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Sorption and desorption of Co(II) on montmorillonite in presence and absence of fulvic acid

Lei Chen,[1]* Xianjin Yu,[1] Zengdian Zhao,[1] Jingshun Pan[2]

[1] *School of Chemical Engineering, Shandong University of Technology, 255049, Zibo, Shandong, P.R. China*
[2] *China Institute of Atomic Energy, P.O.Box 275-24, 102413, Beijing, P.R. China*

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Sorption and desorption of Co(II) on montmorillonite under ambient conditions as a function of pH, ionic strength and fulvic acid are studied by batch technique. The results indicate that the sorption of Co(II) is dependent on pH, and ionic strength. The sorption-desorption hysteresis is found in the desorption tests. Surface complexation is considered as the main sorption mechanism of Co(II) on montmorillonite. The presence of fulvic acid (FA) enhances the sorption of Co(II) on montmorillonite. Montmorillonite is considered as a promising candidate for the solidification and pre-concentration of Co(II) from large volume of solutions.

Introduction

^{60}Co and ^{58}Co are very important radionuclides which are present in liquid wastes released from pressurized water nuclear power reactors, and ^{60}Co is also widely used in research and medical applications. The sorption of radiocobalt on clays or oxides changes the physical-chemical forms of cobalt and thereby controls the migration and diffusion of cobalt in waters and natural environment. YU et al.[1] studied the sorption of Co(II) on bentonite and concluded that surface complexation was the main sorption mechanism. Fulvic acid has little effect at pH<6, a positive effect at pH 6–8 and a negative effect on cobalt sorption at pH>8. Co(II) forms outer sphere complexes with surface hydroxyl groups with the permanent layer sites at bentonite surface with increasing cobalt concentration and pH.[2] NAGY and KÓNYA[3] studied the sorption of cobalt on calcium-montmorillonite and found that Co^{2+} forms strong complexes Co-EDTA. XU et al.[4] studied the sorption of Co(II) on bentonite and found that the sorption of Co(II) on bentonite is irreversible and strong chemical sorption and surface complexation is formed at bentonite surface.

It is well known that humic substances (HS) influence the sorption of metal ions onto all kinds of clays and oxides by their complexation ability with metal ions, their potential involvement in redox reactions and their potential to form coatings on solid surfaces. Generally, the presence of humic substances increases the sorption of metal ions at low pH range. At high pH range, the presence of humic substances has a negative or no influence on metal ion sorption on minerals, as compared with the sorption in the absence of HS. Sorption of radiocobalt and other radionuclides on clay mineral-humic substance hybrids has been studied extensively in the last decades.[4–13]

Based on the results mentioned above, one can see that the sorption mechanisms of Co(II) on clay minerals are not yet sufficiently conclusive. In particular, the effect of humic substances on the sorption of Co(II) by montmorillonite is not clear. In this paper, we consider the sorption-desorption of Co(II) on montmorillonite and the effect of fulvic acid, pH, ionic strength and foreign ions on the sorption of Co(II) is investigated too.

Experimental

Chemicals

The sample of montmorillonite is derived from Lin'an county (China) and well characterized. The N_2-BET surface area is 38.5 m^2/g. The cation-exchange capacity is 0.9 meq/g. The point of zero charge (pH_{zpc}) is 7.8±0.1. The main components of the montmorillonite are listed in Table 1.

Fulvic acid was extracted from weathered coal of Gongxian (Henan Province, China) and had been applied in sorption experiments by other authors.[14]

The concentration of FA was measured by UV-VIS spectrophotometer at wavelength 290 nm.

The cobalt solution was prepared from $CoCl_2·6H_2O$ and the concentration of cobalt was analyzed by spectrophotometry at a wavelength of 592 nm by using xylenol orange and CTMAB.

