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Adsorption performance and mechanism of As(V) uptake over mesoporous Y–Al binary oxide

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ABSTRACT

Mesoporous Y–Al binary oxide was synthesized and employed as adsorbent to remove As(V) from aqueous solution in this study. The adsorbent was synthesized via incipient-wetness impregnation method, and then characterized by N_2 adsorption–desorption, XRD, TEM, EDS and FT-IR. The adsorption performance was tested by batch and column experiments. From the results of batch experiments, it was found that the adsorption processes were abided by pseudo-second-order, which illustrated that the rate limiting step was the "surface reaction". And Langmuir isotherm model was fitted well to the equilibrium experiment data at near neutral, and the maximum adsorption capacity was 62.23 mg/g. Additionally, the coexisting anions of nitrate, silicate and sulphate have no significant interfering effect on As(V) uptake, while the presence of fluoride and phosphate caused the markedly reduction. According to the results of FT-IR spectrum and the pH change in the adsorption process, it could be concluded that the interaction between arsenate and hydroxyl group was involved in the adsorption process. From the results of column experiments, it can be observed that the breakthrough time was increased from 83 min to 125 min due to the incorporation of Y(III) oxide.

1. Introduction

Arsenic contamination in water has been considered as one of the most serious worldwide environmental problems due to its threat to organism safety [1–3]. Therefore, effective process is needed to reduce the amount of arsenic. In general, arsenic exists in the As^{3-}, As^0, As^{3+} and As^{5+} oxidation states, and As^{5+} (As(V)) is regarded as the predominant and thermodynamically stable species [4]. And more attention is demanded to resolve As(V) contamination. Hence, most techniques are employed to remove As(V), such as coagulation, membrane, adsorption, ion exchange, biological, etc. From the mentioned treatment approaches, adsorption has been considered as one of the methods that significantly reduced the energy requirements, chemical requirements, capital requirements and environmental harmful impacts [5].

Metal oxides have attracted much attention to remove As(V) from aqueous solution during the last decades, such as CuO, Al_2O_3, Fe_3O_4, $Fe(OH)_3$ and mixed rare earth oxides [6–13]. However, most of the above mentioned materials have limit adsorption capacities. Therefore, more attention has been paid to get more efficient adsorbents. Among them, researchers have proposed that the adsorption performances are heavily depended on the hydroxyl group and the affinity between As(V) and metal oxide. Additionally, from Han et al.'s report [13], it could be found that the more surface hydroxyl group is in favor of As(V) uptake. As well known, yttrium oxide is rich in hydroxyl group, and exhibit high affinity toward arsenic. However, it is not cost-effective to employ pure yttrium oxide as As(V) adsorbent since the expensive cost. Therefore, searching for a composite material, which containing yttrium oxide, has attracted attention [10,14].

Alumina is one of the most available ingredients to adsorb As(V) from water [12]. However, low adsorption capacity (15.9 mg/g) and slowly adsorption rate (more than 90 h needed to reach equilibrium) limited the application of granular activated alumina [15]. And then, some alumina-containing bimetallic adsorbents (Al–Al, Fe–Al, Cu–Al) are explored by grafted produce, and As(V) adsorption performance is improved [16–18]. A perfect example can be found in the report of Pillewan et al. [18] that As(V) adsorption rate is increased significantly, and adsorption equilibrium is reached within 4 h. However, the adsorption capacity is

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only 2.02 mg/g, which demonstrated that the adsorbent are not ideal and more adsorbents are needed to reach the corresponding legal requirement. Hence, further studies are desirable in this area to get more effective compound material.

Due to the high surface area and controlled porous structure, mesoporous materials are applied in the field of catalysis, biomedical, photovoltaic devices sensing and adsorption [19–22]. In this study, mesoporous Y–Al binary oxide is synthesized by incipient-wetness impregnation method, and employed as As(V) adsorbent. The mesoporous Y–Al binary oxide was characterized by XRD, N_2 adsorption–desorption isotherm, FT-IR spectra, TEM and PZC. The adsorption performance and mechanism of synthesized mesoporous Y–Al binary oxide for removal As(V) from water was investigated. And the adsorption performances were performed by the batch experiments (including the influence of initial pH, adsorbent dosage, contact time, adsorption temperature and coexisting anion on arsenate removal) and column runs. Additionally, the corresponding experiment data were analyzed by adsorption isotherm, dynamics and thermodynamics. And then the adsorption mechanism was also discussed in detail by the pH change in As(V) adsorption process and FT-IR spectra.

2. Experimental

2.1. Materials

Aluminum tri-isopropoxide, yttrium nitrate hexahydrate, concentrated hydrochloric acid, nitric acid, sodium hydroxide, sodium nitrate, sodium phosphate, sodium fluoride, sodium silicate and sodium sulfate were obtained from the Shanghai Chemical Regent Company of China. Nonionic surfactant Pluronic P123 was employed as template, and obtained from Sigma-Aldrich.

