Sorption/Desorption Properties of γ-Al_2O_3 Towards Phosphate Anions

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Summary: Sorption studies of γ-Al_2O_3 towards phosphate anions were conducted at various concentrations and pH. The γ-Al_2O_3 was observed to be an effective anion exchange material for phosphate anions. Phosphate uptake was increased with increase in concentration and a decrease in sorption was observed with increase in pH. Desorption studies were also conducted in the pH range 3 to 9 which showed an increase in desorption with pH rise. Sorption and desorption studies accompanying the pH changes showed that the sorption was caused by electrostatic interactions (ion exchange) rather than pure physisorption i.e., non-electrostatic adsorption.

Introduction

The excessive release of industrial, municipal and agriculture wastes into inland waterways and open ponds are a cause of concern due to pollution of water [1]. Cations like Zn, Fe, Pb, Ni, Cd and anions like chlorides, chromates, nitrates and phosphates are the possible pollutants, which is a direct threat to aquatic as well as human lives [2]. P is the limiting element for profitable crop production, and its control is of prime importance in reducing the accelerated eutrophication of fresh waters [3].

Large phosphorus inputs can increase the biological productivity of surface waters to undesirable levels. Phosphate anions in stored water reservoirs may stimulate uncontrolled algal growth in aqueous environment [4] and scaling in vessels used for cooling purposes in industries [5]. Biological/ chemical precipitation, filtration, reverse osmosis and adsorption techniques reported in the literature have been applied for decontamination of polluted waters but the adsorption technique is found superior over all other methods due to faster regeneration rate, better kinetics and greater selectivity towards certain ions [6]. Therefore, many studies have been carried out in recent years in this field [7].

Earlier researchers successfully applied organic resins for phosphate anions removal [7]. However, subsequent workers diverted their attention towards inorganic adsorbents due to their resistance towards oxidizing agents, high thermal and radiation stabilities [8].

Metal oxides/hydroxides an important class of inorganic adsorbents [9], were studied and were found to act as sink for toxic aqueous anions [10].

Iron hydroxide was successfully applied for sorption of phosphate anions in the pH range from 2 to 14 [11]. Sorption was more at low pH. Yekini *et al.,* [12] observed similar results for phosphate sorption. The study was later extended to hydrous oxide such as goethite, gibbsite and clay minerals [13, 14]. Al_2O_3 widely used for cations removal [15] is also known to have affinity towards phosphate anions [16]. The mechanism of surface charge formation of Al_2O_3 in aqueous medium is well documented in the literature [16].

$$AlO + H^+ \Leftrightarrow AlOH^+ \qquad (1)$$

$$AlOH^+ \Leftrightarrow AlO^- + H^+ \qquad (2)$$

$$AlOH^+ \Leftrightarrow Al^{+3} + OH^- \qquad (3)$$

In present study we intend to undertake sorption and desorption of phosphate anions on γ-Al_2O_3 and to evaluate the mechanism of uptake of phosphate anions by γ-Al_2O_3.

Results and Discussions

Sorption studies

The Sorption of phosphate anions on γ-Al_2O_3 at pH 5 can be seen from Figure 1, which shows that

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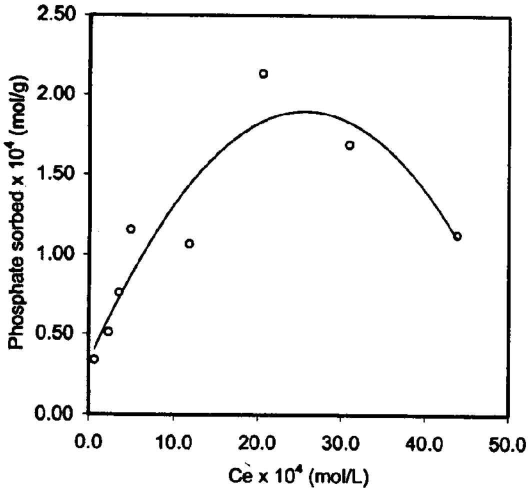

Fig. 1: Sorption isotherms for phosphate anions sorption on Al_2O_3 at pH 5, 303 K.

at low solution concentration phosphate sorption on γ-Al_2O_3 increases sharply and reaches a maxima similar to reported previously for chromate sorption on iron oxide [17]. However after a concentration range of 2.14 x 10^{-4} mol/g sorption decrease as the phosphate concentration increases. Similar, decrease was reported in the literature [18]. These results can be correlated to the increase in positive charge created on the surface as the concentration of phosphate anions increase, consequently, more and more phosphate anions are displaced from the solution on the solid surface. As the concentration further increases the surface charged sites are saturated and the sorption becomes almost constant. These observations are supported in the literature [19].

