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Hydroxyapatite/Carboxymethyl Cellulose Composite: Synthesis, Characterization, Kinetic, Thermodynamic Study for Removal of Cr (III)

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ABSTRACT

In the present work nano-hydroxyapatite (n-HAp)/Carboxymethyl Cellulose (CMC) composite was synthesized. The n-HApCMC composite was tested for the adsorption of Chromium from aqueous solution and compared its removal capacity with nano-hydroxyapatite (n-HAp). Equilibrium data were fitted well in the Langmuir and Freundlich isotherm models. The thermodynamic analysis also established that the adsorption process was endothermic and spontaneous.

Keywords: Adsorption, Heavy metals, Isotherm, Nano-hydroxyapatite/Cellulose

Introduction

Heavy metal pollution has become an environmental problem throughout the world because heavy metals can be accumulated into the food chain and cause serious problems, not only for ecosystems but also for human health [1-5]. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) is a main mineral constituent of teeth, bones and phosphate mineral rocks. It belongs to apatite mineral family [6] However, characteristic of HAp existing in the form of white powder therefore isolating the suspended fine solids from aqueous solutions after adsorption of metal ions is not easy [7]. The annual net yield of photosynthesis is 1.8 trillion tonnes of biodegradable substances, about 40% of which is estimated to be cellulose [8]. Hence the general aim of the study is to investigate adsorption capability of cellulose composites made with nano-hydroxyapatite which, biocompatibility, biodegradability, etc than the individual components and hence be utilized at field conditions. Hybrid polymeric composites namely nano-hydroxyapatite (n-HAp)/Carboxymethyl Cellulose (CMC) were prepared and used for the removal of Cr(III) from drinking water which has not been reported so far. Various parameters namely contact time, pH, coions and temperature were optimized for maximum sorption. The best fit isotherm was identified for the sorption. Suitable mechanism of Cr(III) removal was proposed.

Methods

Synthesis of Nano-Hydroxyapatite (n-HAp)/ Carboxymethyl Cellulose (CMC) Composite

The corresponding n-HApCMC composites were prepared by the precipitation method. The aqueous solution of ammoniumdihydrogen phosphate was added to the mixture of aqueous solution of $Ca(NO_3)_2$ with CMC in the ratio 3:2. The precipitate formed was rinsed with water to reach pH 7. The precipitate obtained was dried at 80 °C to get n-HApCMC composites [9].

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Results and discussion

Characterization of materials

The FT-IR spectra of n-HApCMC (A), CMC (B) and n-HAp (C) were recorded in the region of 500–4000 cm^{-1} and are shown in Fig. 1. The spectra of n- HAp showed a broad band at 1203 cm^{-1} due to asymmetric stretching of PO_4^{3-} and corresponding symmetric stretching was observed at 875 cm^{-1}. The absorption band at 1487 cm^{-1} suggested the presence of CO_3^{2-} [9], which was supposed to have come from atmosphere during the precipitation process. The broad band at 3500 to 3200 cm^{-1} and 1766 cm^{-1} was due to stretching and bending of O–H groups, respectively, present in n-HAp [10]. The FT-IR spectra of n-HApCMC showed a band at 1032 cm^{-1} which was due to stretching vibration of C–O–C group of CMC confirms formation of composite. The peak of PO_4^{3-} group shifted from 1203 to 1132 cm^{-1} due to interaction with CMC. The stretching and bending vibration mode of –OH group of CMC occurred at 3452 and 1627 cm^{-1}, respectively which was overlapped with the bands of O–H groups in n-HApCMC composite.

