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A simple one-pot *in-situ* method for the synthesis of aluminum and lanthanum binary oxyhydroxides in chitosan template towards defluoridation of water

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HIGHLIGHTS

- CS@ALMOH was prepared by simple one-pot *in-situ* method, an eco-friendly approach.
- The prepared material was found to be selective for fluoride removal.
- Maximum DC was observed at 15 min contact time.
- The maximum DC was observed for a wide pH range of 3–9.
- The fluoride removal was by both electrostatic interaction and ion exchange mechanism.

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ABSTRACT

Aluminum and lanthanum binary oxyhydroxides on chitosan template (CS@ALMOH) was synthesized by greener *in-situ* one-pot method for defluoridation of drinking water. Characterization by FTIR, XPS, TGA/DSC and SEM with EDAX revealed that the material was a composite of chitosan and aluminum–lanthanum with primary particle size of micrometer level. The prepared material shows relatively fast adsorption kinetics to fluoride removal within 15 min, good adsorption capacity with wide pH ranges of 3–9 and selectivity. The mechanism of fluoride removal using the synthesized materials were by both electrostatic interaction as well as ion-exchange. Equilibrium sorption results were well described by Freundlich, Langmuir and D–R isotherms and the sorption capacities were approximately 49.54 mg/g for CS@ALMOH and 33.39 mg/g for ALMOH. The sorption process follows pseudo-second-order and intra-particle diffusion kinetic models. This bifunctional adsorbent with aluminum and lanthanum oxyhydroxides impregnated onto chitosan polymeric matrix exhibits a pronounced fluoride adsorption capacity over already reported materials in the literature and the resulting CS@ALMOH material can be used in a broad pH range, which suggests its great potential for the decontamination of fluoride polluted water. The suitability of the CS@ALMOH material has been tested with the field samples collected in a nearby fluoride endemic area.

1. Introduction

Fluorine is one of the few elements that can cause health problems by both its deficiency and excess intake. Low fluorine intake can cause dental carries, while high intake rate may lead to dental or skeletal fluorosis [1]. Unfortunately, dental or skeletal fluorosis effects have been irreversible, leaving prevention as the only cure. The World Health Organization (WHO) established a maximum limit of 1.5 mg/L for fluorides in drinking water [2]. The limit must be lowered to 1 mg/L for fluorides in areas with a warm climate due to higher water consumption [3]. The US Environmental Protection Agency (USEPA) has set the primary standard (enforceable limit) as 4 mg/L for fluoride in drinking water [4]. It is estimated (not accurately) that more than 200 million people consume water with fluoride content higher than the established WHO guidelines. Adsorption method is widely used for defluoridation, which depends on ions in fluid diffusing to the surface of a solid, where they bond with the solid surface or held there by weak intermolecular forces.

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Chitosan contains number of amine and hydroxyl functional groups on the backbone, and can be facilely modified through grafting copolymerization and compounding with many involving sorbents to derive new forms of materials. A number of studies were reported for the removal of fluoride using biopolymer based sorbents, lanthanum entrapped chitosan composite [5], zirconium encapsulated chitosan matrix [6], lanthanum–zirconium chitosan composite [7], hydrous ferric oxide doped alginate beads [8], Fe (III)–Zr(IV) binary oxide loaded calcium alginate beads [9], aluminum loaded alginate beads [10], metal loaded carboxylated alginate acid [11], etc. Similarly, aluminum and lanthanum modified adsorbents showed higher defluoridation capacity due to their high selectivity and chemical affinity towards fluoride than the respective bare alumina and lanthanum. For example, Lee et al. [12] reported that the mesoporous alumina has the maximum fluoride adsorption capacity of 14.26 mg/g. Recently, Saha et al. [13] examined aluminum oxyhydroxide synthesized in chitosan template which has the defluoridation capacity (DC) of 13.47 mg/g. Graphene–aluminum oxyhydroxide interaction and its fluoride uptake studies was clearly explained by Bharathi et al. [14]. The aluminum and lanthanum supported biopolymer composites also possessed higher DC because of their synergistic effect of both the biopolymer and aluminum/lanthanum which could easily form a complex with polymer. Efforts toward the development of new chitosan supported material for faster adsorption of fluoride have been mostly concerned with the presence of plenty of amine groups, because nitrogen possesses a strong affinity for metal and form a complex. From our careful literature survey, there is no study regarding *in-situ* synthesis of aluminum and lanthanum mixed oxyhydroxide in oxygen rich chitosan template for fluoride removal.

