

Effect of shaking time, ionic strength, temperature and pH value on desorption of Cr(III) adsorbed onto GMZ bentonite

Yong-gui CHEN^{1,2,3}, Yong HE^{1,3}, Wei-min YE¹, Wang-hua SUI², Min-min XIAO³

1. Key Laboratory of Geotechnical and Underground Engineering of Ministry of Education, Tongji University, Shanghai 200092, China;
2. State Key Laboratory for GeoMechanics and Deep Underground Engineering, China University of Mining and Technology, Xuzhou 221008, China;
3. School of Civil Engineering and Architecture, Changsha University of Science and Technology, Changsha 410114, China

Received 17 April 2013; accepted 6 June 2013

Abstract: The Cr(III) desorption experiments of Gaomiaozi (GMZ) bentonite in aqueous solutions were performed. The variables affecting the desorption behaviors, such as contact time, concentration of the desorbent, pH value of the solution, temperature and desorption isotherms, were investigated by the batch experiments. The results show that the adsorbed Cr(III) on GMZ bentonite can be easily extracted by the desorbent. Kinetics examination shows that desorption is slower than adsorption, and the desorption rate increases with time and reaches the equilibrium after 3 h. The final desorption ratios of Cr(III) are 89.4%, 56.5% and 77.2% in the desorption solution with 0.1 mol/L HCl, 1 mol/L NaCl, and 1 mol/L CaCl₂, respectively, and the concentration can promote the desorption progress. Furthermore, the results of successive regeneration cycles indicate that the bentonite has a good regeneration ability and reusability. The pH value is an important factor in the Cr(III) desorption from the GMZ bentonite. The results of adsorption and desorption isotherms show that both adsorption and desorption isotherms are consistent with the Freundlich equation. The comparison of adsorption and desorption isotherms implies that the adsorption/desorption hysteresis is negligible and the transport of Cr(III) in bentonite can be described by a reversible adsorption process.

Key words: GMZ bentonite; Cr(III); desorption; isotherms

1 Introduction

In recent years, soil contamination by heavy metals and wastewater disposal is of great concern because of the potential threat to ecosystem functions and human health. Many studies have been focused on the adsorption of heavy metals on different soil materials and under different experimental conditions [1]. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. For instance, in the nuclear industry, radioactive waste contains a variety of radionuclides which have a long half life and will badly pollute the environment if the pollutants are not treated well. Chromium is commonly used in acid electroplating, tanning, painting, dye and

manufacturing, and petroleum refining. If each of the Cr(III) atoms took up only one more atom of oxygen for conversion to a higher valence state, the entire atmospheric oxygen could be stripped out [2]. However, before the earth attains such an anoxic disaster, life will be poisoned by Cr(VI) toxicity as a result of Cr(III) to Cr(VI) conversion.

Among typical methods for wastewater treatment, adsorption by solid adsorbents is an effective method because of its high efficiency, low cost, availability, profitability and convenience to use [3,4]. Bentonite exhibits an enormous surface area when it is hydrated in water. It consists of numerous microscopic platelets, each with negative charges on flat surfaces and positive charges on edges [5]. Due to its physical and chemical properties, such as large specific surface area, cation

exchange capacity, and adsorptive affinity for organic and inorganic ions, bentonite is considered the most promising candidates for use in decontamination and disposal of high level radioactive waste (HLW) [6]. Moreover, several kinds of bentonites have been selected as materials for engineered barrier in HLW repositories in the world, such as MX-80 bentonite, FEBEX bentonite and Kunigel V1 bentonite. In China, the Gaomiaozi (GMZ) bentonite has been considered a potential buffer/backfill material for HLW repository [7].

Up to now, the adsorption of heavy metal ions on bentonite or its mixture materials has been extensively studied in recent years [8]. However, few researchers study the desorption behavior of heavy metal ions from adsorbed bentonite, which is considered to be important to understand the reversibility of adsorption process. Moreover, the transport of toxic metal ions and radionuclides in soil is generally controlled by adsorption. Meanwhile, adsorption hysteresis in environmental sorbents has important implications for pollutant transport [9]. Thus, the study of desorption is conducive to elucidate adsorption process on soil, to recover heavy metal ions from adsorbent, and to multiple regenerate adsorbent.

In the previous work, the adsorption of Cr(III) on GMZ bentonite was studied by equilibrium batch techniques, and the effects of shaking time, pH value, adsorbent dose, ionic strength and temperature were investigated on the adsorption [10]. The aim of this work is to study the desorption characteristics of Cr(III) from adsorbed GMZ bentonite, analyze the reversibility of adsorption process and obtain the desorption isotherms of Cr(III) from GMZ bentonite.

