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Temperature effect on the mechanism of phosphate anions sorption by β-MnO_2

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Abstract

Phosphate anions excess in stored water reservoirs are known to stimulate algal growth and scaling in vessels used for cooling purposes in industries. Several techniques such as ion exchange, adsorption on activated carbon, chemical precipitation and reverse osmosis have been used for its removal. The use of inorganic ion exchangers like oxide/hydroxides has been preferred recently due to their stability at high temperature, to ionizing radiations and high selectivities for specific anion and cations.

In the present investigation phosphate sorption on β-MnO_2 is studied as function of concentration ($1.07–11.85 \times 10^{-1}$ mmol L^{-1}) and temperature (293–313 K) at three different pH values of 3, 5 and 7. The sorption of phosphate is found to decrease with the increase in temperature in the pH range 3–7. Freundlich equation derived from the Law of mass action equation was found applicable to the sorption data. Effect of background electrolyte concentration and FTIR studies showed that mechanism of uptake process was the formation of outer-sphere complexes at all the temperatures under investigation. The thermodynamic parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ values along with isosteric heats of adsorption were calculated, which showed that the solid preferred the multiply charged phosphate at low temperature and pH.

Keywords: β-MnO_2; Point of zero charge; Adsorption; Freundlich isotherm; Surface complexation; Isosteric heat

1. Introduction

Water is a prime need for human survival and industrial development. Effective management of water resources and control of pollution are becoming increasingly important for substantial development and human welfare. With the continuous growth in population, urbanization, industrialization and transportation, the number and amount of the environmentally damaging chemicals and toxic substances entering the biosphere have increased steadily, particularly during the last two decades.

Phosphate anions concentration exceeding about 2 μM in water reservoirs are known to stimulate algal growth (eutrophication), reducing the dissolved oxygen in aqueous environment, which not only kills the aquatic life but also disrupts the natural food chain [1,2]. Besides, the phosphate pollution also causes scaling in vessels used for cooling purposes in industries [3]. It enters the natural waters from various fertilizers industries, domestic sewage, laundries, running water over phosphate rocks and extensive application of manure and fertilizers to soils. The run off from all these sources finds their way to water bodies [2]. It is therefore of the major concern to adopt an effective method for the removal of phosphate from natural aquatic system.

Oxide/hydroxides of aluminum, iron and manganese and other important inorganic ion exchangers are naturally occurring discrete minerals and are mostly used in various processes such as water treatment, nutrient recovery and various engineering processes [4,5]. A number of these inorganic ion exchangers have been employed in the literature to study the sorption of various oxyanions anions like chromate, arsenate and selenate, etc. These researchers used the oxides of iron, aluminum and manganese to study the sorption of chromate, arsenate, selenate and selinite which are thoughts to be toxic in elevated levels both to plants and animals [6–10].

Phosphate in the soil environment is found to be fixed upon organic matter, oxides/hydroxides of aluminum, iron and manganese [11,12]. While a number of studies have been reported in the literature about the phosphate anions sorption upon iron and aluminum oxides/hydroxides [12–15], very little is reported about their interaction with oxides/hydroxides of manganese [16]. The present study therefore takes care of phosphate uptake

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by oxide of manganese (β-MnO_2) as a function of temperature using three different initial pH values of 3, 5 and 7.

2. Experimental

2.1. Reagents

All reagents used were analytical grade. The solutions were prepared in doubly distilled water. KH_2PO_4 supplied by MERCK was used without further purification. Similarly, nitric acid, potassium hydroxide solutions having concentrations 0.1, 0.5 and 1 M and standard buffers of pH 2 and 11 were also prepared in doubly distilled water.

The manganese dioxide purchased from MERCK was characterized as described in the following section.

2.2. Characterization of β-MnO_2

The surface area of the solid β-MnO_2 was determined by well-known nitrogen adsorption BET method. Further air-dried sample of manganese dioxide was subjected to the X-ray analysis using JEOL X-ray diffractometer, model JDX-73 with a Mn-filtered Cu Kα radiation.

The FTIR spectra of the bare and phosphate sorbed β-MnO_2 samples were taken by FTIR spectrometer, model, Perkin Elmer 16pc FTIR. A small quantity of the solid sample was mixed with KBr and was ground to fine powder, using an agate mortar. The fine powder was shaped into a disc form in a special cell under hydraulic pressure of 10 tonnes for 3 min. The discs thus prepared were subjected to the infrared radiation of FTIR spectrometer, and the recorded spectrum was then analyzed from the resulting peaks with known wave numbers.