Procedure

The sorption and desorption were measured by batch technique. All the experiments were carried out under ambient conditions. The stock solution of montmorillonite and sodium nitrate first equilibrated for 2 days, then the cobalt stock solution was added in polyethylene test tubes to achieve the desired

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* E-mail: chenlei761205@sina.com

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background electrolyte concentration. In the test for the investigation of the influence of fulvic acid on Co(II) sorption, the addition sequence was that montmorillonite and sodium nitrate equilibrated for 2 days before the addition of fulvic acid; after 2 days of equilibration, cobalt stock solution was added to the suspension of montmorillonite-fulvic acid. The pH values were adjusted with small amounts of 0.01M HCl or NaOH. After 2 days shaking, the suspension was centrifuged at 6500 rpm for 20 minutes for the separation of solid and liquid phase. Time dependent sorption results indicated that 5 hours was enough to achieve equilibration, thereby, 2 days equilibration was enough to achieve the sorption equilibration of Co(II) on montmorillonite.

For desorption experiments, the suspension of montmorillonite was centrifuged (6500 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.

Results and discussion

Sorption isotherms in the presence/absence of FA

Sorption isotherms of Co(II) on montmorillonite in the presence and absence of fulvic acid at pH 6.5±0.2 and in 0.01M $NaNO_3$ are shown in Fig. 1. The sorption isotherm of Co(II) on mont-FA hybrids is higher than that of Co(II) on bare montmorillonite, which suggests that the presence of FA enhances the sorption of Co(II) on montmorillonite. $CoOH^+$ can be formed in solution and the adsorption process is rapidly completed by interaction with montmorillonite, but also montmorillonite absorbs cobalt ions into the sheets of hydroxyl groups:[15,16]

$$Co^{2+} + H_2O \leftrightarrow CoOH^+ + H^+ \qquad (1)$$

$$\equiv S-O^- + CoOH^+ \leftrightarrow \equiv S-OCoOH \qquad (2)$$

$$(\equiv S-OH)_2 + Co^{2+} \leftrightarrow (\equiv S-O)_2 - Co + 2H^+ \qquad (3)$$

Table 1. Main components of montmorillonite

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

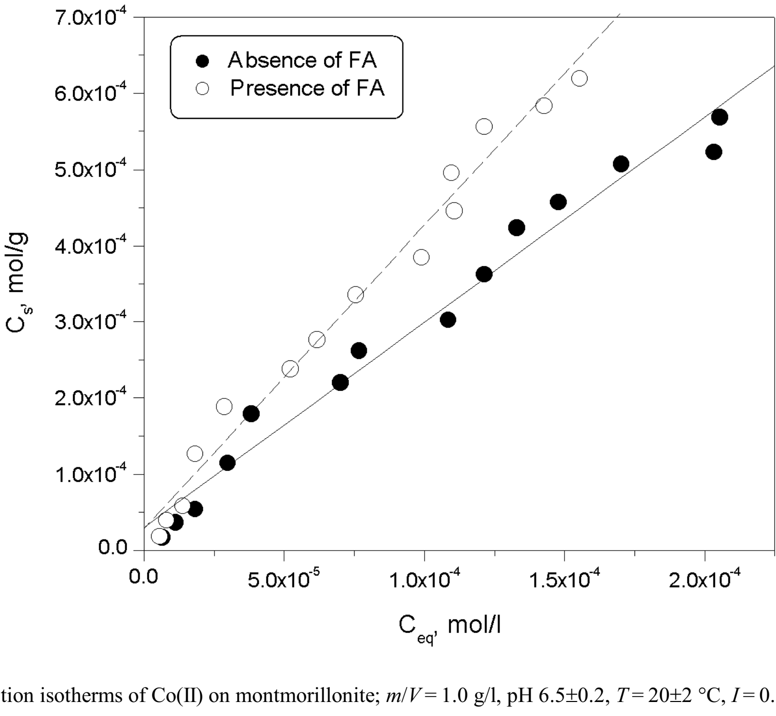

Fig. 1. Sorption isotherms of Co(II) on montmorillonite; $m/V = 1.0$ g/l, pH 6.5±0.2, $T = 20\pm2$ °C, $I = 0.01M$ $NaNO_3$

