



Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgitite composites

Xiaohuan Wang^{a,b}, Yian Zheng^a, Aiqin Wang^{a,*}

^a Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Tianshui Middle Road 18, Lanzhou, 730000, PR China

^b Graduate University of the Chinese Academy of Sciences, Beijing, 100049, PR China

ARTICLE INFO

Article history:

Received 11 November 2008
Received in revised form 22 February 2009
Accepted 23 February 2009
Available online 6 March 2009

Keywords:

Composite
Adsorption
Cu(II)
Kinetics
Isotherm

ABSTRACT

Novel chitosan-g-poly(acrylic acid)/attapulgitite (CTS-g-PAA/APT) composites were applied as adsorbents for the removal of Cu(II) from aqueous solution. The effects of the initial pH value (pH_0) of Cu(II) solution, contact time (t), APT content (wt%) and the initial concentration of Cu(II) solution (C_0) on the adsorption capacity of the composites were investigated. Results from kinetic experimental data showed that the Cu(II) adsorption rate on the composites with 10, 20 and 30 wt% APT was fast and more than 90% of the maximum adsorption capacity for Cu(II) occurred within the initial 15 min. The adsorption kinetics was better described by the pseudo-second order equation, and their adsorption isotherms were better fitted for the Langmuir equation. The results of the five-time consecutive adsorption–desorption studies showed that the composites had high adsorption and desorption efficiencies, which implies that the composites may be used as quite effective adsorbents for the removal of Cu(II) from aqueous solution.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Removal of heavy metals from wastewater can be achieved by coagulation and precipitation [1], ion exchange treatment [2], adsorption [3] and coprecipitation/adsorption [4]. In comparison with the other processes for the treatment of polluted aqueous effluents, the sorption process possesses some advantages, such as flexibility in design and operation, producing superior effluent suitable for reuse without other pollutants. Therefore, adsorption is one of the more popular methods. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants [5,6].

The most widely used adsorbent is activated carbon. However, activated carbon also requires complexing agents to improve its removal performance for inorganic matters [7]. The main disadvantages of using activated carbon as adsorbent are high adsorbent cost, problems of regeneration, and difficulties of separation of powdered activated carbon from wastewater for regeneration. It is now recognized that using low-cost adsorbents to adsorb pollutants is an effective and economical method for water decontamination. Many adsorbents materials have been studied, such as zeolite [8], clay [9], sawdust [10], bark [11], biomass [12], lignin [13], chitosan [14] and other adsorbents [15]. Among these low-cost adsorbents, various clays have been recently focused on study [16–21]. How-

ever, the adsorption capacity and adsorption rate for heavy metals is poor [19].

In recent years, special attention has been given to hydrogel adsorbents. Hydrogels are formed of three-dimensional cross-linked polymer networks of flexible chains, which are able to absorb and retain water and solute molecules. The higher water content and porous structure networks allow solute diffusion through the hydrogel structure [22]. As hydrogels possess ionic functional groups such as carboxylic acid, amine, hydroxyl and sulfonic acid groups, they can absorb and trap metal ions or ionic dyes from wastewater [23,24]. Therefore, a great deal of interest has been observed in relation to the applicability of hydrogels as adsorbents for the removal and separation of metal ions from heavy metal contaminated water [23–26], and the recovery and pre-concentration of precious metal ions from different media [27]. 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 [27].

Hydrogel composites based on polysaccharides and clay may be used as alternative adsorbents for the removal of metal ions or dyes from aqueous solution [28]. Attapulgitite (APT) 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 [29,30]. So, in order to reduce cost of the hydrogel adsorbents, in

* Corresponding author. Tel.: +86 931 4968118; fax: +86 931 8277088.
E-mail address: aqwang@lzb.ac.cn (A. Wang).

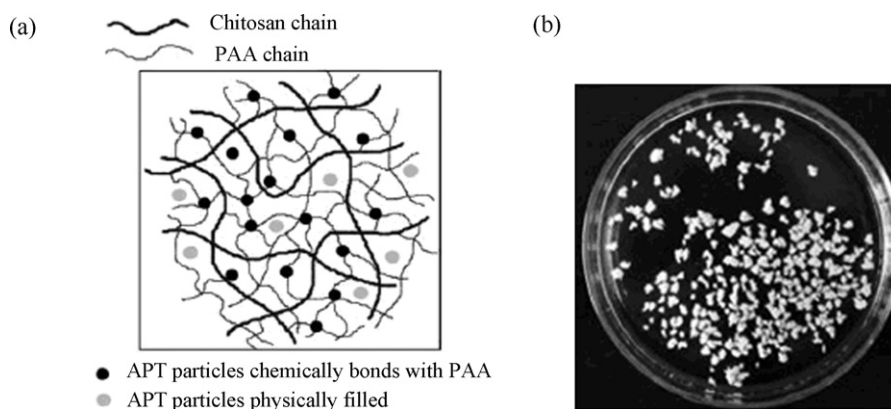


Fig. 1. Schematic structure (a) and digital photo of CTS-g-PAA/APT composite (b).

the present study, several chitosan-g-poly(acrylic acid)/attapulgitite (CTS-g-PAA/APT) composites with different APT content were synthesized and used to remove heavy metal Cu(II) from aqueous solutions. The factors influencing the adsorption capacity of the composites such as the initial pH value (pH_0) of the Cu(II) solutions, contact time (t), APT content (wt%) and the initial concentration of Cu(II) solutions (C_0) were investigated. The adsorption kinetics and isotherms for Cu(II) onto CTS-g-PAA/APT composites were also studied, and the desorption studies of the composites were discussed.

2. Experimental

2.1. Materials

Acrylic acid (AA, distilled under reduced pressure before use), ammonium persulfate (APS, recrystallized from distilled water before use) and *N,N'*-methylenebisacrylamide (MBA, used as received) were supplied by Shanghai Reagent Corp. (Shanghai, China). Chitosan (CTS, degree of deacetylation is 0.85, the average molecular weight is 3×10^5) was supplied by Zhejiang Yuhuan Ocean Biology Co. (Zhejiang, China). Natural Attapulgitite (APT, supplied by Jiangsu Autobang International Co., Ltd., Jiangsu, China)

Table 1

Chemical composition of attapulgitite sample.

