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Adsorption of Pb(II) from Aqueous Solution by Chitosan-*g*-poly(acrylic acid)/Attapulgite/Sodium Humate Composite Hydrogels

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A series of chitosan-*g*-poly(acrylic acid)/attapulgite/sodium humate (CTS-*g*-PAA/APT/SH) composite hydrogels incorporated with various amounts of APT were used as adsorbents for the removal of Pb(II) from aqueous solution. The effects of adsorption (pH and concentration of Pb(II) in solution, dosage and particle size of composite hydrogels) and desorption (the kind and concentration of desorbing agent, recyclability) parameters are discussed in detail from use of a batch adsorption technique. The results showed that the adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II) increases with increasing pH and concentration of Pb(II) in solution but decreases with increasing adsorbent dosage. It is found that the composite hydrogel with a particle size of (40 to 100) mesh is an appropriate choice. The adsorption isotherms of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II) could be described very well by the Langmuir equation, but not the Freundlich equation. Considering the economy and performance, 0.05 M HCl solution is the best desorbing agent. The introduced APT and SH are a benefit for recycling the composite hydrogel, and the adsorption capacity is still higher than 590 $\mathrm{mg \cdot g^{-1}}$ after five consecutive adsorption−desorption processes.

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1. Introduction

Adsorption methods have been frequently used for the removal of pollutants from aqueous solutions owing to the convenience in design, application, and regeneration of the adsorbents.[1]

It has been gradually recognized during the past several years that the application of low-cost and environmentally friendly adsorbents (such as chitosan (CTS),[2] clay,[3] and cellulose[4]) for the removal of pollutants is an economical method for water decontamination. However, there are some problems (including low adsorption capacity and adsorption rate) using these low-cost adsorbents for the removal of heavy metal ions.[5] Approximately 100 min is needed to reach equilibrium for the adsorption of gold(III), platinum(IV), and palladium(II) onto glycine-modified cross-linked CTS [(169.98, 122.47, and 120.39) $\mathrm{mg \cdot g^{-1}}$, respectively].[6]

Recently, the application of hydrogels with a three-dimensional cross-linked polymer network as adsorbents for the removal of heavy metal ions[7,8] and ammonium nitrogen[9] has been paid special attention.[10,11] Hydrogels often contain many hydrophilic functional groups such as −COOH, $-\mathrm{COO^-}$, $-\mathrm{NH_2}$, and −OH depending on its chemical composition,[12] which has endowed hydrogel adsorbents with very high adsorption capacities. The hydrophilic character of hydrogel adsorbents makes them partly swell once immersed in aqueous solution. Thus, the solute molecules could interpenetrate into the network of the hydrogel with water quickly and bind to the functional groups.[13] However, neat polymeric hydrogels often have some limitations such as low gel strength and stability.

On the basis of the above review, it can be seen that it remains necessary to improve the properties of both the environmentally friendly adsorbents and the hydrogel adsorbents.

The preparation of organic/inorganic composite hydrogels by using polysaccharide, monomer, clay mineral, and other bioresources is a good idea to generate novel adsorbent materials and to overcome the flaws mentioned above. It has been proved extensively that the introduction of clay for the preparation of composite hydrogels is an effective way to improve absorbing properties and hydrogel strength of neat polymeric hydrogels.[14−17] However, only a few recent literature studies concerning the application of composite hydrogels as adsorbents for the removal of heavy metal ions can be found, and promising results were obtained.[18]

Attapulgite (APT), a kind of hydrated octahedral layered magnesium aluminum silicate absorbent mineral, has exchangeable cations and reactive −OH groups on its surface.[19] Sodium humate (SH) is composed of multifunctional aliphatic components and aromatic constituents, and so contains a large number of functional groups, such as carboxylates and phenolic hydroxyls.[20] The adsorption capacity of polyacrylamide hydrogel for methylene blue was enhanced by incorporating the proper amount of SH.[7] The synergetic effect of APT and SH could improve water absorbency of the poly(acrylic acid-co-acrylamide) hydrogel.[21] CTS is the most abundant biomass in the world and has been frequently used as an adsorbent for the removal of heavy metal ions.[22] Reactive $-\mathrm{NH_2}$ and −OH groups of CTS are convenient for graft polymerization of hydrophilic vinyl monomers to acquire hydrogels with novel properties. To acquire a novel hydrogel adsorbent with high performance and low cost, the free radical polymerization among CTS, acrylic acid (AA), SH, and APT was carried out on the basis of our previous work about hydrogel composites.[23,24] The adsorption

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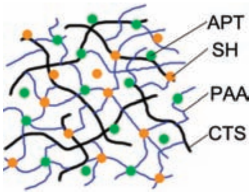

Figure 1. Schematic structure of the CTS-*g*-PAA/APT/SH composite hydrogels.

and desorption parameters are discussed in this study which are very important for practical application of the composite hydrogels.

