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Orthophosphate Removal from a Synthetic Wastewater Using Lime, Alum, and Ferric Chloride

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Abstract

Lime, alum, and ferric chloride were evaluated using a series of jar tests to determine their effectiveness in orthophosphate precipitation from synthetic wastewaters. Calcium phosphate precipitation was most efficient at pH 11.0 and a total carbonate to phosphorus, C_T:P, molar ratio of 15.0. For these conditions, a residual total orthophosphate concentration of 0.12 mg/L-P was observed. The Mg:P molar ratio had little effect on orthophosphate removal from the synthetic wastewater. When alum was used, the minimum residual total orthophosphate concentration observed was 0.21 mg/L-P for an Al:P molar ratio of 3.0 and a pH of 6.0 when pH was adjusted before and during alum addition. When ferric chloride was used, it was found that an Fe:P molar ratio of 3.0 and a pH of 6.0 resulted in the lowest residual total orthophosphate concentration. This value was 0.19 mg/L-P when pH was adjusted before and during iron addition. A multiple regression analysis produced mathematical relationships which can be used to predict residual soluble and residual total orthophosphate concentration for lime, alum, and ferric chloride treatment.

INTRODUCTION

Eutrophication of lakes and reservoirs due to excessive phosphorus levels has prompted numerous studies investigating chemical precipitation of phosphorus from wastewater. This study was conducted to provide a better understanding of the effects of pH, total carbonate concentration, magnesium concentration, aluminum concentration, and iron concentration on the phosphorus precipitation reactions. It was felt that results of such a study would be helpful in explaining the usefulness of chemical precipitation as a treatment for phosphorus removal from wastewater. The reader is referred to books by Snoeyink and Jenkins (*1*) and Stumm and Morgan (*2*) for excellent introductions to the subject of phosphates and their removal.

EXPERIMENTAL METHODS AND PROCEDURES

Precipitation experiments were conducted to study phosphorus removal from wastewater. Different total carbonate, magnesium, aluminum, and iron to phosphorus ratios were applied to a synthetic wastewater at various pH values. Residual phosphorus was measured at each operating point.

Stock solutions of sodium bicarbonate, potassium phosphate monobasic, magnesium sulfate, and aluminum sulfate were prepared by diluting 10 g of each substance to 1 L with distilled water. A 1000-ppm atomic absorption (AA) iron standard was also used.

The number of samples and the various pH and metal to phosphorus ratios used during the precipitation experiments were chosen based on a central composite rotatable experimental design. The design was used to fit a second-order polynomial response surface to data obtained during the testing of the synthetic wastewater. The ranges of pH and metal:P ratios examined in the three phases of this study are presented in Table 1.

The greater the concentration of dissolved chemical species, the greater will be the ionic strength of the solution and the smaller the value of the activity coefficient. Reducing the activity coefficient by increasing the ionic strength of a solution increases the solubility of any solid phase which may form. Thus, in precipitation experiments, ionic strength is an important consideration. However, in this research the final total dissolved solid concentration was general below 200 mg/L. Under such conditions the ionic strength would normally by less than 0.005 *M*, thereby minimizing the effect on solubility.

TABLE 1
Ranges for pH and Metal:P Ratios Examined in Three Phases of Phosphorus Precipitation Study

	pH		C_T:P		Mg:P		Al:P		Fe:P	
Phase	Low	High	Low	High	Low	High	Low	High	Low	High
I	8.00	11.00	0.0	30.0	0.0	5.0				
II	4.00	8.00					0.00	3.00		
III	4.00	8.00							0.00	3.00

Phase I: Effects of pH, Carbonate to Phosphorus Ratio, and Magnesium to Phosphorus Ratio on Calcium Phosphate Precipitation

A series of jar tests were performed with 1 L samples of wastewater. In Phase I the synthetic wastewater was prepared by adding the required volumes of sodium bicarbonate stock solution, potassium phosphate monobasic stock solution, and magnesium sulfate stock solution to give the required carbonate and magnesium to phosphorus ratios. The pH was adjusted during rapid mixing at 120 rpm by dropwise addition of 10 *N*, 1 *N*, or 0.1 *N* sodium hydroxide (NaOH) and an equivalent amount of 10 *N*, 1 *N*, or 0.1 *N* calcium chloride ($CaCl_2$) to simulate lime addition. This method of lime addition was used because of lime's tendency to dissolve slowly. After pH adjustment, the samples were slowly mixed at approximately 20 rpm for 1 h, followed by a 1-h settling period. The pH was maintained throughout the slow mixing period by further addition of 1 *N* or 0.2 *N* NaOH and $CaCl_2$ or 1 *N* or 0.1 *N* HCl. At 30-min intervals from the beginning of the slow mixing period, aliquots were drawn from approximately 1–2 in. below the water surface and filtered through 0.45 μm membrane filters. Analyses to determine soluble orthophosphate concentrations were conducted during the 1-h slow mixing period while both soluble and unfiltered orthophosphate concentrations were determined during the 1-h settling period.