Hence, the present investigation was to evaluate the synthesis of aluminum and lanthanum mixed oxyhydroxides (ALMOH) by greener method and further these oxyhydroxide materials was developed onto chitosan biopolymer as oxygen rich template by *in-situ* method for the removal of fluoride from aqueous solution. The synthesized biopolymeric composite, chitosan@aluminum–lanthanum oxyhydroxides (CS@ALMOH) was characterized using various microscopic and spectroscopic techniques to obtain the nature of the material. Furthermore, the various operating parameters were optimized such as stirring time, result of pH studies, outcome of foreign ions and temperature. The mechanistic way of fluoride removal using the synthesized CS@ALMOH was established with the help of various spectro-analytical techniques.

2. Materials and methods

2.1. Materials

Chitosan was purchased from Pelican Biotech, Kerala, India, ammonia, acetic acid, aluminum nitrate and lanthanum nitrate were purchased from Central Drug House (CDH), New Delhi and all other chemicals and reagents used were of analytical grade. All the solutions were prepared using double distilled water.

2.2. Synthesis of ALMOH and CS@ALMOH composite

The mixed oxides of ALMOH composite adsorbent for fluoride removal were successfully prepared through the co-precipitation method [7,13] by mixing 50 mL of 1 M solution of aluminum nitrate and 50 ml of lanthanum nitrate and stirred for 20 min. Aqueous ammonia (5 M) was added slowly into the aluminum–lanthanum mixed binary solution to facilitate the precipitation of AlOOH–LaOOH mixed oxyhydroxide composite. The precipitate was filtered and washed with plenty of water to remove impurities, and dried at 60 °C in an oven. The dried material was used for the further experiments. The chitosan supported mixed oxyhydroxides composites were synthesized as follows: 1% of chitosan (CS) was dissolved in 2% acetic acid solution and 50 ml of 1 M aluminum nitrate and 50 ml of 1 M lanthanum nitrate solution were added and stirred for 40 min to set homogeneous solution. 5 M aqueous ammonia was slowly added to above solution to form a mixed oxyhydroxide solution at chitosan template. The precipitate was filtered using filter paper and washed with water to remove any impurities present in the composite. The composite material was dried in an oven for about 60 °C for 6 h and the dried material was ground to powder and used for further studies.

2.3. Sorption experiments

In a typical case, a known amount of the sorbent was added to 50 mL of NaF solution with an initial concentration of 50 mg/L. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm and the filtrate was analyzed for fluoride. The influence of various parameters like contact time, pH and the presence of other anions on DC of the sorbents was investigated by varying one parameter at a time and keeping the remaining parameters as constant. For the temperature studies, the effect of initial fluoride concentrations viz., 8, 10, 12 and 14 mg/L at 303, 313 and 323 K on sorption rate was studied by keeping the mass of the sorbent and volume of solution as 50 mL at neutral pH. The solution was then filtered and the residual fluoride ion concentration was measured.

2.4. Analysis

Expandable ion analyzer EA 940 (Orion, USA) with ion selective fluoride electrode BN 9609 (Orion, USA) was used for the quantitative analysis of fluoride [15]. The pH measurements were done with the same instrument with pH electrode. All other water quality parameters were analyzed by using standard methods [16]. FTIR spectra were recorded on a JASCO-460 FT-IR spectrometer in KBr background. The scanning electron microscope (SEM) images were taken using the Vega3Tescan model and elemental spectra of the sorbents were obtained using an energy dispersive X-ray analyzer (EDAX) and were taken during SEM observations which allow qualitative detection and localization of elements present in the material. The XPS measurements were performed with XPS instrument (Carl Zeiss) equipped with Ultra 55 FESEM with EDS. All the spectra were acquired at a pressure using ultra high vacuum with Al Kα excitation at 250 W. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using an Universal V4.5A TA instruments to monitor characteristic physical and chemical changes in biopolymers.

2.5. Adsorption isotherms

The DCs of synthesized materials were calculated according to the equation:

$$q_e = \frac{(C_0 - C_e)}{m} \times v \quad (1)$$

where q_e is the equilibrium adsorption capacity, C_0 and C_e (mg/L) is the initial and equilibrium concentration of adsorbate solution, v is the volume of adsorbate solution (L) and m is the mass of adsorbent (g).

To quantify the performance of synthesized biosorbents, three isotherm models have been widely used namely Freundlich [17], Langmuir [18] and D–R isotherm [19]:

(i) Freundlich isotherm model

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (2)$$