Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21191

81 (2017) 216–222
June

Adsorption of humic acid from aqueous solution onto chitosan-coated attapulgite composites

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Received 17 January 2017; Accepted 7 July 2017

ABSTRACT

Chitosan-coated attapulgite (CCATP) was prepared and applied as sorbent for the sorptive removal of humic acid (HA) from aqueous solution. The effects of various factors such as solution cations, ionic strength and pH on the HA adsorption were investigated, and different models were used to fit the adsorption isotherms and the adsorption kinetics data. The results showed that after modified with chitosan, the HA sorption capacity enhanced greatly onto the attapulgite composites. In the experimental conditions, the sorption capacity of HA onto CCATP decreased with the increasing solution pH and increased with increasing ionic strength. The adsorption isotherms data fitted well with the Freundlich isotherm model ($R^2 = 0.982$), and the adsorption kinetics results could be better fitted by the pseudo-second-order model ($R^2 = 0.911$). The HA-loaded CCATP can be regenerated by using diluted NaOH solution. All results indicated that CCATP was a promising sorbent for removing HA from water.

Keywords: Attapulgite; Chitosan; Humic acid; Sorption

1. Introduction

As a natural organic matter, humic acid (HA) commonly exists in most surface water and ground water [1,2]. The existence of HA in drinking water can lead to color, taste, odor and biological instability in distribution system [3,4]. In addition, HA can react with chlorine during the water treatment process to form groups of carcinogenic disinfection by-products, which affect the human health seriously [5]. Hence, it is necessary to remove HA from water.

Sorption has been found to be a low cost, effective and potential method for removing HA from water, and different types of sorbents were developed and used for the removal of HA from water [6–8]. Recently, natural clay minerals attracted more and more interest as sorbents, based on both the environmental and economic points of view [9–13]. Attapulgite (ATP) clay, also known as palygorskite, is a crystalline hydrated magnesium silicate with a fibrous morphology, and large high-quality reserves existed in Xuyi County, Jiangsu province [14]. ATP has been intensively used as sorbent for removing contaminants due to its large specific surface area, the permanent negative charges on its surface and cation exchange capacity [15–18]. Wang et al. [7] investigated the sorption of low-concentration HA from water by palygorskite, and their study indicated that the electrostatic interaction played an important role in the sorption of HA on palygorskite. Nevertheless, due to the permanent negative charges on its surface, ATP has low affinity to HA which was also negatively charged at pH above 4.0 [7,19]. In order to improve its sorption capacity for negatively charged or neutral contaminants, ATP has been widely treated with the positively charged amino group [6,9,20].

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Chitosan is the N-deacetylated derivative of chitin and is one of the most promising sorbents due to its biodegradability, high-efficiency and non-toxicity [9]. However, due to weak mechanical property and dissolution in strongly acidic and alkali solutions, its practical operation is greatly limited [21]. Chitosan has many reactive $–NH_2$ and –OH groups which are convenient for its graft on the surface of ATP. Considering the interaction between these groups and HA, immobilizing chitosan on ATP will have great potential on the improvement of the sorption capacity for HA.

In our previous work, we have successfully prepared the chitosan-modified attapulgite [21]. The aim of this work is to study the sorption properties of chitosan-modified attapulgite for HA. The materials were characterized by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and zeta potential measurement. The effect of ionic strength and solution pH on HA sorption was investigated, and further the sorption isotherms and kinetics were studied by batch experiments. The regeneration test was carried out and finally the sorption mechanism of HA was also proposed.

2. Experimental setup

2.1. Materials

ATP used in this work was obtained from Xuyi, Jiangsu province of China. HA was purchased from Sigma-Aldrich Chemical Co., Germany, and used without any further purification. Chitosan with a deacetylation degree above 90% (TCI, Japan) was used without any further purification. Other chemicals used were of analytical grade or above. All solutions were prepared using double-distilled water.

