

# Removal of phosphate from aqueous solution with blast furnace slag

Ensar Oguz\*

*Environmental Problems Research Center, Atatürk University, 25240 Erzurum, Türkiye*

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## Abstract

Blast furnace slag was used to remove phosphate from aqueous solutions. The influence of pH, temperature, agitation rate, and blast furnace slag dosage on phosphate removal was investigated by conducting a series of batch adsorption experiments. In addition, the yield and mechanisms of phosphate removal were explained on the basis of the results of X-ray spectroscopy, measurements of zeta potential of particles, specific surface area, and images of scanning electron microscopy (SEM) of the particles before and after adsorption. The specific surface area of the blast furnace slag was  $0.4 \text{ m}^2 \text{ g}^{-1}$ . The removal of phosphate predominantly has taken place by a precipitation mechanism and weak physical interactions between the surface of adsorbent and the metallic salts of phosphate. In this study, phosphate removal in excess of 99% was obtained, and it was concluded that blast furnace slag is an efficient adsorbent for the removal of phosphate from solution.

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## 1. Introduction

Phosphate is an essential macronutrient that spurs the growth of photosynthetic algae and cyanobacteria. Wastewater discharges that reach lakes sensitive to eutrophication often require phosphate removal over and above that normally taking place in primary and secondary treatment [1]. Phosphorus (P) is often present in low concentrations in wastewater as phosphates, including organic phosphate, inorganic phosphate (orthophosphate) and polyphosphate (particulate P). Its release to surface water is of environmental concern, because it is an essential, often limiting, nutrient for growth of organisms in most ecosystems, and is therefore a major cause of eutrophication. Phosphorus removal from wastewater has been widely investigated [2]. The utilization of industrial wastes or by-products for phosphorus removal has been given great attention [3–5].

Eutrophication can in turn disturb the balance of organisms present in the water and affect water quality, mainly through the depletion of oxygen level as the algae decay.

A reduced oxygen level can have harmful effects on fish and other aquatic life, causing reductions in biodiversity. Eutrophication can also affect the recreational value of natural resources. Generally, total phosphorus concentrations in excess of 100 mg P/L provide sufficient nutrient enrichment for eutrophication in the lakes [6].

In wastewater treatment technology, various techniques have been used for phosphate removal. Phosphorus removal techniques fall into three main categories: physical, chemical and biological. Physical methods have proved to be either too expensive, as in the case of electrodialysis and reverse osmosis [7], or inefficient, removing only 10% of the total phosphorus [8]. Enhanced biological treatment can remove up to 97% of the total phosphorus, but this process can be highly variable due to operational difficulties [8]. Chemical treatment is widely used for the removal of phosphate. Lime, aluminum sulfate (alum), and ferric chloride are the common precipitants used for phosphate removal; however, successful results have been obtained using powdered aluminum oxide [9–11], slag [12], fly ash [13,14], half-burnt dolomite [15], tamarind nut shell activated carbon [16,17], activated red mud [18,19], aluminum [20], and gas concrete [21].

\* Tel.: +90 442 231 4601.

E-mail address: eoguz@atauni.edu.tr.

Adsorption is one of the techniques which would be comparatively more useful and economical for this aim. The application of low-cost and easily available materials in wastewater treatment has been widely investigated during recent years [22].

Blast furnace slag is a residue from steel-iron making processes. The use of blast furnace slag in wastewater treatment has been studied extensively in recent years and the results of laboratory investigations showed that blast furnace slag is a good adsorbent for removal of heavy metals from wastewaters [23,24]. Due to the high percentages of alumina and silica, blast furnace slag is a good candidate for use as an economic adsorbent for large-scale use. In this study, phosphate was removed using İskenderun blast furnace slag (blast furnace slag used in this study was supplied from a steel-iron factory in the Hatay-İskenderun province of Turkey). One of the main advantages of phosphate removal by using blast furnace slag over the other chemical treatment methods is the abundance of blast furnace slag and its easy availability, which makes it a strong candidate to remove phosphate economically.

