



Nano α - Al_2O_3 for removal of Hg(II) from water: Adsorption and desorption studies

Qing-Zhou Zhai

Research Center for Nanotechnology, Changchun University of Science and Technology,
Changchun, 7186 Weixing Road, Jilin Province, P. R. China

ABSTRACT

Solid phase method was used to synthesize α - Al_2O_3 using ammonium sulfate as raw material. Powder X-ray diffraction and scanning electron microscopy were used to characterize the product. The synthesized material was used as adsorbent to investigate the effects of acidity, adsorption time, initial concentration of Hg^{2+} , adsorbent dosage and adsorption temperature on the adsorption of Hg^{2+} . The adsorptive results showed that the optimal adsorption conditions are: for the initial Hg^{2+} concentration of 0.80 mg/ml, α - Al_2O_3 amount: Hg^{2+} amount (g/g) = 4.17, pH = 3.5, contact time 10 min, temperature 20 °C. The maximum adsorptive amount of Hg^{2+} was 157.8 mg Hg^{2+} /g (α - Al_2O_3). The effects of desorption of three type desorptive agents HAc, HNO_3 , HCl, were probed. The results indicated that the optimal desorption agent is 0.10 mol/L HCl. When desorption was 10 min, the highest desorption rate could reach 97.92%.

Keywords: mercury(II), nano α - Al_2O_3 , removal, adsorption, desorption, water.

INTRODUCTION

Pollution of heavy metals and other organic compounds pollution are different. For many organic compounds, by nature itself physical, chemical or biological purification, the harmful properties can be reduced or relieved. While the heavy metals can accumulate, they are difficult to be degraded in the environment. At present, due to the heavy metal mining, smelting, processing, it led to a lot of heavy metals such as lead, mercury, cadmium, cobalt entering into the atmosphere, water, soil, causing serious environmental pollution [1]. The heavy metals discharged with wastewater, even if the concentration is small, can be accumulated in the algae and sediments. They are adsorbed by fish and shellfish surface, producing the food chain enrichment, resulting in pollution nuisance. Heavy metals can strongly interact with protein and various enzymes in the human body, causing them to lose activity. It may also be enriched in some organs in the human body. If it exceeds the limit that the body can withstand, acute poisoning, the sub acute poisoning, chronic poisoning can be caused, causing great harm to the human body. Mercury and its compounds belong to highly toxic substances, can be accumulated in the body. Inorganic mercury ions going into the water can be changed into the more toxic organomercurials that enter the body through the food chain and cause systemic poisoning action.

According to the change of metal chemical forms classification in management process, the methods can be divided into: chemical form transformation method and chemical form no change method. According to the processing means classification, the methods can be divided into physical method, chemical method, physical chemistry method and biochemical method etc [1-3]. Processing water by adsorption method mainly relies on the fact that some materials with larger specific surface area and higher surface energy have a stronger adsorption capacity towards the pollutants and separate and remove the pollutants from water, achieving the purpose of purification water. This adsorption interaction can be a strong surface chemistry coordination, complexation, can also be a van der Waals

force or electrostatic attraction physical effect etc. For a long time, adsorption method has been one of the most important water treatment methods, has been widely used in various water supply and wastewater treatment. Using adsorption method to remove the pollutants in water has the advantages of high efficiency, high speed, strong adaptability and easy operation. In addition, as the sorbents are insoluble in water and adsorption occurs only on the solid surface and no further chemical reactions occur, so in general a new chemical substance can not be introduced to the treated water. Activated carbon has a strong adsorption capacity on the part of the heavy metal ions, is capable of removing heavy metal ions from wastewater. But the activated carbon is expensive and regeneration is complex, which is not suitable for treatment of high concentration pollutant wastewater and makes its application limited [4]. Adsorption method can selectively remove heavy metal ions in wastewater, they cannot migrate into environment and cause worse influence on the human environment.

