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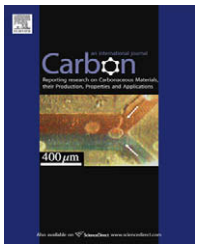

# Preparation and characterization of charcoals that contain dispersed aluminum oxide as adsorbents for removal of fluoride from drinking water

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ABSTRACT

Charcoals adsorbents that contain dispersed aluminum and iron oxides have been synthesized by impregnating wood with salt solutions followed by carbonization at 500 °C, 650 °C or 900 °C. The adsorbents were characterized and their performance for fluoride removal from aqueous solution was evaluated. Aluminum and iron oxides were well dispersed into the porous charcoals. The carbons were amorphous and highly porous. XRD of the adsorbents showed crystalline iron oxide but did not show any form of crystalline aluminum oxides. All the adsorbents showed acidic surface properties. The efficiency of defluoridation was found to depend on the carbonization temperature, the pH of point of zero charge (pHPZC), and the co-existing ions. Substrates prepared at 650 °C with aluminum and iron oxides exhibited the best efficiency with a fluoride sorption capacity of 13.64 mg $g^{-1}$. More than 92% removal of fluoride was achieved within 24 h from a 10 mg $L^{-1}$ solution at neutral pH. Fluoride adsorption kinetic was well fitted by a pseudo-second order model. The amounts of residual Al and Fe in treated solution were pH dependant. At neutral pH, the amounts of dissolved Al and Fe were found to be 0.67 and 1.8 mg $L^{-1}$, respectively.



## 1. Introduction

The quality of drinking water is very important for public safety and the quality of life. The contamination of drinking water with fluoride ions is a real health problem, especially in arid and semi-arid areas where geology provides sources of fluoride ions. For example, the fluoride concentration in groundwater reaches 20 mg $L^{-1}$ and more, in some regions of North Africa, India and China [1–4], this is higher than the standard set by World Health Organization (WHO) which is 1.5 mg $L^{-1}$. Excess fluoride in drinking water causes dental and skeletal fluorosis [3,4] and decreases growth and intelligence [5]. Therefore, many techniques for the removal of fluoride ions from water have been developed to reduce the acuity of their damage to human health and the environmental risks that they induce.

The most commonly used methods for defluoridation of water can be divided into two main categories: precipitation and adsorption [1,6]. The precipitation of fluoride by calcium salts [7–9] and aluminum salts [10–12] has already been investigated. The residual concentration of fluoride ions in water is greater than 2 mg $L^{-1}$ when calcium salts are used [1,6]. On the other hand, Al(III) compounds have good combining affinity with fluoride and reduce the fluoride concentration down

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to 2 mg $L^{-1}$ [4]. However, the precipitation method leads to an increase of total dissolved solids in treated water, resulting in a supplementary difficulty in eliminating residual chemicals in excess [3,13]. Furthermore, a high concentration of aluminum in the treated water may create a danger to human health such as Alzheimer's disease [3,14]. Several adsorbents have been used for removal of fluoride from water such as amorphous alumina [15], low-cost adsorbent [16–18], metal oxides [19,20], activated carbon [21] and especially the activated alumina [22] which is very effective and selective. However, frequent regeneration with aluminum sulfate is needed because of its low adsorption capacity at neutral pH [13], which results in increased difficulty for operation. Moreover, alumina remains expensive for under developed countries and its optimal adsorption for fluoride in acidic pH range limits its use to treat drinking water [15]. Therefore, it is desirable to seek a low-cost adsorbent material which is effective for defluoridation at a pH value of around 7.

Due to its high electronegativity and small ionic size, the fluoride ion is classified as a hard base, which has a strong affinity towards metal ions including Al(III), Fe(III), La(III) [13]. Dispersing a mixture of these metals in a protective matrix would limit the total dissolved solids in treated water, and at the same time would provide high fluoride adsorption capacity. Porous carbons could be a good candidate such as matrix protective. Because of their excellent properties such as large surface area and continuous porosity, porous carbons are used as adsorbent or metal-support [23–26]. The carbon support provides high dispersion and inhibits sintering of metals within its pore structure. Generally, carbon-supported metals are prepared by impregnating carbon with the corresponding metal salt solutions followed by heat treatment. Preparation of adsorbents such as carbon-supported aluminum or iron is scarce in the literature [24,25]. The activated carbon and carbon nanotubes (CNTs) are often used as a source of carbon, which becomes quite expensive for an industrial production. However, there are very little studies on the use of wood instead of the activated carbon as the support or matrix [26], whereas wood is largely available, inexpensive and may lead to mesoporous activated carbons [27]. In this paper, we present a new approach of preparation of new adsorbents by impregnation of wood with aluminum and iron salts followed by a carbonization. The adsorption of fluoride ions by these charcoals that contain aluminum oxide adsorbents is assessed.

