

Preparation and characterization and application of activated alumina (AA) from alum sludge for the adsorption of fluoride from aqueous solutions: new approach to alum sludge recycling

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ABSTRACT

Activated alumina (AA) prepared from alum sludge (AS) was used in removal of fluoride from aqueous solutions. The capacity of AA in the adsorption of fluoride from water was found to be 17.75 mg/g. The maximum efficiency of fluoride adsorption was 96% at the optimum condition ($C = 5$ mg/L, $pH = 7$, $t = 20$ min and adsorbent dosage = 5 g/L). Based on the results, it can be concluded that conversion of AS to AA can be a method for recycling of AS. Also AA can be used for adsorption of fluoride from aqueous solutions. So AS as a substance harmful to the environment turns into AA as a usable material in water treatment.

Key words | activated alumina, defluoridation, fluoride

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INTRODUCTION

Fluoride and its compounds are widely used in different industries such as semiconductor manufacturing, coal-fired power plants, ceramic production, the electrochemical industry, manufacture of rubber and fertilizer, etc. (Tripathy *et al.* 2006). Therefore, the discharge of industrial wastewater containing fluoride can cause pollution of water resources and the environment (Budyanto *et al.* 2015).

Several methods have so far been used to remove fluoride in the water, some of which include adsorption (Daifullah *et al.* 2007; Chen *et al.* 2010; Krupadam *et al.* 2010; Liu *et al.* 2013; Selimoglu *et al.* 2018), precipitation (Saha 1993; Kemer *et al.* 2009; Wang *et al.* 2013), red mud (Meenakshi *et al.* 2008), ion exchange (Vaaramaa & Lehto 2003), electrodialysis (Amor *et al.* 2001), and reverse osmosis (Ndiaye *et al.* 2005).

Adsorption is one of the most widely used methods because of its simplicity of use and availability (Mohapatra *et al.* 2009). Various materials such as red mud, bone

char, zeolite, aluminum–cerium double-metal impregnated activated carbon, granular ferric hydroxide, chitosan, granulation of Fe-Al-Ce nano-adsorbent, low-cost adsorbent and bio-adsorbents have successfully been used to remove fluoride from drinking water (Jagtap *et al.* 2009; Kumar *et al.* 2009, 2011; Buamah *et al.* 2013; Su *et al.* 2013; Kalidindi *et al.* 2016).

Recently, a bulk of new research has been conducted to expand the adsorbents modified with metal ions in order to remove fluoride (Sun *et al.* 2011). On the other hand, the concentration of aluminum as a toxic agent in the aquatic environment, and harmful to human health, is very high in alum sludge (AS) (458–463 mg/g) (Yang *et al.* 2006). The conversion of sludge into sludge-based adsorbents (SBAs) is a more stable and sustainable method for treatment of sludge (Xu *et al.* 2015). Also by conversion of $Al(OH)_3$ to activated alumina (AA), the possibility of its reuse to solve an environmental problem is provided.

The present study sought to examine the production of AA from AS and its use in the removal of fluoride from aqueous solutions with the approach of recycling sludge from water treatment plants.

MATERIALS AND METHODS

Materials

Sodium fluoride was purchased from Merck. All reagents used were of analytical reagent grade.

Preparation and characterization of AA

The AS was used for the preparation of AA (Saha 1994; Moussavi *et al.* 2014; Aghapour *et al.* 2015). Alum recovery from sludge was achieved at a pH of 2.5 by adding sulfuric acid (1N) (Crittenden *et al.* 2012). The sludge was stirred for 30 min at 100 rpm and was then allowed to sediment for 1 h. The supernatant of the sludge was separated from it and used to prepare $\text{Al}(\text{OH})_3$ gel by adding NaOH solution (1N). AA was prepared by the thermal sol-gel method. So, after the pH of the solution reached 8, it was stirred for 15 minutes at 40 rpm and was then allowed to sediment for 1 h. The supernatant of the suspension was then discharged and $\text{Al}(\text{OH})_3$ gel was then dried at 105 °C and calcined for 2 h in air at 700 °C.

AA was characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) was also conducted to study the characterization of AA. Scanning electron microscopy was carried out for phase surface morphology of AA and energy dispersive X-ray analysis (EDAX) was used to examine the elemental composition analysis of Al_2O_3 .

