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A novel ultrasonication method in the preparation of zirconium impregnated cellulose for effective fluoride adsorption

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ABSTRACT

In the present work, we propose for the first time a novel ultrasound assisted methodology involving the impregnation of zirconium in a cellulose matrix. Fluoride from aqueous solution interacts with the cellulose hydroxyl groups and the cationic zirconium hydroxide. Ultrasonication ensures a green and quick alternative to the conventional time intensive method of preparation. The effectiveness of this process was confirmed by comprehensive characterization of zirconium impregnated cellulose (ZrIC) adsorbent using Fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray spectrometry (EDX) and X-ray diffraction (XRD) studies. The study of various adsorption isotherm models, kinetics and thermodynamics of the interaction validated the method.

1. Introduction

The presence of excess fluoride and its consequences require effective remediation methods. The chemical weathering of fluoride containing minerals is one reason for leaching of fluoride into the ground water [1]. Essentially, in India, Andhra Pradesh and Rajasthan are the states where fluoride contamination in the ground water is above the permissible limit. The level of fluoride in drinking water should be between 1.0 and 1.5 mg L^{-1} [2]. There is a need to develop effective adsorbents to bring the fluoride level to this limit and a range of adsorbents have been reviewed for defluoridation [3,4]. The well-known Nalgonda technique [5] which involves the use of lime and alum for fluoride adsorption has been in vogue, nevertheless there are some drawbacks associated with this process. The leaching of excess aluminum with increase in ground water pH is a major concern. Activated alumina [6], alumina impregnated carbon [7], dispersed alumina in charcoal [8] and alumina–chitosan composite [9] are some of the alumina based sorbents used for defluoridation. Magnesia–chitosan composite [10], protonated chitosan beads [11], waste phosphogypsum [12] and kaolinite [13] are some of the other effective adsorbents that have been explored. In view of the small size and high electronegativity of fluoride, it has good tendency interact effectively with rare earth metals such as zirconium and lanthanum. Alginate entrapped Fe(III)–Zr(IV) [14] Zr(IV)–ethylene diamine [15], zirconium impregnated activated charcoal [16] and zirconium impregnated collagen [17], Zr(IV)–metalloporphyrin Fe_3O_4 [18] are some of the zirconium based sorbents reported for adsorption of fluoride.

Since, fluoride ion has strong affinity towards multivalent metal ions including Al(III) and Zr(IV) metal ions [19] biodegradable polymers such as cellulose can be explored as an effective host matrix. Potentiometric sensor for fluoride based on the interaction with zirconium and cellulose has been reported [20]. Zr(IV) phosphate-cellulose acetate nano composite is known for its photocatalytic activity [21]. The objective of the present work is to develop a ultrasound assisted preparation method for Zr impregnated cellulose biopolymer adsorbent thereby leading to its application for the adsorption of fluoride. The high pressure and acoustic cavitation leading to the collapse and formation of the bubbles [22] during ultrasonication ensures a quick, green and effective method in the preparation of the adsorbent compared to the conventional method of mixing-stirring for several hours. The shear forces associated with the acoustic cavitation [23] leads to an increase in surface area and ensures homogenous dispersion of the zirconium oxychloride in the biopolymer through methanol medium. To the best of our knowledge, this is the first report on the use of ultrasonication in the preparation of Zr-impregnated cellulose sorbent for the adsorption of fluoride. The efforts leading to the application of this adsorbent material and the optimization of the experimental parameters are discussed in the following sections.

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2. Experimental

2.1. Chemicals and reagents

Analytical grade reagents and Milli pore water (Elix 3 Millipore unit) was used in preparation of the standard solution of fluoride. A 1000 mg L^{-1} stock solution of fluoride was prepared using sodium fluoride (SD Fine Chemicals, India) and stored in a polyethylene bottle. Working fluoride solutions for the batch adsorption studies were prepared by appropriate dilution. Cellulose was procured from Himedia, India. Zirconium oxychloride and the solvent methanol used in the study were procured from SD Fine Chemicals, India.

2.2. Instrumentation

A probe sonicator (36″ × 16″ × 31″, Frontline, India model no FS-500) which uses ultrasonic (23 ± 3 kHz) signal in producing mechanical vibrations at tip of the probe was used in the preparation of the adsorbent. Stainless steel tips of diameter 6 mm was utilized for sonication and the sonicator was housed in a sound abating chamber. The pH of the aqueous medium was adjusted using appropriate amount of HCl/NaOH using an Li-127 pH meter (Elico, India). Orbital incubator shaker (Biotechnics, India) was used for equilibrating the adsorbent with various concentrations of fluoride. The FT-IR spectra for the ZrIC adsorbent was obtained using a Jasco-4200 FT-IR spectrometer by mixing 0.01 g of the sorbent with KBr in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1}.The XRD spectra of the Zr impregnated cellulose adsorbent was obtained using a Panalytical X-ray spectrometer at a scan rate of 0.5 min^{-1} with CuKα radiation (1.54 Å) and a secondary beam graphite monochromator. The EDX spectrum of the adsorbent was obtained using a JEOL model (JED-2300) analyzer. The particle size of the adsorbent was measured by DLS method using a Malvern nano-ZS particle size analyzer in the range 0.3 nm to 5 μm.

