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# Enriched fluoride sorption using chitosan supported mixed metal oxides beads: Synthesis, characterization and mechanism

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ABSTRACT

Adsorbents, lanthanum (III)–zirconium (IV) mixed oxide (LZMO) and chitosan supported lanthanum (III) and zirconium (IV) mixed oxides beads (CLZMOB), were prepared. The prepared sorbents were characterized using FTIR, SEM with EDAX, XRD and TGA–DSC studies. Sorption studies were performed at different temperatures, equilibrium time, pH values and in the presence of foreign ions in batch mode. Maximum fluoride adsorption occurred at pH 7 for both LZMO and CLZMOB. The kinetic study revealed an optimum equilibrium time as 50 min with an adsorbent dose of 100 mg/L at room temperature. The sorption data were fitted well with Langmuir isotherm. Thermodynamic parameters such as $\Delta G^{\circ}$, $\Delta H^{\circ}$, and $\Delta S^{\circ}$ indicated that the nature of fluoride sorption is spontaneous and endothermic. The column experiment with CLZMOB at neutral pH was successfully employed for the removal of fluoride ions from synthetic fluoride water. 0.1 M NaOH was used for desorption studies and the regeneration ability was tested. Based on the column experiment, a defluoridation model has been illustrated. The results showed that CLZMOB could be an effective sorbent for the removal of fluoride from aqueous solutions.



## 1. Introduction

Fluorosis is a slow, progressive and a crippling malady caused by excess intake of fluoride which affects every organ, tissue and cell in the body and results in health complaints having overlapping manifestations with several other diseases. The primary adverse effects associated with chronic, excess fluoride intake are dental and skeletal fluorosis [1]. Several previous studies concluded that the usage of the high fluoride content of water for food processing significantly elevates the amount of daily fluoride intake through food. Thus the water used for food processing is an essential contributing factor for daily fluoride intake [2,3]. Latest estimates suggest that about 200 million people are under the dreadful fate of fluorosis [4]. There is no treatment for fluorosis, but it can be easily prevented. One such preventive measure is defluoridation of water. According to World Health Organization (WHO) norms, the upper limit of fluoride concentration in drinking water is 1.5 mg/L [5]. Adsorption is characterized as one of the most effective methods due to its simple operation, high treatment efficiency and economy, despite the availability of various traditional technologies, such as membrane [6], precipitation [7], ion-exchange [8] and electrochemical methods [9].

Hybrid materials have attracted much interest in the last few decades, because of their extensive potential applications in various fields of material science ranging from paints, magnetic fluids and high-quality paper coating to microelectronics and biotechnology. Preparation of hybrid material is an economical way for the removal of fluoride with high adsorption capacity [10–14]. Mixed oxides may be the natural key material in scavenging fluoride from the fluoride-rich percolated water. A few oxides/mixed oxides have been successfully used for the removal of fluoride, which includes lanthanum oxides [15], hydrous zirconium oxides [16], zirconium-iron oxide [17], Fe–Ce oxide [18], Fe–Ti nano adsorbent [7], etc. The main advantages of these rare earth elements are their non-leaching nature as they have higher valence. When compared to their efficiency the cost of the material is very less. To the best of our knowledge, this is the first report on the synthesis of lanthanum–zirconium mixed oxides (LZMO) as adsorbent for the adsorption of fluoride from aqueous solution.

Chitosan, a copolymer, is harmless to humans and presents excellent biological properties such as biodegradation in the human body, immunological, antibacterial, and wound-healing activity [19,20]. Chitosan is a well known excellent biosorbent for metal removal in near-neutral solutions because of the presence of a large number of high chemical reactive amine groups, hydroxyl groups of glucose units and the flexible structure of the polymer chain. Viswanathan and Meenakshi [21–23] reported the defluoridation efficiency of lanthanum and zirconium loaded chitosan

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beads and resins. Hence, it was aimed to prepare, chitosan supported lanthanum (III)–zirconium (IV) mixed oxide beads (CLZMOB), an organic–inorganic hybrid sorbent and to study its fluoride removal efficiency in order to exploit the advantage of a synergistic effect.

The primary purpose of the present study is to investigate the mechanism of fluoride sorption onto the surface structures of metal oxides–biopolymer beads obtained by employing both batch and column methods. The development of new adsorbents for selective separation of low-concentration fluoride from aqueous solutions is of great significance. The performance of adsorptive materials is characterized by adsorption speed, adsorption capacity and its selectivity. A comparative evaluation of adsorption capacity of LZMO and CLZMOB was also made and discussed. Various influencing parameters viz., contact time, solution pH, the presence of co-ions and temperature studies on defluoridation capacities (DC) were optimized. The equilibrium sorption data were fitted with various isotherms to find the best fit model for the sorption system.

