Attapulgite-based Adsorbent for Mercury (II) Removal in Aqueous Solution

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Abstract. A new attapulgite-based adsorbent P-ATP was successfully prepared to remove mercury (II) from aqueous solutions *via* grafting reactions. The structures of the products were characterized by Fourier Transform Infrared Spectra (FTIR) and scanning electron microscope (SEM) analysis. The adsorption process was investigated by the batch adsorption experiments. The influence factors including pH, temperature, and contact time were all discussed. To further understand the adsorption process between adsorbents and the heavy metals, pseudo-second-order kinetic model was introduced, and Langmuir adsorption isotherm model was also used to describe the adsorption process. The adsorption capacity of Hg (II) on P-ATP was calculated to be as high as 181.16 mg/g. Furthermore, the adsorbent could be reused after 7 times of adsorption-desorption cycles.

1. Introduction

In recent years, heavy metal pollution in water environments becomes much more serious than ever before [1, 2]. Kinds of heavy metal ions are discharged into rivers, lakes, oceans, and underground waters with the rapid development of economy and modern industry. Among the released heavy metals, mercury is considered to be one of the most toxic elements due to its great harm to the human body. Furthermore, mercury could be enriched in the creatures by the food chain, thus, it makes the creatures at the top of the food chain suffer more damage [3]. Moreover, excess mercury may cause dysfunction of liver, kidney, brain tissue, and other serious problems [4].

Up to now, a great number of chemical and physical techniques have been used to eliminate mercury in water, such as chemical precipitation, ion-exchange, membrane filtration, electrochemical treatment. However, the above methods have obvious disadvantages: either operational complexity or high cost [5]. Therefore, adsorption technique becomes a useful and effective approach for the elimination of mercury in water [6, 7]. Attapulgite (ATP) is a kind of hydrated magnesium aluminum silicate mineral, which is very cheap and easy to be chemically modified via reactions with hydroxyl

groups on the surface or in the porous structures. Besides, attapulgite is not soluble in water, making it easy to be separated from aqueous solutions.

In this work, we report a new attapulgite-based adsorbent for the removal of mercury (II) in aqueous solution. 3-aminopropyltriethoxysilane (KH550) was employed as the coupling reagent, and pyromellitic dianhydride (PMDA) was introduced as the chelating groups for metal ions. The adsorption capacity of mercury (II) was calculated to be as high as 181.16 mg/g. Pseudo-second-order model and Langmuir adsorption isotherm model were also investigated to further understand the adsorption process.

2. Experimental section

2.1. Materials Synthesis

2.1.1. Pretreatment for attapulgite. First, the crude attapulgite was grind to 400 meshes with sieves, and divided into 30 g per group for the following acid pickling. The attapulgite was added in hydrochloric acid (4 mol/L) with a mass ratio of 1:10. The above mixture was heated for 4 hours at 90 $^{\circ}$C, then filtrated and washed by deionized water for several times until the filtrate is neutral. The filtration residue was dried and ready for modification. The pretreatment for attapulgite is to release the hydroxyl groups to active the activity of the raw material.

2.1.2. Modification of attapulgite. 60 g acid-activated attapulgite was added into 1L deionized water, and stirred in a flask to be dispersed uniformly. 30 mL 3-aminopropyltriethoxysilane (KH550) was then added into the above mixture and stirred for half an hour. After the reaction, the mixture was filtrated, washed by deionized water and dried in an oven.

2.1.3. Functionalization of attapulgite. 0.932g pyromellitic dianhydride (PMDA) was dissolved in 60 mL DMF (N, N-dimethylformamide), then 466 mg 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and 372.8 mg N-hydroxysulfosuccinimide sodium salt (NHS) were added into the above mixture. The solution was stirred for 30 minutes, and 2 g KH550-grafted attapulgite was added afterwards. The mixture was stirred for 1 more hour at 80°C. When the reaction was finished, the mixture was filtrated and the filtration residue was dried to obtain the adsorbent P-ATP.

