

# Chitin-like Hollow Alumina Nano-adsorbent for Remediation of Arsenate- contaminated Water: Synthesis by Double Reversed-phase Microemulsion Method and Study of Enhanced Arsenate-removal Ability and Mechanism

**Ting Cai**

Henan University

**Shuang Liang**

Henan University

**Shengbo Wang**

Henan University

**Yi Zhang**

Henan University

**Mochou Gao**

Jilin University

**Yanbao Zhao**

Henan University

**Wensheng Yang**

Henan University

**Xueyan Zou**

[zouxueyan@henu.edu.cn](mailto:zouxueyan@henu.edu.cn)

Henan University

---

## Research Article

**Keywords:** chitin-like hollow alumina, nano-adsorbent, W/O/W microemulsion, synthesis, As(V)-contaminated water, remediation

**Posted Date:** September 10th, 2026

**DOI:** <https://doi.org/10.21203/rs.3.rs-10254756/v1>

**License:** © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.  
[Read Full License](#)

**Additional Declarations:** No competing interests reported.

---

---

# **Chitin-like Hollow Alumina Nano-adsorbent for Remediation of Arsenate-contaminated Water: Synthesis by Double Reversed-phase Microemulsion Method and Study of Enhanced Arsenate-removal Ability and Mechanism**

Ting Cai <sup>1</sup>, Shuang Liang <sup>1</sup>, Shengbo Wang <sup>1</sup>, Yi Zhang <sup>1</sup>, Mochou Gao <sup>1,2</sup>, Yanbao Zhao <sup>1\*</sup>,  
Wensheng Yang <sup>1\*</sup>, Xueyan Zou <sup>1\*</sup>

<sup>1</sup> Institute of Nanoscience and Engineering; School of Law, Henan Provincial Engineering Research Center for AI-enabled Smart Manufacturing of New Materials, National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, School of Life Sciences, College of Pharmacy; Henan Medical School, Henan University, Zhengzhou 450046, China

<sup>2</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry-College of Chemistry, Jilin University, Changchun 130012, China)

\*Corresponding author. E-mail:

Xueyan Zhou: zouxueyan@henu.edu.cn

Yanbao Zhao: zhaoyb902@henu.edu.cn

Wensheng Yang: wsyang@henu.edu.cn

**Abstract:** Arsenic contamination in aquatic systems threatens ecosystems and human health. Chitin-like hollow alumina nanospheres were synthesized via a W/O/W microemulsion system with sodium meta-aluminate and  $\text{NH}_4\text{HCO}_3$  as aqueous phases, and n-hexane with span-80 as oil phase. Precipitate was filtered, washed, freeze-dried to get precursor  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$  (AACH), then calcined at  $500^\circ\text{C}$  for 3 h to obtain  $\text{Al}_2\text{O}_3$  nano-adsorbent, characterized by XRD, SEM, TEM, and FTIR. Its adsorption performance and mechanism for arsenate ions ( $\text{AsO}_4^{3-}$ , i.e., As(V)) were investigated based on batch adsorption experiments as well as adsorption thermodynamics and kinetics simulations. The optimization of synthesis conditions revealed that the  $\text{Al}_2\text{O}_3$  nano-adsorbent synthesized with 0.94 M  $\text{NH}_4\text{HCO}_3$  and 0.5 g span-80 at the reaction temperature of  $45^\circ\text{C}$  and calcination temperature of  $500^\circ\text{C}$  was of chitin-like hollow nanosphere morphology with a specific surface area of  $394.99\text{ m}^2/\text{g}$  and an average pore

---

size of 4.46 nm. It exhibited the highest removal rate of 98.69% for As(V) in the solution of pH 3.0 while its As-removal ability increased with increasing dosage. Besides, the adsorption isotherm and adsorption kinetics for As(V) over Al<sub>2</sub>O<sub>3</sub> nano-adsorbent at 298 K were in accordance with the Langmuir isotherm adsorption model and the pseudo-second order kinetic equation, with saturated adsorption capacity and correlation coefficient of 37.11 mg/g and 99.8%, respectively. In addition, Al<sub>2</sub>O<sub>3</sub> nano-adsorbent retained good removal ability for As(V) during 30 day of consecutive desorption experiments, showing promising potential for the rapid and efficient remediation of As-contaminated water.

**Keywords:** chitin-like hollow alumina; nano-adsorbent; W/O/W microemulsion; synthesis; As(V)-contaminated water; remediation

## 1. Introduction

Increasingly serious heavy metal pollution of water bodies has become one of the major environment and health problems facing mankind, and AsO<sub>4</sub><sup>3-</sup> (As(V)) has attracted widespread attention worldwide due to its extremely high toxicity and hazard. As a human carcinogen identified by WHO and the International Organization for Research on Cancer, as well as the No. 1 toxin in the USEPA list <sup>[1]</sup>, As in aquatic environment poses a significant threat to ecosystems and humans through accumulation in the food chain. Even worse, the long-term consumption of As-containing water can lead to chronic As poisoning, causing cancer <sup>[2]</sup>, skin diseases <sup>[3; 4]</sup>, vascular diseases <sup>[5; 6]</sup>, and diabetes mellitus <sup>[7; 8]</sup>, among others. Arsenic in the environment mainly comes from the weathering of As-containing minerals. However, human production activities, the industrial emissions of wastewater, waste gas, and waste slag, and the use of As-containing pesticides and herbicides in agriculture have also greatly increased the level of As in the environment <sup>[9; 10]</sup>. Some countries and international institutions set a maximum allowable concentration of 10 µg/L for As in drinking water, but globally about 200 million of people have excessive levels of As in their drinking water <sup>[11]</sup>. Therefore, it is urgent to explore remediation materials and techniques for reducing and getting rid of As pollution of water bodies.

Currently available remediation techniques for As(V)-polluted groundwater and

---

wastewater include chemical precipitation <sup>[12]</sup>, ion exchange <sup>[13]</sup>, membrane separation <sup>[14]</sup>, electro-coagulation <sup>[15]</sup>, extraction <sup>[16]</sup>, etc. These techniques, unfortunately, are often of high cost and high energy consumption and may generate excessive toxic sludge to cause secondary pollution <sup>[17]</sup>. Compared with the above remediation techniques, chemical passivation with low-cost, high-efficiency, simple operation, and good scale-up ability is considered to be an economically feasible method for As(V) removal <sup>[18]</sup>. The core of chemical passivation method is the passivator. In recent years, nano-passivators have attracted more and more attention and found wide application in environmental remediation, due to their advantages such as large specific surface area, abundant active sites, and high remediation efficiency. Commonly used nano-remediation agents for As removal include manganese oxides <sup>[19]</sup>, titanium dioxide nanoparticles <sup>[20]</sup>, Iron oxides <sup>[21]</sup>, alumina nanoparticles <sup>[22]</sup>, etc. Among them, nevertheless, the high activity and brittleness of iron-based oxides as well as their high production cost hinder their application in engineering <sup>[23]</sup>. For example, zero-valent iron nanoparticles are highly active and liable to agglomeration and oxidation, which not only greatly reduces their actual remediation capability but also decreases their degradability in water and soil <sup>[24]</sup>. Nano-titanium dioxide has a low utilization of solar energy and its use for large-scale treatment of wastewater is infeasible without expanding the light-gathering area or doping with precious and rare earth metals, which increases the cost of investment.

In the present research, we pay special attention to chitin-like hollow alumina nanospheres (denoted as CLH-Al<sub>2</sub>O<sub>3</sub> NSs, also coded as nano-Al<sub>2</sub>O<sub>3</sub>) as the potential nano-adsorbent for As-contaminated water, since it is advantageous with excellent stability and removal capability for arsenic in water <sup>[25]</sup>. Currently available methods for the synthesis of nano-alumina include high-temperature pyrolysis <sup>[26]</sup>, precipitation <sup>[27]</sup>, water/solvent thermal method <sup>[28]</sup>, sol-gel method <sup>[29]</sup>, etc. These methods, however, often face drawbacks such as high energy consumption and long production cycle while the products are prone to agglomeration. In this sense, double microemulsion method (W/O/W and O/W/O; W refers to water phase and O to oil phase) is of special significance for the synthesis of novel nanomaterials, thanks to its mild synthesis

---

conditions and short production cycle as well as controllable particle size and effectively hindered agglomeration of the synthesized products [30]. Recent advances in nanostructured  $\text{Al}_2\text{O}_3$  fabrication, particularly hollow architectures with tunable porosity [23], have demonstrated exceptional As(V) uptake capacities exceeding 200 mg/g [24]. However, achieving simultaneous control over morphology stability and adsorption kinetics remains challenging. Therefore, we used sodium meta-aluminate solution as the first aqueous phase (W1), span-80 as the emulsifier, n-hexane as the oil phase (O), and ammonium bicarbonate solution as the second aqueous phase (W2) to obtain a W/O/W double reversed-phase microemulsion system. The as-formulated double reversed-phase microemulsion was magnetically stirred at 700 rev/min and 25 °C for 3 h; and the precipitate was pumped, filtered, washed with anhydrous ethanol and distilled water, and freeze-dried in vacuum for 24 h (-71 °C) to obtain precursor  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$  (AACH). The as-obtained precursor AACH was calcined at 500 °C for 3 h to afford CLH- $\text{Al}_2\text{O}_3$  NSs (i.e.,  $\text{Al}_2\text{O}_3$  nano-adsorbent), the target product. This paper reports the synthesis and characterization of the hollow  $\text{Al}_2\text{O}_3$  nano-adsorbent and investigates its adsorption performance and mechanism for arsenate ions in water. It aims at establishing relevant simple, facile, cost-effective, and well scalable synthetic methods for highly efficient and stable nano-adsorbent with promising prospect in remediating As-contaminated water.

## **2. Experimental**

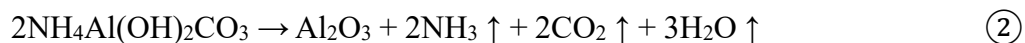
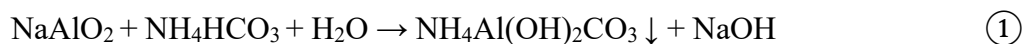
### **2.1 Reagents and apparatus**

Sodium meta-aluminate ( $\text{Na}_2\text{Al}_2\text{O}_4$ , 98.0%, AR) and ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ , 98%, AR) were purchased from McLean Chemical Reagent Company. Span-80 (chemically pure (CP)) was provided by Aladdin Reagent Company. Hexane ( $\text{C}_6\text{H}_{14}$ , 97%, AR) was commercially obtained from Tianjin Fuyu Fine Chemical Company. Sodium arsenate ( $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ , CP) and anhydrous ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 99.7%, AR) were brought from Beijing Chemical Reagent Factory and Anhui Ante Foods Company, respectively.