The aim of the present work was to study the removal of  $\text{PO}_4^{3-}$  in aqueous solution by blast furnace slag. In this study, the adsorption characteristics of phosphate onto blast furnace slag were investigated, including the effect of temperature ranges, agitation rates, adsorbent dose and pHs to remove phosphate.

## 2. Materials and methods

Phosphate was removed from a synthetic wastewater using İskenderun blast furnace slag in a batch reactor. The grain size

Table 1  
Typical analysis of blast furnace slag

Parameter	Component (%)
$\text{SiO}_2$	39.56
$\text{Fe}_2\text{O}_3$	0.33
$\text{Al}_2\text{O}_3$	10.82
CaO	37.68
MgO	6.79
$\text{SO}_3$	0.33
$\text{K}_2\text{O}$	–
$\text{TiO}_2$	–
Sulphide ( $\text{S}^{2-}$ )	–
Chloride ( $\text{Cl}^-$ )	0.125
Undetermined	3.99

of the blast furnace slag used was between 0.03 and 0.02 mm. Blast furnace slag samples were washed with distilled water and then dried at 25 °C. The chemical composition of İskenderun blast furnace slag in Hatay-İskenderun of Turkey was defined using X-ray diffraction spectroscopy and given in Table 1.

The standard phosphate solutions used in the experiments were prepared from anhydrous  $\text{KH}_2\text{PO}_4$ . The adsorption studies have been carried out at phosphate concentrations of 180 ppm  $\text{PO}_4^{3-}$ . A given amount of blast furnace slag was placed in 250-ml volumetric flasks and mixed with 50 ml of stock solution. The experiments were carried out at different temperatures (25, 45 and 65 °C) and pH values. pH adjustments have been done by using solutions of concentrated HCl and NaOH. The mixtures have been filtered using Whatman GF/A filter prior to each measurement. Jar tests were used to define the minimum equilibrium time of removal of phosphate which was defined as 20 min. Phosphate has been measured according to the Vanadomolybdophosphoric

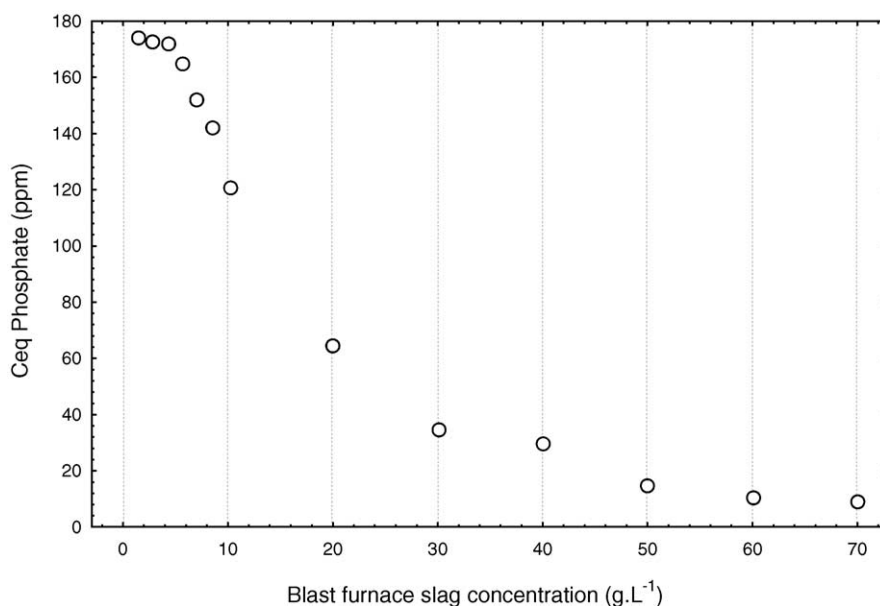


Fig. 1. The effect of blast furnace slag on phosphate concentration in the equilibrium.

