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Study of removal process of manganese using synthetic calcium hydroxyapatite from an aqueous solution

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ABSTRACT

Calcium hydroxyapatite (HAP) was synthesized by a precipitation method, and it was characterized by the XRD technique. The removal of manganese(II) from an aqueous solution on HAP as a function of contact time, pH, ionic strength, temperature, and other monovalent and bivalent ions was studied using a radiotracer, ^{54}Mn, in the batch process. The sorption of manganese on HAP was pH independent ranging from 4 to 6 due to the buffering properties of HAP. The sorption of manganese was rapid, and the percentage of manganese sorption was 99% during the first 20–30 min of the contact time, *when the initial concentration of manganese ions was 1 mg/L (ppm) at pH of 5.* The sorption kinetics showed that the sorption of manganese on HAP could be simulated by the pseudo-second-order kinetic model very well. The maximum sorption capacity of HAP for manganese calculated based on the Langmuir model was ~58.99 mg/g at pH 5.1 and $T = 300$ K. The thermodynamic parameters from the temperature-dependent sorption isotherms indicated that the manganese sorption on HAP was an endothermic and spontaneous process. It was observed that in the presence of bivalent ions like Co^{2+}, the manganese sorption by HAP decreases, whereas it remains same in the presence of monovalent ions like Na^+.

Keywords: Hydroxyapatite; Sorption; Manganese(II)

1. Introduction

With continuous increase in the number of nuclear reactors around the world, the amount of radioactive heavy metals produced also increases in different kinds of nuclear wastes. Radioactive manganese (^{54}Mn) is among the heavy metals produced in the structural and clad materials of fast breeder nuclear reactors due to the high-energy neutron flux encountered in the core. In sodium cooled fast breeder reactors, during routine cleaning of reactor components, ^{54}Mn, an activation product of iron is removed from the components resulting in liquid alkaline waste in the form of aqueous solution of sodium carbonate and

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sodium bicarbonate where sodium concentration is around 2.1 g/L [1]. Both radioactive as well as the inactive manganese have significant influences on our environments. ^{54}Mn has a half life of 312.5 d and gamma energy of 835 keV. Manganese in aqueous solutions can affect both human beings and the aquatic life [2]. High concentration of manganese in human beings can cause brain damage and neural problems [3]. Hence, it is necessary to eliminate the toxic heavy metal ions from wastewater before it is released into the environment. Traditional techniques for the removal of heavy metal ions include chemical precipitation [4], membrane filtration [4,5], sorption on activated carbon [6], ion exchange [7], etc. Among these methods, sorption technique has been used widely, because they offer better volume reduction factor, which is the ratio of initial volume to the final volume, compared to that of chemical treatment methods and are more economical than evaporation methods [8].

Inorganic materials are preferred over organic resins due to some of their interesting properties such as resistance to high radiation as well as high selectivity [9]. There are some inorganic sorbents which are used for the removal of manganese such as kaolinite [10], fly ash [11], carbon nanotube [12], thermally decomposed leaf [13], marble [14], dolomite [14], granular-activated carbon [15], Na–montmorillonite [16], clinoptilolite–Fe system [17], clinoptilolite from Greece [17], etc. However, these materials suffer from either low sorption capacities or efficiencies as shown in Table 1. Hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$, is a member of apatite mineral family. Compared to other heavy metals, little attention has been paid so far on manganese removal by synthetic HAP. The objectives of this work were to (a) synthesize calcium HAP and apply it as sorbents to remove Mn(II) ions from aqueous solutions; (b) investigate the effects of pH, contact time, and manganese concentration on Mn(II) sorption; and (c) study the effect of Co(II) as well as Na(I) ions on Mn(II) sorption.

Table 1
Manganese ions adsorption capacity for different materials

Material	Mn uptake (mg/g)	References
Kaolinite	0.446	[10]
Fly ash	0.2	[11]
Carbon nanotube	0.51	[12]
Thermally decomposed leaf	66.57	[13]
Dolomite	2.21	[14]
Marble	1.20	[14]
Granular-activated carbon	2.54	[15]
Na–montmorillonite	3.22	[16]
Clinoptilolite–Fe system	27.12	[17]
Clinoptilolite from Greece	7.69	[17]
Synthetic HAP	58.9	Our study

2. Experimental

2.1. Reagents

All the chemicals used were of analytical reagent grade pure materials and used without further purification. The radioisotope ^{54}Mn obtained from Board of Radiation and Isotope Technology, India was used as a radiotracer.

