

This article was downloaded by: [CAS Consortium]

On: 30 May 2011

Access details: Access Details: [subscription number 937805357]

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Environmental Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t791546829>

Rapid removal of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgit/sodium humate composite hydrogels

Junping Zhang^{ab}, Yeling Jin^a; Aiqin Wang^{ab}

^a Key Laboratory for Attapulgite Science and Applied Technology of Jiangsu Province, Huaiyin Institute of Technology, Huaian, People's Republic of China ^b Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, People's Republic of China

Online publication date: 03 May 2011

To cite this Article Zhang, Junping , Jin, Yeling and Wang, Aiqin(2011) 'Rapid removal of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgit/sodium humate composite hydrogels', Environmental Technology, 32: 5, 523 – 531

To link to this Article: DOI: 10.1080/09593330.2010.504748

URL: <http://dx.doi.org/10.1080/09593330.2010.504748>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Rapid removal of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgitite/sodium humate composite hydrogels

Junping Zhang^{a,b}, Yeling Jin^a and Aiqin Wang^{a,b*}

^aKey Laboratory for Attapulgitite Science and Applied Technology of Jiangsu Province, Huaiyin Institute of Technology, Huaian, People's Republic of China; ^bCenter of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, People's Republic of China

(Received 9 December 2009; Accepted 24 June 2010)

A series of novel granular chitosan-g-poly(acrylic acid)/attapulgitite/sodium humate (CTS-g-PAA/APT/SH) composite hydrogels were successfully prepared by one-step free radical graft polymerization and applied as adsorbents for the removal of Pb(II) from aqueous solution. The effects of adsorbent composition (including the contents of APT, SH and CTS) on adsorption capacity and adsorption rate were investigated in detail. Results from kinetic experiments showed that the rate of Pb(II) adsorption on the composite hydrogels was quite fast, that more than 90% of the equilibrium adsorption capacity occurs within two minutes and that the adsorption equilibrium could be achieved within 10 minutes. The adsorption kinetics fit well with the pseudo-second order equation. The introduced SH is helpful for both adsorption capacity and adsorption rate. The –COOH and –COO[–] of PAA, –NH₂ of CTS, Ph-O[–] and –COO[–] of SH, as well as cation exchange and Si–OH of APT, participate in adsorption of Pb(II). The synergistic effect of these groups is responsible for the high adsorption capacity and rate.

Keywords: composite hydrogels; adsorption; Pb(II); attapulgitite; sodium humate

1. Introduction

Several treatment processes (including adsorption [1], coagulation and precipitation [2], ion exchange treatment [3] and coprecipitation/adsorption [4], etc.) have been developed over the years to remove heavy metal ions from industrial wastewaters. The adsorption method is the most frequently used because of its flexibility in design and operation as well as easy regeneration of the adsorbent.

It has been gradually recognized that using low-cost and environmentally friendly adsorbents to remove pollutants is an effective and economical method of water decontamination. Many materials have been used as adsorbents including chitosan (CTS) [5], clay [6,7], zeolite [8], sawdust [9], bark [10], lignin [11] and others [12]. However, low adsorption capacity and rate for heavy metal ions are frequently met problems for these low-cost adsorbents [13], which seriously restrict their practical applications. It has been reported that approximately 3 h is needed to reach adsorption equilibrium (33 mg/g) using acid-activated attapulgitite for the removal of Cu(II) from aqueous solution [14]. The adsorption of Au(III), Pt(IV) and Pd(II) onto glycine-modified CTS resin could reach equilibrium (169.98, 122.47 and 120.39 mg/g, respectively) within 100 min [15].

Recently, the application of hydrogels with three-dimensional crosslinked polymeric network as adsorbents for the removal of heavy metal ions [16,17] and ammonium nitrogen [18] has been paid special attention [19–21]. The flexible polymer chains and functional groups of a hydrogel make it swell partly once immersed in aqueous solution, which is convenient for the penetration of solute molecules with water into the network. The solute molecules then bind with the functional groups [22]. Given the limitations of pure polymeric hydrogels such as low gel strength and stability, some inorganic clay minerals including attapulgitite (APT), montmorillonite, vermiculite and sepiolite have been incorporated into pristine hydrogel for the preparation of organic/inorganic composite hydrogels [23–26].

In our previous study, we prepared a series of composite hydrogels, chitosan-g-poly(acrylic acid)/attapulgitite (CTS-g-PAA/APT) [25] and found that such composite hydrogels are excellent adsorbents for Cd(II) ions with high adsorption capacity and fast adsorption rate [6]. Sodium humate (SH) is composed of multi-functional aliphatic components and aromatic constituents, and contains many functional groups such as carboxylates and phenolic hydroxyls [27]. It has also

*Corresponding author. Email: aqwang@licp.cas.cn

been observed that the introduction of SH is of benefit for the improvement of adsorption capacity [16].

In order to acquire a novel hydrogel adsorbent with high performance and low-cost, chitosan-*g*-poly(acrylic acid)/attapulgite/sodium humate (CTS-*g*-PAA/APT/SH) composite hydrogels were prepared in the present study by one-step free radical graft polymerization and applied as adsorbents for the removal of Pb(II) from aqueous solution. The effects of adsorbent composition (including APT, SH and CTS content) on adsorption capacity and adsorption rate were investigated in detail. The adsorption kinetics of the composite for Pb(II) were also studied. In addition, Fourier transform infrared (FTIR) spectra of the samples were taken in order to interpret the adsorption mechanism.