### **2.2 Optimization of reaction conditions for synthesizing $\text{Al}_2\text{O}_3$ nano-adsorbent**

Firstly, a series of  $\text{Al}_2\text{O}_3$  nano-adsorbents (also coded as nano- $\text{Al}_2\text{O}_3$ ) were

synthesized at varying  $\text{NH}_4\text{HCO}_3$  concentrations. Namely, 0.50 g of span-80 was dissolved in 36 mL of hexane while 18 mL of 1.0 mol/L  $\text{NaAlO}_2$  solution was added dropwise at a rate of 2.25 mL/min. The mixed solution was stirred magnetically at 25 °C (500 r/min) for 25 min to form a reversed-phase microemulsion. Seven parallels of the same reversed-phase microemulsion were prepared. Then different amounts (1.99 g, 4.98 g, 7.97 g, 9.36 g, 14.94 g, 19.92 g, and 24.90 g) of  $\text{NH}_4\text{HCO}_3$  were separately dissolved in 126 mL of distilled water while the reversed-phase microemulsion was respectively added dropwise to the  $\text{NH}_4\text{HCO}_3$  solutions under 3 h of magnetic stirring (700 rev/min) at 25 °C. Upon completion of the reactions, the precipitates were pumped, filtered, and washed with anhydrous ethanol and distilled water, each for three times, followed by freeze-drying in vacuum for 24 h (-71 °C) to obtain precursor  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$  (AACH). The as-obtained AACH was calcined at 500 °C for 3 h to obtain CLH- $\text{Al}_2\text{O}_3$  NSs. The reaction formulae for the synthesis of  $\text{Al}_2\text{O}_3$  nano-adsorbent are as follows:



The experiments for optimizing the synthesis conditions of  $\text{Al}_2\text{O}_3$  nano-adsorbent were conducted with varying dosage of span-80 (0.10 g, 0.20 g, 0.35 g, 0.50 g, and 1.00 g) under varying water bath temperature (15 °C, 25 °C, 35 °C, 45 °C, and 55 °C) and calcination temperature (400 °C, 500 °C, 600 °C, 700 °C, and 800 °C). After the optimal levels of span-80 dosage, water bath temperature, and calcination temperature were determined, they were adopted in follow-up experiments for optimizing the synthesis conditions. Based on a series of experiments for optimizing reaction conditions, we suggested that the amount of span-80, the concentration of  $\text{NH}_4\text{HCO}_3$  solution, as well as the water bath and calcination temperatures be selected as 0.5 g, 0.94 mol/L, 45 °C and 500 °C in order to synthesize CLH- $\text{Al}_2\text{O}_3$  NSs with desired comprehensive properties *via* double reversed-phase microemulsion method.

### **2.3 Adsorption performance of $\text{Al}_2\text{O}_3$ nano-adsorbent for arsenate ions at different solution pH values and nano-adsorbent dosage**

Firstly, the effect of solution pH on arsenate ions adsorption by  $\text{Al}_2\text{O}_3$  nano-

---

adsorbent was investigated. Thus 30 mL of  $\text{AsO}_4^{3-}$  solution (50 mg/L) with pH values of 3.0~9.0 (interval 1.0; the pH of the solution was adjusted with 0.1 mol/L  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and 0.1 mol/L  $\text{HNO}_3$ ) was placed into a 50-mL centrifugal tube with a 5-mL pipette gun while 0.025 g of the  $\text{Al}_2\text{O}_3$  nano-adsorbent was added under ultrasonic dispersion for 10 min. The resultant mixed solution was shaken on a shaking table at 25 °C and 60 rev/min for 2 h. Upon completion of shaking, the reaction solution was centrifuged at 8000 rev/min for 5 min and the supernatant was instantly collected and used for inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 2100DV, USA) quantitative detection.

Then the adsorption performance of  $\text{Al}_2\text{O}_3$  nano-adsorbent was examined in relation to the effect of its dosage. For this purpose, different amounts (0.03~0.08 g, interval of 0.01 g) of  $\text{Al}_2\text{O}_3$  nano-adsorbent were separately placed into six of 50-mL centrifuge tubes while 30 mL of  $\text{Na}_3\text{AsO}_4$  solution (77.84 mg/L; pH = 5.0) was respectively added therein. The resultant mixed solutions were shaken at 25 °C and 60 rev/min for 24 h. At the end of shaking, the supernatants were centrifuged for ICP-AES quantification; and corresponding ICP-AES quantification data were used for thermodynamic study.

#### **2.4 Adsorption kinetics of As(V) by $\text{Al}_2\text{O}_3$ nano-adsorbent**

In eight 50-mL centrifuge tubes were separately placed 0.05 g of  $\text{Al}_2\text{O}_3$  while 30 mL of  $\text{Na}_3\text{AsO}_4$  solution (77.84 mg/L; pH = 5.0) was added. The resultant mixed solutions were quickly placed into the shaker and shaken at 60 rev/min and 25 °C for 10 min, 15 min, 20 min, 25 min, 30 min, 35 min, 60 min, 120 min, and 1440 min. Upon completion of shaking, the reaction solutions were centrifuged (8000 rev/min; the same hereafter) to obtain the supernatants for ICP-AES quantitative detection; and the ICP-AES quantitative detection data were adopted for adsorption kinetics study.

#### **2.5 Immobilization of As(V) by $\text{Al}_2\text{O}_3$ nano-adsorbent**

0.08 g of  $\text{Al}_2\text{O}_3$  nano-adsorbent was placed in a 50-mL centrifuge tube and 30 mL of  $\text{AsO}_4^{3-}$  solution (77.84  $\text{mg} \cdot \text{L}^{-1}$ ; pH = 5.0) was added. The as-obtained solution was shaken at 60 rev/min and 25 °C for 24 h, followed by centrifugal separation to afford the supernatant for ICP-AES measurement (the ICP-AES result refers to the content of

---

AsO<sub>4</sub><sup>3-</sup> ions that were not adsorbed and immobilized). Besides, 12 mL of distilled water was added to the as-obtained precipitate and ultrasonically dispersed; and 10 mL of the resultant suspension was centrifuged to obtain the supernatant for ICP-AES measurement (here the ICP-AES result corresponds to the content of physically adsorbed AsO<sub>4</sub><sup>3-</sup> ions). Similarly, 10 mL of distilled water was added into the resulting precipitate, ultrasonically dispersed at 25 °C for 2 h, and centrifuged to obtain the supernatant for ICP-AES analysis to determine the amount of AsO<sub>4</sub><sup>3-</sup> ions at the first desorption. The same procedures were repeated for several times until the as-tested supernatant was free of AsO<sub>4</sub><sup>3-</sup>.

## **2.6 Instruments for preparation and analyses of element composition and surface properties as well as structure characterization of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent**

A high-precision numerical control shaker (ATS-03M2R, China), an electronic balance (BS224S, China), a high-speed centrifuge (TG16-WS, China), a vacuum freeze dryer (freezone 6L, USA), and a chamber resistance furnace (SX-4-10, China) were utilized to prepare Al<sub>2</sub>O<sub>3</sub> nano-adsorbent. An automatic specific surface area and pore size analyzer (BET; JW-BK222, China) was performed to determine the surface properties of the as-synthesized Al<sub>2</sub>O<sub>3</sub> nano-adsorbent; and its microstructure and chemical feature were analyzed with a transmission electron microscope (TEM; JEM-F200/JEM-2100Plus, Japan), a field emission scanning electron microscope (SEM; UK/Carl Zeiss, Germany), an X-ray diffractometer (XRD; DX-2700BH, China), and a Fourier transform infrared spectrometer (FT-IR; VERTEX 70, Germany). Moreover, element composition analysis and concentration detect of AsO<sub>4</sub><sup>3-</sup> ions were conducted by ICP-AES.

## **3. Results and discussion**

### **3.1 Optimizing conditions for preparing nano-Al<sub>2</sub>O<sub>3</sub>**

#### **3.1.1 Effect of NH<sub>4</sub>HCO<sub>3</sub> solution concentration**

The effect of NH<sub>4</sub>HCO<sub>3</sub> solution concentration (0.20, 0.50, 0.80, 0.94, 1.50, 2.00, and 2.50 mol/L) on the morphology of nano-Al<sub>2</sub>O<sub>3</sub> was determined while the dosage of span-80 (0.5 g) and the volume of NaAlO<sub>2</sub> solution (18 mL, 1 mol/L) were kept constant. The reaction was allowed to proceed under 25 °C for 3 h, in association with calcination

at 500 °C for 3 h. The correlation between  $\text{NH}_4\text{HCO}_3$  concentration and  $\text{Al}_2\text{O}_3$  nanostructure geometry, as systematically illustrated in Fig. 1, underscores the tunability of particle morphology through precipitation control. Namely, flake-like  $\text{Al}_2\text{O}_3$  is formed at the  $\text{NH}_4\text{HCO}_3$  solution concentration of 0.20 mol/L (Fig. 1a); when the concentration of  $\text{NH}_4\text{HCO}_3$  solution is kept at 0.50 mol/L,  $\text{Al}_2\text{O}_3$  with mixed flake-sphere morphology is yielded (Fig. 1b).  $\text{Al}_2\text{O}_3$  nanospheres with a size of about 150 nm are produced at an increased  $\text{NH}_4\text{HCO}_3$  solution concentration of 0.80 mol/L (Fig. 1c). When the concentration of  $\text{NH}_4\text{HCO}_3$  further increases to 0.94 mol/L, CLH- $\text{Al}_2\text{O}_3$  NSs with increased size of around 250 nm and surface burrs are obtained (Fig. 1d). Moreover, CLH- $\text{Al}_2\text{O}_3$  NSs with similar morphology are synthesized at the

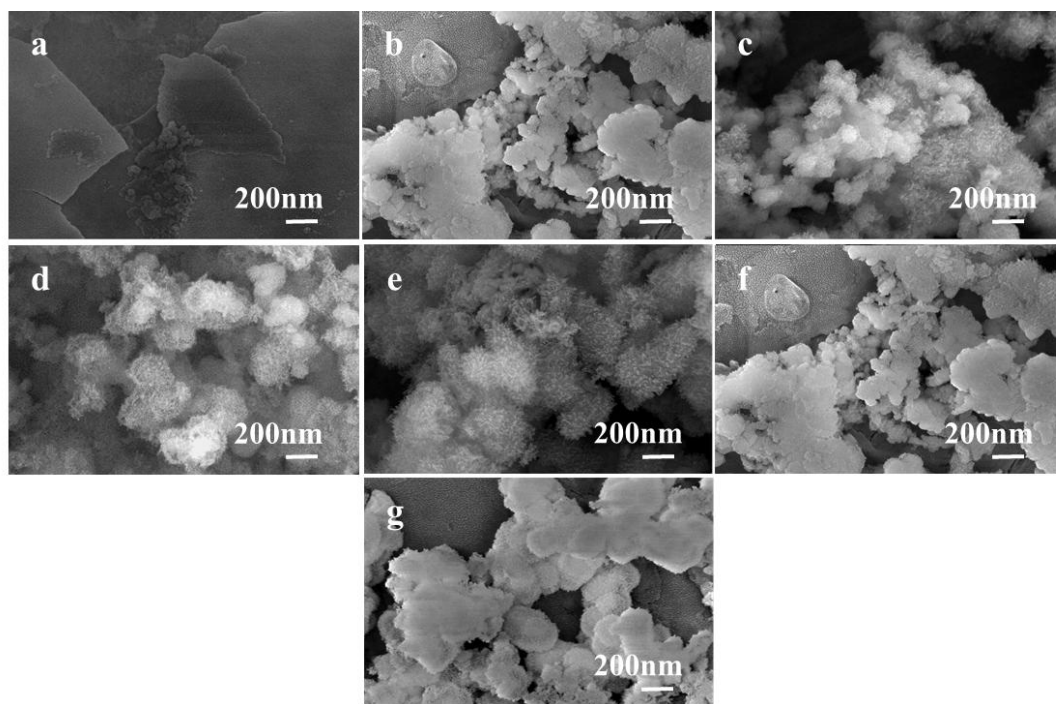


Fig. 1 SEM images of  $\text{Al}_2\text{O}_3$  samples obtained at  $\text{NH}_4\text{HCO}_3$  concentrations of 0.20 mol/L (a), 0.50 mol/L (b), 0.80 mol/L (c), 0.94 mol/L (d), 1.50 mol/L (e), 2.00 mol/L (f), and 2.50 mol/L (g).

