Evaluation of the Point of Zero Charge (pH$_{pzc}$) of Ozone-Treated Activated Alumina for Water Defluoridation

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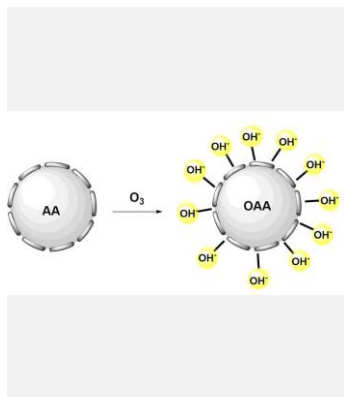
The concentration of fluoride ions (F$^-$) in drinking water is a critical public health concern. To address this, several treatment methods have been developed and used worldwide. Among these methods, adsorption emerges as one of the most effective approaches. In this unit operation, proper characterization of adsorbent materials is essential to understand the mechanism involved. Moreover, treatments on material surface can enhance and improve the performance of the absorbent. Thus, this study aimed to evaluate the effect of ozone treatment to the point of zero charge (pH$_{pzc}$) of activated alumina (AA), an adsorbent commonly used in water to the control of F$^-$.

Introduction

Worldwide, less than 1% of water meets international drinking water standards due to various types of contamination [1]. Among these contaminants, fluoride ions stand out as a significant concern. The presence of fluoride in groundwater has been identified as a critical issue in several countries. It happens because fluoride concentration in public water supplies is a critical factor for human health [1,2]. Consuming water with high fluoride concentrations (greater than 1.5 mg/L) can lead to adverse health effects, such as dental and skeletal fluorosis [3]. Therefore, developing technologies capable of efficiently removing fluoride ions is essential. Adsorption is considered one of the best alternatives for addressing this issue, due to its simplicity, efficiency, and low cost [4]. The efficiency of this process is directly related to the adsorbent material used [5]. Activated alumina (AA) is the most widely used adsorbent for fluoride removal; however, its application is limited by its low adsorption capacity at neutral pH, low adsorption kinetics, and difficulties in regeneration [3,6]. To improve the adsorption capacity and efficiency of AA, surface modifications are necessary, particularly in regions where groundwater is the primary water source and is susceptible to fluoride contamination from anthropogenic or natural sources [7]. Advanced oxidation process (AOPs), which uses ozone combined with catalysts, is known as catalytic ozonation. Depending on the solubility of the catalyst in water, it can be classified as homogeneous or heterogeneous [8,9]. In contrast to ozonation by itself, catalytic ozonation effectively generates hydroxyl radicals even at acidic pH levels [10]. Thus,

evaluating the point of zero charge (pH$_{pzc}$) is of paramount importance, as the increased generation of hydroxyl radicals on the material's surface enhances the adsorption of fluoride ions (F$^-$) [3,7]. The pH$_{pzc}$ of the adsorbent is critical for understanding how the pH of the aqueous solution can influence the adsorption process. The pH$_{pzc}$ represents the pH at which the adsorbent's surface charge is neutral. When the solution's pH is lower than the pH$_{pzc}$, the adsorbent surface is positively charged, favoring the adsorption of negatively charged species such as fluoride. However, when the solution's pH is higher than the pH$_{pzc}$, the adsorbent surface is negatively charged, making it less favorable for fluoride adsorption. Thus, maximum fluoride adsorption typically occurs at a pH lower than the pH$_{pzc}$ [4,7,11]. In light of the aforementioned considerations, the aim of this work was to evaluate the influence of ozone treatment on the point of zero charge (pH$_{pzc}$) of activated alumina and its effects on fluoride removal.

Material and Methods

This study used the "11 points methodology" [6] to determine the point of zero charge (pH$_{pzc}$) of both activated alumina (AA) and ozone-treated activated alumina (OAA). In this method, 0.1 g of the adsorbent material was added to 50 mL of a 0.1 M NaCl solution, under 11 different initial pH values (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12). The pH was adjusted using HCl or NaOH solutions. The mixtures were kept under constant stirring for 24 hours at room temperature (25 ºC). After this period, the final pH of each solution was measured.

Results and Discussion

Figure 1 illustrates the pH_{pcz} for both AA and OAA. The pH_{pcz} corresponds to the value at which the final pH remains constant. This value is obtained on the graph by identifying the point of intersection between the initial pH and final pH curves. The pH_{pzc} values for AA and OAA were assessed to be 7.54 and 8.49, respectively. Based on these results, it can be affirmed that ozonation of AA resulted in an increase in its pH_{pzc}. Since at pH values lower than the pH_{pzc} the surface of the material is positively charged, the adsorption of F^- is favored due to electrostatic attraction between them. Therefore, the use of OAA is expected to result in high fluoride removal over a wide pH range. From pH 8.59 onwards, the adsorption capacity of OAA is expected to decrease due to competition between fluoride ions and hydroxyl ions for the active sites of the material. In addition, as it is negatively charged, the surface of OAA will cause electrostatic repulsion of the fluoride ions, reducing the efficiency of the process [12].

Figure 1. pH_{pzc} de a) AA and b) OAA.
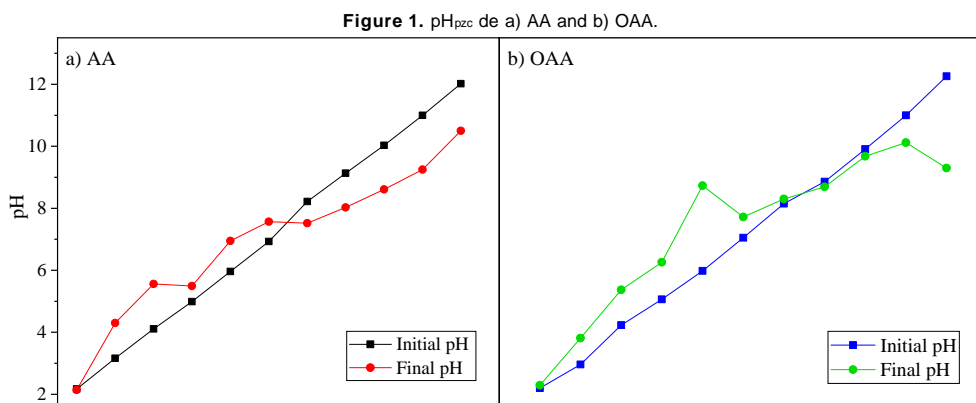
Conclusions

In conclusion, the ozone treatment of activated alumina effectively changed its point of zero charge, enhancing its ability to adsorb fluoride across a large pH range (up to 8.5). This treatment makes AA a more efficient material for water treatment applications.

References

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