Component	wt%
SiO ₂	57.06
MgO	8.63
Al ₂ O ₃	16.59
Fe ₂ O ₃	6.11
CaO	4.55
TiO ₂	0.71
MnO	0.08
K ₂ O	3.51
Na ₂ O	1.35
P ₂ O ₅	0.22
SO ₃	0.42

Table 2

The BET specific surface area, total pore volume and average pore width for CTS-g-PAA polymer and CTS-g-PAA/APT composites.

Sample	BET specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Adsorption average pore width (nm)
CTS-g-PAA	1.83	0.0041	8.99
CTS-g-PAA/10%APT	8.38	0.0343	16.35
CTS-g-PAA/20%APT	19.41	0.0731	15.06
CTS-g-PAA/30%APT	24.66	0.0995	16.13
CTS-g-PAA/50%APT	9.85	0.0284	11.54

was milled and sieved through a 320-mesh screen. The cationic exchange capacity (CEC) of the sample is 30.0 meq/100 g. Chemical composition of APT was determined with a Magix PW 2403 XRF Spectrometer (PANalytical Co.) and the results were shown in Table 1. Copper acetate monohydrate (analytical grade reagent, Cu(CH₃COO)₂ · H₂O, 199.65) was supplied by Shanghai Reagent Corp. (Shanghai, China). Other reagents used were all of analytical grade reagents and all solutions were prepared with distilled water.

2.2. Preparation of CTS-g-PAA/APT composites and their characterization

CTS-g-PAA/APT composites were prepared according to our previous reports [31]. The schematic structure and digital photo of CTS-g-PAA/APT composites were shown in Fig. 1. The preparation procedure of CTS-g-PAA was similar to that of CTS-g-PAA/APT composites except without APT. The products were milled and all samples used for test were sieved through a 80-mesh screen.

IR spectra (Thermo Nicolet NEXUS TM spectrophotometer) showed that the graft reaction has taken place among CTS, AA and APT [31]. The BET specific surface area, total pore volume and average pore width of the samples were measured using an Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP 2020) by BET-method at 76 K, and the results were shown in Table 2.

2.3. Adsorption experiments

All batch adsorption experiments were carried out by mixing 0.1000 g composite sample with 25 mL aqueous solution of copper acetate with the desired concentration and appropriate pH_0 and shaking in a thermostatic shaker bath (THZ-98A) with 120 rpm at 30 °C for a given time. The pH_0 of Cu(II) solution was adjusted to different pH values (2.00, 3.00, 4.00, 5.00, 5.50 and 5.85) with acetic acid or sodium hydroxide solutions using a pH meter (DELTA-320). Batch kinetic experiments were carried out by mixing 0.1000 g sample with 25 mL Cu(II) solution (C_0 : 1220 mg/L, pH_0 5.50) and shaking at 30 °C for predetermined intervals of time. For equilibrium adsorption experiments, 25 mL of various initial concentration of Cu(II) solution was mixed with 0.1000 g sample, then shaken at 30 °C until the equilibrium was established.

The Cu(II) solution was separated from the adsorbent by centrifugation at 4500 rpm for 10 min and the pH of each suspension was measured. Both the initial and the final concentrations of Cu(II) in the solution were measured by EDTA titrimetric method using 0.0050 mol/L EDTA solution as the standard solution and 0.5% xylene orange solution as the indicator. The adsorption capacity of the composites for Cu(II) was calculated through the following

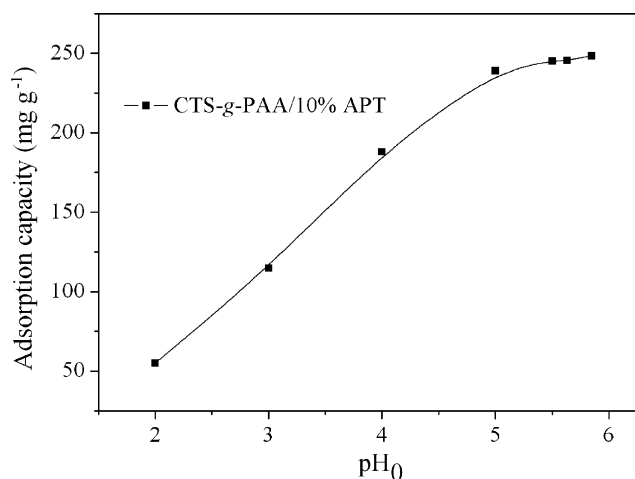


Fig. 2. Effect of pH_0 on the adsorption capacity of CTS-g-PAA/10%APT composite for Cu(II). Adsorption experiments— C_0 : 1220 mg/L; sample dose: 0.1000 g/25 mL; pH range: 2.0–5.85; temperature: 30 °C; equilibrium time: 240 min.

equation:

$$q = \frac{V(C_0 - C)}{m} \quad (1)$$

where q is the amount of Cu(II) adsorbed at time t or at equilibrium (mg/g). C_0 is the initial concentration of Cu(II) solution (mg/L). C is the liquid-phase Cu(II) concentration at time t or at equilibrium (mg/L). m is the mass of the adsorbent used (g) and V is the volume of Cu(II) solution used (L).

2.4. Desorption and regeneration studies

In order to search out an effective reagent for the copper-loaded composites desorption, certain amount of the representative copper-loaded CTS-g-PAA/10%APT sample was prepared and its adsorption capacity for Cu(II) was calculated (241.33 mg/g). The influence of different acid solutions or distilled water on desorption efficiency was studied by mixing 0.1000 g copper-loaded CTS-g-PAA/10%APT sample with 30 mL 0.05 mol/L acid solutions (HCl, HNO₃, H₂SO₄, CH₃COOH) or distilled water and agitating on a magnetic agitator with 220 rpm at room temperature for 60 min.