2.3. Fluoride ion measurement

The concentration of fluoride was monitored using ion selective meter (Model No.98185 Hanna Instruments, USA) and a fluoride ion selective electrode (Model No. HI 4110, Hanna Instruments, USA). The ionic strength was adjusted using TISAB II buffer solutions (pH 5.0–5.5) before measuring the fluoride concentration. The fluoride ion selective electrode was calibrated using 1–100 mg L of standard fluoride solutions to get a maximum slope between 90% and 110%.

2.4. Preparation of Zr impregnated cellulose adsorbent (ZrIC)

The ZrIC biopolymer was prepared with cellulose as the starting material using ultrasonication. The cellulose biopolymer was washed with warm water, dried in an oven at 50 °C and 4.0 g of the biopolymer was dispersed in 30 mL methanol. 2.0 g of zirconium oxychloride was added cautiously to the cellulose solution. The mixture was sonicated for 20 min with a 5 min intermittent time interval and to ensure the completeness of the impregnation, the contents were stirred magnetically for an additional 10 min time duration. The mixture was centrifuged and the and solid adsorbent was filtered using Whatman 42 filter paper and then dried for 2 h at 50 °C. The prepared ZrIC adsorbent was used for further adsorption studies.

2.5. Batch adsorption study

Batch adsorption study was performed by equilibrating 0.5 g of the ZrIC adsorbent material with 50 mL of 5 mg L^{-1} fluoride solution at pH 5.0 for different time intervals fluoride concentration left in the aqueous solution was measured using the fluoride ion selective electrode. The amount of fluoride adsorbed (mg g^{-1}) at equilibrium (q_e) is obtained from the corresponding difference between the initial (C_o) and equilibrium fluoride (C_e) concentrations as

$$q_e = \frac{(C_o - C_e)V}{W}. \quad (1)$$

In the above expression, V is the volume of aqueous solution (L) and W is the weight of the Zr impregnated cellulose adsorbent (g) used for adsorption.

3. Results and discussion

3.1. Characterization

The FT-IR spectrum (Fig. 1) of ZrIC adsorbent shows characteristic peaks corresponding to the O–H, C–H and C–O–C pyranose ring around 3330, 900 and 2901 cm^{-1}, respectively [24,25]. In addition, a peak at 514 cm^{-1} [26] due to stretching vibrations of Zr–O suggests that zirconium atoms are present on the surface of the cellulose biopolymer surface. The peaks characteristic of ZrIC were observed at 841 cm^{-1} (Zr–O–C vibration) and 1710 cm^{-1}(due to partial oxidation of cellulose), respectively [27,28]. The sharpness in the O–H peak intensity after adsorption shows the interaction of zirconium as $Zr(OH)_2^{2+}$ with the surface hydroxyl groups of cellulose. Significant changes occur after the adsorption of fluoride ion with the appearance of deformation peak at 514 cm^{-1} and the peak intensity increased in the range 500–900 cm^{-1} attributed to the adsorption of fluoride on the adsorbent surface.

The EDX spectrum (Fig. 2) confirms the presence of Zr and F elemental peaks on the surface of the cellulose biopolymer and this indicates that zirconium and fluoride are effectively anchored onto the cellulose matrix.

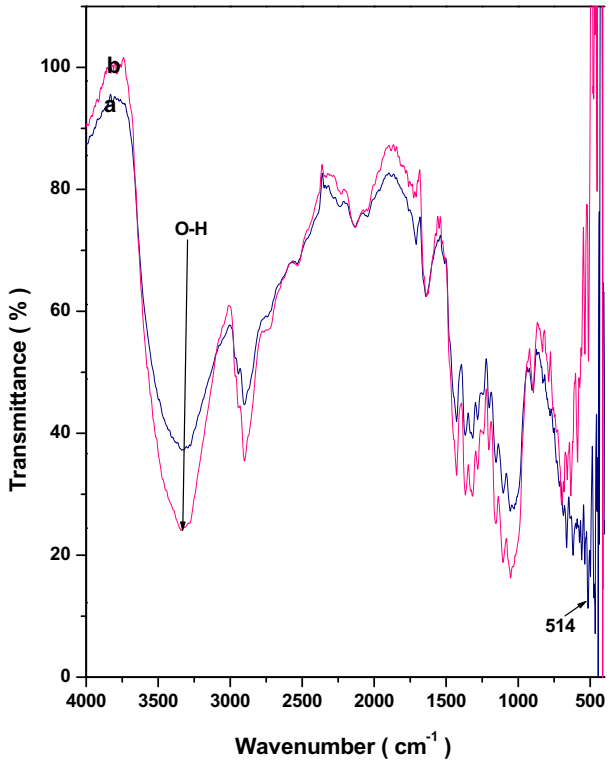

Fig. 1. FT-IR spectrum of Zr impregnated cellulose adsorbent (a) and the fluoride adsorbed (b).