Alumina is a white crystalline powder, with alumina octahedral as the basic structure unit. So far, the crystalline states of 12 aluminas have been found. The alumina that has already been determined have α -, β -, γ -, θ -, κ -, δ -, η -, χ type [5, 6], among which the most widely used one is α -, β - Al_2O_3 . α - Al_2O_3 has a high temperature resistant characteristic. Activated alumina materials generally have the advantages of high stability, acid and alkali resistant, high temperature resistant, usually having high specific surface area, thus they have very strong adsorption ability for many inorganic ions and also have stronger adsorption actions to some organic compounds [7]. Nano material has a surface effect, has very great chemical activity. With the increase of surface atoms, surface energy greatly increases [8]. Nanometer alumina powders have the advantages of large specific surface area, higher chemical activity and thermal stability, high hardness and corrosion resistance and other excellent properties and are widely used in aerospace, luminescent materials, catalyst carrier, artificial gemstones and other field [9-11]. However, according to our knowledge, no report is available regarding the adsorption removal of mercury(II) from aqueous solution using α - Al_2O_3 .

In this paper, solid state method is used to prepare nanometer α - Al_2O_3 powders and powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) are used to characterize the prepared α - Al_2O_3 powders. Hg^{2+} is adsorbed by using the prepared nanometer α - Al_2O_3 , the optimal conditions of adsorption of Hg^{2+} have been established, the mechanism of adsorption is discussed and desorption of the materials is studied.

EXPERIMENTAL SECTION

Reagents

Unless specially stated, all the reagents used in the experiments were of analytical grade. The water was deionised water.

Reagents for the synthesis of α - Al_2O_3 included ammonium aluminium sulfate dodecahydrate ($\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) (Jinshan Chemical Plant, China) and soluble starch ($\text{C}_6\text{H}_{10}\text{O}_5$)_n [Shanghai Company of Chemical Reagents, Chinese Medicine Group, China].

Mercury nitrate was obtained from Chemical Reagent Works of Taixing City, China. Mercury stock standard solution (1 g/L) was prepared from a ready made mercury nitrate (Taixing Chemical Reagent Factory, China). Mercury working solutions were prepared just before use by appropriate dilutions of stock solution. 0.1 mol/L nitric acid and 0.1 mol/L sodium hydroxide solutions were used for adjusting the initial pH value of solutions.

Apparatus

Powder X-ray diffraction (XRD) patterns were collected on a Siemens D5005 diffractometer (Germany) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$ and operating at 40 kV and 30 mA). Typically, the diffraction data were collected from 0.4° to 10° (2θ) with a resolution of 0.02° . The morphology was analyzed with a XL 30 ESEM FEG (American FEI Company) scanning electron microscope. The accelerating voltage used was 20 kV. Mercury content determination was accomplished on a 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China) [12].

Procedure

Procedure for the Preparation of α - Al_2O_3

2.0000 g of ammonium aluminium sulfate dodecahydrate and a 2.0000 g of soluble starch were mixed, placed in a mortar, well mixed and grinded to a thin degree. After it, the mixture was put in a crucible, placed in a muffle oven and the crucible was well covered. The temperature of the muffle oven was adjusted. At 90°C , constant temperature was made for 15 min. At 240°C , constant temperature was made for 40 min. At 800°C , constant temperature was made for 40 min. And finally at 1200°C , constant temperature was made for 1 h. Then, the cover of crucible was

opened. The temperature was adjusted to 750°C for the oven. At 750°C, constant temperature was made for 1 h. Thereby, nanoscale α -Al₂O₃ powders were obtained [12].

