



# Synthesis of metal ion entrapped silica gel/chitosan biocomposite for defluoridation studies



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## ABSTRACT

This article focused on the development of silica gel/chitosan (SGCS) composite for fluoride removal. To enhance the fluoride selectivity of biocomposite, lanthanum-III (La) was incorporated into SGCS composite namely LaSGCS composite. A comparative evaluation of defluoridation capacity (DC) of LaSGCS composite, SGCS composite, silica gel (SG) and chitosan (CS) was made in batch mode. The results showed that LaSGCS composite possesses an enhanced DC of 4900 mg F<sup>-</sup>/kg whereas SGCS composite, SG and CS possess the DCs of 1556, 1296 and 52 mg F<sup>-</sup>/kg, respectively. The various equilibrium parameters, viz., contact time, pH, co-anions, different initial fluoride concentrations and temperature were optimized. The experimental data were analysed using various isotherms and kinetic models. The thermodynamic parameters have been calculated to find the nature of fluoride sorption. The mechanism of fluoride sorption by LaSGCS composite has been proposed. The sorbents were characterized using FTIR, XRD, TGA and SEM with EDAX analysis. A comparison of the DCs of the reported sorbents with that of LaSGCS composite has been made. Suitability of the fabricated biocomposite at field conditions was tested with a field sample taken from a nearby fluoride rife village. The present work provides a budding platform for the development of defluoridation technology.

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## 1. Introduction

Fluorine is the thirteenth most abundant element found in the earth's crust. Fluorine forms stable compounds namely fluorides with other elements. Fluorides are released into the environment due to natural and anthropogenic activities [1]. The presence of fluoride in water can be beneficial or harmful depending on its concentration and total amount ingested. The lower concentration of fluoride in water (<1 mg/L) are useful in preventing tooth decay but higher intake of fluoride leads to an incurable chronic disease namely 'fluorosis'. Fluorosis is a global health problem. Drinking water is the major source of fluoride intake. So, the WHO has specified the tolerance limit for fluoride content in drinking water is 1.5 mg/L [2]. Hence, it is an imperative task to supply water with safe fluoride levels. One of the best options is defluoridation of drinking water.

Established technologies, viz., adsorption [3], ion-exchange [4], precipitation [5], reverse osmosis [6], nanofiltration [7],

electro-coagulation [8,9] and Donnan dialysis [10] have been investigated to reduce fluoride concentration in water. The development of the technology will minimize the pollution towards the sustainable development [11,12]. Adsorption is an effective, eco-friendly and economical technique. A wide variety of materials from natural minerals to synthetic ones have been used as adsorbents to remove excess fluoride content in water namely polymeric resins [3], activated alumina [13], carbon nanotubes [14], chitosan beads [15], polymeric composites [16], double layer hydroxides [17], clay composites [18], hydroxyapatite [19], hybrid ion exchangers [20], etc.

In order to increase the selectivity of adsorption towards particular ion, adsorbents with suitable functional groups and other chemical modifications play the vital role in the adsorption performance. Adsorbent materials carrying thiol or amine functional groups have been shown for their prospective applications [21,22]. In particular, adsorbents with nitrogen-containing functional groups have been widely explored in the adsorption of toxic ions [23–25]. Research concentration has also been paid to development of functional adsorbents for the selective removal of toxic ions [3,26,27]. Nowadays the use of adsorbents containing biopolymers has received great attention because of their biofunctionality, biodegradability and biocompatibility. Chitin and chitosan have

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been extensively used in heavy metal [28–30] and fluoride removal studies [15,16,18,31].

Silica gel powder when it is used as such will cause pressure drop during field applications. To overcome such technological bottlenecks, polymeric composites were prepared by dispersing silica gel onto polymeric matrix. Polymeric composite combines the physical properties of the constituents to obtain new structural/functional properties. Due to the possibility of designing properties, polymeric composite materials have been used for field applications [31]. Recently, the adsorbents with rare earth elements are being paid more attention because of their selective affinity to fluoride, high adsorption capacity, minimum pollution and easy operation [32]. Among the rare earths, La(III) possesses high selectivity towards fluoride.

Hence, in the present investigation, the authors have developed SGCS composite and La(III) incorporated SGCS composite for fluoride removal. A comparative evaluation of DC of CS, SG, SGCS composite and LaSGCS composite was also made and has been discussed in detail. Various sorption influencing parameters on the DC of the sorbent, viz., contact time, pH, initial fluoride concentration, competing co-ions and temperature were optimized. The equilibrium data was fitted with various isotherms and kinetic models. The suitability of the developed LaSGCS composite was tested with a water sample collected from a nearby fluoride endemic village.

