

Adsorption of zinc on manganite (γ -MnOOH): particle concentration effect and adsorption reversibility

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Abstract: The adsorption and desorption processes of Zn(II) on γ -MnOOH as a function of particle concentrations (C_p) were studied. An obvious C_p effect was observed in this adsorption system. The degree of adsorption hysteresis increased greatly with the increasing of C_p , indicating that the extent of the real metastable-equilibrium states deviating from the ideal equilibrium state was enhanced with the increasing of C_p . The C_p -reversibility relationship confirmed the metastable-equilibrium adsorption (MEA) inequality (Pan, 1998a), which was the core formulation of the MEA theory. Because the MEA inequality was based on the basic hypothesis of MEA theory that adsorption density Γ is not a state variable, the C_p -reversibility relationship gave indirect evidence to the basic hypothesis of MEA theory.

Keywords: zinc; γ -MnOOH; adsorption reversibility

Introduction

In studies of adsorption in natural waters, an anomalous phenomenon, “the particle concentration (C_p) effect”, i.e. the decline of the adsorption isotherm (Pan, 1999) or the decrease of the partition coefficient with the increasing of C_p (Voice, 1985), has been observed widely over the last two decades. This phenomenon cannot be explained by classical thermodynamic theory of adsorption, but many laboratory studies on heavy metal or organic chemical adsorption to soils, natural sediments, clays and hydrous metal oxides have observed the C_p effect (O’Connor, 1980; Voice, 1983; Puls, 1991; Cox, 1997). In a specific adsorption system, the partition coefficient should be independent of C_p and keeps constant (Di Toro, 1986). However, in contrast to the above, the C_p effect has indicated that the partition coefficient may be not a constant in a specific condition, because it decreases with the increasing of C_p in some adsorption systems and this implies that previously measured equilibrium adsorption data may show a lack of consistency, thereby making the use and comparison of the data problematic.

Before 1998, most researchers attributed the C_p effect to a variety of experimental artifacts, such as the presence of the third phase, e.g. dissolved organic matter (DOM) phase or “nonsettling” colloid phase (Voice, 1985; Benoit, 1995); or particle-particle interactions (Nyffeler, 1986), or implicit adsorbate competition (Curl, 1984; Higgs, 1986). However, there are still other observations of the C_p effect that cannot be accounted for by experimental artifacts

(Mckinney, 1991). In 1998, Pan and Liss (Pan, 1998a; 1998b) proposed that the C_p effect has fundamental reasons besides some experimental artifacts. In metastable-equilibrium adsorption (MEA) theory (Pan, 2002), it is proposed that a fundamental deficiency in the theoretical foundation of adsorption thermodynamics that adsorption density Γ had been incorrectly used as a thermodynamic state variable in the past. The MEA theory can give a reasonable explanation to the C_p effect. According to MEA theory, Γ is not a thermodynamic state variable. The chemical potential of a given Γ depends on the metastable-equilibrium state of the adsorbed molecules and hence the history of an adsorption process. An adsorption isotherm, when expressed in terms of Γ is therefore fundamentally affected by the kinetics of adsorption processes. By affecting MEA state or adsorption reversibility, C_p can fundamentally influence adsorption isotherms. After the kinetics process of adsorption is finished, or a certain MEA state achieved, changes in C_p will have no physicochemical effect on the adsorption isotherm. In reality adsorption processes may be thermodynamically irreversible and the adsorbed molecules may finally achieve various metastable-equilibrium states on solid surface. The extent of the real metastable-equilibrium states deviating from the ideal equilibrium state determines the inconstancy of traditionally defined equilibrium adsorption constants, which is, in turn, regulated by the reversibility of adsorption reactions. However, the issue of adsorption reversibility is still not well understood in the literature.

Here the MEA theory will be tested by verifying one of its inferences, namely the control of adsorption reversibility on the C_p effect. Experimentally, we used the change of

adsorption hysteresis to approximate a change in adsorption reversibility. In this paper, the adsorption and desorption behavior of the Zn(II)-manganite(γ -MnOOH) system under different C_p conditions has been studied. We will examine the influence of C_p on the adsorption reversibility and on the adsorption isotherm to a larger extent.

