

# Removal of phosphates from aqueous solutions by using bauxite II: the activation study

H Soner Altundoğan\* and Fikret Tümen

Firat University, Department of Chemical Engineering, 23279 Elazığ, Turkey

**Abstract:** In this study, acid treatment and heat treatment methods have been investigated in order to enhance the phosphate adsorption capacity of bauxite. For this purpose, a series of bauxites treated with 0.1–1.0 M HCl and another one heated at various temperatures between 200 and 1000 °C were subjected to standardized orthophosphate adsorption tests. Besides determining chemical and mineralogical compositions, TGA and DTA were performed and point of zero net proton charge (PZNPC), surface area, mean particle size and porosity were measured for selected samples. The results have shown that the acid treatment of bauxite has a negative effect on the phosphate adsorption capability. On the other hand, it has been observed that the phosphate adsorption capacity of bauxite could be increased by heating. The optimum heating temperature was determined as 600 °C. Bauxite heated at 600 °C exhibited about an eight-fold increase in surface area compared with raw bauxite. The results showed that the activation of bauxite occurred via dehydration of boehmite and diaspore, being the hydrated mineral phases. Maximum adsorption efficiencies for ortho-, tripoly- and glycerophosphates were achieved in the slightly acidic pH range. It was found that the adsorption capacities of thermally-activated bauxite for all phosphate species investigated were higher than that of raw bauxite. But the increase in adsorption efficiency is not proportional to the increase in specific surface area. It was found that the relative adsorptivity of phosphate species investigated is in the order of orthophosphate > tripoly(phosphate) > glycerophosphate. In addition, it was found that the desorption trends of these phosphate species were similar to the results obtained for raw bauxite.  
© 2003 Society of Chemical Industry

**Keywords:** phosphate adsorption; bauxite; heat activation; acid activation; activation mechanism

## INTRODUCTION

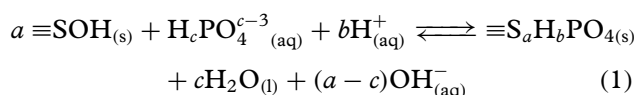
The separation and control of phosphorus during wastewater treatment has become an important issue, due to understanding the increased significance of eutrophication. Conventional methods for removal of phosphorus from wastewater include chemical precipitation, biological processes and ion exchanging–sorption processes. The use of adsorption as a tertiary treatment method for the removal of phosphates is especially promising and has been intensively investigated.<sup>1,2</sup>

As calcium, magnesium, aluminium and iron ions can form insoluble products with phosphates, solid materials containing these elements are considered potential sorbents for phosphorus removal. From natural and synthetic minerals to industrial wastes, a wide variety of adsorbents has been identified and tested for their abilities to uptake phosphorus in this regard. Considerable research has been done in the search for inexpensive adsorbents, especially those developed from various minerals and industrial waste materials.<sup>3–20</sup>

In some earlier studies, on the other hand, adsorbent materials were subjected to activation in order to develop their adsorptive ability by enhancing their reactivity and specific surface area.<sup>16–20</sup> Generally, acid treatment and heat treatment processes have been used for this aim. It has been reported that the phosphate adsorption capacity of red mud could be increased by acid and heat treatments.<sup>21</sup> In a recent study,<sup>21</sup> we have pointed out that an acid treatment of red mud improved its arsenic adsorptivity while heat treatment did not. In some phosphate removal studies, we have also shown that an acid treatment increased the adsorption ability of some industrial wastes such as ferrochrome slag<sup>17</sup> and pyrite cinder.<sup>18</sup> In contrast, it has been reported that the acid treatment decreases the phosphate adsorption capacity of alumina.<sup>22</sup> Also, it is well known that materials containing hydrated mineral phases can be activated by heating, which increases the porosity. In this regard, it has been indicated that heat-activated bauxite is used for decolourising petroleum products and for drying gases and can be reactivated by heating.<sup>23</sup>

\* Correspondence to: H Soner Altundoğan, Firat University, Department of Chemical Engineering, 23279 Elazığ, Turkey  
E-mail: saltundogan@firat.edu.tr  
(Received 4 July 2002; revised version received 4 March 2003; accepted 15 March 2003)

In our study,<sup>24</sup> the adsorption properties of bauxite for various phosphates were investigated on a large scale. In this context, in the first part of the study,<sup>25</sup> the effect of pH on the adsorption of various phosphates onto bauxite has been reported. Bauxite, an abundant ore of aluminium metal and consisting mainly of aluminium and iron oxides and oxyhydrates, is a low-cost sorbent due to its significant affinity with the various type of phosphates and probable reutilization in alumina production after phosphate adsorption. In our recent study, it has been indicated that the adsorption of phosphates onto the surfaces of bauxite could be described by a ligand exchange mechanism, resulting in the formation of inner-sphere complexes, as represented below:<sup>25</sup>



where S refers to a metal atom in a hydroxylated surface, OH to a reactive surface hydroxyl, and  $a$ ,  $b$  and  $c$  are stoichiometric coefficients. It is a fact that the number of active surface sites plays an important role in the phosphate adsorption process. Type and number of phosphate species, of course, is another important factor affecting the adsorption phenomenon. It is known that the total soluble phosphorus in the municipal wastewaters exists in the various forms of ortho-, inorganic condensed and organic phosphates.<sup>26</sup> Not only do different shapes and sizes of phosphate species but hydrolytic reactions taking place also affect the adsorptivity. Additionally, in the case of condensed inorganic phosphates the adsorption process is more complex since the hydrolytic degradation may also be influenced by the catalytic effects of mineral surfaces. On the other hand, adsorptivity of organic phosphates may be dependent on some structural differences such as number and variety of functional groups and number of phosphate groups in the molecule.<sup>27</sup>

In the present paper, the results obtained from the experiments on the bauxite activation section of the study<sup>24</sup> are reported. The main objectives of the present part are to investigate the activation of bauxite with the aim of increasing its phosphate adsorption capacity and to understand the mechanism of activation. For this purpose, acid and heat activation procedures were applied and treated bauxite samples were subjected to adsorption tests and various physicochemical analyses. Also, the pH dependent phosphate adsorption characteristics of activated bauxite were investigated and the results obtained were compared with those from a recent study dealing with raw bauxite.

## MATERIALS AND METHODS

### Materials

Bauxite used in the study was provided from Seydisehir Aluminium Plant, Konya (Turkey). The preparation

of the bauxite sample, its chemical and mineralogical composition and some physicochemical properties have been given in our earlier paper.<sup>25</sup>

The ortho- (OP), tripoly- (TPP) and glycerol- (GP) phosphate solutions used in the experiments were prepared from sodium dihydrogen phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , Merck, 6576), sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ , Sigma, 7758-29-4) and sodium glycerophosphate ( $\text{C}_3\text{H}_5(\text{OH})_2\text{PO}_4\text{Na}_2$ , Merck, 3108) salts.

