

## Adsorption characteristics of Cu(II) from aqueous solution onto poly(acrylamide)/attapulgite composite

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### ABSTRACT

Batch adsorption experiments were carried out to remove Cu(II) ions from its aqueous solutions using a poly(acrylamide)/attapulgite composite. The different parameters effecting on the adsorption capacity such as contact time, initial metal ion concentration, temperature and pH of the solution have been investigated. The adsorption kinetic experiments revealed that there are three stages in the whole adsorption process. It was found that Cu(II) adsorption onto the composite followed pseudo-second-order kinetics and were mainly controlled by the film diffusion mechanism, along with a considerable contribution of the intra-particle diffusion mechanism. Analysis of adsorption results obtained at different temperatures showed that the adsorption pattern on the composite well followed the Langmuir, Freundlich and D-R isotherms, and the characteristic parameters for each adsorption isotherm were also determined. The adsorption process has been found endothermic in nature and thermodynamic parameters have been calculated. The analysis for variations of IR spectra and the values of the mean free energies of adsorption ( $E_a$ ) demonstrated that the chelation model should be the dominating adsorption mechanism. The species of copper salts can affect the adsorption capacity of the composite, which are in the order of  $\text{CuSO}_4 > \text{CuCl}_2 > \text{Cu}(\text{NO}_3)_2 \gg \text{Cu}(\text{CH}_3\text{COO})_2$ .

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### 1. Introduction

Superabsorbents, which are crosslinked hydrophilic polymers, are capable of expanding their volumes due to their high swelling in water. Accordingly they are widely used in many fields, such as hygienic products, horticulture, gel actuators and drug-delivery systems [1–4], as well as the purification of waste water and stabilization of mineral sediments [5,6]. In recent years, it was determined that hydrogels having functional groups such as carboxylic acid, amine, hydroxyl and sulfonic acid groups could be used as complexing agents for the removal of metal ions from aqueous solutions [7,8]. Therefore, a great deal of interest has been observed in relation to the applicability of hydrogels as adsorbent for the removal and separation of metal ions from heavy metal contaminated water [7–10], and the recovery and pre-concentration of precious metal ions from different media [11,12]. Compared with conventional solid adsorbents like ion exchange and chelating resins, main advantages of such materials are easy loading and, in most cases, stripping of cations with simple chemicals, reusability and the possibility of semi-continuous operation. In

addition, high wettability and high swelling of hydrogels also might be beneficial for improving adsorption of target metals [11].

Recently, much attention has been paid to inorganic materials, especially clay minerals for the preparation of superabsorbent composites, such as montmorillonite [11,13], attapulgite [14], kaolin [15], mica [16], etc. Almost all investigations have focused on the improvement of the properties (such as swelling ability, gel strength, mechanical and thermal stability) of superabsorbents. A very interesting property of organic superabsorbents are their ability to control the diffusion process [17,18], it can be expected that the adsorption mechanism and kinetics for heavy metals of the composites prepared by introducing the clay minerals would change in some extent due to the different kinds of active sites and the large amount of micro- and meso-pores present in the clay particles in comparison to organic superabsorbents. Moreover, some naturally occurring clay minerals, which have large specific surface areas and cation exchange capacities, may serve as cost-effective adsorbents for the removal of heavy metals [19]. Hence, an understanding of equilibrium and kinetics of adsorption for these composites is very essential in selection of adsorbent suitable for recovering metals from aqueous solutions. However, little information providing basis to understand the fundamental aspects of the adsorption process can be seen.

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Attapulgite clay is a crystalline hydrated magnesium silicate with a fibrous morphology, large specific surface area and moderate cation exchange capacity, which is beneficial for the adsorption of heavy metals from solution [20]. However, the adsorption capacity for Cu(II) is poor [21]. So, in the present study, a poly (acrylamide)/attapulgite composite was synthesized and used to remove heavy metal Cu(II) from aqueous solutions. The adsorption conditions of Cu(II) onto the composite has been investigated and also the nature of the adsorption process with respect to its kinetic and thermodynamic aspects were evaluated. Finally, Cu(II) adsorption on the composite from aqueous solutions using different copper salts at a range of pH was investigated.

## 2. Experimental

### 2.1. Materials and measurement

Acrylamide (AM, analytical grade, supplied by Shanghai Chemical Factory, Shanghai, China) was purified by a method as reported in the literature [22]. The initiator, ammonium persulfate (APS, analytical grade, supplied by Xi'an Chemical Reagent Factory, Xi'an, China), was recrystallized from water before use. The crosslinker, *N,N'*-methylenebisacrylamide (MBA, chemically pure, supplied by Shanghai Chemical Reagent Corp., Shanghai, China), was used as purchased. Attapulgite micropowder (supplied by Linze Xinyi Co., Gansu, China) was milled through a 320-mesh screen and treated with 37% hydrochloric acid for 72 h, followed by washing with distilled water until pH 6 was achieved, and then dried at 105 °C for 8 h before use. Chemical composition of the acid-activated sample in weight percentage of oxides was: SiO<sub>2</sub> (65.77); Al<sub>2</sub>O<sub>3</sub> (17.52); Fe<sub>2</sub>O<sub>3</sub> (5.29); MgO (5.96); CaO (0.21); Na<sub>2</sub>O (0.43); K<sub>2</sub>O (3.81); TiO<sub>2</sub> (0.81); MnO (0.05); SO<sub>3</sub> (0.03) and P<sub>2</sub>O<sub>5</sub> (0.02).

A stock solution of Cu(II), prepared by dissolving Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O in double distilled water, was taken as the adsorptive solution. Other agents used, such as HCl, NaOH, CuCl<sub>2</sub>·2H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, were all of analytical grade and all solutions were prepared with double distilled water.

FT-IR spectra measurements were done on a Thermo Nicolet NEXUS TM spectrophotometer using the KBr pellets. The spectrum was collected 32 times and corrected for the background noise.