The possible modes of ligand exchange mechanism between montmorillonite and humic substances can be described as:

$$\begin{aligned}&\equiv \mathrm{S-OH_2^+ + {}^-OOC-FA} \leftrightarrow \\ &\leftrightarrow \equiv \mathrm{S-OOC-FA+H_2O}\end{aligned} \tag{4}$$

$$\equiv \mathrm{S}^{-\mathrm{OH}_2^+}_{-\mathrm{OH}} + \mathrm{HOOC-FA} \leftrightarrow \equiv \mathrm{S}^{-\mathrm{O}-}_{-\mathrm{O}-}\mathrm{C-FA+2H_2O} \tag{5}$$

The presence of FA in solution affects the sorption of cobalt on montmorillonite, and the species of cobalt on FA-coated montmorillonite is mainly dominated by both FA and montmorillonite; the formation of ternary complexes such as ≡S–O–Co–FA or ≡S–O–FA–Co occurs on the surface of fulvic acid-bound montmorillonite.[6,12]

At pH 6.5, the surface charge of montmorillonite is positive as the $\mathrm{pH_{zpc}}$ is 7.8. Thereby, the negatively charged FA is easily adsorbed on montmorillonite surface and the strong complexation ability of FA adsorbed on montmorillonite surface with Co(II) enhances the sorption of Co(II) on FA-montmorillonite hybrids. It is necessary to notice that the initial concentration of FA is 8.0 mg/l, whereas the concentration of FA in the supernatant after centrifugation is only (0.5±0.3) mg/l, which suggests that ~95% FA is adsorbed on montmorillonite surface.

The distribution coefficient, K_d, of Co(II) sorption is calculated as:

$$K_{d(sorp)} = \frac{C_{s(sorp)}}{C_{eq(sorp)}} = \frac{C_0 - C_{eq(sorp)}}{C_{eq(sorp)}} \cdot \frac{V}{m} \tag{6}$$

where $C_{s(sorp)}$ is the concentration of cobalt in the solid phase after sorption (mol/g), $C_{eq(sorp)}$ 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 the solution (l), and m is the mass of montmorillonite in solution (g).

In order to distinguish the K_d value of desorption, herein we name K_d value as $K_{d(sorp)}$ in sorption tests and $K_{d(desorp)}$ in the desorption measurements. The K_d values for Co(II) sorption and desorption under different conditions are summarized in Table 2. The relative contribution (*RC*%) of FA on Co(II) sorption is calculated as follow:

$$RC\% = \frac{K_{d(FA)} - K_{d(noFA)}}{K_{d(noFA)}} \times 100\% \tag{7}$$

where $K_{d(FA)}$ is the distribution coefficient of Co(II) sorption on mont-FA hybrids in the presence of FA, and $K_{d(noFA)}$ is the distribution coefficient of Co(II) sorption on bare montmorillonite in the absence of FA. The *RC*% of FA calculated from Eq. (7) is 47%. Considering the concentration of FA (8 mg/l) and that of montmorillonite (1.0 g/l), one can see that FA represents only ~0.8% of the whole mass of montmorillonite, and contributes 47% to Co(II) sorption on mont-FA hybrids.

Sorption-desorption isotherms

Sorption-desorption isotherms of Co(II) on bare montmorillonite and mont-FA hybrids are shown in Figs 2 and 3, respectively. One can see that the desorption isotherms are higher than the sorption isotherms, which indicates that sorption-desorption hysteresis occurs and the sorption is irreversible. The distribution coefficient of Co(II) after desorption tests is calculated as:

$$\begin{aligned}K_{d(desorp)} &= \frac{C_{s(desorp)}}{C_{eq(desorp)}} = \\ &= \frac{C_{s(sorp)} - (C_{eq(desorp)} - C_{eq(sorp)}/2) \times V/m}{C_{eq(desorp)}}\end{aligned} \tag{8}$$

where $C_{s(sorp)}$ is the concentration of Co(II) on solid phase after sorption experiment, $C_{eq(sorp)}$ is the concentration of Co(II) in supernatant after sorption experiment, $C_{eq(desorp)}$ is the concentration of Co(II) in supernatant after the desorption experiment.