Throughout the study, the phosphate concentrations are expressed as mg phosphorus per  $\text{dm}^3$  of solution ( $\text{mg-P dm}^{-3}$ ) in order to be comparable for various types of phosphate.

All solution preparations and dilutions were made using distilled water. The laboratory-ware used in the experiments was always soaked in dilute HCl solution for 12 h and then rinsed with large amounts of distilled water.

### Activation of bauxite

Two different activation procedures were applied. In the first method, 50 g of the fraction of bauxite samples under  $74 \mu\text{m}$  were refluxed with  $1 \text{ dm}^3$  of 0.1–1.0 M HCl solutions at atmospheric conditions for 2 h. After the treatment, the mixtures were filtered by suction. For washing, the filter cakes obtained were slurried in  $1 \text{ dm}^3$  of distilled water for 30 min and filtered. The resulting cakes were then dried at  $100^\circ\text{C}$  for 4 h and preserved in closed vessels.

In the second method, bauxite samples were subjected to heat treatment. For this purpose, a 50 g portion of bauxite samples was placed in a porcelain dish and then heated in a muffle furnace at various temperatures between 200 and  $1000^\circ\text{C}$  for 2 h. After heating, the bauxite samples were cooled in a desiccator, ground to under  $74 \mu\text{m}$  and preserved in closed vessels containing silica gel during the experimental study.

The weight loss was determined for both activation procedures.

### Standardized adsorption experiments

To determine the influence of activation, bauxite samples activated by the different activation procedures were subjected to standardized orthophosphate adsorption tests; all other parameters were kept constant while the pH was varied over a wide range (1.5–12). The experiments were carried out by shaking ( $400 \text{ cycle min}^{-1}$ )  $250 \text{ cm}^3$  glass conical flasks containing 1 g of activated bauxite samples and  $100 \text{ cm}^3$  of orthophosphate solutions having a concentration of  $10 \text{ mg-P dm}^{-3}$  in a temperature-controlled water bath at  $25^\circ\text{C}$  for 2 h. The pH of the mixtures was adjusted by using HCl and NaOH solutions. The experiments were performed at constant ionic strength, provided by NaCl the concentration of which was 0.01 M in all working solutions. The initial pH values of suspensions were measured within a few minutes of the

beginning of the experiments. At the end of the shaking period, the final pH values of the suspensions were measured and the suspensions were then centrifuged at 10 000 rpm for 10 min. The phosphate content of the supernatants was determined immediately, following the methods described below.

### Adsorption and desorption studies

The effect of adsorbent dosage on the adsorption of ortho-, tripoly- and glycerophosphates was investigated by using the most effective activated bauxite sample determined via standardized orthophosphate adsorption tests. In these experiments, all conditions except adsorbent dosage were kept the same as in the standardized adsorption experiments. The adsorbent dosages of 2.5, 5.0 and 10 g dm<sup>-3</sup> were studied for all phosphate species by varying the pH in the range of 1.5–12.

Also, some adsorption experiments were carried out by using mixed binary and ternary phosphate solutions under the similar conditions. In these experiments, total phosphorus concentration was designated as 10 mg-P dm<sup>-3</sup> and the concentration of each species was equal. These experiments were carried out using 5 g dm<sup>-3</sup> of activated bauxite dosage.

In order to determine the desorption behaviour of ortho-, tripoly- and glycerophosphates, a group of experiments was carried out by shaking the phosphate-adsorbed bauxite samples with 100 cm<sup>3</sup> distilled water at 25 °C and over a wide pH range for 2 h. Desorption experiments for ortho-, tripoly- and glycerophosphates were conducted at the dosages of 2.5, 5.0 and 5.0 g dm<sup>-3</sup>, respectively.

### Methods of analysis

Orthophosphate analyses were performed by means of the ascorbic acid method using a Jenway D 500 model UV-Visible spectrophotometer. Analyses of tripoly- and glycerophosphate solutions were accomplished by using this method after converting them to orthophosphate by a sulfuric acid hydrolysis route for tripoly(phosphate) and sulfuric acid–nitric acid digestion route for glycerophosphate.<sup>27</sup>

For mixed phosphate solutions, firstly, total ortho- and tripoly(phosphate) analyses were performed by using suitable methods, as mentioned above. The individual phosphate concentrations were then calculated by subtracting the amount of ortho-, tripoly- or ortho- + tripoly- from the total concentration.

In order to explain the activation mechanism, raw and activated bauxite samples were subjected to additional analyses. For this purpose, XRD analysis (Siemens D-5000 Diffractometer), FT-IR analysis (Mattson 1000), specific surface area analyses (single point N<sub>2</sub>-BET, Micromeritics Flowsorb 2300), porosity analysis (with mercury porosimeter, Micromeritics Poresizer 9310), DT and TG analyses (Shimadzu DTA-TG-DSC system) and particle size analysis (laser particle size analyser, Malvern Inst Master-sizer X) were performed. Also, the point of zero net

proton charge (PZNPC) for raw and activated bauxite samples was determined by a potentiometric titration route.<sup>28</sup> Additionally, in order to determine the solubilized portions of Fe and Al, waste solutions obtained from the acid activation process were analysed for these metals by AAS (Perkin-Elmer 370).

## RESULTS AND DISCUSSION

### Activation study

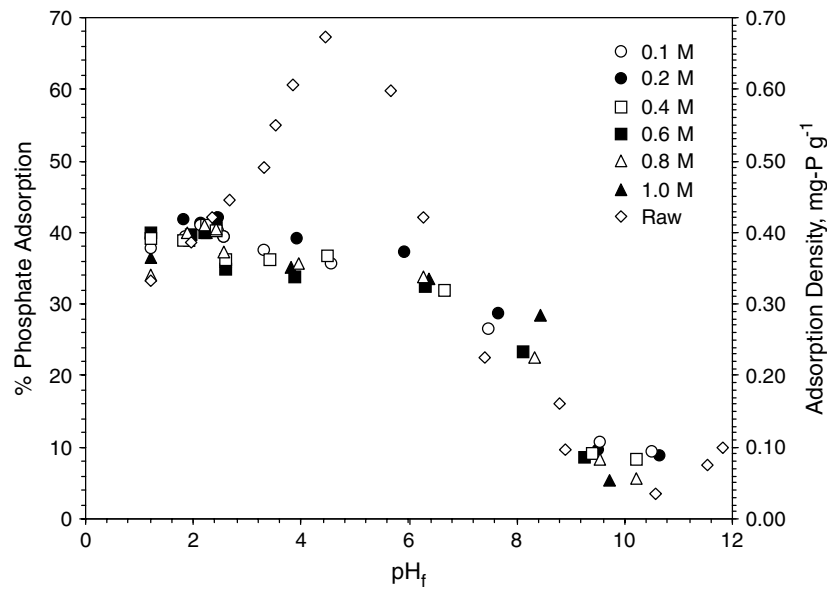
In this part of the study, the effect of activation conditions on phosphate adsorption onto bauxite is discussed in relation to the results of orthophosphate adsorption experiments conducted at standardized conditions.

The effect of final pH (pH<sub>f</sub>) on orthophosphate adsorption by the acid-activated bauxite is shown in Fig 1. It is obvious that the acid treatment has a negative effect on the phosphate adsorption capability of bauxite by decreasing its adsorption capacity to almost half that at the pH at which the adsorption maximum was obtained for raw bauxite. The decrease in adsorption capacity seems to be almost independent of the concentration of HCl used in the range of 0.1–1.0 M.

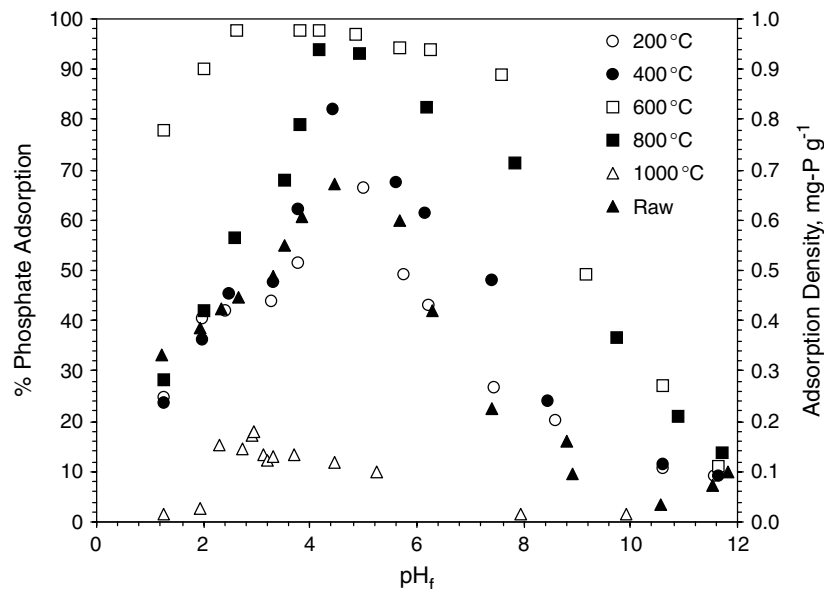
The results of the heat activation study are shown in Fig 2. The phosphate adsorption capacity of bauxite increased on increasing the temperature up to 600 °C. For the narrow pH range of 4.5–5.2, phosphate removal efficiencies are both more than 95% for activated bauxites obtained by heating to 600 and 800 °C. Although the adsorption efficiencies are close, activated bauxite obtained at 600 °C is more effective in the wide pH range of 2.0–8.0; this may be considered as an advantage. The phosphate adsorption efficiency of bauxite decreased sharply on further increase of temperature. For the sample obtained at 1000 °C, adsorption efficiencies were found to be about 15% in the pH range of 2.0–5.0. Consequently, it can be stated that the activated bauxite sample obtained by heating at 600 °C is the most effective and advantageous one. Therefore, this activated product will be called 'activated bauxite (AB)' in the next part of the text.

### Activation mechanism

A considerable amount of Al and Fe is removed from the bauxite by the acid treatment, leading to a weight loss. The percentages of weight loss and Fe and Al dissolved from bauxite depending on the concentration of HCl solution used are given in Table 1. As can be seen, by increasing the amount of HCl used in the treatment, weight loss and amount of solubilized Fe and Al increased. Acid treatment caused a change in the chemical composition of bauxite. It was found that the bauxite treated with 1.0 M HCl contained 61.17% Al<sub>2</sub>O<sub>3</sub>, 8.89% Fe<sub>2</sub>O<sub>3</sub> and 0.31% CaO while these values were 56.91%, 16.95% and 0.91% for raw bauxite,<sup>25</sup> respectively.



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

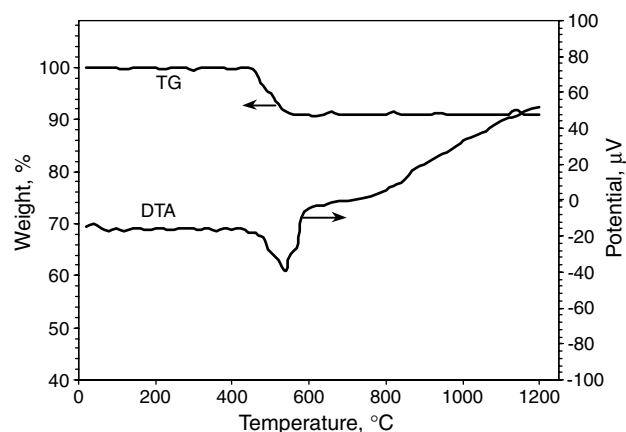
**Table 1.** Amounts of weight loss, and Al and Fe solubilized from bauxite treated by acid solutions

Conc of HCl soln (M)	Weight loss (%)	Solubilized Fe (%)	Solubilized Al (%)
0.1	4.1	1.03	0.29
0.2	5.81	1.52	1.06
0.4	8.86	12.30	2.59
0.6	10.31	18.97	4.22
0.8	13.22	29.55	5.89
1.0	15.93	42.18	8.14

The decrease in adsorption efficiency of bauxite may be attributed to dissolution of Al and Fe, which are

the main constituents, in the active surface sites. The decrease in Ca content may also have a part in efficiency loss. Additionally, XRD analyses showed that the calcite and diaspor phases observed in raw bauxite disappeared in all acid-treated bauxite samples, probably due to dissolution.

In contrast, surface area measurements indicated that the acid treatment has a positive effect on the specific surface area. For example, the  $\text{N}_2$ -BET specific surface areas of raw bauxite and acid-treated bauxite (with  $1.0 \text{ M HCl}$ ) were found to be 11 and  $18 (\pm 0.5) \text{ m}^2 \text{ g}^{-1}$ , respectively. Despite the increases in surface area, decreased values obtained for adsorption capacity supports the suggestion of the partial removal of reactive surface components by acid treatment.