Determination of adsorption isotherm and kinetics

The Langmuir adsorption isotherm model (Equation (1)) was used for mathematical modeling of the adsorption process (Crittenden *et al.* 2012):

$$q = \frac{Bq_m C_e}{1 + BC_e} \quad (1)$$

B and q_m : empirical constants

$q = X/M$: mass of adsorbed material to the mass of adsorbent

C_e = concentration of equilibrium.

Also the pseudo-second-order model (Equation (2)) was used to describe the kinetics of the fluoride adsorption process:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

k_2 : pseudo-second-order rate constant of adsorption (g/(mg min))

q_e and q_t : the amounts of fluoride adsorbed at equilibrium (mg/g) and at time t (min), respectively (Nazari & Halladj 2014).

The samples were passed through a 45 μm Whatman filter and their fluoride concentration was measured according to the SPANDS method. The solid addition method was used to determine the pH of the zero point of charge (pHzpc) of AA. To ensure the reliability of the results, each step was repeated twice.

RESULTS

Characterization of AA

XRD patterns for AA are shown in Figure 1(a). The peak positions at 25.5, 35.1, 37.8, 43.2, 52.6, 57.5, 66.5, 68.2, and 95.1 ° 2 θ on the XRD pattern of AA matches the major peaks of Al_2O_3 . The matching of all major peaks on the XRD patterns of AA with pure alumina (Al_2O_3) identifies the prepared powder as being composed of alumina.

The surface morphologies of AA were characterized using SEM (Figure 1(b)). As seen in Figure 1(b), the surface morphology characterization by SEM demonstrates that AA is composed of micro-agglomerates with a size less than 50 nm.

Elemental analysis of AA was done using EDAX and the results given in Figure 1(b) show aluminum (Al) and oxygen (O) with weight percentages of 34.18% and 52.07% respectively as the main elements in the prepared AA. Also, it shows that the amounts of other elements (sodium = 7.12, sulfur = 6.24, and iron = 1.22 wt%) are negligible in the AA. These findings

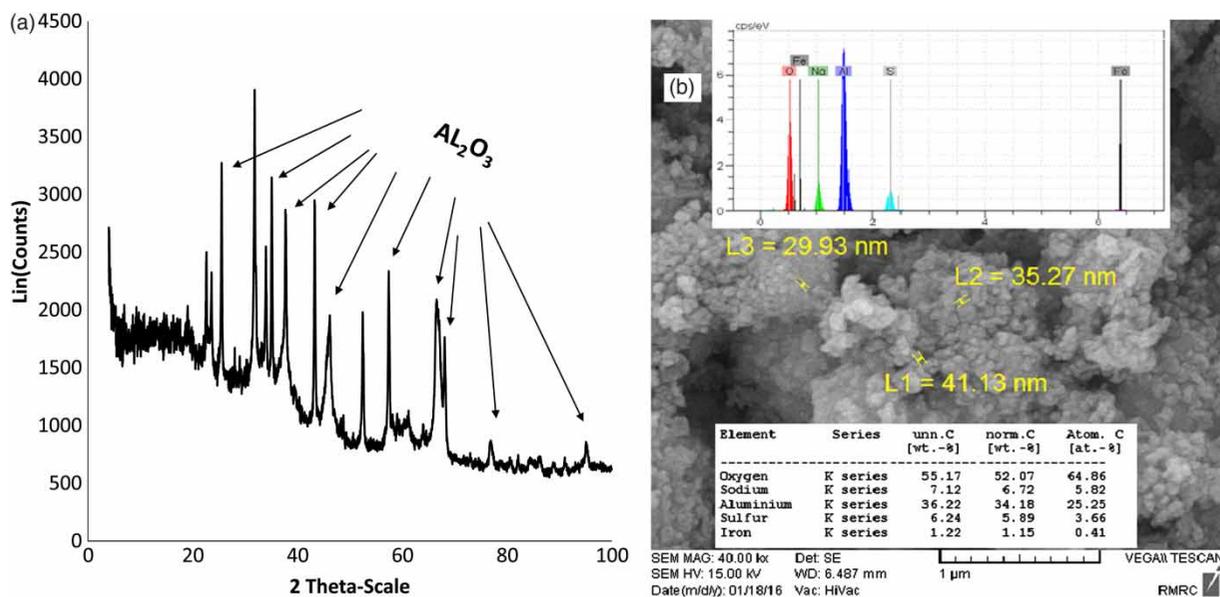


Figure 1 | (a) XRD patterns, (b) SEM micrograph and EDAX analysis of the AA.

indicate that the AA has a high purity. Generally, the ratio of the production of AA from AS was determined to be 38.5%.

