



Adsorptive Performance of Nanoscale α -Al₂O₃ Towards La(III)

QING-ZHOU ZHAI* and LU-GUO CHEN

Research Center for Nanotechnology, Changchun University of Science and Technology, 7186 Weixing Road, Changchun 130022, P.R. China

*Corresponding author: Fax: +86 431 85383815; Tel: +86 431 85583118; E-mail: zhaiqingzhou@163.com; zhaiqingzhou@hotmail.com

(Received: 22 October 2010;

Accepted: 14 May 2011)

AJC-9947

Nanomaterials are ideal adsorptive materials for trace element and have great potential. In this paper, the preparation of α -Al₂O₃ and its adsorptive and desorptive properties towards La³⁺ in aqueous phase were studied. The effect of pH, temperature and time on the adsorption of La³⁺ by nanoscale α -Al₂O₃ was discussed. The results showed that the adsorptive effect of the α -Al₂O₃ on La³⁺ is the best over the range of pH 5-7. Adsorptive rate increases with increasing temperature, but the effect of temperature is not high. Thus, the adsorption is generally carried out at room temperature. When adsorptive time is 20 min, the adsorptive ratio is the highest and reaches 92.14 %. It is found for the studies of desorptive conditions that when 0.1 mol/L AcOH was used as an adsorbent, the desorptive effect of La³⁺ was better. When the desorption was 6 h, the desorptive ratio reached to 97.03 %.

Key Words: Adsorption, La³⁺, Nanoscale α -Al₂O₃.

INTRODUCTION

As the particle diameter of a nanomaterial is very small, the atomic number of surface is relatively very large, surface area and surface binding energy are also accordingly very large, otherwise, surface atoms still have unsaturated property and easily combine with other atoms to tend toward stability, thus nanomaterial has higher chemical activity¹. The surface atoms of nanomaterial can integrate with metal ions in a way of electrostatic action, *etc.*, thus nanomaterials have very strong adsorptive ability to some metal ions and within shorter time adsorptive equilibriums can be reached. Simultaneously, the specific surface areas of nanomaterials are very large, thus they have larger adsorptive capacity². The involved studies used nanometer TiO₂^{3,4} as adsorptive materials to enrich metal ions. Besides nanometer TiO₂, the reports where ZrO₂⁵, Fe₂O₃⁶, ZnO⁷ were used as adsorptive materials are also seen.

In this work, aluminium ammonium sulfate and starch are used as raw materials to prepare nanometer α -Al₂O₃ powders by using solid phase method and powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to characterize the prepared nanometer α -Al₂O₃ powders. The prepared nanometer α -Al₂O₃ powders are used to adsorb La³⁺. From a few aspects such as solution acidity, temperature and adsorptive time, *etc.*, the conditions that influence its adsorption are studied and the mechanism of adsorption is discussed. This paper also studied the desorption of the post-adsorbed lanthanum ion.

EXPERIMENTAL

Ammonium aluminium sulfate dodecahydrate (NH₄Al(SO₄)₂·12H₂O) (Jinshan Chemical Plant, China); soluble starch (C₆H₁₀O₅)_n [Shanghai Company of Chemical Reagents, Chinese Medicine Group]. Unless specially stated, all the reagents used in the experiments were of analytical grade. The deionized water was used throughout.

La³⁺ standard solution: 0.1173 g of lanthanum (spectral purity, Shanghai Company of Chemical Reagents, Chinese Medicine Group) was dissolved in 5 mL of 5 mol/L HCl solution, diluted to 100 mL by water and shaken well. The solution contained 1 mg/mL of La³⁺.

HCl-KCl buffer solution of pH 2.2: 92.48 mL of 0.2 mol/L KCl solution and 7.52 mL of 0.2 mol/L HCl solution were mixed to obtain the HCl-KCl buffer solution of pH 2.2.

Powder X-ray diffraction (XRD) patterns were collected on a Philips PW1710 (Netherlands) diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$ and operating at 40 kV and 30 mA). Typically, the diffraction data were collected from 5-90° (2 θ) with a resolution of 0.02°. Transmission electron microscopic (TEM) images were observed on a Jeol JEM-2010 (Japan) electron microscope. Scanning electron microscopic (SEM) photographs were determined on a Philips XL 30 ESEM FEG (Netherlands) scanning electron microscope. A 722S spectrophotometer (Shanghai Lingguang Technique Co. Ltd., China) equipped with 1-cm cells was used in the determination of absorbance. A HJ-6A digital display constant temperature

water-bath boiler (Jiangsu Jintan Ronghua Apparatus Manufacture Co. Ltd., China) was employed to control experimental temperature.