2.2. Synthesis and characterization of HAP

The HAP was synthesized by a precipitation technique using calcium hydroxide, $Ca(OH)_2$ and orthophosphoric acid, H_3PO_4 in air [18]. The white precipitate so formed was washed thoroughly with distilled water, and then it was heated up to 500°C in a furnace. Finally, the solid was sieved to obtain the powder having a particle size of <75 μm. This powder was used for further characterization and experimental studies. The material was characterized by XRD, Siemens D-500 diffractometer. The zero point charge (pH_{zpc}) of HAP was determined by the batch equilibration method using 0.1 mol/dm^3 KNO_3 as an inert electrolyte.

2.3. Sorption studies

The Mn(II) stock solution (50 ppm) was prepared by dissolving manganese sulfate monohydrate, $MnSO_4 \cdot H_2O$, in distilled water. All the sorption experiments were carried out by the batch process using ^{54}Mn as a radiotracer in such a way that the initial gamma activity of the solution became 40–45 Bq/mL. For this, each of 100 mL aliquots of manganese-containing solutions were transferred into 250 mL glass beakers, and 1 g of sorbent was added into each solution. The beakers were placed in a rotary shaker (50 rpm), and shaken until equilibrium was reached. Small aliquots of the supernatants were taken after filtration from the beaker after each 10 min of shaking. The aliquots were analyzed for their gamma activities using Single Channel Analyzer supplied by the Electronics Corporation of India Limited, India.

2.4. Effect of contact time

The influence of contact time on the manganese removal was analyzed from 10 min to 2,500 min with the concentration of manganese ions in aqueous phase 50 ppm at 298 K. The initial pH was adjusted approximately to pH 5 with nitric acid.

2.5. Effect of pH

Sorption behavior of manganese was studied as a function of pH of the manganese solution. The initial pH of the manganese solution was adjusted from 2 to 8 using nitric acid or sodium hydroxide solutions. For each sorption experiment, 20 ppm of initial manganese concentration and 1 g of adsorbent were used at 298 K. The pH of the solutions was measured using the Eutech Instruments pH 510, before the experiment (initial pH) and after the interaction of HAP with the solution at the equilibrium time (final pH).

2.6. Isotherm studies

Sorption experiments were carried out using a solution of manganese ions with different manganese initial concentrations ranging from 5 to 100 ppm at 298 K. The amount of manganese ion sorbed on the sorbent, and Q_e(mg/g) was calculated from the following equation:

$$Q_e = (C_o - C_e)V/W \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of manganese ions in solution; V is the volume; and W is the weight of the sorbent.

2.7. The effect of temperature

The sorption experiments were studied at 288, 298, 308, and 318 K. In all the experiments, 100 mL of 20 ppm manganese solutions were taken with 1 g of adsorbent at pH 5.2.

2.8. Effect of Co(II) and Na(I) ions

Effect of bivalent cation, Co(II) and monovalent ion, Na(I) on the sorption of manganese was studied with Mn concentration of 20 ppm, while the concentrations of competitive ions were in the range from 10 to 100 ppm at pH 5.3 and 298 K.

3. Results and discussion

3.1. HAP characterization

The XRD spectra of synthetic HAP and manganese-doped HAP indicated that both materials were crystalline as shown in Fig. 1 which suggests that on Mn sorption, the apatite structure remains same. The diffraction patterns of the synthetic HAP compared favorably with the JCPDS cards for HAP. The TGA as well as the FT-IR spectra of HAP was already discussed in our previous study [19]. The observed specific surface area of HAP was obtained around 50 m^2/g, and the zero point charge (pH_{zpc}) was 6.1.