### 2.2. Adsorbent synthesis and their characterization

Polyacrylamide/attapulgite composite was synthesized by our previous reports [14]. AM (7.10 g) was dissolved in 20.0 mL distilled water in a 250 mL four-neck flask, equipped with a stirring rod, a reflux condenser, a thermometer, and a nitrogen line. 20 mL NaOH solution (2 M) and 15.3 mg methylenebisacrylamide was added to the above monomer solution, and then certain amount of attapulgite powder was dispersed in the mixed solution. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the solution, the solution was gradually heated to 40 °C, and then 40.5 mg ammonium persulfate was introduced into the system. The solution was stirred vigorously under nitrogen atmosphere for 3 h, and then another 20 mL NaOH solution was added and the primary product was heated to 95 °C to be saponified for 2 h. After saponification, the product were washed several times with mixed solution of water and methanol (v/v=1:9) to remove any unreacted reactants until pH 7 was achieved. The depurative product was dried in an oven at 70 °C until the weight of the products was constant and gray products were obtained. The product was milled and all samples used for test had a particle size of 200 mesh. Attapulgite content of the composite is 30 wt%. The molar

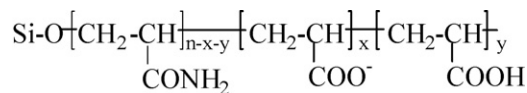


Fig. 1. The schematic structure of the sorbent.

ratio of –COONa, –COOH and –CONH<sub>2</sub> of the composite is 10:3:11. The schematic structure of the sorbent is shown in Fig. 1.

### 2.3. Adsorption studies

Adsorption experiments were evaluated in batch equilibrium mode. All experiments were conducted by mixing 25 mL of aqueous Cu(II) solutions with 0.05 g of the composite. The mixtures were shaken in a thermostatic shaker bath (THZ-98A mechanical shaker) at 120 rpm at desired temperature and contact time, and then the suspensions were centrifuged at 5000 rpm for 20 min. The pH values of initial solutions were adjusted with dilute HCl or NaOH solution by using a Mettler Toledo 320 pH meter. For kinetic studies 3.15 × 10<sup>-3</sup> mol L<sup>-1</sup> was chosen as the initial concentration of Cu(II) solution.

Adsorption experiments were also carried out to obtain isotherms at different temperatures. This was done at 303.2, 313.2 and 323.2 K, respectively. In this group of experiments Cu(II) solutions with different initial concentration, in the range of 3.15 × 10<sup>-3</sup> to 7.08 × 10<sup>-3</sup> mol L<sup>-1</sup>, were selected. Adsorption time of 120 min was chosen to allow attainment of equilibrium at constant temperatures.

To examine the effect of pH, adsorption experiments were conducted at different pH ranging from 2 to 5 at 7.08 × 10<sup>-3</sup> mol L<sup>-1</sup> of Cu(II) solution. Besides Cu(CH<sub>3</sub>COO)<sub>2</sub>, CuCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> and CuSO<sub>4</sub> were also selected to carry out the pH experiments in the same concentration. Normally, pH 6.0 and 303.2 K were selected as adsorption conditions unless otherwise stated.

The initial and the final concentration of Cu(II) in the aqueous salt solution were measured with an atomic absorption spectrophotometer (Perkin-Elmer SIMAA 6000). The adsorption capacity of adsorbent was calculated through the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $q_e$  is the adsorption capacity of Cu(II) on adsorbent (mol g<sup>-1</sup>),  $C_0$  is the initial concentration of Cu(II) (mol L<sup>-1</sup>),  $C_e$  is the equilibrium Cu(II) concentration in solution (mol L<sup>-1</sup>),  $m$  is the mass of adsorbent used (g) and  $V$  is the volume of Cu(II) solution (L). All assays were carried out in triplicate and only mean values were presented.

## 3. Results and discussion

### 3.1. Kinetic studies

Contact time is an important parameter because this factor can reflect the adsorption kinetics of an adsorbent for a given initial concentration of the adsorbate. Fig. 2 shows the effect of contact time on adsorption of Cu(II) by the composite. It is seen that  $q_e$  increases rapidly during the initial adsorption stage and then it continues to increase at a relatively slow speed with contact time and reaches equilibrium point after 90 min, beyond which there was almost no further increase in the adsorption. It was found that Cu(II) adsorption on the composite was a fast process, where >90% of the adsorption took place within the first 10 min. However, attapulgite need 180 min and the maximum adsorption capacity is only 32 mg/g [21].

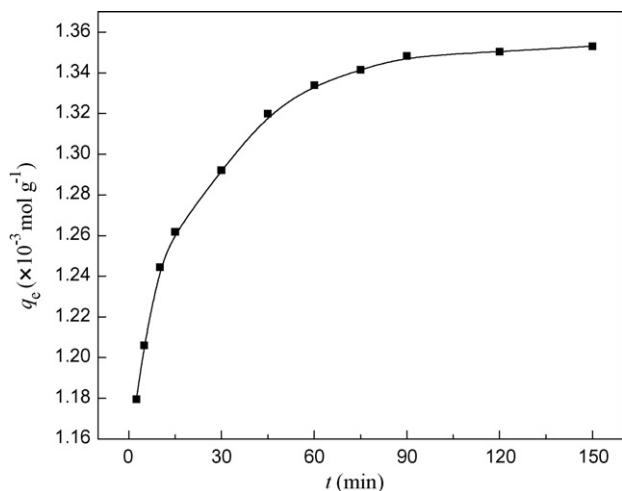


Fig. 2. Effect of contact time on the adsorption of Cu(II) onto the composite.

To examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, pseudo-first-order and pseudo-second-order kinetic equations were used to test the experimental data. The pseudo-first-order kinetic model was suggested by Lagergren for the adsorption of solid/liquid systems and its linear form can be formulated as [23]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

where  $q_t$  is the adsorption capacity at time  $t$  ( $\text{mol g}^{-1}$ ) and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo-first adsorption, was applied to the present study of Cu(II) adsorption. The  $k_1$  and correlation coefficient were calculated from the linear plot of  $\log(q_e - q_t)$  versus  $t$  (figure not shown) and listed in Table 1. It was found that the correlation coefficient for the pseudo first-order kinetic model is high. However, a clearly difference of  $q_e$  between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experimental data.

The kinetic data were further analyzed using Ho's pseudo-second-order kinetics model. It can be expressed as [24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where  $k_2$  ( $\text{g mol}^{-1} \text{min}^{-1}$ ) is the rate constant of the pseudo-second-order adsorption. Fig. 3 shows the plot of  $t/q_t$  versus  $t$  for Cu(II) onto the composite. The  $k_2$ , the calculated  $q_e$  value and the corresponding linear regression correlation coefficient  $r^2$  are given in Table 1. An extremely high correlation coefficient (1.000) was obtained. Moreover, the calculated  $q_e$  value also agrees with the experimental data in the case of pseudo-second-order kinetics. These suggested that the adsorption data are well represented by pseudo-second-order kinetics.

