



Sorption of copper(II) onto super-adsorbent of bentonite–polyacrylamide composites

Guixia Zhao^{a,b}, Hongxia Zhang^c, Qiaohui Fan^c, Xuemei Ren^b, Jiaying Li^b,
Yixue Chen^a, Xiangke Wang^{a,b,*}

^a School of Nuclear Science and Engineering, North China Electric Power University, Beijing, 102206, PR China

^b Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei, 230031, PR China

^c Radiochemistry Laboratory, Lanzhou University, Lanzhou, 730000, PR China

ARTICLE INFO

Article history:

Received 2 July 2009

Received in revised form 25 August 2009

Accepted 27 August 2009

Available online 1 September 2009

Keywords:

Bentonite–polyacrylamide

Super-adsorbent

Cu(II)

Sorption

Thermodynamic data

ABSTRACT

In this work, bentonite embedded in the polyacrylamide (PAAm) gels was used as a novel adsorbent for the removal of Cu(II) from aqueous solution. The sorption and desorption of Cu(II) on bentonite–polyacrylamide (BENT–PAAm) was investigated as the function of pH, ionic strength, adsorbent content, Cu(II) concentrations and temperature. The results indicated that the sorption of Cu(II) on BENT–PAAm was strongly dependent on pH, ionic strength and temperature. The sorption increased from about 9% to 97% at pH ranging from 2.4 to 7. The sorption of Cu(II) on BENT–PAAm increased with increasing temperature and decreasing ionic strength. The sorption of Cu(II) on BENT and on BENT–PAAm was an endothermic and irreversible process. The results of desorption indicated that the adsorbed Cu(II) ions on solid particles were difficult to be desorbed from solid to liquid phase. From the comparison with BENT, BENT–PAAm showed higher sorption capacity with C_{smax} increasing from 29 to 33 mg/g at pH 6.2 and from 11 to 20 mg/g at pH 5.0 for the sorption of Cu(II) from BENT to BENT–PAAm composites. The average standard enthalpy change (ΔH°) and the entropy change (ΔS°) of Cu(II) sorption on BENT–PAAm are higher than those of Cu(II) sorption on BENT. The BENT–PAAm composites can be used as a super-adsorbent for the removal of Cu(II) from aqueous solution.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Copper(II) is a toxic heavy metal ion in industrial wastewater. Trace amount ($\mu\text{g L}^{-1}$) of copper is required and necessary for some organisms as cofactors for the enzymatic activities. However, for most of the organisms, concentrations at ppm (mg L^{-1}) level are known to be toxic because of irreversible inhibition of some enzymes by the heavy metal ions [1]. Due to the mobility and toxicity in natural water ecosystems, the presence of Cu(II) ions in surface water and groundwater poses a major inorganic contamination problem. Up to now, there are various technologies for removing heavy metal ions from solution, including filtration, surface complexation, chemical precipitation, ion exchange, adsorption, electrode position, and membrane processing [2–5]. Among these methods, adsorption is considered one of the best techniques.

Bentonite has attracted great interest in environmental pollution management because of its outstanding properties such as

high swelling ability and cation exchange capacity. As is known, bentonite is classified as a smectic soil composed of an expandable 2:1 type of aluminosilicate clay mineral. It consists of flat particles with characteristic size ca. 10^2 to 10^3 nm with negatively charged surface ions and sodium counterions. The flat plates of clay have a tendency to pack parallel to each other forming liquid-crystalline order. Yang et al. [6] studied the sorption of Ni(II) on bentonite and found that bentonite was a suitable material in the solidification and preconcentration of Ni(II) ions from aqueous solutions. Xu et al. [7] studied sorption and complexation of Co(II) on bare and FA bound MX-80 bentonite. They found that the sorption of Co(II) on bentonite was strongly dependent on pH values. Surface complexation and chemical sorption are the main sorption mechanism. Yu et al. [8] also found the sorption of cobalt by bentonite was ionic strength-independent.

Previous studies showed that sorption of metal ions onto clays were dependent on pH, ionic strength, adsorbent concentration and some organic matter. Polyacrylamide (PAAm) gels content amide bonds indicating good water solubility and strong complexation ability with metal ions. It is widely used in disposing industrial wastewater as a flocculating agent. It was reported that swollen hydro-gels could be strengthened without decreasing their sorption ability via incorporation with the clay particles as a reinforcing

* Corresponding author at: Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei, 230031, PR China. Tel.: +86 551 5592788; fax: +86 551 5592788.

E-mail address: xkwang@ipp.ac.cn (X. Wang).

agent [9]. Although the clay particles are not chemically attached to the network, they act as active fillers and contribute significantly to the elastic modulus of the gel [9]. Many papers have focused on the adsorption of heavy metal ions on clays. However, few referred to the sorption of heavy metal ions on the composites of clays and polymers. Although PAAm can form strong complexes with metal ions in solution, the good water solubility of PAAm greatly hinders the application of PAAm to remove heavy metal ions from wastewater in real work. If PAAm can form composites with clay particles, the solubility of PAAm in aqueous solutions is negligible because the PAAm are connected together with the insoluble clay particles. To date many other properties of such composites have not been studied. These composite materials combine the elasticity and permeability of gels with the high ability of clays to adsorb heavy metal ions. The clay particles embedded in the cross-linked swollen polymer network strengthen the gel and prevent its collapse in bad solvents. On the other hand, immobilization in the cross-linked network prevents coagulation of dispersed clay particles. In particular, the modified composites have the potential to be universal ion-exchange materials, to form complexes with metal ions, providing a wide spectrum of new adsorbent system. However, the application of bentonite–polyacrylamide composites in the removal of heavy metal ions from wastewater has not been reported. In this work, we first prepared bentonite–polyacrylamide composites and compared the sorption abilities of bare bentonite and super-adsorbent of bentonite–polyacrylamide composites. The sorption mechanism of Cu(II) on bentonite–polyacrylamide composites was also discussed.

2. Experimental

2.1. Sample preparation

The bentonite was derived from Gaomiaozhi county (Inner Mongolia, China). Acrylamide (AAm), *N,N'*-methylene-(bis)-acrylamide (BAA), ammonium persulfate (PS), *N,N,N',N'*-tetramethylethylenediamine (TEMED) were purchased from Sinopharm Chemical Reagent Co. Ltd.

The raw bentonite was purified to Na-bentonite by stirring with 1.0 M NaCl under room temperature for one week, and then washed with doubly distilled water until no chloride ion was detected by using 0.1 M AgNO₃ solution. In the end, the sample was dried at 100 °C for 24 h and sieved by 53 μm sieve. The N₂-BET surface area of the sample was 26.14 m²/g. In this work, the Na-bentonite was noted as BENT.