2. Materials and methods

2.1. Materials

AA (distilled under reduced pressure before use), ammonium persulfate (APS, recrystallized from distilled water before use), *N,N'*-methylenebisacrylamide (MBA, used as received) and lead acetate (analytical grade, used as received) were supplied by Shanghai Reagent Corp. (Shanghai, China). CTS (degree of deacetylation = 0.85, average molecular weight = 30×10^4) was supplied by Zhejiang Yuhuan Ocean Biology Co. (Zhejiang, China). APT (supplied by Jiuchuan Clay Technology Co., Jiangsu, China) was milled through a 320-mesh screen before use. The specific surface area of APT is 235 m²/g. SH (supplied by Shuanglong Ltd, Xinjiang, China) with an average molecular weight of 1020 was used as received. Other agents used were all of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of CTS-*g*-PAA/APT/SH composite hydrogels

A series of composite hydrogels from CTS, AA, APT and SH were synthesized according to the following

procedure. An appropriate amount of CTS was dissolved in 30 mL acetic acid solution (1%) in a 250 mL four-neck flask equipped with a mechanical stirrer, a reflux condenser, a funnel and a nitrogen line. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the system, the solution was heated to 60°C and then 0.20 g APS was introduced to initiate CTS to generate radicals. Ten minutes later, the mixed solution of 7.20 g of AA, 0.30 g of MBA and the correct amounts of APT and SH were added. The water bath was kept at 60°C for 3 h. The resulting granular product was transferred into sodium hydroxide aqueous solution (1M) to be neutralized to pH = 7, and then dehydrated three times with 95% ethanol. After wiping off excessive ethanol on the surface using filter paper, the samples were spread on a dish to dry overnight at room temperature. The product was milled and all samples used for testing had a particle size in the range 200–320 mesh.

CTS-*g*-PAA (without APT and SH) was prepared according to the same procedure to study the effect of introducing APT and SH on the adsorbing properties of the composite hydrogels. The samples with various amount of APT (APT1#~APT3#), SH (SH1#~SH3#) and CTS (CTS1#~CTS3#) were prepared to study their influences on adsorption capacity, kinetics and mechanism. The detailed feed composition of the CTS-*g*-PAA/APT/SH composite hydrogels is shown in Table 1.

2.3. Adsorption experiments

All batch adsorption experiments were carried out by mixing 0.1 g of sample with 25 mL aqueous solution of lead acetate (4000 ppm, pH 5.50) and shaking in a thermostatic shaker bath (THZ-98A, 120 rpm, 30°C) for predetermined time intervals. The Pb(II) solution was separated from the adsorbent by centrifugation at 4500 rpm for 10 min. Both the initial and the final concentrations of Pb(II) were measured by the EDTA titrimetric method using 0.0025 M EDTA solution as the standard solution and 0.5% xylenol orange solution

Table 1. Feed composition of CTS-*g*-PAA and CTS-*g*-PAA/APT/SH composite hydrogels.

Sample	APT (g)	SH (g)	CTS (g)	AA (g)	MBA (g)	APS (g)
CTS- <i>g</i> -PAA	0	0	0.72	7.2	0.30	0.20
APT1#	0	0.468	0.72	7.2	0.30	0.20
APT2#, SH2#, CTS1#	0.468	0.468	0.72	7.2	0.30	0.20
APT3#	0.936	0.468	0.72	7.2	0.30	0.20
SH1#	0.468	0	0.72	7.2	0.30	0.20
SH3#	0.468	0.936	0.72	7.2	0.30	0.20
CTS2#	0.468	0.468	1.44	7.2	0.30	0.20
CTS3#	0.468	0.468	2.40	7.2	0.30	0.20

as the indicator. The adsorption capacity of the composites for Pb(II) was calculated according to the following equation:

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

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

2.4. Characterization

The micrographs of CTS-g-PAA and CTS-g-PAA/APT/SH were taken using a scanning electron microscope (SEM) (JSM-5600LV, JEOL Ltd). Before SEM observation, all samples were fixed on copper stubs and coated with gold. FTIR spectra of samples were taken as KBr pellets using a Thermo Nicolet NEXUS TM spectrophotometer.

3. Results and discussion

3.1. Surface micro-morphology analysis

SEM micrographs of CTS-g-PAA, CTS-g-PAA/APT and the CTS-g-PAA/APT/SH (APT 2#) composite hydrogel are shown in Figure 1. These were obtained in order to examine the influence of introduced APT and SH on the surface structure of the composite hydrogel, which may in turn have some influence on the adsorption capacity and the adsorption rate of Pb(II) onto the adsorbent. As can be seen, a tight surface with some post holes is observed for CTS-g-PAA, whereas a relatively loose and fibrous surface is generated after the incorporation of SH and APT (Figure 1(b) and (c)). The change to surface morphology by introducing APT and SH may facilitate the penetration of Pb(II) into network of the CTS-g-PAA/APT/SH composite hydrogels with water, and then improve their adsorption capacity and adsorption rate. Thus the effects of APT, SH and CTS content on adsorption capacity and kinetics of the CTS-g-PAA/APT/SH composite hydrogels are discussed in detail in the following sections.

