Effective removal of lead(II) migrated from kitchen faucets using multi-slice feathery $\gamma$-alumina

Huihui He$^1$, Ligang Luo$^1$, Caiying Lou$^1$, Xihong Che$^1$, Huazhen Yao$^2$ and Ronghui Yuan$^{1,3}$

$^1$Zhejiang Light Industrial Products Inspection and Research Institute, Hangzhou 310007, China;
$^2$Hangzhou Wanxiang Polytechnic, Hangzhou 310023, China

$^3$Email: 366290161@qq.com

Abstract. In this study, $\gamma$-Al$_2$O$_3$ was synthesized using a hydrothermal method and its morphology and chemical composition was characterized by transmission electron microscopy (TEM), energy dispersive X-ray (EDX) and X-ray diffractometer (XRD). The TEM images, EDX and XRD spectrum highlight good crystallization and multi-slice feathery microstructure, involving relatively pure crystal sintering. The Pb(II) concentration analysed by inductively coupled plasma mass spectrometry (ICP-MS) after centrifuging is linked to the $\gamma$-Al$_2$O$_3$ adsorption, and a removal method for Pb(II) from water passing through kitchen faucets is proposed. The Pb(II) value below 0.06 mg g$^{-1}$ relative to the $\gamma$-Al$_2$O$_3$ value reveals 94% adsorption. Further assessment of the alumina separation effect for faucets shows Pb(II) precipitation from the downstream of the valve spool is below 0.16 $\mu$g L$^{-1}$. About 0.12 g adsorbent is mixed with 1.0 L tap water to produce a suspension for effective soaking. The proposed method produced satisfactory results, providing a theoretical basis for authorities to exploit on heavy metal removal from kitchen faucets.

1. Introduction
Considering the rapidly developing economy, heavy metal pollution is attracting increasing attention in modern analytical chemistry. In people’s daily lives, heavy metals are consumed through the food chain or drinking water. Among these elements, lead is one of the most harmful to the digestive, hematopoietic, and immune systems. In particular, it seriously affects early neurodevelopment of infants and young children, and therefore, it has attracted extensive attention from health organizations worldwide [1]. Studies show that lead affects children’s mental development at blood lead concentrations above 100 g L$^{-1}$, causing decline in mental abilities. As lead is a common heavy metal pollutant that is non-biodegradable and difficult to expel from the body, its removal is a priority for protecting the environment and human health [2,3]. The lead from faucets mainly originates from interaction of copper alloy material in them and water. Currently, most faucet producing enterprises utilize copper and casting copper alloy as raw materials. Adding lead to copper improves the processing performance of copper. The lead in copper alloy of the faucet directly migrates into water upon contact, especially over prolonged contact, explaining the higher Pb$^{2+}$ in “overnight water”.

Material size reduction of a material rapidly increases its specific surface area and surface energy, facilitating reaction with metal ions by electrostatic interaction, and thereby enhancing its adsorption capacity [4-6]. An important characteristic associated with the reduction is that the adsorption equilibrium is quickly achieved, making the approach effective for separation and analysis [7-10].
Alumina (Al₂O₃) is a cheap and widely used material with advantages such as temperature resistance, corrosion resistance, high specific surface area and high reactivity. In preparing the alumina by a liquid phase method, a soluble aluminium salt is generally dissolved and a precipitant (e.g. NaOH and CO(NH₂)₂) added to form an alumina precursor like AlOOH, followed by calcining the precursor at 500–800 °C to obtain γ-Al₂O₃ [11-13]. The strong adsorbability of the prepared material highlights potential for dealing with heavy metal pollution, through quick heavy metals adsorption devoid of complicated processing steps. In addition, such material is recoverable after adsorption by purging the heavy metals [14,15].

According to the hydrothermal method, Al(NO₃)₃·9H₂O was used as the aluminium source, while NH₃·H₂O was the precipitating agent, with sodium dodecyl sulfate (SDS) as the surfactant. These reactants were proportionally present in the alumina precursor, with the γ-Al₂O₃ prepared by calcining the precursor. The target element, lead, was separated from water based on the unique structure and excellent adsorption property of γ-Al₂O₃. The morphology and properties of γ-Al₂O₃ were then characterized by Transmission electron microscopy (TEM), energy dispersive X-ray (EDX) and X-ray diffractometer (XRD). The γ-Al₂O₃ was applied for removing Pb²⁺ from soaked kitchen faucet solutions, which is of practical significance. The concentrations of Pb²⁺ from water passing through kitchen faucets after separation were analysed by inductively coupled plasma mass spectrometry (ICP-MS).

