Adsorptive Removal of Mercury by Using New Nano Adsorption

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Abstracts In the present work nano-hydroxyapatite/Carboxymethyl Cellulose (n-HApCMC) composite was synthesized by precipitation method and was characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) crystallography and scanning electron microscopy (SEM). The n-HApCMC composite was tested for the adsorption of Mercury from aqueous solution and compared its removal capacity with nano-hydroxyapatite (HAp). Effect of various physico-chemical parameters such as pH, adsorbent dose, contact time, initial metal ion concentration and temperature on adsorption of metal ions onto n-HApCMC composite was investigated. The adsorption process followed pseudo-second order kinetics and intra-particle diffusion model. 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

1. 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. The selective removal of industrial heavy metals from liquid waste is consequently the subject of considerable ecological and economic interest [1]. Heavy metal ions, aromatic compounds (including phenolic derivatives, and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses. Wastes containing soluble toxic heavy metals require concentration of the metals into a smaller volume followed by recovery and secure disposal. Heavy metals can be removed by adsorption on solid matrices.

Mercury (Hg) emissions from waste incineration are a global problem, indicated by that nearly half of the Hg

emissions reaching the Arctic originates from waste incineration [9]. In most countries, the total Hg emissions from waste incineration are largely underestimated because of poor knowledge about Hg content in wastes and due to economic reasons there are no or only limited analyses available on Hg content in flue gases from a majority of the waste incineration plants in operation [10].

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAp) is a main mineral constituent of teeth, bones and phosphate mineral rocks. It belongs to apatite mineral family. HAp was shown to be efficient for the removal of many toxic metal ions such as lead, cobalt, nickel, copper, zinc, cadmium and uranium in aqueous solutions [2], [4], [8], [11], [12], [14]. 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 [3]. Cellulose, the most abundantly available carbohydrate polymer in nature, is continually replenished by the photosynthetic reduction of CO_2 catalyzed by sunlight—a mechanism that is highly beneficial in mitigating environmental problems resulting from increased atmospheric CO_2 . The annual net yield of photosynthesis is 1.8 trillion tonnes of biodegradable substances, about 40% of which is estimated to be cellulose [13]. 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/Carboxymethyl Cellulose (n-HApCMC) were prepared and used for the removal of Hg (II) 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 Hg (II) removal was proposed.

2. Experimental

2.1. Materials

Carboxymethyl cellulose (CMC) provided by Floka company whose molecular weight is about 4.2×10^8 , potassium dichromate, calcium nitrate, Ammonium dihydrogen phosphate, ammonia were purchased from Merck (Germany) and all other chemicals used were of analytical.

2.2. Methods

2.2.1. Synthesis of Nano-Hydroxyapatite/ Carboxymethyl Cellulose (N-Hapcmc) Composite

n-HAp was synthesized by the reaction of calcium nitrate and ammonium dihydrogen phosphate at a stoichiometric Ca/P ratio of 1.67, with the pH value during mixing, being maintained maintained 10–11 by the addition of ammonia solution. The resulting precipitate was rinsed with water until the wash water was neutral and then dried at 80°C [7]. The corresponding n-HAp/CMC composites were prepared by the precipitation method. The aqueous solution of Ammonium dihydrogen phosphate was added to the mixture of aqueous solution of $\text{Ca}(\text{NO}_3)_2$ with CMC 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 80°C to get n-HApCMC composites.

2.2.2. Characterization of Materials

Characterization -n-HApCMC and its structural and morphological analysis by SEM, XRD and FTIR techniques. The phases present in the magnetic materials were analyzed using a powder X-ray diffract meter (XRD) Philips (Holland), model X' Pert with $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$), and the X-ray generator was operated at 40 KV and 30 mA. Diffraction patterns were collected from $2\theta = 10^\circ$ – 50° .

Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Perkin Elmer) with a spectral resolution of 4 cm^{-1} in the wave number range of 500 – 4000 cm^{-1} . The samples and KBr were fully dried before the FT-IR analyses to exclude the influence of water.

