

# Sorption of Phosphate on Cobalt Hydroxide

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**Summary:** The sorption of phosphate on cobalt hydroxide is studied as a function of temperature (25 - 55 °C) and concentration (1.94 - 3.23 mmol/l). The mechanism of sorption is observed to be the replacement of OH<sup>-</sup> anions from the adsorbent surface by those of phosphate from the aqueous solution. A modified form of the Langmuir equation was used to explain the ion exchange sorption of phosphate on the Co(OH)<sub>2</sub>. The IR studies of phosphate sorption are also made to determine the nature of phosphate ion bonding with the surface of the adsorbent

## Introduction

Due to increasing demands for water and limiting supply of readily usable water in many areas, the idea of its reuse has become very important during the last few years. Phosphate in the reused water has come in to focus as an important problem. Reused water which is used to supplement fresh supplies needs to be stored often in open reservoirs. This constitutes a problem since the excess of phosphate stimulates the algal growth in the aqueous environments [1]. The other major reason is that most of the water consumed by industries is used for cooling and the presence of substantial amounts of phosphate may result in scaling [2].

A number of studies [3-5] have been performed for the removal of phosphate from the aqueous solution by using organic and inorganic ion exchange materials including iron and aluminium hydroxides. However, very little is known about the phosphate interaction with other equally important oxides/hydroxides like Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub>. The

present study, therefore, deals with the adsorption of phosphate on Co(OH)<sub>2</sub> as a function of concentration and temperature.

## Results and Discussion

The phosphate sorption on the Cobalt Hydroxide is observed to increase with the increase in temperature and concentration of the phosphate in the solution (Fig.1, Table 1). The adsorption isotherms obtained in the temperature range 25 - 55 °C are mostly of S- type. These types of isotherms indicate the preference of Cobalt hydroxide surface for OH<sup>-</sup> as compared to the incoming phosphate anions from solution. Similar isotherms were found for the sorption of phosphate on the Fe(OH)<sub>3</sub> [6].

The pH of the solution has greater effect upon the phosphate adsorption by oxides/hydroxides. The initial and the equilibrium pH values after adsorption at different temperatures are given in Table 2. The

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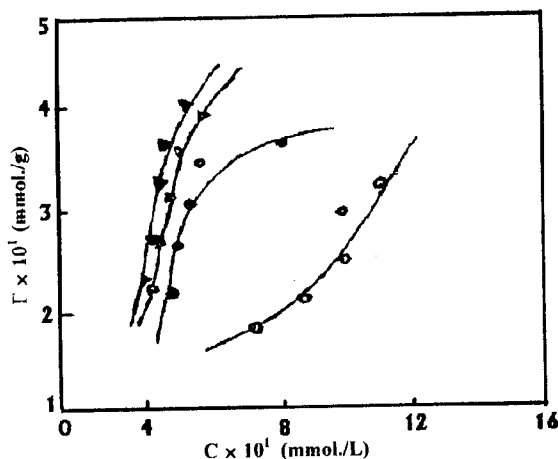
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Table 1. Amount of phosphate adsorbed on cobalt hydroxide at various temperatures

Initial Phosphate Concentration (mmol./L)	Phosphate Adsorbed (mmol./g)			
	25 °C	35 °C	45 °C	55 °C
1.94	0.180	0.218	0.228	0.229
2.26	0.208	0.265	0.269	---
2.58	0.242	0.306	0.311	0.316
2.90	0.287	0.350	0.357	0.363
3.23	0.318	0.361	0.396	0.400

Table 2. Values of equilibrium pH for phosphate adsorption on cobalt hydroxide at various temperatures

Initial phosphate Concentration (mmol./L)	Initial pH	Equilibrium pH			
		25 °C	35 °C	45 °C	55 °C
1.94	5.34	7.28	7.57	7.48	8.06
2.26	5.30	7.26	7.87	7.61	7.83
2.58	4.97	7.29	8.00	7.89	8.05
2.90	4.99	7.46	8.10	7.97	8.08
3.23	5.19	7.50	7.99	7.74	8.08