Method for the determination of mercury

The concentration of mercury in the sample was analyzed using a spectrophotometer by forming a complex with 2-(5-bromo-2-pyridineazo)-5-diethylaminophenol (5-Br-PADAP) in the presence of anionic surface active agent dodecyl sodium sulfate at a wavelength of 562 nm [13]. A linear range of working curve for the determination of mercury using the method was 0 ~ 1.4 $\mu\text{g/ml}$ and the sensitivity apparent molar absorption coefficient of method was $\epsilon_{562\text{ nm}} = 8.26 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Optimum adsorption conditions study

Effect of the initial pH of solution: A total of seven portions of 30 ml of 0.8 mg/ml Hg²⁺ standard solution, were respectively placed into 100-ml beakers. The pH value was respectively adjusted to 1.0, 2.0, 3.0, 3.5, 4.0, 4.5, 5.0. A total of seven portions of 0.10 g of α -Al₂O₃ were weighed and at room temperature (20 ± 1 °C) they were respectively added to the above-stated samples. Under magnetic stirring, adsorption was made for 10 min. And then the sample was placed in a centrifuge tube and under the condition of 8000 r/min centrifuged for 10 min. After taking out the centrifugal tube, the supernatant was taken and according to the above stated *Method for the determination of mercury* the concentration of Hg²⁺ was determined. Its adsorption rate was calculated and the optimum pH of adsorption was obtained.

Effect of contact adsorption time: At room temperature (20 ± 1 °C), a total of eight portions of 30 ml of standard solution of Hg²⁺ of 0.80 mg/ml concentration, were respectively placed in the 8 beakers of 100-ml and respectively adjusted to pH 3.5. A total of eight portions of 0.10 g α -Al₂O₃ were weighed and respectively added to the above-stated sample. After contact adsorption was respectively made for 5, 10, 20, 30, 40, 60, 80, 100 min at room temperature, the sample was placed in a centrifuge tube and centrifuged for 10 min under the condition of 8000 r/min. After taking out the centrifugal tube, the supernatant was taken and according to the above stated *Method for the determination of mercury* the concentration of Hg²⁺ was determined. Its adsorption rate was calculated and optimum adsorption time was obtained.

Effect of temperature: A total of five portions of 30 ml of 0.80 mg/ml Hg²⁺ standard solution, were respectively placed into 100-ml beakers. The pH value was respectively adjusted to 3.5. A total of five portions of 0.10 g of α -Al₂O₃ were weighed and they were respectively added to the above-stated samples. After adsorption was made for 10 min under magnetic stirring at temperature 4, 20, 30, 40, 50 °C, respectively, the sample was placed in a centrifuge tube and under the condition of 8000 r/min centrifuged for 10 min. After taking out the centrifugal tube, the supernatant was taken and according to the above stated *Method for the determination of mercury* the concentration of Hg²⁺ was determined. Its adsorption rate was calculated and the optimum temperature of adsorption was obtained.

Effect of initial Hg²⁺ concentration: A total of five portions of 30 ml of 0.1, 0.3, 0.5, 0.8, 1.0 mg/ml Hg²⁺ standard solution, were respectively placed into five 100-ml beakers. The pH value was respectively adjusted to 3.5. 0.1 g of α -Al₂O₃ were respectively weighed and added to the above-stated samples. After adsorption was made for 10 min under magnetic stirring at room temperature (20 ± 1 °C), the sample was placed in a centrifuge tube and under the condition of 8000 r/min centrifuged for 10 min. After taking out the centrifugal tube, the supernatant was taken and according to the above stated *Method for the determination of mercury* the concentration of Hg²⁺ was determined. Its adsorption rate was calculated and the optimum Hg²⁺ concentration was obtained.

Effect of adsorbent dosage: A total of five portions of 30 ml of 0.80 mg/ml Hg²⁺ standard solution, were respectively placed into five of 100-ml beakers. The pH value was respectively adjusted to 3.5. A total of five portions of 0, 0.05, 0.1, 0.3, 0.5 g of α -Al₂O₃ were respectively weighed and added to the above-stated samples. After adsorption was made for 10 min under magnetic stirring at room temperature (20 ± 1 °C), the sample was placed in a centrifuge tube and under the condition of 8000 r/min centrifuged for 10 min. After taking out the centrifugal tube, the supernatant was taken and according to the above stated *Method for the determination of mercury* the concentration of Hg²⁺ was determined. Its adsorption rate was calculated and the optimum adsorbent dosage was obtained.