2. Experimental section

2.1. Instruments and materials

The instruments and reagents used in this study are as follows. A Talos F200x high-resolution transmission electron microscope (Thermo Scientific, USA), an Ultima IV X-ray diffractometer (Rigaku, Japan), a 5430 bench multi-functional high speed centrifuge (Eppendorf, Germany), a NexION 350X inductively coupled plasma mass spectrometer (PerkinElmer, USA), a Multi N/C310 total organic/inorganic carbon analyser (Jena, Germany), an ASAP 2460 surface area and porosity analyzer (Micromeritics, USA), an AQ3070 residual chlorine analyser (Thermo Scientific, USA), a Seven Excellence acidity meter (Mettler Toledo, USA), electrically heated magnetic agitators (Talboys, USA), an Sx2-5-12 box resistance furnace (Shanghai Yiheng, China), and 500–5000 μL pipettes (Thermo Scientific, USA). The 400 mL hydrothermal reactor was customized with tetrafluoride lining.

The 1000 mg L⁻¹ lead standard solution was obtained from the National Center for Analysis and Testing of Nonferrous Metals and Electronic Materials. Other reagents were of analytical grade, and used without further purification. For the experiment, we used 18.2 MΩ cm⁻¹ ultra-pure water prepared using a Milli-Q Integral ultrapure water meter (Millipore, USA).

2.2. Preparation of γ-Al₂O₃

Hydrothermal synthesis is an effective inorganic synthesis method, involving an aqueous solution as the reaction medium, creating a high-pressure and high-temperature reaction environment, by pressurizing and heating the reagents in a special airtight reaction kettle, thereby dissolving and/or recrystallizing insoluble substances [16]. The properties of materials and their applications largely depend on morphology and phase, with size and dispersion controlled by the preparation method [17-19]. Based on previous functional materials syntheses [20,21], 30 mL of a 0.5 mol L⁻¹ aluminium nitrate solution was mixed with 40 mL of 0.9 mol L⁻¹ ammonia while stirring the mixture at room temperature. Then, 1 mL of 0.1 mol L⁻¹ SDS as the surfactant and 0.2 mol L⁻¹ of ammonia-ammonium chloride as the buffer solution were gradually added to the mixture to maintain the pH of the hydrothermal system at 9.5. The solution was transferred to the hydrothermal reactor and the reactor placed on electrically heated magnetic agitators, followed by continuous stirring at 170 °C for 8 h. The reaction kettle was opened after cooling at the end of the reaction. The precursor was transferred to a funnel for filtration, with the solid phase washed using anhydrous ethanol and ultra-pure water. After
drying and cooling by a vacuum dryer, the solid phase was calcinated for 2 h at 550 °C in a box resistance furnace. The product was then ground to a fine size and stored in a refrigerator using anhydrous ethanol.

2.3. Sample pretreatment and ICP-MS test

Kitchen faucets were randomly selected from supervision batches. The test samples were kitchen faucets randomly selected from a supervised sampling batch. An immersion solution of pH 8 ± 0.5, 122 ± 5 mol L⁻¹ inorganic carbon and 2.0 mol L⁻¹ residual chlorine was prepared to simulate tap water. The acidity meter, total organic/inorganic carbon analyser and residual chlorine analyser were used for calibration and testing. The samples were washed and stabilized.

The matrix, polyatomic ions, oxide and double charges commonly interfere in ICP-MS analysis. Therefore, to obtain stable signals and high sensitivity, the oxide index for the refractory CeO/Ce was maintained at ≤0.025, and the double charge indicator Ce²⁺/Ce at ≤0.03, ensuring negligible interference and presence as plasma in the argon gas. The Pb²⁺ concentrations in the soaking solutions were measured by injecting 1.0 μg L⁻¹ after mixed liquid mass spectrum optimization for tuning the instrument in the kinetic energy discrimination (KED) mode, with helium as the collision response gas.

3. Results and discussion

3.1. Morphology characterization of γ-Al₂O₃

Ultrasonic dispersion of γ-Al₂O₃ in anhydrous ethanol was conducted for 5 min, then a 3 mm diameter wafer was created and placed on a dual copper network, and its microstructure was observed by TEM under an accelerating voltage of 200 kV. The X-ray diffractogram was recorded in a 2θ range of 10–80° at a scan rate of 3° min⁻¹. As seen from Figures 1A–1C, the prepared material has a multi-slice feathery microstructure. The prepared material size by the hydrothermal method and calcination is approximately 1 μm in length and 200 nm in width, and the morphology of the sample was a three-dimensional crystal feathery. The EDX image in Figure 1D displays element compositions at the microscopic level. The results show that the crystal comprises mainly Al and O, with the Cu peak attributed to the copper network used for supporting the sample. As seen from Figure 1E, the diffraction peaks of the sample match the standard spectrum of γ-Al₂O₃ (JCPDS PDF No.10-0425) [22]. All the peaks are narrow and sharp, indicating that the sample is pure and exhibits good crystallization. This indicates that the grain is relatively pure, with no contamination during the sintering process.