For evaluating the reuse value of the composites, 0.5000 g copper-loaded CTS-g-PAA/APT composite sample was agitated with 0.05 mol/L appropriate volume of HCl solution at room temperature for 60 min (dose: 0.1000 g/30 mL). The sample was separated from the solution by centrifugation and washed with distilled water for three times, and then dried for reuse. The consecutive adsorption–desorption process was performed for five times.

3. Results and discussion

3.1. Effect of pH_0 on Cu(II) adsorption

The pH of the metal ion solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Fig. 2 showed the effect of pH_0 of Cu(II) solution on the adsorption capacity of CTS-g-PAA/10%APT composite for Cu(II). It can be seen from Fig. 2 that the adsorption capacity increased sharply from 55.06 to 245.02 mg/g when pH_0 of Cu(II) solution increased from 2.00 to 5.50, and then increased very little (from 245.02 to 248.38 mg/g) with the increase of pH_0 from 5.50 to 5.85. This result may be attributed to the following reasons: at low pH_0 , (i) most of the amino groups of CTS in the composite were ionized and presented in the form of NH_3^+ , electrostatic repulsion between

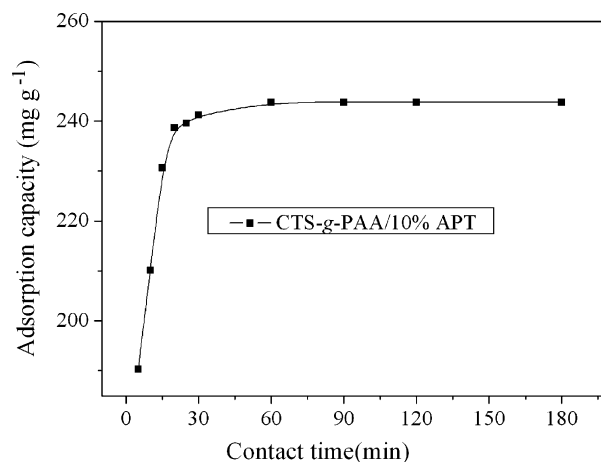


Fig. 3. Effect of contact time on the adsorption capacity of CTS-g-PAA/10%APT composite for Cu(II). Adsorption experiments— C_0 : 1200 mg/L; sample dose: 0.1000 g/25 mL; pH_0 : 5.50; temperature: 30 °C.

Cu(II) and NH_3^+ ions may prevent the adsorption of Cu(II) ions onto the composite; (ii) there are more H^+ ions competed with Cu(II) ions in the solution, which may make the ion-exchange reaction between Cu(II) ions and the exchangeable cations existed in the composite happen very difficultly; (iii) carboxyl groups in the polymer chain existed in the form of $-COOH$ not $-COO^-$, which could make against the adsorption of Cu(II) ions onto the composite. Considering the formation of $Cu(OH)_2$ precipitation when the pH value of Cu(II) solution exceeds 5.50, the pH_0 of 5.50 was selected as the initial pH value of Cu(II) solution for the following adsorption experiments.

3.2. Effect of contact time on adsorption

Contact time is an important parameter of adsorption which can reflect the adsorption kinetics of an adsorbent for an adsorbate solution with the given C_0 and pH_0 values. Fig. 3 showed the effect of contact time on the adsorption capacity of CTS-g-PAA/10%APT composite for Cu(II). It is clear that the adsorption capacity of the composite increased rapidly with the increase of contact time from 0 to 20 min and more than 90% of the equilibrium adsorption capacity for Cu(II) occurred within 15 min. After 60 min, the adsorption capacity became constant and the adsorption reached equilibrium. Therefore, 60 min was selected as the contact time for the adsorption of Cu(II) onto the composites under our experimental conditions.

Fig. 4 showed the pH variation of the suspension (pH_t) with contact time during adsorption process. It can be seen that pH_t decreased rapidly when contact time increased from 0 to 20 min, and then decreased quite little. After the adsorption equilibrium was set up, the pH values of all suspensions did not change any more. The following equations (Eq. (2) and (3)) may be used to explain this phenomenon.



It is known that CTS-g-PAA polymer and CTS-g-PAA/APT composites are three-dimensional cross-linked polymer networks and have lots of $-COOH$, which can be considered as the adsorption sites for ion exchange and chelation. In aqueous solution, on the one hand, $-COOH$ groups on the composites dissociate and become ionized (Eq. (2)). The dissociation of carboxyl groups may give birth to protons, and the quantity of protons increases with the increase of contact time, which cause the decrease of the pH value of the

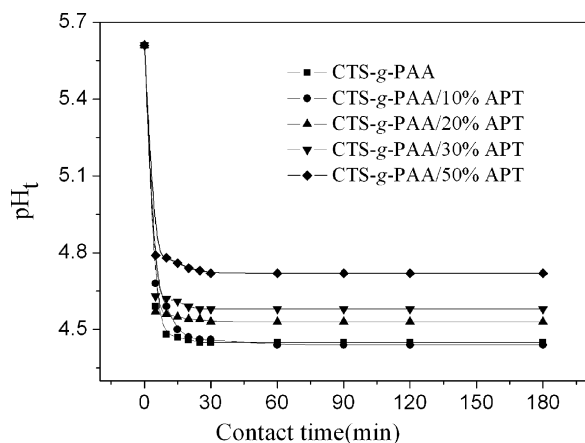


Fig. 4. Variation of the pH value of the suspension with contact time. Adsorption experiments— C_0 : 1200 mg/L; sample dose: 0.1000 g/25 mL; pH_0 : 5.50; temperature: 30 °C.

suspension with the increase of contact time. The ionized carboxyl groups ($-\text{COO}^-$) can bond with Cu(II) ions to form a neutral species and establish equilibrium (Eq. (3)) [32]. On the other hand, the surface of natural APT is negative owing to isomorphous substitution during its form process, and negatively charged sites on the surface of APT particles increase with the increase of APT mass, which can induce more protons to be adsorbed onto APT surface and result in an increase in the pH value of the final solution [29]. Due to the decrease tendency of the suspension pH value caused by the dissociation of carboxyl groups is more obvious than the increase tendency resulted from the negative charges on the surface of natural APT, so, the total effect is that pH_t of the suspension decreased when contact time increased. From Fig. 4 it also can be observed that the decrease extent of pH_t of the suspension (compared with pH_0) decreased with the increase of APT content. This phenomenon is only because that the more negatively charged sites on the surface of APT particles in the composites exist when APT content is higher, which may result in a greater increase in the pH of the final solution. While the adsorption of Cu(II) onto the composites come to the saturation, the pH value of the suspension may keep constant. According to the characteristic of the composite and the pH variation of the suspension (pH_t) with contact time during adsorption processes, it is considered that the ion exchange and chelation may control simultaneously the adsorption process.

In order to further illustrate the adsorption mechanism of CTS-g-PAA/APT composite for Cu(II), Fig. 5 represented the FTIR spectra of

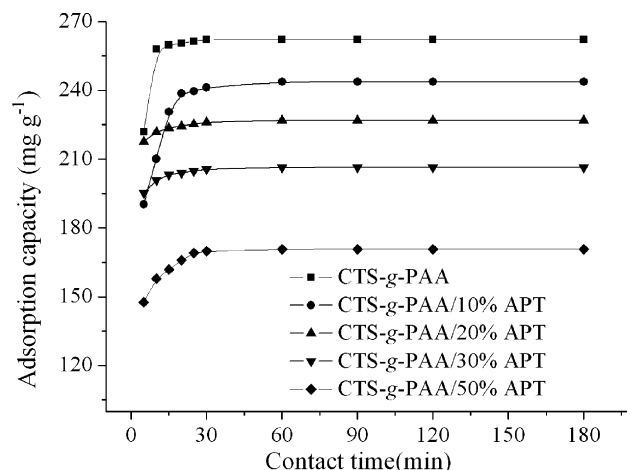


Fig. 6. Variation of the adsorption capacity of CTS-g-PAA/APT composites with different APT content with contact time. Adsorption experiments— C_0 : 1200 mg/L; sample dose: 0.1000 g/25 mL; pH_0 : 5.50; temperature: 30 °C.

the representative CTS-g-PAA/10%APT composite before and after Cu(II) adsorption. From Fig. 5, it can be seen that the IR spectra of the sample after Cu(II) adsorption showed many variations from that of the sample before Cu(II) adsorption. The major differences were listed as follows after adsorption of Cu(II): (i) the wide absorption band at near 3447 cm^{-1} , corresponding to the stretching vibration of $-\text{NH}_2$ groups and $-\text{OH}$ groups, widened and shifted to the lower wave numbers; (ii) the strong absorption band at 1719 cm^{-1} , assigned to the stretching vibration of $\text{C}=\text{O}$ of $-\text{COOH}$ groups, weakened obviously; (iii) the absorption band at 1561 cm^{-1} , assigned to the stretching vibration of $\text{C}=\text{O}$ of $-\text{COO}^-$ groups, was enhanced obviously and shifted to the lower wave numbers; (iv) the absorption band at 1249 cm^{-1} , assigned to the deformation vibration absorption bands of $-\text{OH}$ groups, were enhanced obviously and shifted to the higher wave numbers. All of these changes in FTIR spectra of the representative CTS-g-PAA/10%APT composites before and after Cu(II) adsorption indicates that $-\text{NH}_2$, $-\text{OH}$ and $-\text{COOH}$ groups in the composites were all involved in the adsorption process. So, the chelation should be the dominating adsorption mechanism for Cu(II) onto the composite.

3.3. Effect of APT content (wt%) on adsorption

Fig. 6 showed the variation of the adsorption capacity of CTS-g-PAA/APT composites with different APT content (C_0 : 1200 mg/L;

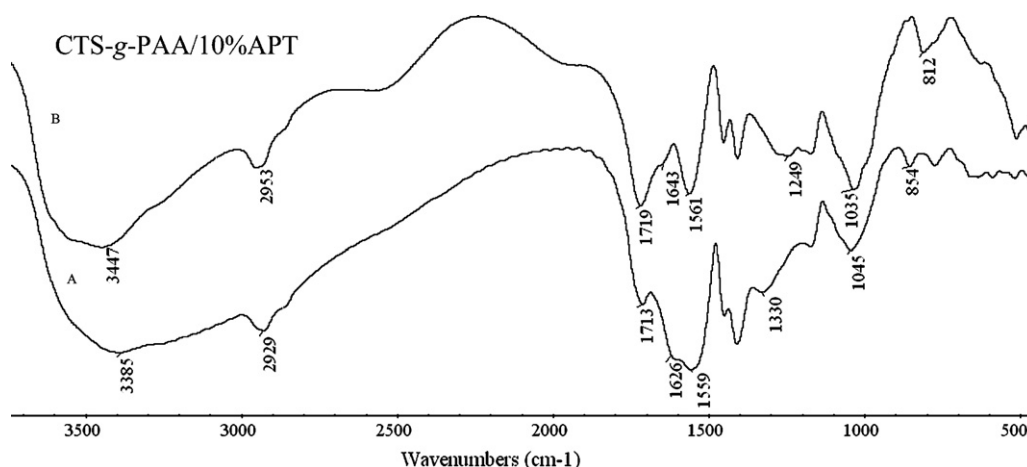


Fig. 5. IR spectra of the representative CTS-g-PAA/10%APT composite before (B) and after (A) Cu(II) adsorption.

Table 3
A comparison of the maximum adsorption capacity of the adsorbents for Cu(II).