Table 2. Average distribution coefficient of Co(II) sorption on montmorillonite

System	Ionic strength	pH	$\overline{K}_{d(sorp)}$, ml/g	$\overline{K}_{d(desorp)}$, ml/g	Hysteresis coefficient, %
Montmorillonite	0.01M $NaNO_3$	6.5	3200 ± 550	5070 ± 860	58
Mont+FA	0.01M $NaNO_3$	6.5	4700 ± 1000	7700 ± 1800	64
Montmorillonite	0.001M $NaNO_3$	6.5	3200 ± 500		
Montmorillonite	0.01M KNO_3	6.5	3120 ± 270		
Montmorillonite	0.01M KNO_3	3.5	670 ± 90		

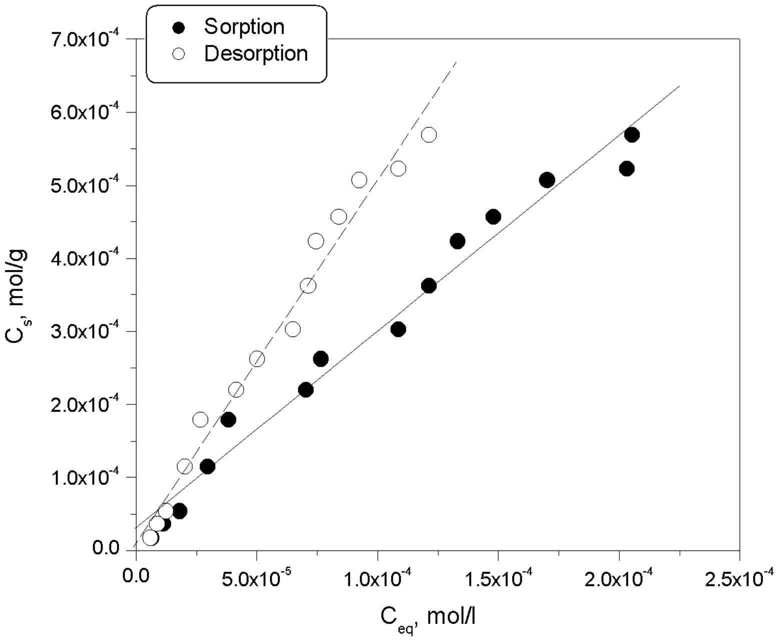

Fig. 2. Sorption and desorption isotherms of Co(II) on montmorillonite; $m/V = 1.0$ g/l, pH 6.5±0.2, $T = 20\pm2$ °C, $I = 0.01$M $NaNO_3$

