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Synthesis of nano-hydroxyapatite chitin/chitosan hybrid biocomposites for the removal of Fe(III)

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ABSTRACT

Biocomposites made up of nano-hydroxyapatite (n-HAp) with chitin and chitosan have been prepared and used for the removal of Fe(III) from aqueous solution. The sorption capacity (SC) of n-HAp, n-HAp/chitin (n-HApC) composite and n-HAp/chitosan (n-HApCs) composite was found to be 4238, 5800 and 6753 mg/kg respectively. Batch adsorption studies were conducted to optimize various equilibrating conditions like contact time, pH and co-ions. The sorbents were characterized by FTIR and EDAX analysis. The sorption process follows Langmuir isotherm. Thermodynamic studies revealed that the sorption of Fe(III) on these composites is spontaneous and endothermic in nature. Both the composites showed higher SC than the n-HAp.

1. Introduction

At present, the presence of heavy metal ions in the environment has received extensive attraction because of their intrinsically persistent nature and toxic effects even at very low concentrations (Moore & Ramamoorthy, 1983; Rapsomanikis & Craig, 1991). Removal of heavy metals from water is usually obtained by physical and chemical processes which include precipitation, solvent extraction, reduction, membrane processes, ion-exchange and adsorption (Alonso, Galan, Gonzalez, & Oritiz, 1999; Bektas, Ağım, & Kara, 2004; Gode & Pehlivan, 2005; Meenakshi & Viswanathan, 2007; Ning, 2002; Pettine, D'Ottone, Companella, Millero, & Passino, 1998; Sedlak & Chan, 1987). One of the new developments in recent years to remove toxic metals is the use of biological origin like chitin, chitosan, lignin and so on (Gonzalez-Davila & Millero, 1998; Jayakumar et al., 2009). Water with high iron content which is considered as heavy metal can be very objectionable in taste, odour or appearance. With severe iron poisoning, much of the damage to the gastrointestinal tract and liver may be the result of highly localized iron concentration and free radical production leading to heptatoxicity through lipid peroxidation and the destruction of the hepatic mitochondria. As a result of the iron storage disease caused due to iron poisoning, the liver becomes cirrhotic. Hepatomia, the primary cancer of the liver, has become the most common cause of death among patients with hemochromatosis. This is an iron storage disease that results from the inability of the intestine to keep out unnecessary iron. Instead, iron gets accumulated in the liver causing siderosis (Cunningham, 1999). Adsorption is the most frequently applied technique owing to its advantages such as variety of adsorbent materials and high efficiency at a relatively low cost.

Adsorption studies of iron onto various adsorbents were carried out by many researchers (Ahalya, Kanamadi, & Ramachandra, 2006; Akaninwor, Wegwu, & Iba, 2007; Karthikeyan, Muthulakshmi Andal, & Anbalagan, 2005). Research works on the removal of cadmium, oxovanadium, cobalt, lead and zinc using hydroxyapatite (HAp) have been reported (Lusvardi, Malavasi, Menabue, & Saladini, 2002; Sandrine, Ange, Didier, Eric, & Patrick, 2007; Sheha, 2007; Smiciklas, Dimovic, Piecas, & Mitric, 2006; Vega, Pedregosa, Narda, & Morando, 2003). However, HAp could not be effectively utilized at field conditions because of their poor strength, low stability, less biocompatibility, etc. Biocomposites (which are made from organic matrix and inorganic fraction) possess amazingly good mechanical strength, biocompatibility and biodegradability (Chen, Wang, & Lin, 2002). Currently chitin and chitosan biopolymers represent an interesting, attractive and more effective sorbents because of their unique characteristics like non-toxicity, hydrophilicity, biocompatibility, biodegradability and biofunctionality (Muzzarelli, 1973; Okuyama, Noguchi, Hanafusa, Osawa, & Ogawa, 1999). Chitin and chitosan have a variety of potential applications in the areas

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of biotechnology, biomedicine and food ingredients (Jayakumar, Reis, & Mano, 2006; Jayakumar, Prabaharan, Reis, & Mano, 2005; Jayakumar, New, Tokura, & Tamura, 2007) and appear to be more useful biopolymers reported for the high potential of adsorption of metal ions (Jayakumar et al., 2009).

