

# Removal As(V) by sulfated mesoporous Fe–Al bimetallic adsorbent: Adsorption performance and uptake mechanism



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## ARTICLE INFO

### Article history:

Received 5 September 2015  
Received in revised form 7 November 2015  
Accepted 21 December 2015  
Available online 22 December 2015

### Keywords:

Fe–Al bimetallic adsorbent  
Mesoporous  
As(V)  
Sulfated  
Adsorption performance  
Uptake mechanism

## ABSTRACT

Sulfated mesoporous Fe–Al bimetallic adsorbent, prepared by a simple method of incipient-wetness impregnation, was employed as an efficient adsorbent to remove As(V) from solution. Removal performance was investigated by batch experiments with various factors, including ferric content, inorganic ferric additive, contact time, initial pH and adsorbent dosage. An interesting result was obtained that demonstrated that anions of inorganic ferric additive have a significant influence on As(V) removal, and the sample obtained from additive 10 wt%  $\text{Fe}_2(\text{SO}_4)_3$  was found to be a highly effective As(V) adsorbent. The experiment data were excellent fitted to Langmuir isotherm and the maximum monolayer uptake was about 98.13 mg/g at near neutral. And solution pH have a negligible influence on As(V) removal in the investigated pH region of 2.5–11.0. More importantly, adsorption equilibrium can be attained within 3 h, which is significantly shorter than that of MA (more than 12 h). Based on the results of batch experiments, pH changes, adsorption energy, XPS analyses and the chemical forms of As(V), the possible uptake mechanisms under the investigated conditions were proposed as follows: (1) during initial pH below 4,  $\text{H}_2\text{AsO}_4^-$  and  $\text{H}_3\text{AsO}_4$  were adsorbed by electrostatic interaction and hydrogen bond, respectively; (2) during initial pH higher than 4, the exchange between sulfate group and  $\text{H}_2\text{AsO}_4^-$  was the dominantly interaction.

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## 1. Introduction

Arsenic pollution in water has been regarded as a worldwide environmental problem due to its serious threaten to organism and its unavoidable contact [1,2]. And much attention has been focused on remove arsenic from contaminated water. Due to the predominant role and the thermodynamic stable,  $\text{As}^{5+}$  species is considered as the chiefly arsenic species to remove from water [3]. However, As(V) species is transformed between  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  under different pH solution, which make it hard to remove effectively. And widely pH wastewater of As(V) are produced by industrial activity that served as the mainly arsenic source in water [4,5]. Therefore, advanced treatment processes are desirable, and most techniques included coagulation, electro-coagulation, precipitation, membrane, ion exchange, adsorption and biological are employed to remove As(V). Among these methods, adsorption process seems to be the most promising

method due to its simple operation, more cost-effective and no harmful byproducts [6].

Adsorption with active carbon [7], zeolite [8,9], bio-sorbent [10,11], resin [12], metal (hydr) oxide [13,14] and byproduct [15] have been widely used to remove As(V) from water. From them, aluminum oxide and iron oxide have focused a great deal of attention due to the high affinity to As(V) species. And alumina has been deemed to one of the most available adsorbents, which classified by United Nations Environmental Program agency [16–18]. However, the low adsorption capacities, slow sorption rate and narrow optimum pH range are presented in traditional aluminum oxide and iron oxide [19–21]. And these characteristics limited their application in the treatment of arsenic pollution. So, further studies are needed in this area.

Since the mainly mechanism of As(V) uptake over metal oxides is the electrostatic attraction between protonated hydroxyl groups and As(V) species ( $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ ), complex metal oxides are attracted considerable attention to overcome the aforementioned drawbacks of traditional aluminum oxide and iron oxide. The binary metal oxide As(V) adsorbents of Fe–Ce, Fe–Zr, Al–Cu and Fe–Mn etc., are synthesized, and demonstrated much higher As(V) uptake than the individual metal oxide [1,21–24]. The results

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could be attributed to the fact that the number of hydroxyl group over binary mixed oxide, which provide As(V) adsorption site, is more than the single metal oxide. Nevertheless, one of the problems is that As(V) adsorption capacities of the aforementioned binary oxides are not larger enough reference to their high cost. And recently, considerable attention and requirement was focused on the As(V) adsorbents with low cost and high capacity [16]. Therefore, economically Fe–Al [25,26] binary mixed (hydr) oxides are explored via coated Fe on alumina with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . However, the maximum uptake of As(V) on Fe–Al adsorbent is only 37 mg/g, which lower than the other above mentioned binary metal oxides [1,21,22–24]. So, improve adsorption capacity of As(V) uptake over Fe–Al based adsorbent are desirable. Additionally, previous research failed to consider the influence of inorganic Fe additive on As(V) uptake over alumina. In particular, little efforts have been attempted to employ  $\text{Fe}_2(\text{SO}_4)_3$  act as the ferric additive to prepare Fe–Al based adsorbent, due to the strong interaction between sulfate group and alumina framework [27,28] and the aim of prepare metal oxide.

In this work, we present an economical and environmental strategy to prepare a new efficient Fe–Al bimetallic adsorbent to uptake As(V), which possess mesoporous structure. The obtained materials were characterized by  $\text{N}_2$  adsorption–desorption, XRD, FT-IR, and XPS. And As(V) adsorption performances were investigated by batch experiments, including the influence of ferric content, inorganic ferric additive, contact time, initial pH and adsorbent dosage. More important, adsorption isotherm, kinetic, pH change, XPS and adsorption energy were also discussed to analyze the interaction between As(V) species and adsorbent, and illustrate As(V) uptake mechanism.