2. Experimental Section

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 the Shanghai Reagent Corp. (Shanghai, China). CTS (degree of deacetylation is 0.85, average molecular weight is $30 \cdot 10^4$) was supplied by the Zhejiang Yuhuan Ocean Biology Co. (Zhejiang, China). APT (supplied by the Jiuchuan Clay Technology Co., Jiangsu, China) was milled through a 320 mesh screen before use. 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 Chitosan-g-poly(acrylic acid)/Attapulgite/Sodium Humate (CTS-g-PAA/APT/SH) Composite Hydrogels. A series of CTS-*g*-PAA/APT/SH composite hydrogels with various amounts of APT were synthesized according to the following procedure. A portion of 0.72 g of CTS was dissolved in 30 mL of 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 of 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, 0.468 g of SH, and the proper amount of APT was added (APT1#, 0 g of APT; APT2#, 0.468 g of APT; APT3#, 0.936 g of APT). The water bath was kept at 60 °C for 3 h. The resulting granular product was transferred into sodium hydroxide aqueous solution (1 M) to be neutralized to pH = 7 and then dehydrated three times with 95 % ethanol. It should be noted that the neutralization of the products was done after polymerization because of the following fact. CTS is a polyelectrolyte, and its amino groups are positively charged in acidic aqueous solution, which makes it soluble. Once the AA monomer is partly neutralized before polymerization, it will become negatively charged sodium acrylate. The strong electrostatic interaction between positively charged CTS and negatively charged sodium acrylate will cause the quick precipitation of CTS, which is vital for the graft reaction between CTS and AA. After wiping off excess ethanol on the surface using filter paper, the samples were spread on a dish to dry overnight at room temperature. The product was milled to a predetermined particle size. CTS-*g*-PAA was prepared according to the same procedure except for the addition of APT and SH. The graft reaction between CTS and PAA is well-known according to the previously reported literature[25,26] and has also been proven by us.[23,24] The schematic structure of a CTS-*g*-PAA/APT/SH composite hydrogel is shown in Figure 1.

2.3. Adsorption Experiments. All batch adsorption experiments were carried out by mixing a certain amount of the samples with 25 mL of aqueous solution of lead acetate of a certain concentration and pH and shaking in a thermostatic shaker bath (THZ-98A) at 120 rpm at 30 °C for 60 min to ensure that adsorption equilibrium is achieved. 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 a ethylenediaminetetraacetic acid (EDTA) titrimetric method using 0.0025 M EDTA solution as a standard solution and 0.5 % xylenol orange solution as the indicator. The adsorption capacity of the composites for Pb(II) was calculated according to the following equation:

$$q_t = \frac{V(C_o - C)}{m} \tag{1}$$

where q_e is the amount of Pb(II) adsorbed at equilibrium ($\text{mg} \cdot \text{g}^{-1}$). C_0 is the initial concentration of Pb(II) solution ($\text{mg} \cdot \text{L}^{-1}$). C is the liquid-phase Pb(II) concentration at equilibrium ($\text{mg} \cdot \text{L}^{-1}$). m is the mass of adsorbent used (g), and V is the volume of Pb(II) solution used (L).

2.4. Desorption and Regeneration Studies. To find an effective reagent for desorption of the Pb(II)-loaded composite hydrogel, a certain amount of the representative Pb(II)-loaded CTS-*g*-PAA/APT/SH sample (APT2#) was prepared, and its adsorption capacity for Pb(II) was calculated (801.90 $\text{mg} \cdot \text{g}^{-1}$). The influence of various reagents on desorption efficiency was studied by mixing 0.1 g Pb(II)-loaded APT2# sample with 25 mL of acid solutions (HCl, HNO_3, H_2SO_4, CH_3COOH) or distilled water and agitating on a magnetic agitator at 220 rpm at room temperature for 60 min. The desorption capacity and desorption efficiency were calculated according to the following equations.

$$\text{Desorption capacity} = C_a V_a / m \tag{2}$$

$$\text{Desorption efficiency} = C_a V_a / q_e \cdot 100 \tag{3}$$

where C_a is Pb(II) concentration in acid solution at desorption equilibrium ($\text{mg} \cdot \text{L}^{-1}$). V_a is the volume of acid solution used for desorption (L). m is the mass of the adsorbent before adsorption of Pb(II). q_e is the amount of Pb(II) adsorbed at equilibrium ($\text{mg} \cdot \text{g}^{-1}$).