Hence the general aim of the study is to investigate adsorption capability of chitin and chitosan composites made with hydroxyapatite which could possess high mechanical strength, biocompatibility, biodegradability, etc than the individual components and hence be utilized at field conditions. Hybrid polymeric composites namely nano-hydroxyapatite/chitin (n-HApC) and nano-hydroxyapatite/chitosan (n-HApCs) were prepared and used for the removal of Fe(III) from drinking water which has not been reported so far. Various parameters namely contact time, pH, co-ions and temperature were optimized for maximum sorption. The best fit isotherm was identified for the sorption. Suitable mechanism of Fe(III) removal was proposed. A field study was also carried out.

2. Materials and methods

2.1. Materials

Chitin and chitosan (85% deacetylated) were supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Calcium nitrate, ammonium dihydrogen phosphate, ammonia and all other chemicals used were of analytical grade.

n-HAp was synthesized by the reaction of calcium nitrate and ammonium dihydrogen phosphate. The pH value during mixing was maintained above 10 with ammonia solution. Then they were mixed with a stoichiometric ratio of Ca to P (=1.67). The precipitate formed was rinsed with water to bring the pH level to 7. The precipitate obtained was dried at 80 °C (Chen et al., 2002; Sairam Sundaram, Viswanathan, & Meenakshi, 2008a). The n-HApC and n-HApCs composites were also prepared by precipitation method. The aqueous solution of ammonium dihydrogen phosphate was added to the mixture of aqueous solution of $Ca(NO_3)_2$ and chitin and chitosan in the ratio 3:2. The precipitate formed was rinsed with water to bring the pH level to 7. The precipitate obtained was dried at 150 °C to get n-HApC and n-HApCs composite (Sairam Sundaram, Viswanathan, & Meenakshi, 2009, 2008b).

2.2. Characterization of the sorbents

The prepared sorbents were characterized by Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra of the samples as solid by diluting in KBr pellets were recorded with JASCO-460 plus model. The results of FTIR spectroscopy was used to confirm the functional groups present, before and after Fe(III) sorption onto the sorbents. Elemental spectra were obtained using an Energy Dispersive X-ray Analyzer (EDAX) with HITACHI-S-3400 model, which allows a qualitative detection and localization of elements in the composite.

2.3. Sorption experiments

The sorption experiments were performed by batch equilibration method. Stock solution of Fe(III) containing 1000 mg/L was prepared and this was used for sorption experiments. The batch adsorption experiments in duplicate were carried out by mixing 0.1 g of sorbent with 50 mL of 10 mg/L as initial Fe(III) concentration. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm. The solution was then filtered and the residual Fe(III) concentration was measured using UV/Vis spectrophotometer (Perkin Elmer – Lambda 35) at 510 nm (APHA, 2005). The pH measurements were carried out with the expandable ion analyzer EA 940 with pH electrode. The thermodynamic parameters of the adsorption were established by conducting the experiments at 303, 313 and 323 K in a temperature controlled mechanical shaker. The SC of the sorbents was studied at different conditions like contact time of the sorbent for maximum sorption, pH of the medium and the effect of other common ions present in water. All other water quality parameters were analyzed using standard methods (APHA, 2005).

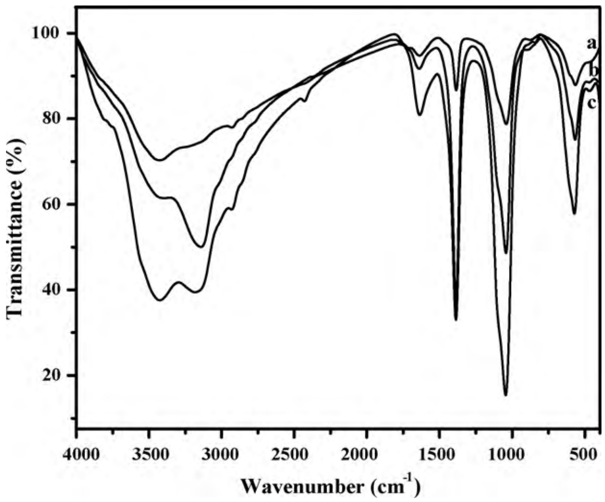


Fig. 1. FTIR spectra of (a) n-HAp (b) n-HApC composite and (c) n-HApCs composite.

Computations were made using Microcal Origin (Version 6.0) software. The goodness of fit was discussed using regression correlation coefficient (*r*) and standard deviation (SD).