2.2. Synthesis and characterization of mesoporous Y–Al binary oxide

Mesoporous Y–Al binary oxide was synthesized by the method of incipient-wetness impregnation. Firstly, mesoporous alumina (MA) was prepared by the procedures that described in previous report [13]. Secondly, 1.3 g $Y(NO_3)_3{\bullet}6H_2O$ was dissolved in denionized water. After yttrium nitrate hexahydrate completely dissolved, 3 g MA was added into the yttrium nitrate solution under stirring. After mixed well, the resulting samples were successively dried at 100 °C for 12 h and then calcined at 400 °C for 3 h. The obtained solid sample was marked as Y–Al.

N_2 adsorption–desorption isotherms of MA and Y–Al binary oxide were tested at −196 °C by ASAP 2020 apparatus. And samples were degassed at 250 °C for 2 h prior to analysis. The Brunauer–Emmett–Teller (BET) method was employed to calculate specific surface area. A Rigaku D/max 2550 PC diffractometer was used to determine powder wide-angle X-ray diffraction (XRD). Transmission electron microscopy (TEM) image and energy dispersive spectrometer (EDS) were recorded by using a JEM-2010 HR transmission electron microscope. The variation in surface groups was identified by Fourier transforms infrared (FT-IR) spectra with a Nicolet 560 IR spectrometer in the form of KBr pellets. The point of zero charge (PZC) of Y–Al binary oxide was measured by method of acid-base titration. And the pH_{pzc} was derived by the linear interpolation of the two points above and below the x-axis.

2.3. Adsorption experiments

The batch arsenate adsorption experiments were carried out in a series of 100 mL conical flasks by mixing adsorbent and arsenate solution under magnetic stirring (200 rpm) conditions, and the resulting mixture was centrifuged after adsorption. Adjustment of pH was done before the addition of Y–Al by adding either HCl or NaOH solution. The arsenic concentrations before and after adsorption were measured by an atomic fluorescence spectrometer (AFS-230E). The adsorption capacity (q_t) was calculated by using Eq. (1):

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

Where, C_0 and C_t are the initial and equilibrium concentration (mg/L) of arsenate solution at time t, respectively. V is the volume of adsorption solution (L), m is the weight of the adsorbent (g).

The adsorption isotherm was performed at a constant adsorbent dosage (2 g/L) and a constant initial pH (6.6 ± 0.1). The initial concentration was variation in the range of 5 mg/L to 200 mg/L. The adsorption kinetic experiments were carried out by adding 0.05 g Y–Al in 50 mL of arsenate solution (44.703 mg/L) with various initial pH (2.03, 4.51, 6.58, 9.03).

3. Results and discussion

3.1. Characterization

Wide angle XRD patterns of MA and Y–Al binary oxide were shown in Fig. 1. From the comparison of MA and Y–Al binary oxide, only six diffraction peaks were appeared, which were indexed to the characteristic of (220), (311), (222), (400), (511) and (440) reflection and ascribed to the γ-Al_2O_3 crystalline [23]. No new peak was observed in the pattern of Y–Al with respect to MA, which can be speculated that Y(III) oxide was highly dispersed on MA in the mixing and calcination process. The result can be proved by TEM image and EDS spectrum. As shown in TEM image (Fig. 2(a)), a negligible contrast of bright/dark was observed, which displayed the markedly contrast to the mesoporous silica based materials [24]. It indicated that the pore structure of Y–Al did not show long-range orderly arrangement, and then the nanorods were in random packing. In addition, it was observed from EDS spectrum (Fig. 2(b)) that the sample was consisted by Al, O and Y, which indicated that Y was obviously incorporated on the MA. And Y–Al binary oxide was successfully prepared.

Fig. 3 illustrates N_2 adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distribution curves of MA and Y–Al binary oxide. It could be seen that the shape of these two isotherms are similar. According to the classification made by International Union of Pure and Applied Chemistry, both of them are typical type IV curves with type-H_1 hysteresis loop [25,26]. Additionally, it was noteworthy that the hysteresis loops of MA shift

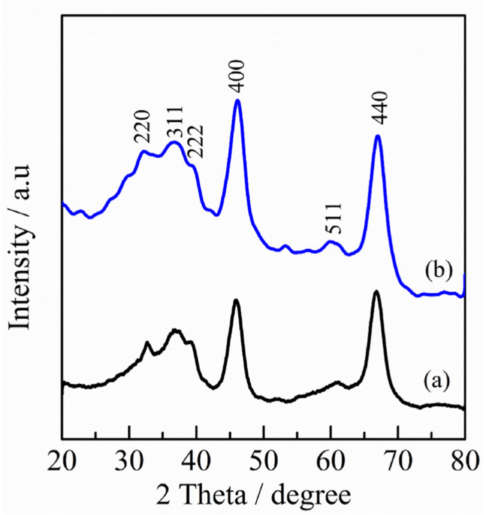

Fig. 1. Wide XRD patterns of (a) MA and (b) Y–Al binary oxide.