2.2. Characterizations of the products

The functional groups of ATP and its derivatives were identified on a Fourier Transform Infrared Spectra (FTIR, Nicolet 6700, USA) in the range of 400-4000 cm^{-1}. The morphology of the products and elements analysis was operated by a JEOL-7800 scanning electron microscope (SEM, Japan). The concentration of the mercury (II) in solution was tested using an atomic fluorescence spectrometer AFS-8220 (Titan instruments, China), and the concentrations of the other heavy metal ions (including Cu (II), Pb (II), and Cr (VI)) in solution were measured by an Atomic adsorption spectrometer (Agilent Technologies 200 Series AA, USA).

3. Results and discussion

3.1. Characterizations of the adsorbents

FTIR was used to identify the functional groups in the adsorbent, and it could also indicate the reaction process *via* the characteristic peaks in different reaction steps. As is shown in Figure 1., the adsorption peaks at 1029 and 471 cm^{-1} are attributed to the Si-O-Si bonds, and the peak at 800 cm^{-1} is attributed to the stretching vibration of Al-O-Si bonds [8].The peak at 882 cm^{-1} is attributed to the Fe-O-Fe bonds. In addition, the peak at 1641 cm^{-1} indicates the zeolitic water [9]. The band at 1441 cm^{-1} is attributed to the carbonate minerals in ATP [10]. After the pretreatment of the raw material,

the carbonate was decomposed by the acid, thus, the adsorption peak disappeared in the FTIR spectra of modified ATP. Furthermore, the adsorption peak at 1640 cm^{-1} is assigned to N-H deformation vibration, which is similar to the adsorption peak of zeolitic water, therefore, it is difficult to identify the above two peaks in FTIR spectra.
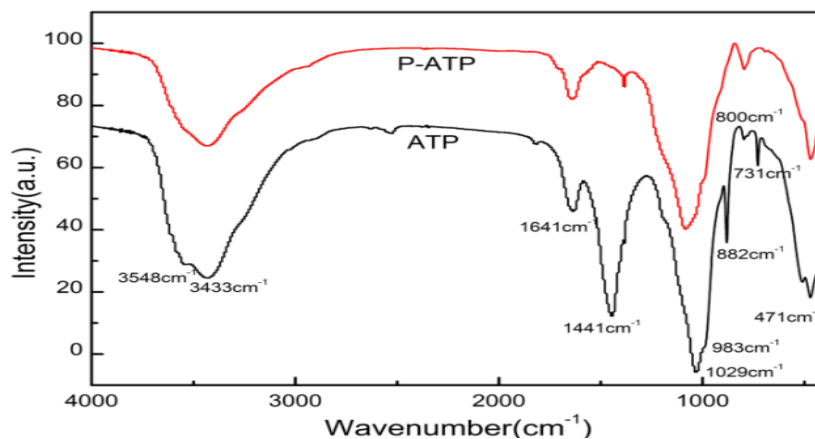

Figure 1. FTIR spectra of ATP and P-ATP.

The SEM images of ATP and its derivatives are shown in Figure 2 and 3. The raw ATP shows blocks of close packed fibres, and these fibres reunites together like needles. The difference of surface morphology between ATP and KH550-grafed ATP are not so obvious, and only the mesopores between the blocks turn smaller. It is worth noting that remarkable morphologic changes has taken place on the PDMA modified ATP (named as P-ATP) that the surface of P-ATP becomes much rougher than its precursor, lots of tiny needles spread out on the surface of the block of the basic material.
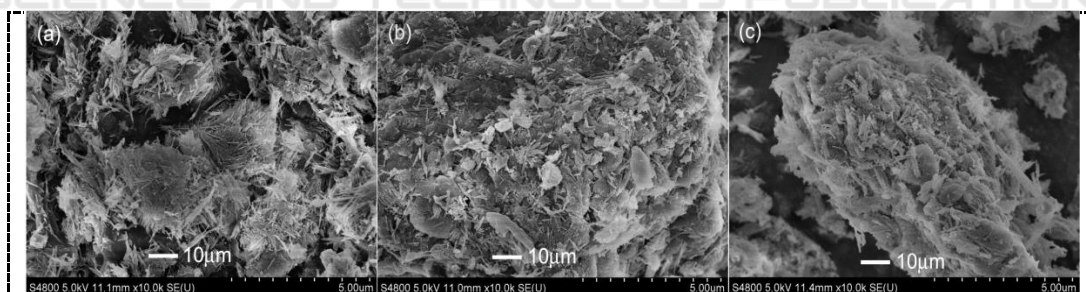

