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Utilization of annealed aluminum hydroxide waste with incorporated fluoride for adsorptive removal of heavy metals

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HIGHLIGHTS

- $Al(OH)_3$-F_{ads} and $Al(OH)_3$-F_{coag} can effectively adsorb As(III), As(V), and Cd(II).
- More significant decrease of S_{BET} and pH_{iep} is observed at higher AT.
- Incorporated-F inhibit the removal of Cd and As as compared to pristine $Al(OH)_3$.
- Elevated AT benefit Cd adsorption whereas inhibit the removal of As(III) and As(V).
- Annealing these aluminas at elevated AT may control fluoride leaching control.

GRAPHICAL ABSTRACT
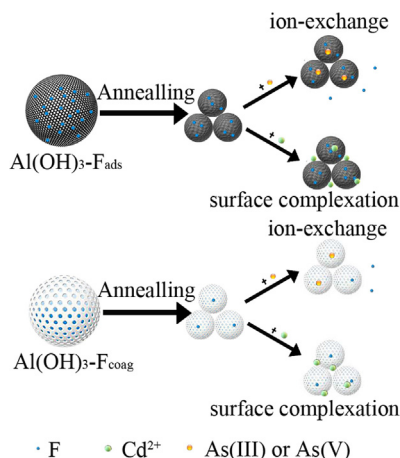
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ABSTRACT

The removal of fluoride by Al hydroxide [$Al(OH)_3$] adsorption and aluminum (Al) coagulation produces spent wastes of $Al(OH)_3$-F_{ads} and $Al(OH)_3$-F_{coag}. This study prepared the annealed $Al(OH)_3$-F_{ads}, $Al(OH)_3$-F_{coag}, and pristine $Al(OH)_3$ at annealing temperature (AT) of 200 °C, 600 °C, and 900 °C, and compared their removal behaviors towards cadmium [Cd(II)], arsenite [As(III)], and arsenate [As(V)]. Annealing treatment decreased their BET surface area (S_{BET}) and isoelectric point (pH_{iep}), and a more significant extent of decrease was observed at elevated AT. The incorporation of fluoride lowered their efficiency towards the removal of Cd(II), As(III), and As(V) as compared to $Al(OH)_3$. The elevated AT benefited Cd(II) adsorption whereas it inhibited the removal of As(III) and As(V) by any of the obtained aluminas, owing to the shift of pH_{iep} to lower pH ranges at elevated AT. The adsorption of Cd(II) increased whereas that of As(III) and As(V) decreased with elevated pH, with electrostatic interactions playing a determining role. The release of fluoride from $Al(OH)_3$-F_{ads} and $Al(OH)_3$-F_{coag} did occur, and it could be controlled by annealing them at elevated AT. The annealed aluminas showed good affinity towards different heavy metals and may be reclaimed for the treatment of industrial wastewater.

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1. Introduction

The discharge of toxic heavy metals such as cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), and mercury (Hg) has caused

serious pollution in rivers, soils, and underground waters in the past several decades in China. Long-term exposure to heavy metals can result in chronic damage to blood composition, lungs, brains, kidneys, liver, and other vital organs, and their mixtures show more significant toxicity than that they were separately existed [1]. Heavy metals also have acute toxicity, and high levels of inorganic arsenic at concentrations of above 60 mg/L in water can even be fatal. Industrial wastewaters are important heavy metal sources, and the control of point sources is easier and more cost-effective compared to the remediation of 'non-point' polluted water environments. However, the intentional or unexpected discharge of wastewater with high levels of heavy metals sometimes occurs in developing countries such as China. To avoid this as much as possible, stringent regulation of pollutant-producing factories is crucially important. On the other hand, the development of low-cost and easy-to-operate technologies also plays an important role.

In the past several decades, various methods such as flocculation [2], adsorption [3–5], ion exchange [6], reverse osmosis [7], electro dialysis [8], and precipitation [9] have been developed for the removal of heavy metals. However, the widespread application of some technologies has been restricted by high costs, the production of excessive amounts of concentrated solutions, and the disposal of secondary sludge and so on. To enable long-term stable operation of treatment facilities, it is important to decrease the treatment costs as much as possible. On the other hand, some industries produce a great deal of solid wastes [10–12], and their safe disposal has received great concern. However, if these spent wastes can be reused for the treatment of wastewater, it not only achieves the reclamation of spent wastes but also reduces the cost of heavy metal removal. This concept would be extremely attractive and cost-effective from an engineering point-of-view, and the utilization of industrial wastes for the adsorption of heavy metals has been widely investigated in the past decade [10–12].