2 Experimental

2.1 Materials

The raw GMZ bentonite used in this work was extracted from the Inner Mongolia, China. It has a grain size of no more than 160 μm , as shown in Fig. 1. The mineralogical composition was quantitatively analyzed by X-ray diffraction method [11]. The bulk composition (mass fraction) was determined as follows: 75.4% montmorillonite, 11.7% quartz, 7.3% cristobalite, 4.3% feldspar, 0.8% kaolinite, 0.5% calcite. It shows that the proportion of montmorillonite is dominant in the GMZ bentonite. The cation exchange capacity (CEC) of GMZ bentonite is 0.773 mmol/g and the specific surface area (SSA) is 570 m^2/g [12].

Stock solutions of Cr(III) with the concentration of 1.923 mmol/L were prepared from its nitrate. The pH values of the system were adjusted by 0.01 mol/L HCl or 0.01 mol/L NaOH to obtain the desired values, which were determined by a PHSJ-3F pH meter. The

desorbents were adjusted with 0.1–2.0 mol/L NaCl (or CaCl_2) solution to the desired values. Fresh dilutions were used for each experiment. All the chemicals used were in analytical grade.

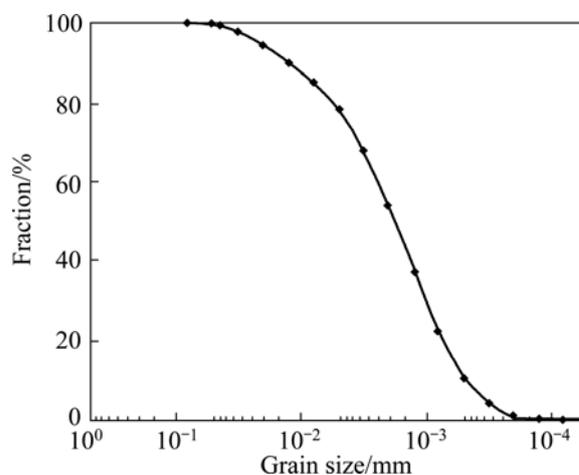


Fig. 1 Grain size distribution of GMZ bentonite used in this work [13]

2.2 Batch desorption studies

Desorption was carried out using the Cr(III) adsorbed GMZ bentonite prepared in the previous work. When adsorption equilibrium reached, the suspension was centrifuged and most of the supernatant was exchanged with the same volume of the background electrolyte solution (i.e. distilled water, NaCl, CaCl_2 , or HCl)[14]. The amount of metal ions desorbed from the GMZ bentonite was then determined by an ultraviolet-visible (UV-Vis) spectrophotometer, WFJ2100, at a wavelength of 540 nm. The adsorbent was finally collected from the solution by filtration, washed with distilled water, and then reused in next adsorption/desorption cycle experiment. The adsorption/desorption experiments were conducted for three cycles.

All batch experiments were conducted with adsorbent soil in a 25 mL Erlenmeyer flasks closed with glass stoppers on a magnetic stirrer at a constant temperature maintained by a thermostatic water bath to elucidate the optimum conditions of pH and ion concentration. The solution pH was carefully adjusted by adding a small amount of HCl or NaOH solution and measured using a pH meter. The effect of pH on the desorption was investigated at pH values between 1.0 and 9.0. The concentrations of Cr(III) solution after desorption were measured by an UV-Vis spectrophotometer. The amount of Cr(III) ions desorbed from GMZ bentonite was determined by the remaining concentrations of Cr(III) ion solution after desorption. The desorption rate was calculated from the equation as follows:

$$w = \frac{q_{\text{des}}}{q_{\text{ads}}} \times 100\% \quad (1)$$

where w is the desorption rate (%); q_{des} is the amount of metal ions desorbed from the bentonite and q_{ads} is the amount of metal ions adsorbed on the bentonite.

Equilibrium distribution coefficient (K_d , L/mg), extensively used for characterizing various heavy metal ions sorption and desorption [15], was calculated as

$$K_d = \frac{q_e}{C_e} \quad (2)$$

where q_e is the amount of Cr(III) adsorbed on bentonite (mg/g); C_e is the aqueous Cr(III) concentration after desorption (mg/L).

3 Results and discussion

3.1 Effect of shaking time on desorption

The influence of shaking time on the desorption is shown in Fig. 2. It is obvious that the amount of desorption increases with shaking time increasing. The maximum desorption capacity was observed after 3 h, beyond which there was almost no further increase in desorption. According to the previous work [10], the adsorption reached equilibrium after 2 h. Obviously, desorption is slower than adsorption. Many studies also indicated that the adsorption rates are significantly higher than the desorption rates (such as Co(II), Pb(II) and Cu(II) ions desorption from bentonite reported by MANOHAR et al [16] and KORKUT et al [5], respectively). This can be explained by differences in activation energies between forward and reverse reactions.

