

# Removal of phosphates from aqueous solutions by using bauxite. I: Effect of pH on the adsorption of various phosphates

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**Abstract:** In this study, the effect of pH on adsorption of various forms of phosphate onto bauxite was investigated. For this purpose, the adsorption and desorption of inorganic (ortho and condensed) and organic phosphate species were studied. It was observed that the adsorption tendency of the various phosphate forms was different and depended on pH. Maximum adsorption efficiencies for all phosphate forms were achieved in slightly acidic conditions (pH 3.2–5.5). The results of adsorption and desorption studies showed that the adsorption of phosphates onto bauxite is based on a ligand exchange mechanism. The adsorption mechanism of inorganic condensed phosphates and organic phosphates is thought to be more complex than that of orthophosphate. It can be stated that the adsorption of organic phosphates is dependent on the functionality, number, and variety of organic groups. The results of experiments carried out with mixed phosphate solutions showed that the adsorption yields of various phosphate forms are dependent on the composition of the solution. The relative adsorptivity of various phosphates was found to be in the general order of hexametaphosphate > pyrophosphate > orthophosphate > tri-polyphosphate > adenosine triphosphate > glycerophosphate > glucose-1-phosphate.

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**Keywords:** phosphate adsorption; bauxite; adsorption of mixed phosphates; surface complexation

## INTRODUCTION

Eutrophication of the water bodies is considered as one of the most important environmental problems and phosphorus has been regarded as a key element in the eutrophication of water reservoirs. Therefore, its removal from municipal and some industrial wastewaters becomes absolutely necessary. The method of chemical precipitation has been considered for the removal of phosphorus from lakes which are seriously damaged by eutrophication.<sup>1</sup>

The phosphorus usually occurs in wastewater and surface water in the form of inorganic (ortho and condensed) and organic phosphates. The removal of phosphates from wastewater can be achieved either through biological treatment and chemical precipitation or a combination of both. These techniques have been used to reduce phosphorus concentrations to below  $1.0\text{mgdm}^{-3}$  in effluent discharged from a municipal wastewater treatment plant.<sup>2</sup> However, they are generally expensive and difficult to apply efficiently since they create considerable volumes of phosphorus-rich sludge which requires disposal. Furthermore, in the case of chemical precipitation, some new pollutants such as chloride and sulfate ions can be introduced into the water. Thus, alternative techniques for the removal of phosphorus are continually being investigated and developed. Since adsorption seems

to be the most economical and applicable of these techniques, attention has been focussed on phosphate adsorbents. Moreover, it has been reported that phosphate removal by adsorption can be used as a tertiary treatment method.<sup>2</sup> In this connection, it has been reported that some large-scale applications of phosphate adsorption are in use.<sup>3</sup>

A range of adsorbents has been investigated for phosphate adsorption; these include aluminas,<sup>4–7</sup> aluminium hydroxide,<sup>8–11</sup> synthetic boehmite,<sup>12</sup> gibbsite,<sup>13</sup> kaolinite,<sup>5</sup> iron(III) hydroxide,<sup>9</sup> goethite,<sup>14–16</sup> alumino haematite,<sup>17</sup> soils,<sup>18</sup> serpentine,<sup>19</sup> porous glass and  $\text{SiO}_2$ ,<sup>20</sup> sand,<sup>21</sup> activated carbon,<sup>22,23</sup> fly ash,<sup>4,24–26</sup> red mud,<sup>27,28</sup> pyrite cinder,<sup>29</sup> ferrochrome slag<sup>30</sup> and blast furnace slag.<sup>31</sup> In these studies, various minerals, commercial materials and some industrial wastes were evaluated for phosphate adsorption and the adsorption characteristics of inorganic orthophosphates have been widely investigated. Approximately 50% of total soluble phosphorus in municipal wastewater exists in the form of condensed and organic phosphates.<sup>32</sup> Although the adsorption characteristics of orthophosphate are well known, further clarification is still needed on the adsorption of condensed and organic phosphates.

The majority of oxidic adsorbents, especially iron and aluminium oxides, have attracted attention among

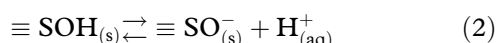
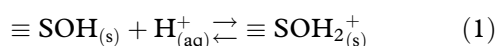
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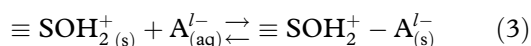
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the adsorbents investigated for removal of anions from aqueous solutions. It is widely held that the mechanism for the adsorption of anions on to oxidic surfaces involves a surface complexation phenomenon in the adsorption process. Depending on the type of connection of an anion to an active surface site, the surface complexes formed are classified as inner and outer-sphere complexes. In opposition to the inner-sphere complexes, there are H<sub>2</sub>O molecules between the active surface sites and the anions in the outer-sphere complexes. Formation of these surface complexes is mostly dependent on the degree of surface protonation or dissociation. It has been reported that the surface reactions could be described as:<sup>12,33–36</sup>

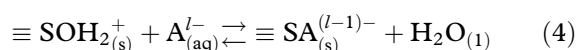


where S is the hydroxylated mineral surface and OH is a reactive surface hydroxyl. If the number of protonated surface groups is more than that of dissociated groups, the surface is positively charged and becomes suitable for anion adsorption. If the amounts of both species are equal, a condition for zero net proton charge (PZNPC) is achieved. Thus, the proposed complex-formation reactions for anions can be illustrated as:<sup>24,37</sup>

In the case of outer-sphere complexes:



In the case of inner-sphere complexes:



where A<sup>l-</sup> represents an anion.

