Synthesis, characterization, and evaluation of simple aluminum-based adsorbents for fluoride removal from drinking water

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HIGHLIGHTS

- Low temperature aluminum (hydr)oxides showed high fluoride adsorption.
- Increased aging temperatures led to higher crystallinity but lower adsorption.
- Addition of sulfate during synthesis yielded basaluminite and increased adsorption.

ARTICLE INFO

ABSTRACT

Simple aluminum (hydr)oxides and layered double hydroxides were synthesized using common chemicals and equipment by varying synthesis temperature, concentrations of extra sulfate and citrate, and metal oxide amendments. Aluminum (hydr)oxide samples were aged at either 25 or 200 °C during synthesis and, in some cases, calcined at 600 °C. Despite yielding increased crystallinity and mineral phase changes, higher temperatures had a generally negative effect on fluoride adsorption. Addition of extra sulfate during synthesis of aluminum (hydr)oxides led to significantly higher fluoride adsorption capacity compared to aluminum (hydr)oxides prepared with extra citrate or no extra ligands. X-ray diffraction results suggest that extra sulfate led to the formation of both pseudoboehmite (γ-AlOOH) and basaluminite ($Al_4SO_4(OH)_{10} \cdot 4H_2O$) at 200 °C; energy dispersive X-ray spectroscopy confirmed the presence of sulfur in this solid. Treatment of aluminum (hydr)oxides with magnesium, manganese, and iron oxides did not significantly impact fluoride adsorption. While layered double hydroxides exhibited high maximum fluoride adsorption capacities, their adsorption capacities at dissolved fluoride concentrations close to the World Health Organization drinking water guideline of 1.5 mg L^{-1} were much lower than those for the aluminum (hydr)oxides.

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1. Introduction

Fluoride in drinking water is a pressing global issue as it can cause dental and skeletal fluorosis when present at levels above the World Health Organization (WHO) drinking water guideline of 1.5 mg L^{-1} (WHO, 2008). Recent modeling efforts show that expansive areas in Africa, Asia and Oceania may be exposed to high levels of fluoride in ground water resources (Amini et al., 2008). As a result, there is a need for efficient fluoride removal technologies that can be applied in drinking water systems around the world. Among candidate technologies, adsorption is efficient, economical, and suitable for household use (Ayoob et al., 2008), and activated alumina is a widely used adsorbent for this purpose (Fawell et al., 2006; Onyango and Matsuda, 2006). However, the high cost of activated alumina, due primarily to the significant energy

required for its manufacture from bauxite ore (Kasprzyk-Hordern, 2004), limits its application in less developed countries. Aluminum (hydr)oxide-based sorbents that can be synthesized under lower energy conditions can be promising for treatment of fluoride contaminated water (Shimelis et al., 2006; Jain and Jayaram, 2009; Liu et al., 2011; Gong et al., 2012; Jiménez-Becerril et al., 2012). In some cases, amendment of these sorbents with the (hydr)oxides of iron (Kuriakose et al., 2004; Dhiman and Chaudhuri, 2007), magnesium (Maliyekkal et al., 2008), or manganese (Maliyekkal et al., 2006; Dhiman and Chaudhuri, 2007; Teng et al., 2009) has been shown to increase fluoride (Maliyekkal et al., 2006, 2008) and arsenic (Kuriakose et al., 2004) adsorption capacities under favorable pH conditions (Maliyekkal et al., 2006), perhaps due to small increases in the pH point of zero charge (pH$_{pzc}$) (Dhiman and Chaudhuri, 2007) and/or adsorption affinity (Kuriakose et al., 2004; Maliyekkal et al., 2006). Layered double hydroxides (LDHs), consisting of alternating layers of hydroxides of mixed metals (e.g., Mg–Al and Zn–Al), intercalated with exchangeable anions

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(including carbonate and chloride), have also shown promise for fluoride adsorption (Lv, 2007; Mandal and Mayadevi, 2008).

The specific aluminum (hydr)oxide phase(s) that precipitate from dissolved aluminum salts depend on the pH, the ligand(s) present in solution, and aging time and temperature. Pseudoboehmite (poorly or finely crystalline boehmite (γ-AlOOH)) may form upon aging of an initial amorphous Al(OH)$_3$ precipitate at room temperature (Aldcroft et al., 1969). The presence of ligands that complex strongly with Al(III) in competition with OH$^-$ can hinder formation of crystalline Al(OH)$_3$ phases and stabilize pseudoboehmite, which has a lower pH$_{pzc}$ (Violante and Huang, 1984). Pseudoboehmite aging at temperatures up to 300 °C increases crystallite size and lowers specific surface area (SSA), but does not promote phase changes (Tottenhorst and Hofmann, 1980; Gong et al., 2012); calcination temperatures of 500–700 °C are required for transformation of pseudoboehmite to γ-Al$_2$O$_3$ (Lippens and de Boer, 1964; Repelin and Husson, 1990; Chary et al., 2008; Gong et al., 2012).

The overall objective of this study was to compare the fluoride adsorption performance of a series of aluminum based adsorbents that could be synthesized using common chemicals, such as water treatment coagulants, and heating equipment, such as kilns, that are readily available in rural areas of developing countries. Specific objectives were to synthesize adsorbents with a range of mineral phases, crystallinities, and surface properties (e.g., SSA and pH$_{pzc}$), by varying synthesis temperature, concentrations of extra ligands, and metal oxide amendments, then to test these sorbents for fluoride adsorption efficiency.