The point zero charge (PZC) of the solid β-MnO_2 was determined by the method of Kinniburgh et al. [17].

2.3. Adsorption studies

Adsorption of phosphate ions on β-MnO_2 was performed on end-to-end shaker bath, labortechnic type LE-209 provided with hooks for 50 mL flasks. Different concentrations of phosphate ions in the range $1.07–11.85 \times 10^{-1}$ mmol L^{-1} were prepared using 0.1 M KNO_3 as a background electrolyte in doubly distilled water diluting from 1000 ppm stock solution. The details of the method used are given elsewhere [18].

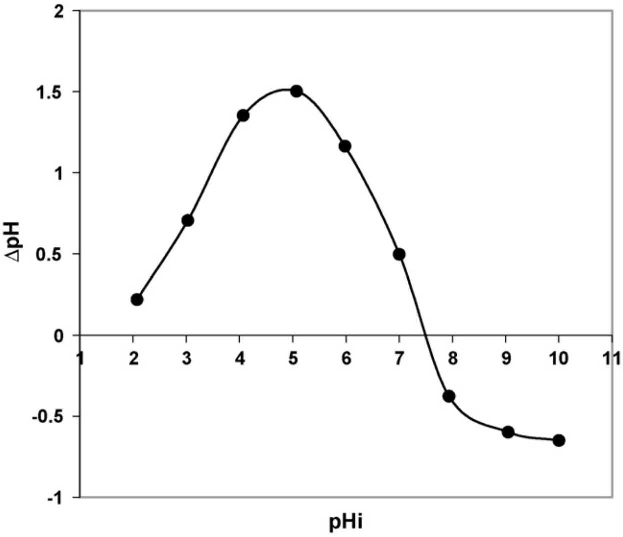

Fig. 1. Plot of pHi vs. ΔpH showing point of zero charge (PZC) for β-MnO_2 at 303 K in the presence of 0.1 M KNO_3.

3. Results and discussion

3.1. Characterization of solid β-MnO_2

The surface area was found to be $214\ m^2\ g^{-1}$ using the well-known nitrogen adsorption BET method. The X-ray diffraction pattern showed the solid to be crystalline β-MnO_2 as reported by Bayliss et al. [19] and also by us elsewhere [18].

The point of zero charge (PZC) value (Fig. 1) for crystalline β-MnO_2 is found to be equal to 7.5, which is reasonably close to the value of Stumm and Morgan [20].

3.2. Sorption studies

The adsorption of phosphate anions as a function of temperature at initial pH values of 3, 5 and 7 are presented in Fig. 2. This multi-plotting figure shows that the sorption of phosphate anions by β-MnO_2 decreases with increase in temperature from 293 to 313 K. Similar variations with temperature for iodate, phosphate, salicylate and selenate anions adsorption onto goethite were reported by a number of authors [21–23].

The pH changes accompanying the phosphate sorption at different temperatures are reported in Table 1. It can be seen that the changes are small at low temperature and tend to increase with

Table 1
Equilibrium pH values for phosphate anion sorption on β-MnO_2 at different temperatures

Initial phosphate $\times 10^{-3}$ concentration (mmol L^{-1})	Initial pH 3			Initial pH 5			Initial pH 7		
	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
107.16	3.34	3.585	3.735	6.406	6.229	5.993	7.113	6.267	6.041
331.37	3.162	3.573	3.877	6.821	6.026	5.975	7.063	5.821	6.280
549.26	3.298	3.595	3.735	6.350	6.005	5.703	6.999	6.167	6.426
770.32	3.242	3.912	3.995	6.250	5.973	5.850	6.987	6.277	6.459
990.32	3.222	3.777	3.842	6.236	5.869	6.009	6.929	6.485	6.509
1080.05	3.271	3.717	3.989	6.307	5.947	5.832	6.960	6.477	6.463
1185.05	3.200	3.741	3.794	6.246	5.879	5.693	6.984	6.821	6.856