**Figure 3.** DTA and TGA results of raw bauxite (heating rate:  $10^{\circ}\text{C min}^{-1}$ ).

In order to have an idea on the heat activation mechanism of bauxite, firstly, differential thermal analyses (DTA) and thermal gravimetric analyses (TGA) were performed. The results are shown in Fig 3. The TGA showed that the significant weight loss begins at  $465^{\circ}\text{C}$ . From the TGA results, it can be seen that the bauxite sample lost about 9.1% of its weight at  $566^{\circ}\text{C}$ . This weight loss figure is in harmony with the result of 9.65% obtained in the heat activation experiment conducted at  $600^{\circ}\text{C}$ . It was observed that an endothermic peak occurs at  $536^{\circ}\text{C}$  in the DTA of bauxite. It has been reported that the single endothermic peak observed between  $510$  and  $580^{\circ}\text{C}$  shows the presence of alumina hydrates in the form of boehmite and diaspor.<sup>29</sup> The weight loss for the range of  $465$ – $566^{\circ}\text{C}$ , to a large extent, corresponds to dehydration of the boehmite and diaspor phases.

The results of XRD analyses of heated bauxite samples are given in Table 2. The major phase conversions observed for the sample heated at  $600^{\circ}\text{C}$  confirm the above findings. Obviously, boehmite and diaspor were converted to  $\alpha$ -alumina at this temperature. Small peaks belonging to calcite, which

**Table 2.** Mineral phases determined by XRD for raw and heat-treated bauxites

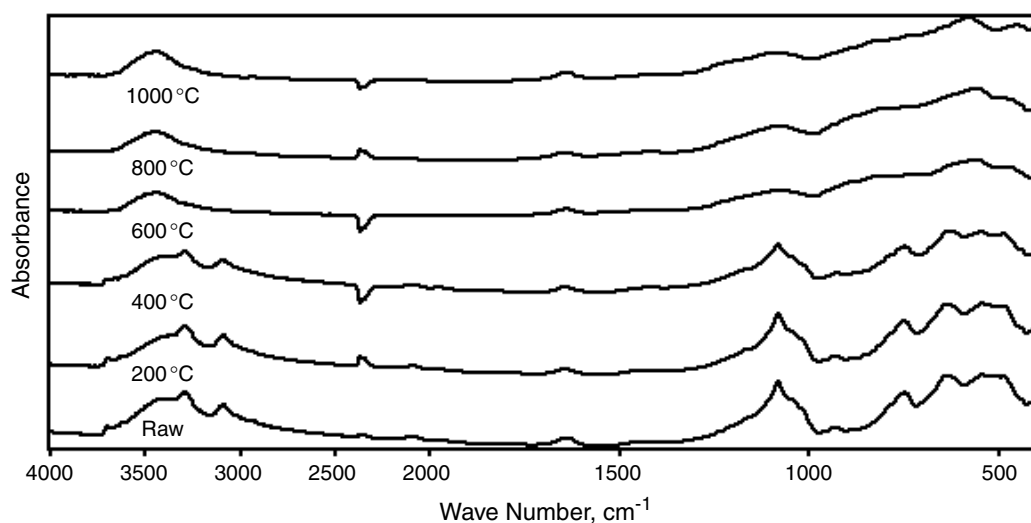
Mineral phase	Bauxite samples					
	Raw	$200^{\circ}\text{C}$	$400^{\circ}\text{C}$	$600^{\circ}\text{C}$	$800^{\circ}\text{C}$	$1000^{\circ}\text{C}$
Boehmite	+	+	+	–	–	–
Diaspor	+	+	+	–	–	–
Kaolinite	+	+	+	+	+	+
Haematite	+	+	+	+	+	+
Calcite	+	+	+	–	–	–
Anatase	+	+	+	+	+	+
Rutile	–	–	–	+	+	+
$\alpha$ -Alumina	–	–	–	+	+	+
Corundum	–	–	–	–	–	+
Quartz <sup>a</sup>	+	–	–	–	–	–

<sup>a</sup> Quartz is a minor mineral phase in raw bauxite (less than 1%).<sup>25</sup>

is a minor component of bauxite, could not be detected in the heat-activated samples obtained at temperatures over  $600^{\circ}\text{C}$ , and may be due to conversion to  $\text{CaO}$ . Also, anatase is partially converted to rutile which is another  $\text{TiO}_2$  modification. In the samples obtained at  $1000^{\circ}\text{C}$ , corundum, being a compact alumina modification, was identified.

The FT-IR spectra of heat-treated bauxite samples are shown in Fig 4. The results of FT-IR analyses support the above findings. The strong bands observed at  $750$ ,  $1073$  and  $3290\text{ cm}^{-1}$  which characterize boehmite in bauxites<sup>29–31</sup> disappeared for heat-activated bauxites obtained at  $600$ ,  $800$  and  $1000^{\circ}\text{C}$ . The IR band of  $3100\text{ cm}^{-1}$  observed for raw and heat-treated samples obtained at  $200$  and  $400^{\circ}\text{C}$  corresponds to stretching vibrations of OH groups. Disappearance of this band in the samples heated to higher temperatures can be attributed to dehydration of hydrated alumina modifications.

The results of mean particle diameter and  $\text{N}_2$ -BET surface area measurements of the raw and heat-activated bauxite samples are given in Table 3. Some other physicochemical properties for raw bauxite and



**Figure 4.** FT-IR spectra of raw and heat-treated bauxite samples (in KBr pellets; wavenumber range:  $400$ – $4000\text{ cm}^{-1}$ ; scan number: 16).

**Table 3.** Some physical and physicochemical properties of raw and heat-treated bauxites

Property	Bauxite samples					
	Raw	200 °C	400 °C	600 °C	800 °C	1000 °C
Single Point N <sub>2</sub> -BET specific surface area (m <sup>2</sup> g <sup>-1</sup> )	11.0 ± 0.5	12.0 ± 0.5	12.0 ± 0.5	86.0 ± 0.5	28.0 ± 0.5	0.8 ± 0.1
Mean Particle diameter (µm)	18.54	21.65	24.85	26.34	26.06	20.73
Apparent density (g cm <sup>-3</sup> )	1.4713	na	na	1.3225	na	na
Skeletal density (g cm <sup>-3</sup> )	2.1311	na	na	3.9884	na	na
Porosity (cm <sup>3</sup> cm <sup>-3</sup> )	0.310	na	na	0.668	na	na
Mean pore radius (µm)	3.689	na	na	0.024	na	na
PZNPC	8.39	na	na	7.87	na	na

na not analysed.

bauxite heated at 600 °C are also included in the table. For the bauxite samples obtained at 600 °C, the single point N<sub>2</sub>-BET specific surface area was found to be increased about eight times with respect to that of raw bauxite. Dehydration of the boehmite and diaspor phases may cause thin capillaries to be formed in the bauxite matrix. An increase in mean particle diameter together with a further decrease in pore radius and with an increase in porosity may support this idea. In accordance with the above discussion and related measurements, water removal from bauxite by dehydration results in an increase in the skeletal density and a decrease in the apparent density. The surface area decreases on further increase in temperature and may be due to the formation of compact constituents such as corundum. In addition, the mean particle diameter of bauxite increases up to 600 °C probably by means of expansion and/or agglomeration of bauxite particles. For the increased temperatures, the mean particle size was found to be slightly decreased. On the other hand, from the PZNPC measurements, it can be stated that the pH value of the zero point of charge for heat-activated bauxite declines towards the neutral zone due to a change in the chemical properties of the surface.

