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Particle concentration effect in adsorption/desorption of Zn(II) on anatase type nano TiO_2

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Abstract

Adsorption/desorption in a new Zn(II)-TiO_2 adsorption system was investigated at different particle concentrations (C_p). TEM, SEM and XRD analyses revealed that the TiO_2 particles were an aggregation of nano-sized (approximately 10 nm) pure anatase-type TiO_2. Adsorption experiments were carried out with particle concentrations of 100, 400 and 1000 mg/L, and their adsorption isotherms were found to decline successively, showing an obvious C_p effect. Desorption experiments indicated that adsorption in this system was irreversible, and the irreversibility increased with increasing C_p. These phenomena could be explained by the MEA (metastable equilibrium adsorption) theory and the C_p effect could be modeled well with an MEA-Freundlich-type C_p effect isotherm equation. This study may help understand environmental behavior of contaminants on ultrafine natural particles.

Key words: Zn(II); anatase-type TiO_2; particle concentrations effect; adsorption; desorption

Introduction

Adsorption of heavy metals on natural particles is an important process regulating their environmental behavior (Honeyman and Santschi, 1998). A fundamental way of describing adsorption is an adsorption isotherm, in which the adsorption density Γ is plotted against the equilibrium concentration of solute in dilute solution (Pan and Liss, 1998a, b). In many cases, an isotherm can well describe adsorption reactions regardless of adsorbent particle concentration (C_p), e.g. in the Zn(II)-δ-MnO_2 system (Li *et al*., 2004) , and various modeling approaches have been developed upon it. However, in certain adsorption reactions the isotherms are found to decline with the increase of C_p, as in Zn(II)-γ-MnOOH system (Pan *et al*., 2004), which is not caused by experimental artifacts and is therefore termed particle concentration effect. The mechanism behind particle concentration effect had not been well understood until 1998 when Pan *et al*. (1998a, b) put forward the MEA (metastable equilibrium adsorption) theory, which pointed out a fundamental deficiency in theoretical foundation of adsorption thermodynamics. According to MEA theory, adsorption density Γ is not a thermodynamic state variable, and can be affected by specific kinetic processes. Different C_p can create such different kinetic paths, and particle concentration effect should be observed widely in adsorption systems. The environmental significance of particle concentrations effect is that adsorption and the consequent desorption of contaminants on natural particles (soil/sediments) can be influenced by the particle concentration and hence determine the transportation and fate of the contaminants.

Owing to the large surface area and unique physicochemical properties, nano and ultrafine particles have drawn much attention in recent years for their roles in adsorption/desorption of contaminants in environment. A good material for the current research is nano TiO_2, which has been widely used in industry at present and has a rapidly increasing exposure to environment, especially under the driving force of nanotechnology. Anatase type nano TiO_2 was selected in this study for its wide practical applications (Huang *et al*., 1996; Watanabe *et al*., 2003; Kim *et al*., 2003; Saripalli *et al*., 2002; Horanyi, 2003) and Zn(II) was chosen as a typical heavy metal in environment, which has been studied comprehensively through both experiments and quantum chemical calculations (Li *et al*., 2004; Pan *et al*., 2004; Qin *et al*., 2004; Zhu and Pan, 2005). The adsorption/desorption in such a Zn(II)-anatase type nano TiO_2 adsorption system has not been reported so far in literature, and it is interesting to explore how C_p will take effect in the adsorption/desorption reactions and whether the particle concentration effect can be well modeled.

In this study, we examined the influence of C_p on adsorption reactions (isotherms), adsorption irreversibility and the relationship between the two, and modeled the

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particle concentration effect with an MEA-Freundlich-type isotherm equation. These data will provide information about this new adsorption system and raise concerns about the roles of nanoparticles in environment. Moreover, this study will verify the prediction from MEA theory about the adsorption on nanoparticles, and help to study further the relationship between microstructure of adsorbed species at molecular level (extended X-ray absorption fine structure (EXAFS)) and their macroscopic adsorption irreversibility.

1 Materials and methods

Anatase type nano TiO_2 was used as the adsorbent in our experiments, which was obtained from the Beijing Century Science & Technology Co. Ltd. All reagents used in our experiments were of analytical grade, except stated otherwise. All adsorption/desorption experiments were carried out at 5°C, because the previous tests showed that particle concentration effect would increase with decreasing temperature (data not shown here).