Phase II: Effects of pH and Aluminum to Phosphorus Ratio on Aluminum Phosphate Precipitation

During this phase the effects of aluminum to phosphorus ratio and pH on aluminum phosphate precipitation were studied. This phase also compared two different treatment schemes. In the first scheme the synthetic wastewater was prepared by adding the correct amounts of aluminum sulfate stock solution and potassium phosphate monobasic stock solution to give the required aluminum to phosphorus ratio. The pH was adjusted using 10 *N*, 1 *N*, and 0.1 *N* NaOH and 1 *N* and 0.1 *N* HCl.

In the second scheme the synthetic wastewater was prepared using only the required amount of potassium phosphate monobasic stock solution to give a final phosphorus concentration of 10 mg/L. The pH was then adjusted to the required final pH value using 0.1 *N* NaOH. The required volume of alum stock solution was added dropwise simultaneously with 0.1 *N* NaOH to maintain a pH of ±0.5 pH units of the required final pH value. The synthetic wastewater was prepared so that the final volume would be near 1 L. The same sampling and analysis procedures were followed in this phase as in Phase I.

Phase III: Effects of pH and Iron(III) to Phosphorus Ratio on Iron Phosphate Precipitation

This phase was identical to Phase II except that different pH values and molar ratios were tested. The two different schemes were again compared.

RESULTS AND DISCUSSION

For clarity, this presentation will be divided into two sections. The first section will be a general analysis and discussion of the results. The second section will provide a statistical analysis of the data. In this section a mathematical model describing orthophosphate precipitation in the synthetic wastewater system will be developed.

General Analysis and Discussion

Phase I: Effects of pH, Carbonate to Phosphorus Ratio, and Magnesium to Phosphorus Ratio on Calcium Phosphate Precipitation

Initially, results of these experiments were analyzed graphically by constructing a plot of the residual soluble orthophosphate concentration versus pH. The residual soluble orthophosphate concentrations plotted were averages of the values obtained over the 2-h sampling period since residual concentrations were essentially independent of time.

The pH versus residual orthophosphate concentration for various Mg:P and C_T:P molar ratios is presented in Fig. 1. The graph shows that the residual soluble orthophosphate concentration decreased significantly as pH was increased from 8 to 11 for all C_T:P and Mg:P ratios. In the pH range of 8 to 8.6, C_T:P and Mg:P ratios had little effect on