3. Results and discussion

3.1. Characterization of the sorbents

Fig. 1a–c depicts the respective FTIR spectra of n-HAp, n-HApC and n-HApCs composites. In Fig. 1a, the stretching vibrations at 632 and 3140 cm^{-1} are due to the hydroxyl groups in n-HAp. The band at 560–610 cm^{-1} and 1000–1100 cm^{-1} in n-HAp corresponds to PO_4^{3-} stretching vibrations (Kuriakose et al., 2004; Mobasherpour, Heshajin, Kazemzadeh, & Zakeri, 2007). In Fig. 1b the band at 1636 cm^{-1} is due to the C=O group of chitin in the composite. In Fig. 1b and c, the –NH group of chitin and chitosan is included in 3140 and 1634 cm^{-1}. The bands at 2850, 1460 and 1383 cm^{-1} are attributed to the vibration of –CH group of chitin and chitosan (Sairam Sundaram et al., 2008a, 2008b, 2009). The vibration bands of C–O group are overlapped with phosphate bands at 1150–1040 cm^{-1}. Fig. 2a and b shows the FTIR spectra of (a) before sorbed and (b) Fe(III) sorbed n-HApCs and similar spectra were observed for n-HApC.

The shifting of –OH stretching vibrations at 3140 cm^{-1} to higher frequencies in the both Fe(III) sorbed n-HApC/n-HApCs composite may be taken as an indicative of adsorption between the sorbent and Fe(III). The presence of FTIR band at 570–590 cm^{-1} in the Fe(III) sorbed composite suggests the bonding between the Fe(III) and the chitosan matrix (Hernandez et al., 2008; Kaushik, Solanki, Ansari, Sumana, & Ahmad, 2009).

EDAX analysis which provides the direct evidence for the sorption of Fe(III) onto the composites. The EDAX spectra of n-HApC and n-HApCs composites confirm the presence of respective ions in the composites (cf. Fig. 3a and b). The Fe(III) sorption has occurred onto the composites was confirmed by the presence of iron peaks in the EDAX spectra of Fe(III) treated composites (cf. Fig. 3c and d).

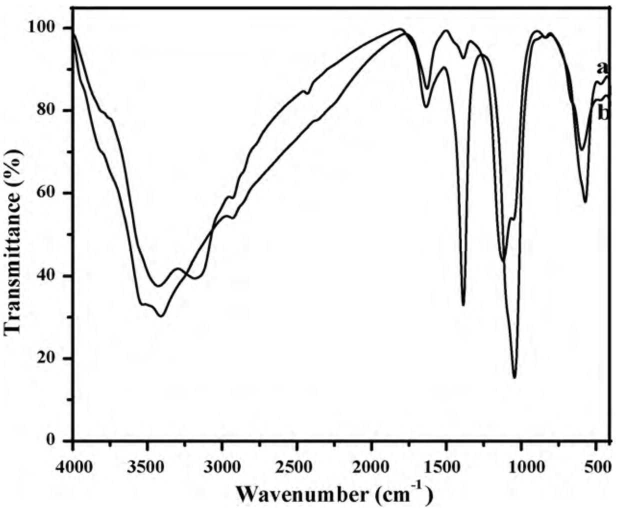


Fig. 2. FTIR spectra of (a) n-HApCs composite and (b) Fe(III) sorbed n-HApCs composite.

3.2. Effect of contact time

The SC of the sorbents was determined by varying contact time in the range of 5–60 min. About 0.1 g of the sorbent was mixed with 50 mL of the stock Fe(III) solution having an initial Fe(III) concentration of 10 mg/L. The contents were shaken thoroughly using a mechanical shaker at 200 rpm and the contents were filtered and analyzed for Fe(III). As is evident from Fig. 4a, the SC of all the sorbents reached saturation at 30 min. Hence, 30 min is fixed as the contact time for the sorbents for further studies. The SC at 30 min contact time of n-HAp, n-HApC and n-HApCs composites was found to 4238, 5800 and 6753 mg/kg respectively.

