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Synthesis of surface coated hydroxyapatite powders for fluoride removal from aqueous solution

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ABSTRACT

This contribution reports the preparation of hydroxyapatite (HAp) and cationic surfactant modified forms of HAp powder for fluoride uptake studies from aqueous solution. The structures of the synthesized sorbents were characterized by FT-IR, SEM with EDAX, XRD and mapping studies. The fluoride adsorption using HAp and modified forms of HAp powder was studied on batch mode. The maximum defluoridation capacity (DC) onto modified forms of HAp powder was 9.369 mg/g from an initial fluoride ion concentration of 10 mg/L as the dosage of 50 mg at room temperature was almost 3–4 times higher than bare HAp whose capacity was found to be 2.63 mg/g. The results indicated that the fluoride adsorption onto modified forms of HAp powder is essentially by an electrostatic attraction and ion-exchange mechanism which depend on the solution pH. Various parameters like contact time, pH, other interfering anions and temperature were optimized. The adsorption data was reasonably explained using Freundlich, Langmuir and D-R isotherms. The calculated values of thermodynamic parameters indicated that the fluoride adsorption is spontaneous and endothermic in nature. The sorption process follows pseudo-second-order and intraparticle diffusion kinetic models. The schematic sketch for fluoride adsorption mechanism by HAp and cationic surfactants modified HAp powder has been proposed. The suitability of the best modified HAp has been tested with the field samples collected in a nearby fluoride endemic area.

1. Introduction

Fluoride is the first element in the halogen family of the periodic table, which does not occur in the elemental state in the environment due to its high reactivity [1]. Fluoride, a typical trace element, is in all places distributed in rock, soil and water. The fluoride ion demonstrates versatile nature, as its concentration in optimum dose (0.5–1.5 mg/L) in drinking water is beneficial to health and excess concentration (>1.5 mg/L) causes serious health effects on human beings. According to the World Health Organization (WHO), the maximum acceptable concentration of fluoride is 1.5 mg/L [2]. Current methods used to remove fluoride from water can be divided into different categories, electrocoagulation [3–5], precipitation [6], membrane techniques [7] and adsorption [8]. Though several methods have been adopted for fluoride removal from aqueous solution, adsorption method is an efficient, simple, economical, energy saving and feasible approach in small water resource systems [9–11]. Different sorbents such as alumina [12] and alumina based sorbents [13,14], activated carbon [15], ion-exchange resins [16,17], bio-polymer based composites [18–20], clay like materials [21,22] and mixed oxides [23–26] have been tried for fluoride removal.

HAp is a naturally occurring mineral which mainly originates in both bone and skeletal tissues. Many authors have proposed HAp as a sorbent for efficient removal of fluoride from aqueous solution [27–36]. HAp has been widely studied for its potential in trapping and removal of toxic heavy metals and anion in ground water and soil [37–39]. In addition, HAp can be comprehensively used in bone substitute, ceramic implants, biomedicine, catalyst or catalyst support, biosensor and sewage treatment [40–44].

However, the natural sorbents and synthesized sorbents showed a lower defluoridation capacity (DC). Thus, there is the need to extend the modification of low cost adsorbents with an affinity towards fluoride ions from aqueous solution. Surface modification technology has been proved to be an efficient and effective technology. Cationic surfactants such as cetyltrimethyl ammonium bromide (CTAB), hexadecylpyridinium chloride (HDPC) and dodecyltrimethyl ammonium bromide (DTAB) mostly contain amine salt and quaternary ammonium salt, which provide more positive sites to the system in which they have been added. Many researchers have attempted to utilize the surface modification technology using these surfactants to enhance the chromium removal [45], nitrate removal [46] and perchlorate removal [47].

Till now there has been no study regarding modification of HAp and hence it is aimed to prepare cationic surfactant layered HAp surface using CTAB, HDPC and DTAB. The objectives of this study are as follows:

i) To carry out surface modification of HAp powder using above said cationic surfactant and explore its DC.
ii) To compare DC of the bare HAp and cationic surfactants modified HAp powder.

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iii) To find out the optimum contact time, pH, the effect of presence of co-ions and temperature.
iv) To establish a suitable mechanism of fluoride removal.

2. Materials and methods

2.1. Materials

Calcium nitrate, ammonium dihydrogen phosphate, sodium fluoride, cetyltrimethyl ammonium bromide (CTAB), hexadecylpyridinium chloride (HDPC) and dodecyltrimethyl ammonium bromide (DTAB) were purchased from Merck. All other chemicals used were of analytical grade and used without further purification.