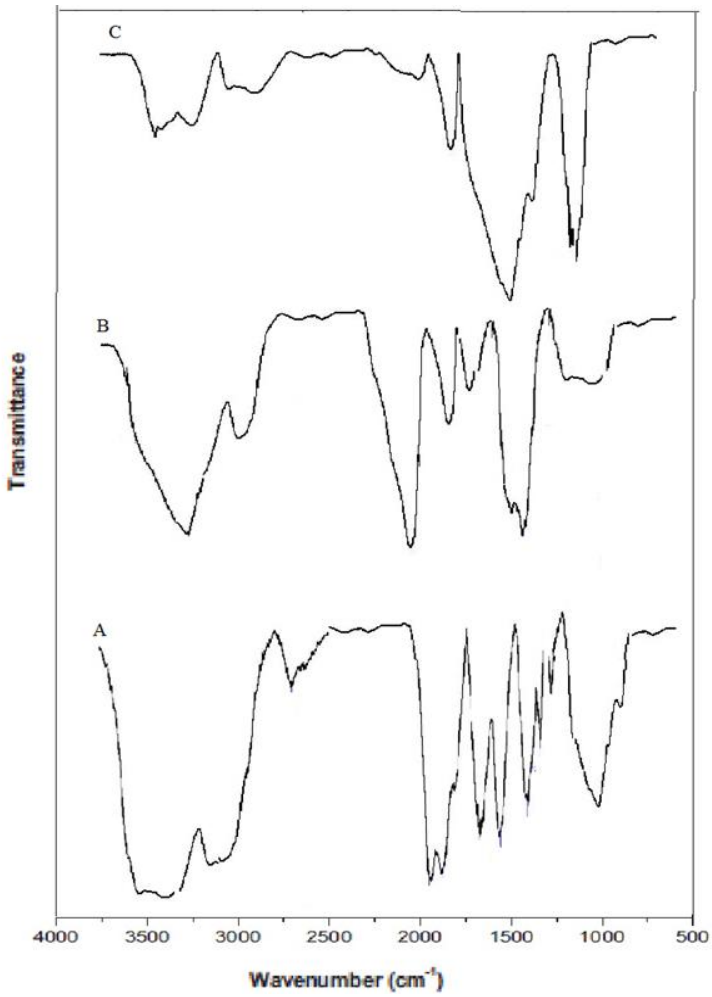

Figure 1. Infrared spectra of n-HApCMC composite (a), CMC (b) and n- HAp (c).

The XRD spectra of CMC, n-HAP and n-HApCMC are shown in Fig. 2. In the XRD pattern of n-HAp, the crystalline peaks at $2\theta = 25.9°$, 31.9°, 32°, 34.5° and 40° confirm the formation of hydroxyapatite. Crystalline peaks of In Fig. 2B, two main diffraction peaks of CMC at 2 $\theta = 32°$ and 46° can be found.n-HAp at $2\theta =$ 26°, 32°, 33.1°, 34.2°, 39.9° and 46° were found in n-HApCMC. This indicated that there was no marked change in the peak structure after the composite formation and confirms that the crystal structure of n-HAp is retained in n-HApCMC composites.

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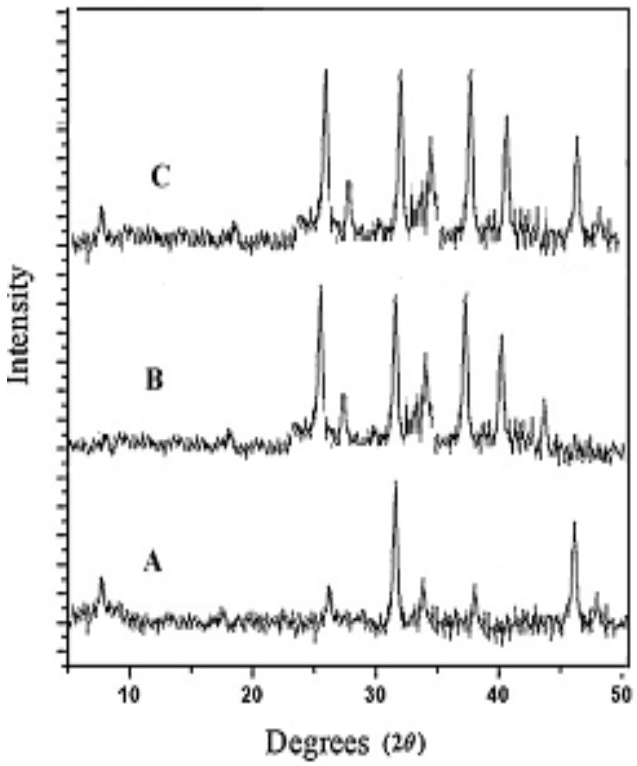

Figure 2. XRD spectra of CMC (a), HAp (b) and n-HApCMC (c).

