

Effect of pH, ionic strength and fulvic acid on the sorption and desorption of cobalt to bentonite

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Received 6 May 2005; received in revised form 15 July 2005; accepted 19 August 2005

Abstract

Humic substances and bentonite have attracted great interest in radioactive waste management. Here the sorption of cobalt on bentonite in the presence and absence of fulvic acid (FA) under ambient conditions was studied. The effects of pH, ionic strength, FA and solution concentrations on cobalt sorption to bentonite were also investigated using batch techniques. The results indicate that the sorption of cobalt is strongly dependent on pH and is independent of ionic strength under our experimental conditions. Surface complexation is considered the main mechanism of cobalt sorption to bentonite. In the presence of FA, little effect of FA on cobalt sorption was found at $\text{pH} < 6$; a positive effect of FA on cobalt sorption was found for $\text{pH} 6\text{--}8$; and a negative effect of FA on cobalt sorption was found at $\text{pH} > 8$. The addition sequences of FA/Co^{2+} to the bentonite suspension on the sorption of cobalt to FA-coated bentonite were also studied. The results indicated that the sorption is not influenced by the addition sequences. Some possible mechanisms are discussed.

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Keywords: Sorption; Cobalt; pH; Fulvic acid; Bentonite

1. Introduction

This paper is an extension of our previous papers (Wang et al., 2000, 2002, 2005a, b), where we studied the sorption, desorption and migration of Co(II) , Eu(III) , Yb(III) and $^{243}\text{Am(III)}$ on alumina, and sorption of U(IV) on bentonite. Effects of pH, ionic strength and humic substances on the sorption and desorption of Co(II) were investigated by using radiotracer ^{60}Co . The results indicated that pH and humic substances influence the sorption of Co(II) on alumina greatly and that strong chemical bonds are formed between the bare alumina surface and Co(II) (Wang et al., 2002). We also studied the effect of pH, ionic strength and fulvic acid (FA) on the sorption of Eu(III) and Yb(III) by alumina under aerobic conditions and found that the sorption of Eu(III) and Yb(III) onto a bare alumina surface is pH-dependent, ionic strength independent and reversible (Wang et al., 2000).

The important radionuclides ^{60}Co and ^{58}Co are present in liquid wastes released from pressurized water from the nuclear power reactors, and ^{60}Co is also widely used in research and medical applications. The sorption of radiocobalt by clay or oxides changes the physical–chemical forms of radiocobalt and controls the migration and diffusion of radiocobalt in waters and environment. So research about cobalt is important for the evaluation of radiocobalt behavior in the environment.

Tewari et al. (1972), Tewari and Lee (1975) studied the sorption of Co^{2+} by several oxides: Fe_3O_4 , Al_2O_3 , MnO_2 , TiO_2 and ZrO_2 . The sorption of Co^{2+} increases markedly with the solution pH between 5 and 8, while above pH 8 Co^{2+} becomes increasingly a surface precipitate of Co(OH)_2 . Eriksen et al. (1999) studied the sorption and diffusion of Co^{2+} in compacted bentonite and found that Co^{2+} forms outer sphere complexes with the permanent layer sites with increasing cobalt concentration and pH forms surface complexes/precipitates with surface hydroxyl groups. Nagy and Kónya (1998) studied the sorption of cobalt on calcium-montmorillonite and found that Co^{2+}

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forms strong complexes Co–EDTA. The ion exchange processes are greatly influenced by the composition of the solution (pH, complex-forming agent). XAFS, TEM and XPS measurements of Co(II) sorption on alumina demonstrate that surface precipitates have formed from solutions that are undersaturated with respect to any known bulk solid phase. The precipitates have a structure similar to that of $\text{Co}(\text{OH})_2(\text{s})$, but are disordered and have a high concentration of Co vacancies (Towle et al., 1997).