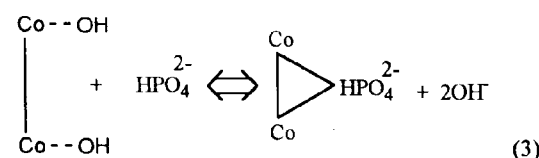
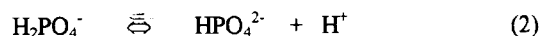
Fig. 1: Phosphate sorption isotherms on  $\text{Co}(\text{OH})_2$  at  $\circ = 25$ ,  $\bullet = 35$ ,  $\Delta = 45$  and  $\blacktriangle = 55^\circ\text{C}$ .

increase in the equilibrium pH can be explained in terms of the desorption of the hydroxide anions from the cobalt hydroxide surface according to the reaction (1).



The negligible pH changes at higher temperatures in the present case are probably due to the adsorption of phosphate as  $\text{HPO}_4^{2-}$ , when the  $\text{OH}^-$  released from the surface are consumed in

neutralizing the  $\text{H}^+$  ions obtained from the deprotonation of the  $\text{H}_2\text{PO}_4^-$  anions according to the following reactions:



Langmuir equation is generally used to illustrate the relationship between the amount of phosphate taken up by the ion exchanger and its equilibrium concentration in solution. This equation is useful in the present case as it gives an idea of the adsorption maximum of the various phosphate species and their energies of interaction with the fixed groups of the ion exchanger. A modified form of the Langmuir equation derived elsewhere [7, 8] was used in this study. The equation can be written as:

$$P = \frac{b}{1 + b/KC} \quad (4)$$

where  $P$  is the amount of phosphate sorbed,  $b$  is the maximum adsorption capacity,  $K$  is the binding energy constant and is equal to  $K_1/K_2$  and  $C$  is the equilibrium concentration of the phosphate solution. The plots of the amount of phosphate sorbed ( $P$ ) vs. reciprocal of the equilibrium concentration ( $1/C$ ) gives linear relationship according to equation (4) which shows that the equation is applicable at all the temperatures under investigations (Fig.2) except at  $25^\circ\text{C}$ , where the data could be fitted to a two slopes equation. Such a behavior by analogy with our previous studies suggests that phosphate is being taken mainly as  $\text{HPO}_4^{2-}$  by  $\text{Co}(\text{OH})_2$  and only at  $25^\circ\text{C}$  both the species  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  are being sorbed. The values of the sorption maxima and binding energy constant are presented in Table 3. As expected values of  $K_1$  for  $\text{HPO}_4^{2-}$  sorption are higher than  $K_2$  for the sorption of  $\text{H}_2\text{PO}_4^-$  at  $25^\circ\text{C}$ . On the basis of binding energy constant, the region 1 of the isotherm can be assigned to the sorption of  $\text{HPO}_4^{2-}$  forming a binuclear bridging complex, while region 2 of the isotherm to the sorption of  $\text{H}_2\text{PO}_4^-$ . Similarly, the sorption maxima  $b_1$  and  $b_2$  may also be assigned to  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  respectively. The values of the sorption maximum  $b_2$  for  $\text{H}_2\text{PO}_4^-$  at  $25^\circ\text{C}$  are double

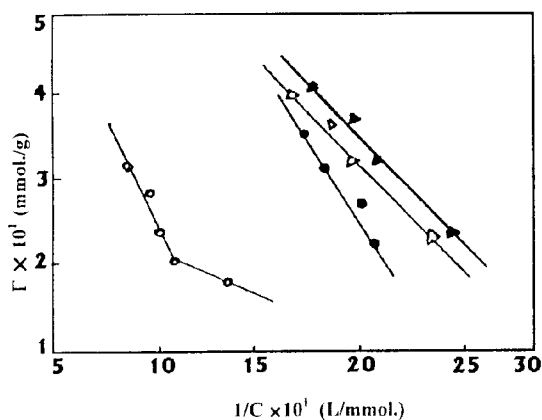


Fig.2: Modified Langmuir isotherms of phosphate sorption at  $\circ = 25$ ,  $\bullet = 35$ ,  $\Delta = 45$  and  $\blacktriangle = 55^\circ\text{C}$ .