The gels of polyacrylamide (PAAm) were prepared by free-radical copolymerization of monomers in the presence of a cross-linking agent in an aqueous suspension of BENT and the fraction of BAA in the monomers was 1 mol%. The gels were prepared as follows: 0.48 g BENT dissolved in 8 mL distilled water was added to 3.32 g 11 wt% monomers solution; and then the obtained suspension was mixed by a magnetic stirrer for 1 h. After this process, 0.0035 mL TEMED and 0.03 mL 10 wt% PS solution were added to the suspension. Polymerization was carried out in a glass tube at 60 °C for 8 h, and then at 25 °C for 24 h. The obtained gels were removed from the tube, and washed with a large excess of distilled water. Then, the gels were dried at 60 °C in the oven and sieved by 53 μm sieve. It has been shown that the degree of conversion during polymerization was higher than 95% [9]. Thus gained composites were named as BENT–PAAm.

2.2. Batch experiments

All solutions were prepared with Milli-Q water. All sorption experiments were carried out under ambient conditions. Stock sus-

pensions of BENT or BENT–PAAm composites, NaNO₃, and Cu(II) stock solution were added in the polyethylene tubes to achieve the desired concentrations of different components. The pH values of the suspension were adjusted by adding negligible volumes of 0.1 or 0.01 M HClO₄ or NaOH. After the suspensions were shaken for 48 h, the solid and liquid phases were separated by centrifugation at 9000 rpm for 30 min at the controlled temperature same to sorption experiments. Our pre-experiments demonstrated that 2 days were enough to achieve the sorption equilibrium. The concentration of Cu(II) was measured by using spectrophotometric analysis with bicyclohexone oxalyldidrazone (BCO) at wavelength 544 nm. The relative errors of the data were less than 5%.

For desorption experiments, after centrifugation at the end of sorption experiments, half of the supernatant was pipetted and the equal volume of background electrolyte solution was added. The pH was adjusted to obtain the same pH value again as in sorption experiments. Then the mixture was shaken and centrifuged at the same conditions as in sorption experiments.

2.3. XRD and FTIR analysis

X-ray powder diffraction (XRD) patterns of the BENT and BENT–PAAm were performed using a MAC Science Co. M18XHF diffractometer with Cu Kα (λ = 0.15406 nm) radiation. The XRD pattern was identified by comparison to the JCPD standards. The diffracted intensities were recorded from 5 to 70 2θ angles. The 2θ-scanning rate was 2°/min. The surface functional groups of BENT and BENT–PAAm were characterized by Fourier transform infrared spectroscopy (FTIR). The samples for the FTIR measurements were mounted on a Bruker EQUINOX55 spectrometer in KBr pellet at room temperature.

2.4. Experimental data analysis

The sorption percentage (%) of Cu(II) on the solid is calculated by the following equation:

$$\text{Sorption}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

Similarly, the amount of copper ion adsorbed on the solid is calculated as follows:

$$C_s = (C_0 - C_e) \times \frac{V}{m} \text{ (mg/g)} \quad (2)$$

As a standard parameter in the assessment of the physico-chemical behavior of metal ions between solid and liquid phases, distribution coefficient (K_d) is calculated using the following equation:

$$K_d = \frac{C_s}{C_e} \text{ (mL/g)} \quad (3)$$

where C_0 (mg/L) is the initial concentration of Cu(II) in suspension; C_e (mg/L) is the equilibrium concentration of Cu(II) in supernatant after centrifugation; V (mL) is the volume of the solution; m (g) is the mass of solid and C_s (mg/g) is the amount of metal ions adsorbed on per weight unit of solid after equilibrium.

In this paper, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were applied to describe the sorption data. The Langmuir model is widely used for modeling equilibrium data. The isotherm is valid for monolayer sorption to surface [10].

$$C_s = \frac{bC_{s\max}C_e}{1 + bC_e} \quad (4)$$

Eq. (4) can be expressed in linear form:

$$\frac{C_e}{C_s} = \frac{1}{bC_{s\max}} + \frac{C_e}{C_{s\max}} \quad (5)$$

where C_{smax} (mg/g), related to the sorption capacity, is the maximum amount of adsorbent at complete monolayer coverage, and b (L/mg) is a binding constant which relates to the heat of sorption.

The Freundlich expression is an empirical equation describing sorption to heterogeneous surface [11]. The Freundlich equation is presented as:

$$C_s = K_F C_e^n \quad (6)$$

Eq. (6) can be expressed in linear form:

$$\log C_s = \log K_F + n \log C_e \quad (7)$$

where K_F ($\text{mol}^{1-n} \text{L}^n \text{g}^{-1}$) represents the sorption capacity when metal ion equilibrium concentration equals to 1, and n represents the degree of dependence of sorption with equilibrium concentration.

The D–R isotherm is more general than the Langmuir, because it does not assume a homogeneous surface or constant sorption potential. The D–R equation is expressed as [12]:

$$C_s = C_{smax} \exp(-\beta \varepsilon^2) \quad (8)$$

Eq. (8) can be expressed in linear form:

$$\ln C_s = \ln C_{smax} - \beta \varepsilon^2 \quad (9)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

where β is the activity coefficient related to mean sorption energy ($\text{mol}^2 \text{kJ}^{-2}$); ε is the Polanyi potential; R is the ideal gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature in Kelvin (K). E (kJ mol^{-1}) is defined as the free energy change required to transfer 1 mol of ions from solution to the solid surfaces, which equals to:

$$E = \frac{1}{\sqrt{2\beta}} \quad (11)$$

The magnitude of E is useful for estimating the type of sorption reaction. If E is in the range of $8\text{--}16 \text{ kJ mol}^{-1}$, the sorption is governed by chemical ion-exchange. In the case of $E < 8 \text{ kJ mol}^{-1}$, physical forces may affect the sorption. On the other hand, sorption may be dominated by particle diffusion if $E > 16 \text{ kJ mol}^{-1}$ [13].

The thermodynamic parameters (ΔH° , ΔS° , ΔG°) for Cu(II) sorption to BENT and BENT–PAAm can be obtained from the temperature dependent data. The free energy change (ΔG°) is calculated by the following equation [14]:

$$\Delta G^\circ = -RT \ln K^\circ \quad (12)$$

where K° is the sorption equilibrium constant. Values of $\ln K^\circ$ are obtained by plotting $\ln K_d$ vs. C_e and extrapolating C_e to zero [15].