$\text{NH}_4\text{HCO}_3$  concentrations of 1.50 mol/L and above (Fig. 1e-g). Therefore, the optimal  $\text{NH}_4\text{HCO}_3$  concentration was determined to be 0.94 mol/L through comprehensive analysis.

### 3.1.2 Effect of span-80 dosage

The effect of span-80 dosage (0.10, 0.20, 0.35, 0.50, and 1.00 g) on the morphology of the products was investigated under fixed  $\text{NH}_4\text{HCO}_3$  concentration of 0.94 mol/L while the  $\text{NaAlO}_2$  solution concentration (18 mL, 1 mol/L) and the other

reaction conditions were kept constant (25 °C, 3 h; in association with calcination at 500 °C for 3 h). Here span-80 acted as an emulsifier, a soft templating agent, and a dispersant <sup>[31]</sup>. Fig. 2 shows the SEM images of the Al<sub>2</sub>O<sub>3</sub> samples synthesized with different masses of span-80. When the dosage of span-80 is less than 0.35 g, Al<sub>2</sub>O<sub>3</sub> nano-adsorbent with inhomogeneous size and a large amount of aggregates is formed. Above span-80 addition of 0.35 g, the resultant CLH-Al<sub>2</sub>O<sub>3</sub> NSs become more dispersed. Therefore, the optimal dosage of span-80 was selected as 0.5 g.

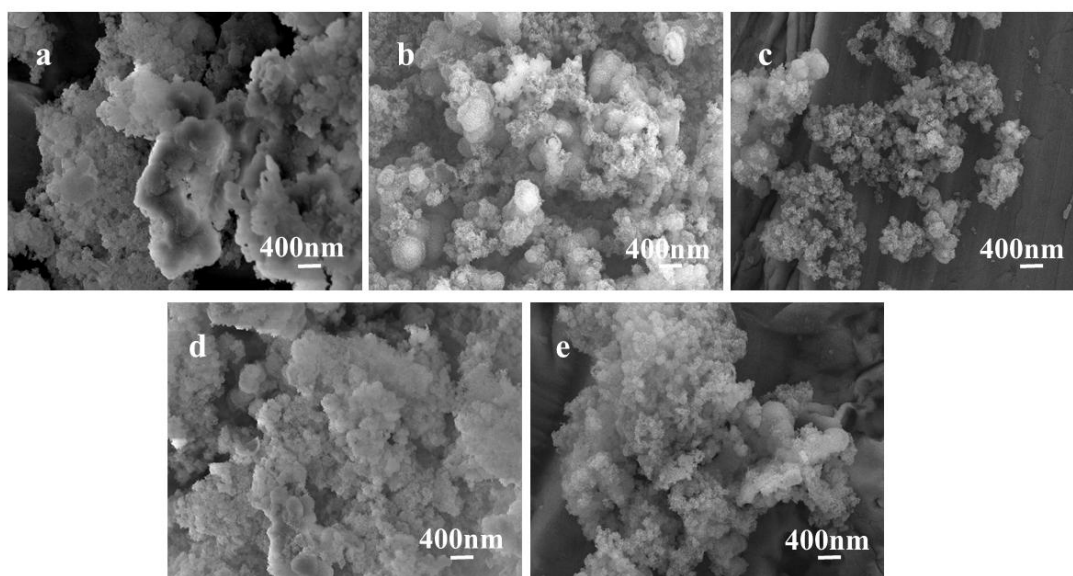


Fig. 2 SEM images of Al<sub>2</sub>O<sub>3</sub> samples obtained with 0.10 g (a), 0.20 g (b), 0.35 g (c), 0.50 g (d), and 1.00 g (e) of span-80.

### 3.1.3 Effect of reaction temperature

The effect of reaction temperature (15 °C, 25 °C, 35 °C, 45 °C, and 55 °C) on the morphology of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent was investigated under the reaction conditions the same as above except for span-80 dosage (0.5 g). As observed in Fig. 3a-c, Al<sub>2</sub>O<sub>3</sub> nanospheres with signs of severe agglomeration as well as an average particle size of 200 nm are obtained at reaction temperatures of 35 °C and below. This is because the Al<sub>2</sub>O<sub>3</sub> nanocrystals are prone to piling up and can hardly form a uniformly dispersed structure at relatively low reaction temperatures. At the reaction temperature of 45 °C, the Al<sub>2</sub>O<sub>3</sub> nano-adsorbent with improved dispersion and increased average particle size of 400 nm is generated in a short reaction time (Fig. 3d), accompanied by the formation of more burrs on the surfaces in association with the increase of specific surface area,

due to accelerated growth of the nanocrystals thereat<sup>[32]</sup>. As the reaction temperature is further increased to 55 °C, CLH-Al<sub>2</sub>O<sub>3</sub> nano-adsorbent with scattered surface burrs is afforded, due to the enhanced collision of the droplets thereat (Fig. 3e). Moreover, as seen in Fig. 3f, the removal rate of AsO<sub>4</sub><sup>3-</sup> upon adsorption by CLH-Al<sub>2</sub>O<sub>3</sub> nano-adsorbent gradually augments with increasing reaction temperature

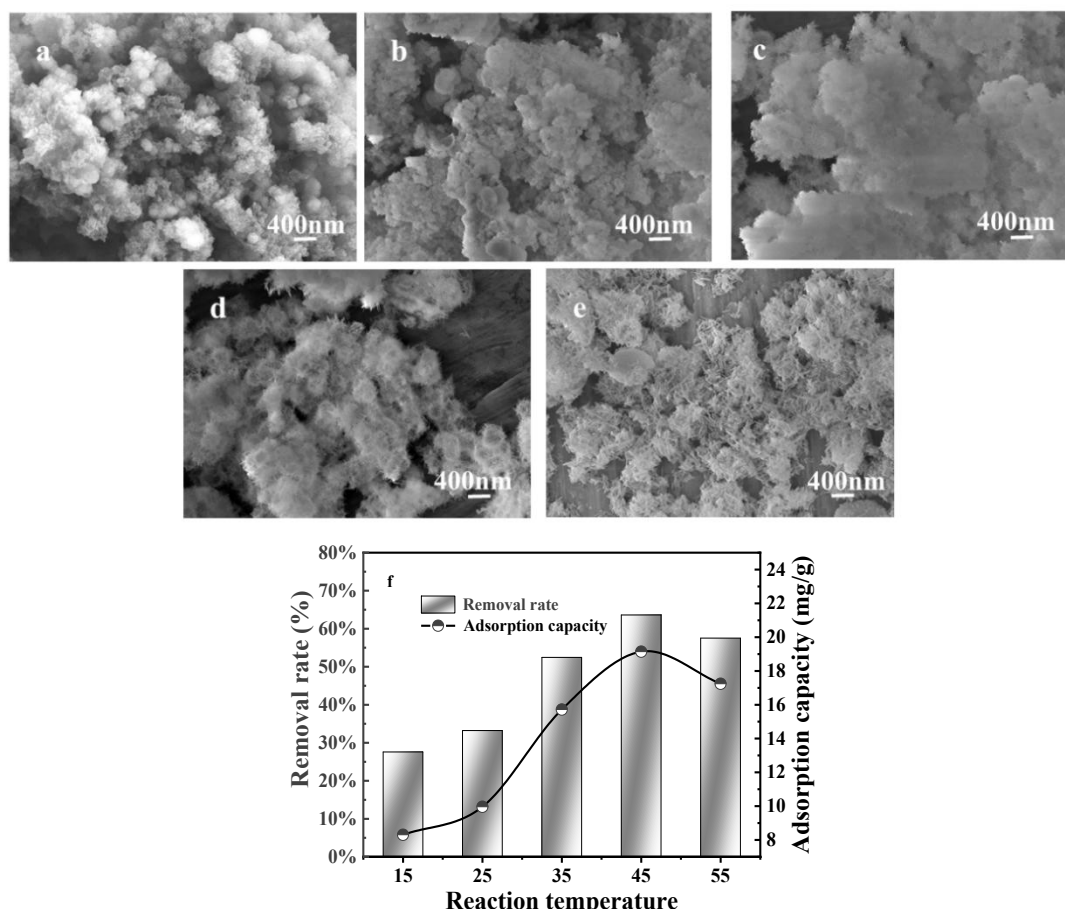


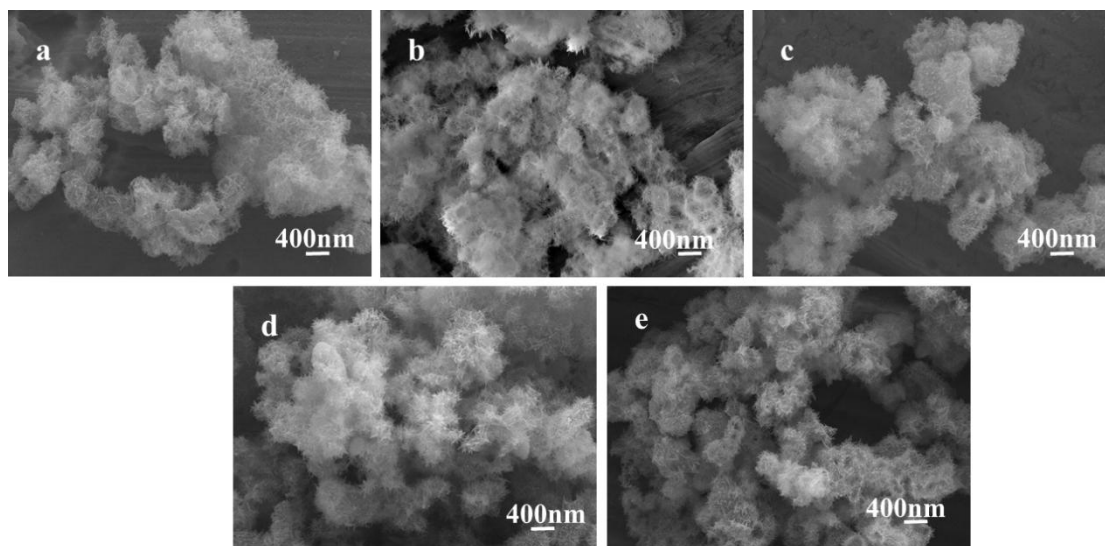
Fig. 3 SEM images of Al<sub>2</sub>O<sub>3</sub> nanospheres synthesized at reaction temperatures of 15 °C (a), 25 °C (b), 35 °C (c), 45 °C (d), and 55 °C (e), as well as relationship among removal rate of AsO<sub>4</sub><sup>3-</sup> and adsorption capacity of Al<sub>2</sub>O<sub>3</sub> nanospheres and reaction temperature (f).

up to 63.61% at 45 °C. This is because increasing reaction temperature favors the formation of Al<sub>2</sub>O<sub>3</sub> nanocrystals with increased dispersion and promotes their contact and interaction with AsO<sub>4</sub><sup>3-</sup>. When the reaction temperature elevates to 55 °C, however, the removal rate declines at a certain degree, which could be because the burrs undergo structural collapse, disturbing the immobilization capability of nano-alumina towards AsO<sub>4</sub><sup>3-</sup>. Therefore, the optimal reaction temperature was suggested to be 45 °C.