3.3. Effect of pH

The removal of Fe(III) from aqueous solution was highly dependent on the solution pH in many cases as it altered the surface charge on the sorbent (Zaid & Mohammed, 2008). The pH of the working solution was controlled by adding HCl/NaOH. SC of all the three sorbents was determined at five different pH levels viz., 3, 5, 7, 9 and 11 and the results are shown in Fig. 4b. A maximum SC was observed at pH 6–8 and a slight decline in SC was observed in both acidic and alkaline medium. There is a competition between H^+ and Fe(III) for the active sites of the sorbent in acidic medium and precipitation of Fe(III) as $Fe(OH)_3$ would decline the SC of the sorbent in alkaline medium. It is apparent from the figure that the pH has significant effect on the SC of both composites but in case of n-HAp a slight decline is observed with increase in pH of the medium. The pH_{zpc} of n-HAp is 7.88 where as for n-HApC and n-HApCs composite it was shifted to 5.95 and 6.97 which clearly indicate the occurrence of structural changes in the composites (Lopez-Ramon, Stoeckli, Moreno-Castilla, & Carrasco-Marin, 1999). After sorption,

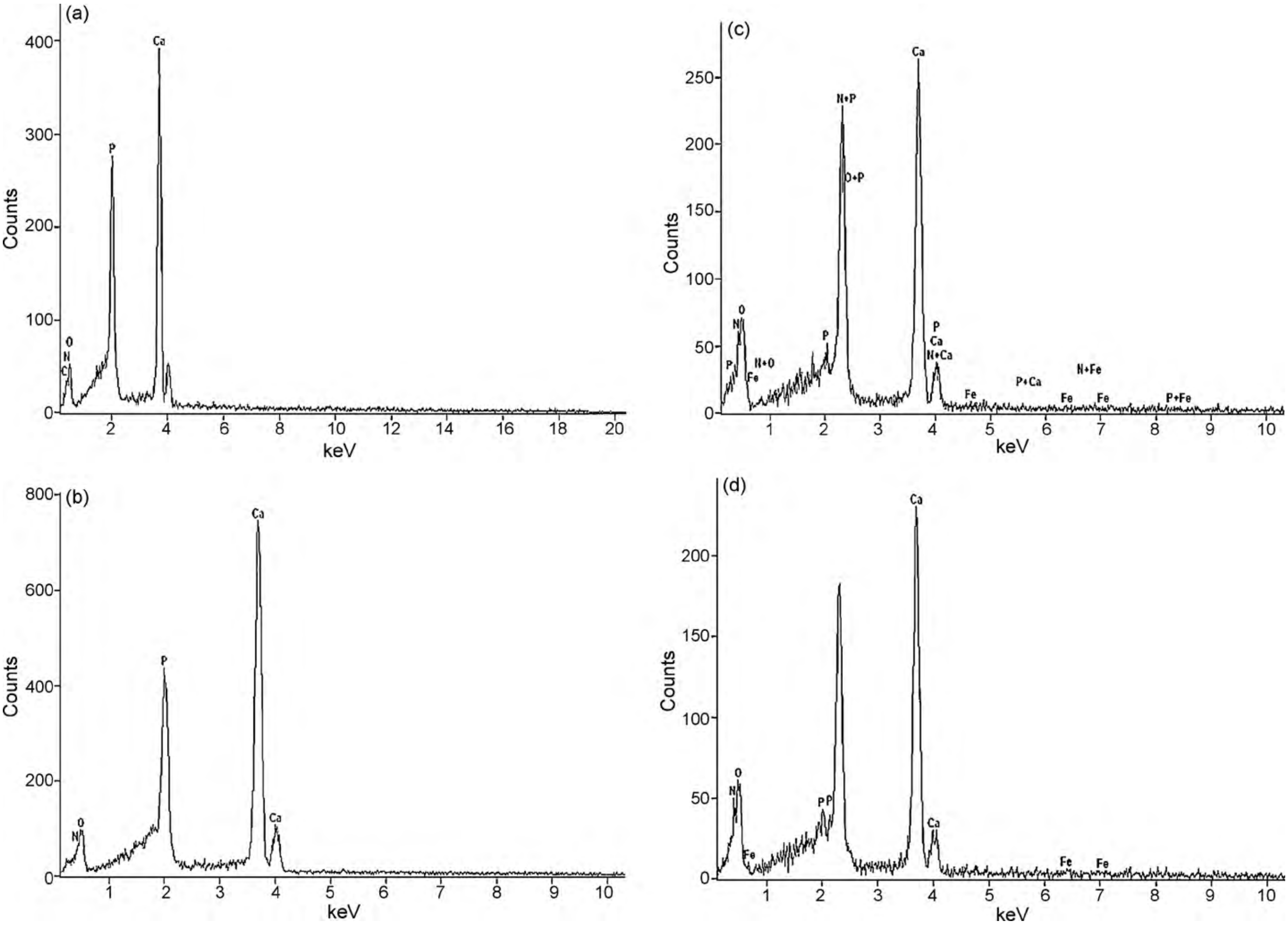


Fig. 3. EDAX spectra of (a) n-HApC composite, (b) n-HApCs composite, (c) Fe(III) sorbed n-HApC composite and (d) Fe(III) sorbed n-HApCs composite.