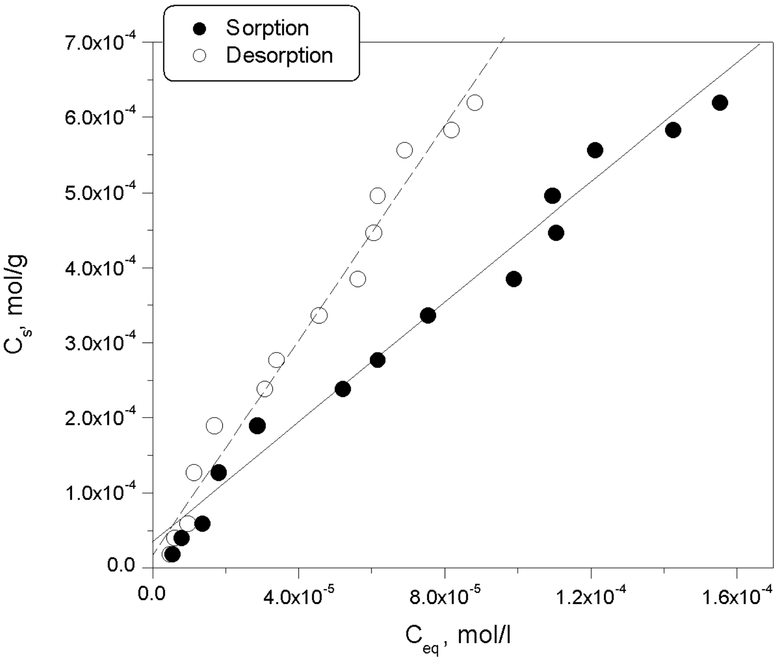

Fig. 3. Sorption and desorption isotherms of Co(II) on montmorillonite in the presence of FA; $m/V = 1.0$ g/l, pH 6.5±0.2, $T = 20\pm2$ °C, $I = 0.01$M $NaNO_3$

The sorption-desorption hysteresis coefficient is calculated as:

$$HC\% = \frac{\overline{K}_{d(desorp)} - \overline{K}_{d(sorp)}}{\overline{K}_{d(sorp)}} \times 100\% \qquad (9)$$

The values of $K_{d(desorp)}$ and $HC\%$ are listed in Table 2. It is clear that HC% of mont-FA system is higher than that of bare montmorillonite, which suggests that Co(II) sorbed on mont-FA hybrids is more difficult to be desorbed than Co(II) sorbed on bare montmorillonite. The high value $HC\%$ of Co(II) sorption on montmorillonite suggests that strong surface complexation or chemical sorption rather than ion-exchange or physical sorption contributes the sorption of Co(II) on montmorillonite or mont-FA hybrids.[4,17]

The linear sorption and desorption isotherms suggest that the sorption of Co(II) on montmorillonite or mont-FA is far from saturation. The high $K_{d(sorp)}$ and $K_{d(desorp)}$ values also indicate that the high sorption ability of Co(II) on montmorillonite, which suggests that montmorillonite is a suitable candidate for the pre-concentration and solidification of cobalt from large volume of waste waters.

Effect of ionic strength

Sorption isotherms of Co(II) on bare montmorillonite at pH 6.5±0.2 in 0.01M and and 0.001M $NaNO_3$ solutions are shown in Fig. 4. Effect of $NaNO_3$ concentration on Co(II) sorption is shown in Fig. 5. From Fig. 4 and the K_d values listed in Table 2, one can see there is no difference under the experimental uncertainty for the sorption of Co(II) under the two $NaNO_3$ concentrations. In Fig. 5, one can see that the percent removal of Co(II) at very low $NaNO_3$ concentrations is a little higher than that at high $NaNO_3$ concentrations if the uncertainty is not taken into account, however, one can also see that there is little difference in the removal of Co(II) over the whole $NaNO_3$ concentrations used in this work if the experimental uncertainty is considered. Thus, we think that sorption of Co(II) on montmorillonite is not appreciable affected by ionic strength because there is no difference in the sorption isotherms (Fig. 4). This ionic strength independent sorption suggests that sorption of Co(II) is not contributed to ion-exchange, which is consistent with the results of sorption-desorption measurements (Figs 2 and 3).