2. Methods

2.1. Adsorbent synthesis

A series of aluminum (hydr)oxides was prepared by hydrolysis of AlCl$_3$ (Sigma–Aldrich), sometimes with addition of sulfate (as sodium sulfate (Acros)) or citrate (as sodium citrate (Sigma–Aldrich)), as well as temperature and pH adjustment (Violante and Huang, 1984, 1993; Watanabe et al., 2002). The overall approach is illustrated in Fig. 1. Briefly, 50 mM AlCl$_3$ was titrated

with 5 M NaOH (Acros) to pH 8.2 (Violante and Huang, 1984) for three sets of conditions: (1) no ligands other than the chloride present in the AlCl$_3$ were added, (2) 0.5 M sulfate was added, and (3) 5×10^{-4} M citrate was added. These concentrations of sulfate and citrate were based on the aluminum: ligand ratios in Violante and Huang (1984), and were intended to produce a similar extent of complexation of aluminum by either sulfate or citrate. (Less citrate was required because citrate is a much stronger complexing agent than sulfate (Violante and Huang, 1984).) The precipitated solids were then aged at either 25 °C (to yield lower crystallinity pseudoboehmite) or 200 °C (to yield higher crystallinity pseudoboehmite) for 1 d, decanted and transferred to dialysis tubing (Fisher, Seamless cellulose dialysis tubing, 12 kDa) and dialyzed for 6 d, during which time deionized water was replaced daily. Next, the solids were centrifuged, air-dried, ground with a mortar and pestle, dried in the oven at 100 °C for 3 h to remove water, and stored in a desiccator. A subset of the solids was then further heated to 600 °C for 4 h to promote the phase transition from pseudoboehmite to γ-Al$_2$O$_3$ (Fig. 1). Some aluminum (hydr)oxide adsorbents were further amended by precipitating (hydr)oxides of iron, magnesium, or manganese on their surfaces (Kuriakose et al., 2004; Maliyekkal et al., 2006, 2008; Dhiman and Chaudhuri, 2007; Teng et al., 2009). These precipitates were generated by mixing a slurry of aluminum (hydr)oxide with 0.747 M Fe(NO$_3$)$_3$·9H$_2$O (Arcos), 1 M MgCl$_2$ (Arcos), or 1.5 M (CH$_3$COOH)$_2$Mn (Arcos) followed by heating at 200 °C for 4 h. After being washed, dried, and dialyzed as before, the metal amended aluminum (hydr)oxides were stored in a desiccator. All aluminum (hydr)oxides are hereafter referenced using the abbreviations in Fig. 1.

A series of LDHs, including Mg–Al–Cl$^-$, Mg–Al–CO$_3^{2-}$, Mg–Al–PO$_4^{3-}$, and Zn–Al–Cl$^-$ was prepared by co-precipitation. Mg–Al LDHs were prepared according to Carriazo et al. (2007). Zn–Al–Cl$^-$ LDH was prepared the same way as Mg–Al–Cl$^-$ LDH, except ZnCl$_2$·6H$_2$O (Fisher) was used instead of MgCl$_2$. Like some of the aluminum (hydr)oxides, Mg–Al–Cl$^-$ LDH was amended by precipitation of an iron (hydr)oxide on its surface by adding 10 g LDH to 7 mL 0.747 M Fe(NO$_3$)$_3$·9H$_2$O, gentle mixing, and drying at 130 °C for 4 h. This sample is called Fe–Mg–Al–Cl$^-$ LDH. One sample of Mg–Al–Cl$^-$ LDH was heated at 500 °C for 4 h, and is denoted Mg–Al–Cl$^-$ LDH-500.
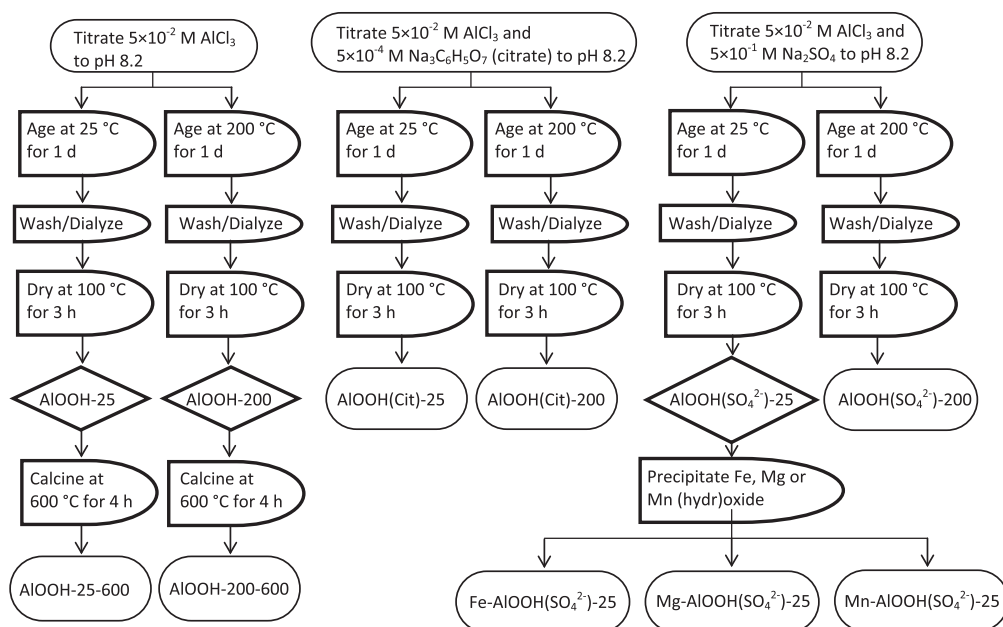

Fig. 1. Aluminum (hydr)oxide synthesis procedures.