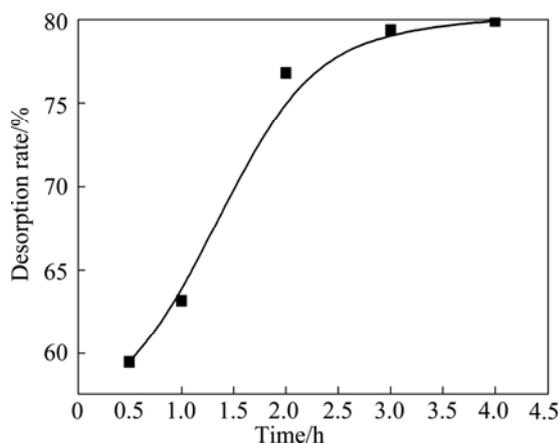


Fig. 2 Effect of shaking time on Cr(III) desorption from GMZ bentonite ($c_0=100$ mg/L, $T=298$ K, $c_{\text{NaCl}}=1.5$ mol/L)

Generally, three models including pseudo first-order, pseudo-second-order and intraparticle diffusion equations [17] are applied to simulate the adsorption

kinetic data. However, it is clear that the 1st and 2nd order models are commonly used for adsorption. To describe desorption kinetics, a modified one was proposed in this work considering the metal–bentonite desorption reaction as the rate-limiting step.

It is assumed in the modified 0-order model that the desorption rate is constant, and independent of the quantity of the Cr(III) filled sites. It can be expressed as

$$\frac{dq}{dt} = -k_{0,\text{des}} \quad (3)$$

where q (mg/g) is the remaining amount of metal bound to the bentonite at time t (min); dq/dt is the desorption rate; $k_{0,\text{des}}$ is the 0-order desorption rate constant (mg/(g·min)).

The pseudo 1st-order model assumes that the desorption rate is proportional to the number of Cr(III) filled sites and can be expressed as

$$\frac{dq}{dt} = -k_{1,\text{des}}q \quad (4)$$

where $k_{1,\text{des}}$ is the 1st-order desorption rate constant (mg/(g·min)).

The modified pseudo-2nd-order model assumes that the rate of desorption is proportional to the square of the number of Cr (III) filled sites and can be expressed as

$$\frac{dq}{dt} = -k_{2,\text{des}}q^2 \quad (5)$$

where $k_{2,\text{des}}$ is the 2nd-order desorption rate constant (mg/(g·min)).

Stepwise numerical integration over time was performed for all three rate expressions according to the following equation:

$$q_{n+1} = q_n - \left(\frac{dq}{dt} \right)_n (t_{n+1} - t_n) \quad (6)$$

where q_n is the amount of Cr(III) remaining on bentonite at time t_n ; q_0 is the initial amount of Cr(III) on bentonite (at time $t_0=0$), as determined from a prior adsorption step. It can be seen from Eq. (6) that the amount of Cr(III) on bentonite at time t_{n+1} will be the amount at time t_n minus the desorption rate multiplied by the incremental time step.

The desorption kinetics of Cr(III) by NaCl from GMZ bentonite were modeled by the 0, 1st and 2nd order models. The results shown in Fig. 3 indicate that the 2nd order model fits the desorption data better than others. This can be explained by the fact that the selected concentrations of the reactant species (desorbents: NaCl and CaCl_2 , or HCl in the case of desorption) are not in the rate-governing range, and the initial excess of the reactants will give a mixed response because the order of desorption is a fractional value between the 1st and 2nd

order. It is fairly well known that metal desorption mainly involves the process of ion exchange, in which protons or other ions of the desorbing agent replace metal ions from the binding sites.

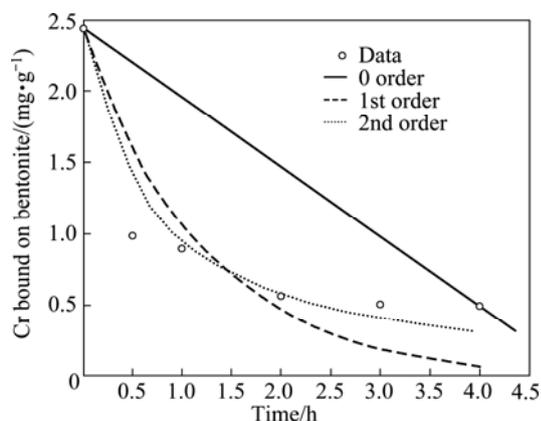


Fig. 3 Kinetics of Cr(III) desorption by NaCl from GMZ bentonite

3.2 Effect of ionic strength on desorption

The previous studies revealed that decreasing of pH or increasing of ionic strength can decrease the adsorption capacity of Cr(III) [10]. Thus, Cr(III) ions can be liberated by washing the adsorbents with acid or salt solutions. The desorption of Cr(III) was studied by different desorbents and by varying the concentration of desorbents of NaCl from 0 to 2.0 mol/L while keeping all other variables (i.e. pH value, shaking time and concentration) constant and the results are shown in Fig. 4 and Table 1.