## 2. Materials and methods

### 2.1. Materials

Chitosan (85% deacetylated) was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). The viscosity of the chitosan solution was determined as 700 (mPa s) by Brookfield Dial Reading Viscometer using electronic drive-RVT model (USA made). The chitosan solution was maintained at a constant viscosity for bead preparation to maintain uniform molecular weight. NaF, NaOH, HCl, $LaCl_3{\cdot}7H_2O$ and $ZrOCl_2{\cdot}8H_2O$ 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 LZMO

The mixed oxides of La–Zr adsorbent for fluoride removal were successfully prepared through the co-precipitation method [14]. A mixture of 0.1 M lanthanum chloride and 0.1 M zirconiumoxychloride solutions were added in 0.01 M HCl in a round bottom flask. Then, the solution was warmed at 80 °C, and hydrolyzed by drop wise addition of 0.1 M NaOH solution. A pure white color gel-like precipitate was formed. The hot flask was cooled to room temperature for 4 h for the white color precipitate to settle down. The precipitate was filtered and washed with plenty of water to remove chloride, and dried at 50 °C in an oven. The dried material was used for the experiments.

### 2.3. Synthesis of CLZMOB

2 g of chitosan was dissolved in (2%, v/v) aqueous solution of acetic acid and stirred for 1 h. About 100 mg of dried LZMO was added into the clear chitosan solution. This solution was mixed well using a stirrer for 2 h. Then, chitosan with mixed oxide solution was dropped into a 0.5 M aqueous NaOH solution to form uniform chitosan beads. After gelling for a minimum of 16 h in 0.5 M NaOH solution, the beads were washed with distilled water to a neutral pH. The wet beads were dried at room temperature to a constant weight and used for further experiments.

### 2.4. Sorption experiments

The equilibrium parameters viz., time, pH, co-ions and temperature studies were optimized by batch equilibration method. In a typical case, 100 mg of the sorbent was added to 50 mL of NaF solution of initial concentration 10 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 were investigated by varying one parameter at a time and keeping the remaining other 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 sorbent as 100 mg and volume of solution as 50 mL at neutral pH. The solution was then filtered and the residual fluoride ion concentration was measured.

### 2.5. 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. The pH measurements were done with the same instrument with pH electrode. All other water quality parameters were analyzed by using standard methods [24]. FTIR spectra were recorded on a JASCO-460 FT-IR spectrometer as KBr pellets. The scanning electron microscope (SEM) images were taken using Vega3 Tescan model and elemental spectra were obtained using an energy dispersive X-ray analyzer (EDAX) spectrum and were taken during SEM observations which allow qualitative detection and localization of elements present in the LZMO and CLZMOB by Bruker Nano GMBH, Germany. X-ray diffraction (XRD) measurements were obtained using X'per PRO model-PANalytical to determine the crystalline phases present in sorbents. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a SDT Q600 V20.9 Build 20 model to monitor characteristic physical and chemical changes in biopolymers.

### 2.6. Sorption isotherms

Two commonly used isotherms namely Freundlich [25] and Langmuir [26] have been adopted to quantify the defluoridation capacity of LZMO and CLZMOB.

The linear form of Freundlich isotherm is represented by the following equation

$$\log q_e = \log k_F + 1/n \log C_e \quad (1)$$

where $q_e$ is the amount of fluoride adsorbed per unit weight of the sorbent (mg/g), $C_e$ is the equilibrium concentration of fluoride in solution (mg/L), $k_F$ is a measure of adsorption capacity and $1/n$ is the adsorption intensity. The linear plot of $\log q_e$ vs. $\log C_e$ indicates the applicability of Freundlich isotherm. The values of $1/n$ are lying between 0 and 1 and the n value lying in the range of 1–10 confirms the conditions favorable for adsorption.

Langmuir isotherm model can be represented in the form of an equation

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (2)$$

where $q_e$ is the amount of fluoride adsorbed per unit weight of the sorbent (mg/g), $C_e$ is the equilibrium concentration of fluoride in solution (mg/L), $Q^0$ is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent and $b$ (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption. The Langmuir constants $Q^0$ and $b$ were calculated from the slope and intercept of plot $C_e/q_e$ vs. $C_e$ respectively. The higher $r$ values indicate the applicability of Langmuir isotherm. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant