Preconcentration and Separation of Cr(VI) Coupled with Controllable Synthesis of Nano $\gamma$-Al2O3 Materials

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ABSTRACT

The $\gamma$-alumina nano materials were acquired through hydrothermal method of controllable synthesis. Optimized methods were used to change the hydrothermal parameters on the synthesis of nano $\gamma$-Al$_2$O$_3$. The preconcentration performance of chromium(VI) was explored comparing with SDS and CTMAB in the presence of precursors which were prepared via Al(NO$_3$)$_3$·9H$_2$O and CO(NH$_2$)$_2$. 170 °C was selected as reaction temperature and SDS was chosen as surfactant. TEM images indicated that the average particle size of granular $\gamma$-Al$_2$O$_3$ was between 100 nm to 400 nm whose dispersion tended to be good. After centrifugation, a certain volume of 2 mol·L$^{-1}$ hydrochloric acid was used as eluent. At the same time, chromium(VI) adsorbed in granular $\gamma$-Al$_2$O$_3$ aggregation was analyzed by inductively coupled plasma mass spectrometry. It was showed that the effect of branch type was not better than the granule type. The adsorption limit of Cr(VI) in $\gamma$-Al$_2$O$_3$ synthesized by SDS was higher than that of CTMAB. Further experiments of the interfering elements showed that Sb, As, total Cr, Se in granular $\gamma$-Al$_2$O$_3$ had higher adsorption rate, which could reach to 90% or more. When eight migrating elements shared some adsorption sites with Cr(VI), the adsorption rate and limitation reduced. The competitive adsorption effect of Ba, Cd, Pb and Hg had little impact on Cr(VI). As a result, this established method had reached the requirements of Cr(VI) combined with separation and detection in environmental sewage which could be used for analysis of other heavy metals.
INTRODUCTION

Nowadays, nanomaterial has attracted great interest because of its unique performance and structure. One of the important features is the surface effect, and can achieve the adsorption equilibrium in a short time, which makes it a more effective mean for the research of material, food, and environmental monitoring\textsuperscript{[1-5]}. Nano alumina possesses many excellent properties, including high temperature resistance, corrosion resistance, large specific surface area, high reactivity, good insulation, and easy molding in low temperatures. Liquid-phase method is applied as the process of preparation of alumina, which dissolve soluble aluminium salt into solution, then add another precipitant, forming aluminum oxide precursor, such as aluminum hydroxide (Al(OH)\textsubscript{3}) or boehmite (AlOOH), finally get nano alumina by calcination\textsuperscript{[6-7]}. Due to low cost, nano $\gamma$-$\text{Al}_{2}\text{O}_{3}$ materials becomes useful materials, which are widely used in many areas such as catalysts, optics, adsorbent, showing lots of advantages\textsuperscript{[8]}. In the process of hydrothermal method, general precursor crystals are obtained, then the $\gamma$-$\text{Al}_{2}\text{O}_{3}$ with the same feature is achieved by calcining\textsuperscript{[9-10]}.

With the rapid development of industry, environmental problem increasingly prominent, more attention is focus on this problem such as sewage, among them, heavy metal pollution is the main part of the water pollution, affecting our daily lives by the water through the process of production. Therefore, the detection of corresponding pollution is becoming more and more attractive\textsuperscript{[11-12]}. Chromium, as one of the pigment composition, is common in printing and dyeing, electroplating, leather and some other industries. In two forms of chromium, chromium(VI) has great harm for our body, which may cause genetic defects or cancer. Therefore, getting rid of chromium(VI) is an important part to protect the environment and human health. Many nano materials have strong adsorption which can be a very suitable material for handling heavy metal pollution, with rapid adsorption of heavy metals without tedious process step as well as the recovery of nano materials through the elution of heavy metals.

According to this study of hydrothermal method, with aluminum nitrate nonahydrate as aluminum source, urea as precipitant, with a certain proportion to form the alumina precursor, preparation of $\text{Al}_{2}\text{O}_{3}$ nanoparticles by calcination. This materials are used on the target heavy metal Cr(VI) by the centrifugal concentration, with a certain volume 2 mol·L\textsuperscript{-1} hydrochloric acid as the eluent eluting Cr(VI) ions on nano $\text{Al}_{2}\text{O}_{3}$ as the effect of desorption. The characterization of morphology and properties of $\text{Al}_{2}\text{O}_{3}$ is detected by transmission electron microscope (TEM) and energy dispersive X-ray spectrum (EDX). The water samples in nature are usually containing a variety of elements, which will change the adsorption limit and the adsorption rate of nano alumina. For the adsorption effect in this kind of complex water samples, it is necessary to explore the features in different morphology of $\text{Al}_{2}\text{O}_{3}$ to improve the adsorption performance on metal or nonmetal ions. It has made significant progress. Therefore, Inductively coupled plasma mass spectrometry (ICP-MS) technique on preconcentration and separation of $\text{Al}_{2}\text{O}_{3}$ for the detection of Cr(VI) will have wide application prospects.
EXPERIMENTAL SECTION

