



Synthesis of a three-dimensional network sodium alginate–poly(acrylic acid)/attapulgite hydrogel with good mechanic property and reusability for efficient adsorption of Cu^{2+} and Pb^{2+}

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Abstract

Water pollution caused by heavy metals has dramatically impacted ecosystems in recent years. For instance, 45.4% of lakes in China are in the category of moderate to high risk of toxic metal pollution, due to excessive mining. There is, therefore, a need for efficient techniques of metal decontamination. Hydrogels are gaining interest as heavy metal adsorbents because of their easy separation, but hydrogel applications are limited due to their poor mechanical property. Here we solve this problem by introducing natural attapulgite into the sodium alginate–poly(acrylic acid) semi-interpenetrating polymer network of the hydrogel. Results show that the compressive stress of the hydrogel with 10% attapulgite, of 1.230 Mpa, was 4.1 times higher than that of pure hydrogel, of 0.299 MPa. The adsorption capacity of hydrogel with 10% attapulgite was high, of 272.8 mg/g for Cu^{2+} and 391.7 mg/g for Pb^{2+} . Even after five cycles of adsorption, the hydrogel with 10% attapulgite still adsorbs 261.7 mg/g Cu^{2+} and 368.1 mg/g Pb^{2+} . Our findings thus reveal that network-structured sodium alginate–poly(acrylic acid)/attapulgite hydrogel holds great potential as an efficient and recyclable adsorbent for heavy metal removal.

Keywords Hydrogel · Attapulgite · Pb^{2+} · Cu^{2+} · Adsorption · Alginate

Introduction

Water pollution caused by heavy metals has dramatically impacted our life in recent years because of their excessive release into aquatic environment (Mudhoo 2012; Kiran et al. 2016). A survey showed that 45.4% of lakes in China were in the category of moderate risk and high risk concerning toxic metals, due to excessive mining, effluent and insecticide discharge (Xu et al. 2017). When the concentration of heavy metals exceeds a certain limit, it is dangerous for human health. For example, excess of lead (Pb^{2+}) affects the mental health of children (Gassowska et al. 2016), and excess of copper (Cu^{2+}) causes many diseases such as hepatocirrhosis and hemolysis (Zhu et al. 2013). Several methods have been reported for metal removal, such as membrane separation (Kurniawan et al. 2006), solvent extraction (Wang et al. 2017) and ion-exchange (Prathap and Namasivayam 2010). Recently, adsorption has been widely applied due to its ready availability and low cost (Keng et al. 2014; Muya et al. 2016).

Hydrogel is an excellent adsorbent because it is recyclable, efficient and provides easy separation (Carvalho et al. 2010; Yin et al. 2008). Natural hydrophilic polymers,

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such as sodium alginate and chitosan, are considered to be good raw materials for hydrogels, but their applications as hydrogels are limited due to their poor mechanical strength (Dragan 2014). The strength of hydrogels can be enhanced by constructing semi-interpenetrating polymer network, for example, by adding poly(acrylic acid) to sodium alginate (Wu et al. 2015), or by adding poly(vinyl alcohol) to chitosan (Wan et al. 2017). However, the mechanical strength of hydrogels decreases significantly after swelling. Some investigations have shown that the addition of clay minerals such as montmorillonite (Kaplan and Kasgoz 2011) and attapulgite (Wang et al. 2011) can improve the mechanical strength of hydrogels and also reduces its cost. Therefore, here we aimed to synthesize a novel hydrogel adsorbent by introducing natural attapulgite into the sodium alginate–poly(acrylic acid) hydrogel. To our best knowledge, this is the first synthesis of an attapulgite-modified hydrogel for heavy metal removal.

Experimental

Materials

Natural attapulgite from Jiangsu Xinyuan Technology Corp. China was crushed to obtain particles of size 200 mesh or less (size less than 61 μm), followed by pretreatment in 1 mol/L hydrochloric acid (HCl) solution for 3 days. This acidified attapulgite was washed with deionized water till neutral pH. Other chemicals, including sodium alginate, ammonium persulfate, acrylic acid, lead chloride and N,N'-methylene-bis-acrylamide, were all purchased from Sinopharm.