It has been reported that the adsorption of the orthophosphate anion on to hydroxylated mineral surfaces occurs by formation of monodentate and bidentate inner-sphere complexes.<sup>38</sup>

In the earlier studies mentioned above, the aluminium oxide-based adsorbents investigated for phosphate adsorption are generally expensive commercial products. Bauxite, which is an important industrial raw material for alumina production, seems to be more economical for phosphate removal processes.

In our study,<sup>39</sup> the adsorption characteristics of various phosphates were investigated on a large scale using bauxite. This paper provides result of some pH studies and some mechanistic considerations which will be useful for the removal of various phosphates using bauxite.

## MATERIALS AND METHODS

A bauxite sample, obtained from Seydisehir Aluminium Plant, Konya (Turkey), was crushed in a jaw crusher, ground in a ball mill and then wet-sieved. The fraction under 74 μm was washed with distilled water by mixing at a 1:5 solid/liquid ratio for 15 min and then filtered and dried at 100 °C for 6h. This material was used in all experiments.

Prepared bauxite sample was subjected to wet chemical analyses.<sup>40</sup> Mineralogical characterization was carried out using a Siemens D 5000 XRD instrument by using a powder diffraction technique. Some physical and physicochemical characteristics of the bauxite sample were determined by using various instrumental analysis techniques such as Single Point N<sub>2</sub>-BET Surface Area measurement (Micromeritics-Flowsorb 2300), density and porosity analysis (Micromeritics-Pore Sizer 9310), particle size distribution analyses (Malvern Inst Mastersizer X). Also, the point of zero net proton charge (PZNPC) for the bauxite sample was determined as a pH value by a potentiometric titration route.<sup>41</sup> The chemical and mineralogical compositions and some physical and physicochemical properties of bauxite used in the study are given in Tables 1 and 2, respectively.

The experimental solutions were made from stock phosphate solutions which were prepared from the following salts:

<u>Orthophosphate</u>	: NaH <sub>2</sub> PO <sub>4</sub> · 2H <sub>2</sub> O (Merck, 6576)
<u>Condensed phosphates</u>	
Tripolyphosphate (TPP)	: Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> (Sigma, 7758-29-4)
Pyrophosphate (TP)	: Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> · 10H <sub>2</sub> O (Merck, 6591)
Metaphosphate (MP)	: (NaPO <sub>3</sub> ) <sub>n</sub> , Graham's salt (Merck, 6529)
<u>Organic phosphates</u>	
α-D-Glucose-1-phosphate (G1P)	: C <sub>6</sub> H <sub>11</sub> O <sub>9</sub> PK <sub>2</sub> (Sigma, 5996-14-5)
Adenosine triphosphate (ATP)	: C <sub>10</sub> H <sub>14</sub> N <sub>5</sub> O <sub>13</sub> P <sub>3</sub> Na <sub>2</sub> (Sigma, 51963-61-2)
Glycerophosphate (GP)	: C <sub>3</sub> H <sub>5</sub> (OH) <sub>2</sub> PO <sub>4</sub> Na <sub>2</sub> (Merck, 3108)

Chemical composition		Mineralogical composition	
Constituent	w/w (%)	Minerals	w/w (%)
Al <sub>2</sub> O <sub>3</sub>	56.91	Boehmite [AlOOH]	59.10
Fe <sub>2</sub> O <sub>3</sub>	16.95	Kaolinite [Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ]	11.34
SiO <sub>2</sub>	8.62	Diaspore [AlO(OH)]	1.76
TiO <sub>2</sub>	2.40	Haematite [α-Fe <sub>2</sub> O <sub>3</sub> ]	15.39
CaO	0.91	Anatase [TiO <sub>2</sub> ]	1.49
CO <sub>2</sub>	0.78	Calcite [CaCO <sub>3</sub> ]	1.29
P <sub>2</sub> O <sub>5</sub>	0.13	Quartz [SiO <sub>2</sub> ]	0.86
V <sub>2</sub> O <sub>5</sub>	0.032	Amorphous substances and others	8.77
S	0.032		
LOI (1000 °C)	12.36		

**Table 1.** Chemical and mineralogical compositions of bauxite

**Table 2.** Some physical and physicochemical properties of bauxite

Physicochemical properties	Value
Mean particle diameter ( $\mu\text{m}$ )	18.54
Modal value ( $\mu\text{m}$ )	38.94
Single Point $\text{N}_2$ -BET Surface Area ( $\text{mg}^{-1}$ )	$11.0 \pm 0.5$
Apparent density ( $\text{g cm}^{-3}$ )	1.4713
Skeletal density ( $\text{g cm}^{-3}$ )	2.1311
Porosity ( $\text{cm}^3 \text{cm}^{-3}$ )	0.310
Mean pore radius ( $\mu\text{m}$ )	3.689
PZNPC	8.39

Phosphate salts were analysed and their phosphorus contents were determined by using an analytical grade diammonium hydrogen phosphate (Merck, 1207) as a standard.