3.2. Exploration of Pb(II) adsorption limit of γ-Al₂O₃

Owing to the high specific surface area and adsorption capacity of γ-Al₂O₃, its Pb²⁺ adsorption characteristics were investigated at different masses. Twelve portions of the prepared alumina solids were accurately weighed and placed in corkscrew colorimetric tubes with a constant volume of ultra-pure water up to 10 mL. Various volumes of the 1.0 mg L⁻¹ lead standard solution were then added, namely 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 mL, respectively. After shaking for 5 min, the samples were transferred to centrifugal tubes. Because it was difficult to completely clear the solutions by allowing them standing for some time, centrifuging was performed at 2000 rpm for 20 min, and then 5 mL of the supernatant were extracted for determining the Pb²⁺ concentrations, with the experiments conducted in triplicate. A blank group without Al₂O₃ was used as a control, aiding in calculating the adsorption rate. According to the constant increase in the Pb²⁺ amounts, the data obtained are plotted in Figure 2. The results show that when the Pb²⁺ to Al₂O₃ ratio in the solution is less than 0.06 mg g⁻¹, the γ-Al₂O₃ adsorption limit is not yet attained, favouring a high Pb²⁺ adsorption rate. This rate reached over 94% without significant fluctuation. When the ratio exceeds 0.22 mg g⁻¹, increasing the Pb²⁺ amount saturates the adsorption capacity of the γ-Al₂O₃.
3.3. Effects of γ-Al₂O₃ separation on Pb(II) precipitation in the faucets
The downstream valve core was filled with the soaking liquid at 23 ± 2 °C. The ends of the sample were sealed with a PTFE or sealing film. The soaking liquid was filled at 9 am on day 1 and replaced every 2 h four times, ending at 5 pm. The cavities of the faucets were filled with the liquid for 16 h, and the first day process repeated from 9 am on the second day. On days 3, 4 and 5, the day 1 procedure was repeated and the extracted fluid stored for 16 h was collected. However, on day 5, the solution was kept for 64 h after replacement at 5 pm, and the soaking liquid poured. The samples were kept till the 8th and 15th day to repeat the complete extraction process of the first cycle. The precipitated lead concentrations (c) for the samples of days 3, 4, 5, 10, 11, 12, 17, 18, 19 collected after soaking for 16 h were measured. Concurrently, the samples of each batch of the inner cavity volume (V_i) and cold-water adjustment factor (CMV) were tested, and the precipitated lead statistics (Q) for 11 batches of kitchen faucets calculated (Table 1).

Figure 1. TEM images (A, B, C), EDX spectrum (D) and XRD spectrum (E) of γ-Al₂O₃ materials.

Figure 2. Adsorption percentage curve of Pb(II) measured with γ-Al₂O₃.
Table 1. Precipitation concentration of Pb (II) for kitchen faucets.a.

| Batch No. | 3rd day | 4th day | 5th day | 10th day | 11th day | 12th day | 17th day | 18th day | 19th day |
|-----------|---------|---------|---------|----------|----------|----------|----------|----------|----------|
| 1         | 16.552  | 9.037   | 5.819   | 4.683    | 7.407    | 9.425    | 7.377    | 5.043    |
| 2         | 3.396   | 5.184   | 2.517   | 8.212    | 4.347    | 6.588    | 10.655   | 4.105    | 9.435    |
| 3         | 7.267   | 11.341  | 8.656   | 9.141    | 9.023    | 5.752    | 8.977    | 4.919    |
| 4         | 4.189   | 2.435   | 2.721   | 1.788    | 5.381    | 0.917    | 4.471    | ND b     |
| 5         | 25.701  | 18.732  | 21.461  | 20.369   | 15.706   | 13.406   | 19.403   | 18.736   | 26.189   |
| 6         | 22.421  | 24.455  | 16.729  | 12.166   | 23.351   | 14.453   | 19.736   | 17.833   | 16.027   |
| 7         | 4.277   | 7.929   | 3.546   | 4.738    | 4.938    | 6.608    | 7.083    | 5.451    | 10.547   |
| 8         | 9.986   | 11.071  | 13.047  | 7.674    | 12.063   | 8.254    | 9.573    | 10.747   | 12.518   |
| 9         | 1.351   | 3.375   | 2.667   | ND       | 1.407    | 4.681    | 1.599    | 4.603    | 1.677    |
| 10        | 17.883  | 15.852  | 14.162  | 25.217   | 18.023   | 17.908   | 17.361   | 16.355   | 13.270   |
| 11        | 14.812  | 13.653  | 8.934   | 11.223   | 7.409    | 7.227    | 13.697   | 9.163    | 14.173   |

a The instrument detection limit of Pb(II) is 0.001 μg L⁻¹.
b ND = Not detected.