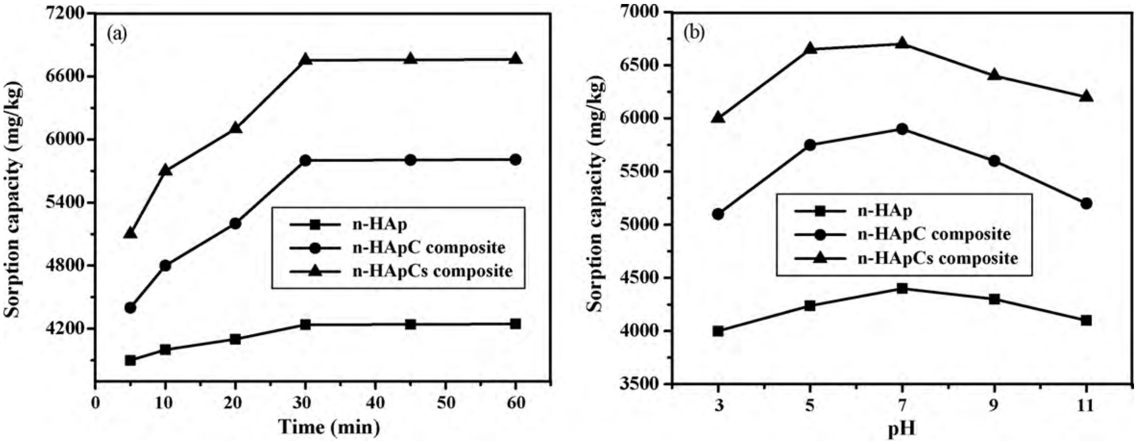


Fig. 4. (a) Effect of contact time on the SC of the sorbents at 303 K. (b) Influence of pH on the SC of the sorbents at 303 K.

Table 1
Freundlich and Langmuir isotherms of the composites.

Sorbents	Temp. (K)	Freundlich isotherm					Langmuir isotherm			
		$1/n$	n	k_F (mg/g) (L/mg)$^{1/n}$	r	SD	Q° (mg/g)	b (L/g)	r	SD
n-HApC composite	303	0.558	1.792	5.726	0.935	0.043	9.554	0.862	0.962	0.006
	313	0.564	1.773	6.358	0.995	0.012	10.853	1.328	0.981	0.005
	323	0.493	2.028	6.515	0.993	0.014	12.962	1.939	0.981	0.006
n-HApCs composite	303	0.849	1.178	5.434	0.991	7.44E−4	9.457	0.220	0.995	9.54E−5
	313	0.793	1.261	5.696	0.980	0.003	10.668	0.336	0.987	0.001
	323	0.748	1.337	5.796	0.989	1.22E−4	12.114	0.472	0.981	3.75E−5

Table 2
Thermodynamic parameters for Fe(III) sorption onto composites at different temperatures.

Sorbents	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
	303 K	313 K	323 K		
n-HApC composite	−3.51	−4.95	−7.79	17.42	52.97
n-HApCs composite	−1.45	−0.70	−0.42	26.99	75.24

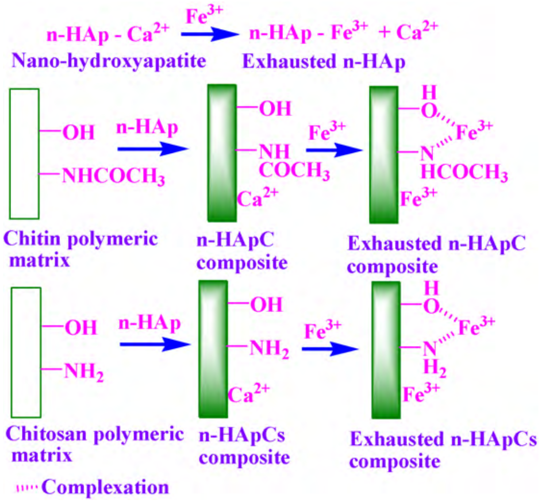
irrespective of initial pH ranges, the final pH of the treated water was found to be neutral due to the pH_{zpc} of these sorbents in neutral pH range. As n-HApC and n-HApCs composites possessed higher sorption capacity than the n-HAp at all pH ranges studied, further studies were limited to n-HApC and n-HApCs composites and throughout the study, the pH of the medium was maintained at pH 3.0 due to the formation of ferric hydroxide at higher pH range.

