

Phosphate removal from water by fly ash: Factorial experimental design

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Abstract

The influence of three variables (phosphate concentration, initial pH of solution (pH_0) and the fly ash dosage) on the removal efficiency of phosphate (% E) and equilibrium pH of solution (pH_{eq}) by using fly ash was studied by means of 2^3 full factorial experimental designs. The parameters coded as x_1 , x_2 and x_3 , consecutively, were used. The parameters were investigated at two levels (−1 and 1). The effects of these factors on dependent variables, namely, % E and pH_{eq} were investigated. To determine the significance of effects, the analysis of variance with 95% confidence limits was used. It was shown that % E and pH_{eq} obtained in this study were found to be 99.6% and 11.16, corresponding to the operating condition of 25 mg l^{-1} , 2 g l^{-1} and 5.5 for the phosphate concentration, fly ash dosage and pH_0 , respectively.

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1. Introduction

Phosphorus is essential to the growth of algal and other biological organisms. Because of algal blooms that occur in surface waters, the amount of phosphorus compounds in domestic and industrial discharges must be controlled using either chemical or biological techniques. The usual forms of phosphorus found in aqueous solutions include orthophosphate, polyphosphate and organic phosphate [1]. The principal phosphorus compounds in wastewater are generally orthophosphate forms together with smaller amounts of organic phosphate [2]. Municipal wastewater may contain from 4 to 15 mg l^{-1} phosphorus as P. However, industrial wastewaters (such as detergent manufacturing and metal coating processes) may contain phosphate levels well in excess of 10 mg l^{-1} [3].

The conventional biological treatment processes have limited phosphate removal capability because microbes utilize phosphorus during cell synthesis and energy transport. As a result, 10–30% of the influent phosphorus only can be removed during biological treatment. Therefore, some of the soluble phospho-

rus compounds are still present in the effluent in the biological treatment process [3]. Biologically, complete phosphorus removal can only be achieved under certain aerobic, anaerobic and anoxic conditions [1]. Other phosphorus removal techniques are chemical treatments like adsorption, chemical precipitation, ion exchange and electro dialysis. Adsorption and chemical precipitation among the above methods have been widely used for phosphate removal [4–6].

The removal of phosphate from aqueous streams consists of the conversion of soluble phosphate to an insoluble solid phase. This solid phase can be separated from water by means of sedimentation or filtration. In wastewater applications, the most common and successful methods to precipitate phosphate involve the dissolved cations Al^{3+} , Ca^{2+} , Fe^{3+} and to a lesser extent of Fe^{2+} . It was found that when iron and aluminium are present in the water, FePO_4 and AlPO_4 forms in the low pH range (<6.5) and at higher pH range (>6.5) iron and aluminium increasingly convert to oxides and hydroxides. A higher pH is more ideal for precipitation of phosphate with calcium as apatites and hydroxyapatites [2,20].

Fly ash is a residue and particulate substance containing metal oxides, carbon and other microelements that result from the combustion of coal in a power plant. So far fly ashes have been used as additive in the cement industry due to its pozzolanic and cementitious properties [7]. But a number of investigation shows that alkaline fly ashes can effectively

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achieve removal of heavy metals (Cd^{2+} , Pb^{2+} , Cu^{2+} , Cr^{3+} , Zn^{2+} , Ni^{2+} , Cr^{6+}) [7,8,11], nutrients (phosphate) [2,4–6] and toxic organic compounds from aqueous solutions [9,10]. Fly ash is widely available and a cheap adsorbent and its alkaline properties make it interesting for use in wastewater treatment for precipitation of metallic ions and phosphates [20,21].

Earlier researches carried out about phosphate removal using fly ash show that phosphate removal has been attributed to adsorption and/or dissolution–precipitation processes [2,4–6,18,19]. The use of fly ash for phosphate removal has been generally carried out as batch and partially as column experiments [4,5]. The addition of fly ash to water because of free lime in the fly ash produces insoluble or low solubility salt when combined with phosphate. Then the solid phase phosphate compounds can be separated from water by sedimentation or classical filtration. But some fly ash particles may remain in the water and cause turbidity.