3.2. Effect of APT content on adsorption

Figure 2(a) shows the effect of APT content on the adsorption capacity and kinetics of CTS-g-PAA/APT/SH for Pb(II). As can be seen, the equilibrium adsorption capacity for Pb(II) is in the order CTS-g-PAA \approx APT1# > APT2# > APT3#. The equilibrium adsorption

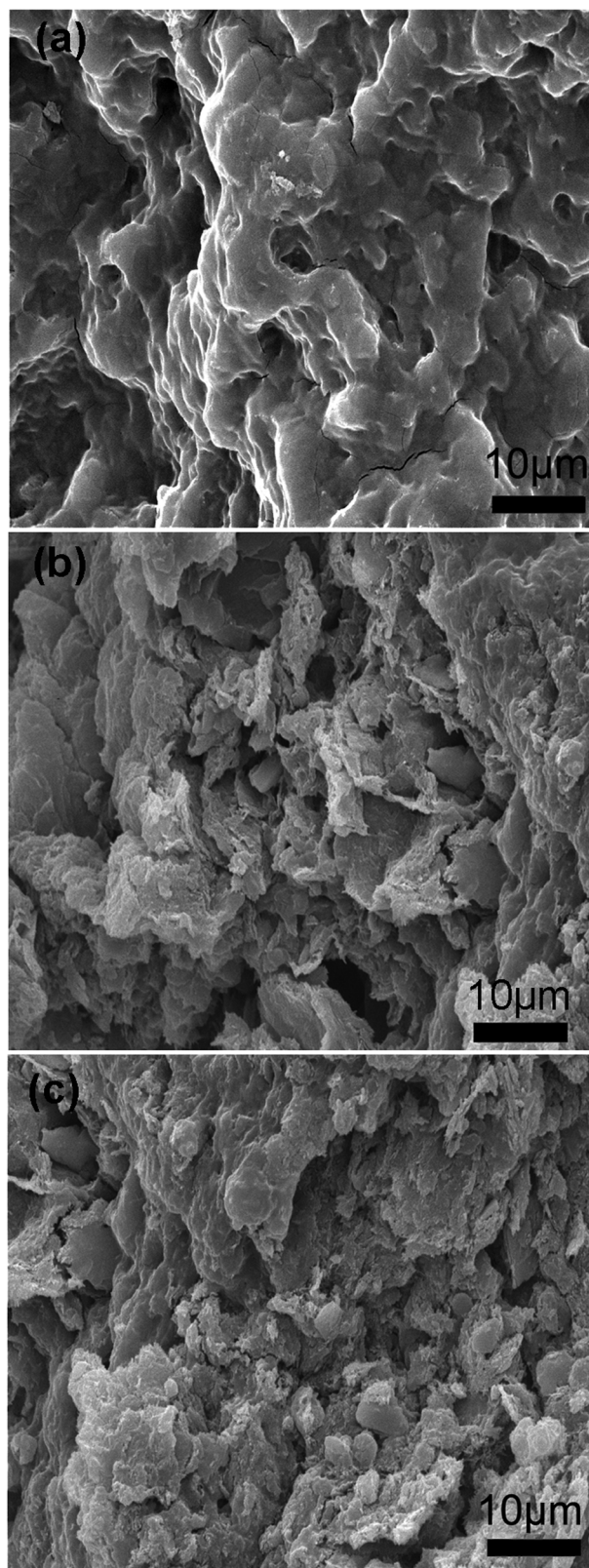


Figure 1. SEM micrographs of: (a) CTS-g-PAA; (b) CTS-g-PAA/APT; and (c) CTS-g-PAA/APT/SH (APT2#).

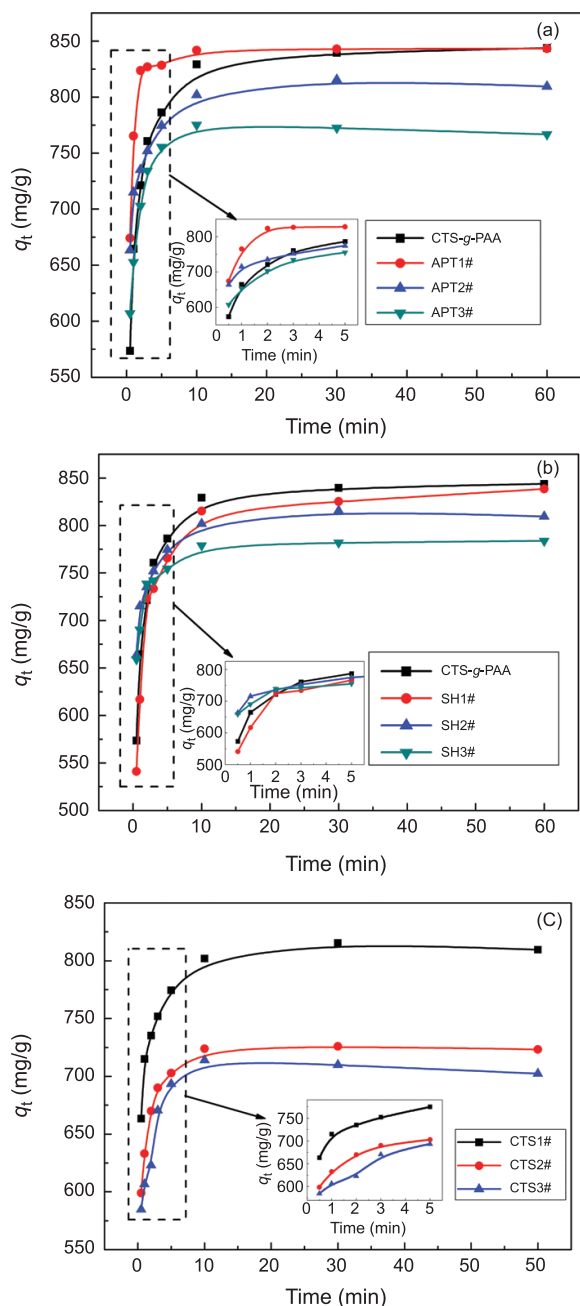


Figure 2. Effects of: (a) APT content; (b) SH content; and (c) weight ratio of CTS to AA on adsorption capacity and adsorption rate of CTS-g-PAA/APT/SH.