All the above findings show that the major factor governing the activation is dehydration, which causes an increase in specific surface area and porosity. It can be noted that the most important parameter is that the temperature must be sufficiently high for dehydration to occur. Further increase in temperature, however, leads to a decline in adsorptivity probably due to a decrease in surface area and formation of some mineral phases having low reactivity.

### Results of adsorption and desorption studies

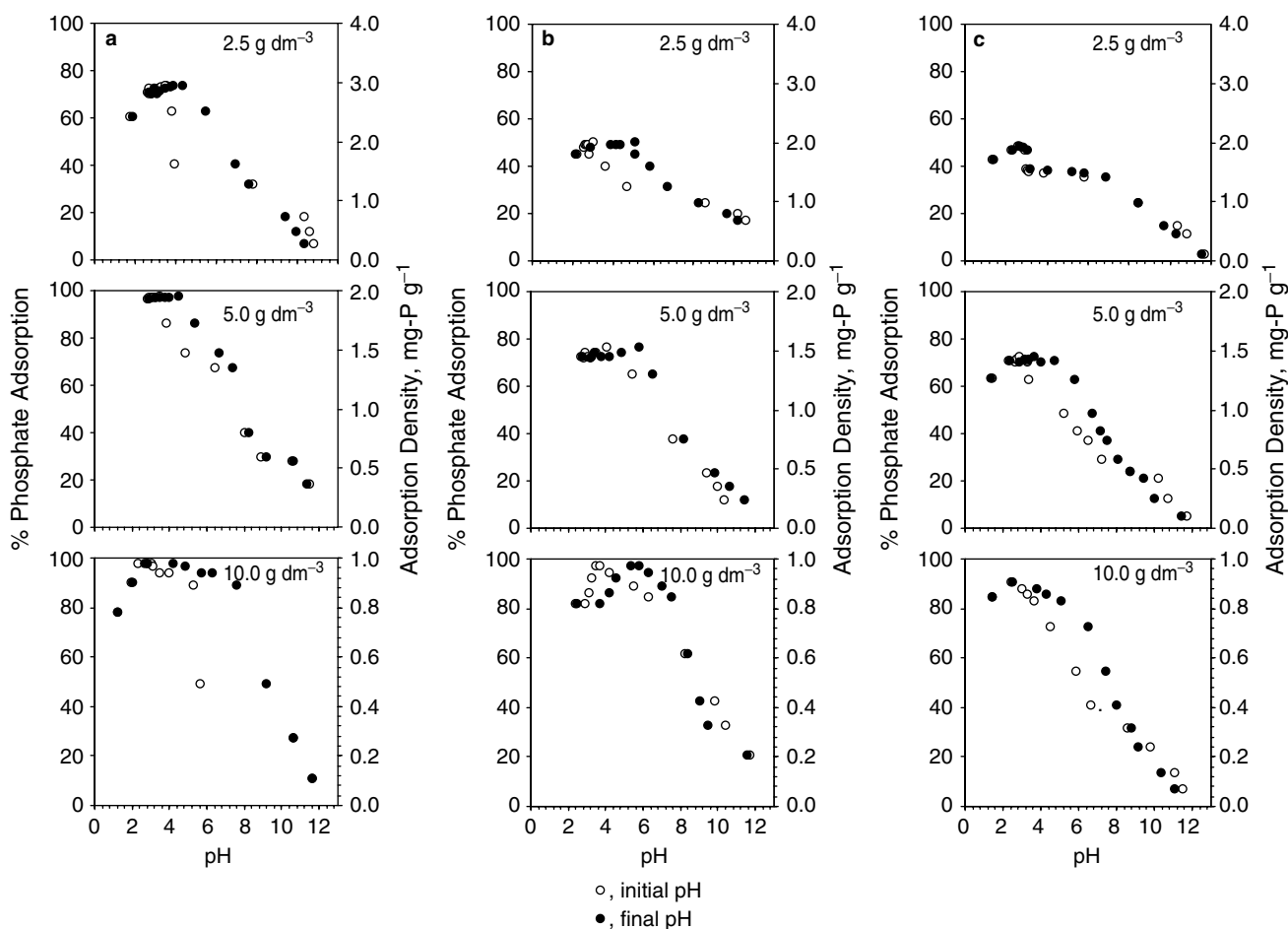
The effect of pH on the adsorption of ortho-, tripoly- and glycerophosphates depending on activated bauxite (AB) dosage are shown in Fig 5. It is clearly seen that AB is effective in the slightly acidic pH range for all phosphate species. The significant differences between initial and final pH values observed implies the validity of a ligand exchange mechanism (eqn (1)), which was discussed in an earlier study.<sup>26</sup> It can

be noted that raw and activated bauxite are both effective over similar pH ranges for various phosphate species. But, the effective pH range is wider and the adsorption capacity is greater for AB than those for raw bauxite. For a comparison, maximum adsorption densities and corresponding pH values observed for raw and activated bauxites are summarized in Table 4.

When the corresponding values for raw and activated bauxite given in Table 4 are compared, adsorptivity seems not to be significantly increased by activation. For example, at the dosage of 10 g dm<sup>-3</sup>, the orthophosphate adsorption densities obtained for raw and activated bauxite are 0.673 and 0.979 mg-P g<sup>-1</sup>, respectively. As can be calculated from these figures, the adsorption density increases only about 1.5 times with respect to raw bauxite. From another viewpoint, the dosages giving similar removal yields can be compared. For example, the orthophosphate removal yield obtained by raw bauxite for the dosage of 10 g dm<sup>-3</sup> (67.3%) can be reached by using activated bauxite with a dosage of 2.5 g dm<sup>-3</sup> (73.8%). This result implies that heat activation of bauxite leads to about a four-fold increase in its orthophosphate adsorptivity, while the specific surface area increases about eight times. Similar results are valid for tripoly- and glycerophosphates as well.