It is also interesting to note that pH has a major effect on the sorption of phosphate anions depicting a strong dependency on pH, Figure 2. The extent of sorption at pH 3 is greater and decreases with rise in pH. Similar, behavior was reported elsewhere [20]. This shows a greater affinity of aluminum oxide for the phosphate anions at low pH values, because the aluminum oxide below the point of zero charge (PZC) [21] i.e., 7.5 is positively charged (reaction 4). Thus, at low pH the magnitude of the positive charge is greater and there is greater interactions of phosphate anions with the solid surface. Similar results were reported by Micheal Sparling and co-workers [22]. In contrast at high pH i.e., close to PZC the surface charge on Al_2O_3 is minimum, therefore, the extent of phosphate sorption is low.

$$\overline{AlO} + H_2O \Leftrightarrow \overline{AlOH}^+ + OH^- \qquad (4)$$

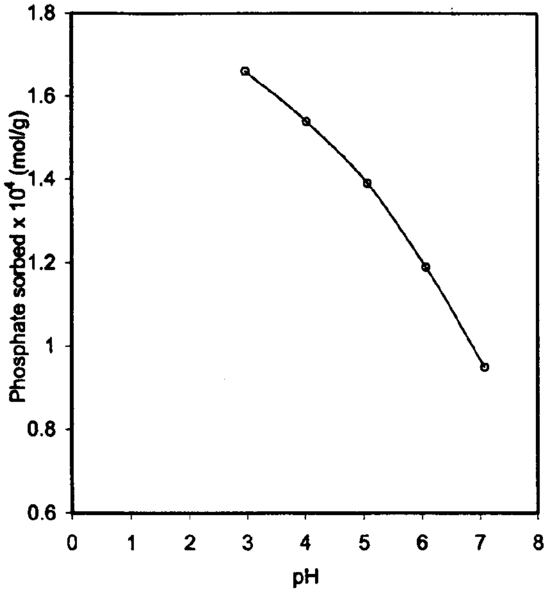

Fig. 2: Effect of pH on sorption of phosphate anions on Al_2O_3 at 303 K.

where AlO and $AlOH^+$ represents the solid Al_2O_3 sorption sites before and after H^+ ions sorption respectively and OH^- is the concentration of hydroxyl ions produced due to ionization of water.

This can also be understood if the pH changes accompanying the phosphate sorption are compared at all the pH (Table 1). At pH 3 the pH changes are greater and higher is the extent of phosphate sorption while at high pH i.e., 7 the pH changes are minimum and lower is the extent of sorption.

Table- 1: Concentrations of phosphate anions sorbed on γ-Al_2O_3 as a function of pH at 303 K

pH adj	pH eq	$H_2PO_4^{-1}$ x 10^4 (mol/g)
2.969	6.034	1.66
4.031	6.423	1.54
5.071	6.493	1.39
6.067	6.871	1.19
7.076	7.713	0.95

pH adj = pH adjusted; pH eq = Equilibrium pH

From the foregoing discussions the mechanism of uptake of phosphate anions by γ-Al_2O_3 can be described with the help of reaction 5,

$$\overline{Al-OH_x^+} + PO_4^{-3} \overset{K}{\Leftrightarrow} \overline{AlO_xPO_4^{-3+x}} \qquad (5)$$

where K is the equilibrium constant.

Desorption studies

The desorption studies of phosphate anions sorbed γ-Al_2O_3 are conducted at 303K in the pH range 3 to 9 and 24 hours equilibration using batch technique, in order to survey the mechanism of sorption and the effect of pH on desorption behavior of γ-Al_2O_3. It can be seen from Figure 3 that the desorption of phosphate anions increases with increase in pH of suspension, Table 2. Similar effect of pH on phosphate desorption was reported in the literature on other oxides [23].