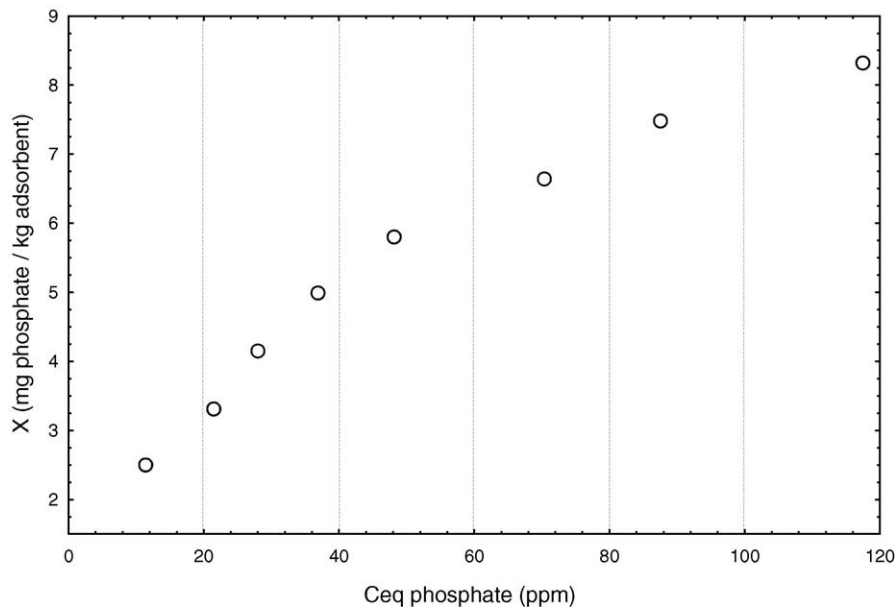


Fig. 2. The Relation between phosphate concentration in the equilibrium and phosphate dose adsorbed per kg blast furnace slag.

Acid Colorimetric Method [25]. The specific surface area of Hatay-İskenderun blast furnace slag particles was measured by using the BET–N2 method.

### 3. Results and discussion

The effect of variation of the blast furnace slag dosage on the removal of phosphate from aqueous solutions was shown in Fig. 1. The Blast furnace slag dosage was varied from 1.4 to 70 ( $\text{g l}^{-1}$ ) and the initial phosphate concentration was 180 ppm. It was apparent that the equilibrium concentration of phosphate decreased with increasing blast furnace slag

doses for a given initial phosphate concentration. This result was anticipated because increasing adsorbent doses provides greater surface area. From Fig. 1, it is evident that for the removal of 180 ppm phosphate in 50 ml, a minimum blast furnace slag dosage of  $60 \text{ g l}^{-1}$  was required.

The variation of removal of phosphate per kg blast furnace slag is shown in Fig. 2. Phosphate concentration was varied from 150 to 500 ppm and the initial blast furnace slag concentration was  $60 \text{ g l}^{-1}$ . It is apparent that the equilibrium concentration of phosphate increased with increasing phosphate concentration for a given constant blast furnace slag concentration. This result was anticipated because the surface area of adsorbent is not enough to remove the total phosphate

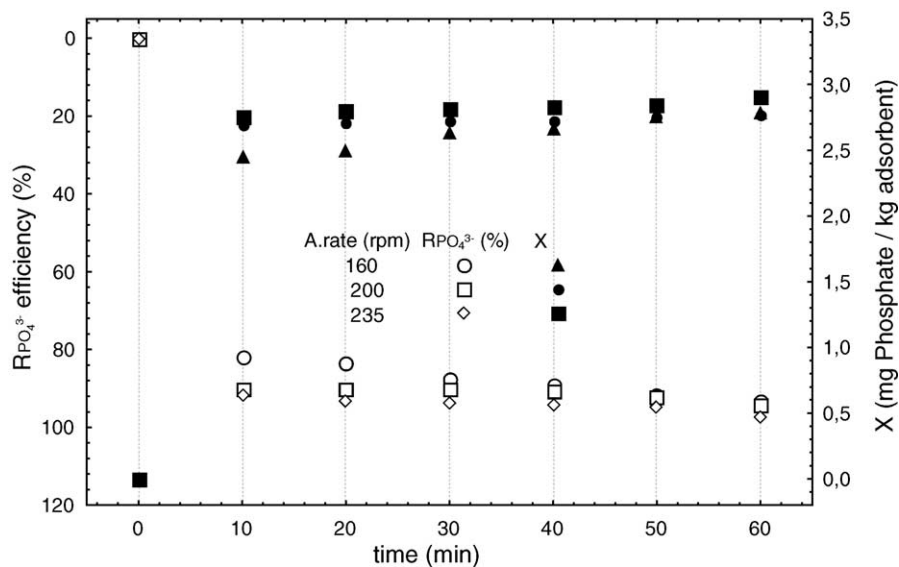


Fig. 3. Effect of agitation rate on adsorption ( $C_0$ : 180 ppm, adsorbent concentration:  $60 \text{ g l}^{-1}$ , pH: 8.5,  $T$ :  $25^\circ\text{C}$ ).

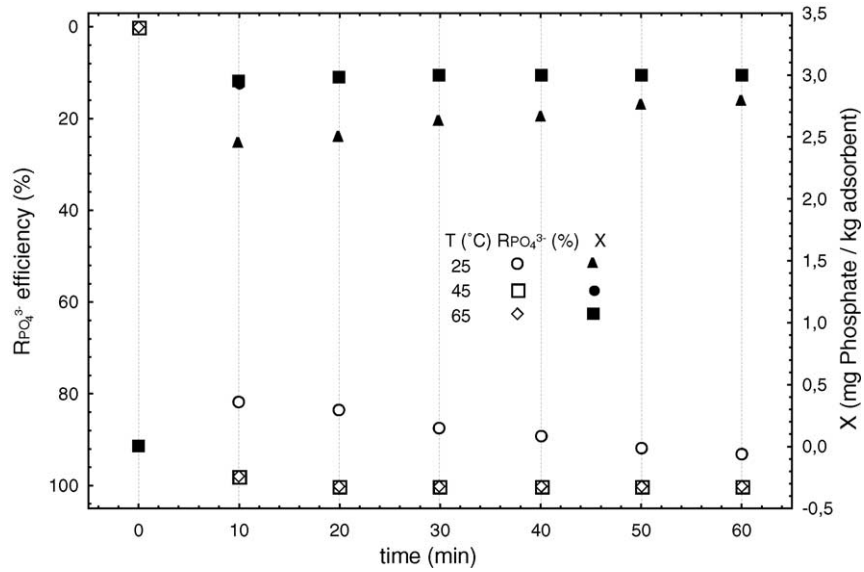


Fig. 4. Effect of temperature on adsorption ( $C_0$ : 180 ppm, adsorbent concentration: 60 g l<sup>-1</sup>, pH: 8.5, A. rate: 160 rpm).

particles from the solution at concentrations above 180 ppm. From Fig. 2, it is evident that for the removal of 180 ppm phosphate in 50 ml, the ratio of  $X$  and phosphate concentration respectively were 2.81 and 180 ppm respectively.

The Langmuir, Freundlich, isotherms models were examined in this study to describe the adsorption equilibrium. Isotherm studies were conducted at an equilibrium time of 60 min and pH of 8.5. The equilibrium data of adsorption of phosphate onto the blast furnace slag fit the Freundlich isotherm according to the correlation coefficient. The Langmuir and Freundlich isotherms models correlation coefficients ( $R^2$ ) were obtained as 0.97 and 0.96 respectively. According to Freundlich isotherms model, the maximum blast

furnace slag capacity to remove 500 ppm phosphate was defined as 6.37 mg g<sup>-1</sup>.