The adsorption rate and adsorption capacity calculation formula is as follows:

$$\text{Adsorption rate} = (C_0 - C_e) / C_0 \times 100\% \quad (1)$$

$$\text{adsorption capacity } Q_e = (C_0 - C_e) \times 30 / W \quad (2)$$

Where C₀ and C_e are the Hg²⁺ concentration in mg/ml at initial and equilibrium time, respectively, W is the weight of

adsorbent in grams. Q_e is adsorption capacity in mg/g.

Desorption of mercury(II) from adsorbent

Experimental material preparation for desorption: 0.10 g of α -Al₂O₃ was weighed and placed in a 30 ml of 0.80 mg/ml Hg²⁺ standard solution. The pH value was adjusted to 3.5. After adsorption was made for 10 min under magnetic stirring at room temperature (20 ± 1 °C), the sample was placed in a centrifuge tube and under the condition of 8000 r/min centrifuged for 10 min. After taking out the centrifugal tube, the supernatant was discarded and (α -Al₂O₃)-Hg composite material was obtained as desorption experimental material, marked as A.

Desorption experiment: The effects of HCl, HNO₃, HAc on Hg desorption in the (α -Al₂O₃)-Hg composite material was studied in order to obtain the optimum desorption agent. Then, the optimum desorption agent concentration was sequentially studied.

A total of five portions of 30 ml of 0.10 mol/L HCl (or HAc, HNO₃) solutions, were respectively taken and placed in 100-ml beakers. A total of five portions of 0.10 g of material A were weighed and respectively placed into the above-stated HCl (or HAc, HNO₃) solutions. After desorption was made for 0, 5, 10, 20, 30 min under magnetic stirring at room temperature (20 ± 1 °C), the sample was placed in a centrifuge tube and centrifuged at the condition of 8000 r/min for 10 min. After taking out the centrifugal tube, the supernatant was taken and according to the above stated "Method for the determination of mercury" the concentration of Hg²⁺ was determined. Desorption rate was calculated and the optimum desorption time was obtained.

$$\text{Desorption rate} = (A/B) \times 100\% \quad (3)$$

Where A is the amount of mercury desorbed from adsorbent and B is the amount of mercury loaded on adsorbent.

Experiment of hydrogen chloride concentration on desorption effect: A total of three portions of 30 ml of 0.010, 0.10, 1.0 mol/L HCl solution, were taken and respectively placed in 100-ml beakers. A total of three portions of 0.10 g of material A were respectively weighed and placed into the above-stated HCl solution. After desorption was made for 10 min under magnetic stirring at room temperature (20 ± 1 °C), the sample was placed in a centrifuge tube and under the condition of 8000 r/min centrifuged for 10 min. After taking out the centrifugal tube, the supernatant was taken and according to the above stated "Method for the determination of mercury" the concentration of Hg²⁺ was determined. Desorption rate was calculated and the optimum hydrogen chloride desorption concentration was obtained.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Results of the powder X-ray diffraction (XRD) characterization of adsorbent show (Fig.1) that the diffraction peaks of product are coincided with those of α -Al₂O₃ [12], indicating that the adsorbent prepared was α -Al₂O₃. By using Scherrer formula the primary particle size of α -Al₂O₃ powders was calculated and the calculated result was 110 nm. Scanning electron microscopy (SEM) images can reflect the shape and size of samples. The SEM micrographs of nanoscale α -Al₂O₃ powders (Fig. 2) display that α -Al₂O₃ powder particles morphology presented global formed and an average particle size of their aggregated products was 140 nm.