Method

The hydrogel without attapulgite was synthesized by the following procedure: acrylic acid (3.60 g, neutralized with NaOH), N,N'-methylene-bis-acrylamide (0.15 g) and water (45.0 mL) were all taken in a 250-mL beaker and stirred at 600 rpm for half hour. Then, sodium alginate (0.30 g) was added into the above solution and kept stirring for another 4.0 h. After sodium alginate was fully dissolved, ammonium persulfate (0.50 g) was dropped into the suspension, then stirring was stopped and the reaction temperature was raised to 45 $^{\circ}\text{C}$ for 1.0 h. The hydrogel was washed by immersing successively in water and ethanol for 15 min. The hydrogel was then cut into small pieces and dried at room temperature.

The synthesis of the hydrogel with attapulgite was similar, but a specified amount of attapulgite was added to the mixed solution before the addition of ammonium persulfate.

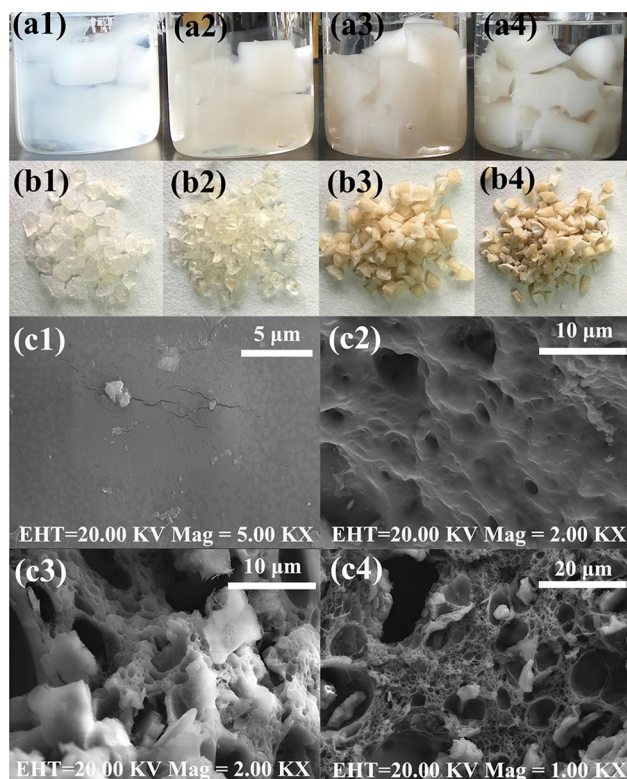


Fig. 1 **a** Digital photographs of hydrogels with different content attapulgite clay: 0% (a1), 10% (a2), 20% (a3) and 30% (a4). **b** The same hydrogels after drying. **c** Scanning electron microscopy of the hydrogels. Note that addition of clay progressively transforms the smooth surface of the initial hydrogel (c1) into a three-dimensional network (c2–c4)

The digital photographs of the final samples are shown in Fig. 1a, b.

The surface microstructures and elemental contents of hydrogels were revealed by scanning electron microscopy (Zeiss Supra55VP). Information regarding chemical bonds was obtained by Fourier transform infrared spectroscopy (Nicolet iS50). X-ray photoelectron spectroscopy (ESCALAB 250XI) was conducted at 150 W using Al K α . The stress–strain curves were obtained using an electronic universal testing machine (MTS Criterion, Model 43). The thermostatic orbital shaker (HZQ-F160) operated at a speed of 120 rpm at 30 $^{\circ}\text{C}$. In the batch adsorption experiments, 25 mg of adsorbents was used to adsorb 25 mL of Cu $^{2+}$ or Pb $^{2+}$ solutions. The concentrations of the solutions (Cu $^{2+}$ and Pb $^{2+}$) are all set as 400 mg/L. The adsorption capacities were calculated using the following equation:

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

where Q_e is the adsorption capacity (mg/g). C_0 and C_e represent the initial and final concentrations of the solution

(mg/L), respectively, and measured by inductively coupled plasma spectrometer (ICP-OES). V and m are volume (mL) of the solution and weight of the adsorbent (g), respectively.