The effect of agitation rate on the removal of phosphate was studied for various contact times. The results are given in Fig. 3. This figure shows that the yield increases slightly with increasing time, and the rate of agitation has affected the adsorbed quantity. This suggests that the diffusion of phosphate ions from the solution to the surface of adsorbent and into the pores has increased with the increase of agitation rate. At time of 60 min, the efficiency of phosphate removal at 235 rpm was approximately 99%. The effect of agitation rate on phosphate quantity adsorbed per kg adsorbent is also shown in Fig. 3. The increase of agitation rate positively affected the attrac-

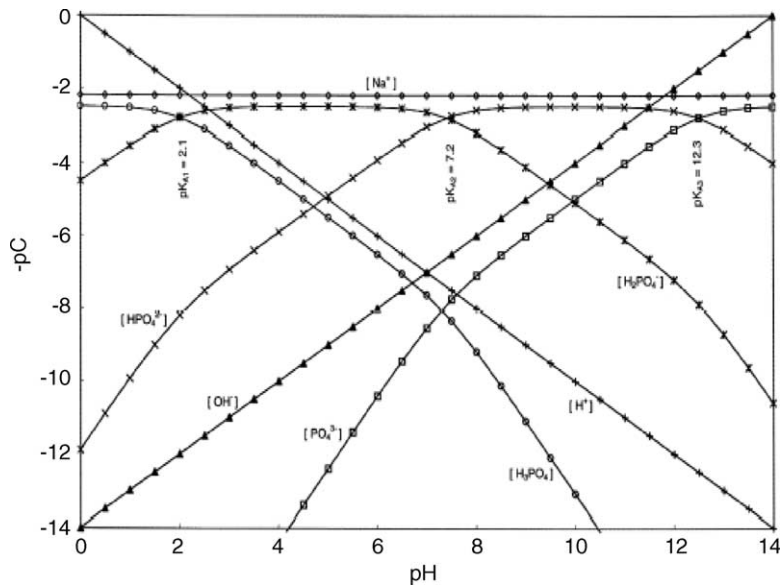


Fig. 5. pC–pH diagram for a  $3.22 \times 10^{-3}$  M  $\text{Na}_2\text{HPO}_4$ .

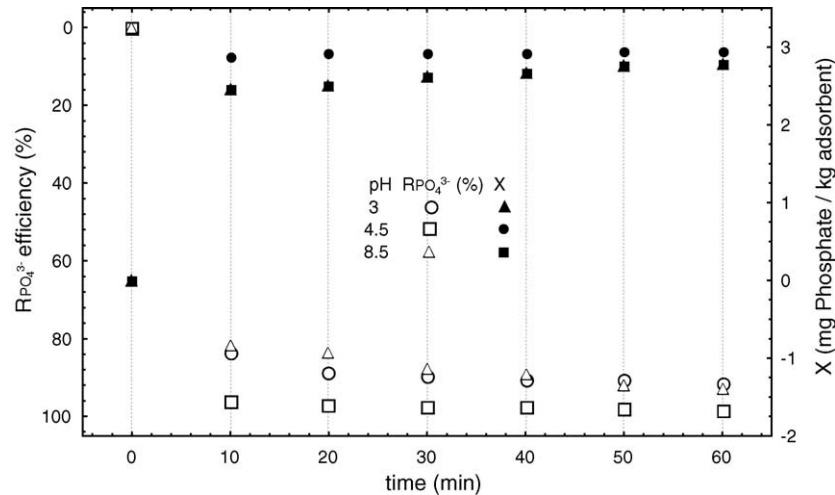


Fig. 6. Effect of pH on adsorption ( $C_0$ : 180 ppm, adsorbent concentration:  $60 \text{ g l}^{-1}$ ,  $T$ :  $25^\circ\text{C}$ , A. rate: 160 rpm).

tion between adsorbate and adsorbent, therefore, the phosphate quantity adsorbed per kg adsorbent increased with an increase in the agitation rate.