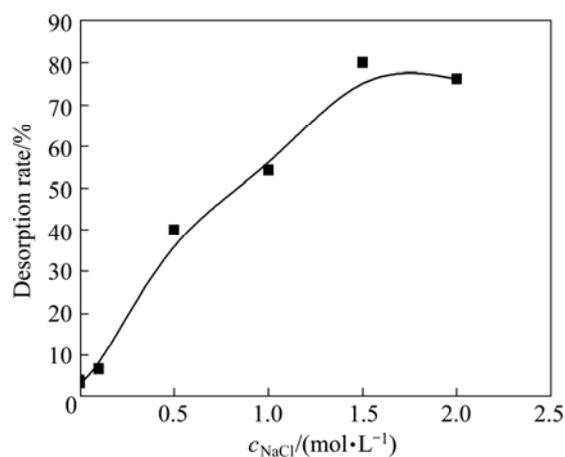


Fig. 4 Effect of NaCl concentration on Cr(III) desorption from GMZ bentonite

The results in Fig. 4 and Table 1 indicate that the highest desorption rates of Cr(III) are 89.4% and 77.2% for HCl and CaCl₂, respectively. The desorption rate gradually increases at the concentration of NaCl from 0 to 2.0 mol/L, maintains a high level around 1.5 mol/L and does not considerably change at high concentration.

These phenomena may be explained by the fact that HCl is a strong acid and can destroy the bonds between bentonite and metal ions.

Table 1 Desorption rate of Cr(III) ions from GMZ bentonite by different desorbents

| Desorbent | Desorption rate/% |
|---------------------------|-------------------|
| Distilled water | 3.4 |
| 0.1 mol/L HCl | 89.4 |
| 1 mol/L NaCl | 56.5 |
| 1 mol/L CaCl ₂ | 77.2 |

Table 1 shows that only 3.4% of the adsorbed Cr(III) ions can be desorbed, indicates that distilled water is not a suitable desorbent. The small amount of desorbed Cr(III) ions can be ascribed to desorption of the Cr(III) ions physically adsorbed on the adsorbent surface. It is suggested that the main adsorption mechanism of Cr(III) ions onto the GMZ bentonite is chemical adsorption, which is too stable to be desorbed by distilled water. BUSINELLI et al [18] studied and pointed out that lead desorption hysteresis by montmorillonite was due to irreversible Pb inner-sphere binding to the mineral edge sites and its precipitation at pH value which is higher than the hydrolysis point of Pb(II).

Different desorption rates of the adsorbed Cr(III) for different desorbent indicate that Cr(III) uptake is also controlled by ion exchange. Previous adsorption studies of U(VI) in smectites indicate that multiple surface species result both from ion exchange and surface coordination reactions [19].

3.3 Multiple cycles of regeneration

NaCl solution was used as the desorbent to regenerate the adsorbent in this work. The adsorption/desorption cycles were tested three times on the regenerated bentonite by the same adsorbent in this work and the results are shown in Fig. 5.

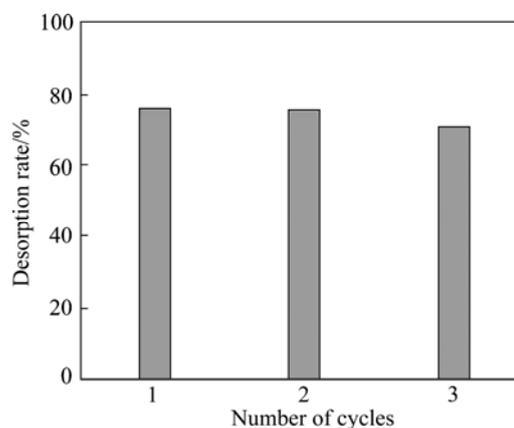


Fig. 5 Adsorption/desorption cycles of Cr(III) on GMZ bentonite

It can be seen from Fig. 5 that the amount of adsorbed or desorbed Cr(III) ions almost remains constant on three cycles. This might be due to the ignorable amount of bentonite lost during the cycle experiments. The decrease of desorption rate no more than 8% shows that the adsorbent is a good potential material to adsorb Cr(III) ions, even though it is reused for few times. The regeneration of adsorbent with 1.5 mol/L NaCl indicates that the adsorption/desorption process is a reversible process. Whereas, it must be mentioned that the adsorbent was modified partly by Na^+ in the first adsorption/desorption cycle, so the adsorbent was Na-bentonite in the following cycles. Similar results were also reported by MANOHAR et al [16], ÖZER et al [20], SAFA et al [21] and ANIRUDHAN and SUCHITHRA [22] who used bentonite as the adsorbent for Co(II), Cu(II), Zn(II) and Pb(II) ions desorption and the adsorbent regeneration studies, respectively.

3.4 Effect of temperature on desorption

The desorption experiments of Cr(III) were performed from GMZ bentonite at 4 different temperatures and the results are shown in Fig. 6.