2.2. Preparation and characterization of the as-made sorbents

A series of chitosan-coated attapulgite (CCATP) composites from chitosan and ATP was prepared according to the method reported previously [21]. The mass ratio of chitosan and ATP was kept at 1:1, 1:5, 1:10 and 1:20, respectively. The resulting materials were milled and all samples used for testing had a particle size of 200 mesh.

FTIR spectra of the materials were acquired on a Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific, USA) in KBr pellet at room temperature. The morphology of the chitosan-modified ATPs was observed using SEM (Model S-3400N II, Hitachi, Japan). XRD patterns were recorded by a X'TRA X-ray diffractometer (ARL Co., Switzerland) using Cu Kα radiation (λ = 0.15406 nm). The zeta potentials of the materials were determined on a zeta potential analyzer (Brookhaven Instruments Corp., USA) according to reference [22].

2.3. Sorption influence of chitosan and ATP ratio

The influence of CCATPs prepared by different mass ratio of chitosan and ATP on HA sorption was conducted at about pH 5.5 using 22-mL glass vials. The initial concentration of HA was kept at 50 mg/L, and the sorbent dosage was 0.02 g. The optimum ratio sorbent was used for the next sorption experiments.

2.4. Batch sorption studies

Batch sorption experiments were conducted using 22-mL glass vials equipped with polytetrafluoroethylene-lined screw caps at room temperature. The pH of the solution was adjusted by adding 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. After reaching sorption equilibrium, the solution was centrifugalized (10,000 rpm, 10 min) and then the supernatant was determined using a UV–Vis spectrometer (Shimazu, Japan) with detecting wavelength at 254 nm [23]. The equilibrium sorption amounts of HA were computed according to Eq. (1):

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

where q_e is the amount of HA sorbed at equilibrium, C_0 is the initial HA concentration, C_e is the equilibrium HA concentration, V is the volume of HA solution and m is the sorbent mass.

The HA sorption isotherm experiments were carried out by adding 0.02 g of CCATP into 20 mL of HA solution with initial concentrations varying from 5 to 60 mg/L.

For sorption kinetics test, 0.50 g of CCATP was fast introduced into a 500-mL three-neck flask containing 500 mL of HA solution with an initial concentration of 50 mg/L under mechanic stirring. 1 mL of the solution was withdrawn at different time intervals.

The initial concentration of HA was kept at 50 mg/L in the subsequent tests. Ionic strength test was carried out by dispersing 0.02 g of sorbents in 20 mL NaCl and $CaCl_2$ solution (0–0.045 mol/L), respectively. The pH effect on HA sorption was investigated in a pH range from 3 to 11. A series of flasks containing 0.02 g of CCATP and 20 mL HA solution with different pH were shaken for 24 h.

2.5. Desorption and regeneration studies

To evaluate the reusability of the sorbent, desorption of HA and regeneration of HA–CCATP were performed in six consecutive cycles. In each cycle, 50 mg/L HA in 20 mL of solution was mixed with 0.02 g CCATP. After stirring for 24 h, the mixed solution was separated by centrifugation and the supernatant was subjected to HA measurements. The resultant HA–CCATP solid was mixed with 20 mL of 0.1 mol/L NaOH solution for 12 h. Prior to the next sorption–desorption cycle, regenerated CCATP was washed thoroughly with double-distilled water till it reaches neutral pH.

3. Results and discussion

3.1. Material characterization

The surface morphology of ATP, chitosan and the as-made sorbents with different mass ratio of chitosan and ATP was characterized by SEM. The obtained results are shown in Fig. 1. As shown in Fig. 1, the surface morphology of CCATP was different from that of ATP. The ATP crystals could not be seen clearly when their surface was covered with chitosan, confirming the combination of ATP with chitosan. As seen from Fig. 1, the morphological differences among the as-made

