

pH effect on phosphate sorption by crystalline MnO₂

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Abstract

The phosphate anions sorption on manganese dioxide was studied as a function of pH in the range 3–9 and at 293 K. The sorption was observed to increase with the increase in concentration of phosphate and decrease with the increase in pH. No effect of the phosphate adsorption upon the PZC of the solid suggested that the only outer sphere complexes were formed on the surface of the solid. The potentiometric titrations studies of the solid were also performed in the presence of different phosphate concentrations (0.53, 1.053, and 2.11 mmol L⁻¹). The calculated p*K*_a values showed that the solid protonation played a dominant role in the uptake of phosphate anions by the solid.

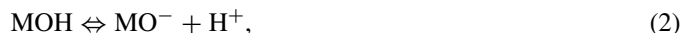
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1. Introduction

In recent years, due to limited water resources the idea of water reuse has become very important. Like metal cations, the presence of an excess of various anions such as phosphates, chromates, nitrates, etc. in water may also cause problems in many natural and engineering systems. Phosphate anions in stored water reservoirs are known to stimulate algal growth and scaling in vessels used for cooling purposes [1]. Several techniques such as ion exchange, adsorption on activated carbon, biological and chemical precipitation and reverse osmosis have been used for removal of phosphate from municipal waste-waters. However, the ion exchange and adsorption methods proved to be more effective due to their low cost, effective treatment in dilute solutions, high uptake capacity, faster regeneration kinetics and greater selectivity [2,3].

The hydrous metal oxides are an important class of inorganic adsorbent [4,5]. They possess pH-dependent surface charges, when immersed in aqueous solution by the protonation and deprotonation of the surface hydroxyl groups by a scheme reported in the literature [6–9], as



where “M” represents the metal cation.

While a number of oxides/hydroxides have been employed in the literature for the uptake of phosphate anions [10,11], very little attention is paid to other environmentally important oxides/hydroxides like MnO₂, etc. Manganese oxide is the 10th most abundant metal in the earth crust and is widely used as a pigment, catalyst, battery material, deoxidizer and in steel making.

Manganese oxides are important scavengers of trace metals and different anion like phosphate, chromate, etc., in the marine and fresh water environment because of the following reasons, e.g., (i) high surface charge, (ii) high cation/anions adsorption capacity, and (iii) large specific surface area. Thus, the trace metal and phosphate concentration in the aqueous system is at least partially dependent on the abundance of manganese oxides. It is also known to have the properties of uptake of metal cations and has been used successfully for the removal of alkali, alkaline earths and transition metal cations [12–15]. However, there are only a few reports in the literature [16] about the sorption of phosphate anions by the manganese dioxide although it is also known to play a major role in phosphate fixation in soils [17]. The present study, therefore, deals with the sorption of phosphate on manganese dioxide as a function of pH and concentration.

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2. Experimental

2.1. Reagents

All reagents used were of 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 sorbent manganese dioxide purchased from Merck was characterized as described in the following section.

2.2. Characterization of the solid

The surface area of the solid manganese dioxide was determined by well-known 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 $\text{CuK}\alpha$ radiation.

The point zero charge (PZC) was determined by the method of Kinniburgh et al. [18].

2.3. Potentiometric titrations studies

Potentiometric titrations of manganese dioxide towards 0.1 M KNO_3 and 0.53, 1.053, and 2.11 mmol L^{-1} phosphate ions at 293 K were performed in a double-walled Pyrex glass cell connected to a thermostated water bath via a water-circulating pump. Thirty milliliters of phosphate ions solution of the desired concentration were taken in a double-walled Pyrex cell, which was kept at constant temperature by circulating water from thermostat. After 30 min of equilibration, 0.1 g MnO_2 was added to the cell solution. The initial pH of the suspensions was measured by using precision pH meter, Orion Model SA 520, with combined glass and calomel electrodes, and was adjusted to pH 3 with 0.1 M HNO_3 . The suspensions were then allowed to equilibrate for 30 min with constant stirring using a magnetic stirrer and any change in the pH was readjusted with standard HNO_3 or KOH . The titration was carried out by stepwise addition of 0.2 ml of 0.1 M KOH solutions using microburette with a very fine capillary tip. The suspension pH was recorded after every two minutes. The titration was continued till the final pH reached 11.