Although the Elovich equation was firstly used in the kinetics of chemisorption of gases on solids, it has been successfully applied for the adsorption of solutes from a liquid solution. The linear form of the Elovich equation [25] is given by

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{4}$$

where  $\alpha$  ( $\text{mol min g}^{-1}$ ) is the initial sorption rate, and the parameter  $\beta$  ( $\text{g mol}^{-1}$ ) is related to the extent of surface coverage and activation energy for chemisorption. The values of  $\alpha$ ,  $\beta$  and the corresponding linear regression correlation coefficient  $r^2$  are given in Table 1. This model does not predict any definite mechanism but

Table 1  
A comparison of pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion kinetic models rate constants calculated from experimental data.

$q_e$ (exp) ( $\times 10^{-3}$ mol g <sup>-1</sup> )	Pseudo-first-order model $k_1$ ( $\times 10^{-2}$ min <sup>-1</sup> )	$r^2$	$q_e$ (cal) ( $\times 10^{-3}$ mol g <sup>-1</sup> )	Pseudo-second-order model $k_2$ ( $\times 10^3$ g mol <sup>-1</sup> min <sup>-1</sup> )	$r^2$	$q_e$ (cal) ( $\times 10^{-3}$ mol g <sup>-1</sup> )	Elovich model $\alpha$ (mol min g <sup>-1</sup> )	$r^2$	Intra-particle diffusion model $k_i$ ( $\times 10^{-5}$ mol g <sup>-1</sup> min <sup>-1/2</sup> )	$r^2$
1.3531	3.8184	0.1781	0.1781	0.9968	0.7740	1.3588	$3.1172 \times 10^6$	0.02192	2.083	0.9939
									1.1676	0.9760

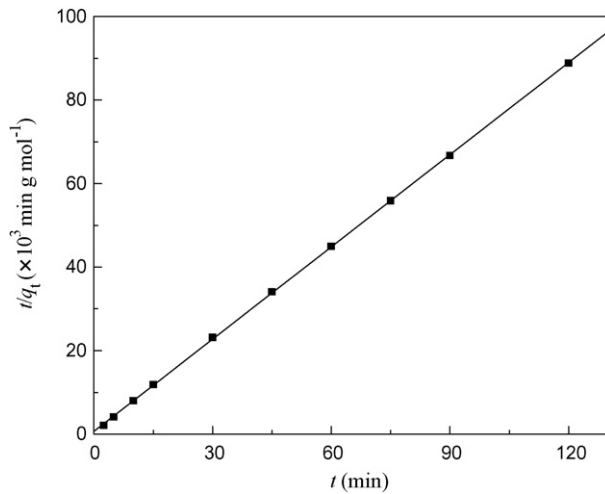


Fig. 3. Pseudo-second-order kinetic plot for the adsorption of Cu(II) onto the composite.

has been found useful in describing chemical adsorption on highly heterogeneous adsorbents. It can be seen clearly from Table 1 that the correlation coefficient is lower than those of the pseudo first, and pseudo second-order equations. The constant  $\beta$  is very small compared with those of references [26,27], indicating the rate of chemisorption is fast in the whole adsorption process.

Adsorption kinetics is generally controlled by different mechanism, of which the most limiting are the diffusion mechanisms, including film diffusion and intra-particle diffusion. The first-order and pseudo-second-order models cannot identify the diffusion mechanism and the kinetic results were then subjected to analyze by the intra-particle diffusion kinetics model for diffusion mechanism, formulated as [28],

$$q_t = k_i t^{1/2} + C \quad (5)$$

where  $k_i$  ( $\text{mol g}^{-1} \text{min}^{-1/2}$ ) is the intra-particle diffusion rate constant and  $C$  ( $\text{mol g}^{-1}$ ) is a constant. The values  $k_i$ ,  $C$  and correlation coefficient calculated from the slope of the plot of  $q_t$  versus  $t^{1/2}$  are shown in Table 1. It was found that the correlation coefficient for the intra-particle diffusion model is lower than those of the pseudo-first-order and the pseudo-second-order models. This indicates that the adsorption of Cu(II) onto the composite doesn't follow the intra-particle diffusion kinetics. In addition, it is necessary to note that the intercept  $C$  as proposed by Eq. (5) was not zero but a large value ( $1.1676 \times 10^{-3} \text{ mol g}^{-1}$ ), indicating that intra-particle diffusion may not be the controlling factor in determining the kinetics of the process.

To determine the actual process involved in the present adsorption, Eq. (6) of the adsorption dynamics can be employed [29].

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left( \frac{1}{n^2} \right) \exp(-n^2 B_t) \quad (6)$$

where  $F$  is the fractional attainment of equilibrium at time  $t$  and is obtained by using Eq. (7),  $n$  is Freundlich constant of the adsorbate and  $B_t$  is a calculated mathematical function of  $F$  (and vice versa) derived from the Reichenberg's table [29].

$$F = \frac{Q_t}{Q_{\infty}} \quad (7)$$

where  $Q_t$  and  $Q_{\infty}$  are amounts adsorbed after time  $t$  and after infinite time, respectively.

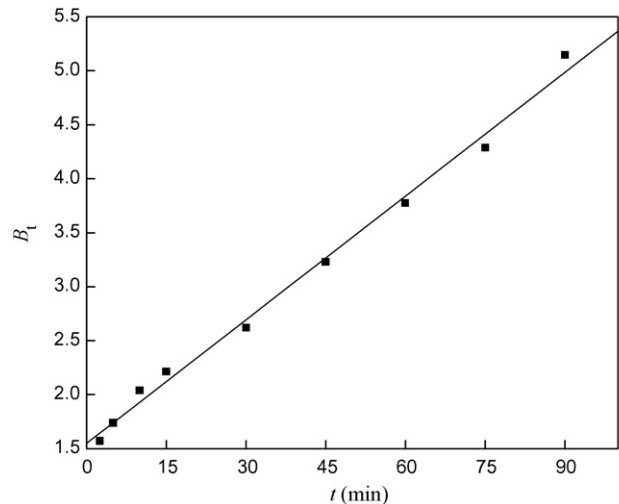


Fig. 4.  $B_t$  versus  $t$  plot for Cu(II) adsorption onto the composite.