Investigations on phosphate removal using different adsorbent such as fly ash slag and baggase shows that phosphate precipitates with calcium as apatites and especially hydroxapatites (HAP), even though the solubility of calcium is primarily regulated by calcite (CaCO_3) [2,5]. It was found that the extent of HAP formation is critically dependent on factors such as degree of supersaturation, pH and initial phosphate concentration [18,19]. Therefore, it is necessary that the effect of the fly ash dosage, initial pH of solution (pH_0) and phosphate concentration on the equilibrium pH (pH_{eq}) which directly affects the formation of HAP must be investigated.

The present work is an attempt to remove phosphate ions in aqueous solution using fly ash and our another aim is to investigate the influence of phosphate concentration, initial pH of solution (pH_0) and the fly ash dosage on the removal efficiency of phosphate (% E) by using experimental design methodology. Experimental design aims at limiting the number of experiments normally required to study the influence of the most important factors involved in a give reactions [17]. The experimental work is carried out using a 2^3 factorial design in order to examine the main effects and their interactions of the parameters considered.

2. Materials and methods

2.1. Materials

Fly ash used in the experiments was obtained from the power plant of Afsin-Elbistan, Turkey and used without further treatment. The chemical composition of used fly ash which was determined previously by Bayat (as oxides in wt.%) was SiO_2 -15.14, Al_2O_3 -7.54, Fe_2O_3 -3.30, CaO -23.66, MgO -4.50, K_2O -0.28, Na_2O -0.57, TiO_2 -1.03, SO_3 -13.22 [8,12]. Specific surface area, bulk density, specific gravity and LOI of the fly ash have been determined as $0.342 \text{ m}^2 \text{ g}^{-1}$, 1.05 g/cm^3 , 2.70 g/cm^3 and 2.31 wt.%, respectively. The particle size distribution of the fly ash was found between 2 and $300 \mu\text{m}$ by Bayat [12]. About 8 wt.% of the fly ash consists of particles with diameter 2– $10 \mu\text{m}$. The ratio of smaller particles than $40 \mu\text{m}$ is nearly 60%. The zero point charge (ZPC) was found to be 7.0 and this pH_{ZPC} was

attributed to the high calcium contents of the fly ash in Bayat's work [8,12]. The other characteristics of fly ash are reported elsewhere [12]. Due to the above specifications of the fly ash used, it is classified as high calcium fly ash i.e., type C fly ash.

The standard phosphate solutions used in experiments were prepared from a stock solution of 1 g P l^{-1} of anhydrous KH_2PO_4 . Diluted HNO_3 and NaOH for pH adjustment of solutions in experiments were used and all chemicals were obtained from Merck. Ca^{2+} was measured by EDTA titration method [13]. The determination of phosphate was done colorimetrically by the yellow vanadomolybdophosphoric acid method according to AWWA [13].

2.2. Experimental techniques

2.2.1. Batch studies

In order to determine phosphate removal capacity and effect on pH_{eq} of the fly ash, batch experiments were conducted using phosphate solutions containing 10, 25, 50 and 100 mg P l^{-1} . The range of phosphate concentrations was selected with regard to concentrations in typical effluent waters. About 100 ml of phosphate solution was poured into the glass beaker of 250 ml and its pH was adjusted with HNO_3 or NaOH . A known amount of fly ash (0.1, 0.5, 1.0 or 2.0 g l^{-1}) was then added to each phosphate solution and mixed with a magnetic stirrer at 200 rpm. Increases in solution pH was monitored using a PC connected – pH meter (WTW Multiline P4) and pH values versus time were recorded. When the pH of the solution remained constant, mixing was stopped and supernatants were filtered through $0.45 \mu\text{m}$ CN membranes prior to analysis. Filtered solutions were then analyzed for phosphate.

2.2.2. Experimental design

The response variables in this study are removal efficiency of phosphate (% E) and equilibrium pH of solution (pH_{eq}). In order to evaluate the influence and interactions of the pH_0 (initial pH), fly ash dosage and initial phosphate concentration, a 2^3 factorial design was used. Each of these operating variables was selected at lower and upper levels and expressed in the following dimensionless form [14]:

(Value of operating variable i)

$$X_i = \frac{-1/2(\text{Its upper limit} + \text{its lower limit})}{1/2(\text{Its upper limit} - \text{its lower limit})}$$

Therefore, each variable is ranked as -1 and 1 at lower and upper levels, respectively. For ease of notation, the effects were designated as in Table 1 which shows the values of the operating variables selected in this study.