Batch adsorption experiments were carried out by shaking  $250 \text{ cm}^3$  glass conical flasks containing 1 g of bauxite samples and  $100 \text{ cm}^3$  of solutions having a concentration of  $10 \text{ mg-P dm}^{-3}$ . The suspensions were shaken ( $400 \text{ cycle/min}^{-1}$ ) in a temperature-controlled vibrating waterbath (Clifton) at  $25^\circ\text{C}$  for 2 h. For the adsorption studies, experiments carried out using mixed phosphate solutions where the total phosphorus concentration was designated as  $10 \text{ mg-P dm}^{-3}$  and the concentration of each species was equal. All adsorption experiments were performed at a constant ionic strength of  $0.01 \text{ M NaCl}$ . The initial pH values of suspensions were adjusted with NaOH and HCl solutions by using a Mettler Delta 3000 pH meter equipped with a combined glass electrode. All dilutions were made using distilled water. The laboratory were used in the experiments was soaked in diluted HCl solution for 12 h, washed, and then rinsed with distilled water.

Ortho-, triply- and glycerophosphates were selected for desorption studies. For this purpose, adsorption experiments were first repeated at their specified pH values. After centrifugation and drying (at  $100^\circ\text{C}$ ) of the solid, the desorption studies were conducted by shaking 1.0 g phosphate-adsorbed bauxite samples with  $100 \text{ cm}^3$  distilled water at  $25^\circ\text{C}$  and different pH values for 2 h. In the adsorption and desorption experiments, at the end of shaking period, the final pH values of the suspensions were measured and these mixtures were centrifuged at 10 000 rpm for 10 min. The supernatants were analysed for phosphate.

Phosphate analyses were performed following the ascorbic acid method using a Jenway D500 model UV-Visible spectrophotometer.<sup>42</sup> A preliminary sulfuric acid hydrolysis procedure was carried out for all solutions containing condensed phosphates before the analyses. For the solutions containing organic phosphates, a preliminary digestion procedure was applied in order to convert organic phosphate to orthophosphate. For this purpose, a sulfuric acid–persulfate digestion route was used for adenosine triphosphate (ATP) and glucose-1-phosphate (G1P).

In the case of glycerophosphate, a sulfuric acid–nitric acid digestion method was used.<sup>42</sup>

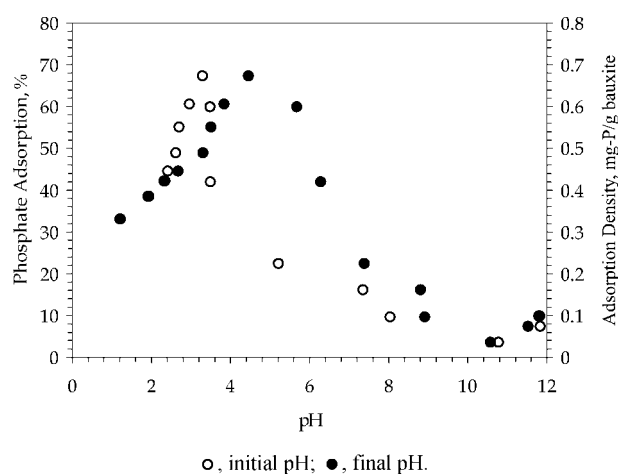
The experiments were performed in duplicate and the mean values were considered. In order to ascertain the reproducibility of the results, the group experiments were repeated a number of times and the results were found to vary within  $\pm 5\%$ .

## RESULTS AND DISCUSSION

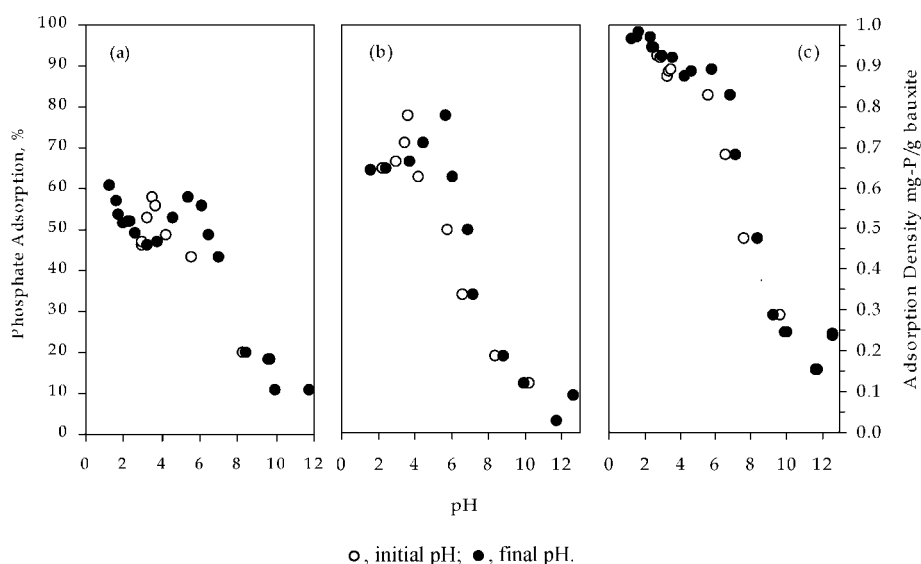
The preliminary studies showed that adsorption of various phosphates could not achieve steady state even after 24 h, but the rates of phosphate concentration change ( $dc/dt$ ) were below  $0.01 \text{ mg-P dm}^{-3} \text{ min}^{-1}$  at the end of the contact period of 2 h. Thus, all adsorption experiments were carried out for 2 h.