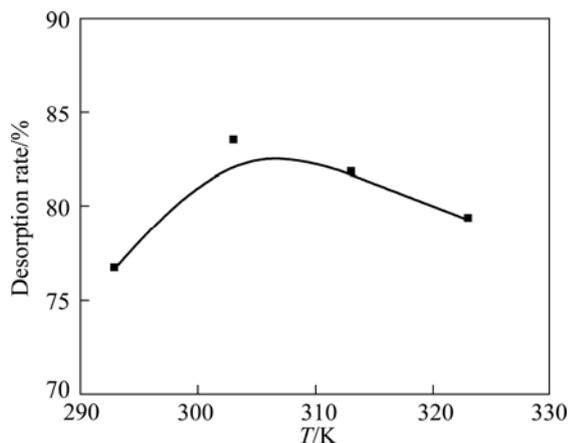


Fig. 6 Effect of temperature on Cr(III) desorption on GMZ bentonite

The results in Fig. 6 indicate that the desorption rate of Cr(III) from GMZ bentonite increases gradually from 293 to 303 K. According to the 2nd order model, the rate limiting step may be a chemical desorption involving valence forces through sharing or exchanging the electrons between Cr(III) and bentonite. Cr(III) ions are difficult to desorb because the energy of making chemical bonds broken provided by simple mechanical agitation at a low temperature is not sufficient. Beyond 303 K, the desorption rate decreases with increasing temperature. It can be found that the desorption process is exothermic at a higher temperature. Above all, the desorption of Cr(III) from the adsorbed GMZ bentonite is not significantly influenced by the temperature.

3.5 Effect of pH on desorption

Since the surface charge of an adsorbent can be modified by changing pH of the solution, or hydrogen ions themselves strongly compete with adsorbates, pH is one of the most important parameters affecting the metal adsorption process. The influence of solution pH on Cr(III) desorption was tested at pH=1, 3, 5, 7, and 9. The results shown in Fig. 7 indicate that the pH value of solution plays an important role in the desorption of Cr(III) from GMZ bentonite. The desorption rate gradually decreases at pH=1–9 and maintains a high level around pH=1. A maximum desorption rate of Cr(III) from GMZ bentonite of 89.4% is observed at pH=1.

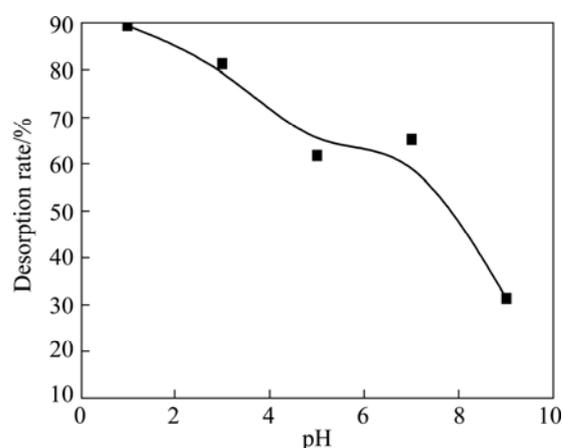


Fig. 7 Effect of pH on Cr(III) desorption from GMZ bentonite

It was found that the adsorption capacity of Cr(III) on GMZ bentonite increased as pH increased from 2 to 7 in the previous works [10]. As a reverse reaction of adsorption, the desorption has reverse results on the pH-dependence in this work. WANG et al [23] reported that the desorption rate of Sr in the gels was 100% when acid solution was used as desorbent, but only 81.4% when KCl solution was used. It can be caused by the fact that besides the adsorption mechanism of ionic exchange on the carboxyl groups, the metal ion is captured by chelation interaction. BHATTACHARYYA and GUPTA [4] covered that the adsorption of Cr(III) reduced with pH at low pH, but it increased with pH at higher pH, which could be due to metal hydroxide precipitation helping Cr(III) retention by the clay.

The desorption mechanism of Cr(III) from GMZ bentonite at low pH can be explained as follows: 1) in acidic region, both the adsorbent and adsorbate are positively charged and the net interaction is the electrostatic repulsion [22]; 2) the positively charged metal ions face a good competition with the higher concentration of H^+ ions present in the reaction mixture. At low pH solution, H^+ ions adsorbed on to the clay surfaces cause a decrease in adsorption of heavy metal ions of Cr(III). On the other side, it causes an increasing

in desorption of heavy metal ions. It has been found that at low pH solution most heavy metals become mobile and adsorption onto clay particles becomes less effective. Moreover, at high pH value of soil, the metal precipitation should also be taken into account at high metal concentrations.

3.6 Adsorption and desorption isotherms

Various isotherm equations were chosen to describe the adsorption and desorption process, namely the Langmuir and Freundlich isotherms. The Langmuir model is the simplest and the most commonly used model to represent the adsorption from a liquid phase by a solid phase. While the Freundlich isotherm is an empirical equation, which assumes the heterogeneity of surface and the exponential distribution of active sites and their energies.