## 2. Materials and methods

### 2.1. Materials

Chitosan (85% deacetylated) was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Silica gel,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ , glacial acetic acid, glutaraldehyde and all other chemicals used were of analytical grade.

### 2.2. Synthesis of silica gel/chitosan (SGCS) composite

Silica gel (SG) was heated at  $110^\circ\text{C}$  for 1 h to activate the surface. About 10 g of SG was immersed in 20 ml of water to make slurry. 2 g of chitosan was dissolved in acetic acid aqueous solution and stirred for 1 h. This solution was added to the silica slurry and then the required amount of glutaraldehyde, the cross-linking agent was added to bind both the silica gel and chitosan matrix. The mixture was stirred for 2 h and soaked in an ultrasonic bath for 30 min. The wet composite was allowed to evaporate at room temperature to complete cross-linking reaction. The dry product obtained was washed thoroughly with distilled water and dried in oven at  $50^\circ\text{C}$ . Finally, the dried SGCS composite was crushed in the ball mill (IKA, Germany) to fine powder and used for fluoride sorption studies.

### 2.3. Synthesis of La(III) loaded silica gel/chitosan (LaSGCS) composite

LaSGCS composite was prepared as described for SGCS composite. 2 g of chitosan was dissolved in acetic acid aqueous solution and 5 g of  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  was added and stirred for 1 h. This solution was added to the silica slurry and then the required amount of the cross-linking agent glutaraldehyde was added. The mixture was stirred for 2 h and soaked in an ultrasonic bath for 30 min. The wet composite was allowed to evaporate at room temperature to complete cross-linking reaction. The dry product obtained was washed thoroughly with distilled water to neutral pH and dried in oven at  $50^\circ\text{C}$ . Finally, the dried LaSGCS composite was crushed in the ball mill (IKA, Germany) to fine powder and used for fluoride sorption studies.

### 2.4. Sorption experiments

Defluoridation experiments were carried out by batch equilibration method in duplicate. About 0.1 g 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 analysed for fluoride. The various influencing parameters like contact time, pH and presence of other anions on the DC of the sorbent were investigated. For the isotherm and kinetic studies, the effect of different initial fluoride concentrations viz., 9, 11, 13 and 15 mg/L at 303, 313 and 323 K on sorption rate was carried out by keeping the mass of the sorbent as 0.1 g and volume of the solution as 50 mL at neutral pH. The solution was then filtered and the residual fluoride ion concentration was measured.

### 2.5. Analysis

The fluoride ion concentration was measured using Thermo Orion Benchtop Multiparameter Kit (Model: VERSA STAR 92) and the fluoride ion selective electrode with the relative accuracy of  $\pm 1$  significant digit, detection limit of 0.02 mg/L and the reproducibility of  $\pm 2\%$  [33]. The pH measurements were done with the same instrument with pH electrode. All other water quality parameters were analysed using the standard methods [34].

### 2.6. Composite characterization

Fourier transform infrared spectrophotometer (FTIR) spectra of the composite were obtained using JASCO-460 plus model to confirm the functional groups present in it. Surface morphology of the composite was examined with scanning electron microscope (SEM) with HITACHI-S-3000H model fitted with an energy dispersive X-ray analyzer (EDAX) which allows a qualitative detection and the localization of elements present in the composite. SEM images enable a direct observation of the surface of the fresh and the fluoride-sorbed composite. BET surface area of the composite was obtained using Micromeritics-Tristar 3000 model. X-ray diffraction (XRD) measurements were obtained using X'per PRO model-PANalytical to determine the crystalline phases present in the sorbents. Thermogravimetric analysis (TGA) of the composite was carried out using SII Exstar 6000-TG/DTA 6300. The pH at zero point of charge ( $\text{pH}_{\text{zpc}}$ ) of the sorbents was determined by pH drift method [35].

### 2.7. Statistical tools

Computations were made using the Microcal Origin (Version 8.0) software. The significance of the data trends and the goodness of plot fit were discussed using the error bar plot, regression correlation coefficient ( $r$ ), chi-square analysis and standard deviation (SD).

## 3. Results and discussion

### 3.1. Effect of contact time

The DCs of SG, SGCS composite and LaSGCS composite varies with the period of time of contact with sorbate solution. So the experiments were carried out with different contact time in the range of 10–60 min with 10 mg/L initial fluoride concentration at 303 K. As it is evident from Fig. 1, that the sorbents reached saturation at 30 min and hence for further studies the contact time was fixed as 30 min. The DCs of LaSGCS composite and SGCS composite are 4900 and 1556  $\text{mg F}^-/\text{kg}$  respectively whereas the SG

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