capacity of APT1# is comparable to that of CTS-g-PAA although 5wt% SH with low adsorption capacity (296.10 mg/g) for Pb(II) is introduced. It is clear that APT content is an important factor affecting the adsorption capacity of the composite hydrogels; the equilibrium adsorption capacity decreases gradually from 843.27 to 766.72 mg/g with increasing APT content from 0 to 10 wt% (for samples APT1#~APT3#).

The decreasing tendency of the adsorption capacity with increasing APT content is attributed to the following facts. APT particles could react with AA and act as crosslinking points in the network [25]. Consequently the crosslinking density of the CTS-g-PAA/APT/SH composite hydrogel increases with increasing APT content, which reduces the elasticity of the polymer chains, and then the equilibrium adsorption capacity decreases [19]. In addition, the carboxyl groups on the network of the CTS-g-PAA/APT/SH composite hydrogel are the main functional groups responsible for the adsorption of Pb(II). The amount of carboxyl groups decreases with increasing APT content. Thus, a decrease in the adsorption capacity of the composites for Pb(II) was observed.

According to our previous studies, introduction of the correct amount of APT to CTS-g-PAA could chemically bond to the network and improve its swelling ratio; however, the excess APT was only physically filled [25]. Since the adsorption capacity of APT (31.06 mg/g) used in this study for Pb(II) is much lower than that of CTS-g-PAA (843.86 mg/g), the physically filled APT is also responsible for the reduction in adsorption capacity. According to Wang *et al.* [28], a similar result has also been observed when using chitosan-g-poly (acrylic acid)/montmorillonite for the removal of methylene blue.

It also can be seen from Figure 2(a) that the adsorption rate of the CTS-g-PAA/APT/SH composite hydrogel for Pb(II) is very fast. More than 90% of the equilibrium adsorption capacity occurs within 2 min (only 1 min is needed for APT1#) and the adsorption equilibrium could be achieved within 10 min. As shown in the insert to Figure 2(a), the adsorption rate of APT1# is evidently higher than that of CTS-g-PAA even though their equilibrium adsorption capacity is almost the same. This phenomenon indicates that the introduced SH is beneficial in improving the adsorption rate as well as the adsorption capacity (as shown above). The adsorption rate decreases with increasing APT content from 0 to 10 wt%. This result indicates that the introduced APT does not benefit the adsorption rate; this may be attributed to the fact that the hydrophilicity of APT is lower than that of CTS-g-PAA. Thus, with increasing APT content, more time is needed for the penetration of Pb(II) into the network with the water molecules and the interaction with the functional groups. Consequently, a lower adsorption rate is observed. Although the equilibrium adsorption capacity of APT2# and APT3# is lower than that of CTS-g-PAA, their initial adsorption rate is still higher than that of CTS-g-PAA. This is attributed to the positive effect of introduced SH on the adsorption rate. Detailed reasons for the positive effect of SH on adsorption capacity and adsorption rate are discussed in the next section.

3.3. Effect of SH content on adsorption

The effect of SH content on adsorption capacity and adsorption rate is shown in Figure 2(b). As can be seen, the equilibrium adsorption capacity for Pb(II) is in the order of CTS-g-PAA > SH1# > SH2# > SH3#. The equilibrium adsorption capacity of SH1# is a bit lower than that of CTS-g-PAA owing to the introduction of 5 wt% APT. This is different from the comparable adsorption capacity of CTS-g-PAA and APT1# (containing 5 wt% SH and 0 wt% APT). The reasons for the lower adsorption when APT is introduced have already been revealed above. As the content of APT is fixed at 5 wt% for samples SH1#~SH3#, the adsorption capacity decreases gradually from 838.57 mg/g to 783.85 mg/g with increasing SH content from 0 to 10 wt%. The decreasing tendency of adsorption capacity with increasing SH content may be attributed to the fact that SH contains a large number of functional groups such as carboxylate, hydroxyl (enolic, phenolic and alcoholic) and amino groups [27]. Thus, SH could chemically bond to the polymeric network during the polymerization process and increase crosslinking density. In addition, excess SH acts only as filler and the amount of functional groups (such as $-\text{COO}^-$) on the polymeric backbone decreases with increasing SH content; this is also responsible for the reduced adsorption capacity of the composite hydrogels.

It also can be seen from the insert of Figure 2(b) that the adsorption rate of the composite incorporated with various amounts of SH is also very high. The introduction of 5 wt% APT into CTS-g-PAA has reduced the adsorption rate of the sample (SH1#). However, the adsorption rate evidently increases with increasing SH content from 0 to 10 wt% when the APT content is fixed at 5 wt%, though the equilibrium adsorption capacities of samples SH2# and SH3# are lower than those of SH1# and CTS-g-PAA.