Scanning electronic microscopy (SEM), the morphology of the surface of -n-HApCMC was investigated using a scanning electronic microscope of XL30 type (Netherlands). The catalyst was covered with pure metallic Ag. The laying down of Ag was carried out using evaporation of the metal under a high vacuum, to give a thickness of around $100 \text{ \AA}$.

pH adjustments were made with digital pH-meter (Sartorius, Model PP-20) using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). Mercury content in each experiment were determined with flame atomic absorption spectrophotometer (Perkin Elmer, Analyst 100).

3. Results and Discussions

3.1. Characterization of Materials

The 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-} [7], 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 [5]. 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 characteristics of n-HAp, n-HApC and n-HApCs composites are shown in Fig. 2. In the XRD pattern of n-HAp, the crystalline peaks at $2\theta = 25.9^\circ$, 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 $2\theta = 32^\circ$ and 46° can be found. n-HAp at $2\theta = 26^\circ$, 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.

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)

3.2. Adsorption Isotherms

The adsorption isotherms were obtained by employing 200 mg of n-HApCMC composite and 25 mL of Waste solution with different concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 $\mu\text{g mL}^{-1}$). These solutions were stirred in a mechanical shaker until they reached adsorption equilibrium. The system was shaken for 90 min and then both phases were separated by filtration. The metal content of the filtrate was determined by atomic spectrometry. Fig. 4 shows equilibrium adsorption isotherm of Hg(II) on n-HApCMC composite at 298 °K. The equilibrium adsorption density q_e is increased with the increase in Hg(II) concentration. At low equilibrium heavy metals concentrations C_e , the equilibrium adsorption densities q_e of the n-HApCMC composite reach almost the same q_e as those at high equilibrium Hg(II) concentrations. It indicates that n-HApCMC composite have high adsorption density even at low equilibrium Hg(II) concentrations. Fig. 4 shows the effect of heavy metals concentration on n-HApCMC composite adsorption. An increase in initial concentration of heavy metals led to an increase in the adsorption capacity of heavy metals on n-HApCMC composite.

Figure 4. Equilibrium adsorption isotherm of Hg (II) on n-HApCMC

This indicates that the initial concentration of heavy metals played an important role in the adsorption capacity of heavy metals on adsorbent. The dotted lines in Figs. 5 and 6 represent a linear regression fit to the results for both isotherms. However, since adsorption data are of a nonlinear nature, nonlinear regressions are also performed on each set of data points. These nonlinear regression fits are represented as solid lines in Figs. 5 and 6.

Figure 5. Freundlich adsorption isotherm at 298 °K

Figure 6. Langmuir adsorption isotherm at 298 °K

The correlation coefficients obtained with both kinds of regression for both adsorption isotherms are summarized in Table 1. The correlation coefficient values in Table 1 indicate that the data fit the Langmuir isotherm better than the Freundlich isotherm, both in case of linear and nonlinear regression.

Table 1. Freundlich and Langmuir adsorption isotherm constants

Metal ions	Langmuir constants			Freundlich constants		
	Q° (mg/g)	b (L/ mg)	R^2	K_F (L/mg)	n	R^2
Hg (II)	9.03	0.276	0.998	2.13	1.82	0.997

3.3. pH Optimization

The removal of Hg(II) at different pH was studied in batch mode. A 25-ml of test solution of fixed concentrations was treated with 200mg of n-HapCMC composite and agitated intermittently for 45 min. The contact time and conditions were selected on the basis of preliminary experiments, which demonstrated that equilibrium was established in 45 min. After this period the solution then both phases were separated by filtration. The metal content of the filtrate was determined by atomic spectrometry. The metal concentration retained in the sorbent phase (q_e , mg/g) was calculated by using Eq. (1)

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Figure 7. Effect of pH on adsorption of Hg (II) on n-HapCMC

Where C_0 and C_e are the initial and final (equilibrium) concentrations of the metal ion in solution (M), V the solution volume (l) and m is the mass of n-HapCMC

composite (g). To study the effect of pH on adsorption, experiments were carried out in the pH range 1–9 for Hg(II). Fig. 7 shows that the removal of metal ions was increased with increasing initial pH of metal ion solution and maximum value was reached at 5-6 for Hg(II).