The standard entropy change (ΔS°) is calculated using the following relationship:

$$\Delta S^\circ = - \left(\frac{\partial \Delta G^\circ}{\partial T} \right)_p \quad (13)$$

The average standard enthalpy change (ΔH°) is then calculated from the equation:

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \quad (14)$$

3. Result and discussion

3.1. Microscopic spectroscopic analysis

3.1.1. XRD analysis of BENT and BENT–PAAm

The XRD patterns of BENT and BENT–PAAm are shown in Fig. 1. It shows that BENT mainly consists of montmorillonite, quartz, feldspar and calcite. Different from BENT, BENT–PAAm does not

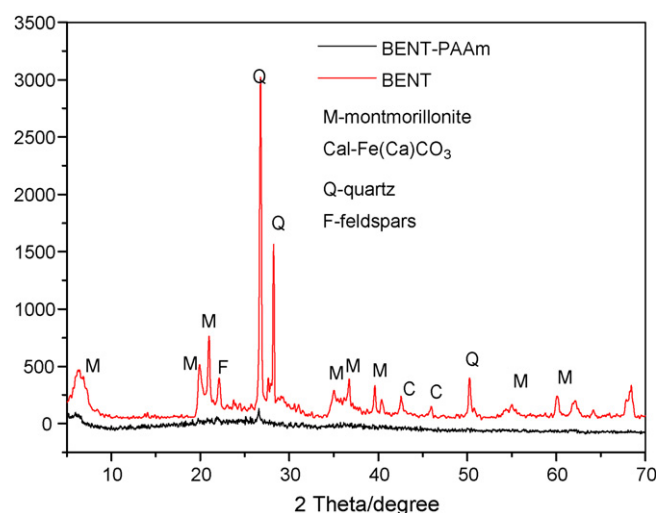


Fig. 1. XRD patterns of BENT and BENT–PAAm.

show sharp signals except the weak band at 26.6° . The results indicate that the polymerization of acrylamide destroyed the structure of BENT, resulting in confusional crystal lattice. This confusional state, which was also reported by Starodoubtsev et al. [9], may be due to the crosslink in the BENT–PAAm.

3.1.2. Fourier transformed infrared spectrums of BENT and BENT–PAAm

The FTIR spectra of BENT and BENT–PAAm are shown in Fig. 2. The broad bands at 3624 and 3429 cm^{-1} are due to the O–H stretching vibration of the silanol (Si–OH) groups and H–OH vibration of the water molecules adsorbed on the solid surface. The band at 1638 cm^{-1} represents the bending H–OH bond of water molecules, which is retained in the matrix. A sharp band at 797 cm^{-1} with inflexion at 779 cm^{-1} confirms the presence of quartz in the sample. The band at 696 cm^{-1} reflects the deformation and bending modes of the Si–O bond [16]. The band at 525 cm^{-1} is due to Al–O–Si bending vibration. The band at 622 cm^{-1} corresponds to the out-of-plane vibrations of coupled Al–O and Si–O [17]. In the spectrum of BENT–PAAm, it is easy to note that there are more characteristic peaks, such as double peaks, 1320 , 1349 cm^{-1} and 1413 , 1453 cm^{-1} ; the C–H typical vibration at 2781 , 2861 , 2925 cm^{-1} , and the strong stretch vibration of carbonyl group at 1659 cm^{-1} . These characteristic peaks are in line with the infrared spectrums of polyacrylamide [18], which confirms the existence of PAAm in the sample. The functional groups on BENT–PAAm composites account for their large adsorption ability because of the interaction between Cu(II) and $-\text{NH}_2$, which will be interpreted in detail in the following section.

3.2. Effect of pH

The pH value of the solution plays an important role in the sorption of Cu(II) on BENT and BENT–PAAm. The sorption of Cu(II) on BENT–PAAm increases from $\sim 9\%$ to $\sim 97\%$ in the pH ranging from 2.4 to 7, and then maintains high level with increasing pH values (see Fig. 3). Similar results were also reported for Cu(II) sorption to TiO_2 [19] and on Al_2O_3 [20]. The pH values of the solution after sorption equilibrium changes a little to the acidic region, which indicates that H^+ is released during the sorption process. In aqueous systems, the surface groups of BENT and PAAm can be protonated in different extents. Therefore, the concentrations of surface species of BENT and PAAm change under different pH values. With increasing pH, the negative charged groups or deprotonated groups increase

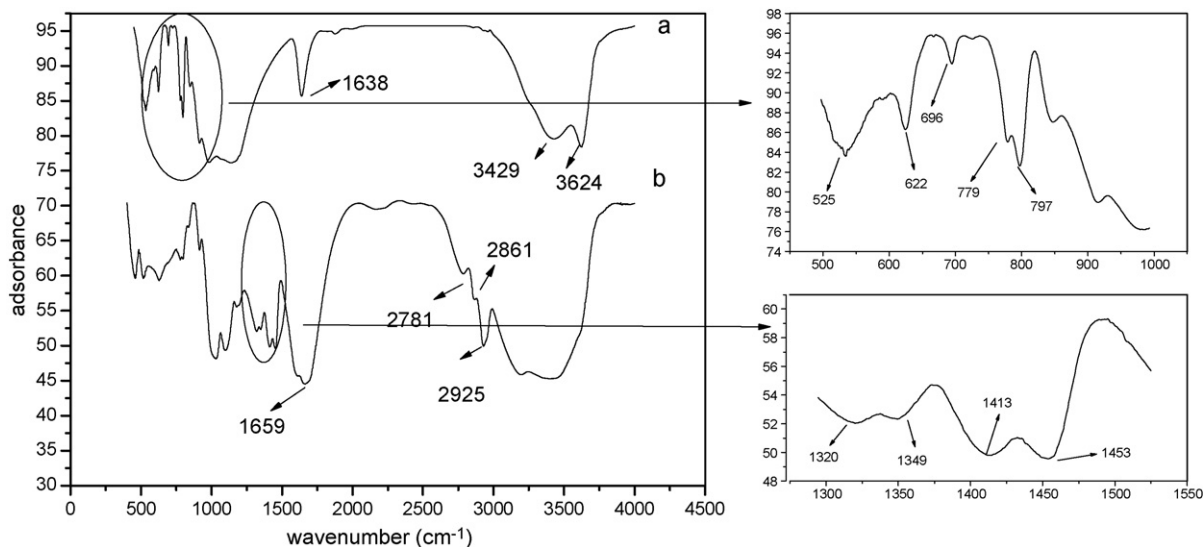


Fig. 2. FTIR spectrum of BENT and BENT-PAAm before and after sorption of Cu(II). (a) BENT; (b) BENT-PAAm.