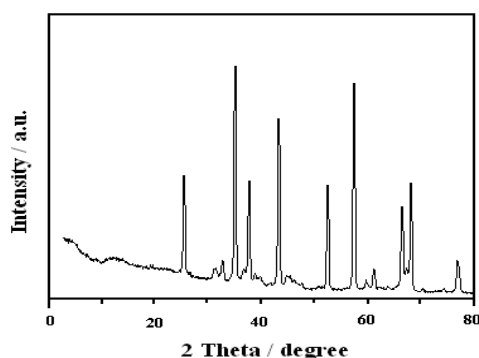


Fig.1: XRD pattern of α -Al₂O₃ sample

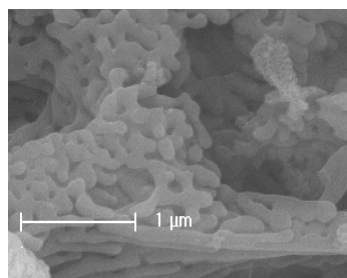


Fig.2: SEM images of α - Al_2O_3 sample

Effect of initial pH value on adsorption

The pH value of the solution can affect the surface charge of an adsorbent as well as affect the degree of ionization and the chemical form of a metal ion. The effect of pH on adsorption of Hg^{2+} by α - Al_2O_3 was studied by varying the initial pH value for an initial Hg^{2+} concentration of 0.80 mg / ml, 0.10 g of α - Al_2O_3 adsorbent dosage and an adsorption time of 10 min at a temperature of 20°C. Figure 3 reveals an effect of solution initial pH value on α - Al_2O_3 adsorption mercury (II). The results showed (Fig. 3) that the rate of Hg^{2+} adsorption went up with the increase of pH value (pH = 1 - 3.5). After pH is raised, hydrogen ion can be neutralized and the competitive effect of hydrogen ion can be reduced, being advantageous to the adsorption of Hg^{2+} by the material. When pH value was 3.5, α - Al_2O_3 showed maximum adsorption rate for Hg^{2+} . Thus, a pH value of 3.5 was selected to be the optimum acidity.

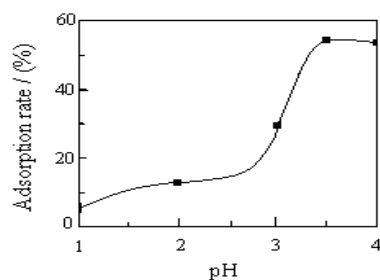


Fig.3: Effect of pH on the adsorption of Hg^{2+}
 $[\text{Hg}^{2+}] = 0.80 \text{ mg/mL}$, 0.10 g α - Al_2O_3 , contact time 10 min, temperature 20 °C.

Effect of adsorbent dosage and mercury(II) initial concentration on adsorption

The adsorption site number for mercury(II) depends on the amount of α - Al_2O_3 . This work studied the effect of α - Al_2O_3 dosage (0 - 10 g / L) on Hg^{2+} (0.80 mg/mL) removal efficiency at pH 3.5 at a temperature of 20 °C. The results indicated that over the range of 0 - 3.3 g / L of α - Al_2O_3 dosage the adsorption percentage of mercury(II) increased with the increase in the α - Al_2O_3 dosage. Maximum removal of Hg^{2+} was obtained over the adsorbent dosage of 3.3 - 15 g / L. 3.3 g / L of α - Al_2O_3 dosage was selected for further work.

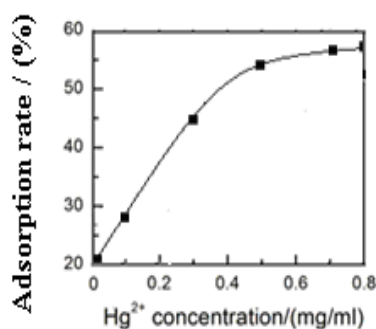


Fig.4: Effect of mercury(II) concentration on adsorption rate
pH 3.5, 0.10 g α - Al_2O_3 , contact time 10 min, temperature 20 °C.