As discussed in our earlier studies [19], the SEM image of the synthetic HAP shows that the surface is heterogeneous indicating the presence of some amorphous matter also. The composition of HAP was analyzed by the energy dispersive X-ray spectroscopy, and it was found that the Ca/P ratio in the HAP samples was 1.60 instead of 1.67 characteristic for stoichiometric

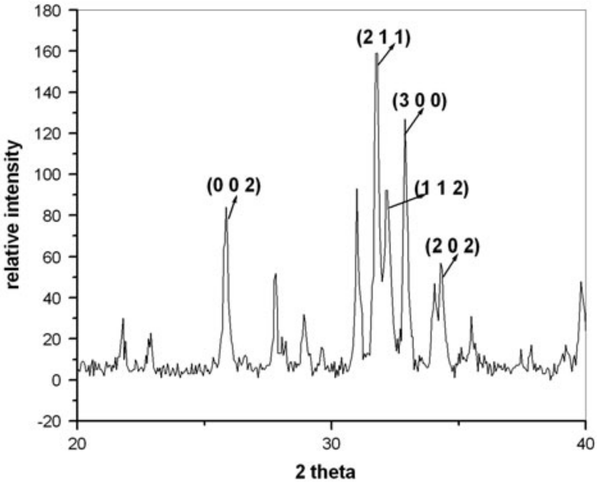

Fig. 1(a). XRD spectra of synthesized hydroxyapatite.

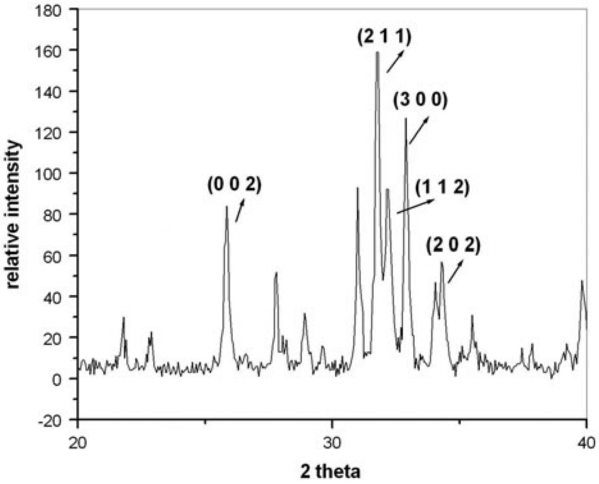

Fig. 1(b). XRD spectra of manganese loaded hydroxyapatite.

HAP which was also verified by the ICP-AES technique (JY Ultima C ICP-emission spectrometer). The slight calcium deficiency may be due to the incomplete reaction between the reactants.

3.2. Effect of contact time

Fig. 2 shows the sorption of manganese ions on HAP under different time intervals. It is seen that the sorption of manganese ions on HAP increases very sharply within 4 h of contact time. It reaches the equilibrium in around 15 h. Initially, Mn(II) ions preferentially occupied many of the active sites of HAP in a random manner; hence, the sorption rate was fast. After some time, most of the active sites were occupied, so rate became slow in the later stages and finally reached a plateau region which showed that no further removal of Mn(II) ions by HAP.

There are different models which can be used to find out the kinetics of the sorption processes (e.g. first-order, pseudo-first-order, and pseudo-second-order reaction models). In our studies here, the pseudo-first-order and pseudo-second-order reaction models were applied to our experimental data to know the sorption rate constant at room temperature. The pseudo-first-order rate equation [20] is expressed as:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (2)$$

where q_e and q_t (mg/g) are the amount of manganese ions sorbed on HAP at equilibrium and time t, respectively; and k_1 is the pseudo-first-order rate constant (min^{-1}). From the slope and intercept of the plot of log (q_e–q_t) vs. t, the first-order rate constant (k_1) and theoretical equilibrium sorption capacities (q_e) were determined, respectively. But the corresponding value of correlation factor (R) for this was found to be very low, and hence is not shown here.