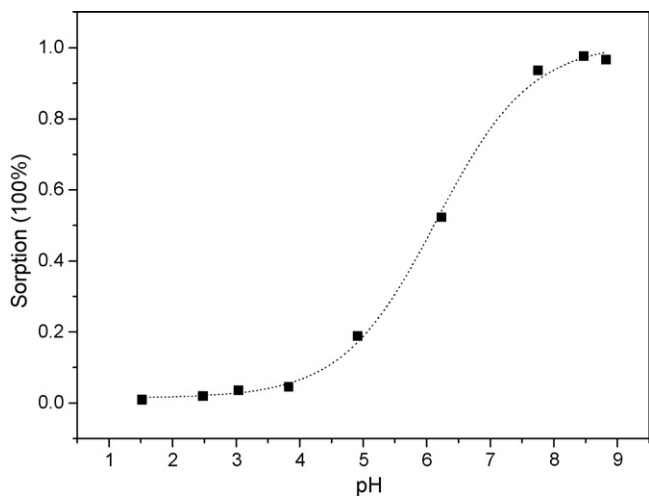
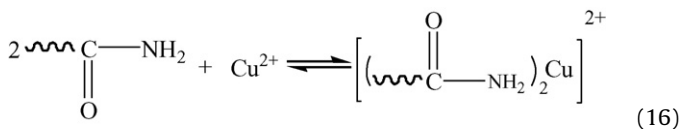
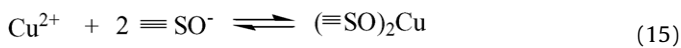
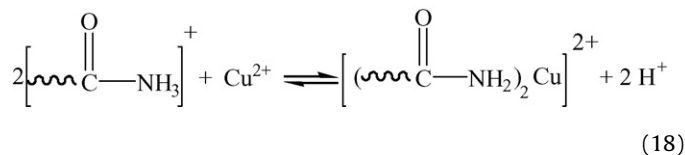


Fig. 3. Sorption of Cu(II) on BENT-PAAm as a function of pH. $T=20\pm 2^\circ\text{C}$, $m/V=0.4\text{ g/L}$, $I=0.0005\text{ M NaNO}_3$, $C_{\text{Cu}}(\text{initial})=10\text{ mg/L}$.

and the hydrolysis of Cu(II) also increases. According to the hydrolysis constants of Cu(II) [21], the distribution species of Cu(II) as a function of pH is shown in Fig. 4. Below pH 6.5, the main species of Cu(II) is Cu^{2+} , and Cu(II) does not form precipitation in this pH region. In the pH above 6.5, $\text{Cu}(\text{OH})^+$ and $\text{Cu}_2(\text{OH})_2^{2+}$ become the main species. In the pH above 9.0, Cu^{2+} is mainly in the precipitation. Considering the strong coordination between Cu(II) and nitrogen, the sorption of Cu(II) on BENT-PAAm can be expressed as followed.



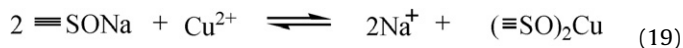
When the surface groups of BENT and PAAm are more protonated, the reaction can be shown as:



3.3. Effect of ionic strength

Fig. 5 shows the effect of ionic strength on the sorption of Cu(II) onto BENT and BENT-PAAm. It indicates that Cu(II) sorption on BENT and on BENT-PAAm is strongly dependent on ionic strength at pH 6.2. It may be due to the SiO^- group whose charge is not compensated form salt bonds with their counterions which are mainly the cations in the solution.

The main process can be expressed as:



Another explanation is that the binding of Na^+ might diminish the density of negative charge on the surface of BENT-PAAm. This supports the theory that electrostatic interaction exists between

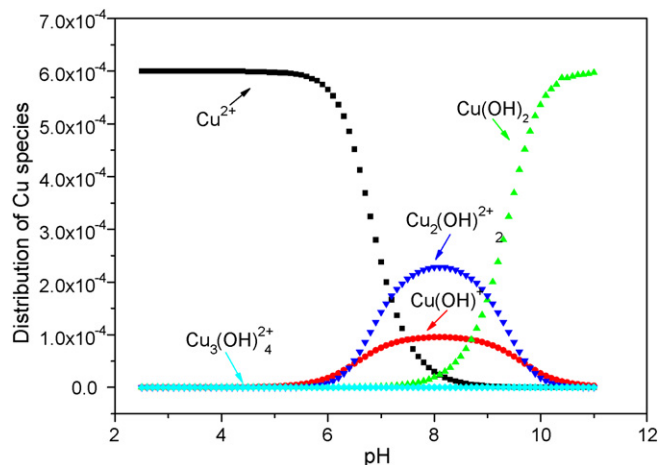


Fig. 4. The distribution of different species of Cu(II) at concentration of $6.0 \times 10^{-4}\text{ mol/L}$ in 0.01 M NaClO_4 and CO_2 -free solutions at 25°C .

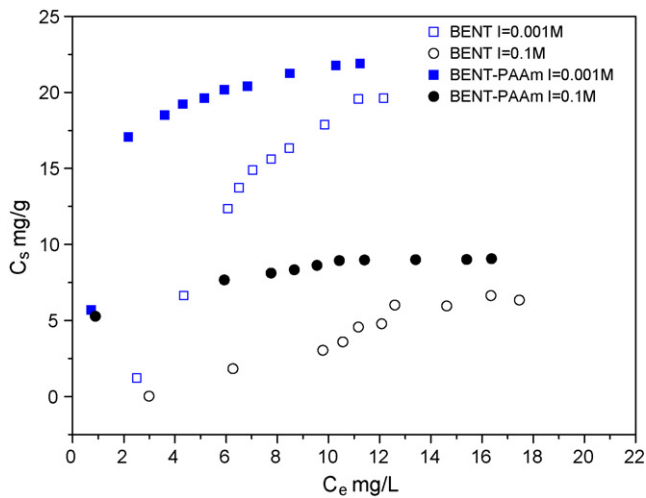


Fig. 5. Effect of ionic strength on the sorption of Cu(II) on BENT and BENT-PAAm. pH = 6.2 ± 0.1 , $T = 20 \pm 2^\circ\text{C}$, $m/V = 0.4\text{ g/L}$.

metal ions and the surface of BENT-PAAm, which is in consistency with the cation exchange process. The exchange process contributes little in case of the interaction between $-\text{CONH}_2$ and Cu^{2+} . It might be related to the fact that $-\text{CONH}_2$ groups can easily form a more stable unit with Cu(II) than ion exchange [22].

Similarly, Chen and Wang [22] reported that the ion exchange and chelation model controlled simultaneously during the Cu(II) sorption process to the poly(acrylamide)/attapulgite composite. The results in Ref. [22] are consistent with the results of our work.

3.4. Effect of BENT-PAAm content

Sorption of Cu(II) as a function of BENT-PAAm content is shown in Fig. 6. One can see that the sorption percentage of Cu(II) increases with increasing BENT-PAAm content in the suspension. The functional sites on BENT-PAAm surfaces increase with increasing of BENT-PAAm content, thereby the sorption percentage of Cu(II) increases reasonably.

In Fig. 6, it is necessary to note that the distribution coefficient (K_d) of Cu(II) on BENT-PAAm does not change with the increasing solid content within the experimental uncertainty, which is consistent with the physicochemical properties of K_d . At low con-

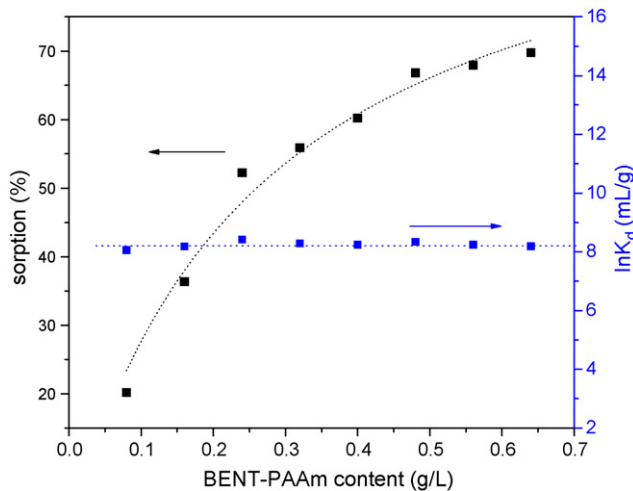


Fig. 6. Variation in sorption percent (%) and distribution coefficient (K_d) of Cu(II) on BENT-PAAm as a function of solid content. pH = 6.2 ± 0.1 , $T = 20 \pm 2^\circ\text{C}$, $m/V = 0.4\text{ g/L}$, $C_{\text{Cu(initial)}} = 15\text{ mg/L}$, $I = 0.0005\text{ M NaNO}_3$.