Sorbent	Maximum adsorption capacity for Cu(II) (mg/g)	Source
Chitosan	17.79 ± 3.2	[34]
N,O-carboxymethyl-chitosan	162.5	[35]
Alumina/chitosan composite membranes	200	[36]
Acid-activated palygorskite	32.24	[37]
CTS-g-PAA	262.25	This paper
CTS-g-PAA/10%APT	243.76	This paper
CTS-g-PAA/20%APT	226.95	This paper
CTS-g-PAA/30%APT	206.39	This paper
CTS-g-PAA/50%APT	170.65	This paper

sample dose: 0.1000 g/25 mL; pH₀: 5.50; temperature: 30 °C). It is clear that wt% was an important factor affecting the adsorption capacity of the composites. As can be seen from Fig. 6, under the same conditions, the adsorption capacities of CTS-g-PAA/APT composites with different wt% are different and the equilibrium adsorption capacity of the composites decreased from 262.25 to 170.65 mg/g, as wt% increased from 0 to 50%. The decrease tendency of the adsorption capacity of composites with increasing wt% may be attributed to the following facts: (i) APT could react with AA and APT particles and act as cross-linking points in the network [31]. And the cross-linking density of the CTS-g-PAA/APT composite may increase with the increase of wt%. The greater the cross-linking density, the worse the elasticity of the polymer chains, which may result in the decrease of the equilibrium adsorption capacity of the composites. (ii) Additionally, during the adsorption processes of CTS-g-PAA and the composites for Cu(II), carboxyl groups are the main functional groups responsible for the adsorption for Cu(II). The higher the APT content, the lower the content of carboxyl groups in the composite. So, increasing the APT content may result in the decrease of the adsorption capacity of the composites for Cu(II). (iii) When APT content exceeds 30 wt%, excess APT acts as a filler in the polymeric network of the composite. Since the equilibrium adsorption capacity of APT for Cu(II) (28.46 mg g⁻¹) is much lower than that of CTS-g-PAA polymer (262.25 mg g⁻¹), the filled APT may greatly decrease the adsorption capacity of the composites. The same phenomenon was also observed by Wang et al. [33].

Fig. 6 also showed the adsorption rate information about the composites with different APT content for Cu(II). It is obvious that the adsorption rate of each sample for Cu(II) was very fast and more than 90% of the equilibrium adsorption capacity occurred within 15 min. Both the adsorption rate of CTS-g-PAA/20%APT composite and CTS-g-PAA/30%APT composite are higher than that of CTS-g-PAA, CTS-g-PAA/10%APT composite and CTS-g-PAA/50%APT composite. Such a result is nearly consistent with the results of the specific surface area, total pore volume and average pore width of the composites (shown in Table 2), which indicates that the specific surface area, total pore volume and average pore width of the composites are the factors controlling the adsorption rate.

Under the same experimental conditions, the equilibrium adsorption capacities of APT and CTS-g-PAA polymer were also measured, they were 28.46 and 262.25 mg/g, respectively. And the equilibrium adsorption capacities of the composites with APT content from 10 to 50 wt% were 243.76, 226.95, 206.39, 170.65 mg/g, respectively. Compared with other adsorbents (listed in Table 3) [34–37], the equilibrium adsorption capacities of the composites are quite high. Meanwhile, from the experimental data, it can be seen that there were differences of 4.89, 11.46, 14.28, 25.29 mg/g between the experimental value and the value calculated by the adsorption capacities of APT and CTS-g-PAA, respectively, if APT and CTS-g-PAA polymer were only compounded physically. Moreover, it can be seen that the differences increased with the increase

of wt%. This result indicated that APT really reacted with the CTS-g-PAA polymer and the introduction of APT into the polymer may improve the adsorption ability of the polymer to some extent. In practical industrial production, one of the most important purposes of the addition of APT into CTS-g-PAA polymer is to largely reduce the cost of adsorbents. Therefore, considering the economic advantage and the adsorption capacity, CTS-g-PAA/APT composites are very potential adsorbents for Cu(II).

3.4. Adsorption kinetics

In order to investigate the controlling mechanism of adsorption process of CTS-g-PAA/APT composites for Cu(II), the pseudo-first order and the pseudo-second order kinetic models were cited to evaluate the experimental data obtained from batch Cu(II) removal experiments. The pseudo-first order kinetic model has been widely used to predict metal adsorption kinetics. It was suggested by Lagergren [38] for the adsorption of solid/liquid systems and its linear form can be formulated as

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (4)$$

Ho and McKay's pseudo-second order kinetics model can be expressed as [39]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t , respectively. k_1 (min⁻¹) is the rate constant of the pseudo-first order adsorption. k_2 (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second order adsorption. All the corresponding parameters obtained from the linear plots of $\log(q_e - q_t)$ versus t and t/q_t versus t were listed in Table 4.

From Table 4, it can be seen that the linear correlation coefficients (R^2) for the pseudo-first order kinetic model are very high. However, there are large differences between the experimental q_e values ($q_{e,exp}$) and the calculated q_e values ($q_{e,cal}$), which indicated the pseudo-first order kinetic model was poor fit for the adsorption processes of CTS-g-PAA polymer and the composites for Cu(II). It can also be found from Table 4 that R^2 for the pseudo-second order kinetic model are all over 0.9999, moreover, the $q_{e,cal}$ values for the pseudo-second order kinetic model are all consistent with the $q_{e,exp}$ values. These suggested that the adsorption processes of CTS-g-PAA polymer and the composites for Cu(II) can be well described by the pseudo-second order kinetic model.

3.5. Adsorption isotherm study

The influence of C_0 on adsorption capacity of Cu(II) onto CTS-g-PAA polymer and CTS-g-PAA/APT composites was shown in Fig. 7. It is clear that C_0 plays an important role in the adsorption processes of Cu(II) onto CTS-g-PAA polymer and the composites. It can be seen from Fig. 7 that the adsorption capacity of the composites for Cu(II) increased with the increase of C_0 and increased more sharply when C_0 did not exceed 1500 mg/L. For CTS-g-PAA/10%APT composite, when C_0 was further increased from 2412 to 3717 mg/L, no further increase of the adsorption capacity was observed. However, such a phenomenon was not observed in the adsorption processes of CTS-g-PAA polymer and other three composites in the predetermined range of C_0 . These may be attributed to the following facts. Generally, the higher the initial Cu(II) concentration, the greater the driving force of the concentration gradient at the solid-liquid interface. And the increase of the driving force of the concentration gradient at the solid-liquid interface may cause the increase of the amount of metal ions adsorbed onto the adsorbent. On the other hand, at low initial Cu(II) concentration, ion exchange and elec-

Table 4

Constants and correlation coefficients of the two kinetic models for Cu(II) adsorption onto CTS-g-PAA polymer and CTS-g-PAA/APT composites.