The sorption and migration of radionuclides in terrestrial environment must be studied to estimate the impact of radioactive waste disposal on the biosphere. Radionuclides are absorbed by inorganic and organic compounds during the migration and diffusion in the terrestrial environment. It is well known that humic substances (HS) may influence the sorption of metal ions onto clays and oxides through their ability to complex metal cations, their potential involvement in redox reactions and their potential to form coatings on solid surfaces. In the presence of humic substances, the sorption of metal ions generally increases at low pH range and then decreases at high pH range, as compared with the sorption in the absence of HS. The increase of sorption is explained by the sorption of HS onto the mineral surface, followed by the interaction of metal ions with surface sorbed HS, whereas the reduction of sorption is explained by the formation of soluble M-HS complexes, which stabilize the metal ions in the aqueous solution.

Based on the experimental results mentioned above, one can see that the sorption mechanisms of Co(II) on bentonite are not yet sufficiently conclusive. Especially, the effect of humic substances on the sorption of Co(II) by bentonite is not clear. Here the sorptions of Co(II) on bare bentonite and FA-coated bentonite were studied by using batch techniques under aerobic conditions. The aims of the study were to study the sorption mechanisms of hydrolysable Co(II) on bentonite and to study the effects of FA, pH and ionic strength on Co(II) sorption on bare and FA-coated bentonite.

2. Experimental

2.1. Materials

All analytical chemicals were purified, but the bentonite was used without any purification. The sample of bentonite was derived from Lin'an county (Zhejiang Province, China) and well characterized. The main components of the bentonite are listed in Table 1. The nitrogen adsorption isotherm at 77 K was measured using a BECKMAN

COULTER SA-3100 Surface Area Analyzer. The surface area of the sample was calculated by the BET method using the adsorption data ranging from $P/P_0 = 0.058$ to 0.200, and its value was $38.5 \text{ m}^2/\text{g}$. The cation exchange capacity was 0.89 meq/g. The point of zero charge (pH_{zpc}) was 7.8 ± 0.1 .

Fulvic acid was extracted from some weathered coal from the area of Gongxian (Henan Province, China) and had been applied in sorption experiments by other authors (Wang et al., 2000 and 2004a). The FA has been characterized in great detail (Tao et al., 1995).

The cobalt solution was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and the concentration of cobalt was analyzed by spectrophotometry at a wavelength of 592 nm by using xylenol orange and CTMAB.

2.2. Procedures

The sorption and desorption were measured using a batch technique. All the experiments were carried out under ambient conditions. The stock solution of bentonite, sodium nitrate, cobalt stock solution, HCl or NaOH and FA stock solution were added in the polyethylene test tubes to achieve the desired background electrolyte concentration, FA concentration and pH of the aqueous solutions. The pH values were adjusted with small amounts of 0.1 M HCl or NaOH.

For desorption experiments, the suspension of bentonite was centrifuged (6000 rpm, 20 min) at the end of the sorption experiments; half of the supernatant was pipetted out and an equal volume of background electrolyte solution with the same pH value was added. Then the mixture was shaken and centrifugation was done under the same conditions as in the sorption experiments.

In addition, the effect of addition sequences on Co^{2+} sorption was studied; the addition sequence is distinguished between: (1) spiking FA to the bentonite dispersion and then adding Co^{2+} after one day (called batch 1); and (2) spiking Co^{2+} to the FA solution and then adding bentonite suspension after 1 day (called batch 2).

All the experimental data were the averages of duplicate or triplicate determinations. The relative errors of the data were about 5%.

3. Results and discussion

3.1. Effect of contact time

The time dependence of sorption kinetics of Co^{2+} on bentonite is shown in Fig. 1. The sorption of cobalt on bare

Table 1
The main chemical component of the bentonite

Component %	Al_2O_3	SiO_2	MgO	Fe_2O_3	K_2O	Na_2O	CaO
	63.04	15.30	3.32	2.04	0.90	0.19	0.11