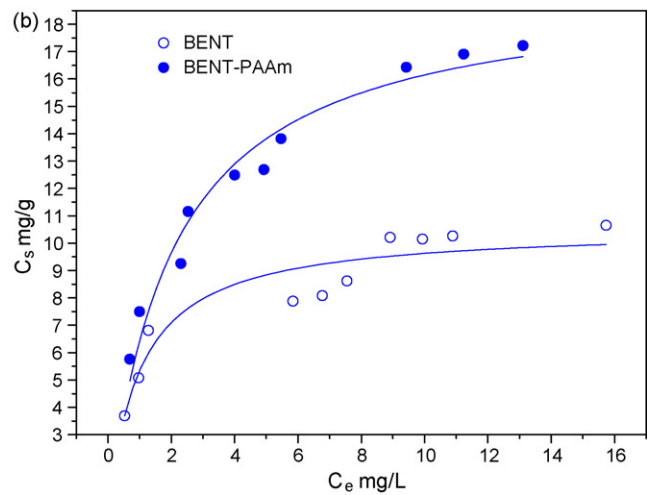
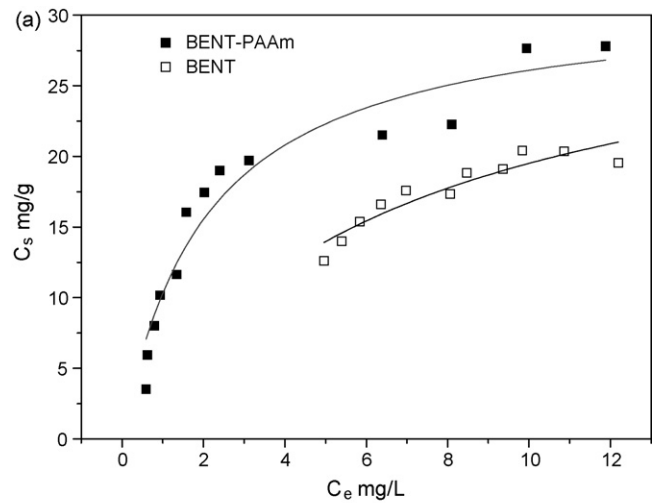


Fig. 7. Adsorption isotherms of Cu(II) on BENT and BENT-PAAm at different pH. (a) pH = 6.2 ± 0.1 ; (b) pH = 5.0 ± 0.1 . $T = 20 \pm 2^\circ\text{C}$, $m/V = 0.4\text{ g/L}$, $I = 0.0005\text{ M NaNO}_3$.

centration of Cu(II) and low content of BENT-PAAm, the K_d value is independent of solid contents.

3.5. Sorption isotherms of Cu(II) on BENT and BENT-PAAm

The sorption of Cu(II) on BENT and on BENT-PAAm at pH values of 6.2 and 5.0, respectively, are shown in Fig. 7. One can see that the sorption isotherm of Cu(II) on BENT-PAAm is much higher than that of Cu(II) on BENT. Langmuir, Freundlich and D-R isotherm models are conducted, respectively, to simulate the sorption data of Cu(II) on BENT and BENT-PAAm (see Fig. 8). The relative parameters are listed in Table 1. It is clear that the Langmuir isotherm model fits the experimental data very well. It shows that C_{smax} increases from 29 to 33 mg/g at pH 6.2 and from 11 to 20 mg/g at pH 5.0 for Cu(II) sorption to BENT to BENT-PAAm composites. The strong coordination between the lone-pair electron of nitrogen and empty orbital of copper contributes to the increased sorption capacity. From the results of D-R model simulation, E value is in the range of 8–16 kJ/mol, indicating that sorption is governed by chemical ion-exchange according to the theory of D-R model [13]. Garmo et al. [23] found that the enrichment of Cu exceeds the estimated capacity for binding of Cd in polyacrylamide gels equilibrated in solutions spiked with Cd only, suggesting that additional binding sites are available for Cu. Wua et al. [20] reported that fulvic acid on $\gamma\text{-Al}_2\text{O}_3$ generated an increase in the total quantity of adsorbed Cu(II) ions.

Table 1
The parameters for Langmuir, Freundlich and D–R isotherms at different temperatures.

Absorbent	Langmuir			Freundlich			D-R			
	C_{smax} (mg g ⁻¹)	b (L mg ⁻¹)	R^2	$\ln K_F$ (mol ¹⁻ⁿ L ⁿ g ⁻¹)	n	R^2	$\beta \times 10^9$ (mol ² kJ ⁻²)	C_{smax} (mmol g ⁻¹)	E (kJ mol ⁻¹)	R^2
BENT pH 6.2	29.43	0.45	0.9355	-3.78	0.49	0.8639	5.31	2.52	9.70	0.8718
BENT-PAAm pH 6.2	32.81	0.19	0.9827	-2.99	0.53	0.8072	5.19	3.68	9.82	0.8322
BENT pH 5.0	11.36	0.66	0.978	-6.31	0.28	0.9136	2.75	0.45	13.50	0.9229
BENT-PAAm pH 5.0	19.89	0.46	0.9924	-5.06	0.36	0.9744	3.57	1.06	11.84	0.9814