The effect of temperature on the removal of phosphate was investigated as a function of contact time. The results were then plotted in Fig. 4. From this figure, it has been determined that 20 min of contact time is enough to remove a considerable amount of phosphate present in aqueous solution at 25 and  $45^\circ\text{C}$ . The solution values of  $\text{FePO}_4$ ,  $\text{AlPO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  in the distilled water at  $25^\circ\text{C}$  are  $10^{-26}$ ,  $7.94 \times 10^{-10}$  and  $7.14 \times 10^{-7}$  respectively. Because of the fact that an increase in the solution temperature increased the solution values of  $\text{FePO}_4$ ,  $\text{AlPO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$ , it was thought that the precipitation of metallic salts such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  was less effective as a result of the electrostatic attraction between adsorbate and adsorbent which affected the removal of phosphate from aqueous solution. This result indicates that the removal of phosphate is mainly based on

physical interactions and hardly the precipitation of metallic salts such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  on the blast furnace slag. The increase of temperature positively affects the removal of phosphate, and the phosphate quantity adsorbed per kg adsorbent increased with increase the temperature as seen in Fig. 4.

In wastewater applications, the most common and successful method to precipitate phosphate involve the dissolved cations such as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  [26]. Solubility diagrams for metal phosphates in pure water show that when iron and aluminum are present, strengite ( $\text{FePO}_4$ ) and variscite ( $\text{AlPO}_4$ ) are the stable solid phases in the low pH range ( $<6.5$ ). The iron and aluminum chemistry becomes increasingly governed by the formation of oxides and hydroxides [26].

The  $[-\text{pC}]-[-\text{pH}]$  diagram for a  $3.22 \times 10^{-3} \text{ M}$   $\text{Na}_2\text{HPO}_4$  solution shown in Fig. 5, indicates that the acidic phosphates ( $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ) are the predominant aqueous species for

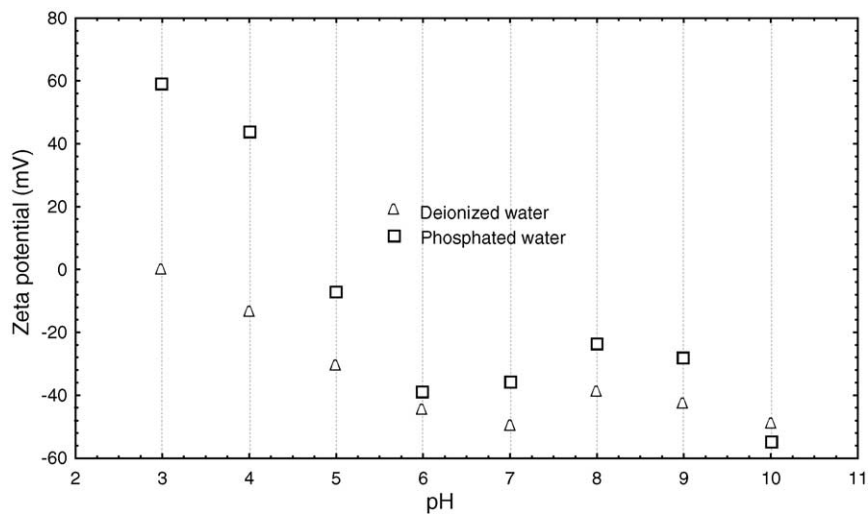


Fig. 7. Relation between zeta potentials and values of pH.