Figure 8 shows the adsorption and desorption isotherms of Cr(III) on GMZ bentonite. The equilibrium data are correlated with the Freundlich isotherm. The Freundlich equation is used

$$q_e = k_F C_e^{1/n} \quad (7)$$

or, in linear form

$$\lg q_e = \lg k_F + 1/n \lg C_e \quad (8)$$

where q_e is the amount of solute adsorbed per unit mass of adsorbent after equilibrium (mg/g); C_e is the equilibrium concentration of metal ions remaining in the bulk solution (mg/L); k_F is the constant indicative of the relative adsorption or desorption capacity of the adsorbent ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$); $1/n$ is the constant indicative of the intensity of the adsorption or desorption. A plot of $\lg q_e$ against $\lg C_e$ gives a straight line, the slope and the intercept of which correspond to $1/n$ and $\lg k_F$, respectively.

According to the definition of a reversible adsorption process, it is assumed that $K_{d,ads} \approx K_{d,des}$ and

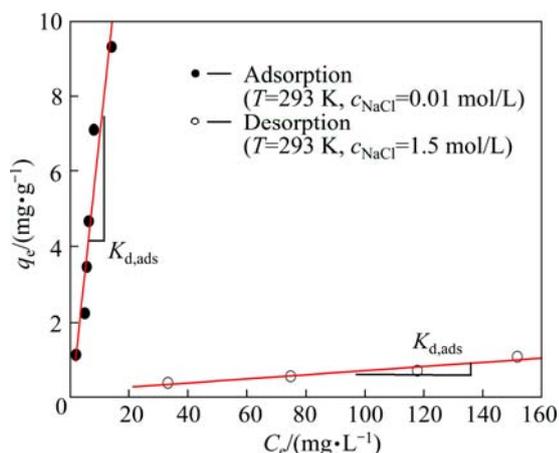


Fig. 8 Adsorption and desorption isotherms of Cr(III) on GMZ bentonite

that adsorption and desorption rates are similar. If $K_{d,ads} < K_{d,des}$, adsorption cannot be considered totally reversible. Hence, taking into account only the above results in the desorbent by NaCl, the adsorption of Cr(III) seems to be reversible. However, the results from Table 1 show that the Cr(III) immersed in distilled water has a low desorption rate, so the adsorption of Cr(III) cannot be considered totally reversible without NaCl or HCl solution. It can be deduced that little part of Cr(III) is weakly adsorbed on the GMZ bentonite, which suggests that most part of Cr(III) is located in the ion exchange sites and is readily accessible. The comparison of adsorption and desorption isotherms in Fig. 8 implies that the adsorption/desorption hysteresis can be negligible by the desorbent of 1.5 mol/L NaCl. Similar conclusions that demonstrate reversible adsorption/desorption process on the bentonite were also drawn by WANG et al [24] and GUO et al [25] for Sr(II), Eu(III) desorption, respectively.

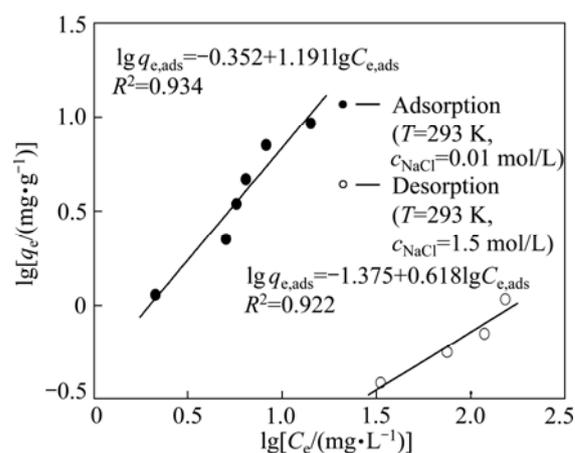


Fig. 9 Freundlich adsorption and desorption isotherms of Cr(III) on GMZ bentonite

The linear plots of $\lg q_e$ versus $\lg C_e$ with $R^2=0.934$ for adsorption isotherm and with $R^2=0.922$ for desorption isotherm are shown in Fig. 9. The results show that the data obtained for Cr(III) adsorption and desorption fit well to the Freundlich model. Some previous adsorption studies of Cr(III) in bentonite indicated that the adsorption data for Cr(III) in the concentration range fit in the Freundlich equation [26]. Similarly, as a reverse reaction of adsorption, the desorption also fits well to the Freundlich model in this work. Similar results have been reported by TURIN and BOWMAN [27], SHIRVANI et al [28] for herbicide and cadmium desorption from Casa Grande and Palygorskite soil, respectively. These studies indicate that both adsorption and desorption isotherms can be satisfactorily described by the Freundlich equation.