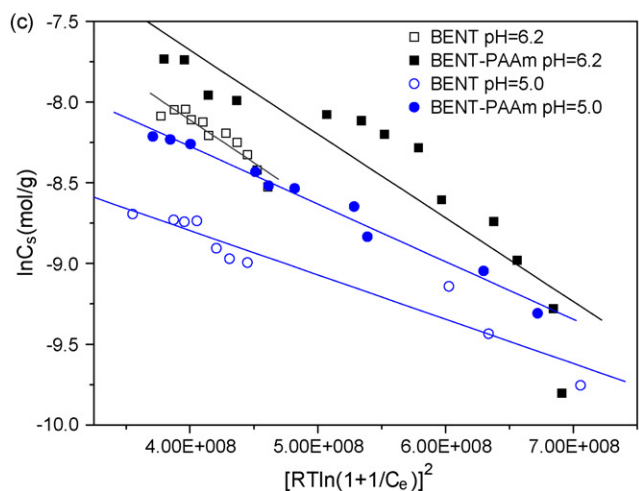
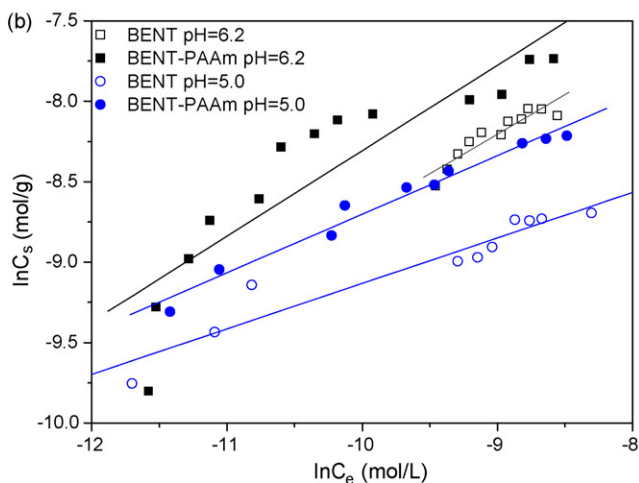
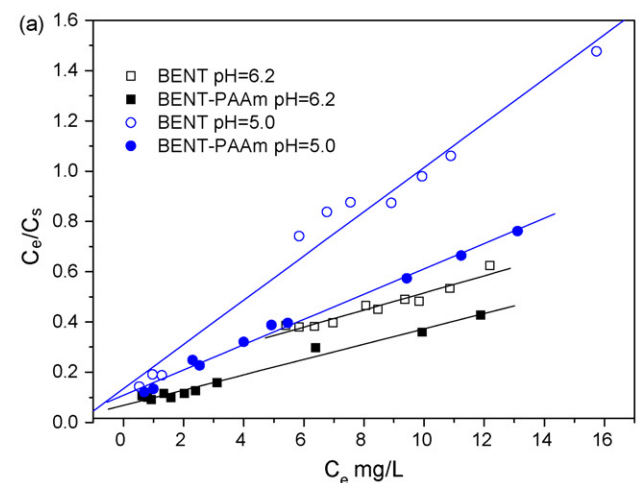


Fig. 8. Langmuir (a), Freundlich (b) and D–R (c) isotherms for Cu(II) on BENT and BENT–PAAm at different pH. $T = 20 \pm 2^\circ\text{C}$, $m/V = 0.4\text{ g/L}$, $I = 0.0005\text{ M NaNO}_3$.

Table 2

Constants of linear fit of $\ln K_d$ vs. C_e ($\ln K_d = A + BC_e$) for Cu(II) sorption on BENT and on BENT–PAAm at $T = 293.15\text{ K}$ and different pH values.

Absorbent	pH	A	B	R^2
BENT	5.0	7.58 ± 0.05	-4227 ± 295	0.9761
BENT-PAAm	5.0	8.43 ± 0.06	-6300 ± 442	0.9760
BENT	6.2	8.36 ± 0.04	-4900 ± 295	0.9787
BENT-PAAm	6.2	9.36 ± 0.07	-11309 ± 2165	0.9009

3.6. Thermodynamic study

In order to investigate the thermodynamic property, sorption experiments of Cu(II) on BENT and on BENT–PAAm were carried out at different temperatures. The thermodynamic parameters (i.e., enthalpy, ΔH° , entropy, ΔS° , and Gibbs free energy, ΔG°) are useful for the evaluation of the sorption process. The linear fit result of $\ln K_d$ vs. C_e at pH 5.0 and 6.2 is tabulated in Table 2. It is obvious that the value of ΔG° at pH 6.2 is larger than that of ΔG° at pH 5.0. Table 3 shows the thermodynamic parameters at pH 6.2 and at different temperatures. The positive value of ΔH° indicates that the sorption process is endothermic, which is an indication of the existence of a strong interaction between BENT and BENT–PAAm with Cu(II). Cu(II) is firstly to be stripped out (at least partially) of their hydration shell, and this process requires energy input. If the exothermicity associated with the sorption of Cu(II) ions onto BENT and BENT–PAAm does not exceed the dehydration energy of Cu(II) ions, the overall energy balance will lead to endothermic behavior. Obviously, ΔH° value of Cu(II) sorption on BENT–PAAm is much larger than that of Cu(II) sorption on BENT, which may indicate that the sorption of Cu(II) on BENT–PAAm is more difficult in kinetics than that on BENT. The Gibbs free energy change (ΔG°) was negative as expected for a spontaneous process under the conditions applied. The decrease of ΔG° with the increase of temperature indicated more efficient sorption at higher temperatures. At high temperatures, ions are readily dehydrated, and therefore their sorption becomes more favorable. The positive values of entropy change (ΔS°) reflected the affinity of Cu(II) ions on BENT and on BENT–PAAm, suggesting some structure changes in adsorbents [24,25]. It is worthwhile to note that the entropy change (ΔS°) of the sorption on BENT–PAAm is higher than that on BENT, which can be explained by the additional interaction between Cu(II) ions and PAAm on the surface of BENT–PAAm composite. The isotherms at different temperatures for BENT and BENT–PAAm are shown in Fig. 9. Fig. 10 shows the linear fit of $\ln K_d$ vs. C_e at different temperatures. The parameters of the linear fit are tabulated in Table 4.

Table 3

Values of thermodynamic parameters for the sorption of Cu (II) on BENT and on BENT–PAAm at pH 6.2.

Absorbent	T (K)	$\ln K^\circ$ (mL g ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
BENT	293.15	8.36	-20.37	20.62	139.82
BENT	318.15	9.02	-23.86	20.62	139.82
BENT-PAAm	293.15	9.36	-22.68	28.46	174.90
BENT-PAAm	313.15	10.37	-27.56	27.78	174.90
BENT-PAAm	328.15	10.58	-30.18	28.53	174.90

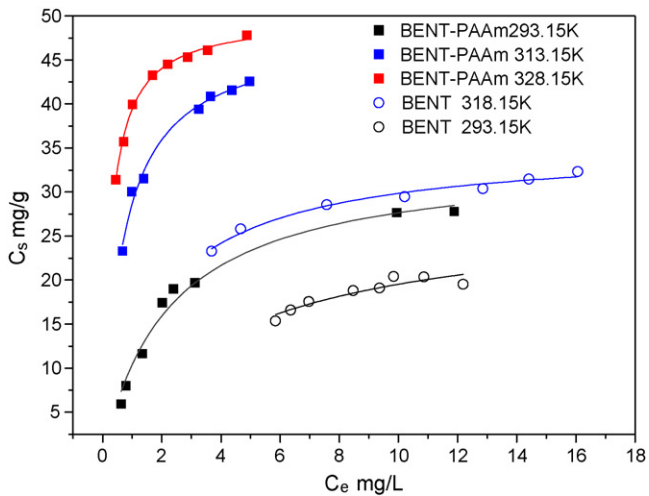


Fig. 9. Sorption isotherms of Cu(II) on BENT and BENT-PAAm at different temperatures. $m/V=0.4$ g/L, $I=0.0005$ M NaNO_3 , $\text{pH}=6.2 \pm 0.1$.