This result is in accordance with the observed effect of introduced SH on the improvement of adsorption rate as described above. A relatively loose and fibrous surface is generated after the introduction of SH as shown in Figure 1(b), which facilitates the penetration of Pb(II) into the composite hydrogels; the enhanced adsorption rate with the introduction of SH was then observed. In addition, the numerous functional groups of SH connected to the polymer network are convenient for the complexing of Pb(II), which also contributes to the improved adsorption rate.

The equilibrium adsorption capacities of APT and SH used in this study and the composite hydrogels with various amount of APT, SH and CTS contents are listed in Table 2. The adsorption capacities of APT and SH are 31.06 and 290.10 mg/g, respectively, whereas the adsorption capacity is more than 700 mg/g

for CTS-g-PAA and all the composite hydrogels. Compared with other adsorbents reported previously as shown in Table 2 [29–32], the equilibrium adsorption capacities of the composite hydrogels are quite high and could be called ‘superadsorbents’. It also can be calculated that the adsorption capacities of the composite hydrogels are higher than the cases when APT, SH and CTS-g-PAA are only physically compounded (as shown in the last row). This result indicates that the introduction of APT and SH into the polymer could improve the adsorption capacity of CTS-g-PAA to some extent despite the decreasing tendency observed (Figure 2(a) and (b)). This is attributed to the fact that APT and SH participate in the graft polymerization with CTS and AA [25,33]. Different from the negative effect of APT on adsorption rate, SH is also beneficial in terms of for the improvement in adsorption rate.

3.4. Effect of CTS content on adsorption

The frequent use of CTS as an adsorbent for the removal of heavy metal ions is attributed to its structure and functional groups [34,35]. The effect of CTS content on the adsorption capacity and rate of the CTS-g-PAA/APT/SH composite hydrogels is shown in Figure 2(c). As can be seen, both the adsorption capacity and adsorption rate decrease with increasing CTS content. This can be explained as follows. Important roles are played by $-\text{COOH}$ and $-\text{COO}^-$ in the adsorption of heavy metal ions [19]. As the weight ratio of CTS to AA increases, the concentration of AA molecules around every CTS polymer chains decreases. Consequently, less AA molecules can be grafted onto the backbone of CTS, which reduces the $-\text{COO}^-$ and $-\text{COOH}$ content of the corresponding composite hydrogel, and then the adsorption capacity decreases. The hydrophilicity of CTS is lower than that of PAA. Less Na^+ ions are generated in the polymeric network owing to the neutralization of the PAA chains of the composite hydrogel with increasing CTS content. Consequently, the difference in osmotic pressure between the polymeric network and the external solution decreases. Thus, the swelling rate of the composite hydrogel falls and is responsible for the decreased adsorption rate.

3.5. Adsorption kinetics

The pseudo-first order kinetic model was suggested by Lagergren [28] for the adsorption of solid/liquid systems. Its linear form can be formulated as

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

Table 2. Comparison of the maximum adsorption capacity for Pb(II).

Adsorbent	Maximum adsorption capacity for Pb (II) (mg/g)	Source	Physically compounded APT, SH and CTS-g-PAA ^a (mg/g)
Crosslinked CTS	34.13 ± 0.93	[29]	–
CTS nanofibres	263.15	[30]	–
Palygorskite	104.28	[31]	–
Modified cellulose	205.9	[32]	–
APT	31.06	This paper	–
SH	296.10	This paper	–
CTS-g-PAA	843.86	This paper	–
APT1#	843.27	This paper	816.47
APT2#, SH2#, CTS1#	809.50	This paper	775.83
APT3#	766.72	This paper	735.19
SH1#	838.57	This paper	803.22
SH3#	783.85	This paper	748.44
CTS2#	723.22	This paper	–
CTS3#	702.35	This paper	–

^aCalculated according to the adsorption capacity of APT, SH and CTS-g-PAA. Their weight ratio is maintained in accordance with the corresponding composite hydrogels.

The pseudo-second order kinetics model can be expressed as follows according to Ho and McKay [35]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where: q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t , respectively; k_1 (per min) is the rate constant of the pseudo-first order adsorption; and k_2 (g/mg/min) is the rate constant of the pseudo-second order adsorption.

The adsorption kinetics curves of Pb(II) on CTS-g-PAA/APT/SH incorporated with various amounts of APT fitted to the pseudo-first order model and the pseudo-second order model are shown in Figure 3. As can be seen, the experimental data do not fit very well with the pseudo-first order model and there is a huge

difference between the pseudo-first order curves and the trend lines. However, the experimental data fit very well with the pseudo-second order model; indeed the pseudo-second order curves and the trend lines almost coincide with each other. Similar results can also be seen for the samples SH1#~SH3# and CTS1#~CTS3#. The corresponding parameters for all the samples obtained from the linear plots of $\log(q_e - q_t)$ versus t and t/q_t versus t are listed in Table 3.

It can be seen that the linear correlation coefficients (R^2) for the pseudo-first order kinetic model are high. However, there are considerable differences between $q_{e,exp}$ and $q_{e,cal}$ according to Equation (2), indicating that the adsorption processes of the composite hydrogels for Pb(II) can not be explained by the pseudo-first order kinetic model. It also can be found from Table 3 that the R^2 values for the pseudo-second order kinetic model are 1; moreover, the $q_{e,cal}$ values for the pseudo-second

Table 3. Constants and correlation coefficients of the two kinetic models for Pb(II) adsorption onto CTS-g-PAA/APT/SH.