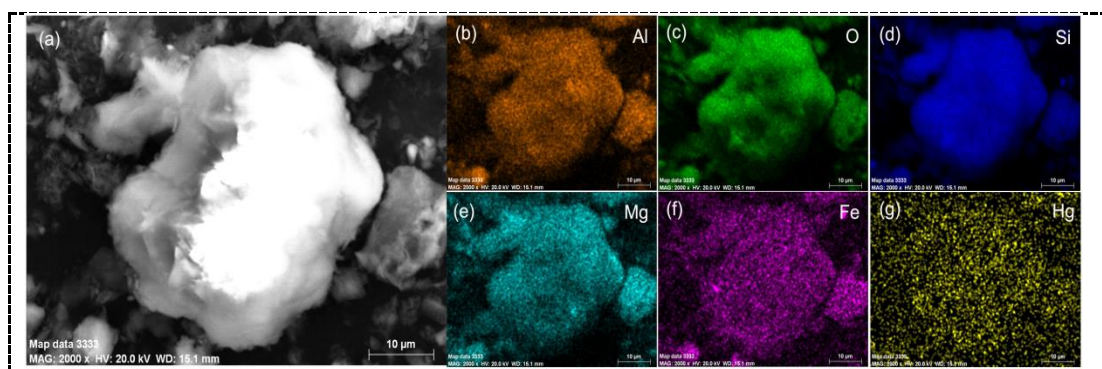**Figure 2.** (a) SEM images of ATP (a), KH550-grafted ATP (b), and PMDA modified ATP (P-ATP) (c).

Figure 3. (a) SEM image of Hg-loaded P-ATP and elemental distribution images of Al (b), O (c), Si (d), Mg (e), Fe (f), and Hg (g).

3.2. Effect of temperature, pH, and contact time on the adsorption

To evaluate the efficiency of the as-prepared adsorbent, the adsorption process for heavy metals should be conducted under the optimum adsorption conditions, including the operation temperature, pH, and contact time.
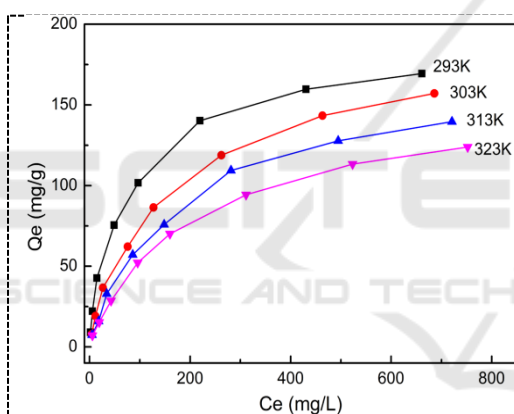

Figure 4. Effect of different temperatures operated on Hg (II) removal process. (pH=5.0, contact time=2 h, adsorbent dose= 1 g/L).
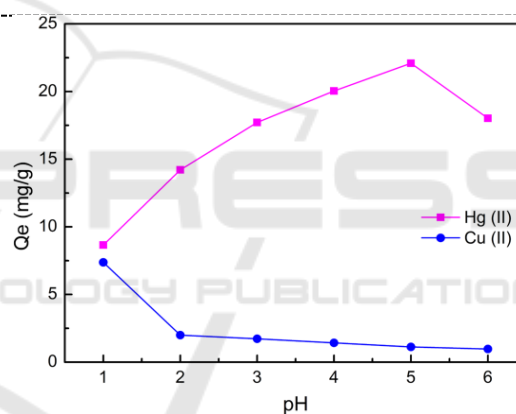
Figure 5. Effect of pH on Hg (II) and Cu (II) removal in aqueous solutions. (T=293 K, contact time= 2 h, adsorbent dose= 1 g/L).