2.4. Adsorption studies

The adsorption of phosphate ions on manganese dioxide was performed on end-to-end shaker bath, Labortechnic type LE-209 provided with hooks for 50 ml flasks. Different concentrations of phosphate ions were prepared in doubly distilled water diluting from 10.53 mmol L^{-1} stock solution.

Before starting the experiment 0.1 g of manganese dioxide was taken in 25 ml of phosphate solution of different concentration in 50 ml conical flasks. Initial pH of the suspensions was recorded and adjusted to the desired pH either by addition of standard solution of HNO_3 or KOH . The flasks were then

transferred to the shaker bath for 24 h keeping the temperature constant at 293 K. After 24 h the suspensions were filtered out and filtrates were analyzed for equilibrium concentration of phosphate ions using the method reported in the literature [19]. The amount of phosphate ions sorbed was computed from difference between initial and equilibrium phosphate ions concentration by using relation:

$$\Gamma = \frac{(C_0 - C_e)V}{1000m}, \quad (3)$$

where Γ is sorption in mmol per gram of sorbent, C_0 and C_e are the initial and equilibrium concentration of phosphate ions in mmol per liter, V is the volume of the solution added to the sorbent, and m is the weight of sorbent.

3. Results and discussion

3.1. Characterization of manganese dioxide

The surface area of the solid was found to be $214 \text{ m}^2 \text{ g}^{-1}$. The X-ray diffraction pattern of solid manganese oxide is shown in Fig. 1. XRD pattern of the sample corresponds mainly to synthetic pyrolusite having tetragonal crystal structure with lattice parameter $a = 4.3999 \text{ \AA}$, $b = 4.3999 \text{ \AA}$, and $c = 2.8740 \text{ \AA}$. The reflection at 1.55, 1.62, 1.969, 2.197, 2.405, and 3.107 \AA d spacing present in the sample pattern are the characteristics peaks of crystalline $\beta\text{-MnO}_2$, i.e., synthetic pyrolusite (JCPDS). The results obtained here are similar to those reported in the literature for $\beta\text{-MnO}_2$ Bayliss et al. [20].

The point zero charge (PZC) was determined by plotting ΔpH (final pH–initial pH) against initial pH yielding the PZC at the pH where $\Delta\text{pH} = 0$ as shown in Fig. 2. The PZC value for manganese dioxide, thus, obtained is equal to 7.5. The value found is reasonably close to the value reported elsewhere [21,22].

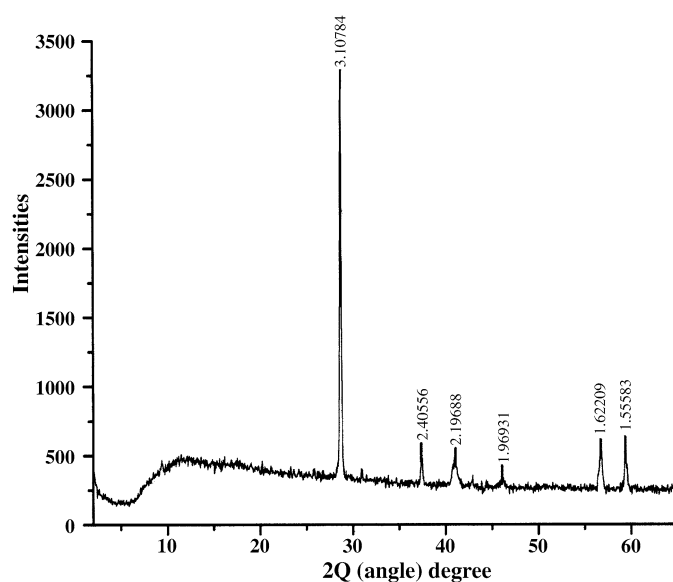


Fig. 1. X-ray diffraction patterns of MnO_2 .

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