Materials and Instruments. Tecnai G2 F30 S-type Twin high-resolution transmission electron microscopy (Philips-FEI company, Dutch). 5430 desktop multi-function high-speed centrifuge (Eppendorf company, Germany). NexION 350X inductively coupled plasma mass spectrometer (PerkinElmer company, USA). SX2-5-12 box type resistance furnace (Yiheng technology co., LTD., Shanghai). Thermal water kettle for custom specifications (with four fluorine lining, 400 mL). 100-1000 μL, 500-5000 μL pipetting gun (Thermo Scientific corporation, USA). Standard stock solution: Cr(VI) and total Cr, As, Cd, Sb, Ba, Hg, Pb standard solution, the concentration of 1000 mg·L\(^{-1}\) bought from nonferrous metals and electronic materials analysis and test center. Al(NO\(_3\))\(_3\)·9H\(_2\)O, CO(NH\(_2\))\(_2\), C\(_{12}\)H\(_{25}\)SO\(_4\)Na, C\(_{16}\)H\(_{33}\)(CH\(_3\))\(_3\)NBr are analytically pure or above, the experimental water is 18.2 MΩ·cm ultrapure water, by the Milli-Q Integral ultrapure water meter (Millipore, USA).

Preparation of γ-Al\(_2\)O\(_3\) nanoparticles. Properties and application values of nano materials mainly depend on the morphology and phase, and the size of the material, shape, dimension, dispersion, and also depend on the preparation method. Therefore, it is primarily necessary to solve the problem of preparation technology of nano materials to obtain stable and reliable nano materials. In room temperature, with 40 mL mol·L\(^{-1}\) aluminum nitrate solution in a beaker, stirred and added 30 mL 1.5 mol·L\(^{-1}\) urea solution, achieved a mixed solution. 1 mL 0.1 mol·L\(^{-1}\) C\(_{12}\)H\(_{25}\)SO\(_4\)Na (SDS, surfactant) was added dropwise to the mixed solution. A buffer solution of 0.2 mol·L\(^{-1}\) NaAc-HAc was used to control the pH values of the solutions. Then it is transferred to the hydrothermal synthesis reactor, placed in the electromagnetic heating, stirring 8 h under 170 °C. After the reaction finished, cooled to the room temperature, opened reaction kettle, filtered to get solid phase and washed with anhydrous ethanol and ultrapure water. After drying in vacuum dryer, the solid was roasting in the muffle furnace for 2 h under 550 °C. The standby nano γ-Al\(_2\)O\(_3\) materials were stored in the anhydrous ethanol in the refrigerator.

ICP-MS analysis. There are many interferences existing in ICP-MS analysis, such as substrate inhibition, polyatomic ions, oxide and double charge. In kinetic energy discrimination (KED) mode, the instrument was attuned by using 1.0 μg·L\(^{-1}\) mixed mass spectrometry fluid to obtain stability signal and high sensitivity for the instrument. The refractory oxide index CeO/Ce ≤ 0.025, double charge indicator Ce\(^{2+}\)/Ce ≤ 0.03 should be ensured to achieve the negligible interference. In the 99.999% purity of helium, the ICP-MS was used to test eight kinds of migrating elements in water samples.

RESULTS AND DISCUSSION

Hydrothermal Parameters for the Effect of the Preparation of Nano γ-Al\(_2\)O\(_3\) Particles.

The particle of the product is bigger without stirring in the reaction after test and easily to form larger particles by gathering in the process of filtering. After the completion of the roasting of nano materials is also difficult to grind in grinding
process. It means that the reunion phenomenon is serious in the process of producing nano materials, the size of obtained nano material is larger, and the adsorption rate of the chromium(VI) is low.