The effect of Hg^{2+} initial concentration (0 - 1.0 mg/mL) on adsorption efficiency was carried out by using 3.3 g / L of α - Al_2O_3 dosage at pH 3.5 at a temperature of 20 °C. It is concluded from the experimental results (Fig. 4) that with the increase of the Hg^{2+} concentration, the adsorption rate grew. When concentration of Hg^{2+} was 0.80 mg/ml, the adsorption rate was a maximum and the optimal adsorption Hg^{2+} concentration was determined to be 0.80

mg/ml.

Effect of contact time on the adsorption of Hg^{2+}

Figure 5 gives results of the effects of different contact time on the adsorptive rate of Hg^{2+} . It can be seen that rapid adsorption of mercury(II) was conducted within the first 10 min, and thereafter adsorption reached equilibrium. Further experiments were conducted at a contact time of 10 min. The reason for causing this phenomenon lies in that in a period of initial stage on the surface of $\alpha\text{-Al}_2\text{O}_3$ adsorbent there were a large number of vacant sites for the adsorption of Hg^{2+} . And after a period of time the remaining vacant surface sites are difficult to be occupied due to the repulsive forces between the solute molecules on the solid phase and in aqueous phase.

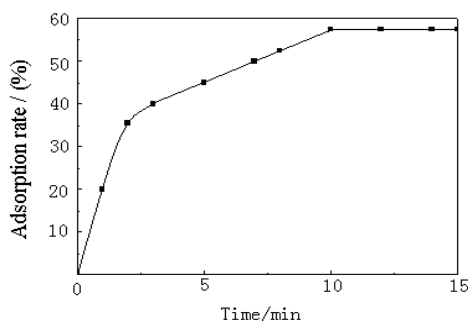


Fig.5: Effect of contact time on mercury(II) adsorption rate
pH 3.5, $[\text{Hg}^{2+}] = 0.80 \text{ mg/mL}$, 0.10 g $\alpha\text{-Al}_2\text{O}_3$, temperature 20 °C.

Effect of temperature on the adsorption of Hg^{2+}

The effect results of temperature on Hg^{2+} adsorption (Fig.6) shows that with increasing temperature over 4 - 20 °C the adsorption rate increased, suggesting that the adsorption is physical adsorption in the temperature range and belongs to the endothermic process. Rise in temperature is beneficial to the progress of adsorption. With the increase of temperature over 20 - 50 °C, the adsorption rate decreased, demonstrating that in the temperature range the adsorption is chemical adsorption, which belongs to an exothermic process. Rise in temperature is not beneficial to the progress of adsorption. From the above results, at 20 °C the adsorptive rate is a maximum, thus the optimal adsorption temperature was determined to be room temperature 20 ± 1 °C.

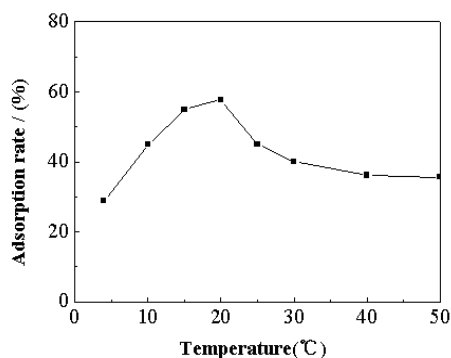


Fig.6: Effect of temperature on the adsorption of Hg^{2+}
pH 3.5, $[\text{Hg}^{2+}] = 0.80 \text{ mg/mL}$, 0.10 g $\alpha\text{-Al}_2\text{O}_3$, contact time 10 min.

The optimum conditions for the adsorption of Hg^{2+} by $\alpha\text{-Al}_2\text{O}_3$ are: for the initial Hg^{2+} concentration of 0.80 mg/ml, $\alpha\text{-Al}_2\text{O}_3$ amount: Hg^{2+} amount (g/g) = 4.17, pH 3.5, contact time of 10 min, room temperature (20 ± 1) °C. At this time, Hg^{2+} maximum adsorption capacity is 157.8 mg (Hg^{2+})/g ($\alpha\text{-Al}_2\text{O}_3$).