3.4. Kinetic Modeling in a Batch System

In order to investigate the mechanism of adsorption kinetic models are generally used to test experimental data. Pseudo-first-order and pseudo-second-order equations can be used assuming that the measured concentrations are equal to surface concentrations. The pseudo-first-order rate Lagergren model is:

$$\frac{dq}{dt} = k_{1,ads} (q_e - q) \quad (2)$$

Where q (mg/g) is the amount of adsorbed heavy metals on the adsorbent at time t and $k_{1,ads}$ (min^{-1}) is the rate constant of first-order adsorption. The integrated form of Eq. (2) is:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}}{2.303} t \quad (3)$$

q_e the equilibrium sorption uptake, is extrapolated from the experimental data at time $t = \text{infinity}$. A straight line of $\log(q_e - q)$ versus t suggests the applicability of this kinetic model. q_e and $k_{1,ads}$ can be determined from the intercept and slope of the plot, respectively. The pseudo-second order kinetic model is expressed as:

$$\frac{dq}{dt} = k_{2,ads} (q_e - q)^2 \quad (4)$$

Where $k_{2,ads}$ (g/mg min) is the rate constant of second-order adsorption. The integrated form of Eq. (4) is:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_{2,ads} t \quad (5)$$

Eq. (5) can be rearranged and linearized to obtain:

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{1}{q_e} t \quad (6)$$

The plot t/q versus t should give a straight line if second order kinetic model is applicable and q_e and $k_{2,ads}$ can be determined from the slope and intercept of the plot, respectively. It is important to notice that for the application of this model the experimental estimation of q_e is not necessary.

3.5. 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 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;

$$q_e = K_f (C_e)^{1/n} \quad (7)$$

This equation is conveniently used in the following linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (8)$$

Where K_f is Freundlich isotherm constant (L/g) 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:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (9)$$

Where q_e is the amount adsorbed at equilibrium (mg/ g), C_e the equilibrium concentration (mg/ L), b a constant related to the energy or net enthalpy of adsorption (L/ mg), and Q^0 the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/ g). 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:

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

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:

$$R_L = \frac{1}{1 + b C_0} \quad (11)$$

Where b is the Langmuir constant and C_0 the initial heavy

metals concentration (mg/L). R_L value indicates the type of isotherm. According to [6]. 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. Fig. 8.

Figure 8. Pseudo-second-order kinetic model fitting for Hg (II) adsorption on n-HapCMC

The effect of temperature on the adsorption of heavy metals on n-HapCMC was investigated by conducting experiments for 30 mg/L of initial metals ion concentrations at 298, 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:

$$\ln \left(\frac{q_e m}{C_e} \right) = \frac{\Delta S^\circ}{R} + \frac{-\Delta H^\circ}{RT} \quad (12)$$

$$\Delta G^\circ = \Delta H - T \Delta S^\circ \quad (13)$$

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

Table 2. Thermodynamic parameters for adsorption of Hg (II) on n-HapCMC

Metal ions	ΔH° (kJ/mol)	ΔS° (Jmol/K)	$-\Delta G^\circ$ (kJ/mol)				
			298 °K	303 °K	308 °K	313 °K	318 °K
Hg (II)	42.769	171.759	8.415	9.273	10.132	10.991	11.850

The values of ΔH and ΔS° were obtained from the slopes and intercepts of the Van't Hoff plots of $\ln (q_e/m/ C_e)$ vs. $1/T$, respectively, thereafter ΔG° values were determined from Eq. (12). The values of thermodynamic parameters are presented in Table 2. The results showed that the ΔG° values are negative and increased in their absolute values with temperature. 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.

4. Conclusions

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 Hg (II) from aqueous solution.

The adsorption process followed pseudo-second-order kinetics and obeyed Langmuir adsorption isotherm for metals ion 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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