Some adsorption experiments were carried out in the binary and ternary mixed phosphate solutions by using activated bauxite. The results obtained from these runs are shown in Fig 6. The pH dependence of phosphate adsorption in multiple systems shows a similar trend to singular systems and all the corresponding pH values at which adsorption maxima occurred are close to one another. The total removal efficiencies determined for binary and ternary systems containing orthophosphates are less than those for singular orthophosphate systems. In contrast, for the binary and ternary systems containing glycerophosphate, total adsorption efficiencies are higher than the corresponding value obtained for single glycerophosphate solutions.

The results obtained from the experiments dealing with single and multiple systems are summarized in Table 5. It must be pointed out that AB has a high affinity for the orthophosphate. However, it can be



**Figure 5.** Effect of pH on the adsorption of various phosphates depending on activated bauxite dosage (a) ortho-, (b) tripoly-, (c) glycerophosphates (10 mg-P dm<sup>-3</sup> phosphate solutions; contact time 2 h; temperature 25 °C; ionic strength: 0.01 M NaCl).

**Table 4.** Maximum adsorption densities and corresponding pH values obtained depending on the dosage of raw and activated bauxites

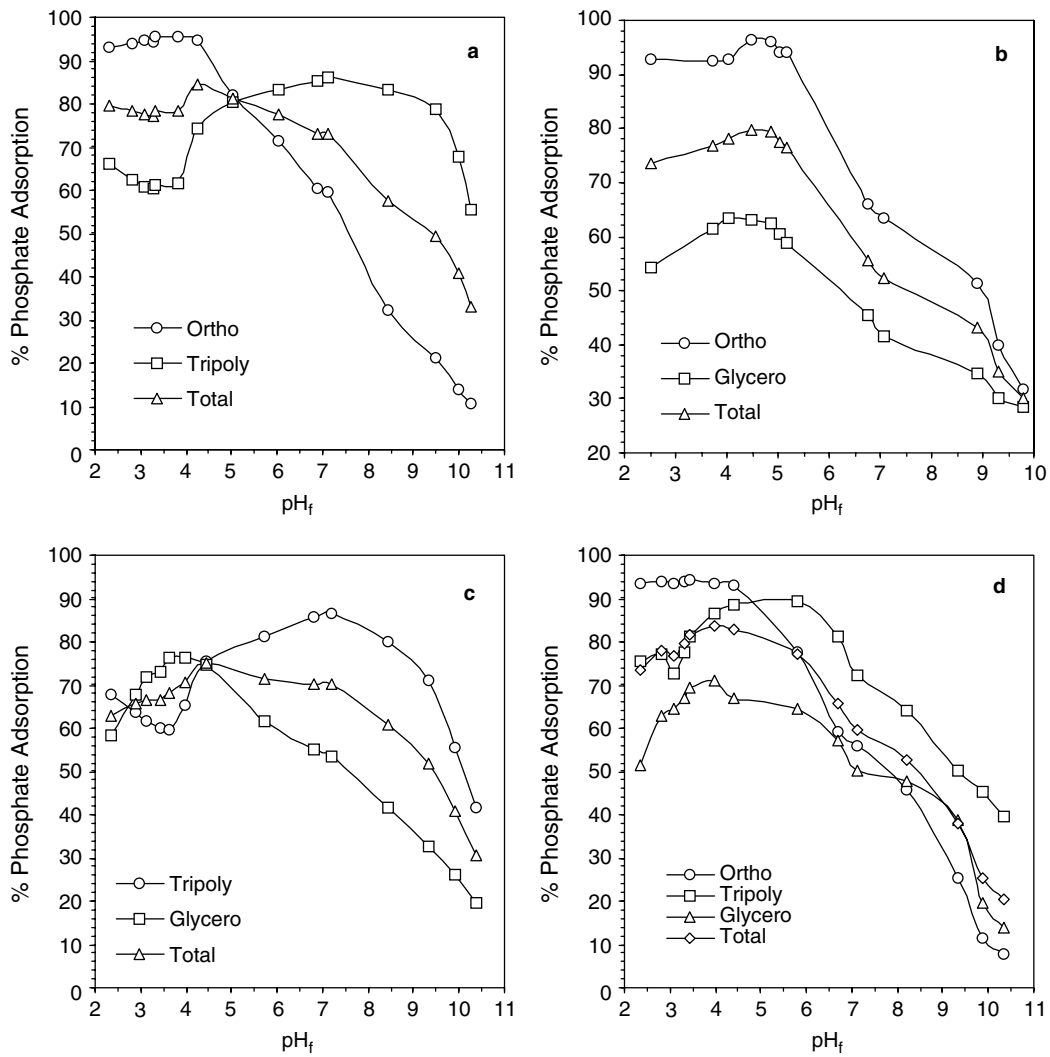
Phosphate type	Dosage (g dm <sup>-3</sup> )	Raw bauxite <sup>a</sup>			Activated bauxite (AB)		
		Maximum removal pH	Removal efficiency (%)	Adsorption density (mg-P g <sup>-1</sup> )	Maximum Removal pH	Removal efficiency (%)	Adsorption density (mg-P g <sup>-1</sup> )
Ortho	2.5		21.3	0.82	4.3	73.8	2.95
	5.0	4.5	39.3	0.79	4.5	97.8	1.96
	10.0		67.3	0.67	4.2	97.9	0.98
Tripoly	2.5		19.9	0.80	5.1	50.1	2.00
	5.0	5.4	34.3	0.69	5.8	76.7	1.53
	10.0		57.7	0.58	5.3	97.5	0.97
Glycero	2.5		16.1	0.64	2.8	48.3	1.93
	5.0	3.2	29.6	0.59	3.7	72.6	1.45
	10.0		39.9	0.40	2.5	90.9	0.91

<sup>a</sup> Previous Studies.<sup>25,26</sup>

concluded that the relative adsorptivity of various phosphates is in the general order of orthophosphate > tripoly(phosphate) > glycerophosphate.

The results of the effect of pH on the desorption of ortho-, tripoly- and glycerophosphates are shown in Fig 7. As seen from the figure, desorption efficiencies of all phosphate species have a minimum at around the pH values at which adsorption maxima were obtained for the corresponding phosphate species. In the strongly basic media, the total amounts of released

phosphate for all species are higher than those for the strongly acidic media. For example, the amounts of desorbed orthophosphate reach 53.53% and 81.49% in the cases of pH ~1 and ~13, respectively. Without any exceptions, desorption trends for all phosphate species were found to be similar to those obtained in the desorption study carried out with raw bauxite.<sup>25</sup> On the other hand, in a similar manner to the previous study, orthophosphate was detected in the eluent obtained in the desorption run of tripoly(phosphate).