Effect of foreign cations

Sorption isotherms of Co(II) on bare montmorillonite at pH 6.5±0.2 in 0.01M $NaNO_3$ and 0.01M KNO_3 solutions, respectively, are shown in Fig. 6. There is little difference in the sorption isotherms and the average distribution coefficients are (3200±550) ml/g and (3120±270) ml/g, respectively. The influence of monovalent Na^+ and K^+ on the sorption of bivalent Co(II) is very weak and one can not see any difference in this work. The results of Co(II) sorption on bentonite[1,4] and alumina[18] indicate that Co(II) sorption is independent of ionic strength. Similar results of Ni(II) sorption on carbon nanotubes and Th(IV) sorption on alumina were also reported by CHEN and WANG.[19,20]

Effect of pH

Sorption isotherms of Co(II) on bare montmorillonite in 0.01M KNO_3 at pH 3.5±0.2 and 6.5±0.2 are shown in Fig. 7. As can been seen in Fig. 7, the sorption isotherm of Co(II) at pH 6.5 is much higher than that of Co(II) at pH 3.5, which indicates that the sorption of Co(II) on montmorillonite is strongly dependent on pH values. Comparing the sorption isotherms at different pH and ionic strength conditions, one can see that the sorption of Co(II) on montmorillonite is dependent on pH and independent of ionic strength, which is in agreement with the sorption mechanism of surface complexation.[10,21]

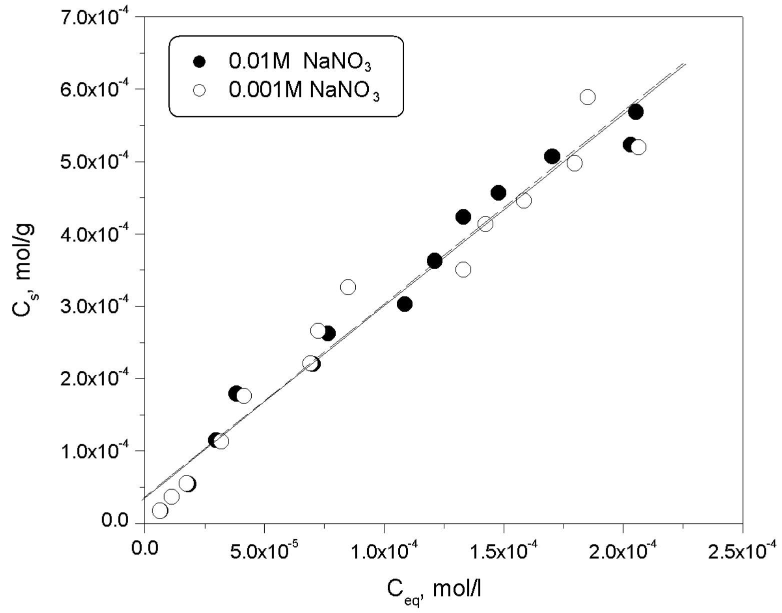

Fig. 4. Sorption isotherms of Co(II) on montmorillonite; m/V = 1.0 g/l, pH 6.5±0.2, T = 20±2 °C

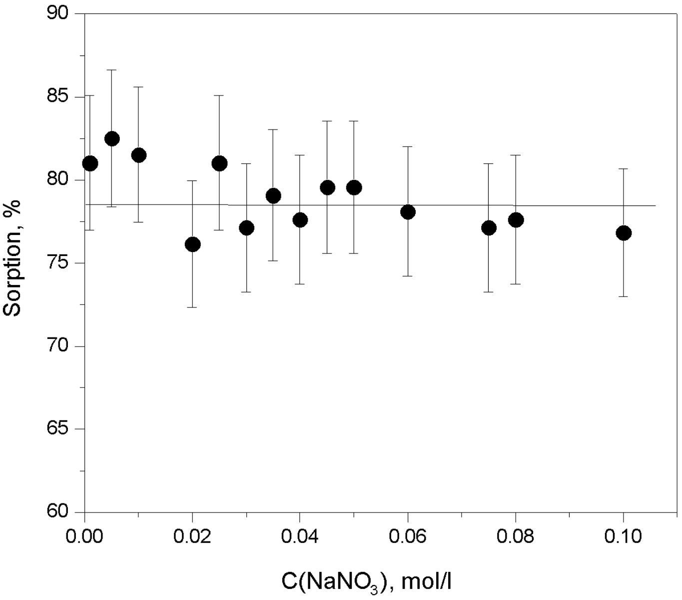

Fig. 5. Effect of ionic strength on the sorption of Co(II) on montmorillonite; $m/V = 1.0$ g/l, pH 6.5±0.2, $T = 20\pm2$ °C, $C_{(\text{Co})\text{initial}} = 2.18\cdot10^{-4}$ mol/l

