



A novel metal coordination enabled in carboxylated alginic acid for effective fluoride removal



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ABSTRACT

This article enlightens the synthesis of carboxylated alginic acid (CAA) and metal ions coordinated CAA (M-CAA) for defluoridation studies in batch mode. The oxidation of alginic acid (AA) with KMnO_4 gives CAA and the metal coordination was enabled in CAA by using high valence metal ions viz., La^{3+} (La-CAA) and Zr^{4+} (Zr-CAA). The synthesized materials Zr-CAA, La-CAA and CAA possess the defluoridation capacities (DCs) of 4064, 3137 and 880 mgF^-/kg respectively. An enhanced DC was observed for metal-coordinated CAA (M-CAA) than CAA. The defluoridation experiments were carried with numerous influencing parameters like contact time, pH and competitor anions for optimization. The characterization of materials was carried out using FTIR, EDAX and SEM analysis. The sorption data was fitted with various isotherms and kinetic models. The values of thermodynamic parameters indicate the nature of fluoride removal is spontaneous and endothermic. At field conditions, M-CAA reduce the fluoride concentration below the tolerance limit.

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1. Introduction

The fluoride enters into the drinking water either by the dissolution of fluoride bearing minerals and/or anthropogenic activities. The amount of fluoride in drinking water leads to beneficial and detrimental effects on health. At lower concentration, it helps to strengthen the teeth and repair the damage caused by early tooth decay before it becomes permanent, but exposed to higher levels ($>1.5 \text{ mg/L}$ as per WHO) leads to fluorosis (WHO, 2006). Researchers developed numerous conventional treatment techniques to remove the excess fluoride from the water bodies namely chemical precipitation (Lu & Liu, 2010), reverse osmosis (Ndiaye, Moulin, Dominguez, Millet, & Charbit, 2005), electro-coagulation (Vasudevan, Lakshmi, & Sozhan, 2009), nanofiltration (Tahaik et al., 2007), ion exchange (Meenakshi & Viswanathan, 2007) and adsorption (Viswanathan & Meenakshi, 2010). In the last decade, adsorption is one of the most promising techniques for fluoride removal due to its ease of operation, uptake capacity, cost-effective and no sludge generation.

Biosorption is the one of the environmentally sound techniques which minimize the operation cost and make the adsorption technology more feasible and eco-friendly. In this scenario, scientists have paid increased attention on the development of bioadsor-

bents using chitin, chitosan, alginate, cellulose, etc., for the removal of toxic ions from the aqueous solution (Googerchian, Moheb, & Emadi, 2012; Jayakumar et al., 2009; Pandi & Viswanathan, 2014; Sairam Sundaram, Viswanathan, & Meenakshi, 2009; Varma, Deshpande, & Kennedy, 2004; Viswanathan & Meenakshi, 2009a; Yu, Tong, Ge, & Zuo, 2013). Among them, alginic acid has been regarded as a fabulous biopolymer because of its unique characteristics such as biodegradability, biocompatibility and non-toxicity. In addition, the reactive carboxyl and hydroxyl functional groups are the attractive features of AA. The functionalization of adsorbent material will increase its selectivity toward a particular ion. In order to effectively utilize the hydroxyl groups in the alginic acid, an oxidation reaction was carried out using KMnO_4 , which converts the hydroxyl groups of AA into carboxyl groups namely carboxylated alginic acid (Jeon, Park, & Yoo, 2002). Recently higher valence metal ions incorporated materials are focused to develop new adsorbents with good performance for the selective removal of fluoride (Paudyal et al., 2013; Viswanathan & Meenakshi, 2008, 2009b). Hence, the higher valence metal ions viz., La^{3+} and Zr^{4+} ions have been utilized for enabling metal coordination with CAA which helps to increase its strength and uptake capacity.

The ultimate aim of the present work is to develop low cost, eco-friendly, functionalized and metal coordinated biomaterials for fluoride removal. Based on the above aspiration, the authors have synthesized carboxylated alginic acid and metal coordinated carboxylated alginic acid for defluoridation studies. A comparative evaluation of CAA and M-CAA was also made. The sorption studies

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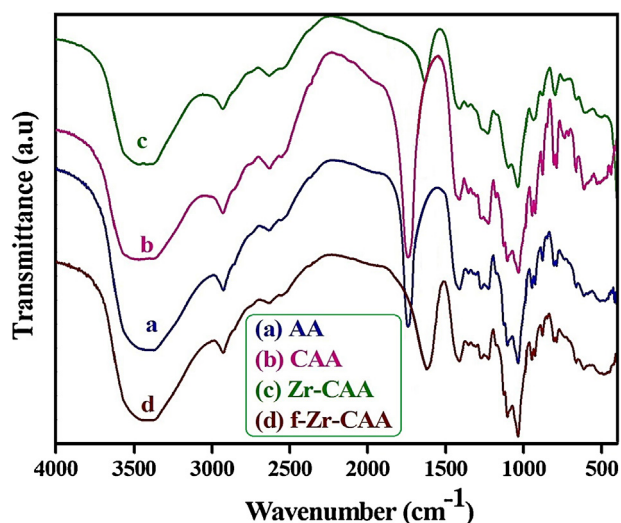


Fig. 1. FTIR spectra of (a) AA, (b) CAA, (c) Zr-CAA and (d) fluoride sorbed Zr-CAA (f-Zr-CAA).

were carried out to optimize various equilibrating conditions like contact time, pH, presence of competitor anions, different initial fluoride concentrations and temperature. Adsorption data have been fitted to various isotherms and kinetic models. The thermodynamic parameters viz., ΔG° , ΔH° and ΔS° have also been calculated and interpreted. The application of the biosorbents at field conditions was also tested by collecting the field fluoride water sample in a nearby fluoride widespread area.