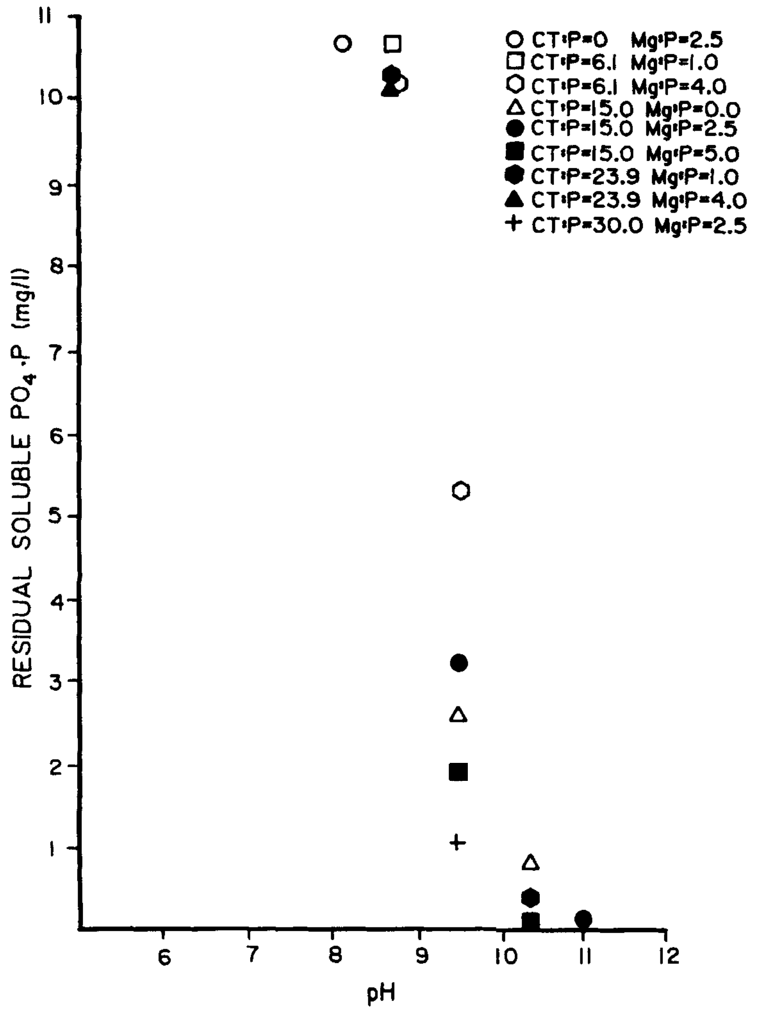

FIG. 1. pH vs soluble residual PO_4-P for various C_T:P and Mg:P ratios.

phosphorus removal. However, in the pH range of 9 to 10 the combined effects of C_T:P and Mg:P ratios on residual soluble orthophosphate concentration were significant. At pH 9.5, residual soluble orthophosphate decreased as the C_T:P molar ratio increased from 0.0 to 30.0. It was thought that at this pH, higher Mg:P ratios would result in higher residual orthophosphate concentrations for a given C_T:P molar ratio, but this effect was only slightly apparent.

At pH values greater than 10, the residual soluble orthophosphate concentration did not decrease significantly with increasing pH. The C_T:P and Mg:P molar ratios also had little effect at the high pH values.

These results support the findings of the Lebanon, Ohio, Sewage Treatment Plant pilot study (*3*), which found that approximately 95% removal of phosphorus was obtained when activated sludge effluent was treated with lime at pH 9.5 and filtered through dual-media filters. The results also agree with the findings of Stamberg et al. (*4*) who found that soluble phosphorus in waters of moderate alkalinity was reduced to less than 0.3 mg/L as P at pH 10.

It should be noted that high C_T:P ratios produced lower residual soluble orthophosphate concentrations in these experiments, an apparent contradiction to the findings of Ferguson and McCarty (*5*) who found that high carbonate levels interfered with calcium phosphate precipitation. At constant calcium concentrations, such would be the case. However, in these experiments lime, $Ca(OH)_2$, was used to adjust the pH to the desired value at each C_T:P molar ratio. Therefore, as the carbonate level increased, the lime required for pH adjustment also increased and the calcium concentration increased. At high carbonate levels, more calcium would be available for precipitation as calcium phosphate and the carbonate interference would be less apparent.

Table 2 shows the comparison between actual and predicted soluble orthophosphate concentrations for various combinations of pH, C_T:P molar ratio, and Mg:P molar ratio. The predicted orthophosphate concentrations were obtained from Seiden and Patel's (*6*) regression analysis line of best fit. The data in the table show that the regression analysis line of best fit does not adequately estimate the residual soluble orthophosphate concentrations measured in the experiments at pH values less than about 9.5. At the higher pH values of 10.4 and 11.0, the measured orthophosphate concentrations were more in agreement with the values predicted by the line of best fit. A possible cause for the difference might be interactions between orthophosphate and ionic species in the actual wastewater which were not included in these experiments with synthetic wastewater.

The effect of Mg:P molar ratio on the soluble orthophosphate

TABLE 2
Comparison of Actual and Predicted Orthophosphate Concentration

pH	Predicted PO_4^{3-} concentration (mg/L-P)	Actual PO_4^{3-} concentration (mg/L-P)	C_T:P	Mg:P
8.0	3.70	10.70	15.0	2.5
8.6	1.42	10.91	6.1	1.0
9.5	0.34	5.33	0.0	2.5
9.5	0.34	1.05	30.0	2.5
10.4	0.09	0.13	6.1	1.0
11.0	0.03	0.10	15.0	2.5

concentration was not as apparent as the effect of pH. Simply plotting the residual soluble orthophosphate concentration versus the Mg:P ratio did not show conclusively any effect that magnesium may have had on orthophosphate removal. More data would be needed to confirm or disprove the findings of Ferguson and McCarty (5) which indicated that increasing the concentration of magnesium from 0 to 0.003 *M* decreased phosphate removal below pH 9, increased phosphate removal between pH 9 and 11, and had little effect above pH 11. The significance of magnesium in phosphorus removal will be further discussed in the statistical analysis section.

Phase II: Effects of pH and Aluminum(III) to Phosphorus Ratio on Aluminum Phosphate Precipitation

This phase is divided into two different treatment schemes. In the first scheme the pH was adjusted to the desired value after the addition of alum to the solution. In the second treatment scheme the pH was adjusted to the desired value and maintained at that value by simultaneously adding 0.1 *N* NaOH with the alum.

Figure 2 shows a plot of residual soluble orthophosphate concentration versus pH for various Al:P molar ratios for the case where pH was adjusted after alum addition. As in Phase I, the residual soluble orthophosphate values are averages of the values obtained over the 2-h sampling period. The results support the findings of most studies which indicate that precipitation of orthophosphate increases with increasing alum dosage and that an optimum pH for orthophosphate precipitation exists near pH 6. The wide variety of points on Fig. 2 shows the effects of both underdosing and overdosing with alum. Figure 3 shows the same

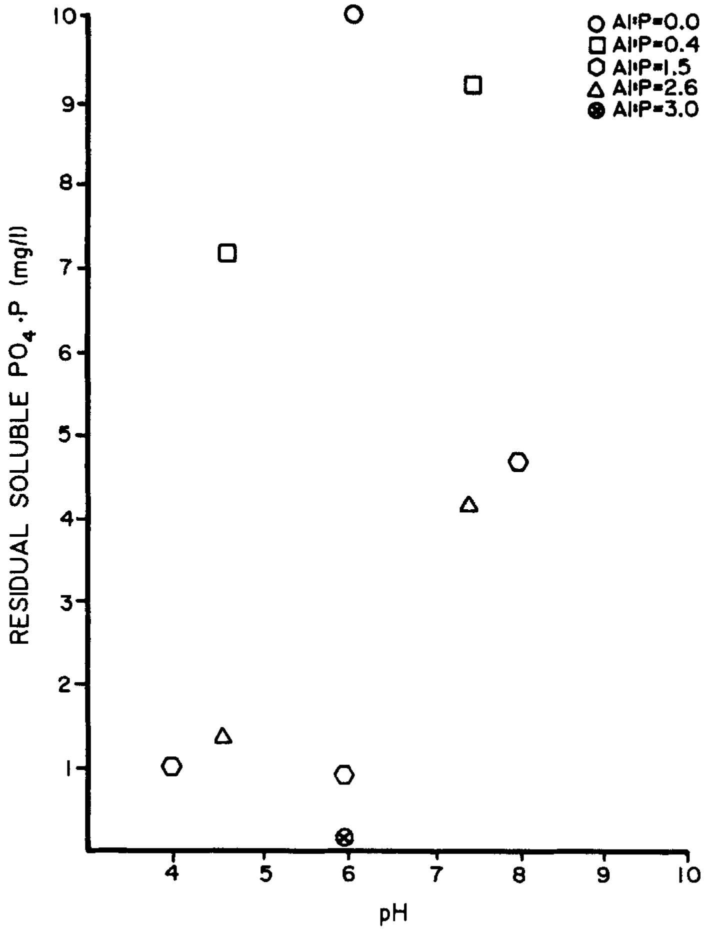

FIG. 2. pH vs soluble residual orthophosphate for various Al:P ratios when pH was adjusted after alum addition.

type plot for the treatment scheme where the pH of the solution was adjusted first and held nearly constant as alum was added.

Ferguson and King (7) pointed out that pH adjustment to the desired value should occur before or with aluminum addition since pH adjustment after precipitation is ineffective in causing further removal of phosphate. To determine how well these experiments support that conclusion, a comparison of the results obtained using the two different treatment schemes was made. Table 3 compares residual soluble