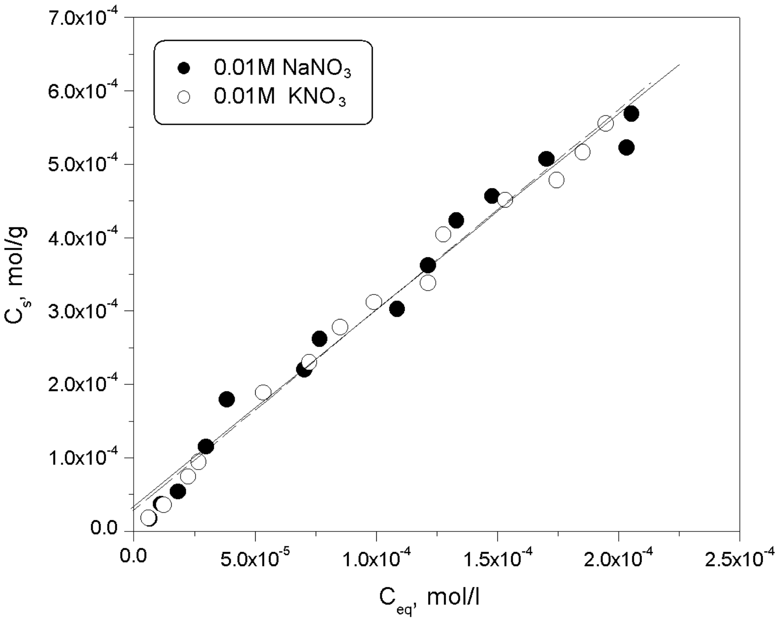

Fig. 6. Effect of foreign ion on the sorption isotherms of Co(II) on montmorillonite; $m/V = 1.0$ g/l, pH 6.5±0.2, $T = 20\pm2$ °C

SEM study

The scanning electron microscope (SEM) analysis of the samples montmorillonite and FA-montmorillonite prepared at pH 6.5 and in 0.01M $NaNO_3$ solutions are shown in Fig. 8. The SEM measurements (HITACHI S-4300, Hitachi, Japan) were performed under vacuum conditions (about 10^{-3}–10^{-4} Pa), and scanned directly to achieve the SEM image.[22] One can see that the sizes of FA-montmorillonite hybrids are bigger than that of montmorillonite. The presence of FA can make montmorillonite easily to form aggregation because of the high oxygen and carboxylic functional groups of FA.