Table 3. Langmuir adsorption maxima (b) and binding energy constant (K) at various temperatures for cobalt hydroxide.

Temperature $^\circ\text{C}$	PART-1		PART-2	
	b1 mmol.P/g	K1 L/g	b2 mmol.P/g	K2 L/g
25	0.36	2.75	0.73	1.61
45	0.81	3.40	-	-
55	0.88	3.28	-	-

in magnitude as compared to the values of the sorption maximum b1 for  $\text{HPO}_4^{2-}$ . It may be due to the fact that two point attachments for  $\text{HPO}_4^{2-}$  are replaced with one point attachment in case of  $\text{H}_2\text{PO}_4^-$ . Further, the values of K1 and b1 i.e. the binding energy constant and sorption maxima for  $\text{HPO}_4^{2-}$  are observed to increase with the increase in temperature, which indicate the preference of the Cobalt hydroxide for  $\text{HPO}_4^{2-}$  at higher temperatures as compared to  $\text{H}_2\text{PO}_4^-$ . As expected, the formation of the binuclear bridging complex (reaction 3) would be more favorable at high temperatures.

#### Infrared (IR) Studies

In order to determine the mechanism of phosphate sorption on cobalt hydroxide, the IR spectra of fully saturated adsorbent along with the blanks are shown in the Fig.3. The appearance of new band at  $1030 - 1040 \text{ cm}^{-1}$  shows the interaction of phosphate with the  $\text{Co}(\text{OH})_2$ . As was suggested by Atkinson et al. [9] the band at  $1040 \text{ cm}^{-1}$  can be associated to  $\text{PO}_2\text{Fe}_2$  groups, when phosphate is adsorbed on goethite. As is evident from the Fig.3,

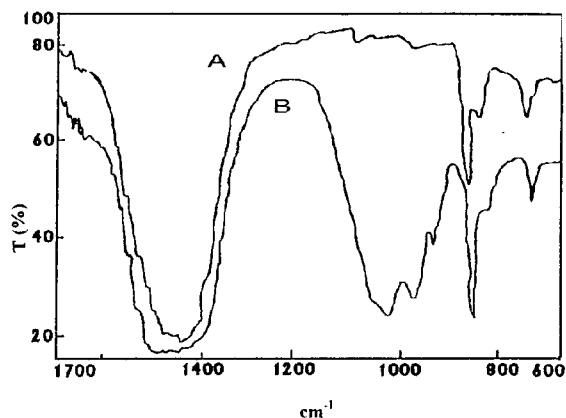
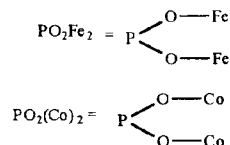


Fig. 3: IR spectra of (A)  $\text{Co}(\text{OH})_2$  only and (B)  $\text{Co}(\text{OH})_2$  fully saturated with phosphate.

the formation of a similar binuclear bridging complex of the type  $\text{PO}_2(\text{Co})_2$  can be suggested also in the present case. The formation of protonated binuclear complex had been also suggested by Nanzyo and Watanabe [10], Parfitt *et al.* [11] and Russell et al.[12] for the sorption of phosphate on iron hydroxide.



#### Experimental

##### Sorption of Phosphate on Cobalt Hydroxide

An exactly weighed amount (0.2 g) of each of Cobalt hydroxide was mixed with 30 ml of  $\text{KH}_2\text{PO}_4$  solution. The concentrations of initial solutions ranged from 1.94 – 3.23 mmol/l. The initial pH was noted with the help of Orion model S A 520 digital pH meter. The mixtures were then shaken on end-to-end shaker in an air thermostat at 25 – 55  $^\circ\text{C}$  for 24 hours, filtered noted the final pH, and the filtrate was analyzed for phosphate and chloride ions by the method given in the literature [13, 14]. The solid residues of the  $\text{Co}(\text{OH})_2$  were then mixed with KBr and crushed to fine powder. The resultant powder was pressed to a pellet and analyzed by SP-3 100 Pye Unicam IR Spectrophotometer.

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