The effect of temperature on the adsorption is shown in Figure 4, lower temperature is confirmed to be better for Hg (II) removal. Besides, the influence of pH is also investigated from pH=1.0 to pH=6.0 as show in figure 5. Higher pH is not considered due to the precipitation generated when the concentration of Hg (II) goes higher. By contrast, lower pH is not suitable for the test either, because H^+ is also positively charged and much smaller than mercury ions, making it a relatively competitive opponent to occupy the finite active sites on the P-ATP particles. Thus, pH=5.0 is selected for the following experiments.
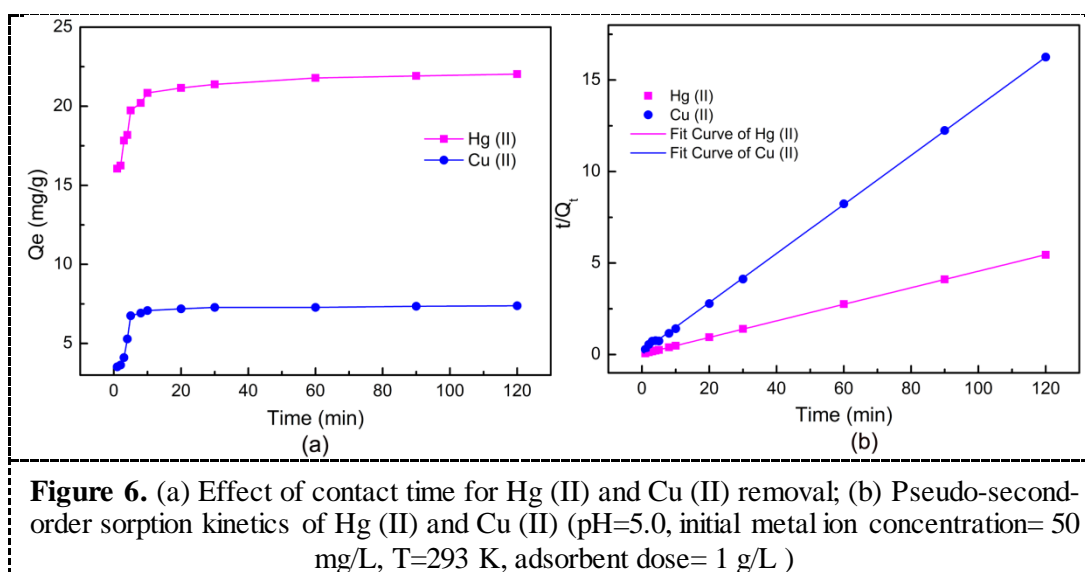
Figure 6. (a) Effect of contact time for Hg (II) and Cu (II) removal; (b) Pseudo-second-order sorption kinetics of Hg (II) and Cu (II) (pH=5.0, initial metal ion concentration= 50 mg/L, T=293 K, adsorbent dose= 1 g/L)

Contact time is also an important factor when the adsorbent is used for the practical application. Figure 6 illustrates the influence of contact time for Hg (II) and Cu (II) removal. At the initial stage in the first 30 minutes, the adsorption rate is very fast due to the unsaturation of the adsorbent, as the adsorption sites are saturated, the adsorption equilibrium is achieved and the adsorption rate is decreased.

Table 1. Kinetic parameters for adsorption of Hg (II) and Cu (II).