1.1 Sample preparation

Anatase type nano TiO_2 suspension of 20 g/L was prepared from dry powder with Milli-Q deionized water. The suspension was prepared several days in advance to make its property stable. A Zn(II) stock solution of 100 mg/L was obtained by dissolving $Zn(NO_3)_2{\cdot}6H_2O$ with Milli-Q water, and was demarcated with standard Zn(II) solution purchased from National Research Center for CRM. The ion strength in the adsorption system was adjusted by a KNO_3 stock solution of 0.1 mol/L. The pH of all stock solutions was controlled below 2 with HNO_3, which were all kept in a refrigerator at 4°C. During experiments, pH electrodes were calibrated with standard buffers at 5°C, and the pH was adjusted to a certain pH value (6.3±0.05) with 1 mol/L or 0.1 mol/L KOH and HNO_3.

1.2 Method

Certain amount of the anatase type nano TiO_2 suspension with Zn(II) solution was mixed, and shaken for 24 h in a shaker set at 200 r/min and 5°C, during mixing the pH was adjusted 3 times to keep the preset pH unchanged. After adsorption equilibrium was reached, the samples were centrifuged at 3000 r/min for 15 min, and then immediately filtered through 0.22 μm filter membrane. The supernatant Zn(II) solution was later measured with VA-differential pulse polarographic analysis (797 VA Computrace, Metrohm, Switzerland), which could detect the soluble Zn(II) with high sensitivity (Good *et al*., 1966).

Desorption processes were conducted by removing 2/3 total volume of the supernatant solution after centrifugation, then topping up to the original volume with 0.1 mol/L KNO_3 stock solution. Shake for 24 h and adjust the pH to 6.3 for 3 times during this equilibrium time. After that, the solution was centrifuged and measured for Zn(II) in the supernatant solution. A second round of desorption was carried out with the same procedure to complete a two-step desorption.

1.3 Characterization

The Characterization of anatase type nano TiO_2 was conducted using scanning electron microscopy (SEM) (S-3000N, Hitachi, Japan) and transmission electron microscopy (TEM) (H-7500, Hitachi, Japan). Particle size of the TiO_2 powder in water solution was characterized with Mastersize 2000 (Malvern Co. Ltd.). The specific surface area of the TiO_2 powder was determined with ASAP-2010 (Micromeritics Inc., USA). Powder X-ray Diffraction (Rigaku, D/MAX-RC, Japan) analysis was applied to determine the mineralogy of the TiO_2 particles.

2 Results and discussion

2.1 Characterization of anatase type nano TiO_2

The physical and chemical properties of anatase type nano TiO_2 were characterized. TEM analysis shows that the TiO_2 powder was in fact comprised of uniform and spheric nanoparticles of about 10 nm, and their aggregation could reach a particle size in micron range as the SEM image revealed (Fig.1). Particle size of the TiO_2 powder in water solution is shown in Fig.2, and their average diameter turned to be slightly smaller than 1 μm (the mode = 0.88 μm), which is in consistent with the direct observation in Fig.1b. The spike in Fig.2 indicated that the TiO_2 formed quite uniform particles in water solution at sub-micrometer level, and its specific surface area was determined to be 200±2 m^2/g. Powder X-ray diffraction analysis was applied to determine the mineralogy of the TiO_2 particles, and their XRD spectrum is shown in Fig.3. It shows that the TiO_2 was almost of pure anatase-type.

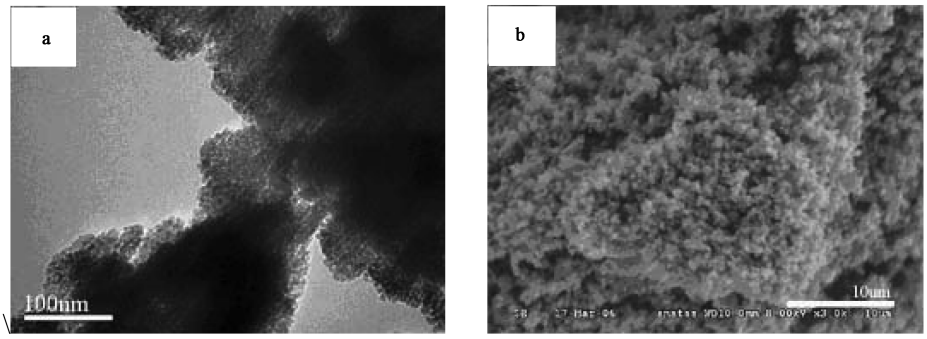

Fig. 1 Nano size TiO_2 morphology by TEM (a) and SEM (b).