2.2. Synthesis and surfactant modification of HAp powder

The HAp was synthesized by precipitation method as per Chen et al. procedure [48]. Briefly, the reaction of calcium nitrate and ammonium dihydrogen phosphate at the pH 10 maintained by adding ammonia yielded HAp. The precipitated form of HAp was rinsed with plenty of water until the solution became neutral. The washed HAp was dried in an oven at 80 °C for 6 h. The preparation of HAp powder modified with cationic surfactants was carried out as follows. Dried HAp powder (10 g) was added to a solution of 50 mL of CTAB at its CMC (1.0 mM) concentrations to prepare CTAB-HAp powder. The mixture was agitated for 5 h and then filtered, washed and dried in an oven at 70 °C for 5 h. A similar procedure was followed to prepare DTAB-HAp and HDPC-HAp powders by adding respective CMC of DTAB (14 mM) and HDPC (0.9 mM) surfactants. The concentration of all the surfactants selected for coating on the HAp powder has been optimized by trial and error method and found that above the CMC, the surfactants form a micelle, which is more stable and remains in the bulk zone. On the other hand, the concentration below the CMC level has no or little effect in enhancing the fluoride sorption. Hence, CMC concentration has been selected as the optimum concentration for all the sorbents and this has been well established by many researchers [45,47]. All the three sorbents viz., CTAB-HAp, DTAB-HAp and HDPC-HAp powders were used for fluoride removal studies in addition to bare HAp.

2.3. Sorption experiments

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

2.4. 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 [49]. The pH measurements were done with the same instrument with pH electrode. The pH_{zpc} of the HAp powder was determined by pH drift method [50]. All other water quality parameters were analyzed by using standard methods [51]. FTIR spectra were recorded on a JASCO-460 FTIR spectrometer using KBr pellets. The scanning electron microscope (SEM) images were taken using the Vega3 Tescan model and elemental spectra were obtained using an energy dispersive X-ray analyzer (EDAX) and mapping images were taken during SEM observations which allow qualitative detection and localization of elements present in the HAp powder, 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.

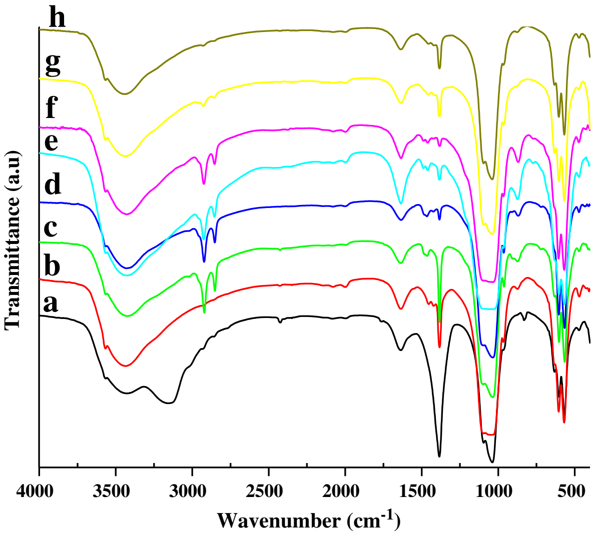

Fig. 1. FTIR spectra of (a) HAp, (b) f-HAp, (c) CTAB-HAp, (d) f-CTAB-HAp, (e) HDPC-HAp, (f) f-HDPC-HAp, (g) DTAB-HAp, and (h) f-DTAB-HAp.

2.5. Computational analysis

Computations were performed using Microcal Origin (version 6.0) software. The significance of trends in the data and the goodness of fit are discussed in terms of the correlation coefficient (*r*), standard deviation (sd), chi-square (χ^2) analysis and non-linear analysis.

3. Results and discussion

3.1. FTIR spectra

The FTIR spectra of the respective sorbents before and after sorption of fluoride viz., (a) HAp (b) fluoride-sorbed HAp (f-HAp), (c) CTAB-HAp,

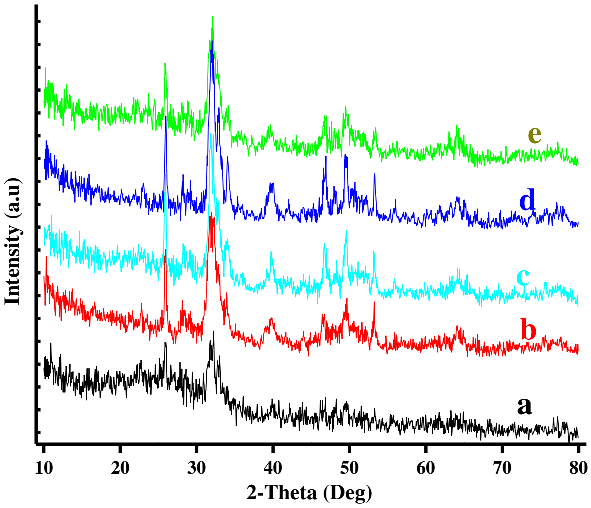

Fig. 2. XRD spectra of (a) HAp, (b) HDPC-HAp, (c) DTAB-HAp, (d) CTAB-HAp, and (e) f-CTAB-HAp.