Table 4

Constants of linear fit of $\ln K_d$ vs. C_e ($\ln K_d = A + BC_e$) for Cu(II) on BENT and on BENT-PAAm at different temperatures at pH 6.2.

Absorbent	T (K)	A	B	R^2
BENT	293.15	8.36 ± 0.04	-4900 ± 295	0.9787
BENT	318.15	9.02 ± 0.08	-5952 ± 440	0.9476
BENT-PAAm	293.15	9.36 ± 0.07	-11309 ± 2165	0.9009
BENT-PAAm	313.15	10.37 ± 0.08	-17522 ± 1453	0.9798
BENT-PAAm	328.15	10.58 ± 0.09	-18834 ± 1826	0.9726

3.7. Sorption and desorption isotherms

In order to investigate the reversibility of the sorption, desorption experiments were carried out after sorption. Fig. 11 shows the sorption and the desorption isotherms, showing that the desorption isotherm is higher than the sorption isotherm. These results indicate that Cu(II) sorption is an irreversible process. The concentration of Cu(II) in the solid phase hardly changes after the concentration of Cu(II) in the solution decreases, which indicates that Cu(II) ions adsorbed on solid particles are not desorbed from solid to liquid phase to re-establish equilibrium under the experimental conditions. The irreversible sorption also indicates that strong surface complexation contributes to the main sorption path of Cu(II) on BENT and on BENT-PAAm.

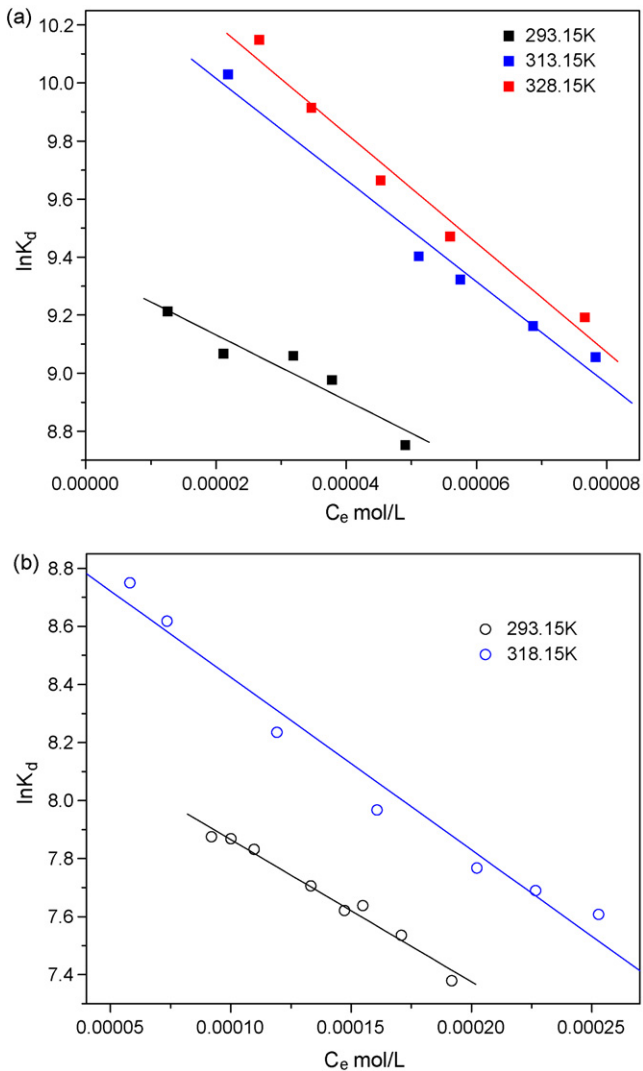


Fig. 10. Linear fit of $\ln K_d$ vs. C_e at different temperatures. (a) Sorption of Cu(II) on BENT-PAAm; (b) sorption of Cu(II) on BENT. $m/V=0.4$ g/L, $I=0.0005$ M NaNO_3 , $\text{pH}=6.2 \pm 0.1$.

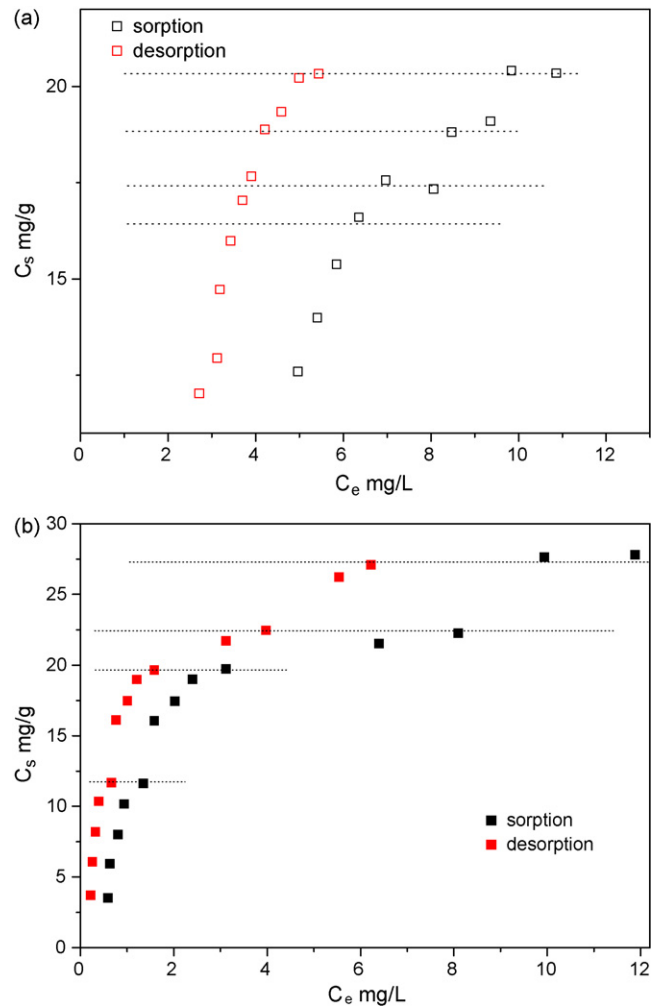


Fig. 11. Sorption-desorption isotherms of Cu(II) on BENT and BENT-PAAm. (a) BENT; (b) BENT-PAAm. $m/V=0.4$ g/L, $I=0.0005$ M NaNO_3 , $\text{pH}=6.2 \pm 0.1$, $T=20 \pm 2$ °C.