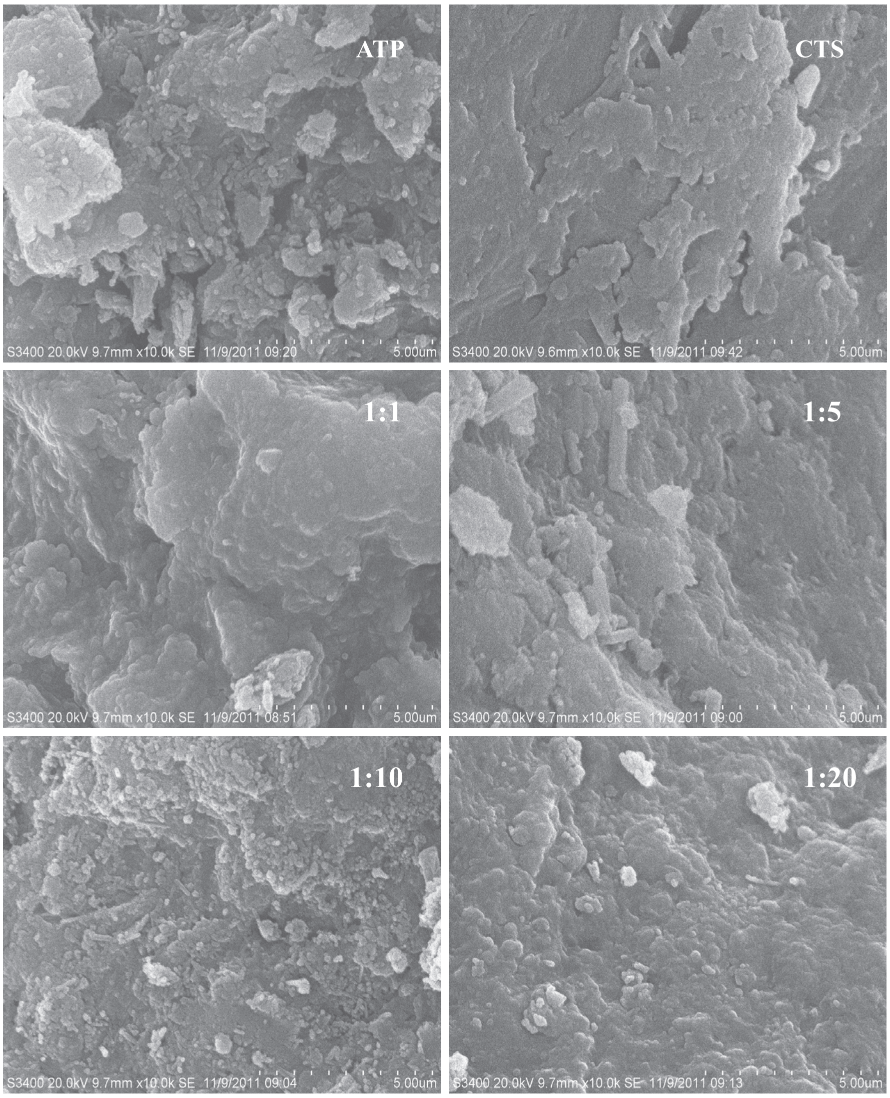

Fig. 1. The SEM images of the acid-activated attapulgite, chitosan and as-made ATPs.

sorbents with different mass ratio of chitosan and ATP were dissimilar to some extent. Moreover, the surface particles of the sorbent with the mass ratio of chitosan and ATP (1:10) were much smaller than that with other ratios.