1 Experimental

1.1 Manganite synthesis and characterization

Manganite was synthesized by oxidizing Mn(II) (as MnSO_4) with 30% H_2O_2 and forcing precipitation with 0.2 mol/L NH_3 (Diovanoli and leuenberger). To remove residual sulfate ions, the brown precipitation was washed by distilled water for several times till near neutral pH. Freshly synthesized manganite was stored as a concentrated suspension (3.0 g/L). Measured BET surface area of manganite was 57.64 m^2/g . The identity and purity (> 99%) of the synthetic manganite was confirmed by powder X-ray diffraction analysis. The particle size fraction ranged from 0.02 to 100 μm (Mastersizer 2000 Analyzer).

1.2 Adsorption and desorption experiments

An adsorption isotherm under a specified C_p condition was produced by preparing a series of initial concentrations of Zn(II) in a series of centrifuge tubes with each tube containing the same concentration of manganite (400 mg/L) (Pan, 1998a; 1998b). The total volume of each tube was made to 25 ml by adding 0.1 mol/L NaNO_3 solution. Adsorption and desorption suspensions were generated by using 0.1 mol/L NaNO_3 to maintain constant ionic strength. 0.1 mol/L NaOH or 0.1 mol/L HNO_3 were used to control a constant pH of 7.5 during the course of the experiment. After this, the tubes were capped and shaken at 25°C for 24 h. After 24 h of equilibration, solids were removed by centrifugation and dissolved metal concentrations were determined by flame atomic absorption spectrometry (AAS).

Desorption experiments were conducted at 25°C by removing the equilibrium supernatant solution after centrifugation, replacing the solution with equal volume of 0.1 mol/L NaNO_3 background solution, adjusting pH to 7.5 and then shaking the mixture for 12 h. The other analytical procedures were the same as described above. The kinetic studies of adsorption and desorption under different C_p conditions proved that the adsorption and desorption reaction of Zn(II) on the manganite surface could attain equilibration within 24 h and 12 h, respectively.

2 Results and discussion

2.1 The C_p effect adsorption isotherm

The adsorption isotherms under three different C_p conditions are shown in Fig. 1.

As C_p increased in Zn-manganite system, the adsorption isotherm clearly declined. The overall adsorption

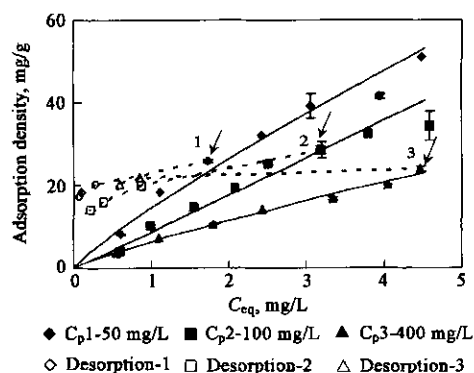


Fig. 1 Adsorption (closed symbols, solid curve) and desorption (open symbols, dotted curves) isotherms of Zn(II) on manganite

isotherms under three C_p conditions could be described by a Freundlich-type C_p effect isotherm equation (Pan, 1998a; 1998b),

$$\Gamma = 66.4 C_p^{-0.406} C_{eq}^{0.91}, \quad (1)$$

where Γ is the adsorption density (mg/g), C_p is the solid adsorbent concentration (mg/L), and C_{eq} is the equilibrium concentration of Zn (mg/L). According to MEA theory (Pan, 1998a), the specific adsorption constant (K_{sp}) is 66.4, and the C_p effect index (n) is 0.406, which is a measure of the degree of the solids concentration effect. The C_p effect isotherm equation introduced a new variable— C_p (solids concentration) into the traditional isotherm equation, and it could describe the relationship between three variables: Γ , C_{eq} , and C_p . From this Freundlich-type C_p effect isotherm equation, we could infer that adsorption density Γ would decrease with increasing the solid adsorbent concentrations (C_p).

