Journal of Water Process Engineering 3 (2014) 144–150

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Synthesis of metal ion loaded silica gel/chitosan biocomposite and its fluoride uptake studies from water

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ARTICLE INFO

Article history:
Received 13 March 2014
Received in revised form 15 June 2014
Accepted 16 June 2014
Available online 25 July 2014

Keywords:
Chitosan
Cerium
Silica gel
Isotherms
Fluoride
Adsorption

ABSTRACT

In this study, novel sorbents, silica gel/chitosan (SGCS) and cerium loaded silica gel/chitosan (Ce-SGCS) composites have been synthesized and their application toward fluoride removal from aqueous solution was discussed under batch equilibrium mode. The synthesized sorbents were characterized using FT-IR, SEM with EDAX and XRD studies. At room temperature, Ce-SGCS has a maximum DC of 4821 mgF$^-$/kg, while for SGCS, the DC was 3470 mgF$^-$/kg only in the optimum contact time of 30 min. Thermodynamic studies revealed that the sorption of fluoride on Ce-SGCS composite is endothermic and spontaneous in nature. For the kinetic studies, the pseudo-second order model could explain the kinetic behavior of fluoride adsorption onto Ce-SGCS composite satisfactorily with a good correlation coefficient than the pseudo-first order model. Field studies were carried out with the fluoride containing water sample collected from a fluoride-endemic area in order to test the suitability of the sorbent at field conditions.

1. Introduction

People in many regions are suffering from fluoride pollution, which is due to high concentration of fluoride in aqueous solution by natural sources, as well as from industries producing hydrofluoric, fertilizer, metal plating, semiconductor and other electronic items. Fluorosis occurs when fluoride ingestion manifested by mottling of teeth in mild cases and embrittlement of bones and neurological damage in severe cases [1]. Acute high oral exposure to fluoride may lead to nausea, vomiting, abdominal pain, diarrhea, drowsiness, headaches, coma, convulsions, cardiac arrest and death [2]. Realizing such harmful effects of fluoride on human health, World Health Organization (WHO) has set the guideline level for fluoride in drinking water at 1.5 mg/L [3].

Current methods used to remove fluoride from water are electrocoagulation [4], precipitation [5], membrane techniques [6] and adsorption [7]. Amongst all the methods mentioned above, adsorption is recognized as the most effective approach for the removal of fluoride due to the low cost, high efficiency and environmental friendly behavior [8].

The composite materials as adsorbents containing natural polymers and inorganic origin have attracted great attention due to their combined advantages. In recent years, biosorption has been recognized as an effective method for the removal of fluoride in water. Chitosan is a poly(D-glucosamine) obtained from deacetylation of chitin. The most important features of chitosan are its biodegradability, biocompatibility, flexibility, versatility and hydrophilicity. Chitosan have a variety of potential applications in the areas of biomedicine [9], food ingredients [10], dye removal [11], metal ions removal [12] and fluoride removal [13,14] studies. Silica gel which is non-toxic and has pore geometry, large BET surface area, narrowly distributed pore sizes and often an ordered pore arrangement [15] was functionalized with chitosan in order to get the silica gel/chitosan composite (SGCS) for fluoride removal studies for the first time. In addition, the rare earth metal Ce(III) have also been combined with silica gel/chitosan composites to extent its defluoridation capacity (DC).

Under various equilibration conditions like contact time, dose, pH and in the presence of competitor co-anions, the fluoride removal studies were carried out. The reasonable mechanism of fluoride removal by this sorbent was suggested.

2. Materials and methods

2.1. Materials

Chitosan was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Its deacetylation degree is 85%. The viscosity of the chitosan solution was determined to be 700 (MPa s) by Brookfield

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http://dx.doi.org/10.1016/j.jwpe.2014.06.005

Dial Reading Viscometer using electronic drive-RVT model (USA make). Silica gel, $Ce(NO_3)_3{\cdot}6H_2O$, NaF, NaOH, HCl, glacial acetic acid, glutaraldehyde, and all other chemicals and reagents were of analytical grade. Double distilled water was used throughout the study.

2.2. *Synthesis of SGCS and Ce-SGCS composites*

Silica gel (SG) was heated at 110 °C for 1 h to activate the surface. 10 g of silica was immersed in 15 mL of distilled water to make slurry. 2 g chitosan was dissolved in 2% acetic acid aqueous solution and stirred for 1 h. This solution was added to the slurry and the mixture was stirred for 2 h. The required amount of glutaraldehyde (5%) was added drop wise and stirred vigorously. The mixture was transferred to a refrigerator at 4 °C for 24 h to undergo complete cross-linking reaction and washed to neutral pH and dried in oven at 40 °C [16]. Finally, the dried hybrid composite was sieved to uniform size and used for fluoride sorption studies.

The Ce-SGCS composite was carried out as follows. About 2 g of chitosan and 5 g of $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in acetic acid mixed with silica gel slurry and stirred for 3 h and then the required amount of 5% glutaraldehyde were added for cross-linking. The Ce-SGCS composite was kept at 4 °C for 24 h and washed thoroughly with distilled water and dried in an oven at 40 °C [16]. Finally, the dried Ce-SGCS composite was sieved to 60 mesh and used for fluoride removal experiments.