Metal ions	$Q_{e,exp.}$ (mg g^{-1})	Pseudo-second-order model		
		$Q_{e,cal.}$ (mg·g^{-1})	$k_2 \times 10^2$ (g·mg^{-1}·min^{-1})	R^2
Hg (II)	22.03	22.22	4.35	0.9999
Cu (II)	7.38	7.46	10.5	0.9997

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + (\frac{1}{Q_e})t \tag{1}$$

The pseudo-second-order model is introduced to describe the adsorption kinetic process which could be expressed as the formula (1), where t is the contact time, Qt and Qe are the adsorption capacity at time t and adsorption equilibrium, respectively. k_2 is the rate constant of pseudo-second-order kinetic model. The relevant kinetic data are calculated and listed in Table 1. The experimental Qe data is close to the calculated ones in this model with the correlation coefficient values R_2 very close to 1, which could be attributed to a chemical adsorption on the P-ATP.
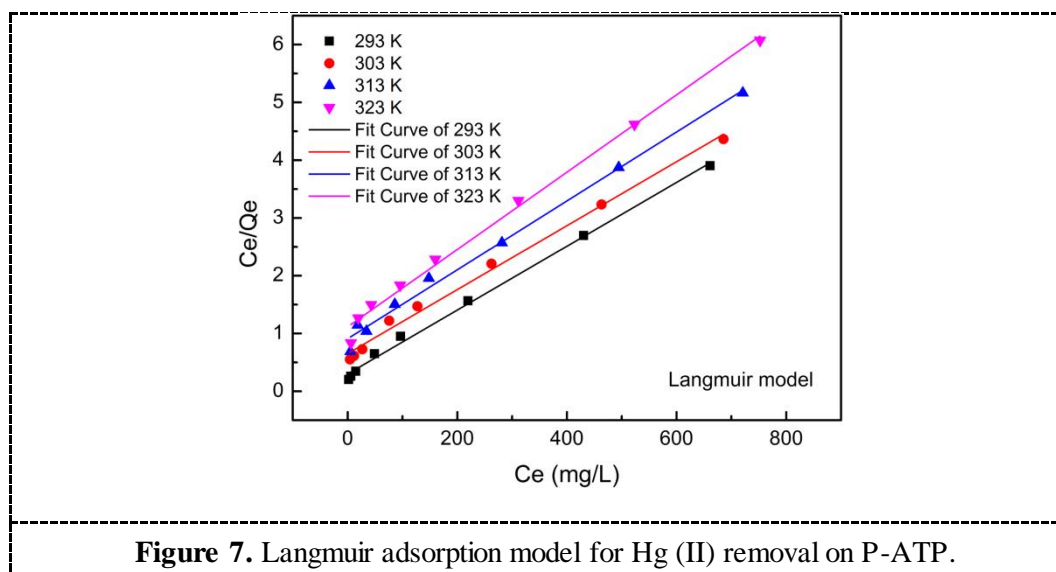
Figure 7. Langmuir adsorption model for Hg (II) removal on P-ATP.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bC_e} \tag{2}$$

In order to analyse the adsorption properties of P-ATP, Langmuir adsorption isotherm model is used to describe the adsorption process. The Langmuir adsorption isotherm model is described as formula (2) [11], where Ce is the equilibrium concentration, Qe is the amount of Hg (II) adsorbed on P-ATP at equilibrium. Qm and b are the maximum adsorption capacity and Langmuir constant, respectively. The fit curves of the Langmuir adsorption isotherm model at different temperatures are shown in Figure 7. The Langmuir model well fits the experimental data with all R_2 close to 1, and we could calculate the equilibrium adsorption capacity of Hg (II) on P-ATP as high as 181.16 mg/g with R_2= 0.9983. Moreover, the results indicate a monolayer adsorption process on P-ATP [12].

3.3. Regeneration of the adsorbent

The adsorbent was regenerated with 1 M HNO_3 solution. After seven times of adsorption-desorption cycles, the adsorption capacity for Hg (II) were measured to be 106.4 mg/g, exhibiting good regeneration properties as well.

4. Conclusions

In this work, PMDA was successfully grafted on ATP with KH550 as a coupling linker and PMDA as a chelating group. The obtained adsorbent exhibited enhanced removal efficiency towards mercury (II) from aqueous solutions. The experimental data could be described with pseudo-second-order kinetic model which indicated a chemical adsorption on P-ATP. Moreover, the adsorption process could be well fitted with Langmuir adsorption isotherm model and could be attributed as a monolayer adsorption. Meanwhile, the adsorption capacity was calculated to be 181.16 mg/g, and the adsorbent exhibited good regeneration properties as well.

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