Sample	Pseudo-first order model				Pseudo-second order model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min ⁻¹)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
CTS-g-PAA	262.25	48.40	0.1732	0.8632	263.16	0.0144	1
CTS-g-PAA/10%APT	243.76	98.27	0.1285	0.9659	243.90	0.0045	0.9999
CTS-g-PAA/20%APT	226.95	13.62	0.0889	0.9836	227.27	0.0242	1
CTS-g-PAA/30%APT	206.39	16.24	0.0986	0.9838	208.33	0.0230	1
CTS-g-PAA/50%APT	170.65	53.26	0.1354	0.9750	172.41	0.0125	1

trostatic attraction are dominant, and the adsorption of Cu(II) by CTS-g-PAA polymer and the composites tends to the possibility of the formation of monolayer coverage of the molecules at the outer interface of the adsorbent. While at the high initial concentration of Cu(II), the chelation between $-\text{COO}^-$ and Cu(II) ions are dominant, and the formation of chelating compounds may result in the increase of the amount of Cu(II) ions adsorbed onto the adsorbent.

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. The correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption [40]. The adsorption data is generally interpreted using the Langmuir and the Freundlich isotherm models. The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. The Langmuir model is represented as follows [41]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (6)$$

The Freundlich model is applied to describe heterogeneous system characterized by a heterogeneity factor of $1/n$. This model describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich model is expressed as follows [42]:

$$\log(q_e) = \frac{1}{n} \log(C_e) + \log K \quad (7)$$

where q_e is the amount of Cu(II) adsorbed at equilibrium (mg/g), C_e is the liquid-phase Cu(II) concentration at equilibrium (mg/L), q_{max} is the maximum adsorption capacity of the adsorbent (mg/g), and b is the Langmuir adsorption constant (L/mg). K is the Freundlich isotherm constant (L/g) and $1/n$ (dimensionless) is the heterogeneity factor. The Langmuir and Freundlich parameters obtained from

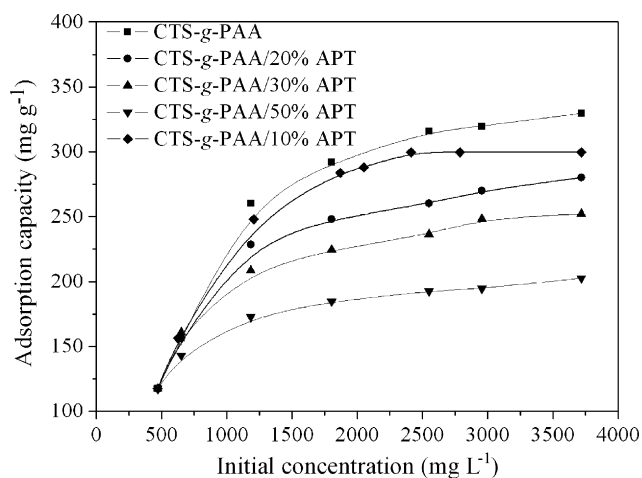


Fig. 7. Effect of the initial Cu(II) concentration of solution on the adsorption capacity of CTS-g-PAA polymer and CTS-g-PAA/APT composites. Adsorption experiments—sample dose: 0.1000 g/25 mL; pH₀: 5.50; temperature: 30 °C; equilibrium time: 60 min.

the plots of C_e/q_e versus C_e and $\log(q_e)$ versus $\log(C_e)$ were listed in Table 5.

The correlation coefficients (R^2) of the linear form of the Langmuir model are closer to 1 than that of the Freundlich model. In addition, the q_{max} values for the adsorption of Cu(II) onto the composites calculated from the Langmuir model are all the same as the experimental data. Obviously, the Langmuir model is much better to describe the adsorption of Cu(II) onto CTS-g-PAA polymer and CTS-g-PAA/APT composites than the Freundlich model. This means the monolayer coverage of Cu(II) on the surface of CTS-g-PAA polymer and the composites.

3.6. Desorption studies and the recycling of CTS-g-PAA/APT composites

Except in the case of precious metals for which the cost of the sorbent is not a limiting criterion, the recycling of the sorbent is a required step in the design of the process. The recovery of metals is also an important parameter for the economics of the process [43]. Desorption studies can help to recover the Cu(II) ions from the composite and regenerate the composite, so that it can be used again to adsorb metal ions. Desorption studies can also help to elucidate the nature of the adsorption process. If the metal adsorbed onto the adsorbent can be desorbed by water, it can be said that the attachment of the metal onto the adsorbent is by weak bonds. If the strong acid, such as HNO_3 and HCl , it can be said that the attachment of the metal onto the adsorbent is by ion exchange. If organic acids, for example, such as CH_3COOH , can desorb the metal, it can be said that the adsorption of the metal onto the adsorbent is by chemisorption [44]. And the sorption of metal cations usually occurs at pH close to neutral and the desorption is usually carried out by contacting with acidic solution [45], though chelating agents can be used.

Table 6 showed the results of desorption experiments. It was clear that the copper-loaded sample cannot be desorbed by distilled water at all, and only 13.03% desorption efficiency was obtained when using 0.05 mol/L CH_3COOH solution as the desorbing agent. The desorption efficiencies of 0.05 mol/L HCl , HNO_3 and H_2SO_4 solution are 86.26%, 84.91% and 85.31%, respectively. Among the four acid solutions, both the desorption capacity and the desorption efficiency of HCl solution are the largest (208.18 mg/g and 86.26%, respectively). HCl is the cheapest among these acid used, in terms of the principle of the economics of the desorption process and the

Table 5

Langmuir and Freundlich constants and correlation coefficients associated with the adsorption isotherms of Cu(II) onto CTS-g-PAA polymer and CTS-g-PAA/APT composites.