Table 1
Values of operating variables used in the designed set of experiments

Operating variable	-1	1
x_1 (phosphate concentration) (mg l^{-1})	25	50
x_2 (fly ash dosage) (g l^{-1})	0.5	2
x_3 (pH_0)	2.9	5.5

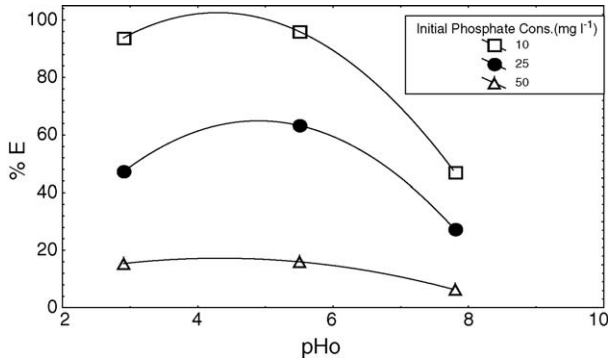


Fig. 1. Variation of phosphate removal percents with pH₀ at different phosphate concentrations (fly ash dosage = 1 g l⁻¹).

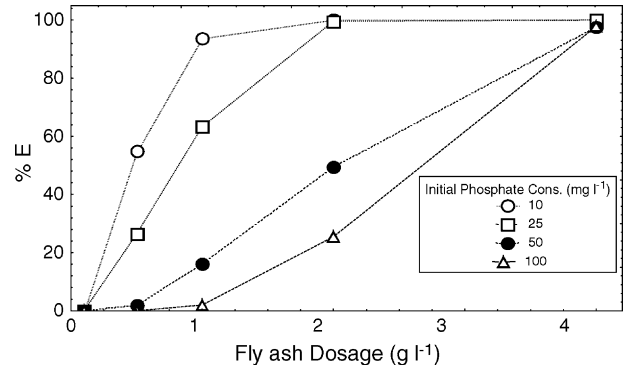


Fig. 2. Variation of phosphate removal percents with fly ash dosage at different initial phosphate concentration (pH₀ = 5.5).

3. Results and discussion

3.1. Effect of Initial pH

Variation of phosphate removal percents with pH₀ at different phosphate concentrations is shown in Fig. 1. As seen from Fig. 1, when pH₀ is increased, first phosphate removal slightly increases and over the pH = 6 reduces for every pH₀. Equilibrium pH values of the solution at pH₀ = 2.9 for 1 g l⁻¹ fly ash dosage were measured as 10.0, 8.13, 7.52 for 10, 25 and 50 mg l⁻¹ of phosphate concentrations, respectively. As phosphate concentration increases, shift of the pH becomes lesser due to buffering properties of the phosphate compounds in the solution.

The extension of the pH change in the system is directly linked to the amount of the CaO in the fly ash and is more intense in a strongly acid medium due to high concentration of hydrogen ions. Calcium concentrations remaining in the solution after equilibrium are shown in Table 2 for phosphate concentration of 25 mg l⁻¹ and at different fly ash dosages. It is seen from Table 2 that Ca²⁺ concentrations in the solution decrease with increasing pH₀ for different fly ash dosages. Relationship between Ca²⁺ and phosphate removal may be explained for two different situations, i.e., for both low and high pH. At the low pH₀ values, Ca²⁺ amount released into the solution is high because CaO turns into Ca(OH)₂ in the water. However, pH_{eq} may be insufficient to form insoluble phosphate compounds due to low initial pH. At high pH₀, dissolution of Ca²⁺ ions reduces even if pH_{eq} is enough to form the insoluble phosphate compound and consequently phosphate removal is lower due to inadequate Ca²⁺ in the solution. Therefore, highest removal efficiency was obtained at medium pH₀ values.