The wide occurrence of fluorosis creates the need for the removal of fluoride from drinking water. Aluminum (Al) based coagulants and adsorbents have been widely used for defluoridation [13,14], inevitably producing a great deal of discharged sludge and spent adsorbents globally. These inorganic solid wastes with high levels of Al and fluoride should be disposed of properly to avoid secondary pollution in soils and underground water and so on. The traditional disposal methods for sewage sludge include farmland application, landfilling, and incineration, whereas for these inorganic sludges and adsorbents, strategies such as landfilling, stabilization, pond disposal, and soil disposal are feasible [15]. In our previous study, in situ prepared AlOxHy, which can be freshly coated onto porous carriers to achieve adsorbent granulation, has been developed and its fluoride removal efficiency has been well evaluated [16]. Once eventually exhausted, the spent AlOxHy with adsorbed fluoride as expressed by $Al(OH)_3$-F_{ads} may be safely disposed of by cheap and convenient means such as solidification in roadbeds or encapsulation in cement–lime mixtures. Coagulation is also a cost-effective defluoridation method, and Al-F complex formation is involved in fluoride removal [13]. The wide application of coagulation for defluoridation is restricted by the large-scale production of spent sludge as expressed by $Al(OH)_3$-F_{coag}. The reclamation of these two solid wastes not only minimizes their discharge into water environments but also is economically valuable. Our previous study indicated that freeze-dried $Al(OH)_3$-F_{ads} and $Al(OH)_3$-F_{coag} are potentially attractive for the removal of heavy metals such as arsenic [17]. However, the experimental freeze-drying procedure is not practically feasible from an engineering point-of-view. Generally, most discharged sludge is dewatered by filter pressing, and the ratios of moisture content can be as high as 70% or more. As for the long-distance transportation of the spent sludge with high moisture content, the cost is much too high and restricts its large-scale reclamation in areas distant from landfills.

To promote their reclamation, these spent sludge may be used as raw materials to prepare commercial adsorbents after being annealed. This economically valuable strategy reduces the moisture content, decreases the transportation cost and expands their application range as much as possible. However, the adsorption efficiency of this spent sludge after thermal pretreatment should be well evaluated.

Based on these considerations, we first prepared two solid wastes obtained from the defluoridation processes of adsorption and coagulation, which were respectively expressed as $Al(OH)_3$-F_{ads} and $Al(OH)_3$-F_{coag}, and pristine $Al(OH)_3$ was also prepared for comparison. The materials were annealed at different temperatures, and were then characterized by XPS, FTIR, and XRD to illustrate the effects of thermal treatment on their characteristics. Finally, the adsorptive behaviors of Cd(II), As(III), and As(V) on these solid wastes were evaluated in terms of adsorption kinetics and the effect of pH, and the mechanisms involved were proposed accordingly.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical-reagent grade and were directly used unless otherwise noted. The stock solutions of fluoride, Al, Cd(II), As(III), and As(V) salts were prepared by dissolving sodium fluoride (NaF), aluminum chloride ($AlCl_3 \cdot 6H_2O$), cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$], sodium arsenite ($NaAsO_2$), and sodium arsenate (Na_3AsO_4) in deionized water, respectively.

2.2. Preparation of $Al(OH)_3$-F solid wastes

The adsorbents $Al(OH)_3$-F_{ads}, $Al(OH)_3$-F_{coag}, and pristine $Al(OH)_3$ were prepared according to the methods described in our previous study [17]. Briefly, the pristine $Al(OH)_3$ was prepared by the stoichiometric reaction between $AlCl_3$ and NaOH. To prepare the $Al(OH)_3$-F_{coag}, NaF solution was added into the $AlCl_3$ solution prior to dosing the NaOH solution whereas NaF solution was introduced after the hydrolysis of Al^{3+} ions to produce $Al(OH)_3$-F_{ads}. To obtain their powders, the suspensions were filtered by 0.45-μm membranes, washed with distilled water, and then freeze-dried.

2.3. Annealing treatment

The $Al(OH)_3$-F_{ads}, $Al(OH)_3$-F_{coag}, and $Al(OH)_3$ powders were respectively annealed in an oven using a heating rate of 8 °C/min up to 200 °C, 600 °C, or 900 °C, and then the annealing temperature (AT) was kept constant for 2 h. The obtained samples were stored in a desiccator before use.

2.4. Batch adsorption experiments

The initial concentrations of Cd(II), As(III), or As(V) were adjusted to 70 mg/L by diluting their stock solutions, and the pH was adjusted thereafter. The species distribution of Cd(II), As(III), and As(V) over wide pH ranges from 3 to 8, as calculated by the Visual MINTEQ software, is illustrated in Fig. S1. $NaNO_3$ solution was added to provide a background ionic strength of 0.01 M. Batch adsorption kinetic experiments were conducted in beakers with magnetic stirring (350 rev min^{-1}) at pH 7.0 ± 0.2 after dosing 200 mg adsorbent into 1000-mL solution (25 ± 1 °C). pH was adjusted during adsorption using 0.1 M NaOH and 0.1 M HNO_3 to minimize pH variation. Sampling was carried out at intervals during adsorption and the obtained samples were filtered through 0.45-μm filter membranes and kept at 4 °C for further analysis.