Keeping other conditions stable, the reaction temperatures are controlled at 150 °C, 170 °C, 190 °C respectively, to observe the difference between the products. At 150 °C, the product is less in the reactor, the reaction efficiency is worse than that obtained at 170 °C, but the character is similar to 170 °C. However, the product produced at 190 °C exhibits large difference on morphology comparing to the products of 150 °C and 170 °C. In the process of filtering out of products from the reaction kettle, slightly white transparent sol precursors are achieved at 150 °C and 170 °C, but the precursor under 190 °C is suspension particles. From the synthetic results, nano alumina generated at 190 °C is different with those obtained at lower temperatures, the further investigation shows that the adsorption ability (190 °C) is inferior to sol.

No surfactant is added into one of the reaction kettle, while the other reaction kettle has 1 mL of 0.1 mol·L\(^{-1}\) C\(_{16}\)H\(_{33}\)(CH\(_{3}\))\(_3\)NBr (CTMAB) in it and other conditions are the same, observing the difference between the reaction products. The results indicate that the product in the reaction kettle without the surfactant in the presence of large particles, after a time, the form of product exhibiting large difference. Adding surfactant can make it well disperse, small particles and not easy to agglomerate.

**Morphology Characterization of γ-Al\(_2\)O\(_3\).**

Scatters Al\(_2\)O\(_3\) sample in ethanol by ultrasound, drops the solution on carbon supported membrane double copper net, put in the transmission electron microscopy, the microstructure was observed under the accelerating voltage of 300 kV. According to the results, the appearance of nano alumina is dendritic by using cationic surfactant CTMAB. In fact, it is a one-dimensional nano chips with partly aggregation (Figure 1). In contrast, the average particle size is between 100 and 400 nm by preparing with anionic surfactant SDS, and dispersion is good. As shown in Figure 2, granular appearance of nano alumina is three-dimensional nano particles. Figure 1C and Figure 2C are the EDX spectrum of element analysis of Figure 1B and Figure 2B, correspondingly, the results show that the chemical composition is Al and O, where Cu and C peak come from the copper mesh support and support membrane.

![Figure 1. TEM images (A,B) and EDX spectrum (C) of dendritic γ-Al\(_2\)O\(_3\) materials synthesized via CTMAB.](image-url)
Exploration of Cr(VI) Adsorption Limit of Granular and Dendritic Nano γ-Al₂O₃.

In the testing samples, there are always few contents of elements, such as environmental water samples, and mineral samples with symbiosis of other metals. Therefore, enrichment and separation are necessary in the determination to eliminate the matrix interference, to improve the sensitivity and reliability of the analytical method. In recent years, due to the unique structure and properties of nano γ-Al₂O₃, combining γ-Al₂O₃ with high specific surface area and good adsorption performance in the analysis of pretreatment, nano γ-Al₂O₃ has been pay extensive attention by scientific workers in some areas such as environment, materials, and analysis[13-16].

In order to investigate different quality of nano alumina for adsorption performance of Cr(VI), we use electronic analytical balance to weight 15, 20, 25 mg of nano alumina granular solid, put them in plastic centrifuge tube, add a certain amount of chromium(VI) solution, oscillate for 5 min, then centrifuge for 30 min to get the supernatant fluid (because it is difficult to make the solution clarifying by standing) to avoid the damage of ICP-MS by nano particles. To determinate the Cr(VI) concentration in the supernatant fluid, a certain volume of 2 mol·L⁻¹ hydrochloric acid is utilized to elute Cr(VI) on nano alumina, meanwhile, setting a blank sample for contrast for calculation of alumina adsorption rate. Improving the Cr(VI) ion concentration constantly, the data constitutes the Figure 3. The results show that the granular nano alumina is more beneficial for the adsorption of Cr(VI) and the adsorption rate is higher. Particle deposition stays in the bottom of the centrifuge tube and the upper liquid keeps clear. When the content of Cr(VI) is less than 0.16 mg·g⁻¹ comparing with the alumina in the solution, the adsorption capacity of nano alumina has not reached its limit, to adsorb Cr(VI) in water samples with
high adsorption rate, which can reach more than 97% with little fluctuation of the adsorption rate. When the ratio is higher than 0.21 mg·g⁻¹, increasing the amount of Cr(VI), the adsorption rate is significantly decreased and without and ability to absorb the rest of the Cr(VI), which means that granular γ-Al₂O₃ has arrived the dynamic adsorption equilibrium in this concentration.