For evaluating the reuse value of the composites, 1.0 g of Pb(II)-loaded CTS-*g*-PAA or APT2# sample was agitated with 250 mL of 0.05 M HCl solution at room temperature for 60 min. The sample was separated from the solution by centrifugation, washed with distilled water three times, and then dried in an oven at 70 °C for reuse. The consecutive adsorption−desorption process was performed five times.

3. Results and Discussion

3.1. Effect of pH of Initial Pb(II) Solution on Pb(II) Adsorption. The pH of the adsorption medium is an important factor influencing adsorption of heavy metal ions onto adsorbents. The effect of pH of Pb(II) solution on adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels is shown in Figure 2. It can be seen from Figure 2 that the adsorption capacity increases sharply from < 100 $\text{mg} \cdot \text{g}^{-1}$ to approximately 600 $\text{mg} \cdot \text{g}^{-1}$ with increasing pH of Pb(II) solution from 2.51 to 3.54 and then increases gradually to about 800 $\text{mg} \cdot \text{g}^{-1}$ with further increasing pH to 5.70. This result is attributed to the following facts. It has been revealed that $-COOH$ and $-COO^-$ of PAA, $-NH_2$ of CTS, $Ph-O^-$, and $-COO^-$ of SH as well as cation exchange and Si−OH of APT participate in the adsorption

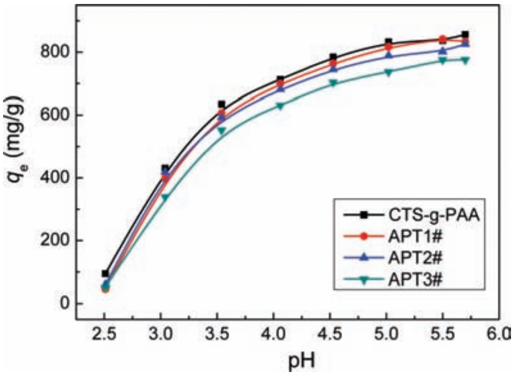

Figure 2. Effect of pH on adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II). Particle size of the adsorbents, (200 to 320) mesh; sample dose, 0.1 g/25 mL; Pb(II) concentration, 4000 mg·L^{-1}.

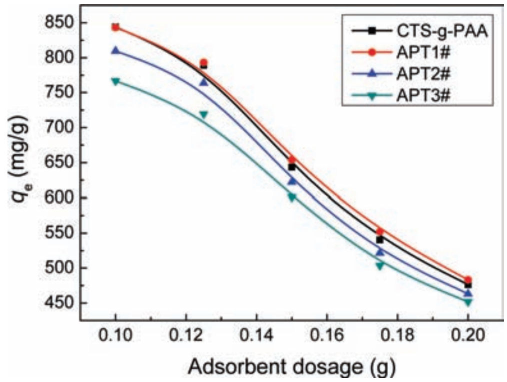

Figure 3. Effect of adsorbent dosage on adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II). Particle size of the adsorbents, (200 to 320) mesh; pH of Pb(II) solution, 5.50; Pb(II) concentration, 4000 mg·L^{-1}.

of heavy metal ions.[18,27] The $-COO^-$ groups from PAA and SH on the network of the composite hydrogel are changed to $-COOH$ at low pH, which is unfavorable for the adsorption of Pb(II) onto the composite. In addition, most of the $-NH_2$ groups of CTS in the composite are protonated and convert to $-NH_3^+$ at low pH. The electrostatic repulsion between Pb(II) and $-NH_3^+$ could also prevent the adsorption of Pb(II) onto the composite. Moreover, the concentration of H^+ ions increases with decreasing pH, which competes with Pb(II) in the solution and makes the ion-exchange reaction between Pb(II) and exchangeable cations in the composite very difficult. Considering the formation of precipitation when the pH of Pb(II) solution exceeds 5.50, the pH of 5.50 was selected as the initial pH of Pb(II) solution for the following adsorption experiments.

