

Sorbent concentration effect on the adsorption of Pb(II) on Fe₃O₄@Mg₂Al-EDTA LDH in aqueous solution

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The adsorption of Pb(II) onto Fe₃O₄@Mg₂Al-EDTA LDH as a function of Fe₃O₄@Mg₂Al-EDTA LDH concentration was studied, and a sorbent concentration effect (*C_s*-effect), namely, adsorption isotherm declines as sorbent concentration (*C_s*) increases, was observed. The experimental data were fitted to the adsorption models including the classic Freundlich model and the surface component activity (SCA) model. The results show that the the Freundlich-SCA equation can adequately describe the *C_s*-effect observed in the batch adsorption tests. In other words, their intrinsic parameters simulated from the experimental data are independent of *C_s* value. In this case, the values of parameters obtained at given *C_s* values can used to predict the adsorption behavior for any *C_s* values.

Key words: Sorbent concentration effect, Freundlich equation, surface component activity model.

INTRODUCTION

In studies of adsorption at the solid-liquid interface, an anomalous phenomenon of “sorbent concentration effect” [1] or “solids effect” [2, 3] (*C_s*-effect), namely, adsorption isotherm declines as sorbent concentration increases, has been observed since the 1980s. Thermodynamically, the adsorption equilibrium constant (or equilibrium partition coefficient) for a given adsorption reaction under constant temperature, pressure, and medium composition (e.g., pH, ionic strength) should be independent of both adsorbate and sorbent concentrations [4]. So, the classic adsorption model cannot explain this anomalous phenomenon because it was derived on the assumption that the adsorption equilibrium constant is independent of the sorbent concentration (*C_s*).

In fact, there has been controversy about the reasons for the *C_s*-effect over the last thirty years. Some researchers [5-8] have attributed the *C_s*-effect to a variety of experimental artifacts, while other researchers [1, 4, 9-15] believed that the *C_s*-effect is a constancy phenomenon based on thermodynamic principles although many artifacts may cause a pseudo *C_s*-effect. Because the substances for which adsorption isotherm apparently declined with increasing *C_s* include inorganic and organic adsorbates in freshwater and marine sediments, quarts, clays and clays minerals, and digested sewage sludge, it seems unlikely that experimental artifacts could explain widespread agreement of a *C_s*-effect for so diverse a set of adsorbates, adsorbents, and investigators [16]. Thus, it can be concluded that the *C_s*-effect is an experimental fact indeed, not an artifact, and there should be a

universal reason that causes the *C_s*-effect although it is still not clear now.

In this study, the sorption of Pb(II) on Fe₃O₄@Mg₂Al-EDTA LDH in aqueous solution was investigated at various *C_s* values. The Freundlich-SCA equation derived from the surface component activity (SCA) model [17-19] was examined for describing the *C_s*-effect observed in the batch adsorption tests.

MATERIALS AND METHODS

Materials

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

Magnetic nanoparticles were prepared by dissolving 0.01 mol of FeCl₂·4H₂O and 0.02 mol of FeCl₃·6H₂O in water solution under stirring at 65°C, and 20 wt% of NH₃·H₂O were added dropwise together at a constant pH value of 10-11. The obtained material (Fe₃O₄) was recovered, washed several times with deionized water until the pH was neutral. The obtained Fe₃O₄ was preserved as suspension.

Fe₃O₄@Mg₂Al-EDTA LDH with a Mg²⁺/Al³⁺ molar ratio of 2:1 was prepared by co-precipitation. An aqueous solution containing 0.1 mol Mg(NO₃)₂·6H₂O and 0.1 mol Al(NO₃)₃·9H₂O was added dropwise to Fe₃O₄ solution with Fe/Mg molar ratio equal to 0.02, under vigorous stirring. During the synthesis, the temperature was maintained at 65°C and pH at 11-12 by the simultaneous addition of EDTA-Na₂ ammonia solution with EDTA-Na₂/Al molar ratio equal to 1. The reaction mixtures were aged for 45 min in mother solution at room

temperature and then filtered, washed with deionized water until the pH was neutral. The filter cakes were further hydrothermally treated at 80°C for 24 h. The sols were dried, triturated and sieved to collect the particles of <74 μm in diameter.