3.2. Effect of fly ash dosage

The effect of fly ash dosage on the removal of the phosphate from aqueous solution at pH₀ = 5.5 is shown in Fig. 2. From Fig. 2, it can be clearly seen that increasing fly ash dosage results in higher removal efficiency. As initial phosphate concentration increase, it is needed to add more fly ash in order to raise the pH_{eq} that is suitable for the formation of the insoluble phosphate compounds. pH_{eq} values decrease with increasing phosphate concentration for a given fly ash dosage. This can be explained by the change of orthophosphate compounds with pH (i.e. conversion of H₃PO₄ ⇒ H₂PO₄⁻ ⇒ HPO₄²⁻ ⇒ PO₄³⁻ with increasing pH). At about pH = 6, H₃PO₄ and H₂PO₄⁻ are the dominant compounds in the solution and HPO₄²⁻ and PO₄³⁻ are present in lesser concentration in comparison with H₃PO₄ and H₂PO₄⁻. The alkaline property (OH⁻) of fly ash is used for the conversion of acidic phosphate compounds and the pH of the solution does not raise a lot. Therefore, in order to increase pH to an adequate value for satisfactory phosphate removal, more fly ash must be added to the water.

3.3. Effect of initial phosphate concentration

At a given pH₀, phosphate removal efficiency for different phosphate concentrations is present in Fig. 3. It can be seen from Fig. 3 that removal percents decreases with phosphate for overall fly ash dosages because buffering properties of phosphate compound and insufficient calcium ions in the solution as discussed previously. Also decreasing of phosphate removal percents with phosphate concentration for different pH values can be seen from Fig. 1.

Table 2

Remaining Ca²⁺ concentrations (mg l⁻¹) in solution and phosphate removal efficiency after equilibrium for 25 mg l⁻¹ phosphate concentration

pH ₀	Fly ash dosage (g l ⁻¹)											
	0.1			0.5			1.0			2.0		
	Ca ²⁺	pH _{eq}	E (%)	Ca ²⁺	pH _{eq}	E (%)	Ca ²⁺	pH _{eq}	E (%)	Ca ²⁺	pH _{eq}	E (%)
2.9	33.6	3.44	5.0	64.8	7.79	17.2	63.2	8.13	47.0	68.8	10.33	99.0
5.5	24.0	6.65	0.0	32.0	8.62	26.0	20.0	9.09	63.0	28.0	11.15	99.6
7.8	7.2	8.75	0.0	4.0	9.78	8.2	4.0	10.15	27.0	4.0	10.78	81.9

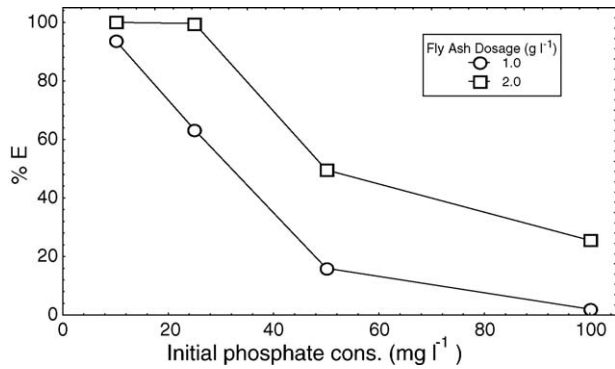


Fig. 3. Variation of phosphate removal percents with initial phosphate concentration at different fly ash dosage (pH₀ = 5.5).

3.4. Effect of phosphate /fly ash ratios

It was seen that fly ash dosage that was added to solution and phosphate concentration of the solution has a considerable effect on the phosphate removal. Therefore, they must be considered together to explain phosphate removal. Variation of the pH_{eq} and phosphate removal percent as a function of pH₀ at different phosphate/fly ash ratios is shown in Fig. 4(a) and (b), respectively. It can be seen from Fig. 4(a) that pH_{eq} has considerably reduced with increasing phosphate/fly ash ratios. As indicated in previous section, an adequate amount of calcium ions and pH higher than 9 must be present in the solution for adequate phosphate removal. It was noted that pH 9 was found as critical value to form hydroxyapatites [5,19]. Consequently, phosphate removal is decreased due to low calcium ions and pH_{eq}. When solubility of CaO decreases at higher phosphate/fly ash rates than 10, removal efficiency reduces. In the case of high phosphate concentration and low pH₀, fly ash dosage can be increased for a higher phosphate removal.