Hysteresis indexes were calculated when hysteresis was observed in the adsorption and desorption isotherms.

The hysteresis index based on the Freundlich exponent [27] is calculated as

$$\eta = \frac{(1/n)_{\text{ads}}}{(1/n)_{\text{des}}} \quad (9)$$

where η is the hysteresis index based on the Freundlich isotherm; $(1/n)_{\text{ads}}$ and $(1/n)_{\text{des}}$ are the exponents of the fitted Freundlich equation in the adsorption and desorption branches, respectively.

The k_F constants for Cr(III) on GMZ bentonite obtained from the desorption isotherms ($k_{F,\text{des}}$) are significantly lower than that calculated from the adsorption isotherms ($k_{F,\text{ads}}$) (Fig. 9). The ratio of Freundlich exponents ($\eta=1.927$) for the adsorption/desorption of Cr(III) on GMZ bentonite is distinctly lower than that reported by SHIRVANI et al [28] for cadmium adsorption/desorption from Palygorskite, which indicates that the adsorption/desorption hysteresis of Cr(III) on GMZ bentonite can be negligible when NaCl solution is used as the desorbent.

4 Conclusions

1) The adsorbed Cr (III) on GMZ bentonite can be easily extracted by NaCl solution and the desorption rate is slower than that of adsorption.

2) The final desorption ratios of Cr(III) are 89.4%, 56.5% and 77.2% in the desorption solution with 0.1 mol/L HCl, 1 mol/L NaCl, and 1 mol/L CaCl₂, respectively, and the concentration can promote the desorption progress.

3) The pH value is an important factor in the Cr(III) desorption from the GMZ bentonite.

4) Both adsorption and desorption isotherms are consistent with the Freundlich model.

References

- [1] GUREL A. Adsorption characteristics of heavy metals in soil zones developed on spilite [J]. *Environmental Geology*, 2006, 51: 333–340.
- [2] KISHAN B K. Assessment of chromium pollution at bual mines, ORISSA [D]. Rourkela: Department of Mining Engineering, National Institute of Technology, 2010: 1–2.
- [3] BRADL H B. Adsorption of heavy metal ions on soils and soils constituents [J]. *Journal of Colloid and Interface Science*, 2004, 277: 1–18.
- [4] BHATTACHARYYA K G, GUPTA S S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review [J]. *Advances in Colloid and Interface Science*, 2008, 140: 114–131.
- [5] KORKUT O, SAYAN E, LACIN O, BAYRAK B. Investigation of adsorption and ultrasound assisted desorption of lead (II) and copper (II) on local bentonite: A modelling study [J]. *Desalination*, 2010, 259: 243–248.
- [6] KAYA A, ÖREN A H. Adsorption of zinc from aqueous solutions to bentonite [J]. *Journal of Hazardous Materials*, 2005, 125: 183–189.
- [7] YE Wei-min, CUI Yu-jun, QIAN Li-xin, CHEN Bao. An experimental study of the water transfer through confined compacted GMZ bentonite [J]. *Engineering Geology*, 2009, 108: 169–176.
- [8] MISSANA T, GARCIA-GUTIERREZ M. Adsorption of bivalent ions (Ca(II), Sr(II) and Co(II)) onto FEBEX bentonite [J]. *Physics and Chemistry of the Earth*, 2007, 32: 559–567.
- [9] SANDER M, PIGNATELLO J J. On the reversibility of sorption to black carbon: Distinguishing true hysteresis from artificial hysteresis caused by dilution of a competing adsorbate [J]. *Environmental Science and Technology*, 2007, 41: 843–849.
- [10] CHEN Yong-gui, HE Yong, YE Wei-min, ZHANG Xiong-fei, LIN Cui-hua. Removal of chromium(III) from aqueous solutions by adsorption on bentonite from Gaomiaozi, China [J]. *Environmental Earth Sciences*, 2012, 67(5): 1261–1268.
- [11] WEN Zhi-jian. Selection and basic properties of the buffer material for high-level radioactive waste repository in China [J]. *Acta Geologica Sinica*, 2008, 82: 1050–1055.
- [12] WEN Zhi-jian. Physical property of China's buffer material for high level radioactive waste repositories [J]. *Chinese Journal of Rock Mechanics and Engineering*, 2006, 25: 794–800. (in Chinese)
- [13] QIAN Li-xin. A fundamental study of GMZ bentonite as buffer material in deep geological disposal for high-level radioactive waste [D]. Shanghai: Tongji University, 2007. (in Chinese)
- [14] ASTM C1733–10. Standard test method for distribution coefficients of inorganic species by the batch method [S].
- [15] LU C, SAMPER J, JOSÉ LUIS CORMENZANA, M A H, MONTENEGRO L, ÁNGEL CUNÑADO M. Reactive transport model and apparent K_d of Ni in the near field of a HLW repository ingranite [J]. *Computers & Geosciences*, 2012, 49: 256–266.
- [16] MANOHAR D M, NOELINE B F, ANIRUDHAN T S. Adsorption performance of Al-pillared bentonite clay for the removal of cobalt(II) from aqueous phase [J]. *Applied Clay Science*, 2006, 31: 194–206.
- [17] HO Y S, MCKAY G. Kinetic models for the sorption of dye from aqueous solution by wood [J]. *Journal Environmental Science, Health (Part B): Process Safety and Environmental Protection*, 1998, 76(B2): 183–191.
- [18] BUSINELLI M, CASCIARI F, BUSINELLI D, GIGLIOTTI G. Mechanisms of Pb(II) sorption and desorption at some clays and goethite-water interfaces [J]. *Agronomie*, 2003, 23: 219–225.
- [19] MCKINLEY J P, ZACHARA J M, SMITH S C, TURNER G D. The influence of hydrolysis and multiple site binding reactions on adsorption of U(VI) onto montmorillonite [J]. *Clays and Clay Miner*, 1995, 43: 568–598.
- [20] ÖZER G, ÖZCAN A, ERDEM B, ÖZCAN A S. Prediction of the kinetics, equilibrium and thermodynamic parameters of adsorption of copper(II) ions onto 8-hydroxy quinoline immobilized bentonite [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2008, 317: 174–185.
- [21] SAFA A, ÖZCAN, ÖZER G, ÖZCAN A. Adsorption of lead(II) ions onto 8-hydroxy quinoline-immobilized bentonite [J]. *Journal of Hazardous Materials*, 2009, 161: 499–509.
- [22] ANIRUDHAN T S, SUCHITHRA P S. Heavy metals uptake from aqueous solutions and industrial wastewaters by humic acid-immobilized polymer/bentonite composite: Kinetics and equilibrium modeling [J]. *Chemical Engineering Journal*, 2010, 156: 146–156.
- [23] WANG Min, XU Ling, PENG Jing, ZHAI Mao-lin, LI Jiu-qiang, WEI Gen-shuan. Adsorption and desorption of Sr(II) ions in the gels based on polysaccharide derivatives [J]. *Journal of Hazardous Materials*, 2009, 171: 820–826.
- [24] WANG Xiang-ke, CHEN Yi-xue, WU Yi-can. Sorption and desorption of radiostrontium on powdered bentonite: Effect of pH and fulvic acid [J]. *Journal of Radioanalytical and Nuclear Chemistry*, 2004, 261(3): 497–500.
- [25] GUO Zhi-jun, XU Jiang, SHI Ke-liang, TANG Yu-qin, WU