Magnetic Fe₃O₄@Mg₂Al-EDTA LDH was characterized by XRD. The magnetization curves were obtained at ambient temperature by vibrating sample magnetometry (VSM, JDM-13) (Fig. 1).

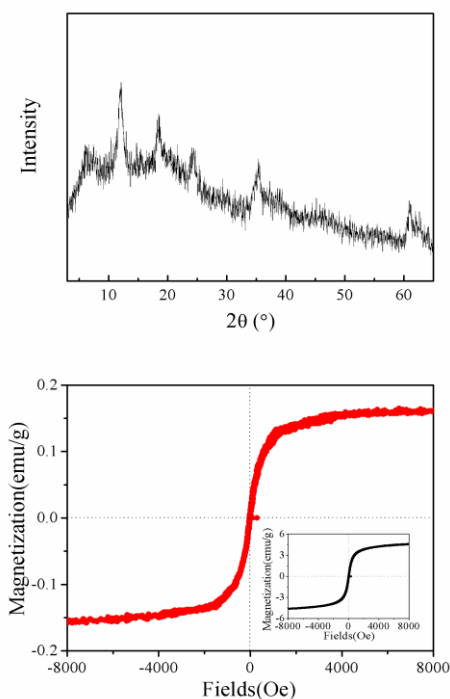


Fig. 1. XRD pattern and magnetization curves of Fe₃O₄@Mg₂Al-EDTA LDH sample and the inset is the magnetization curve of Fe₃O₄

Adsorption experiments

Adsorption tests of Pb(II) on Fe₃O₄@Mg₂Al-EDTA LDH sample were carried out by batch equilibration technique [20-22]. Solutions with various concentrations (0-800 mg/L) of Pb(II) were prepared in 0.01 mol/L of NaNO₃ with Pb(NO₃)₂, and the pH values of the solutions were adjusted to 5.0 with 0.1 mol/L HNO₃ and NaOH solutions. Known masses of Fe₃O₄@Mg₂Al-EDTA LDH samples were mixed with Pb(II) solutions of various initial concentrations in polyethylene centrifugal tubes. The centrifugal tubes were put into a thermostatic water bath shaker at 25±0.2°C for 24 h. Then the suspensions were centrifuged at a speed of 4000 r/min for 5 min. The Pb(II) equilibrium concentrations in the supernatants were determined by flame atomic absorption spectrometry (TAS-990, Beijing Purkinje General Instrument Co., Ltd.). The

equilibrium adsorption amounts were calculated using the following equation:

$$\Gamma_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and the remaining (equilibrium) concentration respectively, Γ_e (mg/g) is the equilibrium adsorption amount, V (mL) is the volume of the suspension and m (g) is the mass of the Fe₃O₄@Mg₂Al-EDTA LDH sample.

RESULTS AND DISCUSSION

Fig. 2(a) shows the adsorption isotherms of Pb(II) on Fe₃O₄@Mg₂Al-EDTA LDH at different Fe₃O₄@Mg₂Al-EDTA LDH concentrations. As can be seen, the adsorption isotherms decline significantly as the sorbent concentrations increase. This phenomenon accords with the law which is described by a C_s -effect. The applicability of current theories to predict the C_s -effect phenomenon was examined as following.

Classical Freundlich equation

As we know, Langmuir model was developed on the basis of the thermodynamic equilibrium theory while Freundlich model was originally an empirical equation. However, it was found that Freundlich equation could be thermodynamically derived based on assuming that the adsorption sites of sorbent are of different energies and the adsorption of sorbate on the sites having same energy level obeys Langmuir equation [23].