3.2. Comparison of the sorption capacities of HA onto ATP and the as-made ATPs

Fig. 2 shows the effect of different mass ratio of chitosan and ATP on the sorption capacity of HA. As can be seen from Fig. 2, with the mass ratio of chitosan and ATP decreasing, the sorption rate of HA initially increased and then decreased obviously. It indicated that the sorbent prepared with the mass ratio of 1:10 of chitosan/ATP was optimum for the sorption of HA. The results may contribute that the sorbent prepared with too large mass ratio of chitosan and ATP had smaller BET surface area. However, less amount of chitosan could not effectively balance the negative charges of ATP, thus a strong electrostatic repulsion between HA and the sorbent existed [21]. Fig. 2 also indicates that the sorption

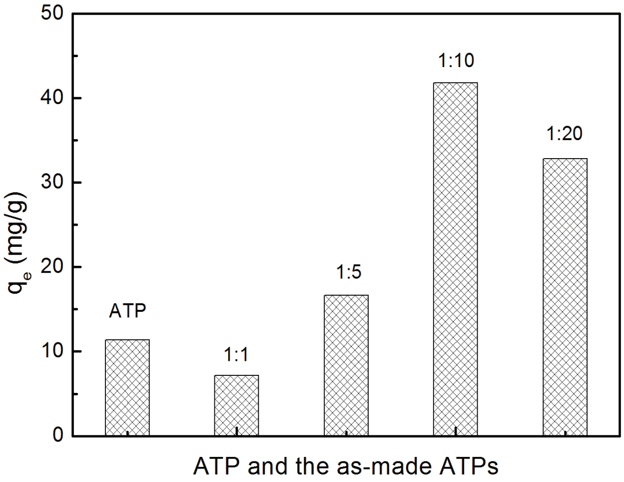

Fig. 2. Comparison of the sorption capacity of HA on ATP and the as-made ATPs.

capacity of HA onto the optimum sorbent was much higher than that of unmodified ATP. Therefore, optimum sorbent with the mass ratio of chitosan and ATP (1:10) (denoted as CCATP) was chosen for the following tests.

3.3. Impacting factors of HA sorption

3.3.1. Effect of ionic strength and solution cations

The sorption capacity of HA on CCATP may be affected by background electrolyte [6]. Fig. 3 displays the effect of ionic strength and solution cations (Na^+ and Ca^{2+}) on HA sorption onto CCATP. Results showed that the presence of the tested cations led to the enhanced HA sorption onto CCATP. The HA sorption capacity increased with increasing the ionic strength, and further increasing the ionic strength, the adsorption capacity gradually reached constant. The dependence of HA sorption on ionic strength implied that the electrostatic interaction played a very important role in HA sorption on CCATP. The enhancement of HA sorption by ionic strength was clearly expressed as other reports [6,7,19,24–28]: (1) the decrease of molecular volume of HA, caused by the increase in ionic strength due to minimization of the electrostatic repulsion between ionized carboxylic groups, which facilitated the sorption; (2) at higher ionic strength, HA diffused faster due to its coiled structure; (3) with increasing ionic strength, the thickness of the diffuse double layer decreased, thus resulting in a shorter distance between the CCATP particles and HA molecules; (4) at higher ionic strength, the solubility of HA was lower, thus favoring the mass transfer of HA from the solution phase to the solid phase of CCATP; (5) Na^+ and Ca^{2+} in aqueous solution could bind with the water molecules, and the competition between HA and water molecules for sorption sites would be reduced.

The results also showed that the effect of the cation ions on enhanced HA sorption was in an order as $Ca^{2+} > Na^+$ (Fig. 3). An increase in ionic strength resulted in an increase of removal efficiency while the divalent cations had a larger effect on the sorption of HA on CCATP than that of monovalent cations. Similar observation was found for HA sorption on ATP on other report [7].

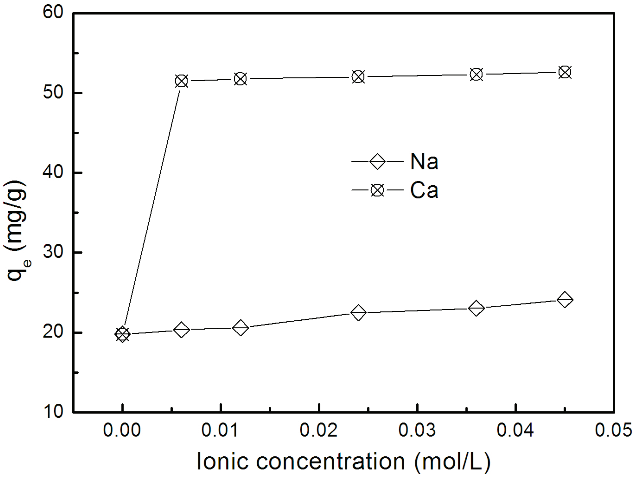

Fig. 3. Effect of ionic strength and solution cations on HA sorption onto CCATP.