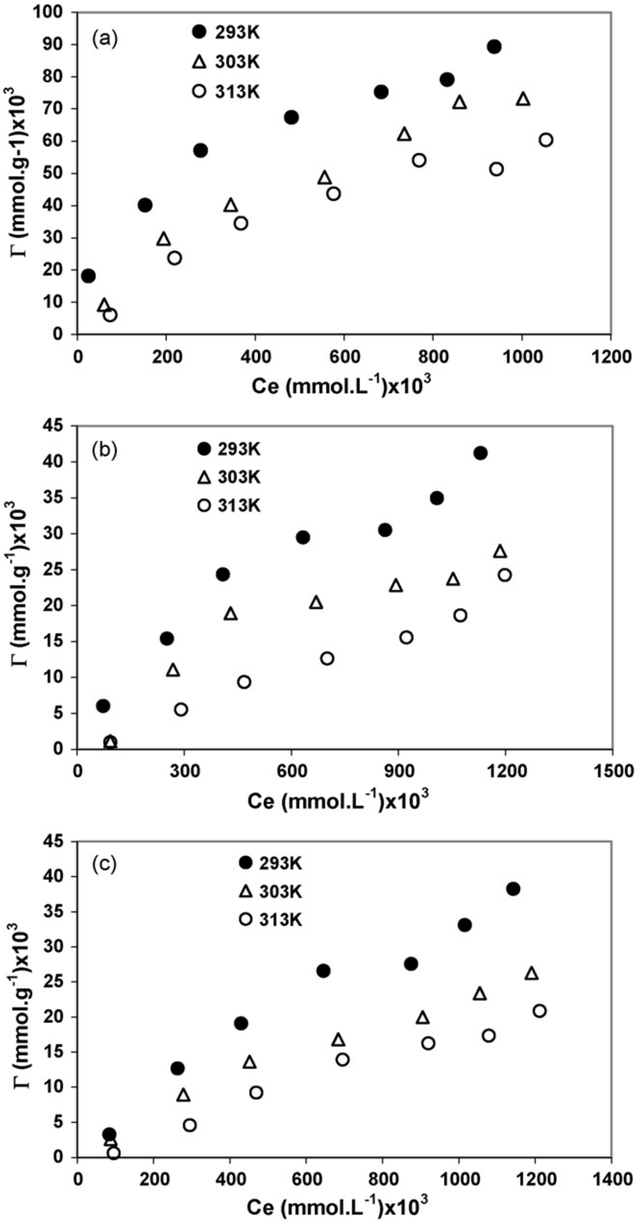

Fig. 2. Phosphate anion sorption isotherms on β-MnO_2 at different temperatures and pH: (a) pH 3; (b) pH 5; (c) pH 7.

the increase in temperature. The trend in pH shift with temperature and phosphate sorption shows that below the PZC, when the solid surface is positively charged, the phosphate anions are taken up by forming outer/inner-sphere complexes according to the mechanisms described below.

$$ROH + H_3{}^+O \Leftrightarrow ROH_2{}^+ + H_2O \qquad (1)$$

$$ROH_2{}^+ + H_2PO_4{}^- \Leftrightarrow ROH_2{}^+ \ldots H_2PO_4{}^- \qquad (2)$$

$$2ROH_2{}^+ + HPO_4{}^{-2} \Leftrightarrow (ROH)_2{}^{2+} \ldots HPO_4{}^{2-} \qquad (3)$$

$$ROH + H_2PO_4{}^- \Leftrightarrow R^+H_2{}^-PO_4 + OH^- \qquad (4)$$

$$2ROH + HPO_4{}^{-2} \rightarrow R_2HPO_4 + 2OH^- \qquad (5)$$

Reactions (2) and (3) take care of outer-sphere complex formation while (4) and (5) are due to the ligand exchange reactions leading to the formation of inner-sphere complexes. Similar outer-sphere and inner-sphere complex formation was proposed by Arai and Sparks for phosphate adsorption on iron hydroxide [12].

The increase in the equilibrium pH with temperature and amount of phosphate uptake at pH3 is probably due to the co-adsorption of proton by the surface according to reaction (1). The decrease of ΔpH at low pH values in Fig. 1 also points towards the same co-adsorption of protons. The proton adsorption accompanying the phosphate sorption on goethite was also reported by Rietra et al. [24].