Performance of adsorption anti-interference

Under the experimental conditions of optimal adsorption $\text{Hg}(\text{II})$ defined by the present article and in the presence of 0.80 mg/mL $\text{Hg}(\text{II})$, when the relative error of adsorption rate is less than $\pm 5\%$, the following amount (mass ratio, *m/m*) coexisting ions have not significant interference: Ca^{2+} (20), Cd^{2+} (5), Cu^{2+} (5), Fe^{2+} (10), Mg^{2+} (15), Pb^{2+} (3), Zn^{2+} (10); Cr^{3+} (3), Fe^{3+} (3); Cl^- (100), NO_3^- (80), H_2PO_4^- (60), SO_4^{2-} (50), $\text{Cr}_2\text{O}_7^{2-}$ (30).

Desorption study

The desorption effect of HCl, HNO₃ and HAc is compared and the results show (Fig.7) that for 0.10 mol/L hydrochloric acid at 10 min mercury (II) desorption rate reached a maximum, reaching 97.92% close to complete desorption. After 10 min, it may be because the desorbed Hg²⁺ concentration was greater and adsorption phenomenon again began to appear, leading to a decrease of desorption rate. Similar phenomena appeared for 0.10 mol/L nitric acid, acetic acid. At 10 min, the desorption rates reached maxima, respectively, being 92.87%, 89.70%. However, compared with hydrochloric acid desorption, the desorption effects of nitric acid and acetic acid were not ideal. From the above three different acid desorption effect, it can be seen that HCl desorption effect was the most ideal, close to complete desorption. So further hydrochloric acid was selected and used to do the effect of acidity on desorption impact. The results of effect of hydrochloric acid concentration on Hg (II) desorption rate is seen in Table 1, showing that when hydrochloric acid was 0.10 mol/L, the desorption rate was a maximum. Its reason is two points: the first is that because after the addition of acid, hydrogen ion or hydronium ions and metal ions compete the active sites on the adsorbent, so the acidity is bigger, the competition ability with metal ion is stronger, the desorption rate is made greater. The second is due to it when acidity is larger, the mechanical strength, surface structure or physicochemical properties of the adsorbent can be destroyed, which, on the contrary, is not conducive to the conduct of desorption.

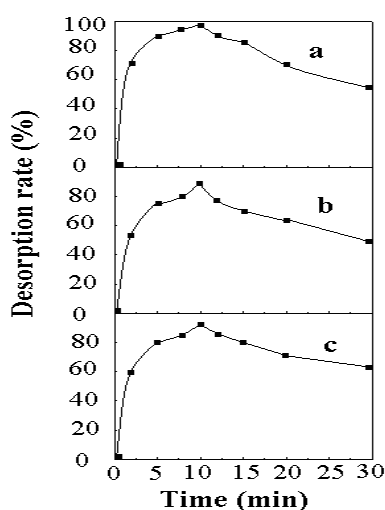


Fig.7: Effect of desorption agent and time on desorption efficiency
(a) HCl, (b) HNO₃, (c) HAc.

Table 1: Effect of the concentration of hydrogen chloride on desorption efficiency

Concentration of hydrogen chloride (mol / L)	Desorption rate (%)
0.010	64.78
0.05	80.33
0.10	96.41
0.50	90.03
1.0	88.30

CONCLUSION

In this paper α -Al₂O₃ was successfully prepared and the average particle size of its aggregated product was 140 nm. The optimum experimental conditions for the adsorption of Hg²⁺ by α -Al₂O₃ were obtained by study. The desorption effects of HAc, HNO₃, HCl three kinds of desorption agents were explored. The optimum desorption agent was 0.10 mol/L HCl. At desorption of 10 min, the highest desorption rate could be reached to 97.92%.

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