3.3.2. Effect of pH

The pH value of the solution plays an important role in the sorption process. The effect of solution pH on the sorption of HA on CCATP was investigated, and the results are shown in Fig. 4. It showed that an increase in solution pH caused an obvious decrease in the HA sorption capacity onto CCATP, indicating that the sorption of HA on CCATP was favored at lower solution pH. The HA solution was considered as a mixture of compounds with weak acidic functional groups, such as carboxylic and phenolic groups [4]. The electrostatic point of HA was about 1.9 [6], and thus HA had negative charges in tested pH range due to the deprotonation of carboxyl or phenolic groups. Previous study showed that ATP could only remove low-concentration HA from water [7]. This might be attributed to the negative charges on the ATP frameworks [15,21], and the hydrophobic interaction might play an important role in HA sorption [4]. However, the HA sorption capacity for CCATP was mainly related to the surface characteristics of chitosan. Dambies et al. [29] reported that when the solution pH was below 5.5, a large number of amino groups on the CCATP surface were protonated, thus the negatively charged HA molecules were easily adsorbed onto the positively charged CCATP surface via the electrostatic interaction. With the increase of solution pH, less amino groups on the CCATP surface were protonated, resulting in the low HA sorption capacity. Furthermore, it had been suggested that HA might exist in a spherical structure at lower pH value but in a rather linear or stretched structure at higher pH [30,31], resulting in less amount of HA adsorbed in the sorbent pores at higher pH.

3.4. Sorption isotherms

The sorption equilibrium plots for the sorption of HA onto CCATP are shown in Fig. 5. It can be seen from the results, the sorption capacity of HA increased as its equilibrium concentration increased. The Langmuir sorption model (Eq. (2)) assumes that sorption occurs at homogeneous sites on the sorbent. The Freundlich sorption model (Eq. (3)) is

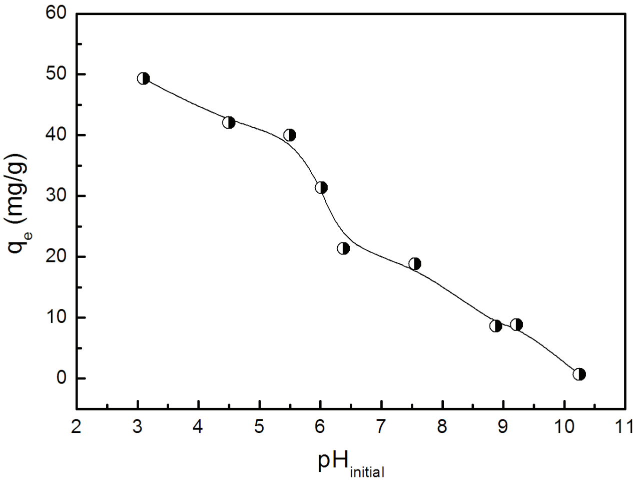

Fig. 4. Effect of pH on the sorption of HA onto CCATP.

generally used to describe the sorption isotherm for heterogeneous surfaces.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \tag{2}$$

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \tag{3}$$

where q_e and C_e are the amounts of HA sorbed (mg/g) and equilibrium concentration (mg/L), respectively; q_m is the maximum HA sorption (mg/g); and K_L is the Langmuir coefficient relating to the strength of sorption. K_F is the Freundlich isotherm constant and $1/n$ (dimensionless) is the heterogeneity factor.

