Evaluation of Ozone-Treated Activated Alumina for Fluoride Ion Removal from Groundwater Samples

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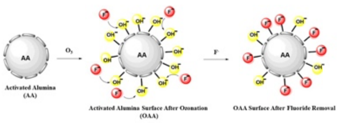

This study investigates the effectiveness of ozone-treated activated alumina (OAA) in removing fluoride ions from groundwater. Using analytical techniques such as FTIR, SEM, EDX, pHpzc and NMR, we evaluated the impact of ozone treatment on the surface characteristics of activated alumina (AA). Batch adsorption tests were performed using groundwater samples collected in Rio Grande do Sul, Brazil. The findings reveal the effectiveness of ozone in increasing the defluoridation capacity of AA, as OAA demonstrates superior fluoride removal efficiency compared to the AA. Overall, OAA shows promise for defluoridation applications due to its improved performance and simplified preparation process.

Introduction

Due to its simple preparation, low cost, easy operation, and affinity with fluoride ions (F^-), activated alumina (AA) is one of the most widely applied adsorbents for water defluoridation [1]. F^- adsorption mechanisms involve the exchange of these ions with the hydroxyl groups present on the surface of AA, electrostatic interaction, and Lewis acid-base interaction. The electrostatic interaction depends on the surface charge of AA, determined by its point of zero charge (pHpzc) and the pH of the solution. If the solution pH is lower than the pHpzc of AA, the surface of AA becomes protonated, facilitating the adsorption of negatively charged species such as F^- [1], [2]. Thus, the adsorption of fluoride ions through AA is highly dependent on the pH of the medium - the pH of the solution to be below 6.0 to achieve maximum adsorption capacity [3]. However, since the pH of groundwater ranges from 5.5 to 8.5 [4], the application of AA for this purpose becomes limited. In addition, this material requires a long contact time to reach adsorption equilibrium[5]. In this context, many researchers have been modifying its chemical and morphological surface properties to enhance the defluorination property of AA. At the same time, AA is used as a catalyst in heterogeneous catalytic ozonation. Studies suggest that various processes occur on the catalyst surface during catalytic ozonation, involving ozone adsorption, decomposition, surface oxidation reactions, and desorption processes [6]. Thus, this work focuses on surface treatment of AA via ozonation and investigates its fluoride ion removal capacity from groundwater samples collected in a rural community.

Material and Methods

Ozone-treated activated alumina (OAA) was produced using an ozone generator (Z100, Ozonebras) following the procedure described by De Paula et al. (2023) . To characterize the materials before (AA) and after ozone modification (OAA), several methodologies were employed, including Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX), determination of the point of zero charge (pHpzc), and Nuclear Magnetic Resonance (NMR) [7], [8]. Groundwater samples contaminated with fluoride ions were collected in Faxinal do Soturno, Rio Grande do Sul, Brazil. Due to fluoride ion contamination, the Rio Grande do Sul Sanitation Company (CORSAN) cannot directly use water from this well - despite its significant potential for water supply. We conducted batch adsorption tests to assess the adsorption capacity and fluoride ion removal efficiency of OAA in a groundwater sample. For comparison purposes, we also performed the same adsorption tests with AA. These tests were carried out in triplicate. For this, we added 0.435 g of each material to 100 mL of the groundwater sample. We maintained the pH and initial fluoride ion concentration at natural conditions. We placed polypropylene Erlenmeyer flasks containing the water sample and adsorbent materials under constant agitation at 150 rpm at room temperature (25°C) for 1 hour. Subsequently, we filtered the samples and determined the final fluoride ion concentration in the solution using ion chromatography (Metrohm 930 Compact IC Flex Ion Chromatograph).

Results and Discussion

The EDS, FTIR, and NMR analyses revealed that ozonation increased the amount of hydroxyl groups on the surface of AA, making it an effective treatment. This led to an increase in fluoride ion adsorption, confirming that OAA is an effective adsorbent material for fluoride ions. Additionally, it was determined that the zero charge point of OAA is at pH 8.5, indicating its electropositive nature on surfaces at pH values lower than 8.5 [7], [8]. The groundwater sample characteristics and the results of adsorption tests with AA and OAA are shown in Table 1. The fluoride concentration in the groundwater sample (3.2 mg/L) exceeds the WHO recommendation (1.5 mg/L), indicating that this groundwater source cannot be used for public supply without treatment. After adsorption with AA, the fluoride ion concentration decreased to 2.7 mg/L, representing a removal efficiency of approximately 16%. In comparison, using OAA reduced the fluoride concentration to 1.5 mg/L (53%), meeting the recommended fluoride ion level for drinking water. However, both removal efficiencies are much lower than those achieved with synthetic F^- solution (>94%). Additionally, Table 1 shows high concentrations of chloride and sulfate ions in the groundwater sample. De Paula et al. (2023) studied the effects of chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) on fluoride removal. Their findings indicate that all three ions decrease the efficiency of OAA in removing fluoride. Moreover, the pH of the groundwater sample (8.5) exceeds the point of zero charge (pHpzc) of AA (7.5) and is the same of OAA (8.5) [7]. As aforementioned, when the solution pH is below the pHpzc, the adsorbent surface becomes positively charged, favoring the adsorption of negatively charged species like fluoride. Thus, we anticipate that maximum fluoride adsorption will occur at a pH below the point of zero charge.

Conclusions

In general, it was found that ozone-treated activated alumina exhibits superior fluoride ion removal efficiency compared to activated alumina, a commercially available material widely used in water treatment systems. Another advantage of ozone-treated activated alumina is that, in comparison to other studies, its preparation is simple, as ozonation does not require the addition of other reagents such as rare earth metals, calcium, zirconium, sulfuric acid, hydroxyapatite, among other materials commonly used for surface modification of activated alumina. Additionally, ozone-treated activated alumina can be used over a wide pH range. Thus, this material has great potential for application in water defluoridation systems.

Table 1. Groundwater sample characteristics and the results of adsorption tests with AA and OAA

Parameter	Experiments results					
	Synthetic sample	Adsorption using AA	Adsorption using OAA	Groundwater sample	Adsorption using AA	Adsorption using OAA
Ions Fluoride (mg/L)	4.4 mg/L	3.2 mg/L	0.25 mg/L	3.2 mg/L	2.7 mg/L	1.5 mg/L
Ions Chloride (mg/L)	-	-	-	178.2 mg/L	178.1 mg/L	176.4 mg/L
Ions Nitrate (mg/L)	-	-	-	2.7 mg/L	3.9 mg/L	3.6 mg/L
Ions Sulfate (mg/L)	-	-	-	382.4 mg/L	394.1 mg/L	387.5 mg/L
pH	8.5	-	-	8.5	-	-

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