3.2. Effect of Adsorbent Dosage on Pb(II) Adsorption. The amount of the adsorbent is an important parameter because it determines the adsorption capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of CTS-*g*-PAA/APT/SH composite hydrogel dosage on adsorption capacity is presented in Figure 3. It is observed that the adsorption capacity decreases almost linearly with increasing amount of adsorbent. This result indicates that the amount of Pb(II) adsorbed per unit weight of the CTS-*g*-PAA/APT/SH composite hydrogel decreases with an increase of adsorbent dosage. The decrease in unit adsorption with increasing adsorbent dosage is mainly due to the fact that the adsorption sites remain unsaturated during the adsorption reaction.[22] The amount of Pb(II) is 100 mg in 25 mL from a 4000 mg·L^{-1} Pb(II) solution. This amount is excess when 0.10 g of adsorbent is charged for the adsorption capacity test and more than 75 % Pb(II) has been removed. With increasing the adsorbent content to 0.15 g, the amount of Pb(II) becomes inadequate. Consequently, a lower adsorption capacity and higher removal ratio of the adsorbent are observed. This phenomenon is more obvious by further increasing adsorbent dosage. The adsorption capacity has decreased to below 500 mg·g^{-1}, and the removal ratio for all of the samples is higher than 90 %.

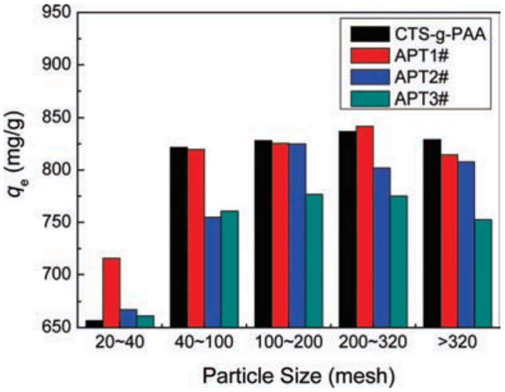

Figure 4. Effect of adsorbent dosage on adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II). Sample dose, 0.1 g/25 mL; pH of Pb(II) solution, 5.50; Pb(II) concentration, 4000 mg·L^{-1}.

3.3. Effect of Particle Size of the Adsorbent on Pb(II) Adsorption. The effect of particle size of the composite hydrogels on Pb(II) adsorption is shown in Figure 4. As can be seen, q_e increases evidently with decreasing adsorbent particle size from (20 to 40) mesh to (40 to 100) mesh. This is an expected result because as the particle size of the CTS-*g*-PAA/APT/SH composite hydrogels decreases, the number of activated adsorption sites on the surface of adsorbent particles increases and more Pb(II) is adsorbed to their surfaces. With further decreasing the particle size to (200 to 320) mesh, q_e shows a slight increase, which indicates that q_e is rarely affected by the particle size of adsorbent in the above conditions. Similar results were observed when palygorskite[28] and sepiolite[29] were used as absorbents for Pb(II). However, the adsorbent with a particle size smaller than 320 mesh has a lower q_e. This is mainly due to the fact that the composite hydrogel particles with a too small size tend to aggregate and become large clusters, which restrict the interaction between the adsorbent and the Pb(II) in the solution. Considering the conditions in actual application, such as energy use and the separation of adsorbent from liquid phase, (40 to 100) mesh is an appropriate choice according to the above study.

3.4. Adsorption Isotherm Study. The influence of initial Pb(II) concentration on the adsorption capacity of Pb(II) onto the CTS-*g*-PAA/APT/SH composite hydrogels is shown in Figure 5. It is clear that initial Pb(II) concentration plays an important role in the adsorption process of Pb(II) onto the adsorbents. It can be seen from Figure 5 that the adsorption capacity of the composites for Pb(II) increases sharply with increasing initial Pb(II) concentration when the concentration is lower than 2469 mg·L^{-1} and then increases gradually by further increasing the concentration to 3950 mg·L^{-1}. This may be attributed to the following fact. Generally, the higher the initial Pb(II) concentration is, the greater the driving force at the solid−liquid interface is. Ion exchange, electrostatic attraction, and chelation are the main driving forces at the solid−liquid interface. The increase of driving force between Pb(II) and the adsorbent at the solid−liquid interface is responsible for the increase of the amount of metal ions adsorbed onto the adsorbent. At low initial Pb(II) concentrations, ion exchange and