For the removal of phosphates from aqueous solutions by adsorption, pH is considered to be an important parameter. The effect of pH on the removal of ortho-, inorganic condensed and organic phosphates is shown in Figs 1, 2 and 3, respectively. The variation of the removal efficiency with pH follows different patterns for the various phosphates. As shown in Fig 1, maximum orthophosphate removal occurs at  $\text{pH}_f$  of 4.45. At this final pH, the removal efficiency of orthophosphate is 67.3%. In addition, the removal efficiencies in acidic conditions are higher than those achieved in basic conditions. Similar findings have been reported in orthophosphate adsorption studies performed using various aluminium-bearing adsorbents such as alumina,<sup>5,6</sup> amorphous aluminium hydroxide,<sup>8–10</sup> boehmite<sup>12</sup> and gibbsite.<sup>13</sup>

There are significant differences between the initial and final pH values of mixtures, which are in Figs 1–3. The adsorption of phosphates on to the hydroxylated mineral surface can be described by a ligand exchange mechanism,<sup>38</sup> which causes an increase in pH stemming from the hydroxyl ions released from the oxidic

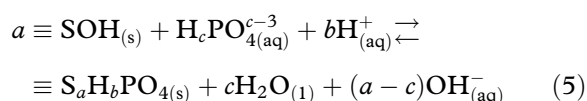


**Figure 1.** The effect of pH on the orthophosphate adsorption by bauxite ( $10 \text{ mg-P dm}^{-3}$  orthophosphate solutions; contact time: 2 h; temperature:  $25^\circ\text{C}$ ; dosage:  $10 \text{ g dm}^{-3}$ ; ionic strength:  $0.01 \text{ M NaCl}$ ).



**Figure 2.** Effect of pH on the adsorption of various condensed phosphate forms by bauxite (a) tripoly-, (b) pyro- and (c) hexametaphosphates (10 mg-P dm<sup>-3</sup> condensed phosphate solutions; contact time: 2 h; temperature: 25 °C; dosage: 10 g dm<sup>-3</sup>; ionic strength: 0.01 M NaCl).

adsorbent:



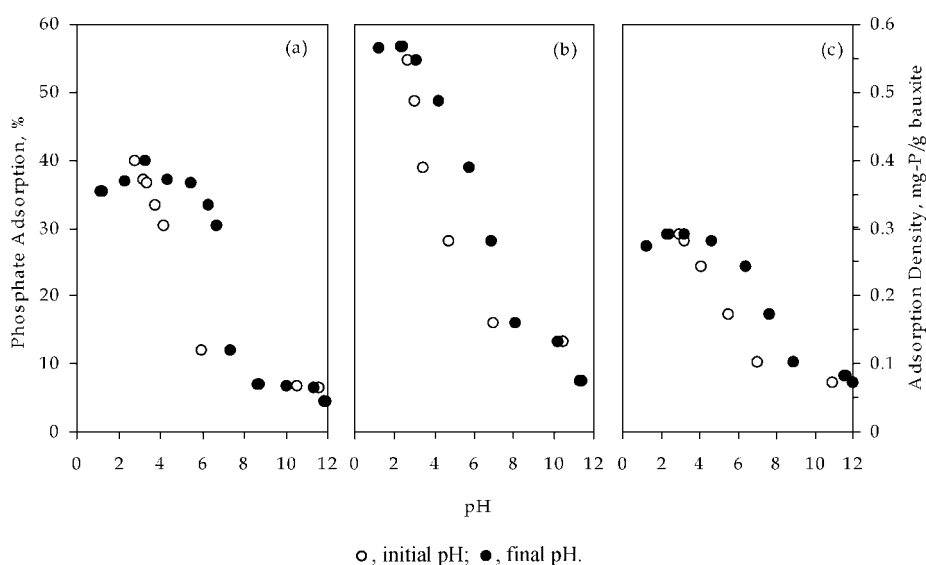
In eqn (5), S refers to a metal atom in a hydroxylated mineral, OH to a reactive surface hydroxyl, *a*, *b* and *c* are stoichiometric coefficients and *c* ≤ 3 is the degree of protonation of the phosphate ion. The reaction product is referred to as an inner-sphere complex since it contains no water molecules between the surface Lewis acid site (S) and the adsorbed ion.<sup>37</sup>

In the aqueous solutions, various types of protonated phosphate species are formed, depending on pH. On the other hand, the PZNPC of the adsorbent has an important role in the adsorption phenomenon. Maximum orthophosphate removal was obtained at the final pH of 4.45; the dominant orthophosphate species being the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ion. The PZNPC value of

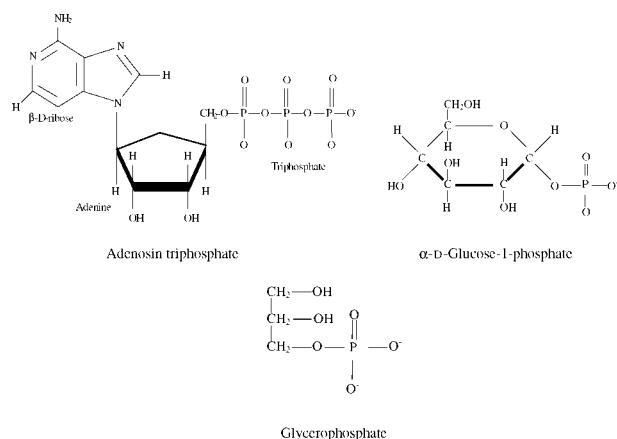
the bauxite used in the study was found to be 8.39, below which the surface is positively charged. Thus, the positively-charged groups on the adsorbent surface may adsorb the dominant phosphate species of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>.