### 3.1.4 Effect of calcination temperature

The effect of calcination temperature (400-800 °C; interval 100 °C) on the

morphology of  $\text{Al}_2\text{O}_3$  nano-adsorbent was investigated under the reaction conditions the same as those of section 3.1.3. As seen in Fig. 4, the  $\text{Al}_2\text{O}_3$  samples formed at different calcination temperatures exhibit similar morphology (Fig. 4a-e), which indicates that the calcination temperature has little influence on the products' morphology. In the meantime, XRD analysis indicates that amorphous alumina is produced at calcination temperatures of 400 °C and 500 °C (Fig 4f). Particularly, the relatively weak XRD signals at  $2\theta$  of 37.60°, 45.86°, and 67.03° demonstrate that the  $\text{Al}_2\text{O}_3$  sample obtained at the calcination temperature of 600 °C is the mixture of nanocrystal and amorphous alumina. As the calcination temperature further rises to 700 °C and above, the as-fabricated target products display XRD signals at  $2\theta$  of 19.45°, 37.60°, 39.49°, 45.86°, 60.89°, and 67.03°, corresponding to the (111), (311), (222), (400), (511), and (440) crystal planes of  $\gamma\text{-Al}_2\text{O}_3$  (PDF 10-0425). This indicates that calcination at 700 °C and 800 °C produces highly pure  $\text{Al}_2\text{O}_3$  nanocrystals. Furthermore, the removal rate of  $\text{AsO}_4^{3-}$  by  $\text{Al}_2\text{O}_3$  nano-adsorbent firstly increases and then decreases with elevating calcination temperature (Fig. 4g); and the target product obtained at calcination temperature 500 °C possesses the highest adsorption capacity of 22.81 mg/g and removal rate of 73.25% for  $\text{AsO}_4^{3-}$ . Therefore, the best calcination temperature for fabricating  $\text{Al}_2\text{O}_3$  nanospheres was recommended as 500 °C.



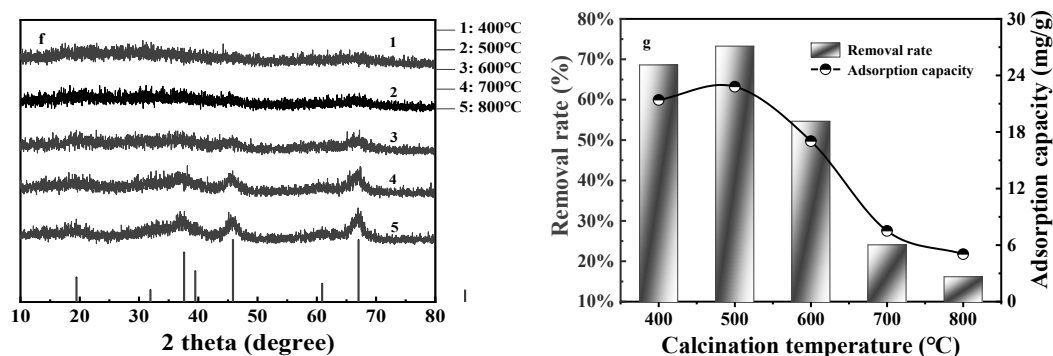


Fig. 4 SEM images of Al<sub>2</sub>O<sub>3</sub> nanospheres obtained at calcination temperatures of 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d), and 800 °C (e), XRD patterns of Al<sub>2</sub>O<sub>3</sub> prepared at calcination temperatures of 400 °C (curve 1), 500 °C (curve 2), 600 °C (curve 3), 700 °C (curve 4), and 800 °C (curve 5) (f), as well as relationship between removal rate of AsO<sub>4</sub><sup>3-</sup> and adsorption capacity of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent and calcination temperature (g).

### 3.2 Structure characterization of Al<sub>2</sub>O<sub>3</sub> nanospheres fabricated under optimal reaction conditions

Fig. 5a-b shows the SEM and TEM images of AACH (the precursor, i.e., Al source). It can be seen that AACH is of a hollow structure with a relatively rough surface (containing flocculent burrs) as well as an average particle size of 400 nm and a shell thickness of 25 nm. After calcination at 600 °C for 3 h, AACH is decomposed to form Al<sub>2</sub>O<sub>3</sub>, NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. Here the as-obtained Al<sub>2</sub>O<sub>3</sub> nanospheres retain the same chitin-like hollow structure as well as particle size and shell thickness of the Al source (see Fig. 5c-d). Besides, 3 h of calcination of AACH at 600 °C leads to the total disappearance of the characteristic diffraction peaks at  $2\theta$  of 15.28°, 21.74°, 27.04°, 30.94°, 35.04°, 40.78°, 44.66°, and 52.86° assigned to the (110), (111), (200), (220), (112), (232), (222), and (312) crystal planes of orthorhombic NH<sub>4</sub>Al(OH)<sub>2</sub>CO<sub>3</sub> (PDF 76-1923) (Fig. 5e). This proves that the precursor is completely transformed into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after being calcined at 600 °C, which is also supported by the XRD data shown in Fig. 5f. Namely, in this case only the characteristic diffraction signals of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> emerge at  $2\theta$  of 45.28° and 67.18°, corresponding to the (400) and (440) facets of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (PDF 10-0425)<sup>[33]</sup>. In other words, the amorphous Al<sub>2</sub>O<sub>3</sub> is completely converted into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocrystal at the calcination temperature of 600 °C.

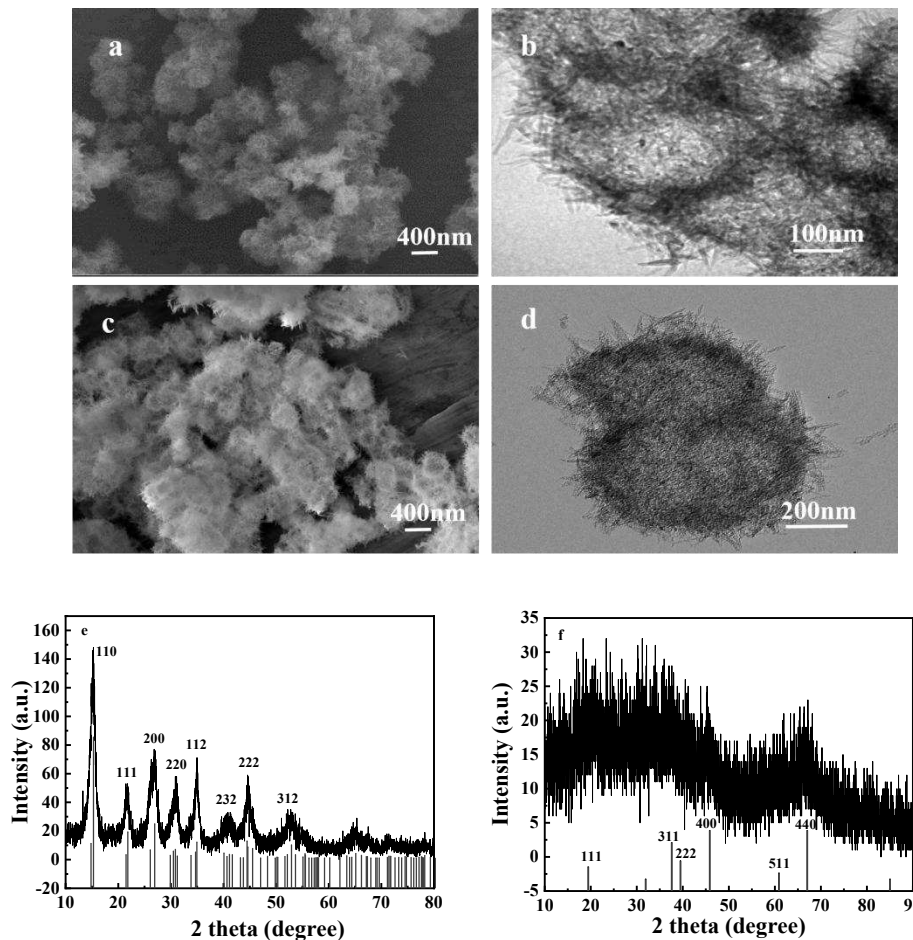


Fig. 5 SEM and TEM images of AACH (a, b) and Al<sub>2</sub>O<sub>3</sub> (c, d) as well as their XRD patterns (e, f).

To determine the specific surface area as well as pore diameter, pore size distribution, and pore volume of Al<sub>2</sub>O<sub>3</sub> nanospheres, we recorded their N<sub>2</sub> adsorption-desorption isotherms. As shown in Fig. 6a, the N<sub>2</sub> adsorption-desorption isotherms refer to typical V-shaped adsorption, exhibiting a clear desorption hysteresis return line. This means that the as-prepared Al<sub>2</sub>O<sub>3</sub> nanospheres exhibit porous structure, which is suitable for the rapid adsorption of bulk molecules. The specific surface area, pore volume, and pore diameter of Al<sub>2</sub>O<sub>3</sub> nanospheres are 394.99 m<sup>2</sup>/g, 1.94 cm<sup>3</sup>/g, and 4.46 nm, respectively (Fig. 6b), higher than those of nano-alumina reported elsewhere [34]. Therefore, it can be inferred that the target products possess many surface active sites, which should be favorable for As removal [35].

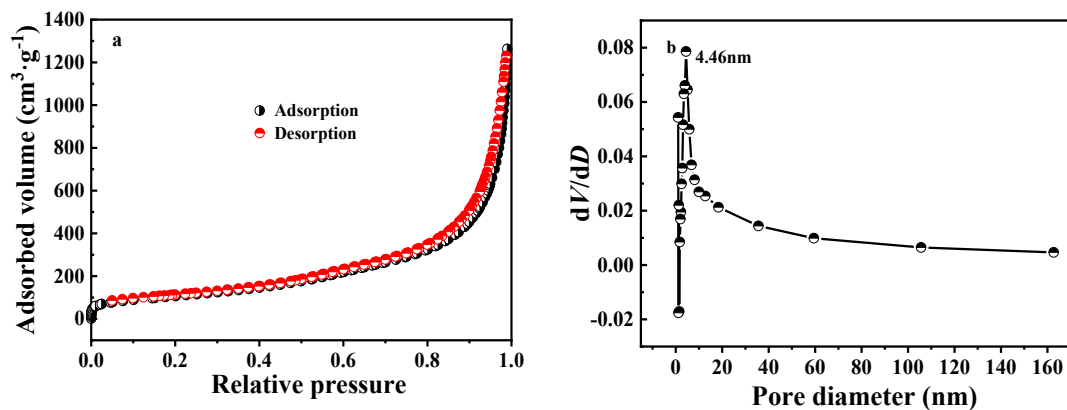


Fig. 6 N<sub>2</sub> adsorption-desorption curves (a) and pore size distribution diagram (b) of Al<sub>2</sub>O<sub>3</sub> nanospheres.

### 3.3 Adsorption behavior of AsO<sub>4</sub><sup>3-</sup> by Al<sub>2</sub>O<sub>3</sub> nano-adsorbent

pH is an important factor affecting the adsorption rate of the adsorbate, and it not only determines the form of the pollutants in water but also the charge of the adsorbent surface [36]. The removal rate of AsO<sub>4</sub><sup>3-</sup> by Al<sub>2</sub>O<sub>3</sub> nano-adsorbent was tested in the pH range of 3.0-9.0, optimum equilibrium time of 120 min, oscillation rate of 60 r/min, initial AsO<sub>4</sub><sup>3-</sup> concentration of 50 mg/L, and adsorbent amount of 0.025 g. As shown in Fig. 7a, the maximum removal rate of AsO<sub>4</sub><sup>3-</sup> by nano-Al<sub>2</sub>O<sub>3</sub> is 98.69% at pH 3.0, and it gradually decreases with increasing pH value. This is because the arsenate ions in aqueous solution of pH 3.0-7.0 are mainly present as HAsO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> [37]. At low pH values, the surface of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent is of positive charge, which is beneficial to enhancing the adsorption of arsenate ions via the electrostatic attraction between the positive and negative charges. When the pH further rises to the isoelectric point (8.0 to 8.5) and above, the removal rate declines to 8.5% [37]. The reason lies in that, at the isoelectric point and above, the surface of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent is negatively charged to induce the electrostatic repulsion between arsenate ions and the nano-adsorbent [38]. This could explain why Al<sub>2</sub>O<sub>3</sub> nano-adsorbent exhibits better passivation efficiency under acidic condition. Considering the environmental pollution by acid rain (pH < 5.6), we selected the pH of the arsenic solution to be 5.0 in the follow-up experiments.