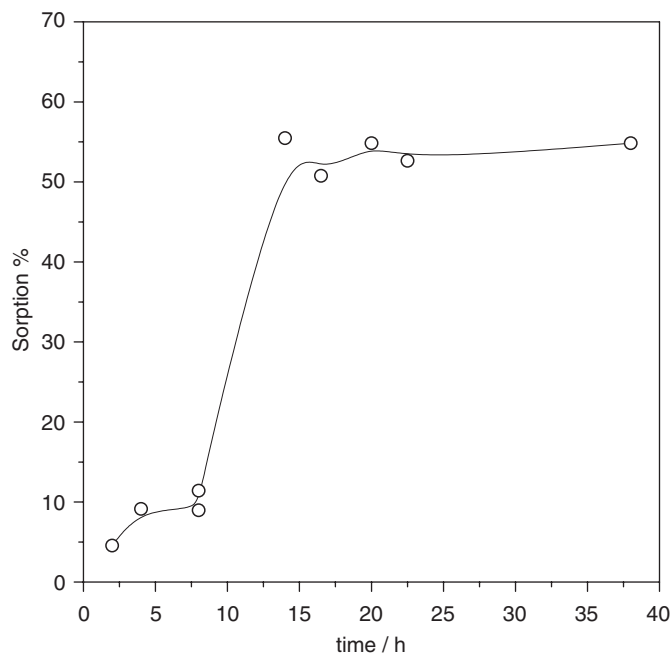
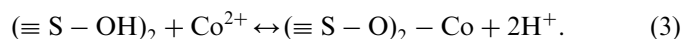
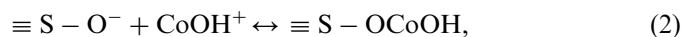
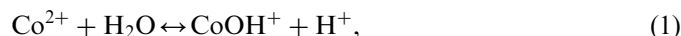


Fig. 1. Time dependence of cobalt sorption on bentonite. $\text{pH} = 6.0 \pm 0.2$, $C(\text{Co}^{2+}) = 3.4 \times 10^{-4} \text{ mol/l}$, $C(\text{NaNO}_3) = 0.01 \text{ mol/l}$, $m/V = 0.2 \text{ g/l}$.

bentonite mainly occurred during the first 15 h and then a steady value of sorption was achieved. Compared with the sorptions of Co^{2+} to other bentonite and kaolinite (Dong et al., 2000), the sorption equilibration was reached quickly and no abnormal sorption shape was found. Twenty-four hours of equilibration time was used in the following experiments according to the time-dependent sorption.

3.2. Effect of pH in the absence of FA

Fig. 2 shows the pH dependence of cobalt sorption on bentonite at ionic strength 0.01 M NaNO_3 . A steep increase of sorption was observed from pH 7 to 9. The step increase in sorption is a typical behavior for the sorption of hydrolysable transition metal ions on bentonite surface (Davis, 1982). CoOH^+ is formed and the adsorption process is rapidly completed by interaction with the negative charge on bentonite, but also bentonite absorbs cobalt ions in the sheets of hydroxyl groups (Yavuz et al., 2003):



The bentonite surface may also be negatively charged, and thus provide sorption sites for cobalt ion:

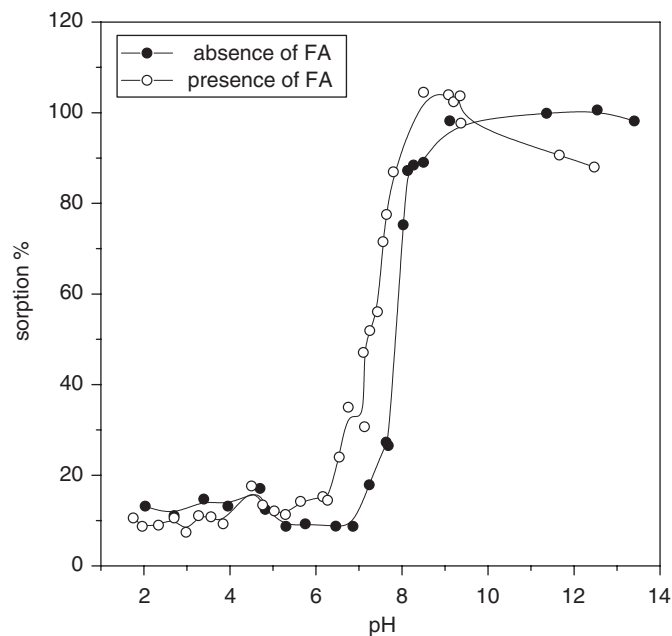
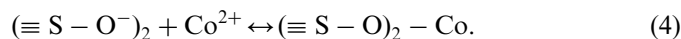