The influence of pH on the adsorption of condensed inorganic phosphates (tripoly-, pyro- and hexameta-) is shown in Fig 2. The maximum removal efficiencies for tripoly-, pyro- and hexametaphosphates are observed at final pH values of 1.24, 5.67 and 1.67, respectively with corresponding percentages of removal of 60.70%, 77.68% and 98.24% for tripoly-, pyro- and hexametaphosphates. The removal of tripolyphosphate follows an interesting pattern. The removal yield of tripolyphosphate decreases as the pH increases up to 3.27 and thereafter, an increase is observed up to pH 5.4. Beyond this value, a sharp decrease is observed.

The adsorption mechanism of condensed phosphates can be explained in terms of the basic principles



**Figure 3.** Effect of pH on the adsorption of various organic phosphate forms by bauxite (a) glycerotri-, (b) adenosine triphosphate and (c) glucose-1-phosphate (10 mg-P dm<sup>-3</sup>. Organic phosphate solutions; contact time: 2 h; temperature: 25 °C; dosage: 10 g dm<sup>-3</sup>; ionic strength: 0.01 M NaCl).



**Scheme 1.** Structures of organic phosphate compounds.

suggested for orthophosphate adsorption. However, the interesting behaviour of tripolyphosphate and high removal efficiency in the adsorption of hexametaphosphate in strongly acidic solutions show that the mechanism governing adsorption of condensed phosphate is more complex. This may be attributed to the different shapes and sizes of various phosphate molecules and also the formation of orthophosphate by hydrolytic degradation during the adsorption process. At the conditions of  $10\text{ mg-P dm}^{-3}$  initial concentration, 2h contact time and  $25^\circ\text{C}$ , the orthophosphate concentrations in the treated tripoly-, pyro- and hexametaphosphate solutions were determined as 0.73, 0.93 and  $0.37\text{ mg-P dm}^{-3}$ . Furthermore, orthophosphate produced by degradation may be partially adsorbed on to the bauxite surface. The hydrolytic degradation may be influenced by the catalytic effects of mineral surfaces. It has been reported that some oxidic constituents such as titanium dioxide, which is readily present in bauxite, have a significant catalytic effect on hydrolytic degradation of tripolyphosphate.<sup>43</sup>

Figure 3 shows the effect of pH on the adsorption of glycerophosphate (GP), adenosine triphosphate (ATP) and glucose-1-phosphate (G1P). Although the organic phosphates studied exhibit similar patterns, their removal efficiencies are quite different. Removal maxima for GP, ATP and G1P were obtained at the same final pH range of 2.2–3.3. In

this pH range, the removal efficiencies were about 38%, 56% and 29%, respectively. It should be noted that GP and G1P, which are organic orthophosphates, exhibit lower adsorptivity than that of ATP which is an organic condensed phosphate. Among these three compounds, there are some structural differences such as shape and size of molecule, number and variety of functional groups and number of phosphate groups. The structures of these organic phosphate compounds are illustrated in Scheme 1.

Shang *et al*<sup>8</sup> have reported that inositol hexaphosphate was adsorbed more effectively than the inositol monophosphate onto goethite because of the differences in the functionality of their phosphate groups. A similar interpretation has been made for inositol hexaphosphate, glucose-1-phosphate and orthophosphate adsorption characteristics.<sup>15</sup>

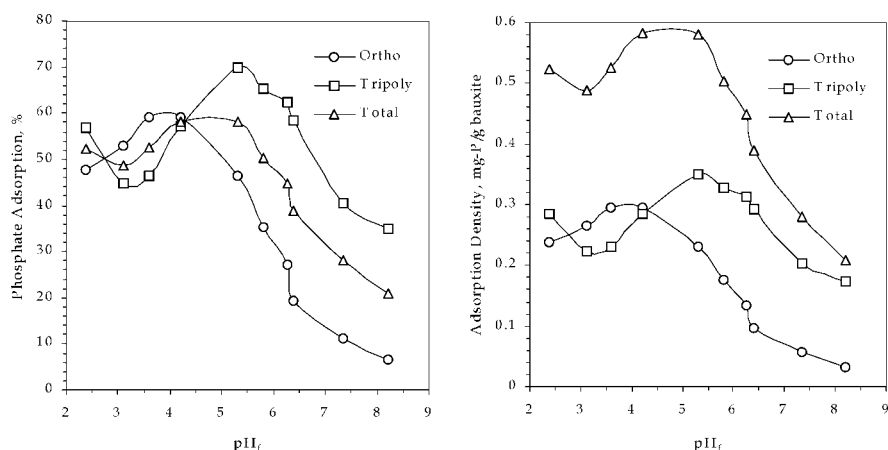
Organic phosphates can also be degraded to orthophosphate in acidic aqueous solutions. In our study, the highest orthophosphate concentrations in the treated solutions were determined as 0.22 and  $0.13\text{ mg-P dm}^{-3}$  for ATP and G1P, respectively, at about  $\text{pH}_f$  1.2.

In the case of the GP, orthophosphate concentrations in the treated solution were below the determination limits for all pH values. It can be concluded that adsorption of organic phosphates is a complex process including a degradation process similar to that of inorganic condensed phosphates.