The Fourier transform infrared (FTIR) spectra of the AA (not shown) shows the main peaks at 3,447, 1,640, 1,152, 840, and 635 cm^{-1} on the spectra that correspond to O-H (water vapor adsorbed from the atmosphere), Al-C (CO_2 adsorbed from the atmosphere), Al-O stretching vibration bending, S=O bending (sulfate), and Al-O stretching vibration respectively (Kumar *et al.* 2011). The main peaks at 1,640, 1,152, and 635 cm^{-1} on the FTIR spectra are attributed to AA and clearly confirm that AA was prepared from AS. Therefore, the results of the characterization of the prepared powder by XRD, SEM, EDAX, and FTIR demonstrate that AA can be successfully prepared from AS.

Influence of pH

The influence of pH on the adsorption of fluoride on AA is presented in Figure 2.

The results showed that a pH increase from 3 to 7 results in an increase in fluoride adsorption and the highest removal efficiency is at pH 7. These results are attributed to the pH_{ZPC} of AA and the distribution of F^- at different pHs. The pH_{ZPC} of AA was determined to be 6.5. The efficiency of adsorption of fluoride decreases with increasing pH from 7 to 11 which is due to the distribution of F^- and HF (Tor 2006; Gong *et al.* 2012).

Due to the formation of HF at acidic pH and coulombic decrease between fluoride and AA, the adsorption at acidic pH decreases. At higher pH levels, due to the accumulation of hydroxyl ions on the surface of the adsorbent and the increase of the number of negative charges, the efficiency decreases. Because of the anionic nature of F^- , the increase in the pH level, which suggests accumulation of negative charges on the surface of the adsorbent, and accordingly the repulsion between the adsorbent and the pollutant, the efficiency of fluoride adsorption reduces (Kumar *et al.* 2009; Sun *et al.* 2011). These findings confirm the results of other researchers demonstrating that the highest removal efficiency of fluoride by AA is at pH 7 (Kamble *et al.* 2007; Kumar *et al.* 2011; Sun *et al.* 2011).

As can be seen in Figure 2, the concentration of residual aluminum in the treated water varies from 0.076 to 2.3 mg/L. A minimum of residual aluminum concentrations (0.076 mg/L) is observed at pH 7 (close to the pH_{ZPC} of AA, 6.5). Therefore, due to the neutrality of the adsorbent surface in the pH_{ZPC} , the maximum adsorption coincides with the pH_{ZPC} and minimum residual aluminum concentrations.

Influence of the adsorbent dosage

Figure 3 shows the fluoride removal as a function of AA dosage. As can be observed in Figure 3, the removal of

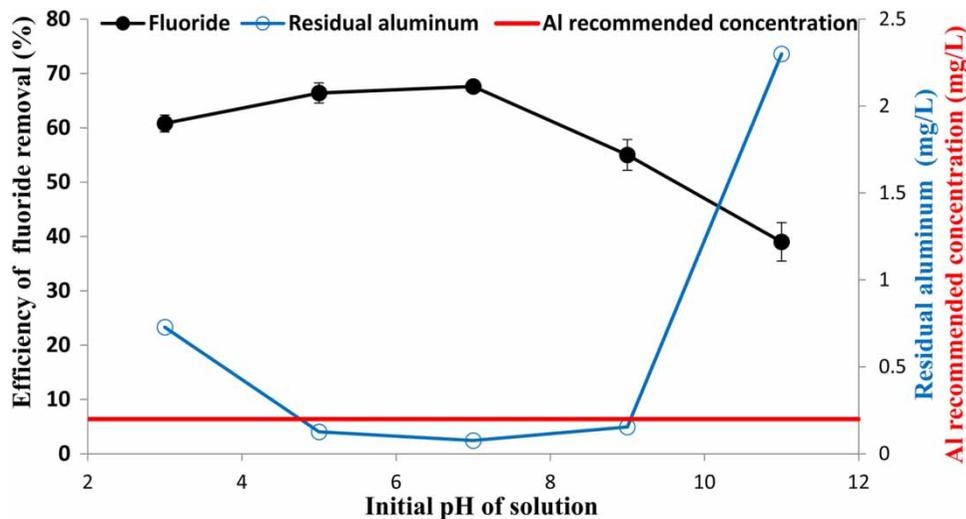


Figure 2 | Effect of initial pH on the fluoride adsorption on the AA.

fluoride by increasing the dosage of AA from 0.1 to 5 g/L has increased from 42.5% to 96%.