Fig. 3 shows the morphology of n-HAp (a) and n-HApCMC composite (b). The n-HAp powder exhibited as particles but in case of n-HapCMC composite aggregates appeared and film of CMC over n-HAp, confirmed the formation of n-HApCMC composite.

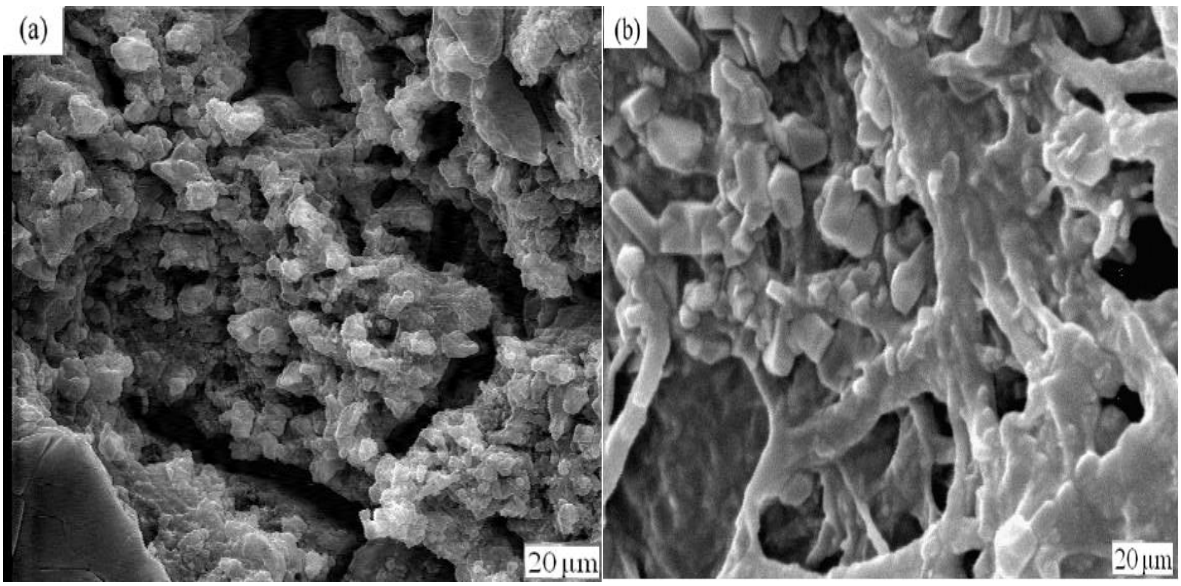

Figure 3. SEM micrograph of n-HAp (a) and n-HApCMC composite (b).

Equilibrium modeling in a batch system

Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational conditions and to design and optimize an operating procedure. The Langmuir and Freundlich equations are

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commonly used for describing adsorption equilibrium for water and wastewater treatment applications. Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between the adsorbent and the adsorbate are described by the adsorption isotherms. The adsorption curves were applied to both the Langmuir and Freundlich equations. The Freundlich isotherm model, which assumes that the adsorption occurs on heterogeneous surfaces, is often expressed as;

$$q_e = K_f (C_e)^{1/n} \quad (8)$$

This equation is conveniently used in the following linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (9)$$