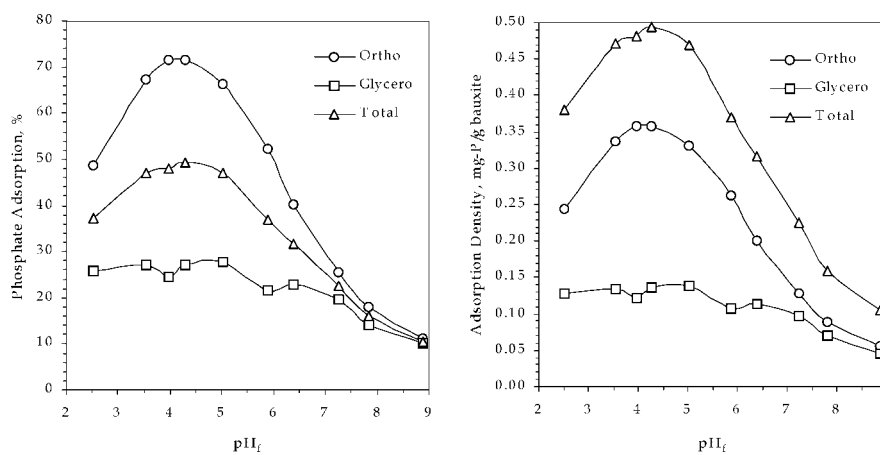
Tripolyphosphate is widely used as a detergent builder. It was found that the glycerophosphate was resistant to conversion into orthophosphate. For these reasons the orthophosphate, tripolyphosphate and glycerophosphate were used in the preparation of the mixed solutions. The results obtained from experiments carried out using mixed phosphate solutions are shown in Figs 4–7.

As seen from the figures, the pH dependence of phosphate removal in multiple systems shows a similar trend to single phosphate systems. It should be noted that the presence of different phosphates together in the solution influenced their adsorptivity.

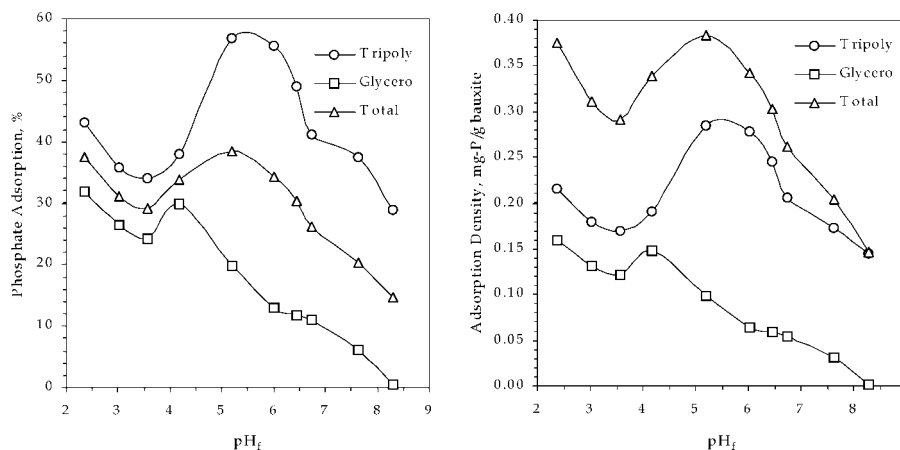
For a comparison, the maximum removal yields and corresponding pH values are given in Table 3. It can be



**Figure 5.** Effect of pH on the phosphate adsorption from mixed ortho–glycerophosphate solution (solutions containing  $5\text{ mg-P dm}^{-3}$  orthophosphate and  $5\text{ mg-P dm}^{-3}$  glycerophosphate; contact time: 2 h; temperature:  $25^\circ\text{C}$ ; dosage:  $10\text{ g dm}^{-3}$ ; ionic strength:  $0.01\text{ M NaCl}$ ).



**Figure 6.** Effect of pH on the phosphate adsorption from mixed tripoly–glycerophosphate solution (solutions containing  $5\text{ mg-P dm}^{-3}$  tripoly phosphate and  $5\text{ mg-P dm}^{-3}$  glycerophosphate; contact time: 2 h; temperature:  $25^\circ\text{C}$ ; dosage:  $10\text{ g dm}^{-3}$ ; ionic strength:  $0.01\text{ M NaCl}$ ).



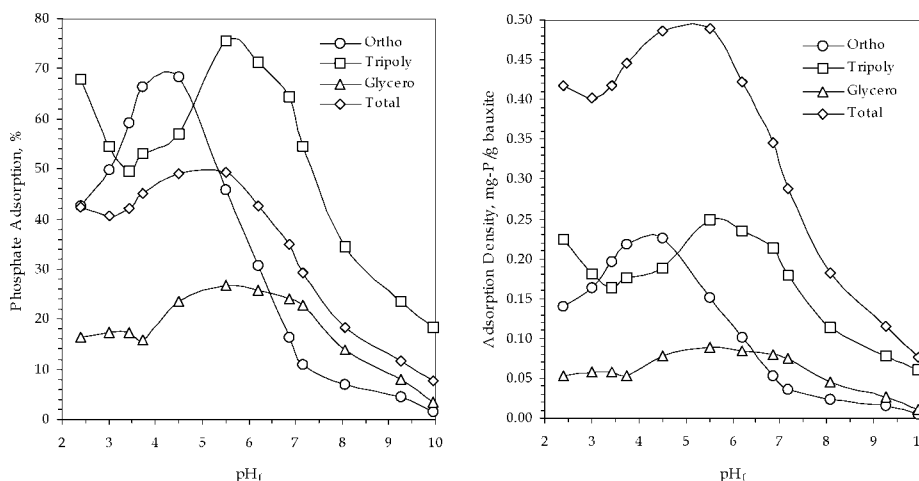
stated that the pH values at which adsorption maxima occurred for multiple systems are close to those of the results from the study of single phosphate systems.