Results and discussion

We synthesized a novel hydrogel adsorbent by introducing natural attapulgite into the sodium alginate–poly(acrylic acid) hydrogel, in order to improve hydrogel strength. We tested adsorption of metals, desorption, pH effect, reusability and mechanical strength.

Characterization of hydrogels

The microscopic surfaces of hydrogels were observed by scanning electron microscopy (SEM). The pure hydrogel showed a smooth and tight surface in Fig. 1c1, whereas the hydrogel with 10% attapulgite shows a loose surface and bone-like three-dimensional structure (Fig. 1c4). This finding confirms that attapulgite promotes the formation of three dimension (3D) network porous structures in hydrogels. The structures of hydrogels with attapulgite are thus more porous compared to conventional hydrogels.

Fourier transform infrared spectroscopy (FTIR) spectra of hydrogels and attapulgite are shown in Fig. 2a. New peaks induced by addition of 10% attapulgite, at 1001 and 528 cm^{-1} , are ascribed to the stretching vibration of Si–O and deformation vibration of Al–O–Si bonds, respectively (Rashidzadeh et al. 2015). These new peaks prove the introduction of attapulgite in the hydrogels. After the introduction of attapulgite, the peak of hydrogel initially at 1047 cm^{-1} , ascribed to the stretching vibration of C–O–C, is shifted to 1028 cm^{-1} , ascribed to the stretching vibration of Si–O–C. This finding reveals that the chains of acrylic acid are linked to attapulgite by Si–O–C bonding at the interface between attapulgite and hydrogel, as well due to physical cross-linking. Major peaks at 3303, 1547 and 1403 cm^{-1} are assigned to the intermolecular hydrogen bonding of –OH, deformation vibrations of –NHR and symmetric stretching vibrations of –COO[−] (Fan et al. 2013), respectively. These strong absorption peaks in the spectrum of the hydrogel suggest that the hydrogel possesses numerous functional groups that could chelate Cu²⁺ and Pb²⁺ ions.

The FTIR spectra of hydrogel with 10% attapulgite exhibits significant differences after adsorption of Cu²⁺ and Pb²⁺ (Fig. 2b). The bands at 3303, 1547 and 1403 cm^{-1} shift to 3141, 1547 and 1403 cm^{-1} after adsorption of Cu²⁺,