The phosphate anions sorption by the solid is observed to increase when the concentration of the background electrolyte (KNO_3) is increased from 0.01 to 0.1 M at pH 5 at all the temperatures under investigation as shown in Fig. 3. Usually the effect of background electrolyte concentration is used in the literature

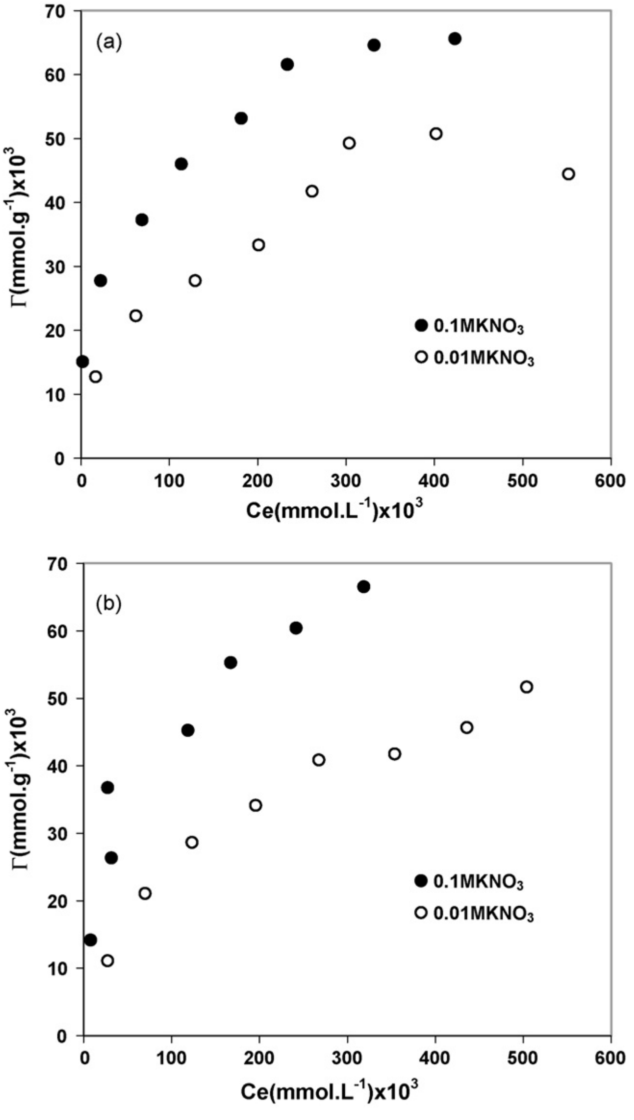

Fig. 3. Effect of back ground electrolyte (KNO_3) concentration on the phosphate sorption by β-MnO_2 at pH 5 and temperature: (a) 308 K and (b) 318 K.

[13,25,26] to decide about the mechanism of the surface reaction to be outer-sphere (reactions (2) and (3)) or inner-sphere complexation process (reactions (4) and (5)). The present data show an increase in the phosphate sorption with the increase in background electrolyte concentration (Fig. 3). Similar increase above the pH 7.5 was attributed by Arai and Sparks [12] to the co-adsorption of Na^{2+} ions by ferrihydrate and by McBride [27] to simple mass action principle. However, an increase in adsorption of Co(II) ions with the increase in background electrolyte concentration was shown to be an outer-sphere complexation process by Weisier et al. [26]. In the present case also the outer-sphere complexation seems to be responsible for the uptake of the phosphate anions by β-MnO_2 when even at higher temperature, phosphate uptake is found to increase with the increase in background electrolyte concentration (Fig. 3). Further no effect of phosphate adsorption upon the PZC [18] and the co-adsorption of protons discussed earlier also points towards the outer-sphere complex formation on the surface. The same conclusion can be drawn from the FTIR spectra, as almost no change was observed in the lattice vibration of the β-MnO_2 at 582 and 475 cm^{-1} after phosphate sorption (Fig. 4). The FTIR spectra for β-MnO_2 is almost similar to the one observed by Buciuman et al. [28]. Similar outer-sphere complexation was found by Yao and Millero [16] for manganese dioxide and Chitrakar et al. [29] for phosphate adsorption by zirconium oxide.