Rearranging the above equation gives:

$$B_t = -\ln(1 - F) - 0.4799 \quad (8)$$

Thus the value of  $B_t$  can be calculated for each value of  $F$  using Eq. (8). The  $B_t$  values were plotted against  $t$  as shown in Fig. 4. The linearity of this plot can be used to distinguish between film diffusion and intra-particle diffusion mechanism. If this plot is a straight line passing through origin, adsorption will be governed by an intra-particle diffusion mechanism, otherwise governed by film diffusion [30]. Seen from Fig. 4, a straight line did not pass through all origin, the linearity of the plot, however, is very high (0.9967). This implies that Cu(II) adsorption onto the composite were mainly controlled by the film diffusion mechanism, along with a considerable contribution of the intra-particle diffusion mechanism.

Based on the above results, it can be concluded that three adsorption stages occurred in the whole adsorption process. Firstly, in the initial 2.5 min, it is known that the Cu(II) species migrate from the bulk liquid phase to the outer surface of adsorbent particles through film diffusion (external mass transfer) and this adsorption process is very fast. Secondly, the portion from 2.5 to 90 min is the gradual adsorption stage, which is has been validated by the above analysis that both film diffusion and intra-particle diffusion were simultaneously operating. The three straight-lines plot for this stage was presented in Fig. 5. It can be considered that a first straight line portion represents macro-pore diffusion, the second and the third one representing meso-pore diffusion and micro-pore diffusion, respectively. Moreover, the three straight lines represented the relative values of intercept  $C$ , which give an idea about the boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect [31]. It is observed that the intercept  $C$  increases with increasing contact time (respectively, 1.1142, 1.1840, 1.2703  $\text{mmol g}^{-1}$  for three linear portions), which implies that film diffusion (boundary layer diffusion) mechanism should become more significant when the adsorption time becomes longer. The third portion (after 90 min) is the final equilibrium stage where the two diffusion mechanisms start to slow down due to the extremely low solute concentration in solution.

### 3.2. Adsorption isotherms

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption systems. Hence, the adsorption of Cu(II) onto the composite at dif-

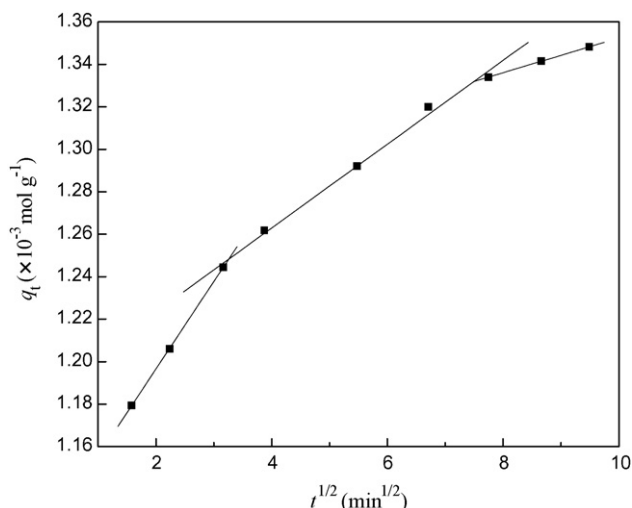


Fig. 5. Intra-particle diffusion kinetic plot for the adsorption of Cu(II) onto the composite.

ferent temperatures are determined as a function of equilibrium (residual) Cu(II) concentration ( $C_e$ ) and the corresponding adsorption isotherms are plotted in Fig. 6. Several isotherm equations are available and three important isotherms are selected in this study, which are namely the Langmuir [32], Freundlich [33] and Dubinin–Radushkevich (D–R) [34] isotherms.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (9)$$

Freundlich equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (10)$$

D–R equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (11)$$

where  $q_e$  is the equilibrium Cu(II) concentration on the adsorbent ( $\text{mmol g}^{-1}$ ),  $C_e$  the equilibrium Cu(II) concentration in solution ( $\text{mol L}^{-1}$ ),  $q_{\max}$  the monolayer capacity of the adsorbent ( $\text{mol g}^{-1}$ ),  $b$  the Langmuir constant ( $\text{L mol}^{-1}$ ) and related to the free energy of adsorption,  $K_f$  the Freundlich constant,  $n$  (dimensionless) is indi-

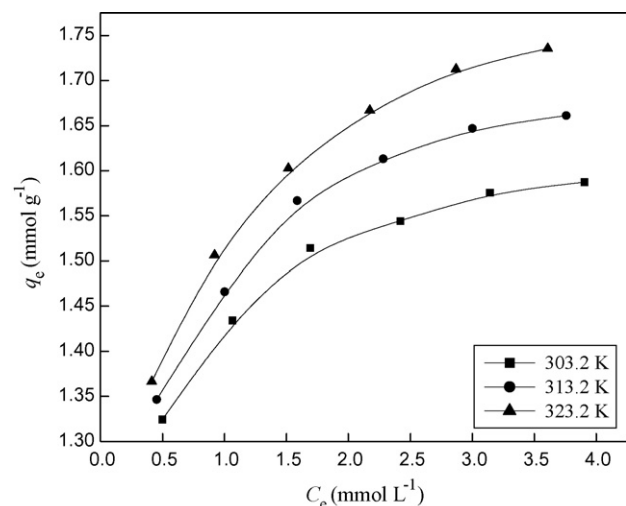


Fig. 6. Adsorption isotherms of Cu(II) on composite at different temperatures.

