Phosphate Sorption on Calcium Carbonate

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Summary: Phosphate sorption on CaCO₃ was undertaken at different temperatures (25 - 55 °C) and concentrations (1.94 - 3.23 mmol/ 1). The sorption of phosphate was found to increase with the increase in both the concentration and temperature. A modified form of the Langmuir equation was used to explain the ion exchange sorption of phosphate on the CaCO₃. The thermodynamic parameters also showed the favourable uptake of phosphate on the CaCO₃.

Introduction

Phosphate in the water has come into focus as an important problem since the excess of phosphate stimulates the algal growth in the aqueous environment [1 - 4]. 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].

One of the best ways to control a pollutant is to reduce its concentration at its source of entry into the sewage system [5 - 7]. Several methods [8 - 9] including ion exchange, adsorption, biological and chemical precipitation and reverse osmosis are used to remove phosphorus from municipal wastewaters. However, ion exchange/adsorption methods are not yet well established as compared to the biological and chemical precipitation methods. The present work is, therefore, carried out with the view to develop cheap, an efficient method for the decontamination of aqueous environments from phosphates.

Results and Discussion

Adsorption of phosphate on CaCO₃ was studied as a function of concentration and temperature of the system. The results obtained are given in the Fig. 1. These isotherms indicate that the phosphate sorption increases with the increase in temperature and concentration of the solution. Similar increase in phosphate adsorption with temperature on calcium carbonate was observed elsewhere [4, 8-10].
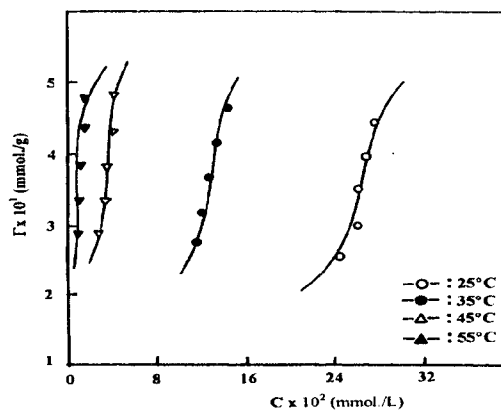

Fig. 1: Phosphate sorption isotherms on CaCO₃ at various temperatures.

As can be seen from Table- 1 with the adsorption of phosphate on calcite there is a sharp increase in the equilibrium pH of the solution at 35 °C. The increase in temperature, however, results in very small changes of the pH in spite of large increase in the adsorption of phosphate. The phosphate ions, thus, replace the OH⁻ anions from the calcite surface at 35 °C due to which a sharp increase in the solution pH is observed. However, further, increase in temperature probably leads to the deprotonation of the $H_2PO_4^-$ anions resulting in compensation of the OH⁻ release from the solid which leads to small changes in the solution pH. The increased sorption of HPO_4^{2-} with the increase in temperature may also be due to the formation of $CaHPO_4$ on the $CaCO_3$ surface as described elsewhere [4, 8-11].

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Table-1. Values of equilibrium pH for phosphate adsorption on calcium carbonate at various temperatures

Initial Phosphate Concentration (mmol./ L)	Initial pH	Equilibrium pH		
		35 °C	45 °C	55 °C
1.94	5.34	8.06	7.47	7.47
2.26	5.30	8.02	7.44	7.60
2.58	4.97	8.07	7.56	7.52
2.90	4.99	8.16	7.48	7.73
3.23	5.19	8.13	7.68	7.73

To determine the mechanism of the process, modified form of the Langmuir equation derived elsewhere [12] was applied to the present data in the form

$$\Gamma = b - b/KC \qquad (1)$$

where Γ is the amount of phosphate sorbed, b is the maximum adsorption capacity, K is the binding energy constant and C is the equilibrium concentration of the phosphate solution. The plots of the amount of phosphate sorbed (Γ) vs. reciprocal of the equilibrium concentration (1/ C) are given in Fig. 2. As can be seen, the present data is fitted to a single line equation at 25 and 35 °C, while at 45 and 55 °C two distinct straight lines are observed (Fig. 2). It can be suggested that at low temperature there is a possibility of a single sorption mechanism, while at higher temperatures the plotted data signify at least two different mechanisms for phosphate adsorption. Reactions, which are responsible for the different slopes noted at 35 and 45 °C may be considered as follows

1. Adsorption taking place at various states on the surface.
2. Adsorption occurring in layers on the surface.
3. Separate mineral species are being nucleated on the surface.