2. Materials and methods

2.1. Materials

Alginic acid used in the work was purchased from Central Drug House (India). KMnO_4 , $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and other chemicals used in the work were of analytical grade and used without further purification. Double distilled water was used to prepare the standard solutions.

2.2. Synthesis of CAA and M-CAA

The carboxylated alginic acid (CAA) was prepared as suggested by Jeon et al. (2002). Briefly, 10 g of alginic acid was added into the 10 mM of KMnO_4 solution and stirred for 30 min at 30 °C. Then the reacted mixture was separated by centrifugation and thoroughly washed with distilled water and then dried at 60 °C for 2 h in hot air oven. The synthesis of metal coordinated carboxylated alginic acid (M-CAA) as follows. About 0.1 mol of La(III) and Zr(IV) solution were prepared separately by dissolving appropriate amount of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 100 mL of distilled water respectively. About 2 g of synthesized CAA was added into the respective metal ion solutions and the mixture was gently stirred for 24 h at room temperature. Finally the mixture was filtered and thoroughly washed with distilled water and then dried at 60 °C for 6 h in hot air oven. The dried sorbents was grinded to fine powder using ball mill (IKA, Germany) and then used for fluoride sorption studies.

2.3. Fluoride sorption experiments

The synthesized materials were utilized as sorbents for the removal of fluoride from the aqueous solution by the batch equilibration method in duplicate. Experiments were conducted by adding 0.1 g of dry sorbent into 50 mL of 10 mg/L sodium fluoride

solution at room temperature. The influence of pH on fluoride sorption by the sorbents was studied by varying the pH of the solution in the range of 3–11 using 0.1 M HCl/NaOH solution. The mixture was shaken in an orbital shaker rotating with a speed of 200 rpm at room temperature. Samples were taken at prefixed time intervals for the analysis of fluoride concentrations in the solutions until sorption equilibrium was reached. Thermodynamic studies were carried out using waterbath shaker with different initial fluoride concentrations, viz., 8, 10, 12 and 14 mg/L in the temperature range of 303, 313 and 323 K. After equilibrating time, the samples were filtered and the final fluoride concentration was determined.

2.4. Analysis

The fluoride concentration was measured using Thermo Orion Benchtop multiparameter kit (VERSA STAR 92) with the fluoride ion selective electrode (Thermo Orion, USA). The pH measurements were made with the same instrument using pH electrode. All other water quality parameters were investigated using standard methods (APHA, 2005). The pH at zero point charge (pH_{zpc}) of the sorbent was determined by pH drift method (Lopez-Ramon, Stoeckli, Moreno-Castilla, & Carrasco-Marin, 1999).

2.5. Characterization techniques

Fourier transform infrared (FTIR) spectra of the materials were carried out using JASCO-460 plus spectrophotometer operated at 1 cm^{-1} resolution in 400–4000 cm^{-1} region using KBr pellets. The surface morphology of the sorbent was imagining by scanning electron microscopy (SEM) with Vega3 Tescan model. SEM images helps to predict the microstructures of the fresh and fluoride treated materials. The qualitative detection and localization of elements present in the materials was identified by energy dispersive X-ray (EDAX-Bruker Nano GMBH, Germany) analyzer.

2.6. Statistical tools

The Microcal Origin (Version 8.0) software was used for the data computation. The regression correlation coefficient (r), standard deviation (sd) and chi-square analysis (χ^2) helps in the prediction of best fit isotherm model.

3. Results and discussion

3.1. Characterization of the sorbents

3.1.1. FTIR analysis

An FTIR spectrum is an essential tool to identify the functional groups present in the adsorbents. Figs. 1a and b represent the FTIR spectra of AA and CAA respectively. A sharp band at 1742 cm^{-1} confirms the presence of carbonyl group in both AA and CAA. In Fig. 1b, the band in the region of 3000–3600 cm^{-1} was quietly narrowed, indicates that the hydroxyl groups in AA were oxidized into carboxylic acid group (Jeon et al., 2002). In Fig. 1c, the C=O stretching vibration was disappeared at 1745 cm^{-1} in Zr-CAA and the band in the region of 3000–3600 cm^{-1} was again narrowed due to –OH stretching of carboxylic acid which indicates the H^+ ions of carboxylic acid are replaced by metal ions. A new band was also observed at around 1605–1652 cm^{-1} for Zr-CAA sorbent, indicating the presence of metal alginate bonds in Zr-CAA (Paudyal et al., 2013). In fluoride sorbed Zr-CAA, the shifting and broadening of bands at 3425 and 1652 cm^{-1} to lower frequencies (cf. Fig. 1d) owing to the electrostatic adsorption between the fluoride and the sorbent (Smith, 1998; Zhou, Zhang, & Guo, 2005). Similar reports were obtained for La-CAA and fluoride sorbed La-CAA material.

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