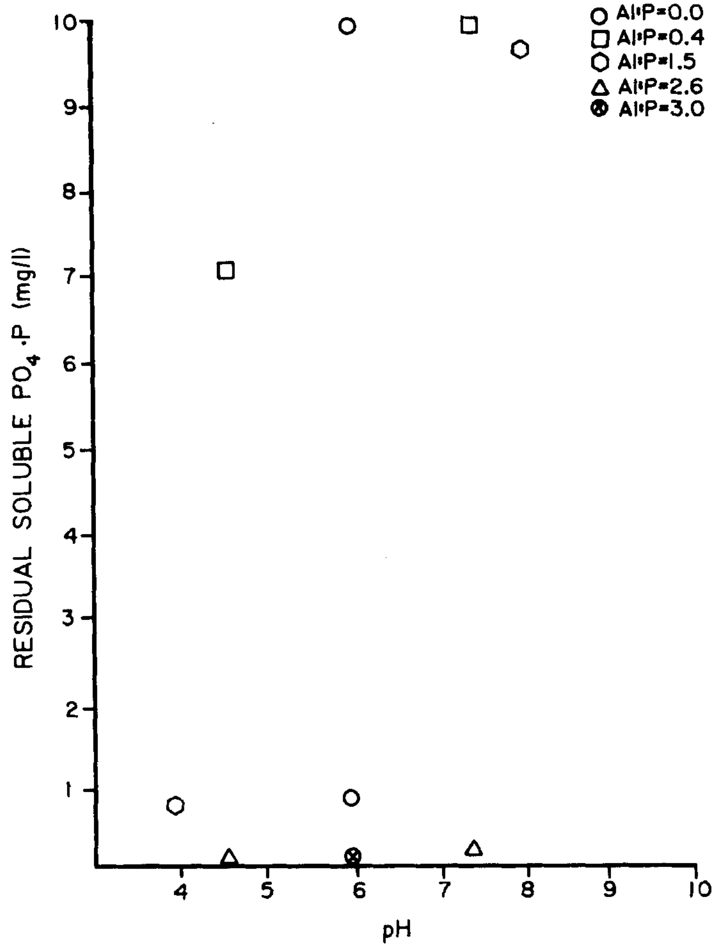

FIG. 3. pH vs soluble residual orthophosphate for various Al:P ratios when pH was adjusted before and during alum addition.

orthophosphate concentrations obtained when pH adjustment occurred after alum addition and residual soluble orthophosphate concentrations obtained when pH adjustment occurred before and during alum addition. The table, along with Figs. 2 and 3, indicates that for certain situations pH adjustment after alum addition gives the best treatment while for other situations pH adjustment before and during alum addition gives the best treatment. For example, data in Table 3 show that for an Al:P molar ratio of 1.5, residual soluble orthophosphate concentra-

TABLE 3
Comparison of Residual Soluble Orthophosphate Values for pH Adjustment After Alum Addition and Before and During Alum Addition

Al:P (molar ratio)	pH	Residual soluble PO_4-P (mg/L) pH adjustment after alum addition (Scheme #1)	Residual soluble PO_4-P (mg/L) pH adjustment before and during alum addition (Scheme #2)
0.0	6.0	10.05	9.95
0.4	4.6	7.16	7.02
	7.4	9.20	9.98
1.5	4.0	1.02	0.77
	6.0	0.93	0.84
	8.0	4.69	9.68
2.6	4.6	1.37	0.15
	7.4	4.18	0.25
3.0	6.0	0.16	0.08

tions were 1.02, 0.93, and 4.69 mg/L-P for pH values of 4.0, 6.0, and 8.0, respectively, when alum was added before pH adjustment. The corresponding residual soluble orthophosphate concentrations when pH was adjusted before and during alum addition were 0.77, 0.84, and 9.68 mg/L-P. The largest difference in residual soluble orthophosphate concentration between the two treatment schemes occurred at pH 8.0. This may be explained by considering that when alum was added before pH adjustment, the initial pH of the solution was lowered. During pH adjustment to the final pH of 8.0, the pH of the solution passed through the minimum solubility point for aluminum phosphate and precipitation of orthophosphate occurred. When the pH of the solution was adjusted to 8.0 before the alum was added and maintained at a nearly constant value during alum addition, the pH of the solution did not pass through the minimum solubility point and very little precipitation occurred. Although both treatment schemes conform to the theory of increasing orthophosphate solubility with increasing pH above the minimum solubility point, pH adjustment before and during alum addition resulted in a much sharper rise in solubility above the minimum solubility point.

Data presented in Table 3 also reflect the effect of overdosing with alum and the corresponding difference between the two treatment schemes. At an Al:P molar ratio of 2.6, pH adjustment before and during alum addition was much more efficient in removing orthophosphate at both pH 4.6 and pH 7.4. For this treatment scheme the pH at the time of initial precipitation was nearer the optimum pH than it was when alum was added after pH adjustment so that more of the excess aluminum was precipitated as aluminum phosphate.

Residual total (unfiltered) orthophosphate concentrations did not indicate a significant difference between the two treatment schemes. However, at pH values near the optimum and at high Al:P molar ratios, pH adjustment before and during alum addition produced precipitate floc sizes which were smaller than those produced when pH was adjusted after alum addition.

Phase III: Effects of pH and Iron(III) to Phosphorus Ratio on Iron Phosphate Precipitation

This phase, like Phase II, was divided into two different treatment schemes which were identical to those used in Phase II except that ferric chloride was used instead of alum.