The variation in the removal rate of AsO<sub>4</sub><sup>3-</sup> ions with the dosage of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent is displayed in Fig. 7b. The removal rate of AsO<sub>4</sub><sup>3-</sup> increases from 45.86% to 82.43% as the nano-adsorbent dosage rises from 0.03 g to 0.08 g, which is because at

the fixed concentration of  $\text{AsO}_4^{3-}$  ions, increasing nano-adsorbent dosage refers to the increased amount of active adsorption sites. At the same time, the adsorption capacity of  $\text{Al}_2\text{O}_3$  nano-adsorbent tends to decrease with elevating dosage, possibly because the saturated adsorption occurs even at a low nano-adsorbent dosage, which, in association with the aggregation at higher dosage, hinders the effective adsorption. To achieve the compromise between the removal rate and adsorption capacity, we fixed the dosage of the  $\text{Al}_2\text{O}_3$  nano-adsorbent as 0.05 g in successive experiments.

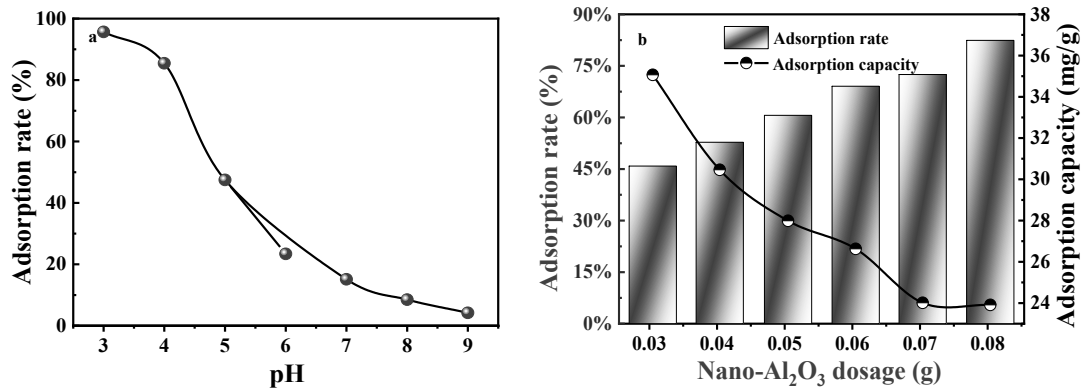


Fig. 7 Relationships between removal rate of  $\text{AsO}_4^{3-}$  ions and solution pH (a) as well as removal rate-adsorption capacity with  $\text{Al}_2\text{O}_3$  nano-adsorbent dosage (b).

### 3.4 Adsorption thermodynamics

The isotherm adsorption curves were measured to reveal the interaction between  $\text{Al}_2\text{O}_3$  nano-adsorbent and  $\text{AsO}_4^{3-}$  ions, with which the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms models were utilized to explore the adsorption mechanism.

Langmuir isotherm model assumes that monolayer adsorption occurs at a finite number of adsorption sites with the same adsorption energy while no migration of the adsorbates takes place on the surface of adsorbent (here  $\text{Al}_2\text{O}_3$  nano-adsorbent) [39]. Based on these assumptions, the Langmuir nonlinear equation is written as below:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{bQ_m} \quad (1)$$

where  $C_e$  ( $\text{mg} \cdot \text{mL}^{-1}$ ) is the equilibrium concentration of  $\text{AsO}_4^{3-}$  ions;  $Q_e$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the amount of  $\text{AsO}_4^{3-}$  ions adsorbed by  $\text{Al}_2\text{O}_3$  nano-adsorbent;  $Q_m$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the maximum adsorption capacity of  $\text{Al}_2\text{O}_3$  nano-adsorbent;  $b$  ( $\text{L} \cdot \text{mg}^{-1}$ ) is the Langmuir isotherm constant. Corresponding linearly fitted adsorption isotherm parameters are presented in

Fig. 8a and Table 1. The maximum adsorption amount of  $\text{AsO}_4^{3-}$  by the nano-adsorbent at 298 K is 37.11 mg/g, and the adsorption equilibrium constant is 0.11. This indicates that the equilibrium adsorption can rapidly achieve while the  $R^2$  of 0.97 means the adsorption process follows the Langmuir isotherm adsorption model. In other words, the adsorption process is dominated by monolayer adsorption.

Freundlich isotherm model is more realistic than the Langmuir isotherm model. The former hypothesizes that the adsorbent-adsorbate interaction on heterogeneous surfaces is governed by multilayer adsorption while the adsorbent surfaces are inhomogeneous (the nature of the adsorption sites varies with locations) <sup>[40]</sup>, described as below:

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln k \quad (2)$$

where  $k$  ( $\text{mg}^{1-1/n}/\text{L}^{-1/n}/\text{g}$ ) is Freundlich isotherm constant; and  $1/n$  is the degree of nonlinearity between  $\text{AsO}_4^{3-}$  ions and the adsorption capacity of  $\text{Al}_2\text{O}_3$  nano-adsorbent. Calculations display that  $n$  equals to 4.03 (between 1 and 10) and  $R^2$  to 0.83, which indicates that the  $\text{AsO}_4^{3-}$  ions can be easily adsorbed by  $\text{Al}_2\text{O}_3$  nano-adsorbent. Therefore, it can be inferred that the adsorption of  $\text{AsO}_4^{3-}$  ions by  $\text{Al}_2\text{O}_3$  nano-adsorbent better follows the Langmuir model.

Temkin isotherm model explicitly takes into account the adsorbent-adsorbate interaction <sup>[41]</sup>. It assumes that adsorption is characterized by the uniform distribution of binding energy up to its maximum, while the heat of adsorption of all molecules in the adsorbed layer decreases linearly with its coverage in the presence of adsorbate-adsorbent interaction. Relevant equations are as follows:

$$Q_e = \frac{RT}{b} \ln A_T C_e \quad (3)$$

$$Q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e \quad (4)$$

$$B = \frac{RT}{b} \quad (5)$$

$$Q_e = B \ln A_T + B \ln C_e \quad (6)$$

where  $A_T$  is the Temkin isotherm equilibrium binding constant (L/g);  $b$  is the Temkin isotherm constant;  $R$  is the gas constant (8.31 J/mol/K);  $T$  is temperature (K); and  $B$  is

the constant related to the heat of adsorption (J/mol). As listed in Table 1, the parameters  $A_T$ ,  $B$ , and  $R^2$ , calculated with the Temkin isotherm model, are 2.29 L/g, 6.64 J/mol, and 0.82, respectively. This means that Temkin isotherm model is less suitable than Langmuir model in describing the adsorption behavior of  $\text{AsO}_4^{3-}$  ions on  $\text{Al}_2\text{O}_3$  nano-adsorbent.

Dubinin-Radushkevich isotherm model: it is usually used to express adsorption mechanisms with Gaussian energy distributions rather than inhomogeneous surfaces [42]. Corresponding mathematical expressions are defined as follows:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (7)$$

$$Q_e = Q_s e^{-B'\varepsilon^2} \quad (8)$$

$$\ln Q_e = \ln Q_m - B'\varepsilon^2 \quad (9)$$

where  $B'$  is the Dubinin-Radushkevich isotherm constant ( $\text{mol}^2/\text{kJ}^2$ ); and  $\varepsilon$  is the Dubinin-Radushkevich isotherm constant. Corresponding calculations demonstrate that  $Q_m$  is 29.25 mg/g while  $R^2$  and the average free energy  $E$  equal to 0.61 and 254.71 kJ/mol, respectively. This indicates that the adsorption of  $\text{AsO}_4^{3-}$  ions by  $\text{Al}_2\text{O}_3$  nano-adsorbent is predominantly governed by physical adsorption. Moreover, similar to the above mentioned, Dubinin-Radushkevich isotherm model demonstrates reduced applicability compared to the Langmuir model in quantitatively characterizing the adsorption behavior of  $\text{AsO}_4^{3-}$  ions on  $\text{Al}_2\text{O}_3$  nano-adsorbent.

The correlation coefficients at 298 K, calculated with Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm adsorption models, are 0.97, 0.83, 0.82, and 0.61, respectively. This means that the adsorption process aligns more closely with the Langmuir isotherm adsorption model and belongs to monomolecular layer adsorption. In other words, the adsorption of  $\text{AsO}_4^{3-}$  ions by  $\text{Al}_2\text{O}_3$  nano-adsorbent can be well described by Langmuir adsorption isotherm model.

Table 1 Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherm parameters.

| Adsorption<br>isotherm<br>models | Parameters      |                      |       |                                                          |     |                |                |                                        |                 |
|----------------------------------|-----------------|----------------------|-------|----------------------------------------------------------|-----|----------------|----------------|----------------------------------------|-----------------|
|                                  | $K_L$<br>(L/mg) | $Q_{\max}$<br>(mg/L) | $R^2$ | $K_F$<br>( $\text{mg}^{1-1/n}/\text{L}^{1/n}/\text{g}$ ) | $n$ | $A_T$<br>(L/g) | $B$<br>(J/mol) | $B'$<br>( $\text{mol}^2/\text{kJ}^2$ ) | $Q_m$<br>(mg/g) |

|                          |      |       |      |       |      |                       |       |
|--------------------------|------|-------|------|-------|------|-----------------------|-------|
| Langmuir                 | 0.11 | 37.11 | 0.97 |       |      |                       |       |
| Freundlich               |      |       | 0.83 | 12.04 | 4.03 |                       |       |
| Temkin                   |      |       | 0.82 |       | 2.29 | 6.64                  |       |
| Dubinin–<br>Radushkevich |      |       | 0.61 |       |      | $7.71 \times 10^{-6}$ | 29.25 |

Note: the initial concentration ( $C_0$ ) of  $\text{AsO}_4^{3-}$  ions is 77.74 mg/L.