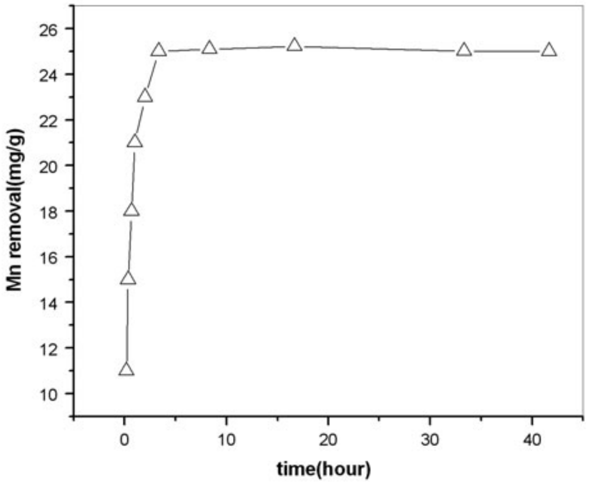

Fig. 2. Effect of time on Mn removal.

The linear form of pseudo-second-order rate expression [20] is:

$$t/q_t = 1/k^{2'}q_e^2 + 1/q_e t \quad (3)$$

where q_e and q_t are the amounts of solute sorbed at equilibrium and time t (mg/g), and $k^{2'}$ is the equilibrium rate constant of pseudo-second-order (g/mg min) equation. As shown in Fig. 2, the sorption of manganese by HAP occurs in two different steps. The first step is the relatively fast sorption and the second step is the slow sorption.

As shown in Fig. 3, the plot of t/q_t vs. t gives a straight line. From the slope of the line, the amount of solute sorbed on HAP was calculated and is given in Table 2. The calculated and experimentally found amounts of solute (Mn^{2+}) sorbed on HAP at equilibrium are 25.22 and 25.13 mg/g, respectively. From the Table 2, it can be concluded that the

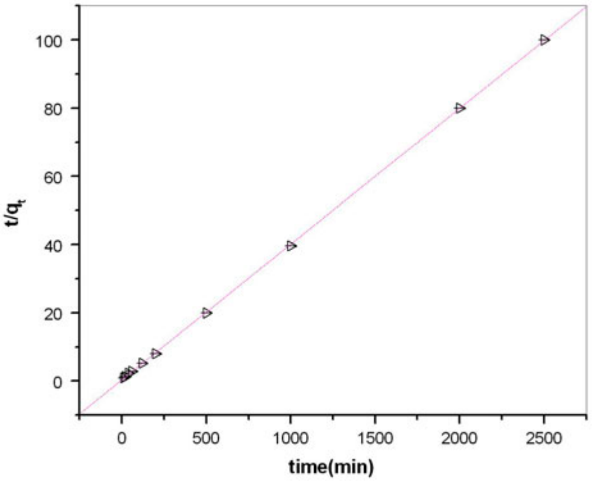

Fig. 3. Linear fit of experimental data using pseudo-second-order kinetic model.

Table 2
The calculated parameters of second-order kinetic model

kinetic model	q_e (mg/g) (cal)	$k^{2'}$ (g/mg min)	R	q_e (mg/g) (exp)
Pseudo-second-order	25.13	4.52×10^{-3}	0.999	25.22

pseudo-second-order sorption describes the sorption of manganese ions on HAP.

The pseudo-second-order model is based on the assumption that the rate-limiting step may be the process of chemisorptions and not the physical sorption [21,22].

3.3. The effect of solution pH

The pH of the solution is one of the most important variables that affect the metal sorption on the sorbent. Fig. 4 shows the effect of pH on the sorption of manganese ions on HAP. If no specific sorption from the solution occurs, acidic and alkaline solutions as reported in the literature (in the initial pH range 4–10) are buffered after the reaction with HAP to its pH_{PZC} value [23]. In the present case, due to the presence of manganese ions in the solution, the pH range has reduced to 4–6 because from pH 6 onwards manganese ions (in solution) started precipitating out from the solution. This was verified by conducting the same experiment without HAP. In the absence of HAP, it was observed that at pH 6, manganese ions started settling down as a precipitate. The figure indicates that between pH 4 and 6, there was almost the same amount of manganese ions removed by HAP. After pH of 6, the removal of manganese increases instantly. This may be due to the precipitation of Mn as its hydroxides and not due to the sorption on HAP.