Figure 4 presents a plot of residual soluble orthophosphate concentration versus pH for various Fe:P molar ratios for the case where pH was adjusted after iron addition. The results, as shown in the figure, tend to support the findings of earlier studies. Soluble orthophosphate concentrations were at a minimum in the pH range of 4 to 6 and increased sharply once the pH was above the optimum range. Increasing the Fe:P ratio significantly decreased the residual soluble orthophosphate concentration at any given pH. For example, Fig. 4 shows that for a pH of 4.6 and a Fe:P molar ratio of 0.4 the residual soluble orthophosphate concentration was approximately 6.9 mg/L-P. These ratios were chosen to illustrate the effect of underdosing and overdosing with iron. Figure 5 presents the corresponding results for the case where pH was adjusted before and during iron addition.

Table 4 gives a comparison of residual soluble orthophosphate concentrations obtained using the two treatment schemes. When iron was added before pH adjustment, the initial pH of the solution was lowered. During pH adjustment to the final pH value, the pH of the solution passed through the optimum range and some precipitation of iron phosphate occurred. For example, for a Fe:P molar ratio of 1.5 and pH values of 4.0, 6.0, and 8.0, residual soluble orthophosphate concentrations were 0.44, 1.51, and 5.48 mg/L-P, respectively, when ferric chloride was added before pH adjustment. The corresponding residual soluble orthophosphate concentrations when pH was adjusted before and during iron addition were 0.12, 1.67, and 8.14 mg/L-P, respectively. Adjusting the pH before and during iron addition resulted in a lower residual

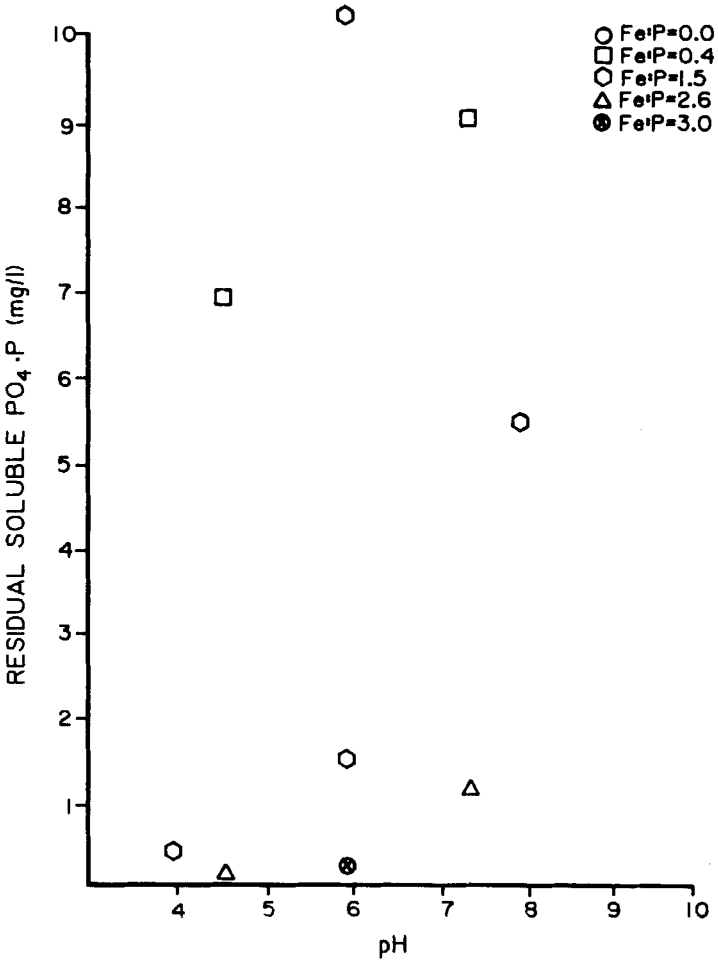

FIG. 4. pH vs residual soluble orthophosphate for various Fe:P ratios when pH was adjusted after iron addition.

orthophopshate concentration at pH 4.0 (near the optimum) but resulted in larger residual concentrations as pH increased beyond the optimum.