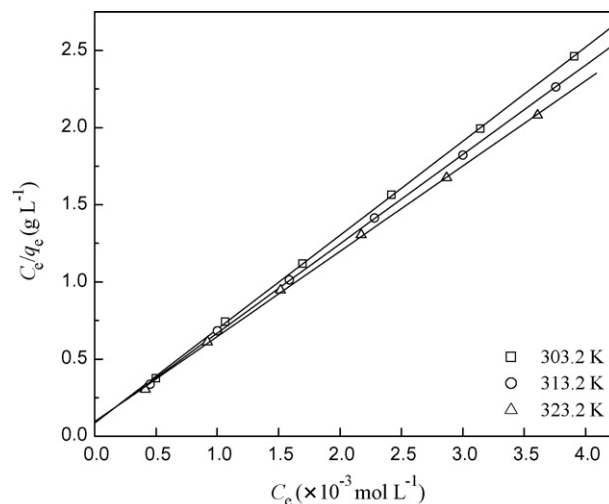


Fig. 7. Langmuir plots for the adsorption of Cu(II) onto the composite at different temperatures.

cator of adsorption intensity,  $\beta$  a constant related to the mean free energy of adsorption ( $\text{mol}^2 \text{kJ}^{-2}$ ),  $q_m$  the theoretical saturation capacity, and  $\varepsilon$  is the Polanyi potential, which is equal to  $RT \ln(1 + (1/C_e))$ , where  $R$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) is the gas constant and  $T$  (K) is the absolute temperature.

The plots of Langmuir, Freundlich and D–R for the adsorption of Cu(II) onto the composite at different temperatures were shown in Figs. 7–9, respectively. The parameters and correlation coefficients were obtained from these plots and listed in Table 2. The fit of the data for Cu(II) adsorption onto the composite suggests that the Langmuir model gave closer fittings than those of Freundlich and D–R models, as is obvious from a comparison of the  $r^2$  in Table 2. In addition, the  $q_{\max}$  increases with an increase in temperature and the analogous behaviors are ascribed by the adsorption capacities ( $K_f$  and  $q_m$ ) as well. The information thus obtained specifies an endothermic nature of the existing process.

For D–R isotherm equation, from the  $\beta$  values the mean energy of adsorption,  $E_a$  can be calculated using the relation [35].

$$E_a = (2\beta)^{-1/2} \quad (12)$$

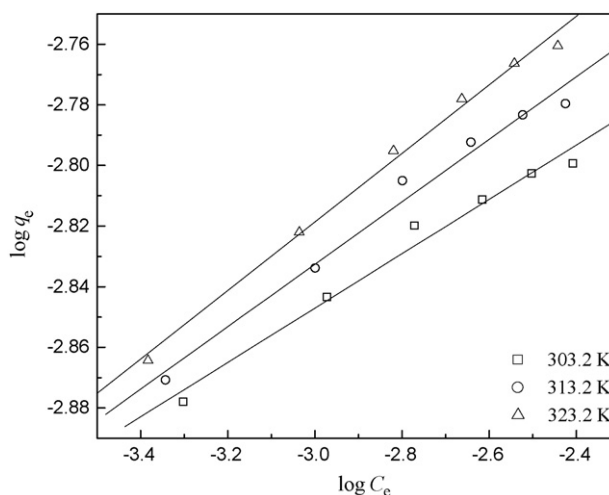
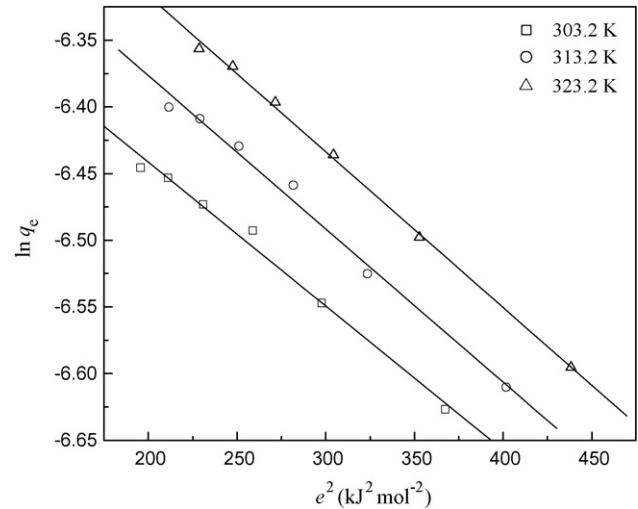


Fig. 8. Freundlich plots for the adsorption of Cu(II) onto the composite at different temperatures.

**Table 2**  
Isotherm constants and correlation coefficients for the adsorption of Cu(II) on composite at different temperatures.

T (K)	Langmuir equation		Freundlich equation		D-R equation		
	$q_{\max}$ ( $\times 10^{-3}$ mol g $^{-1}$ )	$b$ ( $\times 10^3$ L mol $^{-1}$ )	$R_L$	$K_f$ ( $\times 10^3$ mol $^{1-n}$ L $^{1/n}$ g $^{-1}$ )	$q_m$ ( $\times 10^{-3}$ mol g $^{-1}$ )	$\beta$ ( $\times 10^{-3}$ mol $^2$ kJ $^{-2}$ )	$E_a$ (kJ mol $^{-1}$ )
303.15	1.6412	7.2279	0.01916	2.6418	1.9779	1.08	21.517
313.15	1.7275	6.4628	0.02138	2.9952	2.1398	1.15	20.851
323.15	1.8101	5.8786	0.02346	3.3104	2.2799	1.17	20.672



**Fig. 9.** D-R plots for the adsorption of Cu(II) onto the composite at different temperatures.

The mean energy of adsorption is the free energy change when one mole of the ion is transferred to the surface of the solid from infinity in the solution. The value of this parameter can give information about adsorption mechanism. When one mole of ions is transferred, its value in the range of 1–8 kJ mol $^{-1}$  indicates physical adsorption [36], while the value of  $E_a$  is between 8 and 16 kJ mol $^{-1}$ , the adsorption process follows by ion-exchange [37]. The values of  $E_a$  in the present case (Table 2) were determined at different temperatures and found to lie between 20.67 and 21.52 kJ mol $^{-1}$ , indicating that the above two adsorption mechanisms was not dominant and, it is likely other mechanism acted as a more important role in adsorption process.

