The optimization of As(V) removal over mesoporous alumina by using response surface methodology and adsorption mechanism

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HIGHLIGHTS

- Mesoporous alumina was synthesized at room temperature by using P123 as a template.
- Box–Behnken Design was employed to optimize arsenic adsorption process.
- Interactive effects of adsorption parameters on arsenic adsorption capacity were investigated.
- As(V) adsorption mechanisms over MA under different pH conditions were illustrated in detail.

ARTICLE INFO

ABSTRACT

The Box–Behnken Design of the response surface methodology was employed to optimize four most important adsorption parameters (initial arsenic concentration, pH, adsorption temperature and time) and to investigate the interactive effects of these variables on arsenic(V) adsorption capacity of mesoporous alumina (MA). According to analysis of variance (ANOVA) and response surface analyses, the experiment data were excellent fitted to the quadratic model, and the interactive influence of initial concentration and pH on As(V) adsorption capacity was highly significant. The predicted maximum adsorption capacity was about 39.06 mg/g, and the corresponding optimal parameters of adsorption process were listed as below: time 720 min, temperature 52.8 °C, initial pH 3.9 and initial concentration 130 mg/L. Based on the results of arsenate species definition, FT-IR and pH change, As(V) adsorption mechanisms were proposed as follows: (1) at pH 2.0, H_3AsO_4 and $H_2AsO_4^-$ were adsorbed via hydrogen bond and electrostatic interaction, respectively; (2) at pH 6.6, arsenic species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) were removed via adsorption and ion exchange, (3) at pH 10.0, $HAsO_4^{2-}$ was adsorbed by MA via ion exchange together with adsorption, while AsO_4^{3-} was removed by ion exchange.

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1. Introduction

Removing arsenic from contaminated water has attracted considerable attention due to high toxicity for human and other organisms. Moreover, arsenic concentrations (levels) even in natural water of Argentina, Australia, Bangladesh, Vietnam, West Bengal, India, Taiwan and China are far higher than the corresponding rules of these country and area [1–7]. Therefore, several methods including electrocoagulation, precipitation, filtration, reverse osmosis, ion exchange, membrane, biological treatment together with adsorption have been developed for disposing arsenic-contaminated water [8–12]. Among them, adsorption has been recognized as an effective and most extensive technique owing to its high removal efficiency, low cost as well as simple operation. In the past few decades, lots of researches involved arsenic adsorption have been devoted to test the uptake and isotherms of various adsorbents, and the corresponding adsorbents included activated carbon, zeolite, metal oxide (X_mO_n, X = Al, Fe, Ti, Mn, Cu, Zr and their composites), biosorbent, synthetic resin, industrial/agriculture byproducts or wastes etc. [13].

According to the classification made by United Nations Environmental Program agency (UNEPA), activated alumina is one of the most available adsorbents for removing arsenic from contaminated water. Nevertheless, traditional commercial activated alumina (TCAA) generally suffers from the drawbacks of low adsorption capacity, slow adsorption rate and narrow working pH region, which should be closely associated with its ill-defined pore structure together with small surface area. A perfect example can be found in Zhang and co-worker's report that the optimum pH for removing As(V) over TCAA is in a narrow range of 5.5–6.0 and

the removal of As(V) sharply decreased beyond the pH region [14]. Recently, many researchers have tended to improve the performance of TCAA by doping alum, manganese and copper [15–17], while the corresponding adsorption capacity of these modified alumina-based adsorbents is still low.

Since the discovery of the M41S family (silica-based mesoporous materials) has sparked considerable interest in the synthesis of mesoporous materials for the use in the many fields including catalysis [18,19], adsorption [20,21], separation [22,23], sensors [24], optics [25] as well as fabrication of novel nano-object materials [26]. In the past decades, mesoporous alumina (MA) has been synthesized via various methods, and MA with respect to TCAA exhibits more excellent performance in adsorption for many pollutants such as simazine [27], and CO_2 [28], 4-chloro-2-methylphenoxyacetic acid [29].

Of late, limited efforts have been devoted to synthesize MA as high-performance adsorbent for arsenic(V) removal [30–32]. However, these synthesis routes included high-temperature crystallization (100–120 °C) together with the use of expensive aluminum alkoxide (such as aluminum sec-butoxide) and organic solvent (such as sec-BuOH). Moreover, it was documented that nonionic polyethylene oxide (PEO) surfactant with respect to cation and anion templates has attracted much attention due to low-cost, nontoxic and biodegradable [33]. In addition, compared with high-temperature synthesis, low-temperature synthesis is an environmentally friendly method, which will be in favor of energy-saving. Therefore, despite significant progress in the synthesis of MA, further studies in this area, especially in relation to low-temperature synthesis route by using low-cost, nontoxic and biodegradable templates are desirable.

In general, arsenic removal is affected by many factors including As(V) concentration, pH, adsorption temperature and time etc. [34]. In order to assess the effect of experiment parameters on adsorption capacity, the proper use of an adequate experimental design is of particular importance. Response Surface Methodology (RSM), a collection of mathematical and statistical techniques, has been found to be a useful method for studying the mutual interaction between the variables and optimizing the variables in the adsorption process.

This contribution was aimed at the investigation of As(V) adsorption performances over MA, which was prepared with nonionic surfactant P123 and aluminum isopropoxide (AIP) at room temperature. The Box–Behnken Design (BBD) of the RSM [35–37] was employed to investigate the effects of significant operating parameters including initial arsenic concentrations, pH, adsorption time and temperature on arsenic adsorption capability and to find the most suitable combination of variables resulting in maximum As(V) adsorption capability. The second-order polynomial equation (regression model) provided an excellent explanation of the relationship between the response (arsenic adsorption capacity) and these independent parameters. More important, according to the results of arsenic species definition, FT-IR characterization together with pH change during the whole adsorption process, the arsenic adsorption mechanisms over MA under various pH conditions were investigated and illustrated in detail.

2. Experimental

Mesoporous alumina (MA) was synthesized by employing nonionic triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) and aluminum tri-isopropoxide (AIP) as a structure-directing agent and an aluminum source, respectively. The following procedures were used to prepare MA alumina, which were mainly composed of three steps: the first step and the second step consist of the synthesis of aluminum hydroxide gel and the preparation of template solution,

respectively, and the third step was the synthesis of MA. In the first step, 20.4 g of AIP and a small amount of nitric acid (65 wt.%) was added into 160 mL of hot denionized water with vigorously stirring for 2–4 h to yield aluminum hydroxide sol. In the second step, 7.5 g of P123 and 0.24 mol of HCl were added into 150 mL of denionized water with vigorously stirring under room temperature (RT) for 2–4 h. After P123 was completely dissolved, the template solution was formed. In the third step, the solution contained template P123 was added into the aluminum hydroxide sol. After that the mixture was stirred at 40 °C for 12–24 h, and the corresponding pH value was adjusted to 7.0 by using sodium hydroxide solution. Subsequently, the resulting mixture was kept at RT under static conditions for 36–72 h, and the reaction products were filtered, washed with the mixture of water and ethanol, and dried at 105 °C for 24–48 h. Finally, the dried sample was calcined at 400 °C in air for 5 h.

The batch experiments of arsenic adsorption were carried out by mixing adsorbent MA with arsenic solution in a series of 100 mL conical flask under magnetic stirring conditions, and the resulting mixtures were centrifuged after adsorption. Arsenic(V) concentration before and after adsorption was measured by atomic fluorescence spectrometer (AFS-230E), and the As(V) adsorption capacity of MA was calculated using following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where q_t denotes arsenic(V) uptake capacity of MA at contact time t, C_0 and C_t are the arsenic(V) concentrations before and after adsorption, V is the volume of adsorption solution, and m is the weight of adsorbent MA.

2.1. Box–Behnken Design and As(V) adsorption optimization

RSM was employed to investigate the effects of different operating factors on arsenic adsorption capacity, and reveal the optimum conditions for As(V) removal as well as build models. BBD was applied to evaluate the interactive effects of adsorption variables and optimize the adsorption process. The effects of variables (adsorption parameters including pH value, initial concentration, adsorption time and temperature) on adsorption capacity were selected for RSM. The corresponding experiments were carried out in a system with 0.05 g MA and 50 mL As(V) solution, and pH was adjusted by 1.0 M HCl (or 1.0 M NaOH). The range and levels for these variables are coded according to Eq. (2) and summarized in Table 1.

$$x_i = \frac{X_i - X_0}{\Delta x} \tag{2}$$

where x_i and X_i are the coded and the real values of variables. X_0 and Δx are the center point of X_i and the step change in X_i, respectively. Generally, the mathematical relationship between the response Y (arsenic (V) adsorption capacity) and these variables can be described by the following second-order polynomial equation:

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 D + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{44} D^2$$
$$+ \beta_{12} AB + \beta_{13} AC + \beta_{14} AD + \beta_{23} BC + \beta_{24} BD + \beta_{34} CD \tag{3}$$

The validity of the equation was analyzed by using ANOVA (analysis-of-variance), and fit quality of the equation was judged from the coefficients of correlation and P-value.

2.2. Characterization

Powder XRD patterns were performed on a Rigaku D/max 2550PC diffractometer using Cu Kα radiation, operating at 40 kV and 300 mA. N_2 adsorption–desorption isotherm and BET surface