Though many potential artifacts can cause the so-called solids concentration effect, there are two measures to avoid these artifacts in our experiments. First we use a simple model adsorption system—hydrous manganese oxide and Zn^{2+} ions in 0.1 mol/L NaNO_3 mediums, which will preclude the dissolved organic matter (DOM). Second, the adsorption and desorption samples were shaken completely to minimize the particle-particle interactions.

We selected three samples under three C_p conditions to do further desorption experiments (Fig. 1, sample 1, 2, 3 were labeled with arrows). In order to study the influence of C_p on the degree of adsorption hysteresis, we selected sample 1, 2, 3 under three C_p isotherms which adsorption density ($\Gamma_{av} = 26$ mg Zn/g MnOOH) was similar while their equilibrium concentrations of Zn increased with the increasing of C_p . This group of samples was used to study the influence of C_p conditions on the reversibility of adsorbed Zn(II) on the solid surface. By affecting MEA state or adsorption reversibility, C_p can fundamentally influence adsorption isotherms. The adsorption conditions of sample 1, 2, 3 are listed in Table 1.

Table 1 Adsorption conditions for samples (pH = 7.5, 0.1 mol/L NaNO₃ medium)

Sample	C_p , mg/L	[Zn] initial		Adsorption density Γ , mg/g
		C_0 , mg/L	C_{eq} , mg/L	
1	50	3	1.71	25.8
2	100	6	3.17	28.3
3	400	14	4.45	23.9

2.2 Quantitative description of the degree of adsorption hysteresis

Adsorption and desorption isotherms corresponding to the forward and backward reactions were not coincide, indicating that adsorption of Zn(II) onto manganite was not reversible (Scheidtger, 1996). The degree of hysteresis (the angle θ between an adsorption and its corresponding desorption isotherm) was used to approximate a change in adsorption reversibility (Verburg, 1994; Pan, 1998b). Fig. 2 shows the angle θ between an adsorption isotherm (solid line) and its corresponding desorption isotherm (dotted line). We used a trigonometric formula [Eq. (2)] to describe quantitatively the degree of adsorption hysteresis. The detailed explanations were obtained as follows:

$$\cos(\theta) = (a^2 + c^2 + b^2)/2ac, \quad (2)$$

where a is the length of the linear desorption line, b is the intercept of the linear desorption line, and c is the length of the linear adsorption line. According to Eq. (2), we could calculate the degree of hysteresis of sample 1, 2, and 3, respectively. Fig. 3 shows the degree of hysteresis as a function of C_p . As C_p increased in the Zn-manganite adsorption system, the degree of hysteresis increased greatly (indicating high irreversibility in this system).

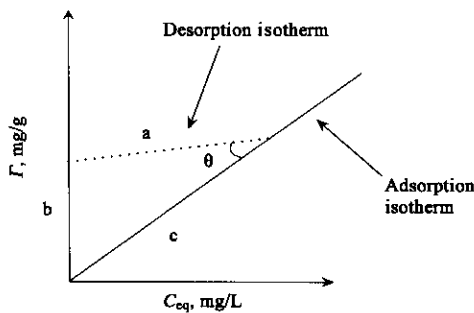


Fig. 2 Schematic representation of the degree of hysteresis between the adsorption and desorption isotherm