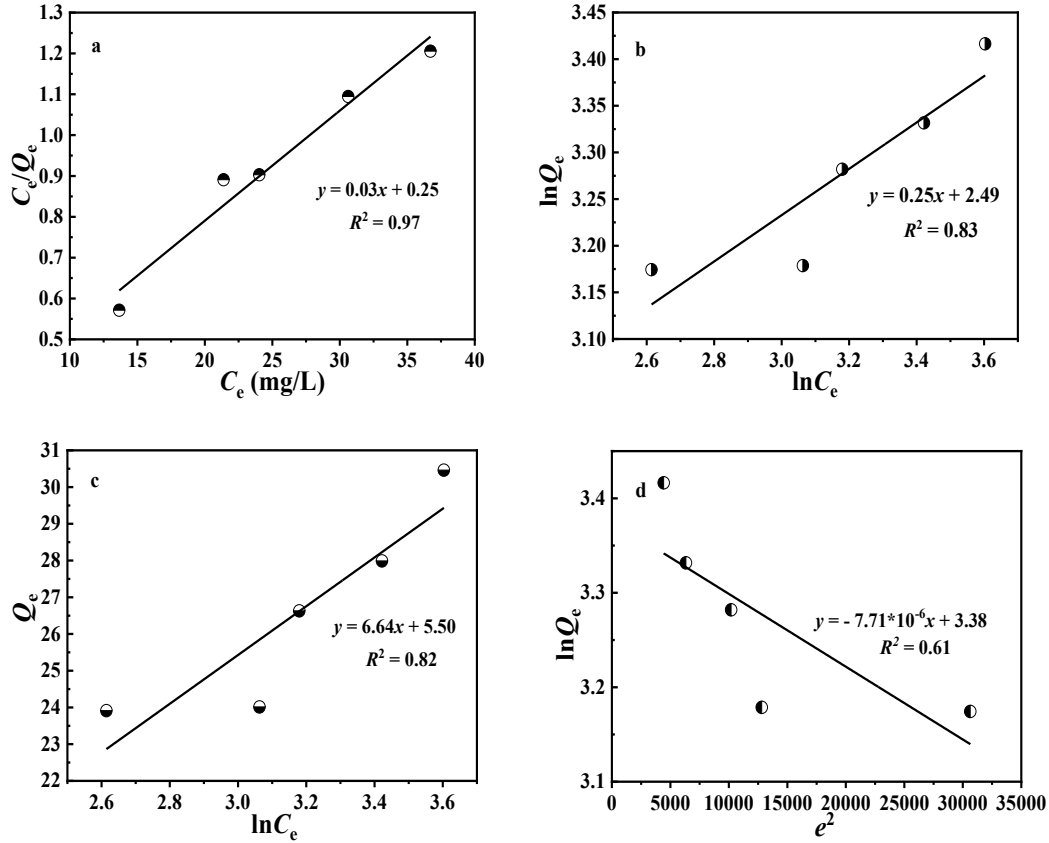


Fig. 8 The adsorption isotherms fitted with Langmuir (a), Freundlich (b), Temkin (c) and Dubinin–Radushkevich models (d).

### 3.5 Adsorption kinetics

The adsorption process of  $\text{AsO}_4^{3-}$  on  $\text{Al}_2\text{O}_3$  nano-adsorbent was further investigated based on adsorption kinetics studies in relation to the adsorption efficiency and mechanism. The most widely used models, i.e., the pseudo-first order <sup>[43]</sup>, the pseudo-second order <sup>[44]</sup>, and intra-particle diffusion kinetic equations <sup>[45]</sup>, were employed to reveal the kinetic adsorption mechanism. The three equations are described as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (10)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (11)$$

---


$$Q_t = K_{\text{int}} t^{\frac{1}{2}} + I \quad (12)$$

where  $Q_e$  is the equilibrium adsorption amount (mg/g);  $Q_t$  is the adsorption amount at time  $t$  (mg/g);  $k_1$  is the primary kinetic adsorption rate constant (/min);  $k_2$  is the pseudo-second order kinetic adsorption rate constant (mg/g/min);  $K_{\text{int}}$  is the rate constant for intra-particle diffusion (mg/g/min<sup>0.5</sup>), and  $I$  is the intercept of the fitted line. Here equation 11 was proposed by Weber and Morris to account for the possibility of diffusion of particles during adsorption. It assumes that the transport process of adsorbates from the solution phase to the surface of adsorbent particles is controlled by one or more steps, i.e., pore diffusion, surface diffusion, adsorption on pore surface, or their combinations. As to equation 12, if the fitted line passes through the origin, i.e., the intercept  $I = 0$ , we can stipulate that the adsorption process is dominated by the intra-particle diffusion mechanism. If  $I \neq 0$ , the intra-particle diffusion mechanism would not be the only rate-controlling step. In this case, aside from intra-particle diffusion mechanism, there are other factors that may also affect the rate of the adsorption process, including chemisorption, charge transport, and the migration of ions or molecules. Furthermore, in a multi-component system, the interaction among particles (e.g., electrostatic attraction or repulsion) can further modulate adsorption dynamics through a hybrid control mechanism.

The results for the adsorption of  $\text{AsO}_4^{3-}$  on  $\text{Al}_2\text{O}_3$  nano-adsorbent fitted with pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic equations are presented in Fig. 9 and Table 2. The correlation coefficients for the intra-particle diffusion model ( $R^2 = 0.96$ ) and the pseudo-second order model ( $R^2 = 0.99$ ) are close to 1.00, larger than that for the pseudo-first order kinetic model ( $R^2 = 0.65$ ); and the adsorption capacity fitted with pseudo-second order model is 19.70 mg/g, relatively closer to the experimental one (27.99 mg/g). Therefore, it can be concluded that the pseudo-second kinetic model is the most suitable for describing the adsorption dynamics of  $\text{AsO}_4^{3-}$  on  $\text{Al}_2\text{O}_3$  nano-adsorbent. Namely, the pseudo-second kinetic

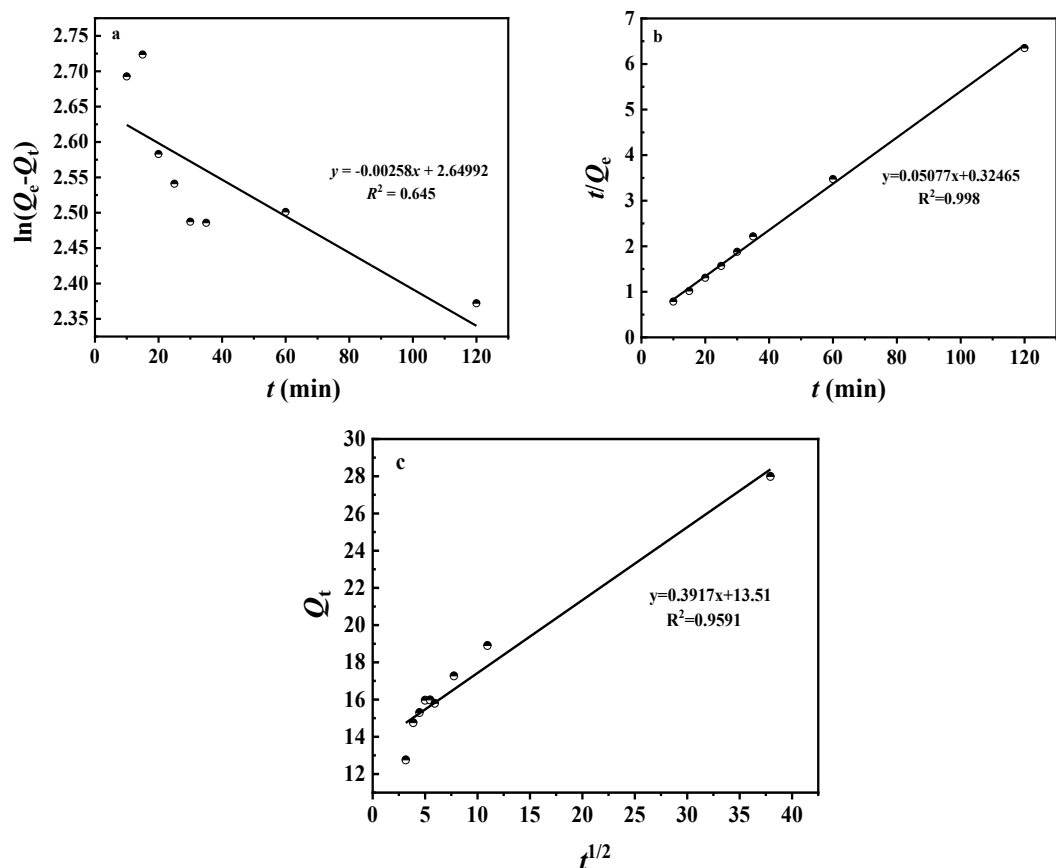


Fig. 9 The adsorption of  $\text{AsO}_4^{3-}$  ions by  $\text{Al}_2\text{O}_3$  nano-adsorbent fitted with the pseudo-first order kinetics (a), the pseudo-second order kinetics (b), and the intra-particle diffusion models (c).

Table 2 The adsorption parameters of  $\text{AsO}_4^{3-}$  ions by  $\text{Al}_2\text{O}_3$  nano-adsorbent fitted with the pseudo-first order kinetics, the pseudo-second order kinetics and intra-particle diffusion models.

| Adsorption<br>kinetics<br>models | Parameters      |                 |       |                     |                                                |       |
|----------------------------------|-----------------|-----------------|-------|---------------------|------------------------------------------------|-------|
|                                  | $k_1$<br>(/min) | $Q_e$<br>(mg/g) | $R^2$ | $k_2$<br>(mg/g/min) | $K_{\text{int}}$<br>(mg/g/min <sup>0.5</sup> ) | $I$   |
| Pseudo-first<br>order            | 0.0026          | 14.15           | 0.65  |                     |                                                |       |
| Pseudo-second<br>order           |                 | 19.70           | 0.99  | 0.0079              |                                                |       |
| Intra-particle<br>diffusion      |                 |                 | 0.96  |                     | 0.392                                          | 13.54 |

Note: the initial concentration ( $C_0$ ) of  $\text{AsO}_4^{3-}$  ions is 77.74 mg/L.

model and the intra-particle diffusion models are suggested to be jointly adopted for better describing the kinetic adsorption behavior of  $\text{AsO}_4^{3-}$  ions over  $\text{Al}_2\text{O}_3$  nano-adsorbent.

### 3.6 Stability of adsorbed products

Nanomaterials can passivate heavy metals through physical and chemical

---

adsorption. Physical adsorption mainly relies on intermolecular forces such as van der Waals force and electrostatic interaction between the nano-adsorbent and the heavy metal ions, and chemical adsorption depends on the chemical bonding there-between. Here the functional groups such as hydroxyl, amino, and carboxyl play key roles in chemical adsorption, because they often can be grafted onto the surface of nanomaterials, thereby chelating with heavy metal ions or forming an ionic bond and/or a covalent bond therewith to efficiently remove heavy metals<sup>[46]</sup>. In the adsorption process, physical adsorption and chemical adsorption usually may coexist, and the chemically adsorbed products often exhibit better stability than the physically adsorbed counterparts. Desorption experiments were conducted to investigate the stability of the adsorbed products between Al<sub>2</sub>O<sub>3</sub> nano-adsorbent and AsO<sub>4</sub><sup>3-</sup> ions. As shown in Fig. 10, the desorption amount on day 0 (corresponding to physical adsorption; the nano-Al<sub>2</sub>O<sub>3</sub>/AsO<sub>4</sub><sup>3-</sup> was washed with deionized water and the supernatant was tested by ICP-AES) is 0.37 mg/g. From day 1 to day 4, the desorption amount tends to rise at a certain degree, which implies that the physically adsorbed AsO<sub>4</sub><sup>3-</sup> ions are nearly completely removed at day 4. From day 4, the desorption amount almost levels off (the daily desorption gradually stabilizes at about 0.05 mg/g), which means that the chemically adsorbed products possess quite high stability (the total desorption amount after 11 day of desorption experiments is 1.70 mg/g). In other words, there are strong chemical interactions between Al<sub>2</sub>O<sub>3</sub> nano-adsorbent and AsO<sub>4</sub><sup>3-</sup> ions. Such strong chemical interactions highly depend on the specific adsorption of AsO<sub>4</sub><sup>3-</sup> ions by Al<sub>2</sub>O<sub>3</sub> nano-adsorbent. Here the specific adsorption refers to electrostatic attraction, hydrogen bonding, and coordination bonding. On the one hand, the electrostatic attraction between the negatively charged AsO<sub>4</sub><sup>3-</sup> ions and positively charged Al<sub>2</sub>O<sub>3</sub> nano-adsorbent under acidic condition (in a certain pH range) largely accounts for the obligatory adsorption therein. On the other hand, the hydroxyl group on the surface of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent can form hydrogen bond or coordination bond with AsO<sub>4</sub><sup>3-</sup> ions, which also contributes to promoting the obligate adsorption.