Fig. 2. Effect of pH on the sorption of cobalt on bare and FA-coated bentonite. $C(\text{Co}^{2+}) = 3.4 \times 10^{-4} \text{ mol/l}$, $C(\text{NaNO}_3) = 0.01 \text{ mol/l}$, $m/V = 0.2 \text{ g/l}$. The values of pH given in Fig. 2 are those after equilibration.

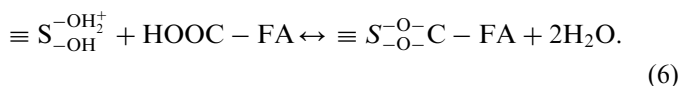
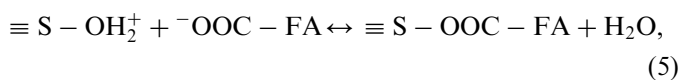
Tewari et al. (1972), Tewari and Lee (1975) studied the sorption of cobalt on oxides and found that the sorption increases markedly from pH 5 to 8. Similar sorption behavior was found for the sorption of cobalt on oxides and bentonite. The pH dependence of cobalt sorption on bentonite indicates that the sorption mechanism is mainly surface complexation (Baeyens and Bradbury, 1997).

3.3. Effect of pH in the presence of FA

The pH dependence of cobalt sorption on FA-coated bentonite is also shown in Fig. 2. The initial concentration of FA in the suspension was 7.1 mg/l. It can be seen that, in the pH range 3–6, there is no difference in the sorption of cobalt on bentonite in the presence and absence of FA; in the pH range 6–9, a positive effect of FA on the sorption of cobalt on FA-coated bentonite is observed; for pH values higher than 9, a negative effect of FA on the sorption of cobalt on FA-coated bentonite is observed. At low pH values, the negatively charged FA is easily adsorbed onto bentonite and the interaction of cobalt ion with surface adsorbed FA is stronger than that of cobalt with bare bentonite; at high pH values, the negatively charged FA is weakly adsorbed onto bentonite and forms stable complexes FA–Co in solution and thus reduces the sorption of cobalt on bentonite (Montavon et al., 2002; Wang et al., 2004a).

The possible modes of ligand exchange mechanism between bentonite and humic substances can be

described as



Many possible modes of humic substances sorption on oxides or clays have been described (Wang et al., 2000; Gu et al., 1994). The presence of FA in solution affects the sorption of cobalt on bentonite, and the species of cobalt on FA-coated bentonite is mainly dominated by both FA and bentonite; the formation of ternary complexes such as $\equiv \text{S} - \text{O} - \text{Co} - \text{FA}$ or $\equiv \text{S} - \text{O} - \text{FA} - \text{Co}$ occurs on the surface of FA-coated bentonite (Wang et al., 2004b, Takahashi et al., 2002).

3.4. Effect of ionic strength

Fig. 3 shows the dependence of $\log K_d$ on the ionic strength from 0.001 to 2 M NaNO_3 for the sorption of cobalt on bare bentonite. As can be seen from Fig. 3, the $\log K_d$ values were almost independent of ionic strength from 0.5 to 2 M, and the $\log K_d$ values at 0.01 and 0.1 M were slightly larger. One can draw the following conclusion: that the sorption of cobalt on bare bentonite was insensitive to the ionic strength. The results of this work are very similar to those of cobalt sorption on kaolinite and bentonite (Dong et al., 2000).