3.5. Factorial design for removal experiments

A 2³ complete factorial design can be performed with the values of the operating variables as shown in Table 1. This results

Table 3
Experimental results of 2³ designs for the % E and pH_{eq}

Experiments	x ₁	x ₂	x ₃	Y ₁	Y ₂
1	-1	-1	-1	17.16	7.79
2	1	-1	-1	1.5	7.18
3	-1	1	-1	99.41	10.33
4	1	1	-1	41.22	7.71
5	-1	-1	1	26.4	8.63
6	1	-1	1	1.1	7.62
7	-1	1	1	99.6	11.16
8	1	1	1	49.56	8.04

Table 4
Results of regression analyzing for % E (Y₁)

	Coefficient	S.E.	t-value
Intercept	41.99375	0.134519	-
x ₁	-18.6488	0.134519	-138.633
x ₂	30.45375	0.134519	226.3903
x ₃	2.17125	0.134519	16.14086
x ₁ x ₂	-8.40875	0.134519	-62.5098
x ₁ x ₂ x ₃	2.22375	0.134519	16.53114

in eight tests with all possible combinations of x₁, x₂ and x₃. % E (Y₁) and pH_{eq} (Y₂) were measured for each of these tests as shown in Table 3.

The complete factorial model that can be used to fit the data in Table 3 is:

$$\hat{Y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{123}x_1x_2x_3 \quad (1)$$

where \hat{Y} is the response calculated by model, x₁, x₂, x₃, coded variables, b_i, b_j, b_{ij}, b_{ijk}, are the coefficients estimated by the model. The Microsoft Excel was used for regression and graphical analysis of the data obtained. Regression analysis was performed to fit the response function (% E and pH_{eq}) with the experimental data. (Respectively, Tables 4 and 5).

The model expressed by Eq. (1), where the variables take their coded values, represent % E (Y₁) as a function phosphate

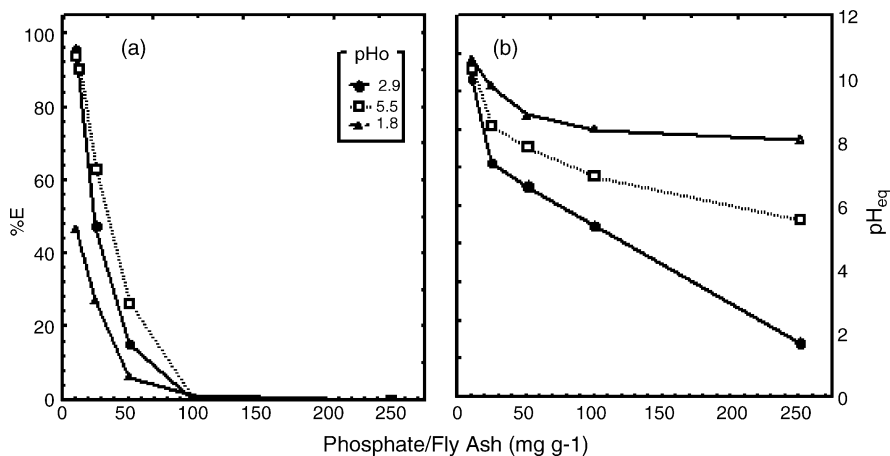


Fig. 4. Variation of the pH_{eq} and phosphate removal percent as a function of pH₀ at different phosphate/fly ash ratios.