The FT-IR spectra of Al<sub>2</sub>O<sub>3</sub> nano-adsorbent before and after AsO<sub>4</sub><sup>3-</sup> adsorption are presented in Fig. 10<sup>[47]</sup>, where the FT-IR spectrum of amorphous Al<sub>2</sub>O<sub>3</sub> is presented for

comparison. The absorption bands at  $3442\text{ cm}^{-1}$  and  $1633\text{ cm}^{-1}$  are assigned to the stretching vibration and bending vibration of -OH group; and the weak absorption band at  $1525\text{ cm}^{-1}$  is attributed to Al-OH stretching vibration. Besides, the strong absorption band at  $500\text{--}1000\text{ cm}^{-1}$  is attributed to the Al-O-Al bonding, which confirms the successful synthesis of the target nano-adsorbent. Moreover, the FT-IR spectra of the  $\text{Al}_2\text{O}_3$  before and after adsorbing  $\text{AsO}_4^{3-}$  ions show no significant changes, which suggests that FT-IR under current characterization conditions can hardly detect chemical bond formation between the adsorbent and the  $\text{AsO}_4^{3-}$  ions. This observation, however, does not preclude the existence of surface complexation mechanisms that may occur below the detection limit of FT-IR spectroscopy. As reported elsewhere, such spectral invariance could arise when the formed chemical bonds share similar vibrational characteristics with pre-existing surface groups.

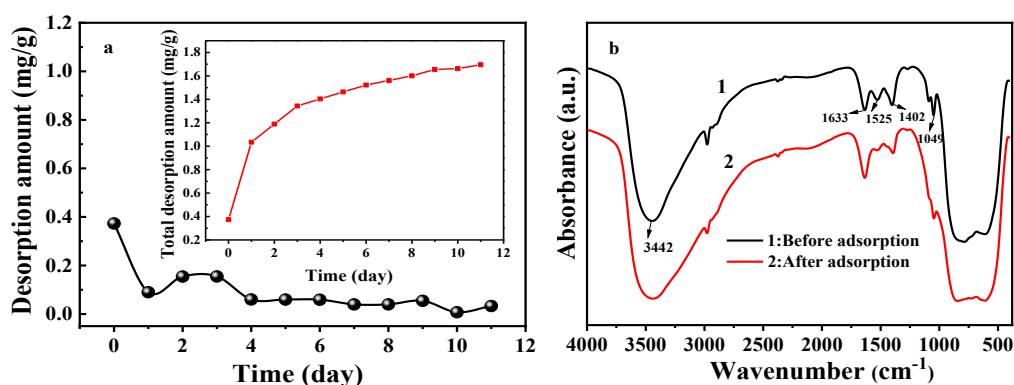


Fig. 10 Variation of desorption amount of nano- $\text{Al}_2\text{O}_3/\text{AsO}_4^{3-}$  with time (a) and FT-IR spectra of  $\text{Al}_2\text{O}_3$  nano-adsorbent before (curve 1) and after (curve 2) adsorbing  $\text{AsO}_4^{3-}$  (b).

### 3.7 Schematic diagram for the preparation of $\text{Al}_2\text{O}_3$ nano-adsorbent and the adsorption of $\text{AsO}_4^{3-}$ ions

The preparation of  $\text{Al}_2\text{O}_3$  nano-adsorbent by the double microemulsion method is schematically illustrated in Fig. 11. On the one hand, the reverse phase microemulsion is formulated by dispersing the aluminum source ( $\text{NaAlO}_2$  solution, i.e., WP-1) in a continuous n-hexane oil phase (OP) to obtain the W/O reverse phase microemulsion. On the other hand, the as-obtained W/O reverse phase microemulsion is dispersed in  $\text{NH}_4\text{HCO}_3$  solution (WP-2), the precipitant, to allow the reaction of  $\text{NaAlO}_2$  and  $\text{NH}_4\text{HCO}_3$  via the diffusion of either the aluminum source or the precipitant through the oil layer between the inner and outer aqueous phases. The diffusion of the ions in

the oil phase depends on the transport in the form of “anticlusters” [48]. In the aqueous phase, all ions exist in the hydrated state. When the water shell is close to the interface, anticolloidal micelles are formed at OP/WP-1 and WP-2/OP, due to the interactions between water molecules and the hydrophilic polar head of span-80. Once the anticolloidal micelles are formed, they can diffuse through the oil layer from the initial aqueous phase to the second aqueous phase, during which the direction and process of the diffusion depends on the osmotic pressure or ion concentrations in the two aqueous phases. As the ions diffuse through the oil layer and encounter counteracting ions in the second aqueous phase, they will precipitate along the spherical interface and form AACH nanospheres, the precursor calcined to yield CLH- $\text{Al}_2\text{O}_3$  NSs, the target product  $\text{Al}_2\text{O}_3$  nano-adsorbent.

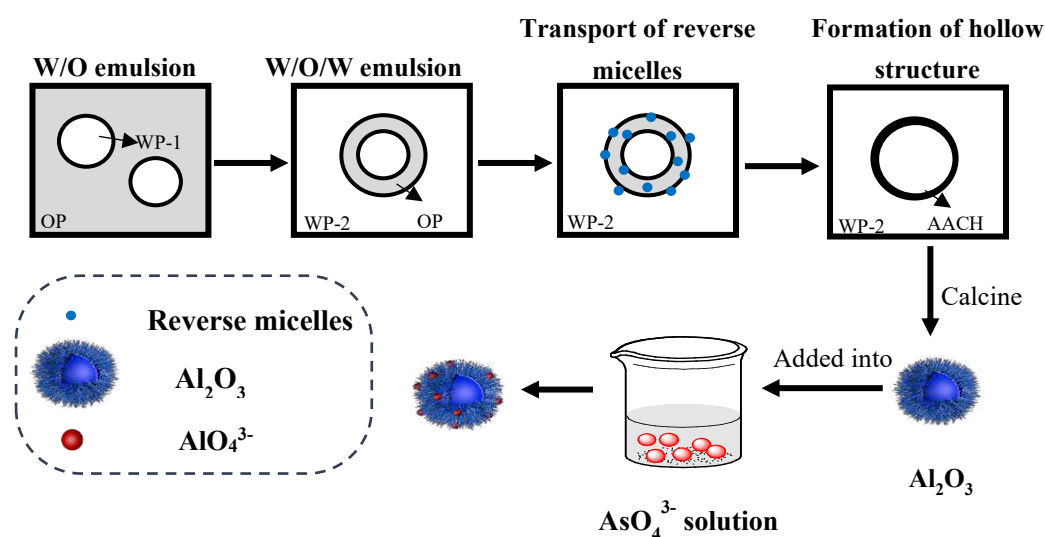


Fig. 11 Schematic diagram for fabricating W/O and W/O/W reversed phase microemulsions as well as synthesis of  $\text{Al}_2\text{O}_3$  nano-adsorbent and its adsorption performance towards  $\text{AsO}_4^{3-}$ .

#### 4. Conclusions

CLH- $\text{Al}_2\text{O}_3$  nano-adsorbent was prepared by a facile double reversed-phase microemulsion method. The as-prepared  $\text{Al}_2\text{O}_3$  nano-adsorbent has an average particle size of 400 nm, a specific surface area of 394.99  $\text{m}^2/\text{g}$ , a pore volume of 1.94  $\text{cm}^3/\text{g}$ , and a pore diameter of 4.46 nm. The dosage of span-80, the  $\text{NH}_4\text{HCO}_3$  solution concentration, and water bath temperature have large effects on the morphology of the target product; and the  $\text{AsO}_4^{3-}$  solution pH has a significant effect on the adsorption performance of the CLH- $\text{Al}_2\text{O}_3$  nano-adsorbent. CLH- $\text{Al}_2\text{O}_3$  nano-adsorbent exhibits

---

the highest removal rate of  $\text{AsO}_4^{3-}$  (98.69%) at a solution pH of 3.0; and its adsorption capacity increases with increasing dosage while the removal rate of  $\text{AsO}_4^{3-}$  ions gradually decreases therewith. The adsorption of  $\text{AsO}_4^{3-}$  ions by  $\text{Al}_2\text{O}_3$  nano-adsorbent at 298 K follows the Langmuir isotherm adsorption model and the pseudo-second order kinetics equation, referring to a saturated adsorption capacity of 37.11 mg/g and a correlation coefficient of 99.8%. Moreover, CLH- $\text{Al}_2\text{O}_3$  nano-adsorbent retains good immobilization ability for  $\text{AsO}_4^{3-}$  ions during 30 day of consecutive desorption experiments, showing promising potential for the rapid and efficient remediation of As-contaminated water.

### **Acknowledgements**

The authors acknowledge the financial support provided by Henan Provincial Key Research, Development and Promotion Special Project (Science and Technology Breakthrough, 252102231052); Project of International Cooperation and Exchanges of the National Natural Science Foundation of China (82020108017); the Fellowship of China Postdoctoral Science Foundation (2021M690913); the Open Foundation of State Environmental Protection Key Laboratory of Soil Environmental Management and Pollution Control (MEESEPC202310); Science and Technology Project of Kaifeng city (2202002); Henan University Open Foundation for Undergraduates in Scientific Laboratories and Platforms (20242401244); and Fund of Scientific Experimental Platform for Undergraduates of Henan University (20252404267; 20252412271; 20252412272; 20252412277).

### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **References**

- [1] Xu HQ, Jia Y, Sun ZD et al (2022) Environmental pollution, a hidden culprit for health issues. *Eco-Environment & Health* 1(1): 31-45. <https://doi.org/10.1016/j.eehl.2022.04.003>
- [2] Zhou XX, Speer RM, Volk L (2021) Arsenic co-carcinogenesis: inhibition of DNA repair and

---

interaction with zinc finger proteins. *Seminars in Cancer Biology* 76 86-98.