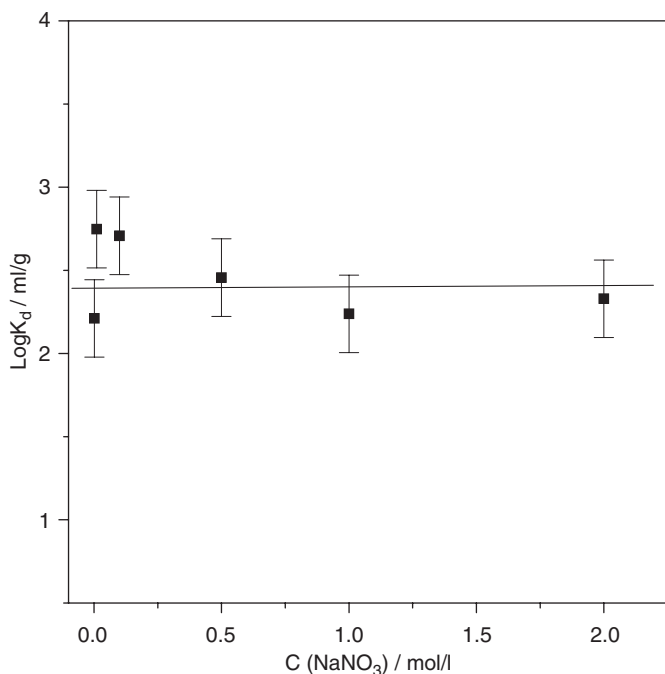


Fig. 3. Effect of ionic strength on the sorption of cobalt on bare bentonite. $C(\text{Co}^{2+}) = 3.4 \times 10^{-4}$ mol/l, $C(\text{NaNO}_3) = 0.01$ mol/l, $m/V = 0.2$ g/l.

The distribution coefficient, K_d , for sorption and desorption was calculated from

$$K_d = \frac{q}{C_{\text{eq}}} = \frac{C_0 - C_{\text{eq}}}{C_{\text{eq}}} \cdot \frac{V}{m}. \quad (7)$$

Here q is the concentration of cobalt in the solid phase after sorption (mol/g), C_{eq} is the concentration of cobalt in the solution phase after sorption (mol/l), C_0 is the initial concentration (mol/l), V is the volume of solution (l), and m is the mass of bentonite in solution (g).

The strongly pH-dependent and ionic strength-independent cobalt sorption to bentonite indicates that the sorption mechanism is surface complexation rather than ion exchange (Baeyens and Bradbury, 1997). Surface complexation is strongly pH-dependent and weakly ionic strength-dependent; the surface sites change with the change of pH values, and thus the sorption exhibits pH dependence.

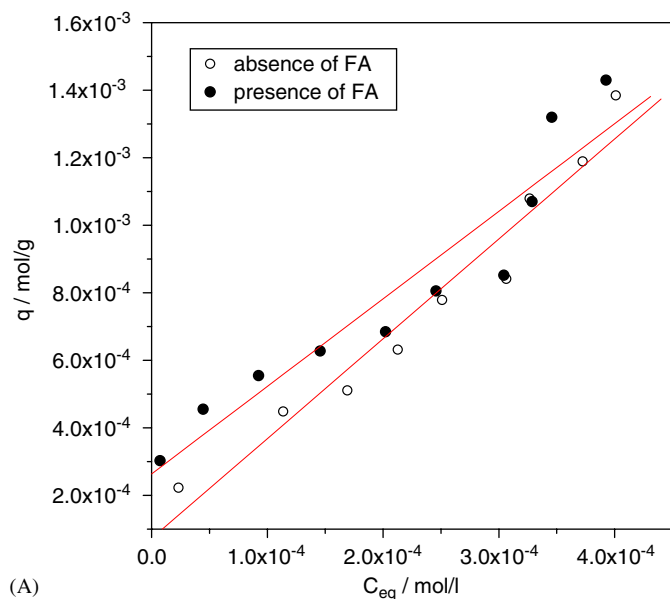
3.5. Sorption isotherms in the presence and absence of FA