Sample	Langmuir equation			Freundlich equation		
	q_{max} (mg/g)	b (L/mg)	R^2	K	n	R^2
CTS-g-PAA	333.33	0.0235	0.9988	169.94	11.72	0.9951
CTS-g-PAA/10%APT	303.03	0.0328	0.9987	145.55	9.99	0.9816
CTS-g-PAA/20%APT	277.78	0.0169	0.9975	138.68	11.36	0.9824
CTS-g-PAA/30%APT	250.00	0.0220	0.9977	135.99	13.11	0.9879
CTS-g-PAA/50%APT	200.00	0.0189	0.9984	95.06	10.57	0.9963

Table 6

The influence of desorbing agents on the desorption capacity and desorption efficiency of Cu(II) from the representative copper-loaded CTS-g-PAA/10%APT composite sample.

The desorbing agent	The desorption capacity (mg/g)	The desorption efficiency
Distilled water	0	0
Nitric acid	204.94	84.91%
Acetic acid	31.46	13.03%
Sulfuric acid	205.89	85.31%
Hydrochloric acid	208.18	86.26%

reduction of the cost of the utilization of adsorbent, 0.05 mol/L HCl aqueous solution was selected as the desorbing agent for copper-loaded CTS-g-PAA/APT composites.

In order to evaluate the reuse value of the composites, the consecutive adsorption–desorption process was performed for five times. The concentration of 0.05 mol/L of HCl solution was used as the desorbing agent. Fig. 8 showed the relationship between the time for reuse and the adsorption capacity of the representative samples (CTS-g-PAA polymer and CTS-g-PAA/30%APT composite) for Cu(II). It can be seen that the adsorption capacity of CTS-g-PAA/30%APT composite decreased firstly with the increase of the time for reuse and then increased. However, the adsorption capacity of CTS-g-PAA polymer decreased all along. This result may be attributed to the following facts: during the adsorption–desorption processes, HCl solution was used as the desorbing agent and protonated amino groups in the composite, which may cause the decrease of the adsorption capacity of the composite. On the other hand, the sample after desorption need to be dried in an oven (85 °C) for 8 h. Thus, each adsorption–desorption process must go with an acid-treated process and a heat-treated process, and both the acid-treated process and the heat-treated process may increase the adsorption capacity of APT [30]. So, after several times for reuse, the adsorption capacity of CTS-g-PAA/30%APT composite began to increase slowly.

In addition, during the five-time consecutive adsorption–desorption processes, the average desorption efficiency of each CTS-g-PAA/APT composite was over 75%, which suggested that the adsorption of Cu(II) onto CTS-g-PAA/APT composites carried out mainly by electrostatic attraction. And all of these also further substantiated the discussion of the effect of pH value on adsorption and indicated that CTS-g-PAA/APT composites possessed of the potential of regeneration and reuse.

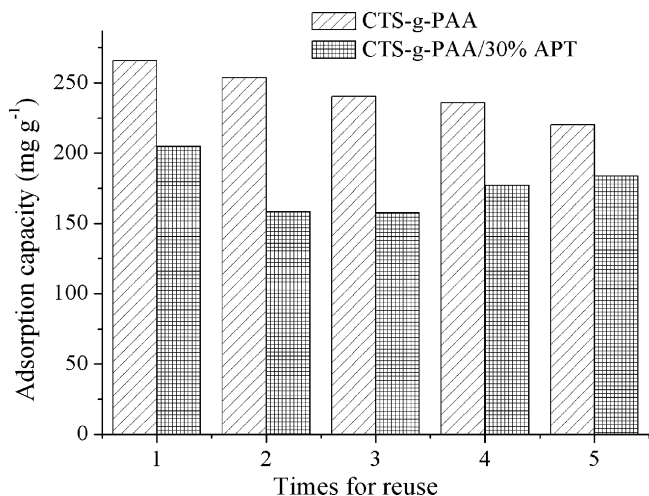


Fig. 8. Relationship between the time for reuse and the adsorption capacity of CTS-g-PAA polymer and CTS-g-PAA/30%APT composite for Cu(II).

4. Conclusions

The introduction of APT clay into CTS-g-PAA polymeric network could reduce the cost of adsorbents and generate a loose and porous surface, which might improve the adsorption ability of composites to some extent. The results of the adsorption kinetics and isotherms showed that the adsorption processes of the composites for Cu(II) were all better fitted by the pseudo-second order equation and the Langmuir equation, respectively. The monolayer coverage of Cu(II) on the surface of the composites was in the ascendant. The high adsorption capacity and average desorption efficiency during the consecutive five-time adsorption–desorption processes of CTS-g-PAA/APT composites implied that the composites possess the potential of regeneration and reuse. In conclusion, it can be said that the composites are quite effective adsorbents for the removal of Cu(II) from aqueous solution.

Acknowledgements

The authors thank for jointly supporting by the National Natural Science Foundation of China (No. 20877077), Taihu Project of Jiangsu Provincial Sci. & Tech. Department (No. BS2007118) and Science and Technology Support Project of Gansu Provincial Sci. & Tech. Department (No. 0804GKCA03A).