<https://doi.org/10.1016/j.semcancer.2021.05.009>

[3] Chen QY, Costa M (2021) Arsenic: A Global Environmental Challenge. *Annual Review of Pharmacology* 61 47-63. <https://doi.org/10.1146/annurev-pharmtox-030220-013418>

[4] Shi RC, Nambudiri EV (2017) Nambudiri, Arsenic in Dermatology—From Dermatologic Therapy to Carcinogen. *Jama Dermatol* 153 905. <https://doi.org/10.1001/jamadermatol.2017.2658>

[5] Wang Y, Ma L, Wang C et al (2024) Cardiovascular adverse effects and mechanistic insights of arsenic exposure: a review. *Environmental Chemistry Letters* 22 (3) 1437-1472. <https://doi.org/10.1007/s10311-023-01677-0>

[6] Du SF, Liu LP, Wang HJ et al (2020) Arsenic in the Pathway to Cardiovascular Diseases: Arsenic May Mediate Lipid Profile in Adults. *Current Developments in Nutrition* 4(S2) 1630-1630. [https://doi.org/10.1093/cdn/nzaa063\\_028](https://doi.org/10.1093/cdn/nzaa063_028)

[7] Miranda JS, Spratlen, Umans JG et al (2018) Arsenic, One-Carbon Metabolism and Diabetes-Related Outcomes in the Strong Heart Family Study. *ISEE Conference Abstracts* 121 (2) 728-740. <https://doi.org/10.1289/isesisee.2018.O04.01.16>

[8] Spaur M, Fernandez GM, Chen Q et al (2024) Association of Water Arsenic With Incident Diabetes in U.S. Adults: The Multi-Ethnic Study of Atherosclerosis and the Strong Heart Study. *Diabetes care* 47 1143-1143. <https://doi.org/10.2337/DC23-2231>

[9] Sasireka R, Vinoth R, Abhishek S et al (2024) Arsenic and Environment: A Systematic Review on Arsenic Sources, Uptake Mechanism in Plants, Health Hazards and Remediation Strategies. *Topics in Catalysis* 67 325-34. <https://doi.org/10.1007/s11244-023-01901-9>

[10] Patel KS, Pandey PK, Martn-Ramos P et al (2023) A review on arsenic in the environment: contamination, mobility, sources, and exposure. *RSC Advances* 13 19. <https://doi.org/10.1039/D3RA00789H>

[11] Yan Z (2020) Global solutions to a silent poison. *Science (New York, N.Y.)* 368 818-819. <https://doi.org/10.1126/science.abb9746>

[12] Cao PL, Qiu KY, Zou XY, Zhang Z (2020) Mercapto propyltrimethoxysilane- and ferrous sulfate-modified nano-silica for immobilization of lead and cadmium as well as arsenic in heavy metal-contaminated soil. *Environmental Pollution* 266 115152. <https://doi.org/10.1016/j.envpol.2020.115152>

- 
- [13] Rathi BS, Kumar PS, Ponprasath R et al (2021) An effective separation of toxic arsenic from aquatic environment using electrochemical ion exchange process. *Journal of Hazardous Materials* 412 125240. <https://doi.org/10.1016/j.jhazmat.2021.125240>
- [14] Judit, Floch, Miklos et al (2004) Application of ZW-1000 membranes for arsenic removal from water sources. *Desalination* 162(1) 75-83. [https://doi.org/10.1016/S0011-9164\(04\)00029-3](https://doi.org/10.1016/S0011-9164(04)00029-3)
- [15] Bandaru SRS, Roy A, Gadgil AJ et al (2020) Genuchten, Long-term electrode behavior during treatment of arsenic contaminated groundwater by a pilot-scale iron electrocoagulation system. *Water Research* 175 10. <https://doi.org/10.1016/j.watres.2020.115668>
- [16] Guo G, Zhang D, Lei M et al (2023) Phytoextraction of As by *Pteris vittata* L. assisted with municipal sewage sludge compost and associated mechanism. *The Science of the total environment* 164705. <https://doi.org/10.1016/j.scitotenv.2023.164705>
- [17] Podgorski J, Berg M (2020) Global threat of arsenic in groundwater. *Science* 368 845-850. <https://doi.org/10.1126/science.aba1510>
- [18] Bi XY, Meng S, Zhang Y et al (2024) Study of adsorption capacity and mechanism of nano-alumina for arsenic ion by isothermal adsorption model simulations. *Environmental Technology & Innovation* 34 34103560-34103561. <https://doi.org/10.1016/j.eti.2024.103560>
- [19] Li F, Yin H, Zhu T et al (2024) Understanding the role of manganese oxides in retaining harmful metals: Insights into oxidation and adsorption mechanisms at microstructure level. *Eco-Environment & Health* 3 89-106. <https://doi.org/10.1016/j.eehl.2024.01.002>
- [20] Yang P, Qin F, Dai G et al (2019) Reducing the Leachability and Bioaccessibility of Arsenic in Soils using Supported Nano Titanium Dioxide. *Soil and Sediment Contamination: An International Journal* 28 347-359. <https://doi.org/10.1080/15320383.2019.1575335>
- [21] Deng J, Mi S, Qu C et al (2025) Enhanced As(III) adsorption-oxidation via synergistic interactions between bacteria and goethite. *Eco-Environment & Health* 4 100131-100131. <https://doi.org/10.1016/j.eehl.2024.12.001>
- [22] Han C, Li H, Pu H et al (2013) Synthesis and characterization of mesoporous alumina and their performances for removing arsenic(V). *Chemical Engineering Journal* 217 1-9. <https://doi.org/10.1016/j.cej.2012.11.087>
- [23] Luo H, Zeng Y, He D et al (2020) Application of iron-based materials in heterogeneous advanced oxidation processes for wastewater treatment: A review - ScienceDirect. *Chemical*

---

Engineering Journal 434. <https://doi.org/10.1016/j.cej.2020.127191>

[24] Lu WC, Wang ZB, Bu YP et al (2023) Removal of heavy metals in water using nano zero-valent iron composites: A review. *Journal of Water Process Engineering* 53 121. <https://doi.org/10.1016/J.JWPE.2023.103913>

[25] Prabhakar R, Samadder SR (2018) Low cost and easy synthesis of aluminium oxide nanoparticles for arsenite removal from groundwater: A complete batch study. *Journal of Molecular Liquids* 250 192-201. <https://doi.org/10.1016/j.molliq.2017.11.173>

[26] Hu X, Liu Y, Tang Z et al (2012) Fabrication of high-surface-area  $\gamma$ -alumina by thermal decomposition of AACH precursor using low-temperature solid-state reaction. *Materials Research Bulletin* 47 4271-4277. <https://doi.org/10.1016/j.materresbull.2012.09.019>

[27] Parida KM, Pradhan AC, Das J et al (2009) Synthesis and characterization of nano-sized porous gamma-alumina by control precipitation method. *Materials Chemistry & Physics* 113 244-248. <https://doi.org/10.1016/j.matchemphys.2008.07.076>

[28] Li Y, Wang W, Qin F et al (2024) Synthesis of monodisperse spherical nano alumina by hydrothermal method and its mechanism study. *Ceramics International* 50 39467-39474. <https://doi.org/10.1016/J.CERAMINT.2024.07.323>

[29] Li L, Liu X, Wang G et al (2020) Research progress of ultrafine alumina fiber prepared by sol-gel method: A review. *Chemical Engineering Journal* 421 127744 <https://doi.org/10.1016/J.CEJ.2020.127744>

[30] Shum H, Bandyopadhyay A, Bose S et al (2009) Double Emulsion Droplets as Microreactors for Synthesis of Mesoporous Hydroxyapatite. *Chemistry of Materials* 21 5548-5555 <https://doi.org/10.1021/cm9028935>

[31] Said S, Mikhail S & Riad M (2020) Recent processes for the production of alumina nanoparticles. *Materials Science for Energy Technologies* 3 344-363. <https://doi.org/10.1016/j.mset.2020.02.001>

[32] Liang WY, Wang GH, Peng C et al (2021) Recent advances of carbon-based nano zero valent iron for heavy metals remediation in soil and water: A critical review. *Journal of hazardous materials* 426 127993-127993. <https://doi.org/10.1016/j.jhazmat.2021.127993>

[33] Gholizadeh Z, Aliannezhadi M, Ghominejad M et al (2023) High specific surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles synthesized by facile and low-cost co-precipitation method. *Scientific*

---

Reports 13(1) 6131-6131. <https://doi.org/10.1038/s41598-023-33266-0>

[34] Ferreira ND, Klegues MOR, Michael BA et al (2022) Synthesis and characterization of nano  $\alpha$ -alumina by an inorganic sol-gel method. *Materials Science & Engineering B* 280 98. <https://doi.org/10.1016/j.mseb.2022.115690>

[35] Ghosh S, Prabhakar R, Samadder SR et al (2019) Performance of  $\gamma$ -aluminium oxide nanoparticles for arsenic removal from groundwater. *Clean Technologies and Environmental Policy* 21 121-138. <https://doi.org/10.1007/s10098-018-1622-3>

[36] Smedley PL, Kinniburgh DJ (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17 517-568. [https://doi.org/10.1016/S0883-2927\(02\)00018-5](https://doi.org/10.1016/S0883-2927(02)00018-5)

[37] Kim DJ, Kim H, Lee JK, Dependence of the rheological behaviour of electrostatically stabilized alumina slurries on pH and solid loading. *Journal of Materials Science* 33 (1998) 2931-2935. <https://doi.org/10.1023/A:1004398428917>

[38] Zowada R, Foudazi R (2019) Porous Hydrogels Embedded with Hydrated Ferric Oxide Nanoparticles for Arsenate Removal. *Acs Applied Polymer Materials* 1(5) 1006-1014. <https://doi.org/10.1021/acsapm.9b00047>

[39] Arjang S, Motahari K, Saidi M (2018) Experimental and Modeling Study of Organic Chloride Compounds Removal from Naphtha Fraction of Contaminated Crude Oil Using Sintered  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Nanoparticles: Equilibrium, Kinetic and Thermodynamic Analysis. *Energy & Fuels* 32(3) 4025-4039. <https://doi.org/10.1021/acs.energyfuels.7b03845>

[40] Chen XP, Ren YC, Qu GF et al (2023) Ning Ping A review of environmental functional materials for cyanide removal by adsorption and catalysis. *Inorganic Chemistry Communications* 157. <https://doi.org/10.1016/J.INOCHE.2023.111298>

[41] Zhou Q, Duan Y, Chen M et al (2017) Studies on Mercury Adsorption Species and Equilibrium on Activated Carbon Surface. *Energy & Fuels* 31 14211-14218 <https://doi.org/10.1021/acs.energyfuels.7b02699>

[42] Samad A, Kazem M, Majid S (2018) Experimental and Modeling Study of Organic Chloride Compounds Removal from Naphtha Fraction of Contaminated Crude Oil Using Sintered  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Nanoparticles: Equilibrium, Kinetic, and Thermodynamic Analysis. *Energy & Fuels* 32 4025-4039. <https://doi.org/10.1021/acs.energyfuels.7b03845>

- 
- [43] Asuquo E, Martin A, Nzerem P et al (2017) Adsorption of Cd(II) and Pb(II) ions from aqueous solutions using mesoporous activated carbon adsorbent: Equilibrium, kinetics and characterisation studies. *Journal of Environmental Chemical Engineering* 5 679-698. <https://doi.org/10.1016/j.jece.2016.12.043>
- [44] Godoi FCD, Rabelo RB, Silva MA et al (2014) Introduction of copper nanoparticles in chitosan matrix as strategy to enhance chromate adsorption. *Chemical Engineering and Processing: Process Intensification* 83 43-48. <https://doi.org/10.1016/j.cep.2014.07.002>
- [45] Nassar NN (2010) Asphaltene Adsorption onto Alumina Nanoparticles: Kinetics and Thermodynamic Studies. *Energy & Fuels* 24 4116-4122. <https://doi.org/10.1021/ef100458g>
- [46] Wu Y, Pang H, Liu Y et al (2019) Environmental remediation of heavy metal ions by novel-nanomaterials: A review. *Environmental Pollution* 246 608-620. <https://doi.org/10.1016/j.envpol.2018.12.076>
- [47] Dolganov AV, Balandina AV, Chugunov DB (2020) Sorption of Fluoride Ions onto Cellulose and Aluminum Oxide Composites. *Russian Journal of Inorganic Chemistry* 65 1770-1775. <https://doi.org/10.1134/S0036023620110030>
- [48] Cheng J, Chen JF, Zhao M (2007) Transport of ions through the oil phase of W1/O/W2 double emulsions. *Journal of Colloid & Interface Science* 305 175-182. <https://doi.org/10.1016/j.jcis.2006.09.055>

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GraphicalAbstract.docx](#)
- [Highlights.docx](#)
- [NoveltyStatement.docx](#)