Therefore, due to the high adsorption capacity of AA and taking into consideration the economic conditions, the adsorbent dosage of 0.2 g/L was chosen as the favorable dosage. This result is in accordance with the results of other researchers demonstrating that by increasing the absorption, the efficiency of fluoride removal increases (Nigussie *et al.* 2007; Kagne *et al.* 2008; Biswas *et al.* 2009). But the favorable adsorbent dosage of AA (0.2 g/L) is significantly lower than that reported by others (>5 g/L) which may be attributed to

the structure of AA, its high effective surface area, and pore volume that are reported to be 151.7 m²/g and 1.09 cm³/g respectively (Kumar *et al.* 2011).

Effect of reaction time

The results of the effect of reaction time on the fluoride removal in pure water (distilled water) and actual water (tap water) are presented in Figure 4.

Based on Figure 4, the rate of fluoride removal by AA increases by increasing the reaction time and at 20 minutes

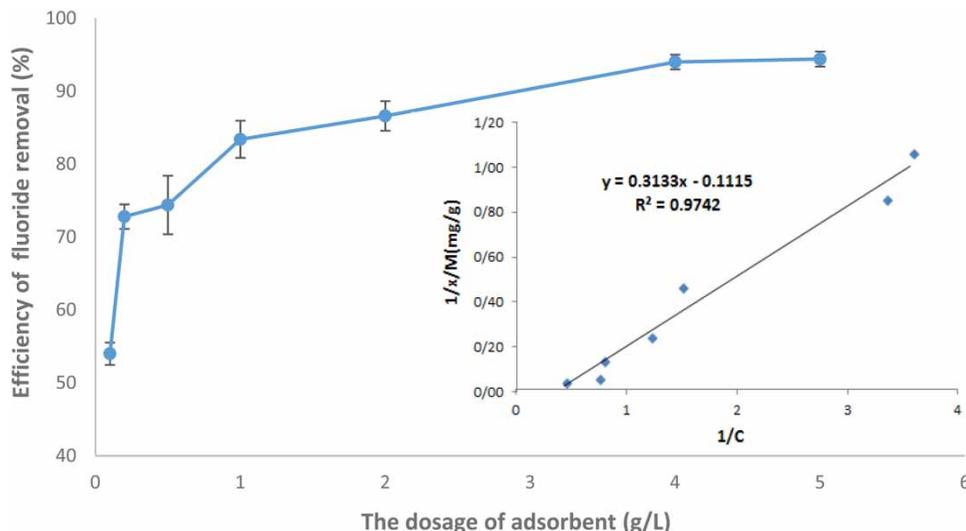


Figure 3 | Effect of the adsorbent dosage and isotherm of the fluoride adsorption.

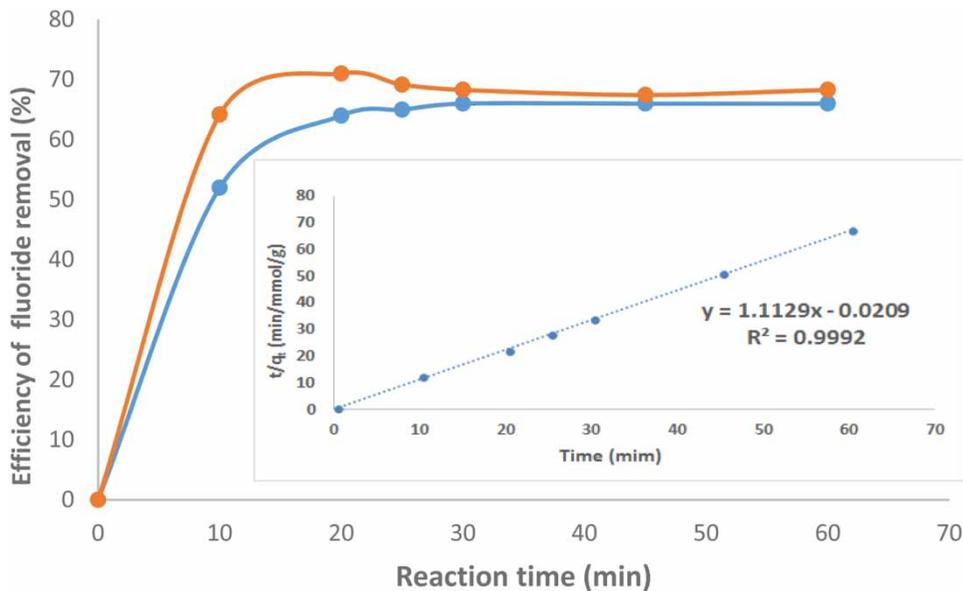


Figure 4 | Effect of reaction time and the kinetics of fluoride adsorption.