## 2. Experimental

### 2.1. Material preparation

Scandinavia spruce wood with a density of 0.37 was used for the preparation of charcoals. The modified carbons were prepared according to the following procedure. The wood samples of parallelepipedic form ($3.8 \times 3.3 \times 1.3$ cm) were dried beforehand in an oven at 105 °C for 24 h, and they were impregnated with a boiling mixture of 1 M $AlCl_3$ and 1 M $FeCl_3$ aqueous solution for 90 min. After the heating, the samples remained immersed in the aqueous solution for 2 h. The impregnated woods were removed from the solution, then dried in the open air for 2 h and finally dried in an oven at 105 °C for 24 h. These dried impregnated wood samples were placed in a steel dish in a muffle furnace and heated to 500 °C, 650 °C or 900 °C for 1 h. It was found advantageous to restrict the access of air during carbonization. The resulting samples were ground to the form of particles less than 200 μm and stored for further characterization. Samples of aluminum–iron dispersed in carbon are denoted AlFexxx/C where xxx refers to the carbonization temperature.

### 2.2. Characterization techniques

Scanning electron microscopy (SEM) images and energy dispersive analysis of X-rays (EDAX) were performed at the Center of Scanning Electron Microscopy of Rennes University on Jeol JSM 6400 equipment operating at an accelerating voltage of 20 kV.

X-ray powder diffraction (XRD) data were collected at room temperature with a Siemens diffractometer operating with the parafocusing Bragg–Brentano geometry, using Cu $K\alpha_{1,2}$ radiation ($\lambda$ = 1.5406/1.5444** Å) and equipped with a diffracted beam graphite monochromator to limit fluorescence due to the iron content in the samples. The diffraction patterns were collected at 40 kV and 30 mA, over the angular range 10–80° (2$\theta$) with a counting time of 14s $step^{-1}$ and a step length of 0.02° (2$\theta$).

The $pH_{PZC}$ was measured as follows: 100 mg of AlFexxx/C samples were contacted with 50 mL of 0.05 M $NaNO_3$ deaerated solution with a pH range of 3–11. Blanks with no carbon were also run in the same initial pH values. After shaking for 24 h at 250 rpm at room temperature, the final pH of the solution was measured and was plotted against the initial pH. The $pH_{PZC}$ was determined as the pH of $NaNO_3$ solution that did not change after the contact with the samples.

The concentration of total acidic and basic groups on AlFexxx/C surface was determined from NaOH and HCl uptake, respectively. 100 mg of AlFexxx/C samples were placed in 50 mL of 0.05 M NaOH or 0.05 M HCl. Sealed beakers that contained samples or blanks were shaken for 24 h and filtered. Then 10 mL of each filtrate were titrated with 0.05 M of either NaOH or HCl solution. The difference between the NaOH or HCl consumption by the blank and samples was calculated and translated to the equivalent acid or base content per gram of charcoal.

The chemical stability of the inorganic content of the charcoals was studied by measuring the release of Al and Fe in solution. The concentration of dissolved Al and Fe were measured with a spectrophotometer (Hach) using Aluver 3 and Ferover reagents for Al and Fe, respectively. The inorganic content of the charcoals was calculated from the ash weight after an exhaustive combustion of the charcoals in an oven at 650 °C for 24 h.

### 2.3. Fluoride adsorption experiments

A 1000 mg $L^{-1}$ $F^-$ stock solution was prepared by dissolved 1.1050 g of NaF (analytical grade) in 500 mL of deionized water. All the solutions for fluoride removal experiment and analysis were prepared by appropriate dilution from the stock solution. The defluoridation experiments were carried out by