Samples	$q_{e,exp}$ (mg/g)	Pseudo-first order model			Pseudo-second order model		
		$q_{e,cal}$ (mg/g)	k_1 (/min)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg/min)	R^2
CTS-g-PAA	843.86	242.21	0.2870	0.9766	848.21	0.0038	1
APT1#	843.27	99.79	0.4286	0.8816	844.59	0.0149	1
APT2#, SH2#, CTS1#	809.50	138.74	0.2372	0.9817	813.20	0.0076	1
APT3#	766.72	220.80	0.5295	0.9944	769.60	0.0133	1
SH1#	838.57	256.33	0.2483	0.949	842.55	0.0030	1
SH3#	783.85	120.23	0.3190	0.9688	785.64	0.0091	1
CTS2#	723.22	144.41	0.4180	0.9901	725.53	0.0119	1
CTS3#	702.35	204.83	0.5150	0.9875	705.35	0.0160	1

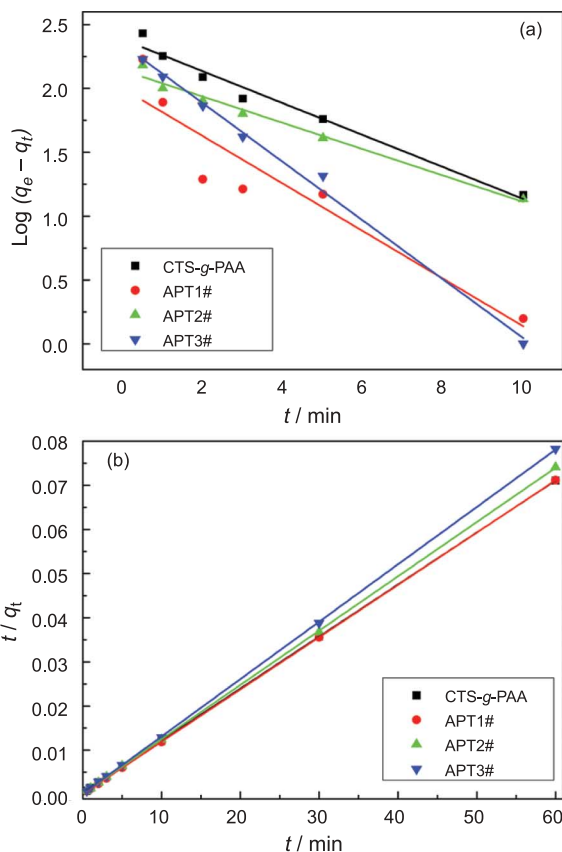


Figure 3. Adsorption kinetics of Pb(II) onto CTS-g-PAA/APT/SH incorporated with various amount of APT: (a) pseudo-first order model; and (b) pseudo-second order model.

order kinetic model are all consistent with the $q_{e,exp}$ values. These results indicate that the adsorption processes of the CTS-g-PAA/APT/SH composite hydrogels for Pb(II) can be well simulated by the pseudo-second order kinetic model.

3.6. Adsorption mechanism

In order to interpret the adsorption mechanism of the CTS-g-PAA/APT/SH composite hydrogel for Pb(II), Figure 4 represents the FTIR spectra of SH and the representative CTS-g-PAA/APT/SH composite hydrogel (APT2#) before and after Pb(II) adsorption. The absorption bands at 1707, 1612, 1377 and 1238 cm^{-1} in the spectrum of SH are attributed to C=O stretching of $-\text{COOH}$, C=O stretching of $-\text{COO}^-$, C–O stretching of $-\text{COO}^-$ and stretching of phenolic C–O, respectively. After adsorption of Pb(II), the absorption bands at 1612, 1377 and 1238 cm^{-1} shift to 1576, 1363 and 1225 cm^{-1} , respectively. However, no obvious change in the absorption of C=O stretching of $-\text{COOH}$ is observed. This result indicates that $-\text{COO}^-$ and phenolic C–O groups of SH participate in the reaction with Pb(II).

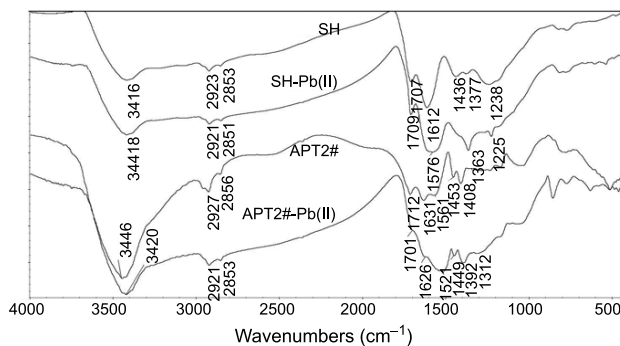


Figure 4. FT-IR spectra of SH and CTS-g-PAA/APT/SH composite hydrogel (APT2#) before and after Pb(II) adsorption.

The absorption bands at 1712, 1631, 1561 and 1408 cm^{-1} in the spectrum of APT2# are attributed to C=O stretching of $-\text{COOH}$ of PAA, $-\text{NH}_2$ of CTS, C=O and C–O stretching of $-\text{COO}^-$ of PAA, respectively. These absorption bands have shifted to 1701, 1626, 1521 and 1392 cm^{-1} , respectively, after the adsorption of Pb(II). In addition, the absorption bands at 1701 and 1626 cm^{-1} were obviously weakened. These changes in the FTIR spectrum of APT2# indicate that $-\text{COOH}$ and $-\text{COO}^-$ of PAA as well as $-\text{NH}_2$ of CTS take part in reactions with Pb(II). It has been reported that the adsorption of APT for Cu(II) is mainly attributed to the cation exchange of Pb(II) with metal ions between layers of APT and Si–OH of APT [14]. The adsorption of Pb(II) onto APT may be according to the same mechanism.