3.4. Isotherm studies

The sorption of manganese as a function of different manganese concentrations (5–100 ppm) was studied at 298 K, and the results are shown in Fig. 5. It is observed that with increasing manganese concentration, the removal of manganese by HAP also increases until the equilibrium reached. On the other hand, the percentage of removal is higher in diluted manganese solutions as shown in Fig. 5. This is due to the fact that there will be more number of active sites per gram of the sorbent available at higher dilution.

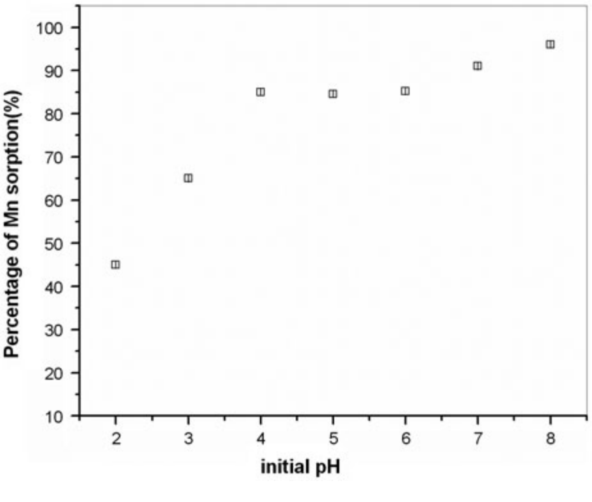

Fig. 4. Effect of pH of solution.

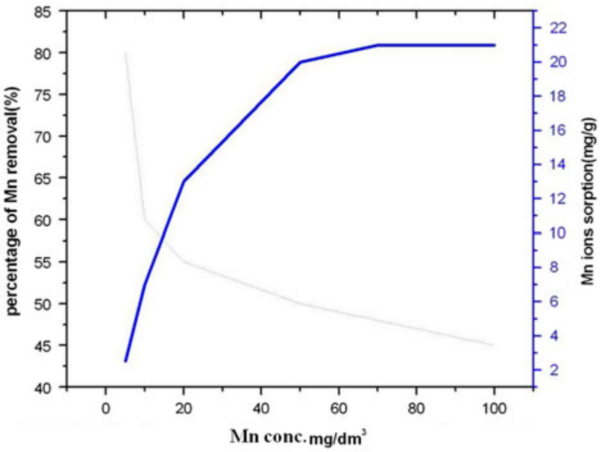

Fig. 5. Relationship between equilibrium metal concentration, amounts of Mn^{2+} sorbed (solid line), and percentage of Mn removal (dash line).

The Langmuir and Freundlich models are used here to describe the equilibrium sorption isotherms.

The Langmuir equation can be written as [24,25]:

$$C_e/Q_e = 1/X_m K + 1/X_m C_e \tag{4}$$

where Q_e (mg/g) and C_e (mg/dm^3) denote the equilibrium concentrations of sorbate in the solid and the liquid phase, respectively; X_m (mg/g) is the maximum sorption capacity; and K (dm^3/g) is the Langmuir constant related to the energy of adsorption. A linearized plot (Fig. 6) of C_e/Q_e vs. C_e will give the values X_m and K.

The Freundlich model can be expressed by the following equation [26]:

$$\log(q_e) = \log(K_f) + 1/n \log(C_e) \tag{5}$$

where q_e (mg/g) is the total amount of manganese ions sorbed per unit weight of HAP at equilibrium; C_e (mg/L) is the concentration of the manganese ions in the solution at equilibrium; K_f is the equilibrium constant indicative of sorption capacity; and n is an empirical constant. K_f and $1/n$ can be determined from the linear plot (Fig. 7) of log (q_e) against log (C_e). The calculated values of Langmuir and Freundlich