Figs. 4A and B show the sorption isotherms of cobalt on bare and FA-coated bentonite at $\text{pH } 6.3 \pm 0.2$ and 7.3 ± 0.2 , respectively. From Fig. 4, one can see that the sorption isotherms of cobalt on bare or FA-coated bentonite are linear at both pH values; this suggests that the sorption of cobalt is far from saturation. At $\text{pH } 6.3 \pm 0.2$, there is little difference in the sorption of cobalt on bare and FA-coated bentonite; however, the sorption isotherm of cobalt on FA-coated bentonite is higher than that of cobalt on the bare bentonite at $\text{pH } 7.3 \pm 0.2$. The concentration of FA in the supernatant was measured by UV-vis spectrophotometry; the results indicate that about 97% of FA was adsorbed onto bentonite surface at both pH values. Such results indicate that the contribution of FA on cobalt sorption at $\text{pH } 7.3$ is higher than that at $\text{pH } 6.3$. The presence of FA enhances the sorption of cobalt on bentonite and the complexes of FA-Co are stronger than that of Co-bentonite.

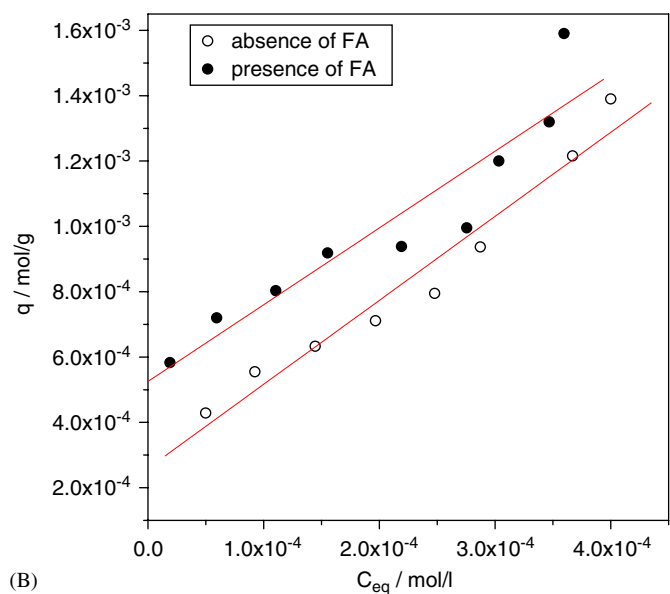
The sorption of positively charged Co^{2+} onto the positively charged bentonite at $\text{pH} < 8$ is the direct evidence of formation of chemical bonds between the bentonite surface and Co^{2+} . The strong sorption of Co^{2+} on bentonite suggested the formation of precipitate, the chemical sorption or the strong complexation of Co(II). However, the concentration of Co(II) used here was so low that pure $\text{Co}(\text{OH})_2$ precipitate cannot be formed. Thus, a transition from the adsorption to the surface-induced precipitation took place and the bentonite surface acted as a template for the formation of the surface precipitate (Wang et al., 2002).

3.6. Effect of addition sequence on cobalt sorption

Fig. 5 shows the cobalt sorption isotherms for batch 1 and 2 tests. From Fig. 5, one can see that the sorption of cobalt on FA-coated bentonite was not influenced by the



(A)



(B)

Fig. 4. Sorption isotherms of cobalt on bare and FA-coated bentonite. $m/V = 0.2$ g/l, $C(\text{FA}) = 7.1$ mg/l. (A) $\text{pH} = 6.3 \pm 0.2$; (B) $\text{pH} = 7.3 \pm 0.2$.

addition sequence after equilibration. The effect of humic substances on radionuclide sorption to clay minerals or oxides is different for different humic substances and sorbents. Wang et al. (2000) studied the effect of the addition sequence of Yb(III)/FA to alumina suspension on the sorption of Yb and found that the addition sequence influenced the Yb sorption. The effect of the addition sequence of Cm(III)/HA to alumina suspension on the sorption of Cm was studied by TRLFS. The results indicated the sorption of Cm(III) was not influenced by the addition sequence; however, the microstructure of Cm in the ternary systems was different for the different addition sequences, before any long-period equilibration (Wang et al., 2004b). Takahashi et al. (2002) studied the species of Cm(III) on FA–montmorillonite hybrid by