It can be concluded from Figure 4 that $-\text{COOH}$ and $-\text{COO}^-$ of PAA, $-\text{NH}_2$ of CTS, Ph–O $^-$ and $-\text{COO}^-$ of SH, as well as cation exchange and Si–OH of APT, participate in adsorption of Pb(II). Owing to the co-existence of these functional groups and the fact that Pb(II) is a divalent cation, a Pb(II) cation may bind to two different functional groups. This means that the various functional groups on the network of the CTS-g-PAA/APT/SH composite hydrogel could interact with the interpenetrated Pb(II) simultaneously. This may be the original reason for the observed improved adsorption properties with the introduction of APT and SH. It also can be concluded that the synergistic effect of various functional groups is superior to the single one. In order to describe the adsorption of Pb(II) onto the CTS-g-PAA/APT/SH composite hydrogel clearly, the schematic structure of the composite hydrogel after the adsorption of Pb(II) is shown in Figure 5.

4. Conclusions

The novel CTS-g-PAA/APT/SH composite hydrogels were successfully prepared and used as adsorbents for the removal of Pb(II) from aqueous solution. The

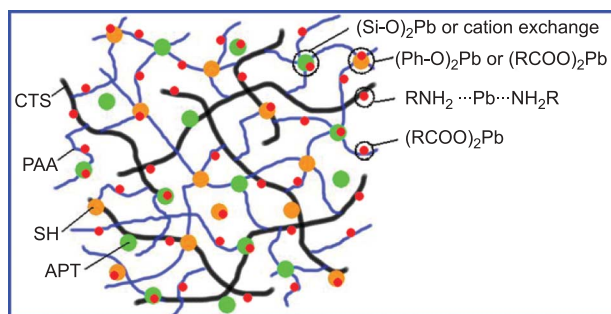


Figure 5. Schematic structure of the CTS-g-PAA/APT/SH composite hydrogel after the adsorption of Pb(II).

introduction of APT and SH can increase the adsorption capacity of the composite hydrogel, whereas only SH is beneficial for the adsorption rate. The composite hydrogels show very high adsorption capacity and adsorption rate owing to the synergistic effect of various functional groups. The pseudo-second order model can be used to describe the adsorption process of the composite hydrogels for Pb(II) very well. It should be noted that introduction of APT and SH reduces the production cost of the adsorbent, which is important for practical applications. Thus, the CTS-g-PAA/APT/SH composite hydrogels are very promising adsorbents for Pb(II) considering their economic advantage, high adsorption capacity and adsorption rate.

Acknowledgements

The authors are thankful for the joint support of the National Natural Science Foundation of China (No. 20877077), Science and Technology Support Project of Gansu Provincial Science and Technology Department (No. 0804GKCA03A) and the Foundation of Key Laboratory for Attapulgite Science and Applied Technology of Jiangsu Province (No. HPK200901).