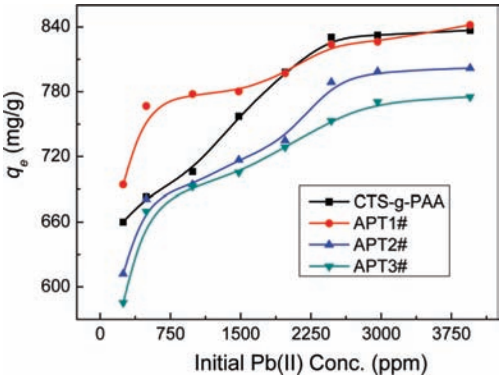

Figure 5. Effect of pH on adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II). Particle size of the adsorbents, (200 to 320) mesh; sample dose, 0.1 g/25 mL; pH of Pb(II) solution, 5.50.

electrostatic attraction are dominant. With increasing Pb(II) concentration, the chelation between $-COO^-$ and Pb(II) becomes dominant, and a quick increase of adsorption capacity is observed. By further increasing initial Pb(II) concentration, the Pb(II) could only interact with the remaining functional groups of the composite hydrogels, and a slow increase of adsorption capacity is observed.

It also can be seen from Figure 5 that the adsorption capacity is always in the order of APT1# > CTS-*g*-PAA > APT2# > APT3# when the initial Pb(II) concentration is smaller than 1975 $mg \cdot L^{-1}$, whereas the order is APT1# > CTS-*g*-PAA > APT2# > APT3# by further increasing the initial Pb(II) concentration. This result indicates that the introduced SH is of benefit for improving the adsorption capacity of the composite hydrogel at lower Pb(II) concentrations, which is very important for practical applications. It has been revealed that the introduced SH could improve adsorption rate and adsorption capacity.[7] This effect is more evident when the initial concentration of Pb(II) decreases from 4000 $mg \cdot L^{-1}$ to lower than 1975 $mg \cdot L^{-1}$. This may be attributed to the fact that the chelation constants between functional groups of SH and Pb(II) are higher than those between CTS-*g*-PAA and Pb(II).

The interaction between adsorbate and adsorbent are frequently interpreted using the Langmuir and the Freundlich isotherm models. 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.[30] The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. The Langmuir isotherm model is represented by eq 4.[31] The Freundlich isotherm model is applied to describe heterogeneous systems 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 isotherm model is expressed by eq 5.[32]

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{4}$$

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log K \tag{5}$$

where q_e is the amount of Pb(II) adsorbed at equilibrium ($mg \cdot g^{-1}$), C_e is the liquid-phase Pb(II) concentration at equilibrium ($mg \cdot L^{-1}$), q_{max} is the maximum adsorption capacity of the adsorbent ($mg \cdot g^{-1}$), and *b* is the Langmuir adsorption constant ($L \cdot mg^{-1}$). *K* is the Freundlich isotherm constant ($L \cdot g^{-1}$), and 1/*n* is the heterogeneity factor.

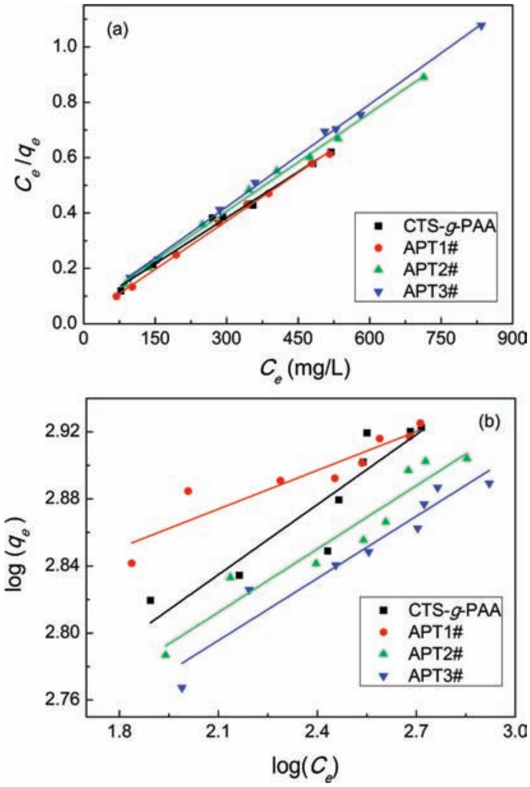

Figure 6. (a) Langmuir and (b) Freundlich plots for the adsorption of Pb(II) onto the CTS-*g*-PAA/APT/SH composite hydrogels.