Where K_f is Freundlich isotherm constant (L g^{-1}) and n_F is Freundlich isotherm exponent. Values of K_F and n_F were calculated from the intercept and slope of plots ln q_e vs ln C_e and a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The value of n_F should be greater than one confirming good adsorption of heavy metals onto n-HapCMC composite. Langmuir isotherm, which assume that a monolayer of heavy metals is formed on a relatively regular adsorbent surface, using the partially protonated groups of the adsorbent. The Langmuir isotherm has been successfully applied to many real sorption processes and is expressed as follows:

$$q_e = \frac{Q^0 b\, C_e}{1 + bC_e} \quad (10)$$

Where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}), b a constant related to the energy or net enthalpy of adsorption (L mg^{-1}), and Q_0 the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg g^{-1}). Q_0 represents a practical limiting adsorption capacity when the surface is fully covered with heavy metals and allows the comparison of adsorption performance, particularly in the cases where the adsorbent did not reach its full saturation in experiments. The Langmuir equation can be described by the linearized form as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (11)$$

By plotting (C_e/q_e) versus C_e, Q^0 and b can be determined if a straight line is obtained. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L, which is defined by:

$$R_L = \frac{1}{1 + bC_0} \quad (12)$$

Where b is the Langmuir constant and C_0 the initial heavy metals concentration (mg L^{-1}). R_L value indicates the type of isotherm. According to [12], R_L values between 0 and 1 indicate favorable adsorption. For evaluating the adsorption kinetics the pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data. It was observed that the q_e values estimated by first-order kinetic model differ substantially from those measured experimentally, suggesting that the adsorption is not a first-order reaction. The correlation coefficients for the second-order kinetic model are nearly equal to 1 and the theoretical values of q_e also agree very well with the experimental values. This suggests that the adsorption of heavy metals on n-HapCMC follows the second-order kinetic model. Tab. 4 and Fig. 6 and 7.

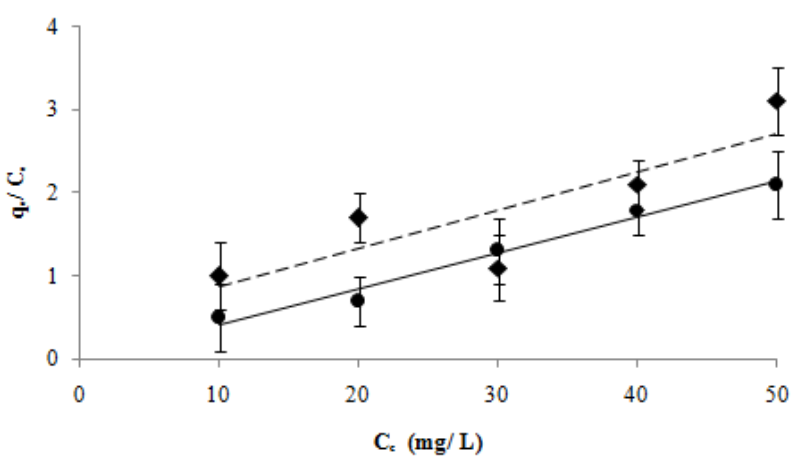

Figure 6. Langmuir adsorption isotherm at 293 °K.

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Table 4
Freundlich and Langmuir adsorption isotherm constants.

	Langmuir constants			Freundlich constants		
	Q° (mg/g)	**b (L/ mg)**	**R^2**	**K_F (L/mg)**	**n**	**R^2**
n-HAp	9.03	0.276	0.998	2.13	1.82	0.997
n-HApCMC	12.89	0.612	0.997	4.09	1.58	0.994