References

- [1] A. Demirbas, *Heavy metal adsorption onto agro-based waste materials: a review*, *J. Hazard. Mater.* 157 (2008), pp. 220–229.
- [2] L. Charentanyarak, *Heavy metals removal by chemical coagulation and precipitation*, *Water Sci. Technol.* 39 (1999), pp. 135–138.
- [3] A. Dąbrowski, Z. Hubicki, P. Podkościelny, and E. Robens, *Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method*, *Chemosphere* 56 (2004), pp. 91–106.
- [4] R.J. Crawford, D.E. Mainwaring, and I.H. Harding, *Adsorption and coprecipitation of heavy metals from ammoniacal solutions using hydrous metal oxides*, *Colloids Surf. A* 126 (1997), pp. 167–179.
- [5] Y.C. Chung and C.Y. Chen, *Competitive adsorption of a phthalate esters mixture by chitosan bead and α -cyclodextrin-linked chitosan bead*, *Environ. Technol.* 30 (2009), pp. 1343–1350.
- [6] X.H. Wang and A.Q. Wang, *Removal of Cd(II) from aqueous solution by a composite hydrogel based on attapulgite*, *Environ. Technol.* 31 (2010), 745–753.
- [7] M. Şölenner, S. Tunali, A.S. Özcan, A. Özcan, and T. Gedikbey, *Adsorption characteristics of lead(II) ions onto the clay/poly(methoxyethyl)acrylamide (PMEA) composite from aqueous solutions*, *Desalination* 223 (2008), pp. 308–322.
- [8] E. Erdem, N. Karapinar, and R. Donat, *The removal of heavy metal cations by natural zeolites*, *J. Colloid Interf. Sci.* 280 (2004), pp. 309–314.
- [9] Y. Bulut and Z. Tez, *Removal of heavy metals from aqueous solution by sawdust adsorption*, *J. Environ. Sci.* 19 (2007), pp. 160–166.
- [10] S. Al-Asheh, F. Banat, and R. Al-Omari, *Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data*, *Chemosphere* 41 (2000), pp. 659–665.
- [11] D. Parajuli, K. Inoue, and K. Ohto, *Adsorption of heavy metals on crosslinked lignocatechol: a modified lignin gel*, *React. Funct. Polym.* 62 (2005), pp. 129–139.
- [12] V. Bekiari and P. Lianos, *Ureasil gels as a highly efficient adsorbent for water purification*, *Chem. Mater.* 18 (2006), pp. 4142–4146.
- [13] K.G. Bhattacharyya and S.S. Gupta, *Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review*, *Adv. Colloid Interface Sci.* 140 (2008), pp. 114–131.
- [14] H. Chen, Y.G. Zhao, and A.Q. Wang, *Removal of Cu(II) from aqueous solution by adsorption onto acid-activated palygorskite*, *J. Hazard. Mater.* 149 (2007), pp. 346–354.
- [15] A. Ramesh, H. Hasegawa, W. Sugimoto, T. Maki, and K. Ueda, *Adsorption of gold(III), platinum(IV) and palladium(II) onto glycine modified crosslinked chitosan resin*, *Bioresour. Technol.* 99 (2008), pp. 3801–3809.
- [16] J.Z. Yi and L.M. Zhang, *Removal of methylene blue dye from aqueous solution by adsorption onto sodium humate/polyacrylamide/clay hybrid hydrogels*, *Bioresour. Technol.* 99 (2008), pp. 2182–2186.
- [17] R. Akkaya and U. Ulusoy, *Adsorptive features of chitosan entrapped in polyacrylamide hydrogel for Pb^{2+} , UO_2^{2+} , and Th^{4+}* , *J. Hazard. Mater.* 151 (2008), pp. 380–388.
- [18] Y.A. Zheng and A.Q. Wang, *Evaluation of ammonium removal using a chitosan-g-poly (acrylic acid)/rectorite hydrogel composite*, *J. Hazard. Mater.* 171 (2009), pp. 671–677.
- [19] X.H. Wang, Y.A. Zheng, and A.Q. Wang, *Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite composites*, *J. Hazard. Mater.* 168 (2009), pp. 970–977.
- [20] V. Bekiari, M. Sotiropoulou, G. Bokias, and P. Lianos, *Use of poly(N, N-dimethylacrylamide-co-sodium acrylate) hydrogel to extract cationic dyes and metals from water*, *Colloid Surf. A* 312 (2008), pp. 214–218.
- [21] H. Kaşgöz, S. Özgümüş, and M. Orbay, *Modified polyacrylamide hydrogels and their application in removal of heavy metal ions*, *Polymer* 44 (2003), pp. 1785–1793.
- [22] E.K. Yetimoğlu, M.V. Kahraman, and Ö. Ercan, *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), pp. 451–460.

- [23] A. Li, A.Q. Wang, and J.M. Chen, *Studies on poly(acrylic acid)/attapulgitic superabsorbent composite. I. Synthesis and characterization*, J. Appl. Polym. Sci. 92 (2004), pp. 1596–1603.
- [24] F. Santiago, A.E. Mucientes, M. Osorio, and F.J. Poblete, *Synthesis and swelling behaviour of poly(sodium acrylate)/sepiolite superabsorbent composites and nanocomposites*, Polym. Int. 55 (2006), pp. 843–848.
- [25] J.P. Zhang, Q. Wang, and A.Q. Wang, *Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgitic superabsorbent composites*, Carbohydr. Polym. 68 (2007), pp. 367–374.
- [26] J.P. Zhang, H. Chen, and A.Q. Wang, *Study on superabsorbent composite III. Swelling behaviors of polyacrylamide/attapulgitic composite based on acidified attapulgitic and organo-attapulgitic*, Eur. Polym. J. 41 (2005), pp. 2434–2442.
- [27] M.H.B. Hayes, P. MacCarthy, R.L. Malcolm, and R.S. Swift (ed.), *Humic Substances II. In Search of Structure*, John Wiley & Sons, Chichester, UK, 1990.
- [28] L. Wang, J.P. Zhang, and A.Q. Wang, *Removal of methylene blue from aqueous solution using chitosan-g-poly (acrylic acid)/montmorillonite superadsorbent nanocomposite*, Colloid Surf. A 322 (2008), pp. 47–53.
- [29] A.H. Chen, S.C. Liu, C.Y. Chen, and C.Y. Chen, *Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin*, J. Hazard. Mater. 154 (2008), pp. 184–191.
- [30] S. Haider and S.Y. Park, *Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu(II) and Pb(II) ions from an aqueous solution*, J. Membrane Sci. 328 (2009), pp. 90–96.
- [31] H. Chen and A.Q. Wang, *Kinetic and isothermal studies of lead ions adsorption onto palygorskite clay*, J. Colloid Interface Sci. 307 (2007), pp. 309–316.
- [32] L.V.A. Gurgel, O.K. Júnior, R.P. Freitas Gil, and L. Frédéric Gil, *Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride*, Bioresour. Technol. 99 (2008), pp. 3077–3083.
- [33] J.H. Liu, Q. Wang, and A.Q. Wang, *Synthesis and characterization of chitosan-g-poly(acrylic acid)/sodium humate superabsorbent*, Carbohydr. Polym. 70 (2007), pp. 166–173.
- [34] S.L. Sun and A.Q. Wang, *Adsorption kinetic of Cu(II) ions using N, O-carboxymethyl-chitosan*, J. Hazard. Mater. B 131 (2006), pp. 103–111.
- [35] A.H. Chen, S.C. Liu, C.Y. Chen, and C.Y. Chen, *Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin*, J. Hazard. Mater. 154 (2008), pp. 184–191.