Table 1. Langmuir and Freundlich Constants and Coefficients of Determination Associated with the Adsorption Isotherms of Pb(II) onto the CTS-*g*-PAA/APT Composite Hydrogels

	Langmuir equation			Freundlich equation		
	q_{max}	*b*				
sample	$mg \cdot g^{-1}$	$L \cdot mg^{-1}$	R^2	*K*	*n*	R^2
CTS-*g*-PAA	900.90	0.0218	0.9889	346.94	7.17	0.8209
APT1#	862.07	0.0528	0.9983	515.41	12.98	0.8506
APT2#	847.46	0.0227	0.9953	353.14	7.94	0.9106
APT3#	813.01	0.0235	0.9981	343.76	8.10	0.9176

The adsorption of Pb(II) onto CTS-*g*-PAA/APT/SH incorporated with various amounts of APT fitted to the Langmuir (plotting C_e/q_e vs C_e) and Freundlich (plotting $\log(q_e)$ vs $\log(C_e)$) isotherm models is shown in Figure 6. As can be seen, the experimental data do not fit very well to the Freundlich isotherm model, and there is a great difference between the Freundlich plots and the trend lines. However, the experimental data fit very well to the Langmuir isotherm model. The Langmuir plots and the trend lines are almost entirely coincident with each other. The corresponding parameters for all of the samples obtained from the linear plots of Langmuir and Freundlich isotherm models are listed in Table 1. It can be seen that the linear coefficients of determination (R^2) for the Freundlich isotherm model are lower than 0.92, which indicate that this model does not describe very well the adsorption processes of the composite hydrogels for Pb(II). It also can be found from Table 1 that R^2 values for the Langmuir isotherm model are close to 1. In addition, the q_{max} values for the adsorption of Pb(II) onto the composite hydrogels calculated from the Langmuir model are in close proximity to the experimental data. Obviously, the Langmuir model is much better to describe the adsorption of Pb(II) onto the CTS-*g*-PAA/APT/SH composite hydrogels than the Freundlich model. This indicates that a monolayer coverage of Pb(II) has formed on the surface of the composite hydrogels.

Table 2. Influences of Acid Type and Concentration on the Desorption Capacity and Desorption Efficiency of Pb(II) from the Representative Pb(II)-Loaded CTS-*g*-PAA/APT/SH Composite Hydrogel (APT2#)

acids	desorption capacity (mg·g^{-1})	desorption efficiency (%)
distilled water	0	0
0.05 M HNO_3	600.70	74.91
0.05 M CH_3COOH	96.47	12.03
0.05 M H_2SO_4	603.91	75.31
0.05 M HCl	623.40	77.74
0.025 M HCl	562.37	70.13
0.1 M HCl	637.35	79.48

3.5. Desorption and Recycling of CTS-g-PAA/APT/SH Composite Hydrogels. Desorption and recycling of an adsorbent are very important parameters for its design and practical application. Desorption is beneficial for the separation and enrichment of Pb(II) ions as well as the regeneration of the composite. In addition, the nature of the adsorption process may be further elucidated through desorption studies. The effects of acid type and concentration on the desorption capacity and desorption efficiency of Pb(II) from the representative Pb(II)-loaded CTS-*g*-PAA/APT/SH composite hydrogel (APT2#) are shown in Table 2. As can be seen, no Pb(II) could be desorbed by distilled water indicating that Pb(II) is stably adsorbed to the composite hydrogel. The desorption efficiencies of 0.05 M HNO_3, CH_3COOH, H_2SO_4, and HCl solutions are 74.91 %, 12.03 %, 75.31 %, and 77.74 %, respectively. The obviously lower desorption efficiency of 0.05 M CH_3COOH solution may be attributed to its weak acidity. The desorption capacity and desorption efficiency of 0.05 M HCl, HNO_3, and H_2SO_4 are comparable, which indicates that these three acids have no evident difference when used for the desorption of Pb(II) from the composite hydrogel. It also can be seen from Table 2 that the increase of HCl concentration from (0.025 to 0.05) M has great influence on desorption capacity and efficiency. However, a further increase of HCl solution concentration to 0.10 M does not show evident improvement. Considering the above results and economics of the desorption process, 0.05 M HCl solution is the best choice for the desorption of Pb(II) from the CTS-g-PAA/APT/SH composite hydrogels.