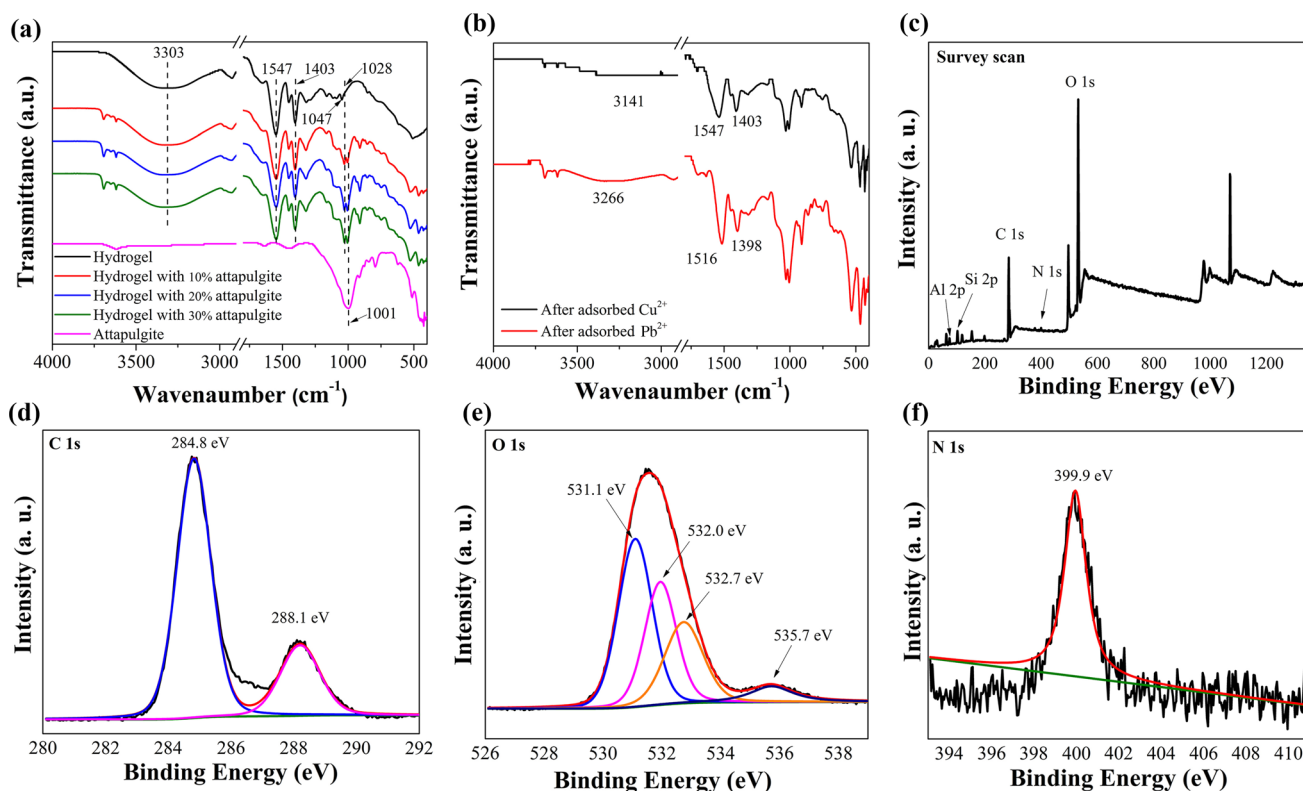


Fig. 2 a Fourier transform infrared spectroscopy of hydrogels with different content attapulgite (0, 10, 20 and 30%) and b hydrogels with 10% attapulgite after absorbing Cu²⁺ (black) and Pb²⁺ (red). X-ray

photoelectron spectroscopy of hydrogels with 10% attapulgite: c survey scan, d C1s, e O1s, f N1s

meanwhile shift to 3266, 1516 and 1398 cm^{-1} after adsorption of Pb^{2+} . The spectral shifts are caused by the strong interaction between these groups ($-\text{OH}$, $-\text{NHR}$ and $-\text{COO}^-$) and Cu^{2+} and Pb^{2+} (Zhu and Li 2015).

The X-ray photoelectron spectroscopy (XPS) of the hydrogel with 10% attapulgite complemented the FTIR data in Fig. 2c–f. Peaks attributed to Al 2p and Si 2p are observed in the survey scan spectrum (Fig. 2c). In the high-resolution spectrum, the broad peak of C1s before adsorption is fitted into two peaks at 284.8 and 288.1 eV, which are attributed to the C–H bond and amide bond, respectively (Fig. 2d) (Hoffmann et al. 2005). The asymmetric shape of O1s peak before adsorption can be deconvoluted into four peaks at 531.1, 532.0, 532.7 and 535.7 eV, which were assigned to O–H, C–O, C=O and carboxyl bond, respectively (Fig. 2e) (Zhang et al. 2015). N1s peak at 399.9 eV corresponds to the N–H bond (Fig. 2f). All results confirm the successful synthesis of the hydrogel with attapulgite.

Effect of attapulgite content on hydrogel adsorption

The metal adsorption capacity of the hydrogel was tested with increasing attapulgite clay content (Fig. 3a). Results show that the adsorption capacity only decreases from 282.6 mg/g to 249.9 for Cu^{2+} and from 396.1 mg/g to 362.5 for Pb^{2+} after introducing 30% attapulgite. This finding is in agreement with previous results showing a decrease in the adsorption capacity of hydrogels with increasing amount of attapulgite (Zhu et al. 2015). Overall, the present results show that adsorption of metal ions slightly decreases with adding attapulgite clay content.

Effect of pH on hydrogel adsorption

The adsorption of Cu^{2+} and Pb^{2+} was affected by the pH of the solution (Fig. 3b). Results show that the adsorption capacities of hydrogels were lower at lower pH values, especially lower than 2. This is explained by the competition between protons (H^+) and Cu^{2+} and Pb^{2+} ions (Bae et al. 2016). Raising the pH to 3.0 highly increases the adsorption capacities due to deprotonation. At pH of 4 and higher, adsorption capacities did not change (Fig. 3b). This is explained by the saturation of surface adsorption sites (Liu et al. 2012; Zhang et al. 2013). Overall, our results show that metal ion adsorption increases highly above pH 2.