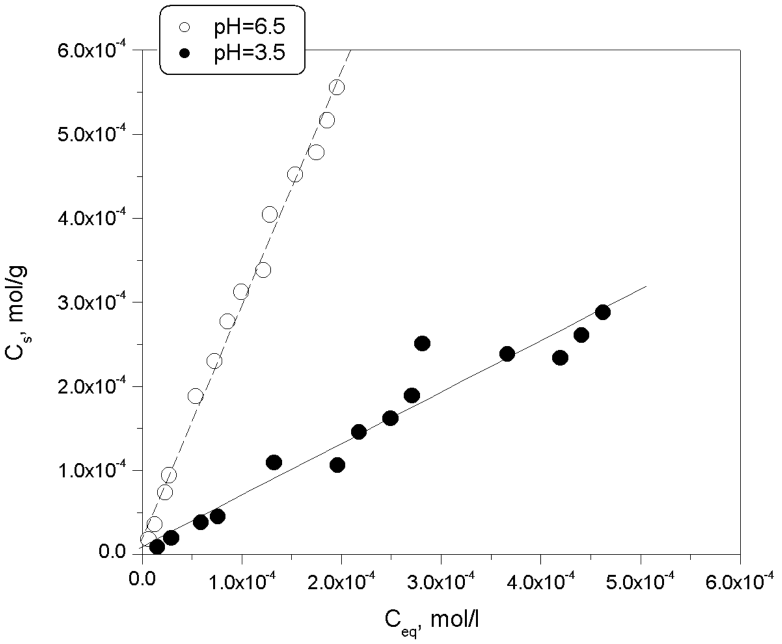

Fig. 7. Effect of pH on the sorption isotherms of Co(II) on montmorillonite; $m/V = 1.0$ g/l, $I = 0.01$M KNO_3, $T = 20\pm2$ °C; (●) pH 3.5±0.2; (○) pH 6.5±0.2

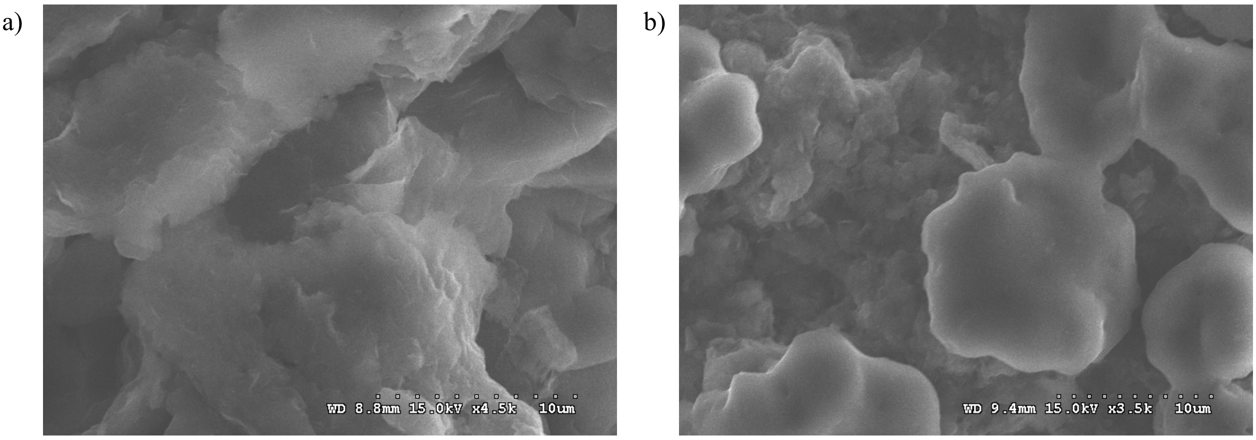

Fig. 8. SEM image of FA-montmorillonite (a); and montmorillonite (b)

The differences in the particle sizes and surface structures of FA-montmorillonite and montmorillonite can cause the different sorption abilities. One can think that SEM analysis is a good method to observe the surface structures and colloid particles of sorbent, which are important for the evaluation of sorption ability of sorbent, which is related to the sorption behavior of metal ions in natural environment.

Conclusions

Sorption and desorption of Co(II) on montmorillonite as a function of pH, ionic strength, foreign ions and fulvic acid were considered. The following conclusion can be achieved from the results. Sorption of Co(II) on montmorillonite is dependent on pH values. Generally the sorption increases with increasing pH values. Sorption of Co(II) on montmorillonite is independent of ionic strength. Surface complexation rather than cation exchange contributes the sorption of Co(II) on montmorillonite. Fulvic acid enhances the sorption of Co(II) on mont-FA hybrids at pH 6.5 studied in this work. Sorption of Co(II) on montmorillonite is irreversible. Co(II) sorbed on montmorillonite is difficult to be desorbed from the solid phase. Sorption of Co(II) on montmorillonite is far from saturation under our investigation. Montmorillonite is a promising candidate for pre-concentration and solidification of Co(II) from large volume of solutions.

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