To explore the influence of γ-Al₂O₃ on the Q value according to the calculated adsorption limit, a suspension of 0.12 g of alumina mixed in 1.0 L tap water was prepared and stored in a polypropylene bottle. The suspension was used to fill the cavity of the faucets and kept for 24 h before the liquid phase was poured. The kitchen faucets samples were washed again, followed by the test immersion liquid addition. The other conditions remained unchanged for the test for 19 days. The extraction liquid from the valve core downstream was collected, with a parallel test set as the reference. After centrifuging, the extracted solution was filtered by a 0.2 μm drainage membrane, and the precipitated Pb²⁺ concentrations were determined. The extraction solution was analysed by ICP-MS in the KED mode, with the concentrations calculated (Table 2).

Table 2. V_L, CMV and comparison of Q via γ-Al₂O₃ value via γ-Al₂O₃.

| No. | V_L (L) | CMV | Q (μg L⁻¹) | Q via γ-Al₂O₃ |
|-----|---------|-----|------------|--------------|
| 1   | 0.036   | 0.961 | 0.325      | ND           |
| 2   | 0.021   | 0.914 | 0.192      | ND           |
| 3   | 0.049   | 0.957 | 0.427      | ND           |
| 4   | 0.030   | 0.924 | 0.051      | ND           |
| 5   | 0.027   | 0.955 | 0.908      | 0.132        |
| 6   | 0.016   | 1.000 | 0.317      | 0.094        |
| 7   | 0.018   | 0.927 | 0.089      | ND           |
| 8   | 0.070   | 0.893 | 0.768      | ND           |
| 9   | 0.017   | 0.882 | 0.063      | ND           |
| 10  | 0.008   | 0.846 | 0.106      | ND           |
| 11  | 0.085   | 0.939 | 1.041      | 0.156        |

ND = Not detected.

a The limit requirement of Q is ≤5 μg L⁻¹.

The results show that the γ-Al₂O₃ strongly adsorb the Pb²⁺ from kitchen faucets. The samples were adsorbed by γ-Al₂O₃, and then filtered by the membrane after shaking and centrifugation. The Pb²⁺ in the valve core downstream was below 0.16 μg L⁻¹. The consumption of γ-Al₂O₃ material was extremely low, with less than 0.12 g L⁻¹. The implementation of this method is attributed to the special structure of the γ-Al₂O₃ and its excellent adsorption performance. The Brunauer-Emmett-Teller (BET) method was used to investigate the specific surface of γ-Al₂O₃, and the specific surface area was
determined to 139.5 m$^2$ g$^{-1}$. The material with multi-slice feathery microstructure has a larger surface area, which can contact well with the solution, so as to absorb more heavy metal ions. Following is the proposed adsorption mechanism: The main driving force of adsorption is electrostatic action, which can be described using the second order adsorption kinetic equation. Furthermore, the Pb$^{2+}$ onto adsorbent is fitted well with the Langmuir isothermal adsorption model, indicating that this adsorption process is dominated by single molecule adsorption [16]. In addition, subsequent desorption tests show that the $\gamma$-Al$_2$O$_3$ dried after purging with hydrochloric acid is reusable with good chemical stability and good adsorption performance.

4. Conclusion
Multi-slice feathery $\gamma$-Al$_2$O$_3$ was prepared by the hydrothermal method. A method for adsorption of Pb$^{2+}$ distributed in water was established with $\gamma$-Al$_2$O$_3$ as the adsorbent. This approach was applied for separation of Pb$^{2+}$ present in kitchen faucets. The results before and after the addition of alumina were compared. The Pb$^{2+}$ precipitation downstream of the valve were satisfactory after alumina treatment. Practically, domestic kitchen faucets soaked in a suspension containing 0.12 g L$^{-1}$ alumina dispersed in tap water effectively separated and removed Pb$^{2+}$ from the faucets. This method exhibited advantages of low cost and simple operation. Therefore, the approach is of great significance, with broad application prospects for studying the removal of portable heavy metal ions from actual samples by $\gamma$-Al$_2$O$_3$.

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