References

- [1] L. Charerntanyarak, Heavy metals removal by chemical coagulation and precipitation, *Water Sci. Technol.* 39 (1999) 135–138.
- [2] A. Dąbrowski, 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.
- [3] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: a review, *J. Hazard. Mater.* 157 (2008) 220–229.
- [4] R.J. Crawford, D.E. Mainwaring, I.H. Harding, Adsorption and coprecipitation of heavy metals from ammoniacal solutions using hydrous metal oxides, *Colloids Surf. A: Physicochem. Eng. Aspects* 126 (1997) 167–179.
- [5] J.C. Morris, W.J. Weber Jr., Preliminary appraisal of advanced waste treatment processes, *Public Health Serv. Public.* (1962) W24–W62.
- [6] J.C. Morris, W.J. Weber Jr., Adsorption of biochemically resistant materials from solution 1, *Public Health Serv. Public.* (1964), 999-WP-11.
- [7] B. Sandhya, A.K. Tonni, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.* 97 (2003) 219–243.
- [8] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, *J. Colloid Interface Sci.* 280 (2004) 309–314.
- [9] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, *Miner. Eng.* 19 (2006) 463–470.
- [10] Y. Bulut, Z. Tez, Removal of heavy metals from aqueous solution by sawdust adsorption, *J. Environ. Sci.* 19 (2007) 160–166.
- [11] S. Al-Asheh, F. Banat, R. Al-Omari, et al., Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, *Chemosphere* 41 (2000) 659–665.
- [12] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, *Bioresour. Technol.* 98 (2007) 2243–2257.
- [13] D. Parajuli, K. Inoue, K. Ohto, Adsorption of heavy metals on crosslinked lignocatechol: a modified lignin gel, *React. Funct. Polym.* 62 (2005) 129–139.
- [14] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.* 30 (2005) 38–70.
- [15] V. Bekiari, P. Lianos, Ureasil gels as a highly efficient adsorbent for water purification, *Chem. Mater.* 18 (2006) 4142–4146.
- [16] K.G. Bhattacharyya, S.S. Gupta, Adsorptive accumulation of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) from water on montmorillonite: influence of acid activation, *J. Colloid Interface Sci.* 310 (2007) 411–424.
- [17] D.L. Guerra, R.R. Viana, C. Airoidi, Adsorption of mercury cation on chemically modified clay, *Mater. Res. Bull.* 44 (2009) 485–491.
- [18] P. Liu, T.M. Wang, Adsorption properties of hyperbranched aliphatic polyester grafted attapulgite towards heavy metal ions, *J. Hazard. Mater.* 149 (2007) 75–79.
- [19] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review, *Adv. Colloid Interface Sci.* 140 (2008) 114–131.
- [20] M.F. Brigatti, S. Colonna, D. Malferrari, et al., Mercury adsorption by montmorillonite and vermiculite: a combined XRD, TG-MS, and EXAFS study, *Appl. Clay Sci.* 28 (2005) 1–8.
- [21] P. Srivastava, B. Singh, M. Angove, Competitive adsorption behavior of heavy metals on kaolinite, *J. Colloid Interface Sci.* 290 (2005) 28–38.
- [22] C.L. Bell, N.A. Peppas, Biomedical membranes from hydrogels and interpolymer complexes, *Adv. Polym. Sci.* 22 (1995) 125–176.

- [23] V. Bekiari, M. Sotiropoulou, G. Bokias, et al., 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.
- [24] E.K. Yetimoğlu, M.V. Kahraman, Ö. Ercan, et al., *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.
- [25] H. Kagöz, S. Özgümü, M. Orbay, Preparation of modified polyacrylamide hydrogels and application in removal of Cu(II) ion, *Polymer* 42 (2001) 7497–7502.
- [26] H. Kagöz, S. Özgümü, M. Orbay, Modified polyacrylamide hydrogels and their application in removal of heavy metal ions, *Polymer* 44 (2003) 1785–1793.
- [27] 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.
- [28] T. Alexandre, R. Marcos, V. Adriano, Removal of methylene blue from an aqueous media using a superabsorbent hydrogel supported on modified polysaccharide, *J. Colloid Interface Sci.* 301 (2006) 55–62.
- [29] H. Chen, A.Q. Wang, Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay, *J. Colloid Interface Sci.* 307 (2007) 309–316.
- [30] W.J. Wang, H. Chen, A.Q. Wang, Adsorption characteristics of Cd(II) from aqueous solution onto activated palygorskite, *Sep. Purif. Technol.* 55 (2007) 157–164.
- [31] J.P. Zhang, Q. Wang, A.Q. Wang, Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgit superabsorbent composites, *Carbohydr. Polym.* 68 (2007) 367–374.
- [32] K.A. Dashkhuu, Y.G. Ko, U.S. Choi, Adsorption and equilibrium adsorption modeling of bivalent metal cations on viscose rayon succinate at different pHs, *React. Funct. Polym.* 67 (2007) 312–321.
- [33] L. Wang, J.P. Zhang, A.Q. Wang, Removal of methylene blue from aqueous solution using chitosan-g-poly (acrylic acid)/montmorillonite superabsorbent nanocomposite, *Colloids Surf. A: Physicochem. Eng. Aspects* 322 (2008) 47–53.
- [34] S.L. Ilauro, A. Claudio, A thermodynamic investigation on chitosan-divalent cation interactions, *Thermochim. Acta* 421 (2004) 133–139.
- [35] S.L. Sun, A.Q. Wang, Adsorption kinetics of Cu(II) ions using *N,O*-carboxymethyl-chitosan, *J. Hazard. Mater.* 131 (2006) 103–111.
- [36] G.C. Steenkamp, K. Keizer, H.W.J.P. Neomagus, et al., Copper(II) removal from polluted water with alumina/chitosan composite membranes, *J. Membr. Sci.* 197 (2002) 147–156.
- [37] 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.
- [38] S. Lagergren, About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens, Handlingar*, Band 24 (1898) 1–39, No. 4.
- [39] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [40] E.L. Grabowska, G. Gryglewicz, Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon, *Dyes Pigm.* 74 (2007) 34–40.
- [41] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [42] H.M.F. Freundlich, Über die adsorption in lasungen, *Z. Phys. Chem.* 57 (1906) 385–470.
- [43] R.W. Coughlin, M.R. Deshaies, E.M. Davis, Chitosan in crab shell wastes purifies electroplating wastewater, *Environ. Prog.* 9 (1990) 35–39.
- [44] I.D. Mall, V.C. Srivastava, G.V.A. Kumar, et al., Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution, *Colloids Surf. A: Physicochem. Eng. Aspects* 278 (2006) 175–187.
- [45] G. McKay, H.S. Blair, J.R. Gardner, Two resistance mass transport model for the adsorption of acid dye onto chitin in fixed beds, *J. Appl. Polym. Sci.* 33 (1987) 1249–1257.