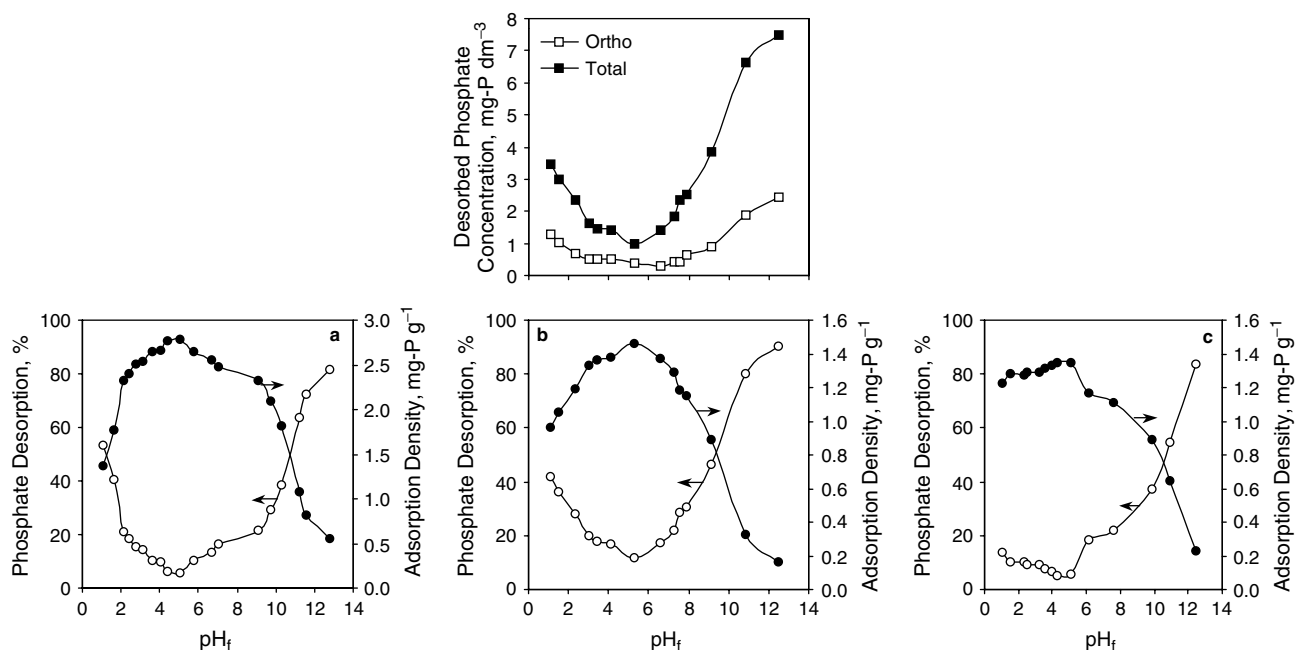


**Figure 6.** Effect of pH on the phosphate adsorption from mixed binary and ternary phosphate solutions (total phosphorus concentration is  $10 \text{ mg-P dm}^{-3}$  and concentration of each species is equal; contact time 2 h; temperature  $25^\circ\text{C}$ ; dosage  $5.0 \text{ g dm}^{-3}$ ; ionic strength:  $0.01 \text{ M NaCl}$ ).

**Table 5.** Maximum adsorption percentages of phosphates and corresponding pH values in multiple phosphate solution systems

Single solution system									
	Ortho			Tripoly			Glycero		
pH	4.46			4.05			3.67		
Remov efficiency (%)	98.0			76.7			72.7		
Binary solution system									
	Ortho–Tripoly			Ortho–Glycero			Tripoly–Glycero		
	OP	TPP	Total	OP	GP	Total	TPP	GP	Total
pH	3.34	7.13	4.24	4.49	4.85	4.49	7.21	3.62	4.46
Remov efficiency (%)	95.6	86.3	84.5	96.4	62.6	79.8	86.7	76.3	75.3
Ternary solution system									
	Ortho		Tripoly		Glycero		Total		
pH	3.45		5.81		3.99		3.99		
Remov efficiency (%)	94.2		89.6		71.0		83.7		





**Figure 7.** Effect of pH on the desorption of various phosphate species from phosphate-adsorbed activated bauxite samples (a) orthophosphate ( $2.952 \text{ mg-P g}^{-1}$  samples; dosage:  $2.5 \text{ g dm}^{-3}$ ), (b) tripoly(phosphate) ( $1.657 \text{ mg-P g}^{-1}$  samples; dosage:  $5.0 \text{ g dm}^{-3}$ ), (c) glycerophosphate ( $1.423 \text{ mg-P g}^{-1}$  samples; dosage:  $5.0 \text{ g dm}^{-3}$ ) (contact time 2 h; temperature  $25^\circ\text{C}$ ).

These findings show the existence of an hydrolytic degradation phenomenon during the adsorption and desorption processes for tripoly(phosphate), which was suggested in our earlier study.<sup>25</sup> However, when orthophosphate fractions determined in eluates obtained from the AB–tripoly(phosphate) desorption study are compared with those values of raw bauxite, the degradation degrees are found to be at about the same level. In adsorption and desorption runs conducted with glycerophosphate solutions, orthophosphate was not detected in related eluates.

## CONCLUSION

From the above the following conclusions can be drawn.

In spite of the surface area of bauxite being increased by acid treatment, treated bauxite has a lowered phosphate adsorption capability which may be due to dissolution of surface constituents located at active sites.

Heat treatment has been found to have a significant activation effect on the phosphate adsorption capacity of bauxite. Standardized orthophosphate adsorption tests have shown that the most effective adsorbent is obtained by heating the bauxite at  $600^\circ\text{C}$ . It has been determined that hydrated alumina modifications of boehmite and diaspore, being main components of bauxite, convert to  $\alpha$ -alumina at  $600^\circ\text{C}$  and higher temperatures, and  $\alpha$ -alumina converts to corundum at  $1000^\circ\text{C}$ . XRD, FT-IR, DTA and TGA studies support these findings. Also, the surface area of activated bauxite obtained by heating at  $600^\circ\text{C}$  is found to be about  $86 \text{ m}^2 \text{ g}^{-1}$  which is about eight

times that of raw bauxite. In addition, the porosity increases approximately two times by heating it at  $600^\circ\text{C}$ . Higher heating temperatures cause a decrease in the surface area. Also, it has been found that heat treatment causes an increase in mean particle diameter up to  $600^\circ\text{C}$  and thereafter a decrease has been observed. When compared with the values of raw bauxite, however, decreased apparent density and pore radius but increased skeletal density have been observed for activated bauxite obtained by heating at  $600^\circ\text{C}$ .