Classical Freundlich equation is represented as [23, 24]:

$$\Gamma_e = K_F C_e^{n_F} \quad (2)$$

where Γ_e is equilibrium adsorption amount, C_e is equilibrium concentration, K_F and n_F are Freundlich constants.

The Eq. (2) can be expressed by the following linear form:

$$\lg \Gamma_e = \lg K_F + n \lg C_e \quad (3)$$

The adsorption data of Pb(II) on Fe₃O₄@Mg₂Al-EDTA LDH were fitted with the Freundlich equation (see Fig.2). It was found that Freundlich equation can adequately describe the adsorption equilibrium for a given C_s value, and all the correlation coefficients (R^2) are greater than 0.98. The fitted Freundlich parameters, K_F and n_F , for various C_s values are presented in Table 1. This dependence of the Freundlich parameters on C_s showed that the classical Freundlich model cannot predict the C_s -effect. That is to say, using the Freundlich parameters obtained with given C_s values to predict the adsorption behavior of

adsorbate at other C_s values will be inaccurate.

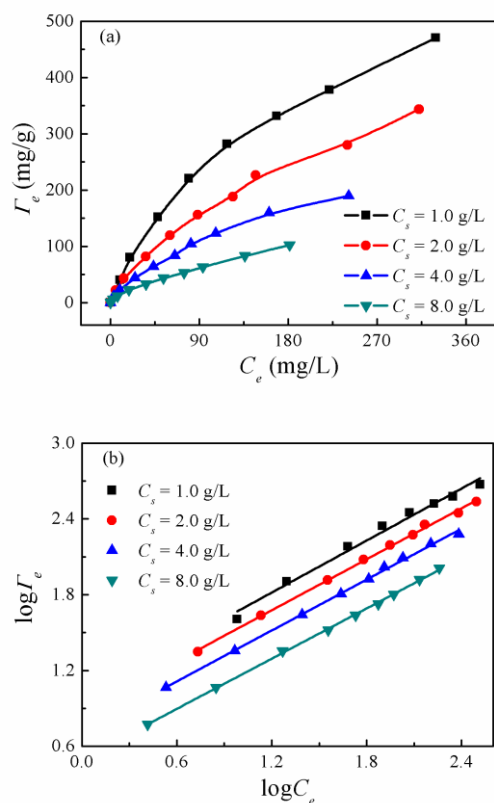


Fig. 2. Adsorption isotherms (a) and linear correlation plots for the classical Freundlich equation (b) at different sorbent concentrations

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

C _s (g/L)	n _F	K _F	R ²
1.0	0.686	9.877	0.985
2.0	0.673	7.400	0.998
4.0	0.671	5.319	0.998
8.0	0.663	3.154	0.999

The fact that Freundlich equation can adequately describe the adsorption behavior for a given C_s value indicates that Freundlich equation is available for the real adsorption systems studied. Therefore, the deviation of the prediction of Freundlich equation from the experimental data for different C_s values should be because the effect of C_s on adsorption was not accounted for in the derivation process of the classical Freundlich equation.

Examining using the Freundlich-SCA equation

Considering the deviation of a real adsorption system from an ideal one, we proposed a alternative model, surface component activity (SCA) model [17-19]. It suggests that (1) the surface of the sorbent is uniform, that is, all the adsorption sites are equivalent; (2) all adsorption occurs through the same mechanism; (3) at the maximum adsorption, only a monolayer is formed; (4) the molecular size

of solute and solvent are similar; (5) surface component (adsorption site or adsorbed solute) activity coefficient is not equal to unity because of the deviation of a real adsorption system from a ideal one. A C_s-dependent Freundlich equation (or Freundlich-SCA equation) can be derived as following,

$$\Gamma_e = K_S \cdot f_{H_2O}^s \cdot C_e^{n_S} \quad (4)$$

The linear form of Eq. (4) is

$$\lg\left(\frac{\Gamma_e}{f_{H_2O}^s}\right) = n_S \lg C_e + \lg K_S \quad (5)$$

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

The C_s-dependent function of f_{H₂O}^s is an exponential form,

$$f_{H_2O}^s = \exp(-\gamma C_s^\alpha) \quad (6)$$

where γ and α are empirical constants. Then,

$$K_F = K_S \exp(-\gamma C_s^\alpha) \quad (7)$$

Thus, the C_s-dependent function of f_{H₂O}^s can be estimated from the relationship between the experimental measured K_F values and C_s values.