However, comparing the data of phosphate adsorption on calcium carbonate with its adsorption on iron hydroxide (6) where similar results were observed, it can be concluded that separate phosphate mineral species are being nucleated at the CaCO₃ surface. At low temperature, sorption of $H_2PO_4^-$ and at high temperature sorption of both the
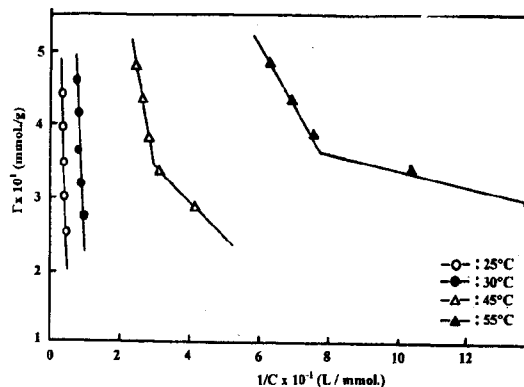

Fig. 2. Modified Langmuir isotherms of phosphate sorption at various temperatures.

phosphate species $H_2PO_4^-$ and HPO_4^{2-} takes place. Similar behaviour was also reported by Griffin and Jurinak [4], while studying the sorption of phosphate on CaCO₃.

The values of adsorption maxima (b) and the binding energy constant (K) are given in Table 2. As expected, the values of adsorption energy K_1 of HPO_4^{2-} are much higher than that of K_2, energy of sorption of $H_2PO_4^-$. Similarly the values of the adsorption maxima b_2 for HPO_4^{2-} are almost twice of the values of b_1, the adsorption maxima for HPO_4^{2-} as two point attachments for $H_2PO_4^-$ is replaced with one point attachment for $H_2PO_4^-$. Further, the values of both binding energy constants K_1 and K_2 increase with the increase in temperature.

Table- 2. Adsorption maxima (b) and binding energy constant (K) at various temperatures for calcium carbonate

Temperature (°C)	PART 1		PART 2	
	b1 mmol.P/ g	K1 L/ g	b2 mmol.P/ g	K2 L/ g
25	-	-	1.18	4.74
35	-	-	1.20	11.43
45	0.48	103.4	1.03	45.31
55	0.47	360.5	0.94	126.92

The values of the standard thermodynamic parameters ($\Delta H°$ and $\Delta S°$) are calculated from the plot of Fig. 3, according to equation 2. Knowing the values of $\Delta H°$ and $\Delta S°$ the values of $\Delta G°$ can be computed from equation (3).

Table-3. Thermodynamic data for calcium carbonate at various temperatures

Temperature (°C)	PART 1			PART 2		
	$\Delta G°$ kJ / mol	$\Delta H°$ kJ / mol	$\Delta S°$ J / mol.K	$\Delta G°$ kJ / mol	$\Delta H°$ kJ / mol	$\Delta S°$ J / mol.K
25	-6.68			-5.10		
35	-10.39			-8.34		
45	-14.10	103.88	371.00	-11.58	91.51	324.00
55	-17.09			-14.83		
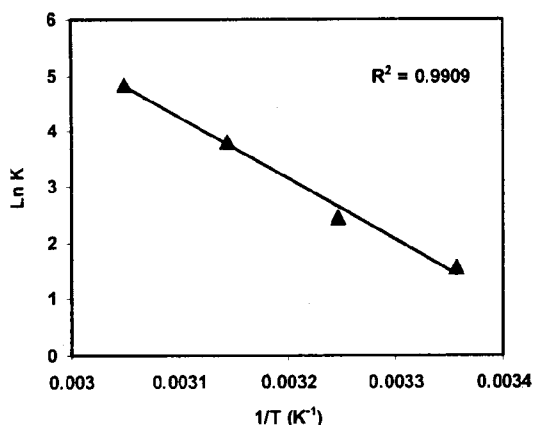
Fig. 3: Plot of Ln K vs. 1/ T for CaCO₃.

$$\ln K = \Delta S° / R - \Delta H° / RT \qquad (2)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (3)$$

As can be seen from the Table-3 the values of $\Delta G°$ for both the regions of the isotherm are negative showing the spontaneity of the process. Further, for HPO_4^{2-} the values $\Delta G°$ are more negative than those for $H_2PO_4^{-}$ confirming the preference of the calcium carbonate for the doubly charged HPO_4^{2-} ions in the temperature range 25-55 °C.

Both the values of thermodynamic parameters $\Delta H°$ and $\Delta S°$ are positive. The values of $\Delta S°$ for HPO_4^{2-} are more positive as compared to $H_2PO_4^{-}$, indicating a greater stability of the surface $CaHPO_4$ complexes as compared to Ca $(H_2PO_4)_2$. The positive values of $\Delta H°$ indicate the endothermic nature of the process [13] which shows that sorption of phosphate increases with the increase in the temperature [14]. The values of $\Delta H°$ are much higher than those obtained in the case of oxides/ hydroxides (6) showing the pronounced effect of temperature on $CaCO_3$. The higher values

of the $\Delta H°$ also confirm the chemical nature of the sorption process.

Experimental

Sorption of Phosphate on CaCO₃

Adsorption experiments of phosphate on $CaCO_3$ over a range of concentration (1.94 – 3.23 mmol/ 1) and temperature (25 – 55 °C) were conducted in polypropylene batch reaction vessels using 0.2 g $CaCO_3$ in 30ml KH_2PO_4 solution. The initial pH of the suspension was noted and the suspension was then equilibrated for 24 hours at 25 – 55 °C to attain a true equilibrium. The final pH was recorded before the filtration of suspension. The filtrate was analyzed for phosphate ions by the method given elsewhere [15].

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