In contrast with the results obtained from single phosphate solutions, the removal efficiency of tripolyphosphate was found to be higher than that of orthophosphate for binary and ternary phosphate systems containing tripoly- and orthophosphate. This may arise from the catalytic effect of the mineral surface and acid, which causes a partial conversion of tripolyphosphate to the ortho form.

The results obtained from tripoly–glycero and ortho–glycero binary systems support this idea. Although the individual removal yield of glycerophosphate is low in the glycero–tripolyphosphate system, this value for the tripoly form for this system is lower than that of the tripoly–ortho system. Accordingly, the individual orthophosphate removal percentages for the ortho–glycero pair are higher than that of the ortho–tripoly system (Figs 4–7).

The phosphate-adsorbed bauxite samples were subjected to desorption experiments. The bauxite

**Figure 7.** Effect of pH on the phosphate adsorption from mixed ortho–tripoly–glycerophosphate solution (total phosphorus concentration is  $10\text{ mg-P dm}^{-3}$  and concentration of each species is equal; contact time: 2 h; temperature:  $25^\circ\text{C}$ ; dosage:  $10\text{ g dm}^{-3}$ ; ionic strength:  $0.01\text{ M NaCl}$ ).



**Table 3.** Maximum removal pH and corresponding adsorption percentage of phosphates in single, binary and ternary mixed solution systems

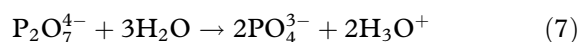
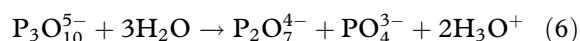
Single solution system										
	Ortho			Tripoly			Glycero			
pH	4.45			5.41			3.23			
Remov eff, %	67.3			57.71			39.98			
Binary solution system										
	Ortho-Tripoly			Ortho-Glycero			Tripoly-Glycero			
	OP	TPP	Tot	OP	GP	Tot	TPP	GP	Tot	
pH	4.20	5.31	4.20	3.98	5.04	4.29	5.19	4.17	5.19	
Remov eff, %	59.19	69.94	58.18	71.66	27.60	49.36	56.88	29.78	38.33	
Ternary solution system										
	Ortho			Tripoly			Glycero			Total
pH	4.50			5.51			5.51			5.51
Remov eff, %	68.40			75.52			26.79			49.41

samples obtained from adsorption of ortho-, tripoly- and glycerophosphate at optimum conditions were contacted with solutions at various pH values. These solutions were prepared from distilled water and HCl or NaOH.

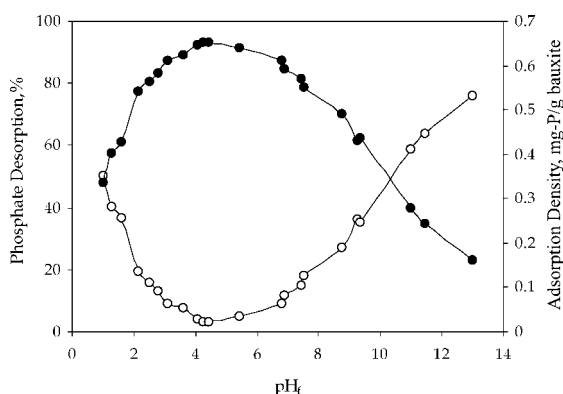
The results of the effect of pH on the desorption of orthophosphate are given in Fig 8. As expected, the amount of desorbed orthophosphate is of a minimum at around the same pH at which adsorption is optimal. In the strongly acidic (pH~1) and basic (pH~13) media, the amounts of released orthophosphate reach values of 50.32% and 75.83%, respectively. These findings confirm that the ligand exchange mechanism for anion adsorption, suggested by earlier investigators,<sup>12,38</sup> is valid for the bauxite-phosphate system.

Figure 9 shows the results of the tripolyphosphate desorption study. It can be stated that the desorption trend of tripolyphosphate is similar to that of orthophosphate. In the adsorption study, it was determined that a portion of tripolyphosphate was converted to orthophosphate. Thus, this conversion was followed by determining the orthophosphate concentration in the supernatants obtained from tripolyphosphate

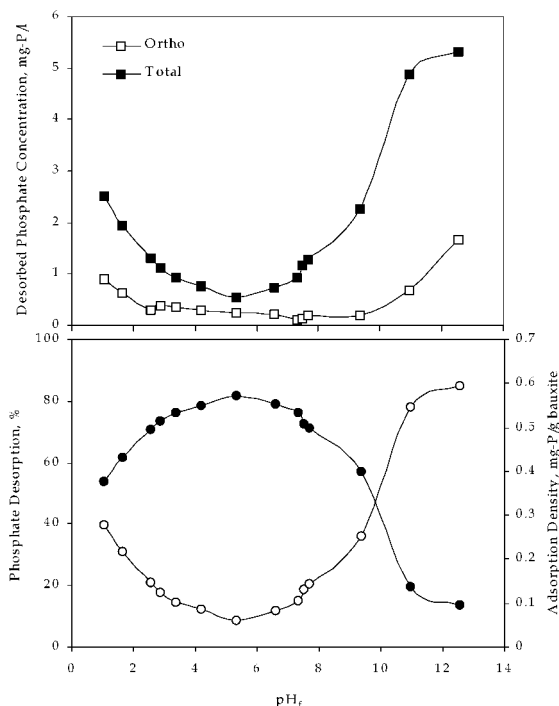
desorption experiments. The existence of orthophosphate in the desorption solutions may be attributed hydrolytic degradation of tripolyphosphate during either the adsorption or desorption processes. The mechanism of hydrolytic degradation can be explained through eqns (6) and (7).