It is known that there are three kinds of adsorption sites for the composite, i.e.  $-\text{COO}^-$ ,  $-\text{COO}^-\text{Na}^+$  and  $-\text{CONH}_2$ , which can be considered as the adsorption sites for electrostatic attraction (physical adsorption), ion-exchange and chelation, respectively. The effect of various adsorption temperatures on the adsorption capacity of the composite were studied by FT-IR and are shown in Fig. 10. It can be seen from Fig. 10 that there is obvious variations of absorption bands after adsorption in comparison to those of unadsorbed sample. After Cu(II) adsorption, peak at 1565  $\text{cm}^{-1}$  ascribed to  $\nu_s\text{C}=\text{O}$  in  $-\text{COO}^-$  and  $-\text{COO}^-\text{Na}^+$  almost disappeared and the intensity of peak at 1122  $\text{cm}^{-1}$  ascribed to  $\nu_s\text{C}-\text{O}$  in  $-\text{COO}^-$  and  $-\text{COO}^-\text{Na}^+$  evidently weakened, which both indicated that the two groups participated in the adsorption process. The absorption band of  $-\text{CONH}_2$  group shifted from 1652  $\text{cm}^{-1}$  to 1630  $\text{cm}^{-1}$  when the adsorption temperature becomes higher. Moreover, with the increase of adsorption temperature, the peak at 1401  $\text{cm}^{-1}$  ascribed to  $\nu_s\text{C}-\text{N}$  gradually weakened. These confirmed the participation of  $-\text{CONH}_2$  group for Cu(II) adsorption.

In fact, in present study there were a spot of  $-\text{COO}^-$  and  $-\text{COO}^-\text{Na}^+$  was a major form in the composite due to the thorough saponification. So, it can be considered that  $-\text{COO}^-\text{Na}^+$  and  $-\text{CONH}_2$  were two dominating groups. According to the values of  $E_a$ , which have exceeded range corresponding to ion-exchange, indicating that the chelation model should be the dominating adsorption mechanism. 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. Based on the above analysis, it is considered that the ion exchange and chelation model controlled simultaneously during the adsorption process, but the chelation model should be the dominating adsorption mechanism for Cu(II) onto the composite. The possible mechanisms of Cu(II) adsorption onto the composite are schemat-

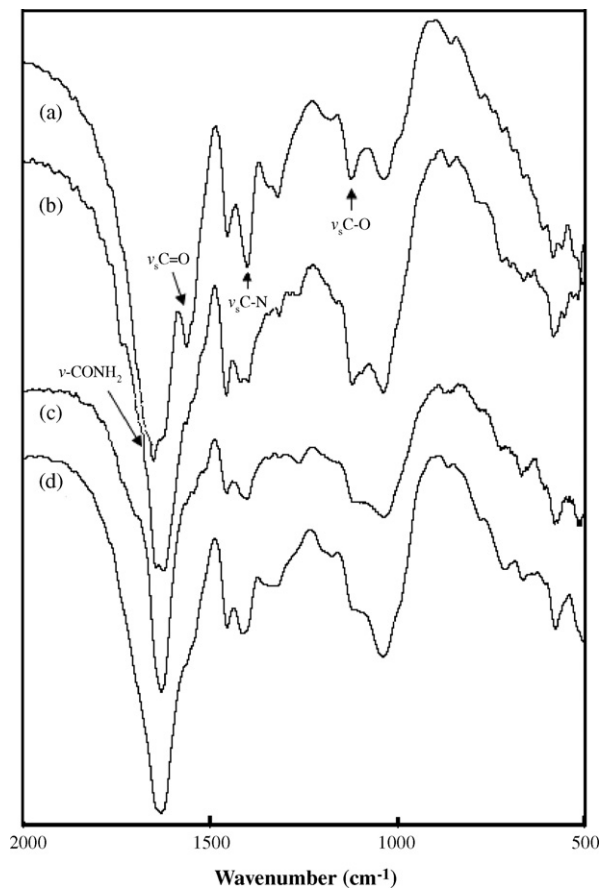


Fig. 10. IR spectrum of (a) the composite, samples after adsorption at (b) 303.2 K, (c) 313.2 K and (d) 323.2 K.

ically presented in Fig. 11. Furthermore, it can be concluded by the variations in intensity and position of characteristic peaks (Fig. 10) that ion-exchange and chelating effects both should become more prominent at higher temperature.

Through the discussion for isotherm constants, it can predict whether an adsorption system is favorable or unfavorable. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter,  $R_L$  [38], which is defined by

$$R_L = \frac{1}{1 + bC_0} \quad (13)$$

where  $C_0$  is the highest initial metal concentration. As seen from Table 2, at all temperatures the  $R_L$  values were between 0 and 1.0, indicating that adsorption of Cu(II) onto the composite are all favorable. Moreover,  $R_L$  values changed slightly from 0.0232 to 0.0195

Table 3  
Thermodynamic parameters for the adsorption of Cu(II) onto the composite.

T (K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
303.15	-22.395		
313.15	-22.843	8.4055	0.09985
323.15	-23.318		

with decreasing temperatures, denoting that the ongoing adsorption process is much more favorable at lower temperatures, yet the trend is not evident in the range of selected temperatures.

### 3.3. Thermodynamic parameters

Thermodynamic parameters including change in the Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) are the actual indicators for practical application of an adsorption process. According to values of these parameters, what process will occur spontaneously can be determined. The thermodynamic data were evaluated from Langmuir isotherms using following equations:

$$\Delta G^\circ = -RT \ln b \quad (14)$$

$$\Delta H^\circ = -R \left( \frac{T_2 T_1}{T_2 - T_1} \right) \ln \left( \frac{b_2}{b_1} \right) \quad (15)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (16)$$

where  $b$ ,  $b_1$ ,  $b_2$  are the equilibrium constants at different temperatures as presented in Table 3.

Obtained thermodynamic parameters are given in Table 3. As shown in the table, the negative values of  $\Delta G^\circ$  imply the spontaneous nature of the adsorption process. Further, the decrease in the values of  $\Delta G^\circ$  with the increasing temperature indicates the adsorption was more spontaneous at higher temperatures [39]. Generally, the change in free energy for physisorption is between  $-20$  and  $0$  kJ mol<sup>-1</sup>, but chemisorption is a range of  $-80$  to  $-400$  kJ mol<sup>-1</sup> [40]. The values of  $\Delta G^\circ$  obtained in this study are within the ranges of neither the physisorption nor chemisorption, indicating that the other adsorption such as complexation was likely the dominating mechanisms. The result of analysis for  $\Delta G^\circ$  again confirms clearly the mechanism of adsorption stated in isotherms model studies.