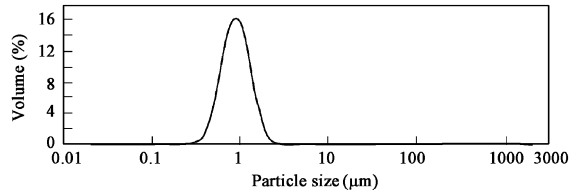

Fig. 2 Particle size distribution of the nano size TiO_2 in water solution.

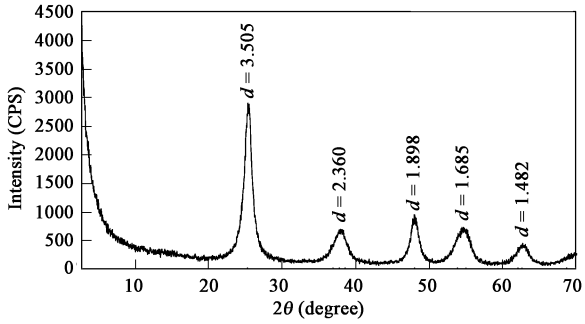

Fig. 3 XRD spectrum of the anatase type nano TiO_2.

2.2 pH edge and adsorption kinetics

A proper pH value was needed to conduct Zn(II)-anatase type nano TiO_2 adsorption experiments, and it was determined by the pH edge experiment as pH=6.3 (Fig.4a), where the percentage of adsorption capacity was approximately 40%.

The zeta potential of the TiO_2 suspensions was measured in 0.01 mol/L KNO_3 solution (Fig.4b), with the point of zero charge (PZC) = 6.2.

To determine the period required for equilibrium in the batch experiments, kinetic experiments were conducted in a 1-L foil-shaded conical flask with a particle concentration of 400 mg/L. The kinetic curve is shown in Fig.5, from which an equilibrium time of approximately 15 min could be observed. For full adsorption equilibrium, an equilibrium time of 24 h was applied in the following experiments.

2.3 Adsorption/desorption experiments

Adsorption experiments were carried out at three different particle concentrations, 100, 400, 1000 mg/L, and three corresponding isotherms with data from two parallel experiments are plotted in Fig.6. It was clear that the isotherms declined with the increase of C_p, and the isotherm at C_p = 1000 mg/L was less than half of that at C_p = 100 mg/L, showing an obvious particle concentration effect.

The two-step desorption experiments were carried out on three selected adsorption samples from the three isotherms (Fig.6), which had similar equilibrium concentrations (2.5–3.5 mg/L). It was noted that the desorption lines did not coincide with the corresponding adsorption isotherms, indicating that all the adsorption reactions were irreversible. The angle between adsorption and its

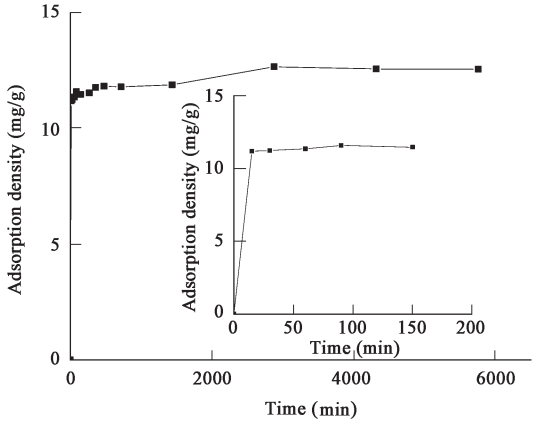

Fig. 5 Adsorption kinetics of Zn(II) on anatase type nano TiO_2.

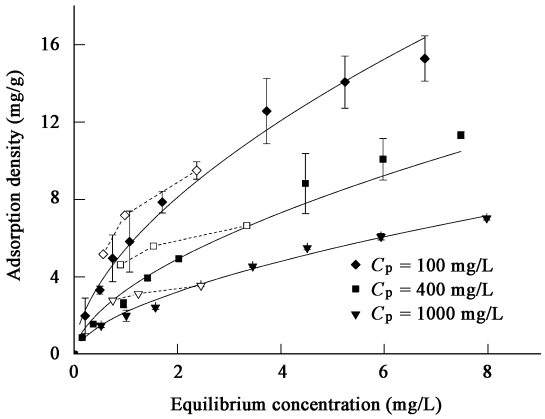

Fig. 6 Adsorption isotherms and their simulating curves under three different C_p conditions for adsorption of Zn(II) on anatase type nano TiO_2. Points were experimental data. Lines were modeled results using the MEA–Freundlich-type particle concentration effect isotherm equation. The open symbols were for two-step desorption data.