reaches the maximum level (71%), and after 20 minutes the efficiency remains almost constant. This is due to the reduction of fluoride concentration and the reduction of operation efficiency in the adsorbent (Dolati *et al.* 2017). So, this is because in the initial stage of absorption, a lot of empty places are available and over time, these places are occupied by fluoride molecules. In previous studies, the removal rate was reported to be high in the first 30 min and then reduced (Kamble *et al.* 2007; Sundaram *et al.* 2009).

In this study, given that the removal happens after 20 min and no basic change is observed after this interval, 20 min was considered as the time equilibrium. Therefore, it becomes clear that compared with the adsorbents used in previous studies, AA could remove fluoride in low contact time and low adsorbent dose (Wajima *et al.* 2009; Deng *et al.* 2011). This can be ascribed to the high effective surface area and the pore volume of AA.

Given that the presence of anions and cations in water can affect the absorption of fluoride with AA. The effect of reaction time was repeated using actual water containing common anions and cations such as Ca (64 mg/L as CaCO_3), Mg (35 mg/L as CaCO_3), Na (14.5 mg/L), HCO_3^- (356 mg/L as CaCO_3), SO_4^{2-} (27 mg/L) and Cl (6.5 mg/L). As shown in Figure 2, the use of actual water instead of pure

water, reduced the efficiency of fluoride removal with AA at reaction times of less than 30 min. However, its effect is negligible at reaction times longer than 30 minutes.

Determination of adsorption isotherms and kinetics

As can be seen from Figure 3, the results of this study revealed that adsorption isotherms of fluoride on AA could be fitted well by the Langmuir isotherm ($R^2 = 0.9742$). It indicating that fluoride adsorption onto AA is favorable. Also, it showed that the adsorption process might be a homogeneous adsorption.

The capacity of AA in the adsorption of fluoride from water under favorable operating conditions ($C_0 = 5$ mg/L, $\text{pH} = 7$, $t = 20$ min, and adsorption dosage = 0.2 g/L) was found to be 17.75 mg/g at room temperature. The adsorption capacity of AA (17.75 mg/g) compared with other adsorbents reported in previous studies shows that AA has higher adsorption capacity than commercial nano-alumina (14 mg/g) (Kumar *et al.* 2011; Tomar *et al.* 2014).

As Figure 4 shows, the results of this study revealed that the adsorption kinetics of fluoride on AA could be fitted well by the pseudo-second-order model ($R^2 = 0.9992$). This indicated the applicability of the pseudo-second-order model for the adsorption kinetics of activated AA. Due to good

agreement of experimental data with the pseudo-second-order model, it can be used to favorably explain fluoride adsorption on AA. Therefore, the adsorption of fluoride on to AA is suitable for the pseudo-second-order reaction. This result has been confirmed by different researchers (Kamble *et al.* 2010; Kumar *et al.* 2011; Gong *et al.* 2012). So, it indicates that adsorption by AA can be a method to remove fluoride from aqueous solution. The production of alumina from AS is also important, in terms of the life cycle analysis of aluminum, the life cycle of aluminum in AS, from entering the water and environment and accumulation in the soil of plants, and in animals and humans, has changed to AA, which is an insoluble substance in water. Meanwhile, alumina is a natural substance in the environment and soil. On the other hand, this AA is recyclable in acidic conditions after use in water purification. Thus, by providing alumina from AS, the life cycle of an important part of the alumina can be altered. Therefore, by converting aluminum into AS, environmental pollution can be reduced to aluminum.

CONCLUSIONS

The results of this study demonstrate that AA can be successfully prepared from AS. The AA has high potential for the removal of fluoride from aqueous solutions. AA has a good correlation with the Langmuir isotherm model. The capacity of AA in adsorption of fluoride from water under optimum conditions was found to be 17.75 mg/g. The maximum efficiency of fluoride adsorption by AA from aqueous solutions was 96%. Therefore, prepared AA from AS can be a practical, reliable method to remove fluoride from aqueous solution. Also, by converting aluminum into AS, environmental pollution can be reduced to aluminum.

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