Positive  $\Delta H^\circ$  suggest endothermic reaction. The positive value of  $\Delta S^\circ$  suggests the increased randomness at the solid/solution interface during the adsorption of Cu(II) onto composite. In adsorption of Cu(II), the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system [38]. Also, in the case of physisorption which may also contribute to the total adsorption process can cause increase in entropy because of the water molecules released from the hydrated

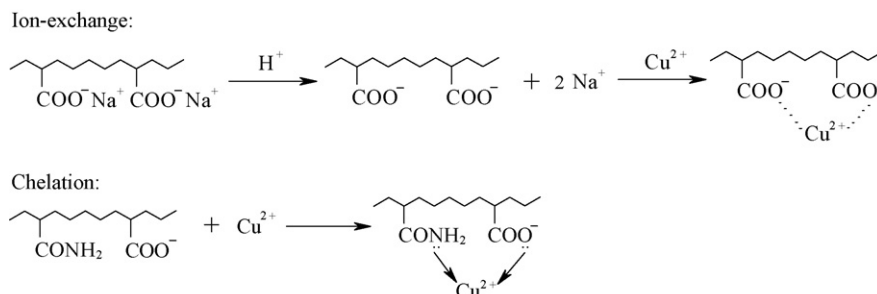


Fig. 11. Mechanisms of removal of copper ions by the composite.

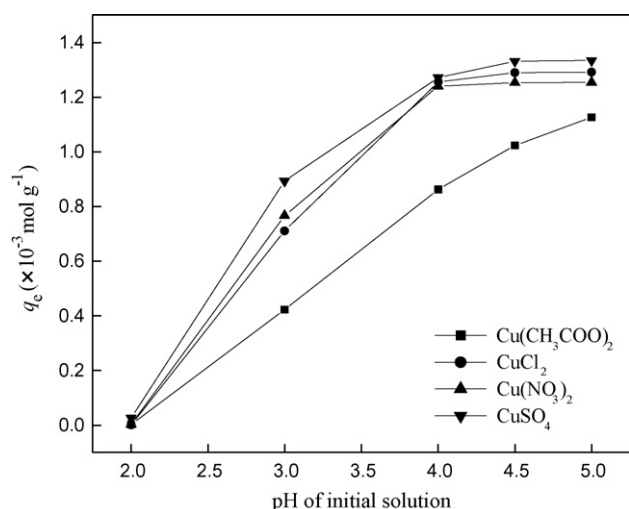


Fig. 12. Effect of initial pH on the adsorption of Cu(II) onto the composite using different copper salts.

ions or water molecules present on the surface during the adsorption process.

### 3.4. Effect of pH and different copper salts

In order to understand better the adsorption mechanism, the effect of the pH of initial solution on the adsorption of Cu(II) to the composite was examined in the pH range of 2–5 using the four types of copper salts in this section and the results were shown in Fig. 12. Clearly, the adsorption capacities were found to be low at lower pH values and increased with increase in pH. This can be explained with competitive adsorption of H<sup>+</sup> ions and metal ions for the same active adsorption site. As the pH increased, the adsorption surface becomes less positive due to the decrease of proton competition for the adsorption sites and therefore electrostatic attraction and ion-exchange between the metal ions and the surface of composite are likely to be increased.

It is interesting to note that there were different trend in adsorption capacity with an increasing pH for different copper salts in range of pH values from 2.0 to 5.0. For three types of inorganic copper salts, i.e. CuCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> and CuSO<sub>4</sub>, the  $q_e$  all increases drastically with an increase in pH of the initial solution from 2 to 4, and then remains almost constant as the pH becomes higher. In contrast to the three inorganic copper salts, the  $q_e$  increases almost linearly with increasing pH of Cu(II) solution when Cu(CH<sub>3</sub>COO)<sub>2</sub> was used. This may be further specified that in the present study the functional groups existed in the composite mainly contributed to metal uptake by chelation which is pH-dependent when Cu(CH<sub>3</sub>COO)<sub>2</sub> was used.

The above result implied that species for the same metal may affect the Cu(II) adsorption onto the composite and the different adsorption processes maybe occur. In general, there was a orderliness of the adsorption capacity as follows: CuSO<sub>4</sub> > CuCl<sub>2</sub> > Cu(NO<sub>3</sub>)<sub>2</sub> >> Cu(CH<sub>3</sub>COO)<sub>2</sub>. The trend of adsorption capacity versus pH for Cu(II) on the composite using acetate salt is obviously difference, it may be related to the property of acetate anions. The reasons for the difference using acetate salt and other inorganic salts are still not clear and need further study.

## 4. Conclusions

Adsorption processes of Cu(II) onto the poly(acrylamide)/attapulgite composite were found to undergo three stages and fol-

low pseudo-second order type adsorption kinetics. Intra-particle diffusion was found to take part in adsorption processes but it could not be accepted as the primary rate-determining step. The adsorption pattern on the composite seems to follow the Langmuir, Freundlich and D–R isotherms. According to the variations of IR spectra and the mean free energies of adsorption ( $E_a$ ), it can be safely concluded that the ion exchange and chelation model controlled simultaneously during the adsorption process, but the chelation model should be the dominating adsorption mechanism. The calculated values of different thermodynamic parameters clearly indicate that the ongoing adsorption process is feasible, spontaneous and endothermic in nature. The trend of adsorption capacity versus pH were different using Cu(CH<sub>3</sub>COO)<sub>2</sub>, CuCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> and CuSO<sub>4</sub>, this suggested that anionic kinds for the same metal may affect the Cu(II) adsorption onto the composite. According to the adsorption capacity for Cu(II), it is said that the poly(acrylamide)/attapulgite composite can be used as an effective adsorbent for the removal of Cu(II) from aqueous solution.