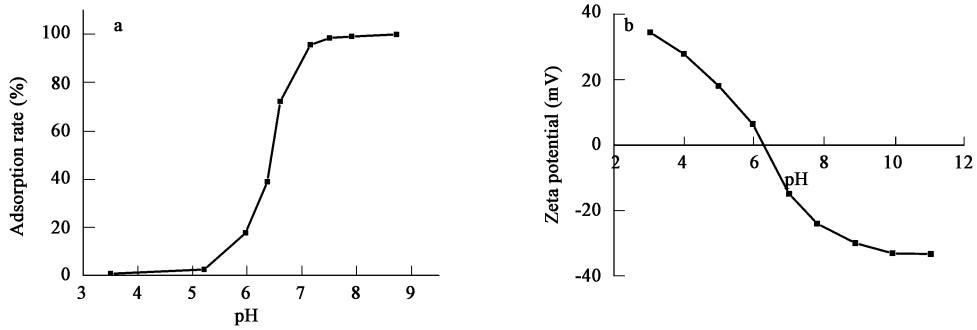

Fig. 4 Adsorption pH edge of Zn(II) on anatase type nano TiO_2 at PZC=6.2 (a) and zeta potential of TiO_2 suspensions (b).

corresponding desorption isotherms was usually used to describe quantitatively the degree of adsorption hysteresis (Qin *et al*., 2004), and it was calculated as 8.9, 22.5 and 32.7°C for the isotherms of 100, 400, 1000 mg/L respectively. Although absolute values of the angle might vary with the data points on the isotherms, the changes in angle would be able to reflect the basic trend in irreversibility when data points were selected with similar equilibrium concentrations. Therefore, the adsorption irreversibility in this Zn(II)-anatase type nano TiO_2 system could be ensured to increase with increasing C_p, which was in line with the previous work (Pan *et al*., 2004; Qin *et al*., 2004).

These adsorption/desorption phenomena, particle concentration effect and its relationship with adsorption irreversibility in particular, could not be explained by conventional adsorption thermodynamics, but could be well interpreted with MEA theory, which attributed these to different microstructures of adsorbed molecules on solid surfaces (Pan and Liss, 1998a; Pan *et al*., 2004). It was needed to point out that the MEA theory was also applicable to describing adsorption on nanoparticles, although the surface characteristics could be very different from that of larger ones. As relative work was seldom reported in literature, these data would provide new information for the Zn(II)-TiO_2 adsorption/desorption system, and more investigations were required to assess the roles of nano and ultrafine particles in transportation and fate of contaminants (heavy metals) in environment.

2.4 Modeling

Pan and Liss (1988a) proposed in their MEA theory a metastable-equilibrium adsorption inequality, and applied it to the Freundlich (or Langmuir) isotherm equation to obtain an MEA-Freundlich-type isotherm equation to describe C_p effect quantitatively:

$$\Gamma = K_{sp} \times C_p^{-n} \times C_e^{\beta} \quad (1)$$

where, K_{sp} is an equilibrium adsorption constant, C_e is the equilibrium concentration of solute in dilute solution, n is the magnitude of particle concentration effect, and β is a constant under isothermal conditions.

Data from the Zn(II)-anatase type nano TiO_2 adsorption at different C_p (Fig.6) were modeled with the MEA-Freundlich-type particle concentration effect isotherm equation, and the parameters were determined as:

$$\Gamma = 28.8 C_p^{-0.362} C_e^{0.577} \quad (2)$$

This generalized equation simulated all the data in this adsorption system (Fig.6), and the correlation between the data points and adsorption isotherms was good (R^2=0.98). This made it possible to quantify isotherms with particle concentration effect with one equation, instead of three different equations using original Freundlich data fitting. According to this equation, the adsorption density Γ would decrease with increasing C_p (C_p effect).

3 Summary

The anatase type nano TiO_2 used in this study was characterized as an aggregation of nano-sized particles (approximately 10 nm) with a mode of 0.88 μm in water solution. Several conclusions could be drawn from the adsorption/desorption experiments in the Zn(II)-anatase type nano TiO_2 adsorption system:

This adsorption system displayed an obvious particle concentration effect at 5°C. The overall adsorption isotherms under three C_p conditions could be described with one MEA-Freundlich-type particle concentrations effect isotherm equation as:

$$\Gamma = 28.8 C_p^{-0.362} C_e^{0.577}$$

Two-step desorption experiments indicated that Zn(II)-anatase type nano TiO_2 adsorption system was irreversible, and the irreversibility increased with increasing C_p.

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