Preparation of nanoscale α -Al₂O₃: In this work, a nanoscale α -Al₂O₃ was prepared using solid phase thermal diffusion method⁸ and the steps are as follows:

2 g of ammonium aluminium sulfate dodecahydrate and 2 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.

Adsorption of La³⁺ in solution by nanoscale α -Al₂O₃: 100 mL of 10 μ g/mL of La³⁺ solution was added to a 250 mL conical flask and 0.25 g of nanoscale α -Al₂O₃ was added to it. Under a definite temperature and a definite pH, oscillations were lasted out for 20 min and then centrifugated for 20 min. An upper layer clear solution was taken and the residual La³⁺ concentration was determined by the spectrophotometric method. Adsorptive ratio of La³⁺ by the nanoscale α -Al₂O₃ was worked out under each condition.

Procedure for the determination of La³⁺: In 10 mL calibrated flasks, in turn were added different amount of 10 μ g/mL working solution of La³⁺, 1.0 mL of 0.05 % (w/v) DBC-ASA solution and 1 mL of pH 2.2 HCl-KCl buffer solution. The mixture was diluted to the mark with water, shake well, placed for 20 min. Absorbance was determined at 632 nm with 1 cm cells using a corresponding reagent blank as reference⁹. The results showed that Beer's law was obeyed over the range of 0-1.0 μ g/mL for La³⁺. Based on the experimental data obtained a linear regression equation was worked out: $A = 0.8936C + 0.0417$ (A: absorbance, C: μ g/mL), with a correlation coefficient of $\gamma = 0.9993$. From this the following formula was figured out:

$$C = \frac{(A - 0.0417)}{0.8936} \quad (1)$$

According to the following formula, the adsorptive ratio and adsorptive amount of La³⁺ in solution adsorbed by nanoscale α -Al₂O₃ were calculated.

$$\eta (\%) = \frac{(C_0 - C)}{C_0} \quad (2)$$

In the formula, η is adsorptive rate, C_0 is the initial concentration of solution (μ g/mL), C is the equilibrium concentration in solution when adsorption achieved equilibrium (μ g/mL), V is solution volume (mL), m is the mass of nanoscale α -Al₂O₃ (g).

Procedure for the effect of pH on adsorption: 100 mL of 10 μ g/mL La³⁺ working solution was added to a 250 mL conical flask and 0.25 g of nanoscale α -Al₂O₃ was added as an adsorber. 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide were, respectively used to adjust different pH. By performing the adsorption of La³⁺ in solution by nanoscale α -Al₂O₃, adsorptive ratio of La³⁺ in solution by nanoscale α -Al₂O₃ was calculated and pH-adsorptive rate curve was drawn.

Procedure for the effect of temperature on adsorption:

100 mL of 10 μ g/mL La³⁺ working solution was added to a 250 mL conical flask and 0.25 g of nanoscale α -Al₂O₃ was added as an adsorber. 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide were, respectively used to adjust pH = 7 under different temperature. Adsorptive ratio of La³⁺ in solution by nanoscale α -Al₂O₃ was calculated and temperature-adsorptive rate curve was drawn.

Procedure for the effect of time on adsorption:

100 mL of 10 μ g/mL La³⁺ working solution was added to a 250-mL conical flask and 0.25 g of nanoscale α -Al₂O₃ was added as an adsorber. 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide were, respectively used to adjust pH = 7 under different time. Adsorptive ratio of La³⁺ in solution by nanoscale α -Al₂O₃ was calculated and time-adsorptive rate curve was drawn.

Procedure for the experiment of desorption: The desorptive performance for nanoscale α -Al₂O₃ adsorption La³⁺ was studied by using EDTA, oxalic acid, acetic acid. The solutions, for which under the optimum adsorptive experimental conditions adsorption achieved equilibrium, were filtered. Afterwards, the nanoscale α -Al₂O₃ on filter papers were, respectively placed in 0.1 mol/L EDTA, 0.1 mol/L oxalic acid and 0.1 mol/L acetic acid for desorption. Desorptive ratio was calculated and desorptive time-desorptive ratio curve was drawn.

RESULTS AND DISCUSSION

Characterization of nanoscale α -Al₂O₃: Results of the XRD characterization of nanoscale α -Al₂O₃ are shown in Fig. 1. The diffraction peaks in the figure are coincided with those of α -Al₂O₃ as reported by Zhai and Lai⁸. Therefore, it showed that the sample prepared was α -Al₂O₃. By using Scherrer formula:

$$D = \frac{k\lambda}{(\beta \cos \theta)} \quad (3)$$

where, D = size of primary particle (nm), $k = 1.075$ (global crystal), $\lambda = 0.154178$ nm, β = integrated peak width measured (rad), θ is diffraction angle, peak location is 2θ value.