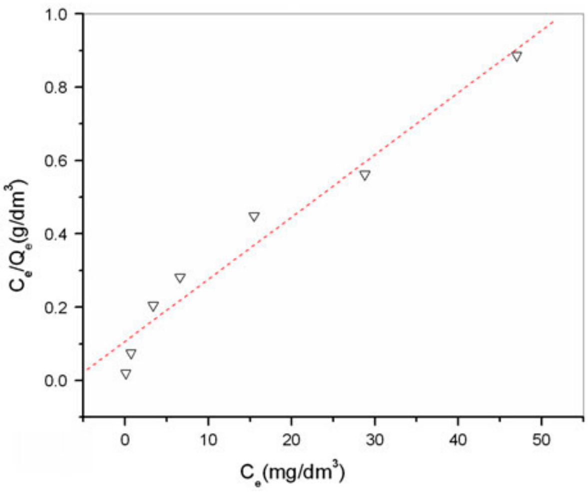

Fig. 6. Linear fit of experimental data using Langmuir isotherm.

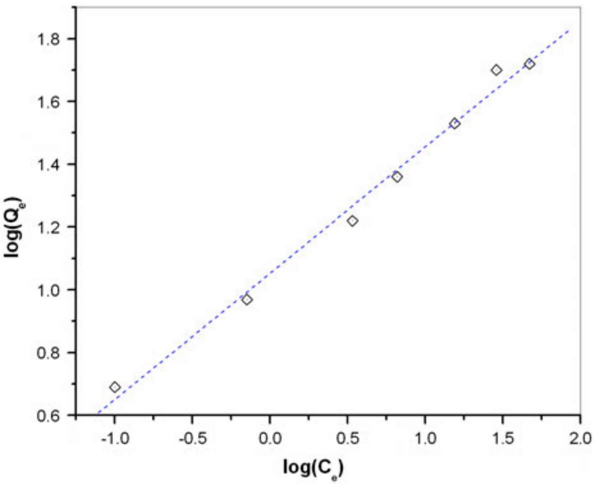

Fig. 7. Linear fit of experimental data using Freundlich isotherm.

constants are shown in Table 3. It is seen from the table that the sorption of manganese ions on HAP correlated well ($R = 0.995$) with the Freundlich equation as compared to the Langmuir equation under the concentration ranges studied.

Table 3
Parameters of the Langmuir and Freundlich isotherm models

Langmuir	Freundlich
X_m (mg/g): 58.99	$1/n$: 0.40192
K (dm^3/g): 0.1584	K_f: 11.30 (L/g)
R: 0.978	R: 0.995

3.5. Thermodynamic studies

The distribution coefficients (K_d) of manganese on HAP could be described as:

$$K_d = (C_0 - C_e)/C_e \times (V/m) \tag{6}$$

where C_0 and C_e are the initial and equilibrium concentrations of manganese ions in solution (mg/L); V is the volume of the solution (mL); and m is the mass of the sorbent (g).

The variation of ln K_d with inverse temperature, $1/T$, gives a straight line as shown in Fig. 8 by the following equation:

$$\ln K_d = (-\Delta H^\circ/RT) + (\Delta S^\circ/R) \tag{7}$$

where K_d is the distribution coefficient (mL/g); ΔS° is the standard entropy (kJ mol^{-1} K^{-1}); ΔH° is the standard enthalpy (kJ mol^{-1}); T is the temperature in K; and R (8.314 J mol^{-1} K^{-1}) is the universal gas constant. From the slope and intercept of the straight line in Fig. 9, the values of ΔH° and ΔS° are calculated, respectively.

On the other hand, the free energy of sorption, ΔG°, is calculated by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

The values of ΔG°, ΔH°, and ΔS° are given in Table 4. As shown in the table, the positive value of ΔH° (53.42 kJ mol^{-1}) indicates that the sorption of

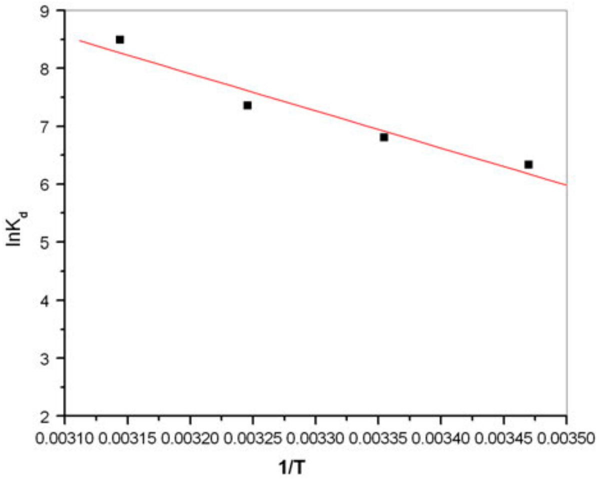

Fig. 8. Effect of temperature on distribution coefficient (K_d).

