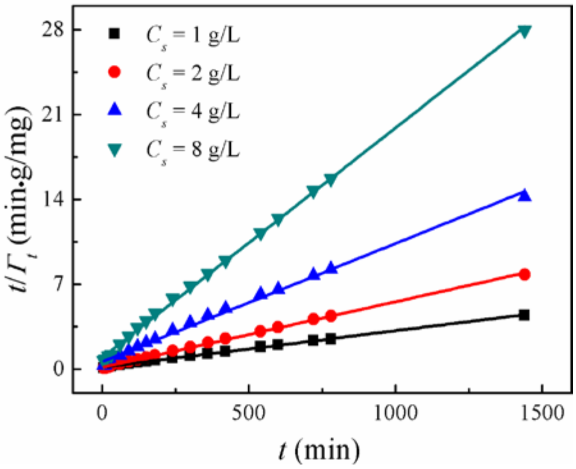

Fig. 6. Pseudo-second-order sorption kinetics

The parameters are listed in Table 2. Pseudo-second-order kinetic model [20] is expressed as:

$$\frac{t}{\Gamma_t} = \frac{t}{\Gamma_e} + \frac{1}{\Gamma_e^2 k_2} \qquad (7)$$

where k_2 (g/mg·min) is the rate constant of pseudo-second-order sorption. The fitted parameters for various C_s values are presented in Table 2. The values of k_2 changed with C_s. This phenomenon indicates that the C_s-effect also exists in the sorption kinetics.

Table 2. Parameters of the pseudo-second-order kinetic equation at different sorbent concentrations

C_s (g/L)	Γ_e (mg/g)	k_2 (g·mg^{-1}·min^{-1})	R^2
1.0	357.1	5.47×10^{-5}	0.996
2.0	181.5	1.99×10^{-4}	0.998
4.0	102.4	1.60×10^{-4}	0.995
8.0	52.66	3.86×10^{-4}	0.999

The equilibrium partition coefficient of Pb (II) between solid and liquid phase can be obtained by sorption kinetics data. The partition coefficient (K_p) is the ratio of the solid-phase and dissolved concentrations of chemicals at equilibrium. It can be expressed as:

$$K_p = \frac{\Gamma_e}{C_e} \qquad (8)$$

The partition coefficient-SCA equation can be derived as follows:

$$K_p = \exp(-\gamma C_s^{\alpha}) K_p^0 \qquad (9)$$

where K_p^0 is the intrinsic partition coefficient of a given system, which is independent of sorbent concentration. The change of K_p with C_s for the sorption system was fitted to Eq. (9) using a non-linear least-squares method (Excel Solver) (see Fig. 7), and the best-fit values of the empirical constants, γ, α and K_p^0, are 0.559, 0.455 and 3.239. The values of γ and α are similar to those obtained by the Freundlich-SCA equation for the sorption isotherm.

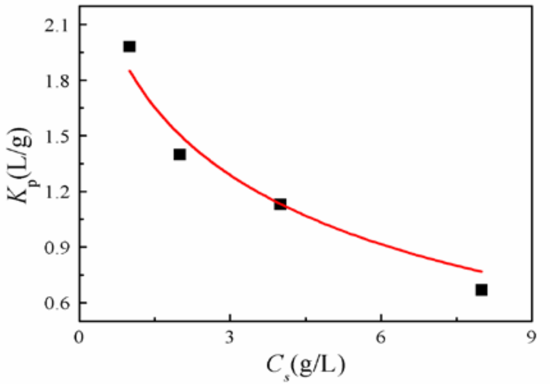

Fig. 7. Simulated variation curve of the partition coefficient with sorbent concentration

CONCLUSION

A significant C_s-effect was observed in the sorption of Pb(II) on Mg-Al-EDTA LDH. The classic Freundlich model and the pseudo-second-order kinetic equation sorption can well describe the sorption isotherm and kinetic process at a given C_s value but cannot describe the C_s-effect observed. The C_s-effect data can be described using the Freundlich-SCA equation and partition coefficient-SCA equation. We believe that the C_s-effect can be attributed to the deviation of the real sorption system from an ideal one. This study confirms the applicability of the SCA model for describing the sorption process with the C_s-effect.

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