Desorption, reusability and mechanical strength

We studied on the effect of time and HCl concentration on desorption of metal ions by hydrogels with 10% attapulgite. Results show that desorption ratios for Cu^{2+} and Pb^{2+} increased with HCl concentration and contact time (Fig. 3a,

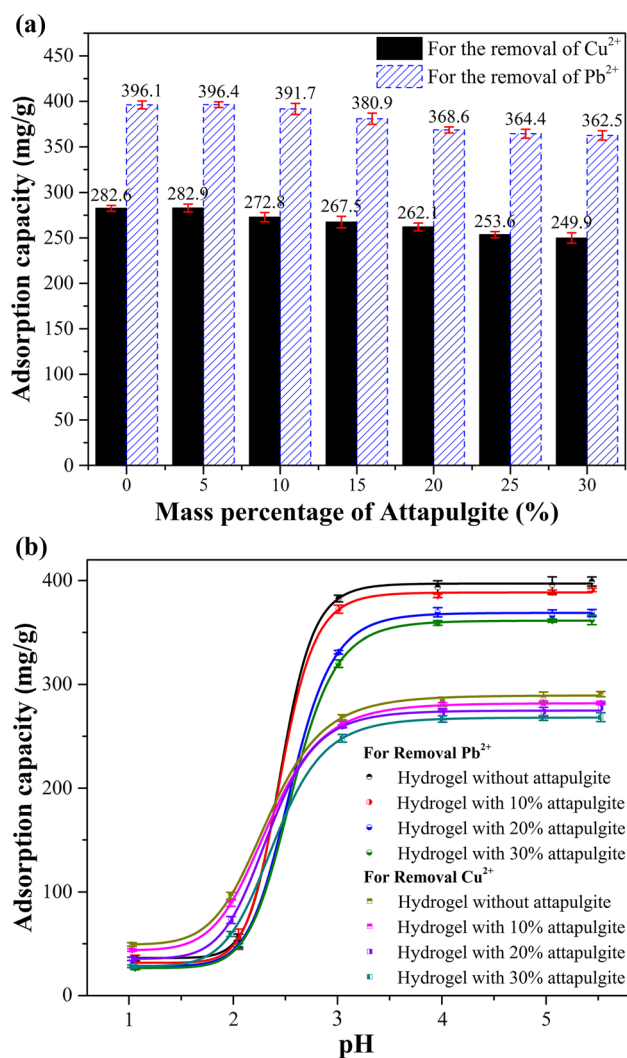


Fig. 3 Effects of attapulgite content and the initial pH of solution on adsorptions of Cu^{2+} and Pb^{2+}

b). The desorption rate reached 90% using 2 mol/L HCl during 2 h.

Moreover, we studied on the reusability of desorbed hydrogel with 10% attapulgite. The desorbed hydrogel was reused for the next adsorption process. First, concerning hydrogel with 10% attapulgite, the results show that, after five cycles, the adsorption capacities decreased from 282.9 mg/g to 261.7 mg/g for Cu^{2+} and decreased from 391.7 mg/g to 368.1 mg/g for Pb^{2+} (Fig. 4c). Due to the fragility of hydrogel alone (without clay) after one cycle, its structure was broken after three cycles (Fig. 4d). Moreover, the hydrogel with 10% attapulgite remained intact after five cycles (Fig. 4e). Overall, the finding shows that addition of clay highly improves the reusability of hydrogels.