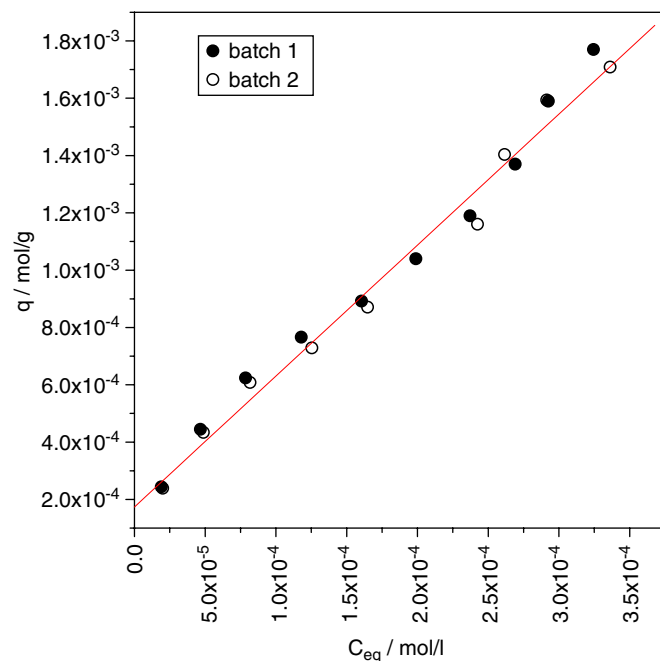


Fig. 5. Effect of addition sequences FA/ Co^{2+} on cobalt sorption to bentonite. $\text{pH} = 7.5 \pm 0.2$. $C(\text{Co}^{2+}) = 3.4 \times 10^{-4}$ mol/l, $C(\text{NaNO}_3) = 0.01$ mol/l, $C(\text{FA}) = 7.1$ mg/l, $m/V = 0.2$ g/l.

laser-induced fluorescence spectroscopy. Their results indicate that the species of Cm(III) on FA–montmorillonite hybrid is dominated by both FA and montmorillonite. From the results of this work and the references mentioned above, one can see that the species of Co(II) on FA-coated bentonite is dominated by both bentonite and FA on bentonite surface.

3.7. Sorption and desorption isotherms

Figs. 6A and B show the sorption and desorption isotherms of cobalt on bare bentonite (Fig. 6A) and on FA-coated bentonite (Fig. 6B), respectively, at $\text{pH} 6.3 \pm 0.2$. As can be seen from Fig. 6, the sorption and desorption isotherms are linear and the isotherm of desorption is much higher than that of sorption. This illustrates that sorption–desorption hysteresis occurred in the sorption of cobalt on bentonite. The sorption of cobalt on bentonite is irreversible. It is necessary to note that little cobalt was desorbed from the bare bentonite surface or FA-coated bentonite surface; the amount was within the experimental uncertainty during the desorption measurement. The results of this work indicate that strong surface complexes are formed at the surface of bentonite by chemical sorption rather than physical sorption.

The concentration of cobalt on bentonite in desorption tests is calculated from

$$q' = q - \left(C'_{\text{eq}} - \frac{C_{\text{eq}}}{2} \right) \cdot \frac{V}{m}, \quad (8)$$