Both Langmuir and Freundlich equation were applied to the sorption data. However, only the Freundlich equation was found applicable to the data in the form

$$\log \Gamma = \frac{1}{n}\log \mathrm{Ce} + \log K \qquad (6)$$

The values of n and pK calculated from the plots of this Eq. (6) are presented in Table 2. The values of n and K of the Freundlich plots (Fig. 5) are usually correlated in the literature with the

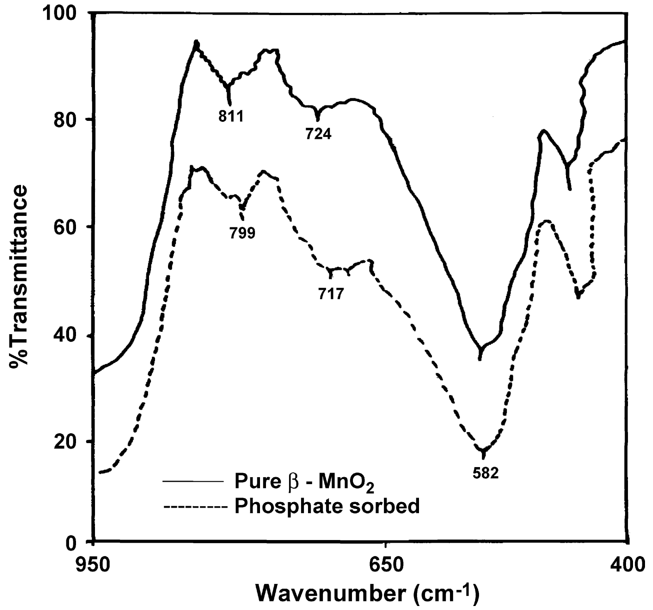

Fig. 4. FTIR spectra pure and 11.85×10^{-1} mmol L^{-1} phosphate sorbed β-MnO_2.

Table 2
n and pK values calculated from Freundlich equation

Temperatures (K)	n values			pK values		
	pH 3	pH 5	pH 7	pH 3	pH 5	pH 7
293	2.32	1.49	1.11	1.04	1.42	1.45
303	1.39	0.86	1.17	1.10	1.53	1.63
313	1.22	0.84	0.73	1.19	1.71	1.72

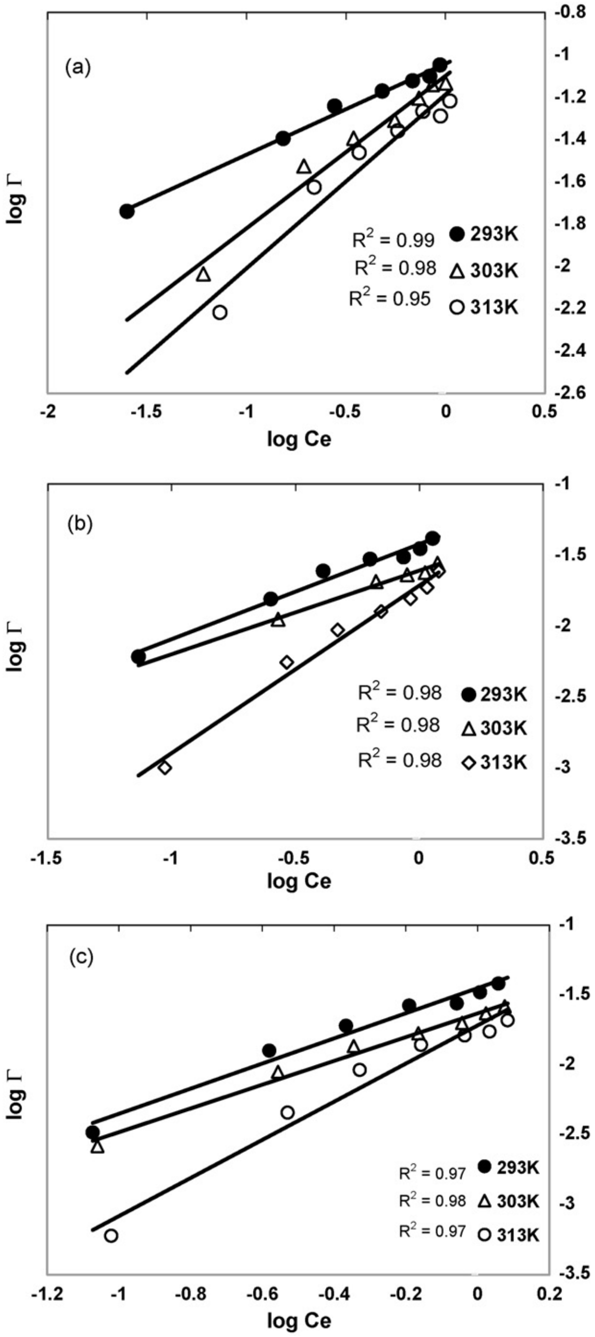

Fig. 5. Freundlich plots for phosphate anions sorption at different temperatures: (a) pH 3; (b) pH 5; (c) pH 7.

surface heterogeneity and sorption capacity of the adsorbent. Freundlich equation was also found applicable to the phosphate sorption data on zirconium oxide by Chitrakar et al. [29].