- Wang-suo, TAO Zu-yi. Eu(III) adsorption/desorption on Na-bentonite: Experimental and modeling studies [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2009, 339: 126–133.
- [26] KHAN S A, RIAZ-UR-REHMAN, KHAN A. Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite [J]. Waste Management, 1995, 15: 271–282.
- [27] TURIN H J, BOWMAN R S. Sorption behavior and competition of Bromacil, Napropamide, and Prometryn [J]. Journal of Environmental Quality, 1997, 26(5): 1282–1287.
- [28] SHIRVANI M, KALBASI M, SHARIATMADARI H, NOURBAKHSH F, NAJAFI B. Sorption–desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: Isotherm hysteresis [J]. Chemosphere, 2006, 65: 2178–2184.

振荡时间、离子强度、温度和 pH 值对 GMZ 膨润土中 Cr(III)解吸特性的影响

陈永贵^{1,2,3}, 贺勇^{1,3}, 叶为民¹, 隋旺华², 肖明明³

1. 同济大学 岩土及地下工程教育部重点实验室, 上海 200092;
2. 中国矿业大学 深部岩土力学与地下工程国家重点实验室, 徐州 221008;
3. 长沙理工大学 土木与建筑学院, 长沙 410114

摘要: 对吸附在高庙子(GMZ)膨润土上的 Cr(III)进行解吸实验, 研究振荡时间、解吸溶液离子强度、温度和 pH 值等因素对解吸特性的影响规律。结果表明: 高庙子膨润土上 Cr(III)的解吸过程较易发生; Cr(III)的解吸动力学过程较吸附过程慢, 实验条件下解吸过程在 3 h 后达到平衡; 当使用 0.1 mol/L HCl、1 mol/L NaCl 和 1 mol/L CaCl₂ 作为解吸液时, Cr(III)的最终解吸率分别达 89.4%、56.5% 和 77.2%; 增大解吸溶液的离子浓度能够促进解吸过程的发生; pH 值对 Cr(III)解吸过程有重要影响; 吸附/解吸过程较符合 Freundlich 等温模型。GMZ 膨润土在处理 Cr(III)废水时具有较好的再生能力, 可以多次重复利用。

关键词: 高庙子膨润土; Cr(III); 解吸; 等温线

(Edited by Chao WANG)