Residual total (unfiltered) orthophosphate concentrations were also higher at pH values above the optimum when pH was adjusted before iron addition. This treatment scheme also produced smaller floc sizes at pH values above the optimum when Fe:P molar ratios of 1.5 or less were

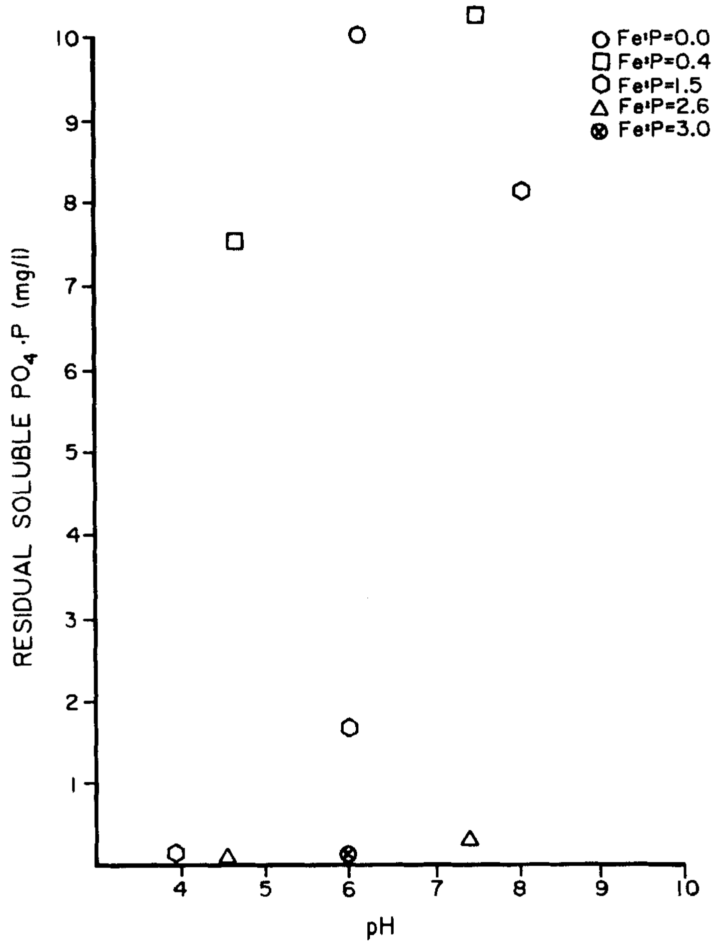

FIG. 5. pH vs residual soluble orthophosphate for various Fe:P ratios when pH was adjusted before and during iron addition.

used. At Fe:P molar ratios greater than 1.5 (overdosing), large amounts of precipitate formed.

Statistical Analysis and Discussion

In each of the three experimental phases a central composite rotatable experimental design was used to fit a second-order polynomial response

TABLE 4
Comparison of Residual Soluble Orthophosphate Values for pH Adjustment After Iron Addition and pH Adjustment Before and During Iron Addition

Fe:P (molar ratio)	pH	Residual soluble PO_4-P (mg/L) pH adjustment after iron addition (Scheme #1)	Residual soluble PO_4-P (mg/L) pH adjustment before and during iron addition (Scheme #2)
0.0	6.0	10.28	10.02
0.4	4.6	6.93	7.54
	7.4	9.06	10.28
1.5	4.0	0.44	0.12
	6.0	1.51	1.67
	8.0	5.48	8.14
2.6	4.6	0.15	0.11
	7.4	1.15	0.30
3.0	6.0	0.25	0.10

surface. This type of experimental design was chosen for several reasons. First, a regression equation describing the response surface can be developed based on relatively few experimental observations. Also, provisions can be included in the experimental design for degrees of freedom for estimating experimental error and the lack of fit of the second-order polynomial response surface. Finally, the standard error of a predicted value is constant for all combinations of pH and molar ratios tested. Thompson (*8*) pointed out that the quadratic function describing the response surface can be easily formed by the addition of terms to the linear or first-ordered function. However, Thompson also pointed out that the ability of the quadratic polynomial to fit the response surface can be severely restricted by the fact that it is symmetrical about the optimum. Another disadvantage of the quadratic polynomial is its sensitivity to outliers.

In each of the three phases, a separate response surface was developed for residual soluble orthophosphate and residual total orthophosphate. In the calcium phosphate experiments, the regression model fit was

$$\begin{aligned} x = {} & b_0 + b_1\mathrm{C_T{:}P} + b_2(\mathrm{C_T{:}P})^2 + b_3\mathrm{Mg{:}P} + b_4(\mathrm{Mg{:}P})^2 + b_5\mathrm{pH} \\ & + b_6\mathrm{pH}^2 + b_7(\mathrm{C_T{:}P})(\mathrm{Mg{:}P}) + b_8(\mathrm{C_T{:}P})(\mathrm{pH}) + b_9(\mathrm{Mg{:}P})(\mathrm{pH}) \\ & + e_{\mathrm{lof}} + e \end{aligned}$$

where C_T:P = total carbonate to phosphorus ratio
Mg:P = magnesium to phosphorus ratio

pH = negative logarithm of the hydrogen ion activity
e_{lof} = lack of fit error
e = pure error
b_i = regression coefficients