In addition, we also studied on the effect of adding clay on the mechanical strength of the hydrogels. Results show that the pressure of the hydrogel with 10% attapulgite

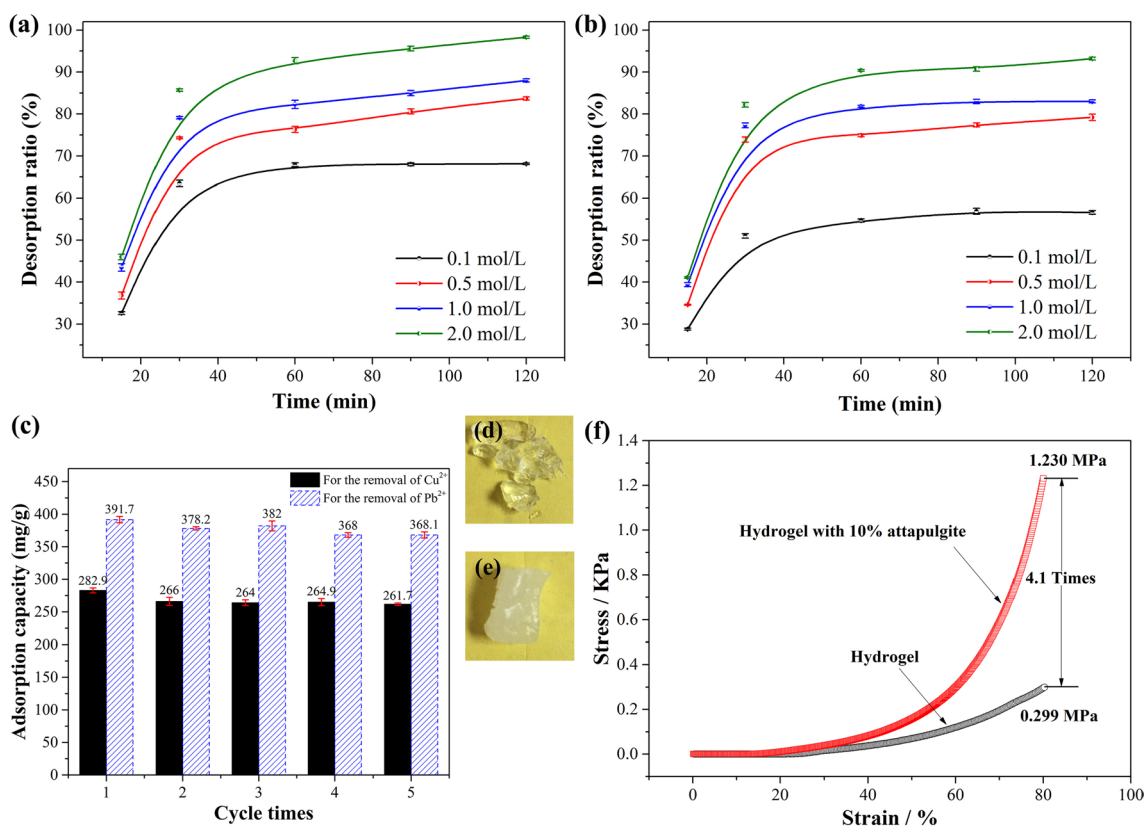


Fig. 4 Desorption ratios of hydrogels with 10% attapulgite for adsorptions of Cu²⁺ (a) and Pb²⁺ (b) ions in HCl solution with different concentrations. c Cycle test on the adsorption capacities of hydrogel with 10% attapulgite for Cu²⁺ and Pb²⁺ ions; digital photographs

of hydrogel alone after three cycles (d) and hydrogels with 10% attapulgite after five cycles (e); f stress–strain curves for hydrogel alone and hydrogel with 10% attapulgite (water content: 80%)

(1.230 MPa) is 4.1 times higher than that of hydrogel (0.299 MPa) in Fig. 4f. These findings are in agreement with reports suggesting that the mechanical strength of a hydrogel can be effectively improved by adding clay to the hydrogel (Kong et al. 2017).

Conclusion

Our results overcome the poor mechanical properties of hydrogels used in heavy metal removal from aqueous system. The compressive stress of semi-interpenetrating polymeric 3-D network-structured hydrogel increases from 0.299 to 1.230 MPa by addition of 10% attapulgite. Adsorption experiments show that the adsorption capacity of the hydrogel with 10% attapulgite was as high as 272.8 and 391.7 mg/g for Cu²⁺ and Pb²⁺, respectively. The hydrogel with 10% attapulgite can also retain 261.7 and 368.1 mg/g of Cu²⁺ and Pb²⁺, respectively, after five cycles.

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