![Figure 3. The limitation curve of granular γ-Al₂O₃.](image)

With different quality of dendritic nano alumina for parallel test, the data can be seen in Figure 4. When the content of Cr(VI) is less than 0.13 mg·g⁻¹ comparing with the aluminum oxide in the solution, the adsorption rate of dendritic nano alumina for Cr(VI) in the solution is relatively low, only about 92%. Accordingly, the adsorption limit of Cr(VI) by dendritic nano alumina is lower than granular nano alumina, and with the ratio gradually increases to 0.16 mg·g⁻¹, the adsorption rate is significantly reduced, which shows that the adsorption ability of dendritic nano alumina is becoming saturated.

For the saturated adsorptions from two different morphology of nano alumina, particles is better than branches, as three dimensional nano materials for visible granular nano alumina, adsorption sites of particles is more than dendritic material, and the contact area of heavy metal ions is also greater than the latter one. Therefore, choosing the nano alumina particles to conduct the following experiments on impurity element interference for adsorption.
The Effect for γ-Al₂O₃ Adsorption of Cr(VI) by Impurity Elements.

In order to further explore other interfering elements in water samples of absorption of chromium(VI) of γ-Al₂O₃, weight 40 mg alumina solid in plastic centrifuge tube accurately, add 3 mL solution of eight kinds of commonly migrating elements (Sb, As, Ba, Cd, total Cr, Pb, Hg, Se) with low concentration, respectively, to ensure that it is no more than the adsorption cap of granular nano alumina, oscillate for 5 min, centrifuge for 30 min and take the supernatant fluid for the analysis of the content of rest elements, meanwhile, set up a blank experiment for contrast, repeat 3 times, the results are shown in Table 1.

**TABLE 1. THE AVERAGE ADSORPTION RATE OF GRANULAR Γ-Al₂O₃ FOR 8 KINDS OF ELEMENTS.**

| Element | Sb | As | Ba | Cd | Cr | Pb | Hg | Se |
|---------|----|----|----|----|----|----|----|----|
| Average rate(%) | 90.4 | 97.2 | 2.0 | 0.7 | 90.5 | 0.1 | 10.6 | 96.9 |

The Table 1 shows that under the same concentration of mixture of elements, the adsorption rates for Sb, As, total Cr, Se are higher and reach to more than 90% by granular γ-Al₂O₃. But for Ba, Cd, Pb, Hg, the adsorption effect is poorer. To verify this conclusion, considering the As, Pb as examples, configuring Cr(VI)-As mixed solution, and Cr(VI)-Pb mixed solution, which is used in the latter experiment, the method is the same as the previous, the data lists in Table 2.

**TABLE 2. THE AVERAGE ADSORPTION RATE OF GRANULAR Γ-Al₂O₃ IN MIXED SOLUTION.**

| Element | Mixed solution of Cr(VI) and As | Mixed solution of Cr(VI) and Pb |
|---------|---------------------------------|---------------------------------|
|         | Cr(VI) | As | Cr(VI) | Pb |
| Average rate(%) | 92.9 | 95.7 | 98.6 | 0.2 |
When Cr(VI) and As existing, adsorption rates of nano alumina for these two elements are still high, but for Cr(VI) and Pb, Pb adsorption rate is still very low to ignore. The adsorption rate of Cr(VI) is almost the same under the influence of Pb, so we believe that these four elements have little influence for the adsorption of Cr(VI). When total Cr, As, Se, Sb existing, the adsorption by $\gamma$-Al$_2$O$_3$ is partly higher than that of Cr(VI).

More kinds of interfering elements exist, more complex the competitive adsorption will be. For further investigation of the other elements (such as As) for the impact on the adsorption of Cr(VI), we utilize the Cr(VI)-As to explore the limit curve of adsorption of mixed solution of Cr(VI) (Figure 5). In Cr(VI)-As mixture solution, adsorption rate of Cr(VI) for granular nano alumina slightly drops from 97% to 95%, and adsorption limit falls from 0.21 mg·g$^{-1}$ to 0.17 mg·g$^{-1}$, correspondingly. It shows that the total Cr, As, Se, Sb is not completely occupied the adsorption sites of Cr(VI). The sharing part of the competitive adsorption with Cr(VI) may mainly affect the adsorption sites, causing the deterioration of adsorption limit.