The change of the K_F with C_s for the adsorption system was fitted to Eq. (7) 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 0.449 and 0.626.

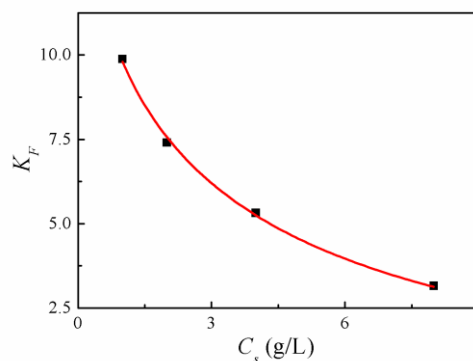


Fig. 3. Relationship between K_F and C_s

Using the simulated γ and α values, the normalized non-linear plot of (Γ_e / f_{H₂O}^s) vs. C_e for the studied system was obtained (see Fig.4(a)). A unique curve independent of C_s was obtained from experimental data. Fig.4(b) presents the normalized plot of lg(Γ_e / f_{H₂O}^s) vs. lgC_e. As can be seen, a unique fairly straight line for various C_s values was obtained. The K_S and n_S values obtained from the slope and intercept of the linear plot are 0.677 and 17.9. The correlation coefficients (R²) of

the non-linear and linear plots are higher than 0.98, indicating that the Freundlich-SCA equation can adequately describe the C_s -effect observed in the studied system.

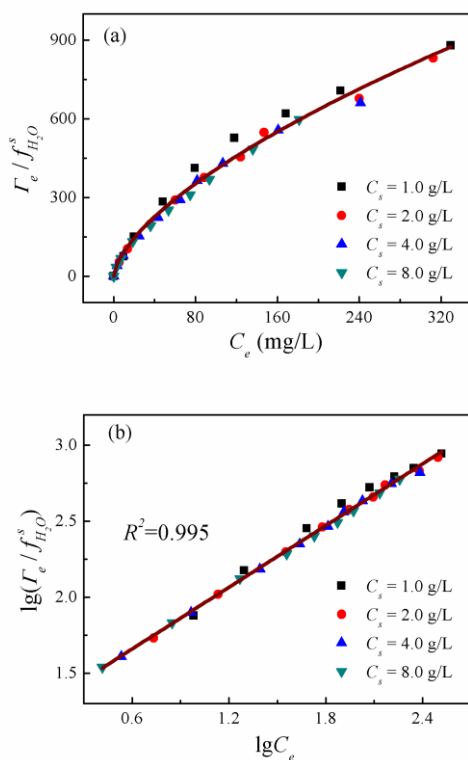


Fig. 4 The Freundlich-type MEA isotherm (a) and linear correlation plot of the Freundlich-type MEA model (b)

CONCLUSION

The adsorption of Pb(II) onto Fe₃O₄@Mg₂Al-EDTA LDH in the studied conditions is subject to the C_s -effect in which the adsorption isotherm declines as the sorbent concentration increases. The above fitting result of the adsorption data with Freundlich-SCA equation shows that Freundlich-SCA equation can be used to describe the C_s -effect observed in the batch adsorption tests. In this case, the values of parameters obtained at given C_s values can be used to predict the adsorption behavior for any C_s values.

The SCA model supposes that it is the interaction between the sorbent particles that induces the deviation of a real adsorption system from an ideal one, just as the deviation of a real solution from an ideal one. With increasing the C_s value, the interaction between the sorbent particles strengthens, resulting in the decrease of the effective adsorption site density, therefore, the adsorption isotherms decline.

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