The removal efficiencies of phosphates obtained with activated bauxite are higher than those of raw bauxite. It can be concluded that the activation of bauxite via dehydration causes an increase in the number of active surface sites, which have an important role in phosphate adsorption. But, this increase is not proportional to the increase in specific surface area. In addition, all mechanistic considerations for raw bauxite are valid for adsorption of phosphates onto activated bauxite. The Relative affinities of three different phosphate species against activated bauxite have been found to be in the order of orthophosphate > tripoly(phosphate) > glycerophosphate.

Our future papers will consider the kinetic and thermodynamic evaluations of phosphate adsorption onto bauxite and activated bauxite.

## ACKNOWLEDGEMENTS

This study was supported by the Research Foundation of Firat University under Project No FUNAF-118. We would like to thank to Etibank Seydişehir Aluminum Plant for the bauxite analyses.

## REFERENCES

- 1 Nesbitt JB, Phosphorus removal-the state of the art. *J Water Pollut Cont Fed* **41**:701–703 (1969).
- 2 Yeoman S, Stephenson T, Lester JN and Perry R, The removal of phosphorus during wastewater treatment: a review. *Environ Pollut* **49**:183–233 (1988).
- 3 Shang C, Huang PM and Stewart JWB, Kinetics of adsorption of organic and inorganic phosphates by short-range ordered precipitate of aluminum. *Canad J Soil Sci* **70**:461–471 (1990).
- 4 Shang C, Stewart JWB and Huang PM, pH effect on kinetics of adsorption of organic and inorganic phosphates by short-range ordered precipitate of aluminum and iron. *Geoderma* **53**:1–14 (1992).
- 5 Bleam WF, Pfeffer PE, Goldberg S, Taylor RW and Dudley R, A <sup>31</sup>P solid state nuclear magnetic resonance study of phosphate adsorption at the boehmite–aqueous solution interface. *Langmuir* **7**:1702–1712 (1991).
- 6 Van Riemsdijk WH and Lyklema J, Reaction of phosphate with gibbsite (Al(OH)<sub>3</sub>) beyond the adsorption maximum. *J Colloid and Interface Sci* **76**:55–66 (1980).
- 7 Chen YSR, Butler JN and Stumm W, Kinetic study of phosphate reaction with aluminum oxide and kaolinite. *Environ Sci* **7**:327–332 (1973).
- 8 Brattebo H and Odegaard H, Phosphorus removal by granular activated alumina. *Wat Res* **20**:977–986 (1986).
- 9 Ognalaga M, Frossard E and Thomas F, Glucose-1-phosphate and myo-inositol hexaphosphate adsorption mechanisms on goethite. *Soil Sci Soc Am J* **58**:332–337 (1994).
- 10 Barron V, Herruzo M and Torrent J, Phosphate adsorption by aluminous hematites of different shapes. *Soil Sci Soc Am J* **52**:647–651 (1988).
- 11 Mehadi AA and Taylor RW, Phosphate adsorption by two highly-weathered soils. *Soil Sci Soc Am J* **52**:627–632 (1988).
- 12 Bulusu KR, Kulkarni DN and Lutode SL, Phosphate removal by serpentine mineral. *Ind J Environ Hlt* **20**:268–271 (1978).
- 13 Dalas E and Koutsoukos PG, Phosphate adsorption at the porous glass/water and SiO<sub>2</sub>/water interfaces. *J Colloid and Interface Sci* **134**:299–304 (1990).
- 14 Bhargava DS and Sheldarkar SB, Use of TNSAC in phosphate adsorption studies and relationship. Literature, experimental methodology, justification and effects of process variables. *Wat Res* **27**:303–312 (1993).
- 15 Tümen F, Removal of phosphates from aqueous solutions by fly ash. *J FU Sci and Technol* **3**:123–130 (1988).
- 16 Yamada H, Kayama M, Saito K and Hara M, A fundamental research on phosphate removal by using slag. *Wat Res* **20**:547–557 (1986).
- 17 Tümen F, Arslan N, Özer A and Bildik M, Phosphate adsorption from aqueous solutions by activated ferrochrome slag. *J FU Sci and Technol* **3**:41–51 (1988).
- 18 Tümen F, Arslan N, Dağaçan E and Bildik M, Phosphate removal by pyrite cinder. *Doğa Tu J Eng and Environ* **13**:83–93 (1989).
- 19 Koumanova B, Drame M and Popangaloca M, Phosphate removal from aqueous solutions using red mud wasted in bauxite Bayer's Process. *Resour Conserv Recy* **19**:11–20 (1997).
- 20 Shiao SJ and Akashi K, Phosphate removal from aqueous solution by activated red mud. *J Water Pollut Cont Fed* **49**:280–285 (1977).
- 21 Altundoğan HS, Altundoğan S, Tümen F and Bildik M, Arsenic adsorption from aqueous solutions by activated red mud. *Waste Manag* **22**:357–363 (2002).
- 22 Gangoli N and Thodos G, Phosphate adsorption studies. *J Water Pollut Cont Fed* **45**:842–849 (1973).
- 23 Treyball RE, *Mass Transfer Operations*, 3rd edn. McGraw-Hill International Edition, Singapore (1981).
- 24 Altundoğan HS, Phosphate removal from waters by using Bauxite. PhD Thesis, Graduate School of Natural And Applied Science, University of Firat (1998). (in Turkish).
- 25 Altundoğan HS and Tümen F, Removal of phosphates from aqueous solutions by using bauxite: I. Effect of pH on the adsorption of various phosphates. *J Chem Technol Biotechnol* **77**:77–85 (2002).
- 26 Jenkins D, Ferguson JF and Menar AB, Chemical processes for phosphate removal. *Wat Res* **5**:369–389 (1971).
- 27 APHA, *Standard Methods for The Examination of Water and Wastewater*, 17th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA (1989).
- 28 Tamura H, Katayama N and Furuichi R, Modeling of ion exchange reactions on metal oxides with the Frumkin Isotherm. 1. Acid–base and charge characteristic of MnO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> surfaces and adsorption affinity of alkali metal ions. *Environ Sci Technol* **30**:1198–1204 (1996).
- 29 Gado P and Orban M, Mineralogical and textural investigation of bauxite: red mud and alumina, Group Training in Production of Alumina, UNIDO, Aluterv-FKI, Budapest (1979).
- 30 Solymar K, Zöldi J, Toth AC, Feher I and Bulkai D, Manual for laboratory, Group Training in Production of Alumina, UNIDO, Aluterv-FKI, Budapest (1979).
- 31 Merenkova BM and Tsekhovol'skaya DI, Quantitative determination of bauxite mineral composition by IR spectroscopy. *Industrial Laboratory* **50**:767–770 (1985).