![Figure 5](image_url)

**Figure 5.** The effect of Cr(VI) and As on the limitation curve of granular $\gamma$-Al$_2$O$_3$.

**CONCLUSIONS**

Nano $\gamma$-Al$_2$O$_3$ was synthesized by hydrothermal method, mainly carried on the morphology characterization of $\gamma$-Al$_2$O$_3$ material. Some optimized methods were used to change the hydrothermal parameters on the synthesis of $\gamma$-Al$_2$O$_3$ and its adsorption performance of Cr(VI) was explored. We selected 170 °C as reaction temperature and SDS as surfactant. After centrifugation, a certain volume of 2 mol·L$^{-1}$ hydrochloric acid as eluent combined with ICP-MS analysis. The results showed that the adsorption effect of branch type is not better than the grain type. The adsorption limit of Cr(VI) of $\gamma$-Al$_2$O$_3$ which is synthesized by SDS is higher than that of CTMAB.

Eight migrating elements were investigated to understand the adsorption limit of competitive adsorption of Cr(VI) on granular $\gamma$-Al$_2$O$_3$. The experiments of the interfering elements show that Sb, As, total Cr, Se in granular $\gamma$-Al$_2$O$_3$ have higher adsorption rate, which can reach to 90% or more. When sharing some adsorption
sites with Cr(VI), the Cr(VI) adsorption rate and adsorption limit reduced. The competitive adsorption effect of Ba, Cd, Pb and Hg will have little impact on Cr(VI) adsorption. As a result, this method has been applied in Cr(VI) concentration and separation of environmental water samples and determination. And it can also be extended to other heavy metals, exhibiting wide application prospect.

ACKNOWLEDGMENTS

This work was supported by The Analysis and Measurement Fund of Zhejiang Province (No. 2016C37075).

REFERENCES

[1] R.J.B. Peters, Z.H. Rivera, G.V. Bemmel, H.J.P. Marvin, Development and validation of single particle ICP-MS for sizing and quantitative determination of nano-silver in chicken meat, Anal. Bioanal. Chem. 406 (2014) 3875-3885.
[2] W.M. Zeng, N.Y. Chen, L.H. Gui, J. Wang, L. Gao, J.K. Guo, Synthesis of Al₂O₃ nanopowders using inorganic salt and its physical chemistry, J. Inorg. Mater. 13 (1998) 887-892.
[3] L.D. Mitchell, P.S. Whitfield, J. Margeson, Sucrose synthesis of nanoparticulate alumina, J. Mater. Sci. Lett. 21 (2002) 1773-1775.
[4] D.M. Mitrano, E.K. Lesher, B. Anthony, Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry, Environ. Toxicol. Chem. 31 (2012) 115-21.
[5] S. Miao, Z.Q. Shen, F.X. Ling, Z.M. Zhang, Preparation and characterization of one-dimensional nanostructure Al₂O₃ carrier, Ind. Catal. 20 (2012) 38-42.
[6] M. Zhang, R. Zhang, G.C. Xi, Y. Liu, Y.T. Qian, From sheet to fibers: a novel approach to γ-AlOOH and γ-Al₂O₃ 1D nanostructures, J. Nanosci. Nanotechnol. 6 (2006) 1437-1440.
[7] H.W. Hou, Y. Xie, Q. Yang, Preparation and characterization of γ-AlO(OH) nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry, Environ. Toxicol. Chem. 31 (2012) 115-21.
[8] L. Zhang, Y.J. Zhu, Microwave-assisted solvothermal synthesis of AlOOH hierarchically nanostructured microspheres and their transformation to γ-Al₂O₃ with similar morphologies, J. Phys. Chem. C, 1 (2008) 16764-16768.
[9] M. Karimi, A.M.H. Shabani, S. Dadfarnia, Magnetic nanoparticles coated with ionic liquid as a sorbent for solid phase extraction of chromium(VI) prior to its determination by electrothermal atomic absorption spectrometry, J. Braz. Chem. Soc. 27 (2016) 144-152.
[10] C. Cui, M. He, B.B. Chen, B. Hu, Chitosan modified magnetic nanoparticles based solid phase extraction combined with ICP-OES for the speciation of Cr(III) and Cr(VI), Anal. Methods 6 (2014) 8577-8583.
[11] H. Tavallali, G. Deilamy-Rad, P. Peykarimah, Preconcentration and speciation of Cr(III) and Cr(VI) in water and soil samples by spectrometric detection via use of nanosized alumina-coated magnetite solid phase, Environ. Monit. Assess. 185 (2013) 7723-7738.
[12] H.M. Jiang, T. Yang, Y.H. Wang, H.Z. Lian, X. Hu, Magnetic solid-phase extraction combined with graphite furnace atomic absorption spectrometry for speciation of Cr(III) and Cr(VI) in environmental waters, Talanta. 116 (2013) 361-367.