For the present case, however, it can also be shown that the value of the n is related to the stoichiometry of the sorption reaction. The monodentate surface reaction may be assumed to takes place as

$$\mathrm{SOH_2^+} + \frac{1}{n}P^{-n} \Leftrightarrow \mathrm{SOH_2^+}\ldots\frac{1}{n}P^{-n} \tag{7}$$

where n is the charge of the phosphate anions being sorbed by the solid. Accordingly, the n values may vary from 1 to 3 for the sorption of $H_2PO_4^-$, HPO_4^{-2} and PO_4^{-3}, respectively.

Applying the Law of mass action to the reaction (7) and equating the equilibrium concentration of phosphate to Ce and amount of phosphate sorbed to Γ, the following equation can be written

$$K = \frac{\Gamma}{[\mathrm{SOH_2^+}][\mathrm{Ce}]^{1/n}} \tag{8}$$

For constant pH taking the $[SOH_2^+]$ as constant, Eq. (8) reduces to

$$K = \frac{\Gamma}{[\mathrm{Ce}]^{1/n}} \tag{9}$$

After taking the log, Eq. (9) transforms to the well-known Freundlich adsorption isotherm (6).

Eq. (6) when applied to the sorption data in the pH range 3–7 at all the temperatures under investigation gives a straight line as shown in multi-plotting Fig. 5.

It can be seen from Table 2 that the values of n vary from 1 to 3 which show that the charges of the phosphate anions being sorbed are $H_2PO_4^-$, HPO_4^{-2} and PO_4^{-3}, respectively. The n values are found to decrease both with temperature and pH, indicating that at low values of pH and temperature, the solid prefers the multiply charged anions. The same conclusion can be drawn from the pH changes given in Table 1. The increase in pH at 3 and 5 and decrease in pH at 7 points towards the deprotonation of the phosphate anions before their sorption by the solid β-MnO_2. The decrease in pH due to phosphate anions deprotonation must be the highest at pH 3. The pH changes at pH 3, however, reveal that the phosphate deprotonation is accompanied by the surface protonation reactions of the solid. Further, the pH increase due to surface protonation reaction is greater as compared to phosphate deprotonation reactions at pH 3 and 5 leading to an overall increase in the equilibrium pH of the solution. As for as the effect of temperature on pH changes is concerned, one would expect a smaller decrease in pH on account of the reduced sorption at higher temperature. However, the observed changes in pH show that deprotonation of phosphate anions far exceeds its sorption by the solid at higher temperatures. As no such surface protonation would occur at pH 7, a decrease in equilibrium pH is observed on account of the deprotonation of the phosphate anions from H_2PO^- to HPO_4^{-2}. The selective sorption of multivalent ions in the presence of a large excess of univalent ions is termed as electroselectivity and is well known for oxides and organic ion exchangers [29–31]. Similarly the PO_4^{-3} adsorption at pH values ≥6 has also recently postulated in the literature by Kiyoshi Okada et al. [32].

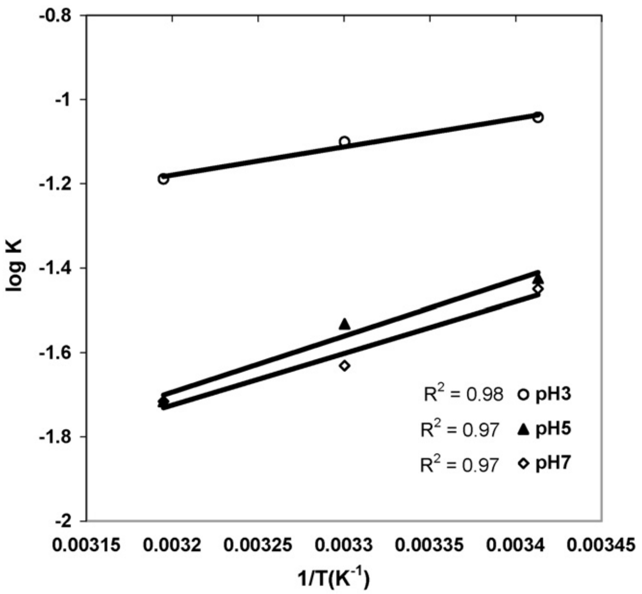

Fig. 6. Plot of log K vs. $1/T$ at different pH values for phosphate sorption.