## 2. Experimental

### 2.1. Chemicals

Aluminum tri-isopropoxide, ferric sulfate, ferric chloride, ferric nitrate nonahydrate, sodium hydroxide, hydrochloric acid (37%) and nitric acid (65%) were purchased from China National Medicine Group Shanghai Chemical Reagent Company. Nonionic surfactant Pluronic P123 was employed as template, and obtained from Sigma–Aldrich.

### 2.2. Preparation of adsorbent

Mesoporous alumina (MA) used in this study was prepared by nonionic triblock copolymer and aluminum tri-isopropoxide as report in our previous work [29]. Incipient-wetness impregnation method was employed to prepare sulfated mesoporous Fe–Al bimetallic adsorbent (Fe–MA). For one thing, different content ferric sulfate (calculated as Fe was 0 wt%, 5 wt%, 10 wt% and 15 wt%) was dissolved in deionized water. For another, MA and ferric sulfate solution were mixed together. After mixed well, the mixture was dried for 12 h at  $100^\circ\text{C}$ , and the obtained solid was calcined at  $400^\circ\text{C}$  for 3 h. The sample marked as Fe–MA.

For comparison, ferric chloride and ferric nitrate was grafted on mesoporous alumina via the similar process of ferric sulfate, respectively. The content of ferric chloride and ferric nitrate was calculated as 10 wt% Fe.

### 2.3. Batch experiments

100-mL conical flasks were used to perform batch adsorption experiments. The adsorbent and As(V) solution were mixed together under magnetic stirring. At the scheduled time, the resulting mixture (solid adsorbent and liquid As(V)) was separated with centrifuge. HCl or NaOH was added into As(V) solution to

adjusted the pH value. Arsenic content in solution was determined by an atomic fluorescence spectrometer.

To estimate the obtained materials, 0.05 g adsorbent was put into a conical flask, which contain 50 mL As(V) solution with 44.703 mg/L, with room temperature for 12 h under  $\text{pH } 6.6 \pm 0.1$ . The experiments for evaluated the adsorption isotherm were carried out by varied initial concentration from 11.187 mg/L to 223.325 mg/L under a constant adsorbent dosage (0.6 g/L), and adjusted solution pH to  $6.6 \pm 0.1$ . The adsorption kinetic experiments were performed by fixing concentration at 44.703 mg/L with a series contact time (0.5–12 h). In the experiments of pH influence on As(V) removal, the As(V) concentration was kept at 44.703 mg/L, and the initial pH values were controlled at the range of 2–11.

### 2.4. Characterization

Thermogravimetry analysis was performed using TG-60H thermogravimetric analyzer. The samples were tested in flowing air with a heating rate of  $10^\circ\text{C}/\text{min}$ .  $\text{N}_2$  adsorption–desorption isotherms of MA and Fe–MA were tested at  $-196^\circ\text{C}$  by ASAP 2020 apparatus. The Brunauer–Emmett–Teller (BET) method was employed to calculate specific surface area from  $\text{N}_2$  adsorption–desorption isotherms. A Rigaku D/max 2550PC diffractometer was used to determine powder wide-angle X-ray diffraction (XRD). The variation in surface groups of MA and Fe–MA was identified by Fourier transforms infrared (FT-IR) spectra with a Nicolet 560 IR spectrometer. A PHI 5000 Versa Probe instrument was used for X-ray photoelectron spectra (XPS) measurement. 284.6 eV of C1s peak was employed as the criterion to corrected charging effects on binding energies.

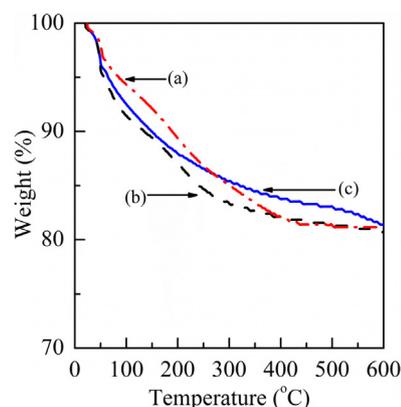
## 3. Results and discussion

### 3.1. Adsorbent characterization

#### 3.1.1. Thermogravimetric analysis

TG profiles are determined in air to examine the thermal treatment temperature of the as-synthesized Fe–Al bimetallic adsorbent, which obtained from different ferric salts.

It is obviously that the weight losses of these three materials can be deemed to be two stages (Fig. 1). In the first step, ca. 5% of the weight loss have been observed in the  $0\text{--}50^\circ\text{C}$  for all investigated adsorbents, which is ascribed to the loss of some physically adsorbed water. However, the weight loss are completely different in the second stage. The second weight loss for additive  $\text{Fe}(\text{NO}_3)_3$  and  $\text{FeCl}_3$  is occurred in  $50\text{--}390^\circ\text{C}$  and  $50\text{--}340^\circ\text{C}$ ,



**Fig. 1.** Thermogravimetric curves for as-synthesized Fe–Al bimetallic adsorbent prepared from different ferric additive. (a)  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , (b)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and (c)  $\text{Fe}_2(\text{SO}_4)_3$ .

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