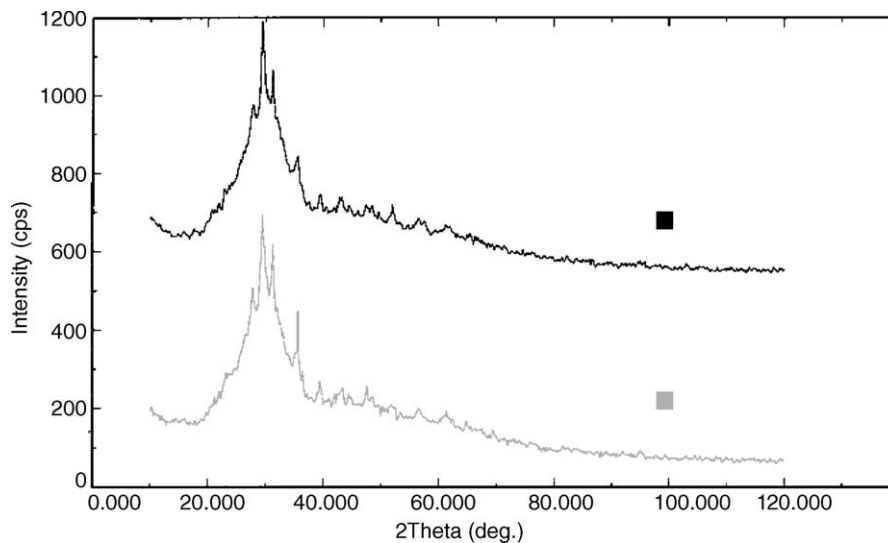


Fig. 8. X-ray diffraction diagram of the blast furnace slag before (□) and after adsorption (■) ( $C_0$ : 180 ppm, pH: 8.5,  $T$ : 25 °C, A. rate: 160 rpm).

the pH range of 3–9 [27], and polyphosphates ( $H_2P_3O_{10}^{-3}$ ,  $HP_3O_{10}^{-4}$ ,  $HP_2O_7^{-3}$ ) may also be present in the same pH range [26]. As seen in Fig. 5, at high levels of pH (9–13), basic solution, the precipitation of  $AlPO_4$ ,  $FePO_4$  and  $Ca_3(PO_4)_2$  occur on the surface of the blast furnace slag.

At the pH range of 3–8.5, phosphate removal probably occurs with ion exchange mechanisms of phosphate hydrolysis products ( $H_2PO_4^-$ ,  $HPO_4^{2-}$ ) and the precipitation of the metallic salts of phosphate ( $Al^{3+}$ ,  $Ca^{2+}$ ,  $Fe^{+3}$ ). At higher values than  $pH \leq 8.5$ , it was thought that phosphate removal take place by precipitation mechanism and the weak physical interactions between the surface of adsorbent and the metallic salts of phosphate. It was thought that phosphate removal decreased at pH 8.5 because of stronger competition with

hydroxide ions on adsorbent surface. Removal of phosphate by blast furnace slag increased at pH 4.5, but decreased at values of pH 3 and 8.5. The effect of pH on the adsorption of phosphate on the blast furnace slag was presented in Fig. 6. At the result of these study, it was thought that the pH of the aqueous solution is an important controlling parameter in the adsorption process as seen in Fig. 6.

The values of zeta potential of the particles were measured by using a microelectrophoresis cell (zeta meter 3.0+). From Fig. 7, zeta potential values of the slag particles at pH (3–10) in the distilled water were lower than in the  $PO_4^{3-}$  solution. The dominant species in the  $PO_4^{3-}$  solution were electrostatically attracted by adsorbent particles and then adsorbed on the surface of blast furnace slag particles. Adsorption of

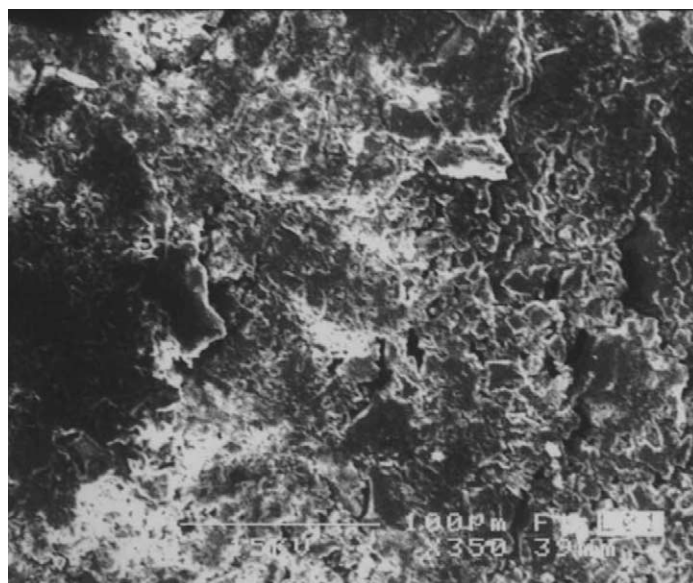


Fig. 9. SEM micrograph of the particles of blast furnace slag before adsorption ( $C_0$ : 0 ppm, pH: 8.5,  $T$ : 25 °C, A. rate: 160 rpm).