2.3. *Sorption experiments*

Defluoridation experiments were carried out by a batch equilibration method in duplicate. In a typical case, 0.1 g of the sorbent was added to 50 mL of fluoride 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 influences of various parameters like contact time, pH and presence of other anions on DC of the sorbents were also investigated. The thermodynamic parameters of the adsorption were established by conducting the experiments at 303, 313 and 323 K in a temperature-controlled mechanical shaker.

2.4. *Characterization of sorbents*

The concentration of fluoride ions present in the solution was measured using an expandable ion analyzer EA 940 with the fluoride ion selective electrode BN 9609 (Orion, USA) [17]. TISAB II (Total Ionic Strength Adjustment Buffer II) was added to all fluoride standards and samples to control the ionic strength. The relative accuracy of ±1 significant digit, detection limit of 0.02 mg/L and reproducibility of ±2% were obtained using TISAB buffer. The pH measurements were made with the same instrument with pH electrode. All other water quality parameters were analyzed by using standard methods [18]. A JASCO-460 plus Fourier transform infrared spectroscopy (FTIR) was used to verify the presence of functional groups in the adsorbent before and after sorption of fluoride in aqueous solution. The surface morphology of the composite before and after fluoride sorption was studied using scanning electron microscope (SEM) with Vega3 Tescan model. Elemental spectra were obtained using an energy dispersive X-ray analyzer (EDAX) during SEM observations which allows qualitative detection and localization of elements in the composite. X-ray diffraction (XRD) measurements were obtained using X'per PRO model-PANalytical to determine the crystalline phases present in sorbents.

Computations were made using Microcal Origin (Version 6.0) software. The goodness of fit is discussed using error bar plot, regression correlation coefficient (r), chi-square (χ^2) analysis and standard deviation (sd).

3. Results and discussion

3.1. *Characterization of the sorbents*

3.1.1. *FTIR analysis*

Fig. 1a and b depicts the FTIR spectra of Ce-SGCS and fluoride sorbed Ce-SGCS composite. The broad and intense peak at 3413 cm^{-1} was assigned to O—H group of chitosan of composite. The band at 2937 cm^{-1} is due to asymmetric vibration of C—H. The stretching vibration of 1640 cm^{-1} was related to C—N [19]. The strong peak at 1432 cm^{-1} was C—H bending vibration, and the peak at 1110 cm^{-1} corresponds to Ce—OH stretching vibration of chitosan [20]. The band at 465 cm^{-1} indicates the Si—O—Si bending vibration of Ce-SGCS composite [12,21]. All these bands confirm the co-existence of cerium, chitosan and silica gel in Ce-SGCS composite. A slight broadening of band at 3413 cm^{-1} in the fluoride sorbed Ce-SGCS composite may be taken as an indicative of electrostatic adsorption between the sorbent and the fluoride (Fig. 1b) [22,23].

3.1.2. *XRD studies*

XRD curves of SG, CS, SGCS and Ce-SGCS composite are shown in Fig. 2. Silica gel showed the characteristic peaks at $2\theta = 11.6°$, 20.7°, 25.6°, 29.7°, 31.7° and 49.2° and chitosan flakes showed characteristic peaks at $2\theta = 10.1°$, 20.3°, 26.0° and 42.0° in Fig. 2a and b. the respective XRD patterns of SGCS and Ce-SGCs composite are shown in Fig. 2c and d. Ce-SGCS composite shows the characteristic peaks at $2\theta = 28°$, 25°, 48°, 13° indicates the presence of cerium in this composite [24,25]. Further, the peaks for SGCS and Ce-SGCS composite suggested that the crystalline area lies between $2\theta = 20–30°$. The changes on the crystallinity may be attributed to the introduction of bulky nature of chitosan polymeric group, which demonstrate that the conjugations of silica and chitosan polymeric chain were mixed well at molecular level [26,27].

3.1.3. *SEM analysis*

Scanning electron micrographs was employed to depict the surface morphology of Ce-SGCS composite before and after the defluoridation process. Fig. 3a and b indicates the SEM images of Ce-SGCS composite before and after sorption of fluoride, respectively. The alteration of the surface morphology in the fluoride sorbed (f-Ce-SGCS) composite indicates the sorption of fluoride onto the composites. This is further supported by EDAX spectra of Ce-SGCS

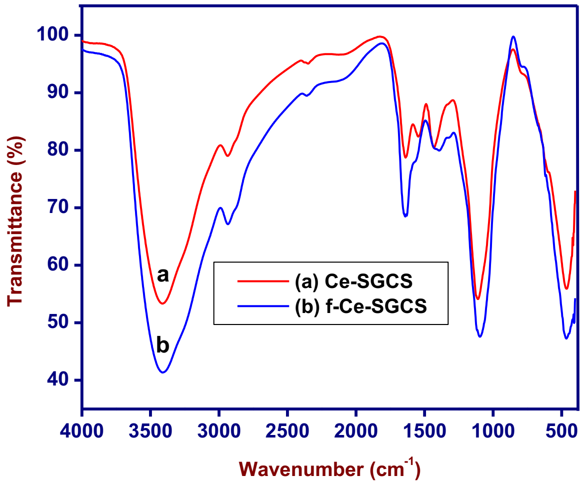

Fig. 1. FTIR spectra of (a) Ce-SGCS and (b) f-Ce-SGCS composites.