The fitted parameters using the above two models obtained by linear regression analysis are listed in Table 1. In comparing with the calculated correlation coefficients in Table 1, both isotherm models were reasonably fitted to the equilibrium data for the HA sorption onto CCATP; however, the results indicated that the Freundlich model seems to fit better with the experimental data than the Langmuir model. Since n values for the Freundlich equation are close to 1 for CCATP, the surface heterogeneity could be assumed to be less significant [32].

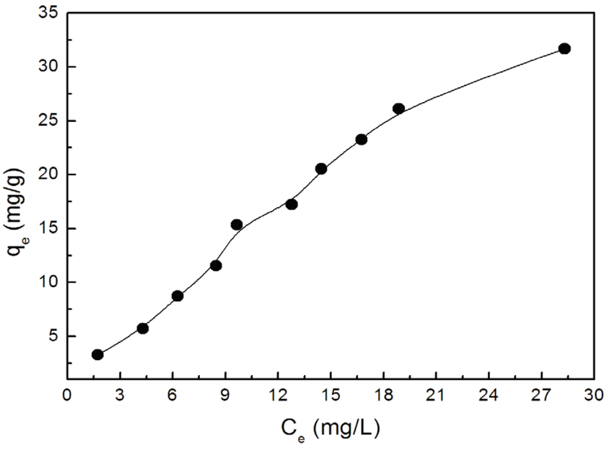

Fig. 5. Sorption isotherm of HA onto CCATP.

Table 1
Sorption isotherms parameters for HA sorption onto CCATP

Langmuir equation			Freundlich equation		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
51.2	0.0376	0.967	1.86	1.14	0.982

3.5. Sorption kinetics

Fig. 6 showed the kinetic data for the sorption of HA on CCATP. The sorption capacity of HA on CCATP increased during the 300 min, and then HA sorption reached equilibrium within almost identical sorption time. The pseudo-first-order model (Eq. (4)) and pseudo-second-order model (Eq. (5)) were applied to describe the kinetic behaviors of HA sorption on CCATP:

$$\text{Ln}(q_e - q_t) = \text{Ln}q_e - K_1 t \tag{4}$$

$$\frac{\text{t}}{q_t} = \frac{1}{K_2 q_e^{\;2}} + \frac{t}{q_e} \tag{5}$$

where q_e is the amount of sorbed HA at equilibrium (given in units of mg/g), and q_t is the amount of sorbed HA at time t (also given in units of mg/g), and K_1 is the rate constant of pseudo-first-order sorption (1/min). K_2 is the constant of pseudo-second-order rate (mg/(g min)).

The fitting parameters and theory data obtained from linear fitting were listed in Table 2. As shown in Table 2, the correlation coefficient R^2 for the pseudo-first-order sorption model was very low ($R^2 = 0.596$), and there was a large difference of sorption capacity between the experimental data and calculated one, indicating that pseudo-first-order sorption model was not suitable to fit the experimental data. However, the pseudo-second-order equation was demonstrated to be a better model for HA sorption with the higher correlation coefficient ($R^2 = 0.911$) than the pseudo-first-order equation, and the sorption capacity calculated by the pseudo-second-order sorption model was very close to the experimental value. Therefore, it could be concluded

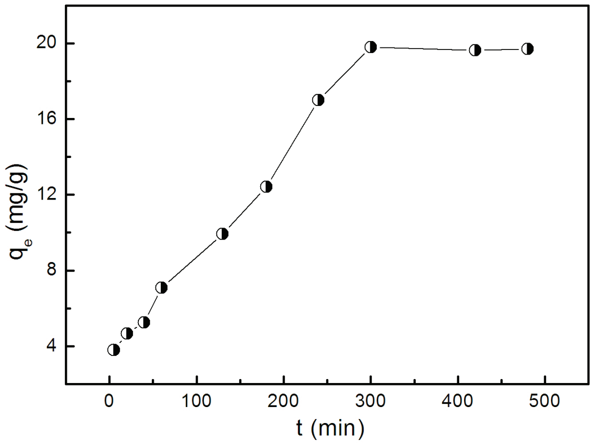

Fig. 6. Sorption kinetics of HA onto CCATP.

Table 2
Kinetic parameters for HA sorption onto CCATP

q_{exp} (mg/g)	Pseudo-first-order equation			Pseudo-second-order equation		
	K_1 (1/min)	q_{cal} (mg/g)	R^2	K_2 (g/(mg min))	q_{cal} (mg/g)	R^2
19.8	–0.0337	180	0.596	3.49×10^{-4}	24.5	0.911

that the pseudo-second-order sorption model was suitable to describe the sorption kinetics of HA sorption onto CCATP.

3.6. Sorption mechanism

The FTIR spectra of CCATP, CCATP after sorption (HA–CCATP), and HA are shown in Fig. 7. Compared with the spectrum of CCATP, the main changes of HA–CCATP spectrum are as follows: peaks at 1,578 and 1,427 cm^{-1} become weaker, and the peaks shift to shorter wavelength, affected by the N–H bending and C–O bending of HA. Furthermore, new peaks at about 2,950; 3,585 and 3,620 cm^{-1} represent the characteristic of the C–H$_2$ stretching vibration [33] and O–H stretching vibration. The appearance of new peaks and shifted peaks confirmed that HA had been sorbed onto CCATP.

XRD patterns of ATP and CCATP are shown in Fig. 8. The important diffraction peaks showed no shift in peak location after modification. The invariability of *d*-spacing of ATP after modification suggested that HA modification might be on the surface.

Zeta potentials of CCATP and HA–CCATP are shown in Fig. 9. It was expressed in our previous work [21] that ATP had permanent negative charges on its surface. However, after chitosan coated on ATP, the negative charges decreased, which could be attributed to the positively charged amino groups of chitosan. As shown in Fig. 9, HA sorption led to the increase of negative charges in the tested pH range, which suggested that HA had been uptaken by CCATP. The change of zeta potentials of CCATP and HA–CCATP was in accord with that of pH analysis discussed above.

3.7. Regeneration of the sorbent

The regeneration of sorbent is a crucial factor in the practical application of the sorbent [34]. Low sorption capacity of HA onto CCATP at high solution pH implied that alkali treatment might be a feasible approach to regenerate CCATP from HA–CCATP. In this study, batch experiments were conducted to desorb HA from HA–CCATP using diluted NaOH solution. Due to the high stability of CCATP under alkali conditions, HA–CCATP was regenerated using 0.1 mol/L NaOH solution and the regenerated sorbent was reused in six consecutive cycles. The sorption rate of the regenerated sorbents is shown in Fig. 10. The results showed that the regenerated sorbents also had very well sorption ability for HA. The relatively high desorption efficiency of HA from HA–CCATP might be attributed to the fact that, in the basic solution, the positively charged amino groups were deprotonated and the electrostatic attraction between CCATP and HA molecules became much weaker [35].

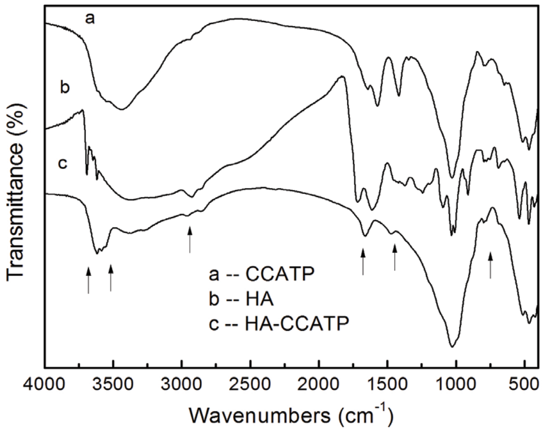

Fig. 7. FTIR spectra of CCATP (a), HA (b) and HA–CCATP (c).

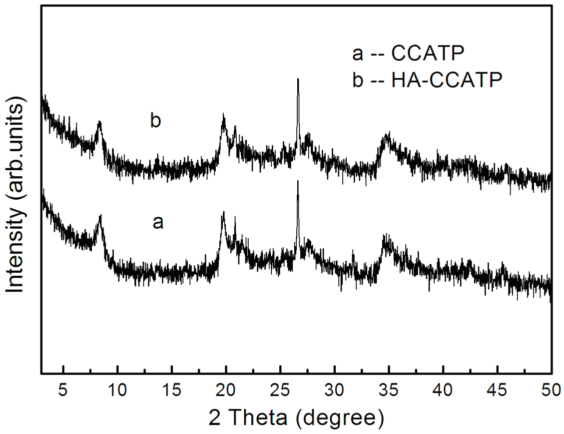

Fig. 8. X-ray diffraction patterns of CCATP (a) and HA–CCATP (b).

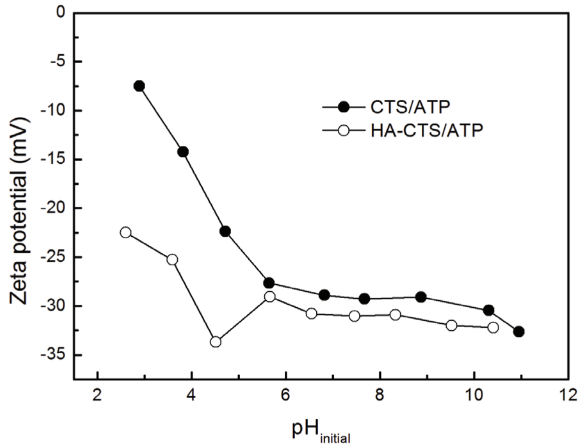

Fig. 9. Zeta potentials of CCATP and HA–CCATP.

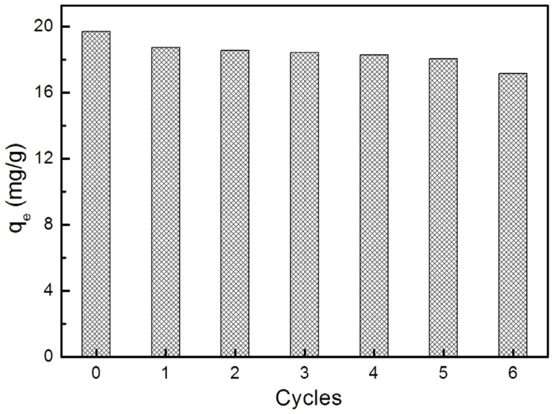

Fig. 10. HA sorption on CCATP and regenerated CCATP.

4. Conclusions

In this work, chitosan-modified ATP was prepared and applied for the sorption of HA. The materials were characterized by SEM, powder XRD, FTIR and zeta-potential measurement. The sorption capacity of CCATP for HA and the effects of various factors on HA sorption were investigated. Results showed that CCATP had much higher HA sorption capacity than ATP. The HA sorption capacities for CCATP decreased with increasing solution pH and increased with increasing ionic strength. Freundlich isotherm model and pseudo-second-order model fitted better for the sorption isotherms and adsorption kinetics of HA on CCATP. The HA-loaded CCATP can be regenerated by the 0.1 M NaOH solution treatment. The regenerated CCATP also had good sorption ability for HA, which showed that CCATP was a promising sorbent for removing HA from water.

Acknowledgments

This work was supported by the Foundation of State Key Laboratory of Pollution Control and Resources Reuse of China (No. PCRRF13008), China Postdoctoral Science Foundation (No. 2013M541646), The Science and Technology Key Project of Henan Province (No. 162102310389) and the Key Project of the Education Department of Henan Province (No. 14A610012).

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