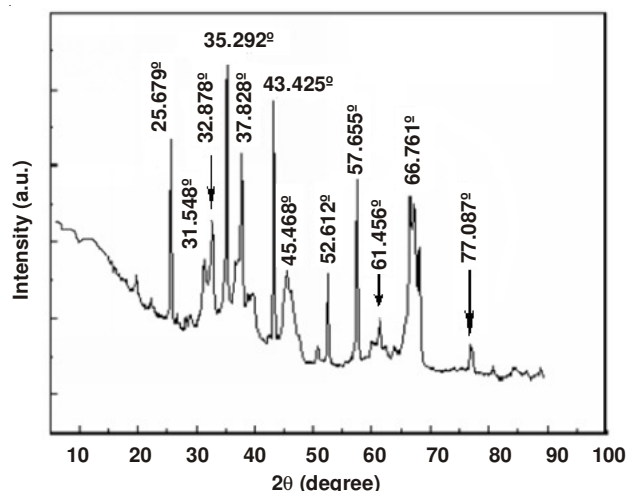


Fig. 1. XRD pattern of sample α -Al₂O₃ powder

The primary particle size of α -Al₂O₃ powders was calculated and the calculated result was 110 nm.

This basically coincides with the result measured by TEM (Fig. 2). It is observed by TEM that the prepared nanoscale α -Al₂O₃ sample particles presented global shape. The SEM micrographs of nanoscale α -Al₂O₃ powders are shown as Fig. 3. The results measured by SEM showed that nanoscale α -Al₂O₃ powder particles presented global form and an average particle size of its aggregated products was 140 nm.

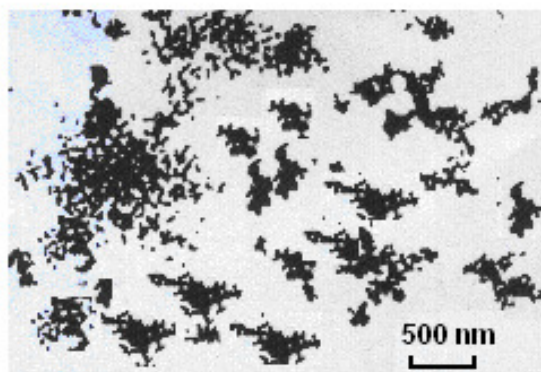


Fig. 2. TEM images of sample α -Al₂O₃ powder

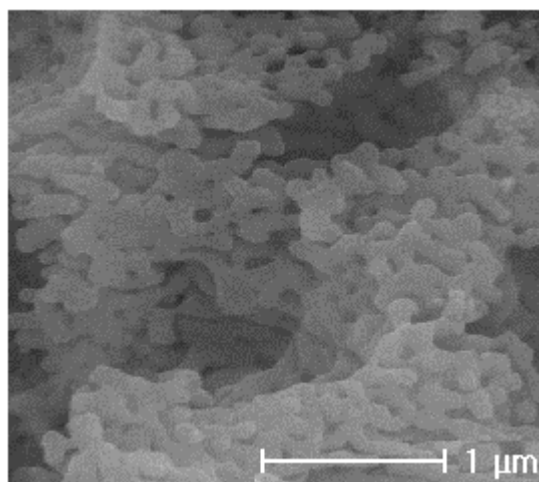


Fig. 3. SEM images of sample α -Al₂O₃ powder

Effect of pH on adsorption: pH value is one of the major factors that can influence adsorptive action. The results of effect of pH on adsorption are shown in Fig. 4. Fig. 4 shows that the adsorption of La(III) by α -Al₂O₃ was strongly influenced by pH. When pH was low (pH < 5), the adsorptive ratio was lower. However, when pH was more than 5, the adsorptive rate rapidly augmented. As alumina formed hydroxylated surface in aqueous solution, these surface hydroxyls would be protonated or deprotonated because the pH value was different. On the outside surface of alumina existed 3 kinds of groups: Al-OH₂⁺, Al-OH, Al-O⁻. When pH debased, it was advantageous to the formation of Al-OH₂⁺ and made the surface take positive charges. Furthermore, on lowering of pH, more the positive charges taken were. These charges and La³⁺ caused repulse, which was disadvantageous to adsorbing La³⁺. The Al-O⁻ and La³⁺ caused electrostatic attraction, which was advantageous to the adsorption of La³⁺.