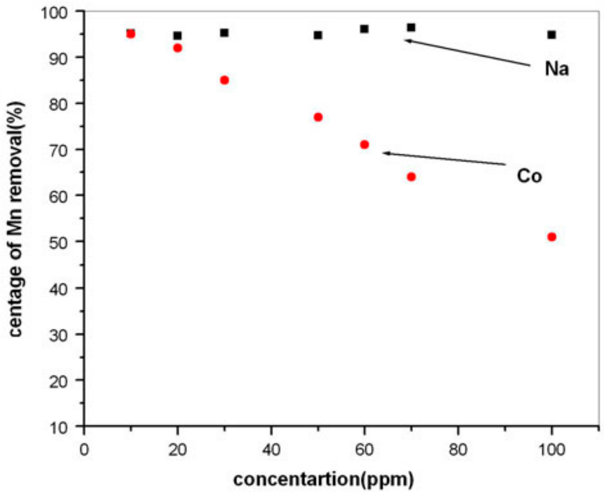

Fig. 9. Effect of Co(II) and Na(I) ions on sorption properties of HAP on Mn(II).

Table 4
Thermodynamic parameters for Mn(II) sorption onto HAP

ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1})	ΔG° (kJmol^{-1})			
		288 K	298 K	308 K	318 K
53.42	0.236	−14.55	−16.91	−19.27	−21.62

manganese ions on HAP is an endothermic process. The negative values of ΔG° at different temperatures indicate that the sorption on manganese on HAP is a spontaneous process. The decrease in ΔG° value with increase in temperature shows that with an increase in temperature of the system, the sorption of manganese by HAP will also increase. Similarly, the positive value of ΔS° indicates that the degree of randomness increases with sorption i.e. with sorption of manganese ions on HAP from an aqueous solution, the loss of hydrated water molecules previously attached with manganese ions also will be more.

3.6. Effect of Co(II) and Na(I) ions

It is observed that (Fig. 9), in the presence of bivalent ion such as Co(II), the sorption of manganese ions on HAP decreases as cobalt ions are also sorbed along with manganese. As a result, there will be fewer sites available for manganese, so sorption decreases. On the other hand, in the presence of monovalent ions like Na(I), the sorption of manganese by HAP is not at all affected. This is due to the solubility of sodium phosphate, whereas cobalt phosphate like other divalent phosphate is insoluble in aqueous solution.

4. Conclusion

In the present investigation, sorption of Mn(II) on synthetic HAP was studied as a function of contact time, pH, ionic strength, temperature, and other monovalent and bivalent ions. The experiments have shown that:

(1) The kinetic study demonstrated pseudo-second-order kinetic rather than pseudo-first-order kinetics for Mn(II) sorption on synthetic HAP. The contact time of approximately 15 h was required to reach the equilibrium.
(2) The sorption of Mn(II) on HAP can well be defined by the Freundlich equation as compared to the Langmuir equation under the concentration ranges studied. The maximum sorption capacity of HAP for Mn(II) calculated based on the Langmuir model was ~58.99 mg/g at pH 5.1 and $T = 300$ K.
(3) The sorption of Mn(II) on HAP was pH independent ranging from 4 to 6 due to the buffering properties of HAP. After pH of 6, the sorption of manganese increases instantly, which is due to the precipitation of Mn as its hydroxides.
(4) The XRD results show that on Mn sorption, the structure of apatite remains same.
(5) Presence of Co(II) in Mn(II) aqueous solutions affects the sorption of Mn(II) on HAP. On the other hand, Na(I) ions are not having any influence on it.

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