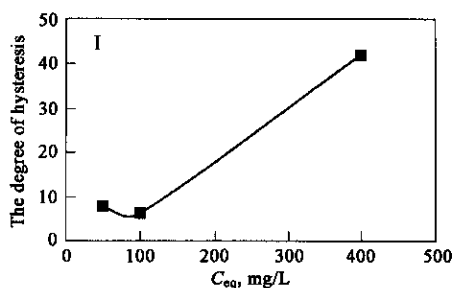


Fig. 3 The degree of hysteresis as a function of C_p

2.3 The C_p -reversibility relationship

For sample 1, 2, and 3 with a fixed Γ , the degree of hysteresis increased with the increasing of C_p , suggesting that the extent of irreversibility was enhanced with the increasing of C_p . According to MEA theory (Pan, 1998a), adsorption density Γ is incorrectly used as a state variable in the existing thermodynamics adsorption theories, so a fixed Γ can represent different thermodynamic states depending on the different metastable-equilibrium states of the adsorbate on the solid surface. By affecting the adsorption kinetics (because the adsorption rate strongly depends on C_p), C_p can fundamentally affect the extent of metastable-equilibrium states deviating from the ideal equilibrium state. The extent of the real metastable-equilibrium states deviating from the ideal equilibrium state determines the inconstancy of traditionally defined equilibrium adsorption constants, which is, in turn, regulated by the reversibility of adsorption reactions. Though we do not directly measure the energy state of the adsorbate on wet surfaces, we could use the C_p -reversibility relationship to verify the basic hypothesis of MEA theory.

2.4 pH conditions of the experiments

The adsorption of Zn(II) on manganite under three C_p conditions as a function of pH is presented in Fig. 4. The pH-edge of Zn(II) adsorption to manganite displayed the typical sigmoid curve characteristic for transition metal (Benjamin, 1981). The pH adsorption curves under different solid adsorbent concentrations are approximately parallel and shift toward lower pH with increasing adsorbent concentration (C_p). At pH 7.5, fractional adsorption was above 70% at the highest C_p (400 mg/L), while fractional adsorption reduced to 40% at lower C_p (50 mg/L).

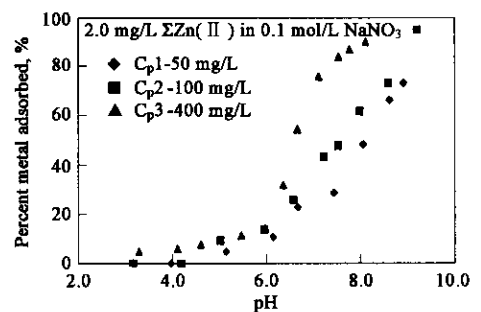


Fig. 4 The pH-adsorption edges as a function of C_p

Suspensions of manganite ($C_p = 400$ mg/L) in 0.1 mol/L NaNO₃ medium were prepared in order to check for solubility as a function of pH (Fig. 5). Manganite will disproportionate into Mn(II) and Mn(IV) in acidic pH range (Hem, 1983), while in the neutral or alkaline pH range ($\text{pH} \geq 7$), the aqueous Mn concentration was below the detection limit of 0.2 $\mu\text{mol/L}$ of AAS. At pH 7.5 where the adsorption and desorption experiments were conducted, γ -MnOOH could persist for a considerable length of time and all

samples were understaturated with respect with formation of amorphous $Zn(OH)_2(s)$ ($\log K_{sp} = 12.66$ in 0.1 mol/L medium; Baes, 1976).

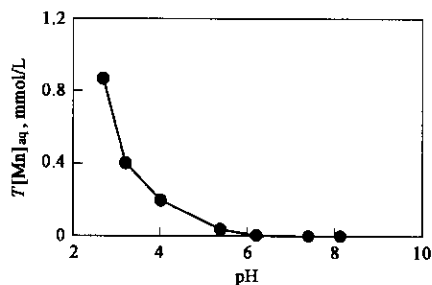


Fig. 5 Soluble Mn concentration in equilibrium with γ -MnOOH as a function of pH. The particle concentration of suspensions of manganite in 0.1 mol/L $NaNO_3$ medium is 400 mg/L

3 Conclusions

In a 0.1 mol/L $NaNO_3$ solution of pH 7.5, the $Zn(II)$ -manganite adsorption system displayed a clear C_p effect. The overall adsorption isotherms under three C_p conditions could be described a Freundlich-type C_p effect isotherm equation ($\Gamma = 66.4 C_p^{-0.406} C_{eq}^{0.91}$). The adsorption and desorption isotherms were not coincide, indicating that adsorption of $Zn(II)$ onto manganite was not reversible. For three samples (sample1, 2, 3) with a given Γ , the degree of hysteresis increased greatly with the increasing of C_p . The result implied that a fixed Γ could represent different thermodynamic states depending on the different metastable-equilibrium states of the adsorbate on the solid surface.

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