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## References

- [1] F.L. Buchholz, A.T. Graham, *Modern Superabsorbent Polymer Technology*, Wiley-VCH, New York, 1998, pp. 1–152.
- [2] X.H. Sun, G. Zhang, Q. Shi, B.C. Tang, Z.W. Wu, Study on foaming water-swelling EPDM rubber, *J. Appl. Polym. Sci.* 86 (2002) 3712–3717.
- [3] M.T. Ende, D. Hariharan, N.A. Peppas, Factors influencing drug and protein transport and release from ionic hydrogels, *React. Polym.* 25 (1995) 127–137.
- [4] A.S. Hoffman, Hydrogels for biomedical applications, *Adv. Drug. Deliv. Rev.* 54 (2002) 3–12.
- [5] G.S. Chauhan, H. Lal, Novel grafted cellulose-based hydrogels for water technologies, *Desalination* 159 (2003) 131–138.
- [6] C.A. Finch, *Specialty Polymers*, Wiley, New York, 1982.
- [7] V. Bekiari, M. Sotiropoulou, G. Bokias, P. Lianos, Use of poly(*N,N*-dimethylacrylamide-co-sodium acrylate) hydrogel to extract cationic dyes and metals from water, *Colloids Surf. A* 312 (2008) 214–218.
- [8] E.K. Yetimoğlu, M.V. Kahraman, Ö. Ercan, Z.S. Akdemir, N. Kayaman Apohan, *N*-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid based hydrogels: synthesis, characterization and their application in the removal of heavy metals, *React. Funct. Polym.* 67 (2007) 451–460.
- [9] H. Kagöz, S. Özgümü, M. Orbay, Preparation of modified polyacrylamide hydrogels and application in removal of Cu(II) ion, *Polymer* 42 (2001) 7497–7502.
- [10] H. Kagöz, S. Özgümü, M. Orbay, Modified polyacrylamide hydrogels and their application in removal of heavy metal ions, *Polymer* 44 (2003) 1785–1793.
- [11] H. Kaşgöz, A. Durmuş, A. Kaşgöz, Enhanced swelling and adsorption properties of AAm-AMPSNa/clay hydrogel nanocomposites for heavy metal ion removal, *Polym. Adv. Technol.* 19 (2008) 213–220.
- [12] T. Kinoshita, Y. Ishigaki, K. Nakano, K. Yamaguchi, S. Akita, S. Nii, F. Kawazumi, Application of acrylate gel having poly(ethylene glycol) side chains to recovery of gold from hydrochloric acid solutions, *Sep. Purif. Technol.* 49 (2006) 253–257.
- [13] W.F. Lee, L.G. Yang, Superabsorbent polymeric materials. XII. Effect of montmorillonite on water absorbency for poly(sodium acrylate) and montmorillonite nanocomposite superabsorbents, *J. Appl. Polym. Sci.* 92 (2004) 3422–3429.
- [14] J.P. Zhang, A. Li, A.Q. Wang, Superabsorbent composite. X. Effects of saponification on properties of polyacrylamide/attapulgite, *Polym. Eng. Sci.* 46 (2006) 1762–1767.
- [15] J.H. Wu, Y.L. Wei, J.M. Lin, S.B. Lin, Study on starch-graft-acrylamide/mineral powder superabsorbent composite, *Polymer* 44 (2003) 6513–6520.
- [16] W.F. Lee, Y.C. Chen, Effect of intercalated reactive mica on water absorbency for poly(sodium acrylate) composite superabsorbents, *Eur. Polym. J.* 41 (2005) 1605–1612.
- [17] A.H. Muhr, J.M.V. Blanshard, Diffusion in gels, *Polymer* 23 (1982) 1012–1026.
- [18] W. Davison, H. Zhang, In situ speciation measurements of trace components in natural waters using thin-film gels, *Nature* 367 (1994) 546–548.
- [19] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.* 97 (2003) 219–243.



- [20] H. Chen, A.Q. Wang, Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay, *J. Colloid Interface Sci.* 307 (2007) 309–316.
- [21] H. Chen, Y.G. Zhao, A.Q. Wang, Removal of Cu(II) from aqueous solution by adsorption onto acid-activated palygorskite, *J. Hazard. Mater.* 149 (2007) 346–354.
- [22] M.P. Raju, K.M. Raju, Design and synthesis of superabsorbent polymers, *J. Appl. Polym. Sci.* 80 (2001) 2635–2639.
- [23] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens, Handlingar* 24 (1898) 1–39.
- [24] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process. Biochem.* 34 (1999) 451–465.
- [25] H.A. Taylor, N. Thon, Kinetics of chemisorption, *J. Am. Chem. Soc.* 74 (1952) 4169–4173.
- [26] E. Bulut, M. Özacar, I.A. Şengil, Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design, *Microporous Mesoporous Mater.* 115 (2008) 234–246.
- [27] N. Thinakaran, P. Panneerselvam, P. Baskaralingam, D. Elango, S. Sivanesan, Equilibrium and kinetic studies on the removal of Acid Red 114 from aqueous solutions using activated carbons prepared from seed shells, *J. Hazard. Mater.* 158 (2008) 142–150.
- [28] W.J. Weber Jr., J.C. Morriss, Kinetics of adsorption on carbon from solution, *J. Sanitary Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–60.
- [29] D. Reichenberg, Properties of Ion-exchange resins in relation to their structure. III. Kinetics of exchange, *J. Am. Chem. Soc.* 75 (1953) 589–597.
- [30] S.B. Wang, H.T. Li, L.Y. Xu, Application of zeolite MCM-22 for basic dye removal from wastewater, *J. Colloid. Interface Sci.* 295 (2006) 71–78.
- [31] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, *Dyes Pigments* 51 (2003) 25–40.
- [32] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [33] H.M.F. Freundlich, Ueber die adsorption in lösungen, *Z. Phys. Chem.* 57 (1906) 385–470.
- [34] M.M. Dubinin, L.V. Radushkevich, Equation of the characteristic curve of activated charcoal, in: *Proceedings of the Academy of Sciences, 55. Physical Chemistry Section USSR, 1947*, pp. 331–333.
- [35] J.P. Hobson, Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure, *J. Phys. Chem.* 73 (1969) p2720.
- [36] M.S. Onyango, Y. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, *J. Colloid Interface Sci.* 279 (2004) 341–350.
- [37] F. Helfferich, *Ion Exchange*, McGraw-Hill Book Co., New York, 1962.
- [38] C. Namasivayam, K. Ranganathan, Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater, *Environ. Pollut.* 82 (1993) 255–261.
- [39] B.S. Chu, B.S. Baharin, Y.B. Che Man, S.Y. Quek, Separation of vitamin E from palm fatty acid distillate using silica. I. Equilibrium of batch adsorption, *J. Food. Eng.* 62 (2004) 97–103.
- [40] M.J. Jaycock, G.D. Parfitt, *Chemistry of Interfaces*, Onichester, Ellis Horwood Ltd., 1981.