Table 5
Results of regression analyzing for pH_{eq} (Y₂)

	Coefficient	S.E.	t-value
Intercept	8.5575	0.080254	–
x ₁	–0.92	0.080254	–11.4637
x ₂	0.7525	0.080254	9.376538
x ₃	0.305	0.080254	3.800457
x ₁ x ₂	–0.515	0.080254	–6.41717
x ₁ x ₂ x ₃	–0.0125	0.080254	–0.15576

Table 6
ANOVA for the model regression representing % E

Source	df	SS	MS	F
Regression	5	10844.59	2168.917	14982.59
Residual	2	0.289525	0.144763	
Total	7	10844.88		

df: degree of freedom, SS: Sum of square, MS: Mean squares.

concentration (x₁), fly ash dosage (x₂) and pH₀ (x₃).

$$Y_1 = 41.99 - 18.65x_1 + 30.45x_2 + 2.17x_3 - 8.41x_1x_2 + 2.22x_1x_2x_3 \quad (2)$$

The statistical significance of the model equation was evaluated by the *F*-test analysis of variance (ANOVA) which revealed that this regression is statistically significant at 95% of confidence level. The model presented a high determination coefficient (*R*₂ = 0.999) explaining 99.9% of the variability in the response (Table 6).

Another response studied was the pH_{eq}. The mathematical model representing pH_{eq} (Y₂) in the experimental region studied can be expressed by Eq (3).

$$Y_2 = 8.55 - 0.92x_1 + 0.75x_2 + 0.305x_3 - 0.515x_1x_2 - 0.0125x_1x_2x_3 \quad (3)$$

Table 7 shows the analysis of variance for the model used to estimate pH_{eq} as a function of phosphate concentration, fly ash dosage and pH₀. The regression is highly significant at 95% of coefficient (*R*² = 0.992), thus explaining 99.2% of the total variation in the surface in the response, the rest (1%) being explained by the residues. This is proof that the model describes well, the region studied [15].

The analysis of data obtained in this study shows that fly ash dosage had the strongest effect on % E and pH_{eq}. Increasing fly ash dosage increases % E and pH_{eq}. The *b*₂ coefficient is the largest positive coefficient for all the model equations. (see

Table 7
ANOVA for the model regression representing pH_{eq}

Source	df	SS	MS	F
Regression	5	14.1685	2.8337	54.9966
Residual	2	0.10305	0.051525	
Total	7	14.27155		

df: degree of freedom, SS: Sum of square, MS: Mean squares.

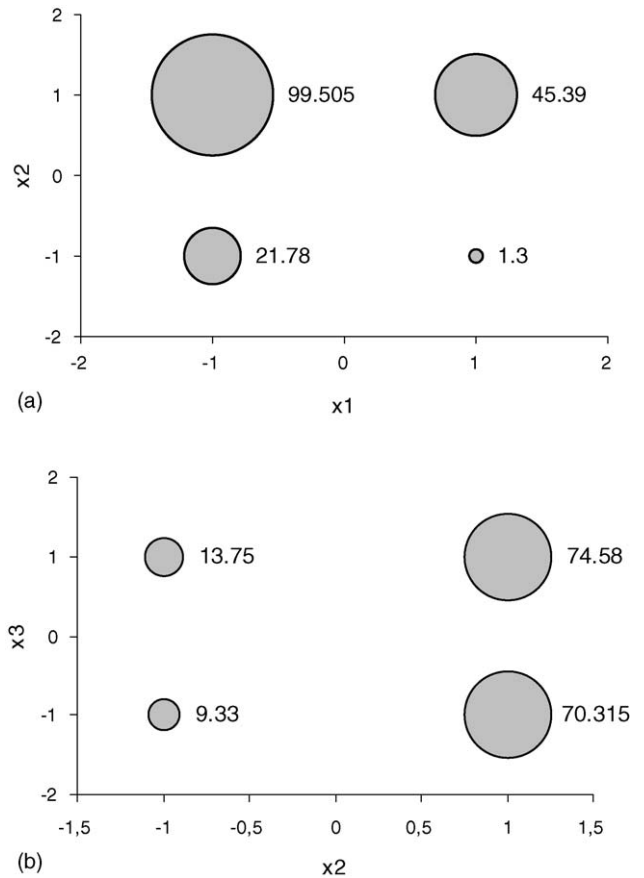


Fig. 5. Interaction effect of phosphate concentration and fly ash dosage (a) and fly ash dosage and pH₀ for % E (b). The balls represent a certain weight for the response variable and the values are the average of the response variables.