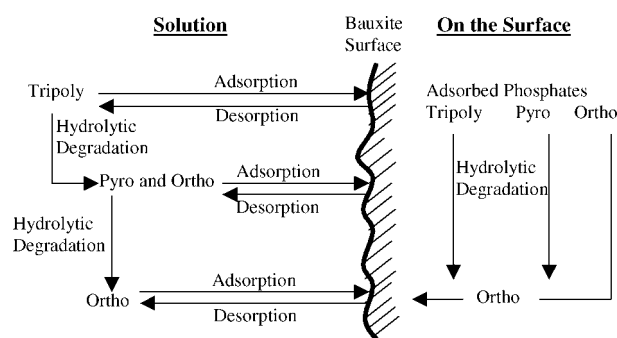
In the desorption experiments carried out with tripolyphosphate-adsorbed bauxite samples, 39.9% of



**Figure 8.** Effect of pH on the desorption of orthophosphate from phosphate-adsorbed bauxite samples ( $0.652\text{mg-Pg}^{-1}$  samples, contact time: 2h).



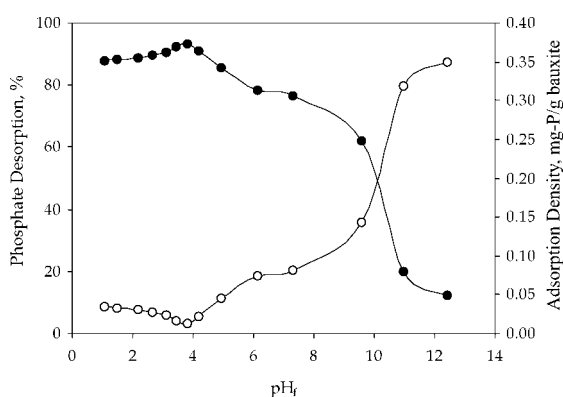
**Figure 9.** Effect of pH on the desorption of tripolyphosphate from phosphate-adsorbed bauxite samples ( $0.627\text{mg-Pg}^{-1}$  samples, contact time: 2h).



**Scheme 2.** The scheme of adsorption and desorption of tripolyphosphate.

phosphate was found to be desorbed at pH 1.04. In addition, the presence of  $0.9 \text{ mg-P dm}^{-3}$  orthophosphate in the solution obtained at the end of the desorption period shows that 35.95% of the phosphate is degraded. In fact, this amount is a minimum. Because the remaining phosphate on the surface may be partially in the form of orthophosphate, it can be stated that a significant portion of tripolyphosphate undergoes degradation during adsorption–desorption processes. In basic conditions, although the degree of phosphate desorption is much higher, the amount degraded is relatively lower. For example, 84.7% of phosphate is desorbed at pH 12.56 while the portion of orthophosphate in the final solution is 31.1%.

The scheme of adsorption and desorption of tripolyphosphate is illustrated in Scheme 2. The desorption results for glycerophosphate are shown in Fig 10. Although the pH dependence of glycerophosphate desorption is similar to ortho- and tripolyphosphate, desorption yields of glycerophosphate in the acidic medium are relatively low. Maximum desorption efficiency of glycerophosphate is determined as 87.2% at final pH 12.4. The amount of orthophosphate probably produced via degradation was found to be below the determination limits. These results show that the glycerophosphate does not readily convert to the ortho form under the adsorption and desorption conditions applied.



**Figure 10.** Effect of pH on the desorption of glycerophosphate from phosphate-adsorbed bauxite samples ( $0.385 \text{ mg-P g}^{-1}$  samples, contact time: 2h).

## CONCLUSION

Based on the results of this study of the effect of pH on the removal of various phosphates from aqueous solutions by adsorption with bauxite, the following conclusions can be drawn.

The adsorption of ortho-, inorganic condensed and organic phosphates on bauxite has been found to be firmly dependent on pH and maximum removal efficiencies of three phosphate types have been obtained at slightly acidic conditions. Experiments undertaken with the solutions of binary and ternary mixed phosphates show that the composition of the solution is another factor affecting adsorption. Increase in pH accompanying the adsorption process leads to a mechanism involving a ligand exchange. Results obtained from desorption experiments support this idea.

The adsorpties of ortho- and inorganic condensed phosphates towards the bauxite are similar and rather higher than those of organic phosphate. The relative affinities of all the studied phosphate species organic phosphates have been found to be in the general order of hexametaphosphate > pyrophosphate > orthophosphate > tripolyphosphate > adenosine triphosphate > glycerophosphate > glucose-1-phosphate.

It has been determined that inorganic condensed phosphates convert into orthophosphates during the adsorption due to the catalytic effects of mineral surface and acid. Consequently, it can be stated that the removal of inorganic condensed phosphates occurs through adsorption, desorption, and degradation or their combination. Further more the degree of degradation of these inorganic condensed phosphates is in the order of pyrophosphate > tripolyphosphate > hexametaphosphate. The results from experiments conducted with different types of organic phosphates show that adsorption efficiency is influenced by the number and variety of functional groups.

The use of bauxite for adsorption of phosphates from aqueous medium seems to be more advantageous than that of other materials such as alumina. Bauxite, ground for alumina production, can be utilized in phosphate adsorption before the Bayer Process. Thus, it may be concluded that the bauxite is a low-cost adsorbent for phosphate adsorption. A further article on increasing the phosphate adsorption capability of bauxite by activation, is in preparation.

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