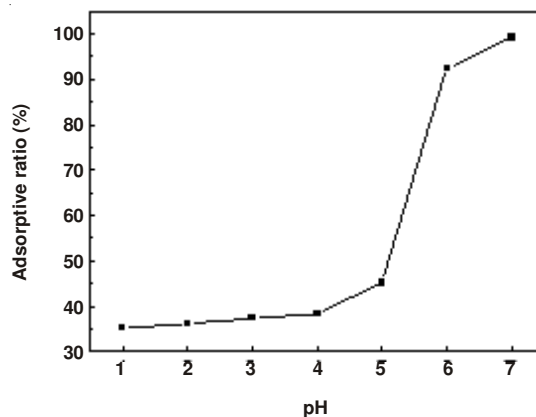
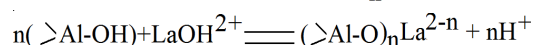
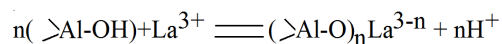


Fig. 4. Effect of pH on the adsorption of La³⁺

The existing form of La(III) ion in solution is also closely correlative to the pH value of the solution. The existing form of ion is different, the adsorptive ability on an adsorbent is also different. Due to the effect of double electric shell, the La(III) concentration on alumina surface could be far higher than that in the solution. Therefore, on the surface of alumina a large amount of LaOH₂⁺ might exist. Therefore, the adsorption of La(III) was mainly in the form of La³⁺ and its first order hydrolyzed product LaOH₂⁺ was adsorbed, because the surface of alumina took positive electric charge (the pH of isoelectric point is equal to 8.02). The adsorption of La(III) on alumina is deduced to be:



Effect of temperature on adsorption: The results of effect of temperature on adsorption are shown in Fig. 5. The results of effect of temperature on adsorption show that as temperature increased, the adsorptive ratio increased a little. However, the effect of temperature was not great. This mainly is because the vibration of La³⁺ quickened in the solution when temperature raised. This made La³⁺ be more easily adsorbed on nanoscale α -Al₂O₃.

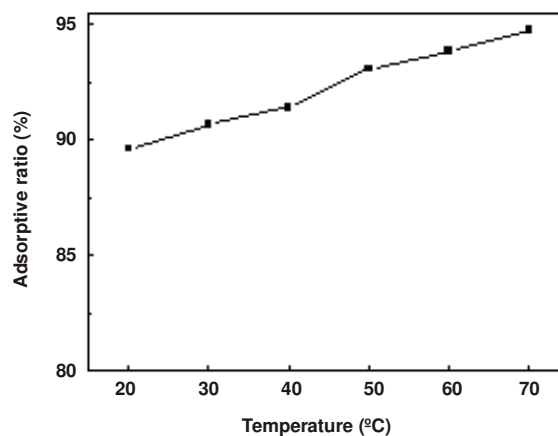


Fig. 5. Effect of temperature on the adsorption of La³⁺

Effect of time on adsorption: The results of time on adsorption show (Fig. 6) that adsorptive time was *ca.* 15 min,

the adsorptive rate of La^{3+} adsorbed by nanoscale $\alpha\text{-Al}_2\text{O}_3$ and time presented an ascending relationship. Over 15-20 min, adsorption reached an equilibrium and all the adsorptive ratios were above 90 %. At 20 min, the adsorptive rate was maximum and achieved 92.14 %. At this time, the adsorptive amount of La^{3+} by $\alpha\text{-Al}_2\text{O}_3$ was 3.696 mg/g. Afterwards, adsorptive ratio began to descend. This is mainly because the adsorption of La^{3+} by nanoscale $\alpha\text{-Al}_2\text{O}_3$ is physical adsorption. The adsorption of La^{3+} on alumina generally subjected according to three steps: (1) outside diffuse; (2) internal diffuse; and (3) La^{3+} on surface was adsorbed. After a majority of La^{3+} was adsorbed, due to long time vibration the La^{3+} adsorbed on the surface of nanoscale $\alpha\text{-Al}_2\text{O}_3$ could partially be desorbed as time lengthened. Therefore, the desorptive rate decreased a little.