Eqs. (2) and (3)) It is known that the larger the coefficient, the larger is the effect of related parameter. The positive sign also shows that there is a direct relation between the parameter and dependent variable [16]. The *b*₁ coefficient is the largest negative coefficient for Y₁ and Y₂. Decreasing phosphate concentration decreases % E and pH_{eq} and its increase decreases the removal rates due to low pH as shown in Fig. 3.

Eq. (2) is also seen that two-variable or three-variable interactions are significant. Evidence of large negative (x₁x₂) and positive (x₁x₂x₃) interactions is very strong and therefore cannot be neglected from the model. Fig. 5 illustrates the possible positive and negative two-variable interactions among the variables x₁, x₂, x₃ for Y₁. These results support the findings related to the effect of phosphate/fly ash ratios in Section 3.4. Because it has been found that the lower phosphate/fly ash ratios, the higher removal rates, i.e., low phosphate and high fly ash dosage.

For Y₂, it is seen that three variable interactions are insignificant. Therefore, it can be neglected from the model. Fig. 6, illustrates the possible positive and negative two-variable interactions among the variables x₁, x₂, x₃ for the mathematical model representing pH_{eq} (Y₂).

The maximum removal efficiency of phosphate (% E) and pH_{eq} obtained in this study was found to be 99.6% and 11.16, corresponding to the operating condition of 25 mg l⁻¹, 2 g l⁻¹

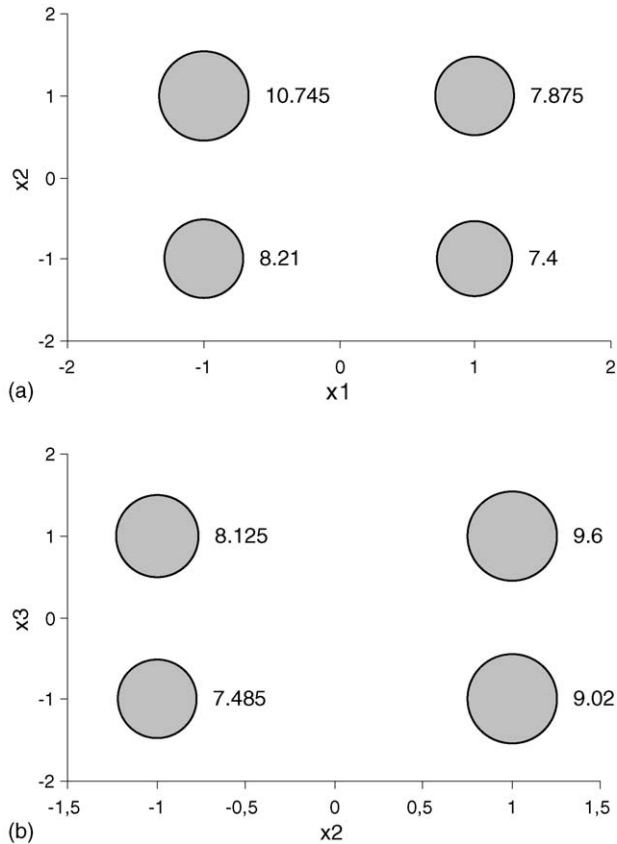


Fig. 6. Interaction effect of phosphate concentration and fly ash dosage (a) and fly ash dosage and pH_0 for pH_{eq} (b). The balls represent a certain weight for the response variable and the values are the average of the response variables.

and 5.5 for the phosphate concentration, fly ash dosage and pH_0 , respectively.

4. Conclusion

The obtained results for removal of phosphate ions from aqueous solution in contact with fly ash show an increasing capacity with increasing fly ash dosage at medium pH values. In addition, it has been shown that adequate amount of calcium ions and higher equilibrium pH than 9 must be supplied for maximum phosphate removal. The results of this research showed that fly ash dosage had significant effect on the removal efficiency of phosphate (% E) and pH_{eq} . Fly ash dosage and pH_0 have a positive effect, whereas phosphate concentration has a negative effect on the % E and pH_{eq} . The interaction effect between phosphate concentration and fly ash dosage was an important significant factor for removal efficiency of phosphate (% E) and pH_{eq} .

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