To evaluate the recycling of the composite hydrogel, the consecutive adsorption−desorption process was performed five times. The effect of reuse times on the adsorption capacity of CTS-*g*-PAA and APT2# for Pb(II) is shown in Figure 7. It can be seen that the adsorption capacity of CTS-*g*-PAA and APT2# decreases evidently during the first two recycles. This is attributed to the fact that HCl solution was used as the desorbing agent during the desorption process. Thus, a part of the $-NH_2$ groups from CTS of the composite hydrogel are protonated, and the $-COO^-$ groups are changed to $-COOH$. In addition, a part of adsorption sites on the network of APT2# may bind stably with Pb(II) and cannot be desorbed by 0.05 M HCl solution. Moreover, the gel strength may have been changed during the consecutive adsorption−desorption process and then cause the decrease of the adsorption capacity. With further increasing reuse times, a gradual decrease of adsorption capacity is observed for CTS-*g*-PAA, whereas a bit of an increase of adsorption capacity is observed for APT2#. This difference between CTS-*g*-PAA and APT2# indicates that the introduced APT and SH are beneficial for the recycling of the composite hydrogel. This result may be because a more stable network of CTS-*g*-PAA/APT/SH has been formed and the functional groups of CTS, PAA, APT, and SH could interact with Pb(II) simultaneously. The synergistic effect of various functional groups is helpful to keep its adsorption capacity. In addition, the sample after desorption needs to be dried at 70 °C. Thus, each adsorption−desorption process must go with an acid-treated process and a heat-treated process. Both the acid-treated process and the heat-treated process could increase the adsorption capacity of APT,[33] which may be also the reason for the observed slight increase of adsorption capacity with further increasing reuse times.

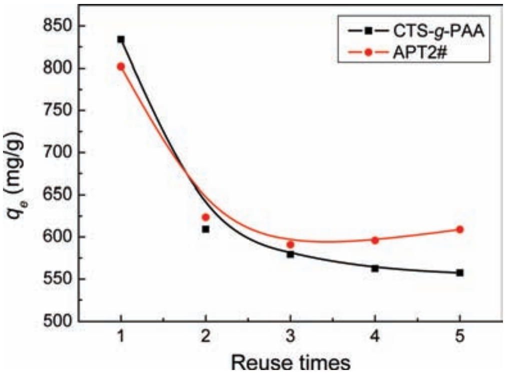

Figure 7. Relationship between the reuse times and the adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II).

It also can be seen from Figure 7 that the average desorption efficiency of APT2# is over 75 % and the adsorption capacity is always higher than 590 mg·g^{-1} during the five consecutive adsorption−desorption processes. This means that the CTS-*g*-PAA/APT/SH composite hydrogel is a high-performance recyclable adsorbent.

4. Conclusions

The adsorption and desorption parameters of the novel CTS-*g*-PAA/APT/SH composite hydrogel for the removal of Pb(II) from aqueous solution were investigated and discussed in this study. The adsorption capacity of the CTS-*g*-PAA/APT/SH composite hydrogels for Pb(II) increases with increasing pH and concentration of Pb(II) in solution but decreases with increasing adsorbent dosage. A particle size of (40 to 100) mesh is an appropriate choice for the practical application of the composite hydrogel. The Langmuir equation can be used to describe the adsorption of Pb(II) onto the composite hydrogel very well. It is found that the adsorbed Pb(II) could be desorbed from the composite hydrogel efficiently using 0.05 M HCl solution. In addition, the introduced APT and SH are helpful for the recycling of the composite hydrogel, and the adsorption capacity is kept higher than 590 mg·g^{-1} after five times of consecutive adsorption−desorption processes. This work has built a solid foundation for the practical application of this novel composite hydrogel as an adsorbent for the removal of Pb(II). The results indicate that the composite hydrogel is a high-performance, low-cost, and recyclable green adsorbent.

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