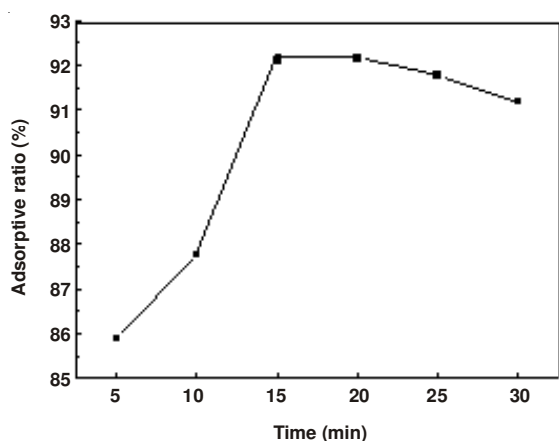


Fig. 6. Effect of time on the adsorption of La^{3+}

Studies on desorptive agent and desorptive time: By studying the elution process of metal ion La^{3+} adsorbed *via* desorptive agents EDTA, oxalic acid, acetic acid, the desorptive results are shown as Table-1. The results showed that the desorptive effects of both EDTA and oxalic acid were not as good as that of acetic acid. When adsorption was at 6 h using acetic acid, the desorptive ratio could reach 97.03 %. Desorbing La^{3+} by AcOH, the desorptive ratio was high. The reason is that the electronic density of La^{3+} excessively concentrates and in outside layer there are vacant orbits. The complex, which was formed by the La^{3+} and the hydroxylation surface of alumina, was not stable. Under the condition that acidity was stronger, the complex was destroyed due to the competition reaction between H^+ in the solution and the metal ions. However, when $\text{H}_2\text{C}_2\text{O}_4$ was used as desorptive agent, it is mainly because the $\text{C}_2\text{O}_4^{2-}$ of oxalic acid and La^{3+} could form a precipitation that was adsorbed on the surface of $\alpha\text{-Al}_2\text{O}_3$ and this resulted in that the desorptive effect was not good. The complex that EDTA and the hydroxylation surface of alumina formed was more stable than that it and La^{3+} formed. Thus, the desorptive effect was not good.

TABLE-1
DESORPTIVE RESULTS OF La^{3+}

Desorptive agent	EDTA	$\text{H}_2\text{C}_2\text{O}_4$	HOAc
Desorptive ratio (%)	15.78	58.39	97.03

The desorptive curve is shown as Fig. 7 using acetic acid as desorptive agent. Within 6 h desorptive ratio increased as time increased. At 6 h, it reached a maximum of 97.03 %. Afterwards, the desorptive ratio began to decrease.

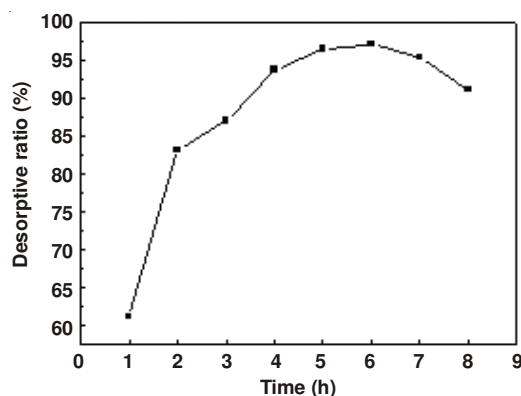


Fig. 7. Effect of desorptive time on the desorption (AcOH as desorptive agent)

Conclusion

- The $\alpha\text{-Al}_2\text{O}_3$ powders prepared by solid phase thermal diffusion method were characterized by XRD, TEM and SEM, showing that the particles presented global shape and primary particle size of $\alpha\text{-Al}_2\text{O}_3$ was 110 nm and the average particle size of its aggregated products was 140 nm.
- Adsorptive studies of nanoscale $\alpha\text{-Al}_2\text{O}_3$ towards La(III) indicated that under the optimum conditions the adsorptive ratio was 92.14 %. Thus, nanoscale $\alpha\text{-Al}_2\text{O}_3$ has stronger adsorptive ratio towards La(III), being a better adsorptive agent of La(III).
- The optimum pH is equal to 7 for the adsorption of La(III) by nanoscale $\alpha\text{-Al}_2\text{O}_3$. The adsorptive ratio increased as temperature increased but the effect of temperature was not great. Therefore, generally adsorption is made at room temperature.
- The optimum adsorptive time of equilibrium for La(III) was 20 min.
- It was discovered from the desorptive studies that using 0.1 mol/L AcOH the desorptive effect for La^{3+} was better. When desorptive time was 6 h, the desorptive ratio could reach 97.03 %. When $\text{H}_2\text{C}_2\text{O}_4$ was used to desorb and precipitation could be produced, the desorptive effect was not good. And a stability of the complex that EDTA and La(III) formed was not as good as the one of the complex that EDTA and alumina hydroxylated surface substance formed, the adsorptive effect was also not ideal.

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