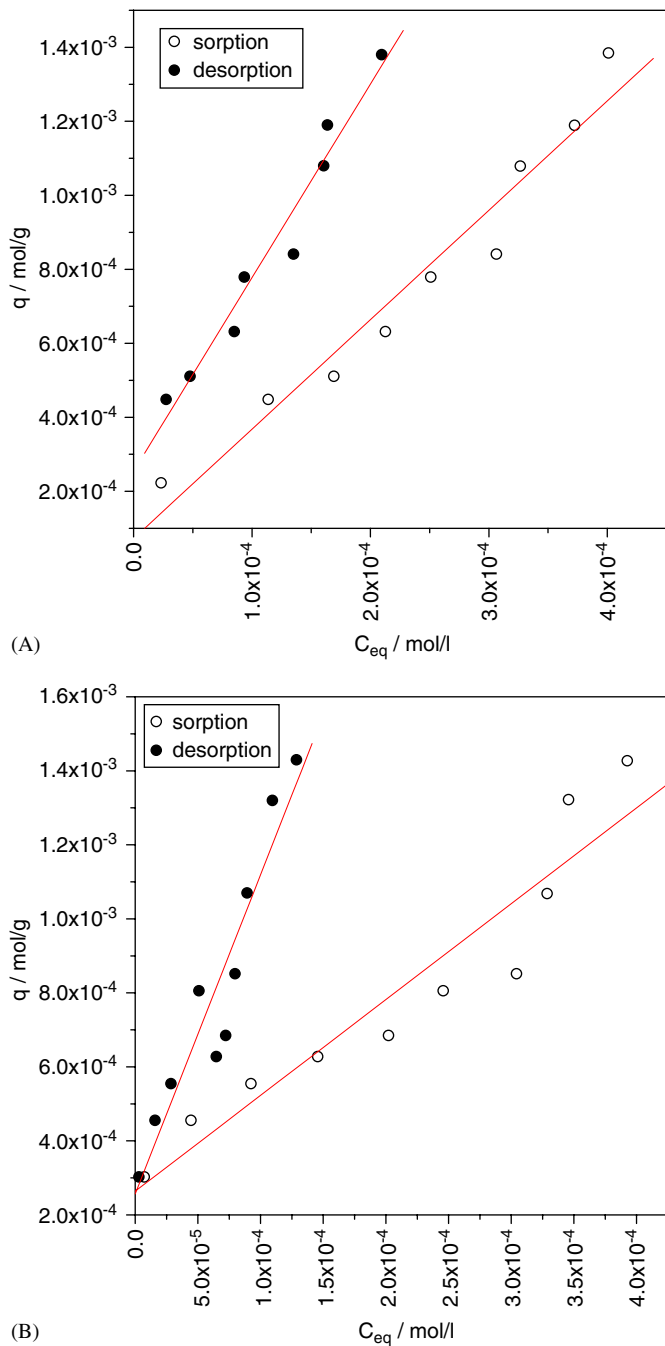


Fig. 6. Sorption and desorption isotherms of cobalt on bentonite. pH = 6.3 ± 0.2 , $m/V = 0.2$ g/l, $C(\text{NaNO}_3) = 0.01$ mol/l. (A) absence of FA; (B) presence of FA, $C(\text{FA}) = 7.1$ mg/l.

where q' is the concentration of cobalt in the solid phase after desorption (mol/g), q is the concentration of cobalt in the solid phase after sorption (at the beginning of desorption test) (mol/g), C'_{eq} is the concentration of cobalt in solution after desorption (mol/l), C_{eq} is the concentration of cobalt in solution after sorption (at the beginning of desorption test) (mol/g), V is the volume of solution (l) and m is the mass of bentonite in solution (g).

4. Conclusions

The present experimental work studied the effects of pH, ionic strength and FA on sorption of cobalt by bentonite under aerobic conditions. The sorption of cobalt on bentonite was shown to be pH-dependent and ionic strength-independent. The presence of FA significantly influenced the sorption of cobalt on bentonite. The effect of FA on cobalt sorption was pH dependent. The competition between the complexation of adsorbed FA and the dissolved FA in solution with cobalt can explain the observations of cobalt sorption on FA-coated bentonite.

Based on the results of this work, one can conclude that the fate of metal ions in the environment depends on the pH, the nature of solid surface, the nature of humic substances, and the natures of organic or inorganic compounds in the environment. Furthermore, it was possible to describe the complex interactions of the metal ions–humic substances–bentonite ternary system by (1) metal complexation by free surface hydroxyls of bentonite; (2) metal–humic substance complexation in aqueous phase; and (3) metal–humic substance complexation by humic substance adsorbed on the bentonite surface.

Acknowledgements

Financial supports from the Centurial Project of Chinese Academy of Sciences, National Natural Science Foundation of China (No.20501019) and the Anhui Natural Science Foundation (No. 03045104) are acknowledged.

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