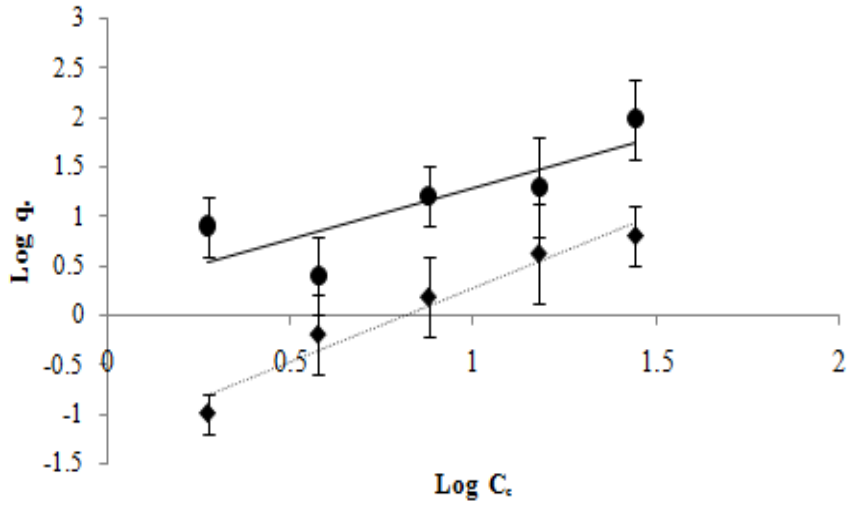

Figure 7. Freundlich adsorption isotherm at 293 °K.

The effect of temperature on the adsorption of heavy metals on n-HapCMC was investigated by conducting experiments for 100 mg/L of initial metals ion concentrations at 293, 303, 308, 313, and 318 °K. It was observed that on increasing the temperature percentage removal of heavy metals increased. This showed that the adsorption process was endothermic in nature.

The thermodynamic parameters Gibb's free energy (ΔG°), enthalpy (ΔH) and entropy (ΔS°) were calculated using the following equations:

$$ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta s^0}{R} + \frac{-\Delta H^0}{RT} \quad (13)$$

$$\Delta G^0 = \Delta H - T\Delta S^0 \quad (14)$$

Where m is the adsorbent dose (g L^{-1}), C_e is concentration of metals ion (mg L^{-1}), q_e is the amount of metals ion at equilibrium in unit mass of adsorbent (mg g^{-1}), q_e/ C_e is called the adsorption affinity. ΔH, ΔS° and ΔG° are change in enthalpy (kJ mol^{-1}), entropy (J $(mol\ K)^{-1}$) and free energy (kJ mol^{-1}), respectively. R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

The values of ΔH and ΔS° were obtained from the slopes and intercepts of the Van't Hoff plots of ln (q_em/ C_e) vs. 1/ T, respectively, thereafter ΔG° values were determined from Eq. (13). The values of thermodynamic parameters are presented in Table 5. The results showed that the ΔG° values are negative and increased in their absolute values with temperature [13].

Table 5
Thermodynamic parameters for adsorption of Cr (III) on n-HApCMC and n-Hap.

	ΔH° (kJ/mol)	**ΔS° (Jmol/K)**	**- ΔG° (kJ/mol)**				
			293 °K	**303 °K**	**308 °K**	**313 °K**	**318 °K**
n-HAp	42.769	171.759	8.415	9.273	10.132	10.991	11.850
n-HApCMC	57.823	223.871	8.890	10.001	11.129	12.248	13.368

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This result suggested that a high temperature is favoured for the adsorption of heavy metals on n-HapCMC composite, indicated a spontaneous adsorption process. The values of heat of adsorption, ΔH is positive for metals ion, indicated that the adsorption process of heavy metals on n-HapCMC composite was endothermic. A positive ΔS suggested that heavy metals were not stable on the adsorption sites of n-HapCMC composite probably due to the increase in translational energy of metals ion.

Conclusion

This study showed that the binding of nano-HAp powder with cellulose makes it convenient to use practically and its removal capability was also retained in n-HApCMC which makes n- HApCMC composite as an effective adsorbent for the removal of Cr(III) from aqueous solution. Taguchi statistical method as an efficient, effective, and without the need for a large number of experiments indicated that the Hydroxyapatite/ Carboxymethyl Cellulose nanocomposite as a new adsorbent, no cost, and without secondary pollutant has a high efficiency for Cr(III) removal from aqueous solution. The adsorption process followed pseudo-second-order kinetics and obeyed Langmuir adsorption isotherm for metal ions studied. The negative values of ΔG° suggested that the adsorption was spontaneous in nature. The positive value of ΔH and ΔS indicated endothermic adsorption process and increased randomness at surface–solution interface, respectively.

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