3.4. *Effect of common ions in the medium*

The SC of the sorbents in the presence of other common cations which are normally present in water viz., Ca^{2+} and Mg^{2+} ions was investigated with a fixed initial concentration of 200 mg/L of these ions by keeping 10 mg/L as initial Fe(III) concentration at room temperature. These ions have slight effect on SC of both the sorbents which may be attributed to the fact that the there is a competition between the common ion and Fe(III).

3.5. *Sorption isotherms*

To quantify the sorption capacity of composites for Fe(III) sorption, two-parameter equations namely Freundlich and Langmuir have been adopted (Freundlich, 1906; Langmuir, 1916).



Scheme 1. Fe(III) sorption by the sorbents.

The data obtained from these two models were given in Table 1. The values of $1/n$ lying between 0 and 1 confirm the favorable conditions for adsorption. The k_F values of both the sorbents that are found to increase with increase in temperature confirm the endothermic nature of sorption. The values of Q° for both the composites that are found to increase with increase in temperature again confirm the endothermic nature and temperature dependence of the sorption process. The higher r values obtained for both the sorbents indicate the applicability of Freundlich and Langmuir

Table 3
Field trial results of the sorbents.

Water quality parameters	Before treatment	After treatment		
		n-HAp	n-HApC composite	n-HApCs composite
Fe(III) (mg/L)	1.50	Nil	Nil	Nil
pH	7.65	8.60	7.56	7.53
Cl^- (mg/L)	1704	1065	868	865
Total hardness (mg/L)	1160	1080	920	900
Total dissolved solids (mg/L)	4650	2250	2000	2000

isotherm. However to identify a suitable isotherm model for the sorption of Fe(III) on composites, the best fit isotherm was calculated using the values of standard deviation (SD). The lower values of SD with higher *r* values obtained for Langmuir isotherm indicates the applicability of Langmuir isotherm for both the composites.

3.6. Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the adsorption, viz., standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the method suggested by Khan and Singh (1987).

The calculated values of thermodynamic parameters are shown in Table 2. The thermodynamic treatment of the sorption data indicates that ΔG° values were negative at all temperatures investigated. The negative values of ΔG° confirm the spontaneous nature of Fe(III) sorption by the sorbents. The positive value of ΔS° indicates that the freedom of Fe(III) is not too restricted in the sorbents. The positive value of ΔH° for Fe(III) removal confirms the endothermic nature of sorption process by both the composites.

3.7. Mechanism of Fe(III) sorption

The mechanism of Fe(III) sorption by n-HAp, n-HApC and n-HApCs composites was governed by adsorption as well as ion-exchange as shown in Scheme 1. In case of n-HApC and n-HApCs composites in addition to these forces, sorption by chelation of the Fe(III) with the lone pair of electron from nitrogen has also taken place due to amino and hydroxyl groups in the composites. Hence a high increase in the SC was observed for n-HApC and n-HApCs composites than the n-HAp due the combined effect of respective chitin and chitosan with n-HAp.

3.8. Field study

The suitability of n-HAp, n-HApC and n-HApCs composites was tested with a field sample taken in a nearby village. About 0.1 g of sorbent was added to 50 mL of water sample and the contents were shaken with constant time at room temperature. The results are presented in Table 3. There is a significant reduction in the levels of other water quality parameters in addition to Fe(III). It is evident from the result that both the composites can be effectively employed for removing the Fe(III) from water than n-HAp.

4. Conclusions

The Fe(III) sorption characteristics of composites were studied under various equilibrium and thermodynamic conditions. Composites displayed good selectivity towards Fe(III) removal. The SC of n-HApC and n-HApCs composites are higher than the n-HAp. Sorption of Fe(III) on composites was influenced by pH and in the presence of co-ions. After sorption, irrespective of initial pH ranges, the final pH of the treated water was found to be neutral. Fe(III) sorption follows Langmuir isotherm. The nature of sorption process is spontaneous and endothermic. The main advantage of n-HApC and n-HApCs composites over n-HAp is that they can be shaped into any desirable form as they are biocompatible and hence could be utilized for field applications.

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