4. Conclusions

- (a) Sorption of Cu(II) on BENT or on BENT–PAAm is strongly dependent on pH, Cu(II) initial concentration and ionic strength. Surface complexation and ionic exchange contribute to the sorption of Cu(II) on BENT and on BENT–PAAm.
- (b) BENT–PAAm performs a better sorption property than BENT at the same experimental condition, which may be due to its strong coordination between Cu(II) and the nitrogen on the surfaces of BENT–PAAm. The sorption of Cu(II) on BENT and on BENT–PAAm is irreversible.
- (c) Sorption of Cu(II) on BENT or on BENT–PAAm is a spontaneous process and increases with the increase of temperature. The ΔS° of Cu(II) sorption on BENT–PAAm is much larger than that on BENT, which may be also because of the strong coordination between the nitrogen and PAAm. The larger ΔH° may be due to the larger activation energy of the sorption onto BENT–PAAm.
- (d) The degree of polymerization and cross-linkage should be low enough to maintain the high surface area and dispersion of BENT. In our experiment, the synthesis of BENT–PAAm was in obturator not vacuum, which ensured the low polymerization and cross-linkage. Further research is necessary to investigate the relationship between the percent of PAAm in the BENT–PAAm composite and the sorption capacity of BENT–PAAm. The BENT-polymers complex would become a kind of super-adsorbent considering its simple synthesis and high adsorption ability.

Acknowledgments

Financial supports from the Natural Science Foundation of China (20971126, 20677058, J0630962), 973 project (2007CB936602) from Ministry of Science and Technology of China and Special Foundation for High-level Waste Disposal (2007-840) are acknowledged.

References

- [1] M.Y. Pamukoglu, F. Kargi, Copper(II) ion toxicity in activated sludge processes as function of operating parameters, *Enzyme Microb. Technol.* 40 (2007) 1228–1233.
- [2] X.K. Wang, C.L. Chen, J.Z. Du, X.L. Tan, D. Xu, S.M. Yu, Effect of pH and aging time on the kinetic dissociation of $^{243}\text{Am}(\text{III})$ from humic acid coated $\gamma\text{-Al}_2\text{O}_3$: a chelating resin exchange study, *Environ. Sci. Technol.* 39 (2005) 7084–7088.
- [3] K. Trivunac, S. Stevanovic, Removal of heavy metal ions from water by complexation-assisted ultrafiltration, *Chemosphere* 64 (2006) 486–491.
- [4] X.K. Wang, X. Zhou, J.Z. Du, W.P. Hu, C.L. Chen, Y.X. Chen, Using of chelating resin to study the kinetic desorption of $\text{Eu}(\text{III})$ from humic acid- Al_2O_3 colloid surfaces, *Surf. Sci.* 600 (2006) 478–483.
- [5] A. Dabrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, *Chemosphere* 56 (2004) 91–106.
- [6] S.T. Yang, J.X. Li, D.D. Shao, J. Hu, X.K. Wang, Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA, *J. Hazard. Mater.* 166 (2009) 109–116.
- [7] D. Xu, D.D. Shao, C.L. Chen, A.P. Ren, X.K. Wang, Effect of pH and fulvic acid on sorption and complexation of cobalt onto bare and FA bound MX-80 bentonite, *Radiochim. Acta* 94 (2006) 97–102.
- [8] S.M. Yu, A.P. Ren, C.L. Chen, Y.X. Chen, X.K. Wang, Effect of pH, ionic strength and fulvic acid on the sorption and desorption of cobalt to bentonite, *Appl. Radiat. Isot.* 64 (2006) 455–461.
- [9] S.G. Starodoubtsev, A.A. Ryabova, A.T. Dembo, K.A. Dembo, I.I. Aliev, A.M. Wasserman, A.R. Khokhlov, Composite gels of poly(acrylamide) with interaction with cationic surfactants, ESR and SAXS Study, *Macromolecules* 35 (2002) 6362–6369.
- [10] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [11] X.L. Tan, C.L. Chen, S.M. Yu, X.K. Wang, Sorption of Ni^{2+} on Na-rectorite studied by batch and spectroscopy methods, *Appl. Geochem.* 23 (2008) 2767–2777.
- [12] M.M. Dubinin, The potential theory of adsorption gases and vapors for adsorbents with energetically nonuniform surfaces, *Chem. Rev.* 60 (1960) 235–241.
- [13] A. Ozcan, E.M. Oncu, A.S. Ozcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite, *Colloid Surf. A* 277 (2006) 90–97.
- [14] D. Akar, T. Shahwan, A.E. Eroglu, Kinetic and thermodynamic investigations of strontium ions retention by natural kaolinite and clinoptilolite minerals, *Radiochim. Acta* 93 (2005) 477–486.
- [15] F.E. Bartell, T.L. Thomas, Y. Fu, Thermodynamics of adsorption from solutions. IV. Temperature dependence of adsorption, *J. Phys. Chem.* 55 (1951) 1456–1462.
- [16] D. Xu, X.L. Tan, C.L. Chen, X.K. Wang, Adsorption of $\text{Pb}(\text{II})$ from aqueous solution to MX-80 bentonite: Effect of pH, ionic strength, foreign ions and temperature, *Appl. Clay Sci.* 41 (2008) 37–46.
- [17] H. Zaitan, D. Bianchi, O. Achak, T. Chafik, A comparative study of the adsorption and desorption of oxylyene onto bentonite clay and alumina, *J. Hazard. Mater.* 153 (2008) 852–859.
- [18] Y.K. Ke, H.R. Dong, *The Enrichment of Analytical Chemistry: Spectroscopic Analysis*, Chemical Industry Press, Beijing, 1998, 1059.
- [19] M.S. Kim, K.M. Hong, J.G. Chung, Removal of Cu(II) from aqueous solution by adsorption process with anatase-type titanium dioxide, *Water Res.* 37 (2003) 3524–3529.
- [20] C.H. Wua, C.F. Linb, H.W. Mab, T.Q. His, Effect of fulvic acid on the sorption of Cu and Pb onto $\gamma\text{-Al}_2\text{O}_3$, *Water Res.* 37 (2003) 743–752.
- [21] A. Richter, V. Brendler, C. Nebelung, Blind prediction of Cu(II) sorption onto goethite: current capabilities of diffuse double layer model, *Geochim. Cosmochim. Acta* 69 (2005) 2725–2734.
- [22] H. Chen, A.Q. Wang, Adsorption characteristics of Cu(II) from aqueous solution onto poly(acrylamide)/attapulgite composite, *J. Hazard. Mater.* 165 (2009) 223–231.
- [23] O.A. Garmo, W. Davison, H. Zhang, Interactions of trace metals with hydrogels and filter membranes used in DET and DGT techniques, *Environ. Sci. Technol.* 42 (2008) 5682–5687.
- [24] H. Genc-Fuhrman, J.C. Tjell, D. Mcconchie, Adsorption of arsenic from water using activated neutralized red mud, *Environ. Sci. Technol.* 38 (2004) 2428–2434.
- [25] H.S. Altundo Gan, S. Altundo Gan, F. Tumen, M. Bildik, Arsenic removal from aqueous solutions by adsorption on red mud, *Waste Manage.* 20 (2000) 761–767.