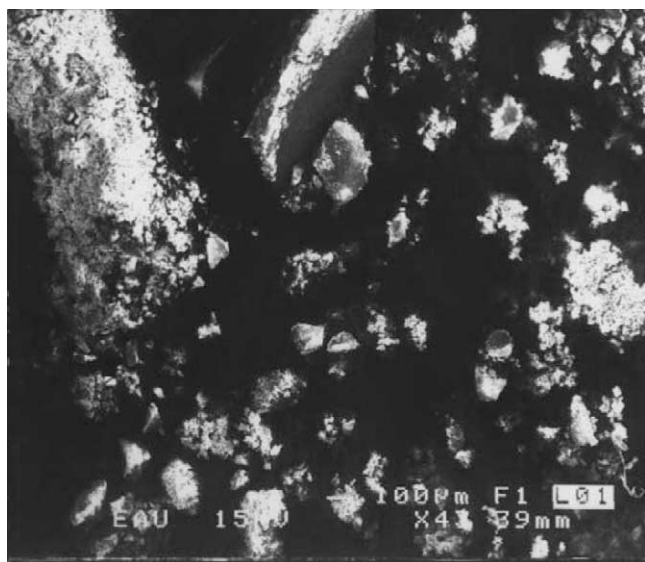


Fig. 10. SEM micrograph of the particles of blast furnace slag after adsorption ( $C_0$ : 180 ppm, pH: 8.5,  $T$ : 25 °C, A. rate: 160 rpm).

$\text{PO}_4^{3-}$  salts on the blast furnace slag particles and  $\text{H}^+$  ions in the solution caused a positively increase of zeta potential values. The increase in the zeta potential values of blast furnace slag particles was a sign of adsorption of  $\text{PO}_4^{3-}$  salts from aqueous solutions.

Fig. 8 shows X-ray diffraction spectroscopy scans of blast furnace slag before and after adsorption. The blast furnace slag has specific chemical composition intensities at different  $2\theta$  (deg). As seen in Fig. 8 (■), after adsorption of phosphate onto blast furnace slag, a considerable shifting of peaks was observed from 20 to 120 $2\theta$  (deg) as seen in Fig. 8. Fig. 8 also shows that the phosphate adsorbed electrostatically on blast furnace slag modified the peaks of chemical composition intensities on the blast furnace slag (■). In this study, according to the X-ray spectra, it was thought that there was an electrostatic (coulomb) attraction between salts of phosphate ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{+3}$ ) and blast furnace slag particles. This interaction increased at value of pH 4.5. Thus, the adsorption spectra of chemical compositions onto the blast furnace slag changed as seen in Fig. 8 (■). The results of X-ray analysis in Fig. 8 clearly reveal the presence of phosphate salts on the structure of adsorbent after adsorption process.

In order to see the surfaces of particles before and after adsorption, scanning electron microscopy (SEM) images for the samples of the raw and treated adsorbents were obtained. These micrographs are presented in Figs. 9 and 10. A representative experiment under the given conditions such as 25 °C, pH: 8.5, a contact time of 60 min, an agitation rate of 160 rpm, and an initial phosphate concentration of 180 ppm was carried out to obtain the material shown in the micrograph.

In this experiment, almost 99% of the phosphate in the aqueous solution has been removed. The micrograph obtained after adsorption indicates that the pores of the particles of the adsorbent have been covered with adsorbate.

#### 4. Conclusion

The results of this study indicate that blast furnace slag is an effective adsorbent for the removal of phosphate in aqueous solutions. Phosphate removal ratios of 99% were obtained. It was found that the amount of phosphate adsorbed on blast furnace slag depends on pH, temperature and agitation rate of the solution.

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