As for as the values of pK (Table 2) are concerned, they are observed to increase with increase in temperature at all the pH values. The increase in the pK values with temperature is expected, as the multiply charged phosphate anions would form a stronger surface complex as compared to the singly charged phosphate anions. Thus the pK values also are in agreement with the fact that the solid prefers the HPO_4^{-2} anions at low values of temperature and pH. This similarity shows that the outer-sphere complexation of the phosphate anion with the solid plays the dominant role in the over all process of the uptake of the anions by the solid.

3.3. Thermodynamic parameters

The standard thermodynamic parameters for phosphate sorption on β-MnO_2 were calculated from the plots of log K versus $1/T$ (Fig. 6) using the well-known relation and are given in Table 3.

$$\log K = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{10}$$

where K has the usual meaning, R (8.314 JK^{-1} mol^{-1}) the molar gas constant, T absolute temperature and ΔS° and ΔH° are the

Table 3
Standard enthalpy, entropy and free energy changes for phosphate anion sorption on β-MnO_2 calculated from Freundlich equation

pH	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})		
			293 K	303 K	313 K
3	−12.85	−63.69	18.65	19.29	19.93
5	−25.63	−113.92	33.35	34.80	35.63
7	−23.47	−107.56	31.49	32.57	33.64

changes in entropy and enthalpy of the system. The plots drawn according to the Eq. (10) are presented in Fig. 6.

The standard enthalpy and entropy changes for phosphate anion sorption on β-MnO_2 are given in Table 3. The values of ΔH° are negative at the pH values 3, 5 and 7 showing the exothermic nature of the process, i.e., the sorption is observed to decrease with increase in temperature. The ΔS° values are also negative at all the pH values under investigation.

Knowing the values of ΔH° and ΔS°, the values of standard free energy ΔG° for phosphate anions sorption are calculated using the following well-known relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (11)$$

Table 4
Isosteric heat of sorption for phosphate anion on MnO_2 at different pH

$\Gamma \times 10^3$ mmol g^{-1}	pH 3 ($\overline{\Delta H}$, kJ mol^{-1})	pH 5 ($\overline{\Delta H}$, kJ mol^{-1})	pH 7 ($\overline{\Delta H}$, kJ mol^{-1})
5.00	−55.23	−38.23	−23.87
10.0	−56.06	−45.95	−32.56
15	−57.17	−53.74	−44.92
20.0	−58.43	−56.63	−45.67