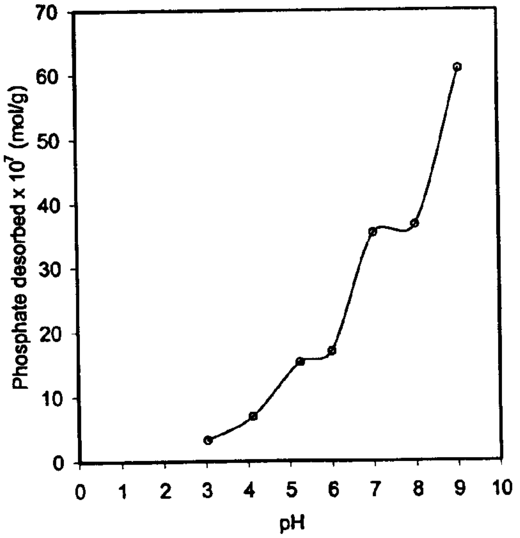

Fig. 3: Plot of phosphate anions desorbed vs pH on Al_2O_3 at 303 K.

Table- 2: Equilibrium pH and phosphate anions release from γ-Al_2O_3 at 303 K

pHadj	pHeq	$H_2PO_4^{-1}$ x 10^7 (mol/g)
3.037	3.431	3.26
4.111	4.437	6.93
5.253	4.737	15.35
6.007	4.642	17.03
7.017	5.490	35.35
8.005	5.488	36.61
9.077	6.311	60.82

It can be suggested that at low pH the surface has specific interactions towards phosphate anions i.e., the magnitude of surface charge on the surface is more therefore, the electrostatic interactions between the surface positive charge and phosphate anions are more consequently, less is the phosphate anions release. In contrast, at high pH the surface and phosphate anions interactions are less and the phosphate desorption is more. Comparing the pH changes and the amount of phosphate ions desorption along with the point of zero charge of aluminum oxide, it is concluded that the OH^- ions replaces for phosphate anions and reaction 5 progress in backward direction which impart surface regeneration to aluminum oxide.

57% phosphate anions was desorbed when the aluminum oxide was equilibrated with 0.1 M potassium hydroxide (KOH) however, complete regeneration was possible by equilibrating with 0.2 M KOH indicating the surface to be of economical importance for recovery and purification purposes.

Experimental

All the reagents used were of analytical grade and were used as supplied. 0.1 M HNO_3 and 0.1 M KOH was prepared for pH adjustment. Buffers of pH 2 and 11 were also prepared in doubly distilled water for standardization of pH meter.

The adsorbent γ-Al_2O_3 was purchased from Merck and was used as such.

Stock solution of phosphate (1000 ppm) was prepared in doubly distilled water from KH_2PO_4 provided by Merck.

Adsorption studies

The adsorption studies of phosphate anions on γ-Al_2O_3 were performed in an end-to-end shaker bath, Labortechnic type LE-209, provided with hooks for 50ml conical flasks. Different concentrations of phosphate anions were prepared in doubly distilled water. Before starting the experiment 0.1g of Al_2O_3 was taken in 50ml Pyrex glass flask, to which 20ml of phosphate solution was transferred. Initial pH of the suspensions was recorded and was adjusted to the desired pH either by the addition of standard HNO_3/KOH. The flasks were then transferred into the shaker bath for 24 hours at constant temperature. After 24 hours, the suspensions were centrifuged/ filtered out and the filtrate was analyzed for the equilibrium concentration of phosphate anions. The equilibrium concentrations of phosphate anions were measured spectrophotometrically using the method reported in the literature (24). Spectronic 20-D was used for phosphate analysis at 882 nm.

Desorption studies

Desorption studies for phosphate anions from γ-Al_2O_3 were performed in the pH range 3 to 7 and at temperature 303 K. 20 mL of distilled water was added to 0.1g of phosphate sorbed γ-Al_2O_3. The pH of the suspensions was adjusted to the desired one either by KOH/HNO_3. The suspensions were kept shaking in shaker bath at 303 K. After 24hours of equilibration, pHs of the suspensions were recorded and were filtered through a Whatman filter paper.

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