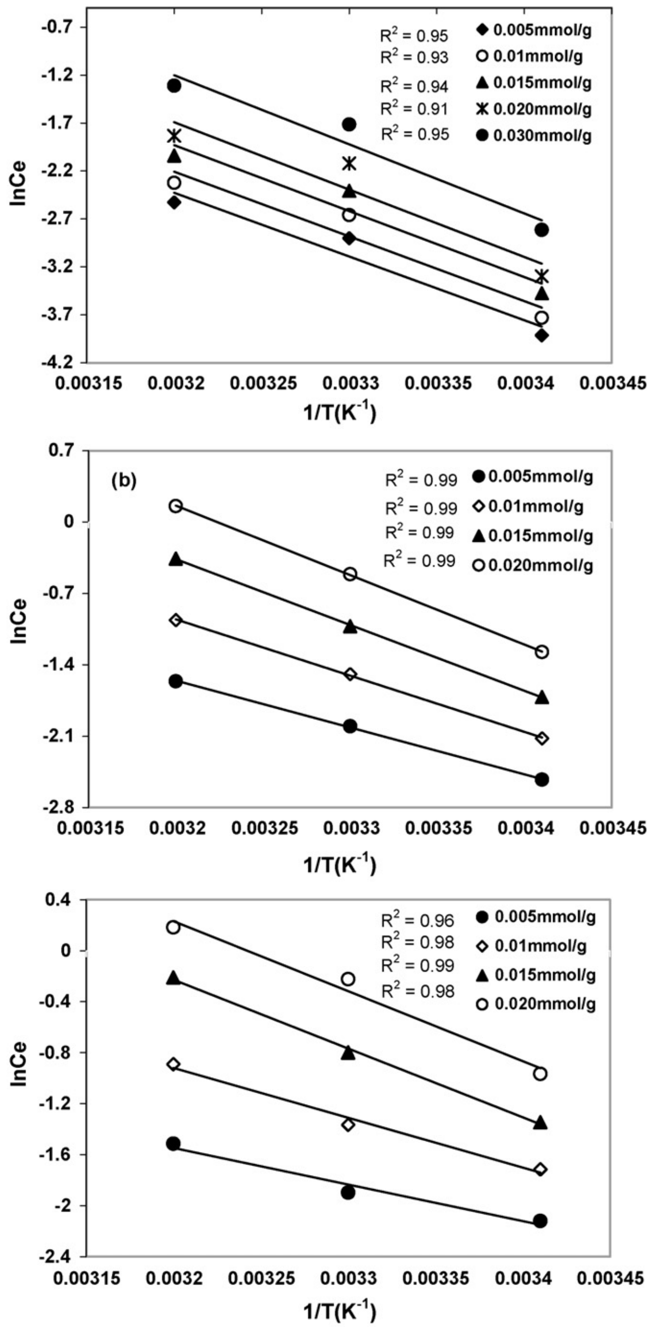

Fig. 7. Plots of Clausius Clapeyron equation for phosphate sorption on β-MnO_2: (a) pH 3; (b) pH 5; (c) pH 7.

The value of ΔG° calculated from Eq. (11) presented in Table 3 show that these are positive at all the pH and temperatures under investigation which demonstrate the non-spontaneous behavior of the sorption process. Moreover, at all the pH values they are observed to increase with increase in temperature. This increase in ΔG° values with temperature and pH indicates that the sorption process is unfavourable both at high temperatures and pH.

Isosteric heat of sorption for β-MnO_2 are also calculated from the well-kwon Clausius Clapeyron equation by plotting ln Ce(r) versus $1/T$ according to relation (12) as

$$[\ln \mathrm{Ce}]_\Gamma = \frac{\Delta H}{RT} + \mathrm{Constant} \qquad (12)$$

The plots are drawn according to Eq. (12) and are shown in Fig. 7. As can be seen the $\ln \mathrm{Ce}_{(\Gamma)}$ varies linearly with temperature for all the constant phosphate anion sorbed. The $\overline{\Delta H}$ values calculated from the slopes of the lines are reported in Table 4. These values are also negative for all the pH values 3, 5 and 7 and show the exothermic nature of the process. These values are observed to be more negative at pH 3 and are found to increase in magnitude with the increase pH. This behaviors also points towards the fact that the solid is more selective towards the doubly charged phosphate anions at pH 3, i.e., $HPO_4{}^{-2}$, though their concentration at this pH value is very low. With the increase in extent of adsorption, however, the solid tends to loose its selectivity towards the multiply charged anions, as the differences in the isosteric heat of adsorption decreases with the increase in pH, which is evident from the data in Table 4 for the sorption of 20 mmol g^{-1} of the solid. The proton adsorption enthalpy was found to be −38.9 kJ mol^{-1} by Machesky et al. [33]. As the sorption of $HPO_4{}^{-2}$ would require the simultaneous sorption of two protons according to reaction (5), therefore the isosteric heat of adsorption observed at pH 3 are much more exothermic than that at pH 7 particularly for low values of the phosphate adsorption, where the sorption of $H_2PO_4{}^{-}$ would require the sorption of only one proton by the solid according to reaction (2). Similar values of the isosteric heat of adsorption for phosphate anion on goethite were observed elsewhere [21].

4. Conclusions

From the foregoing discussion, it can be concluded that the adsorption of phosphate is favoured by β-MnO_2 both at low pH and temperature. The pH changes accompanying the sorption process, increase in phosphate sorption with the increase in back ground electrolyte concentration and the FTIR spectra show that the process responsible for the uptake of the phosphate anions is outer-sphere surface complexation at pH range 3–7 and temperature 293–313 K. Thermodynamic parameters derived from the Freundlich equation points towards the electroselectivity of the β-MnO_2. The solid prefers the doubly charged HPO_4^{-2} as compared to singly charged $H_2PO_4^{-}$ anions, a fact which is also proved by the isosteric heat of adsorption calculated from the Clausius Clapeyron equation.

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