In the aluminum and iron phosphate experiments, the regression model fit was

$$x = b_0 + b_1(\text{M}_e\text{:P}) + b_2(\text{M}_e\text{:P})^2 + b_3\text{pH} + b_4\text{pH}^2 + b_5(\text{M}_e\text{:P})(\text{pH}) + e_{\text{lof}} + e$$

where x, pH, b_i, e_{lof}, and e = as previously defined
$\text{M}_e\text{:P}$ = metal to phosphorus molar ratio

The calcium phosphate precipitation experiment was designed to estimate the relationship between residual orthophosphate concentration and carbonate to phosphorus molar ratio, magnesium to phosphorus ratio, and pH. The aluminum phosphate and iron phosphate precipitation experiments were designed to estimate the relationship between residual phosphate concentration and aluminum to phosphorus molar ratio, iron to phosphorus molar ratio, and pH. A regression analysis was performed for both residual soluble and residual total orthophosphate to determine which first-order terms, which second-order terms, and which interaction terms for the various parameters should be included in the relationship.

The 5% significance level was chosen as the significance level at which the parameters in the relationship were tested. A regression analysis was performed to determine the significance of each of the terms mentioned above in the residual soluble orthophosphate equation. In addition, the significance of the lack of fit error term was also calculated. If the lack of fit error term was significant, then the model did not adequately describe the actual data and more terms were possibly needed in the equation. Table 5 contains the regression equations for all three experimental phases. The terms whose significance level was $\leqslant 0.05$ are significant and are reflected in these equations.

Phase I: Calcium Phosphate Precipitation in the Synthetic Wastewater

Figure 6 shows the surface response plot for residual soluble orthophosphate versus pH and $\text{C}_\text{T}\text{:P}$ molar ratio for calcium phosphate

TABLE 5
Regression Equations for Various Treatment Techniques[a]

Treatment	Equation number	Residual phosphorus concentration (mg/L)	Regression equation	R^2
a	(1)	Soluble =	$176.45 - 0.183(C_T{:}P) - 31.31(pH) + 0.004(C_T{:}P)^2 + 1.40(pH)^2$	0.913
a	(2)	Total =	$166.58 - 0.212(C_T{:}P) - 0.130(Mg{:}P) - 29.16(pH) + 0.004(C_T{:}P)^2 + 1.29(pH)^2$	0.907
b	(3)	Soluble =	$22.78 - 7.84(Al{:}P) - 5.19(pH) + 1.93(Al{:}P)^2 + 0.519(pH)^2 - 0.218(Al{:}P)(pH)$	0.993
b	(4)	Total =	$69.16 - 4.50(Al{:}P) - 20.99(pH) + 1.14(Al{:}P)^2 + 1.82(pH)^2 - 0.398(Al{:}P)(pH)$	0.927
c	(5)	Soluble =	$32.89 - 5.70(Al{:}P) - 9.77(pH) + 1.65(Al{:}P) + 0.989(pH)^2 - 0.463(Al{:}P)(pH)$	0.937
c	(6)	Total =	$69.91 - 4.99(Al{:}P) - 20.97(pH) + 1.05(Al{:}P) + 1.80(pH)^2 - 0.291(Al{:}P)(pH)$	0.927
d	(7)	Soluble =	$16.59 - 7.31(Fe{:}P) - 3.28(pH) + 1.69(Fe{:}P)^2 + 0.372(pH)^2 - 0.183(Fe{:}P)(pH)$	0.986
d	(8)	Total =	$29.60 - 5.74(Fe{:}P) - 7.76(pH) + 1.55(Fe{:}P)^2 - 0.751(pH)^2 - 0.393(Fe{:}P)(pH)$	0.993
e	(9)	Soluble =	$20.65 - 5.58(Fe{:}P) - 5.30(pH) + 1.47(Fe{:}P)^2 + 0.599(pH)^2 - 0.414(Fe{:}P)(pH)$	0.948
e	(10)	Total =	$-40.69 + 3.74(Fe{:}P) + 15.97(pH) - 2.52(Fe{:}P)^2 - 1.25(pH)^2$	0.890

[a] a = lime treatment.
b = pH adjusted after alum addition.
c = pH adjusted before and during alum addition.
d = pH adjusted after iron addition.
e = pH adjusted before and during iron addition.
C_T:P = carbonate to phosphorus molar ratio.
Mg:P = magnesium to phosphorus molar ratio.
Al:P = aluminum to phosphorus molar ratio.
Fe:P = iron to phosphorus molar ratio.

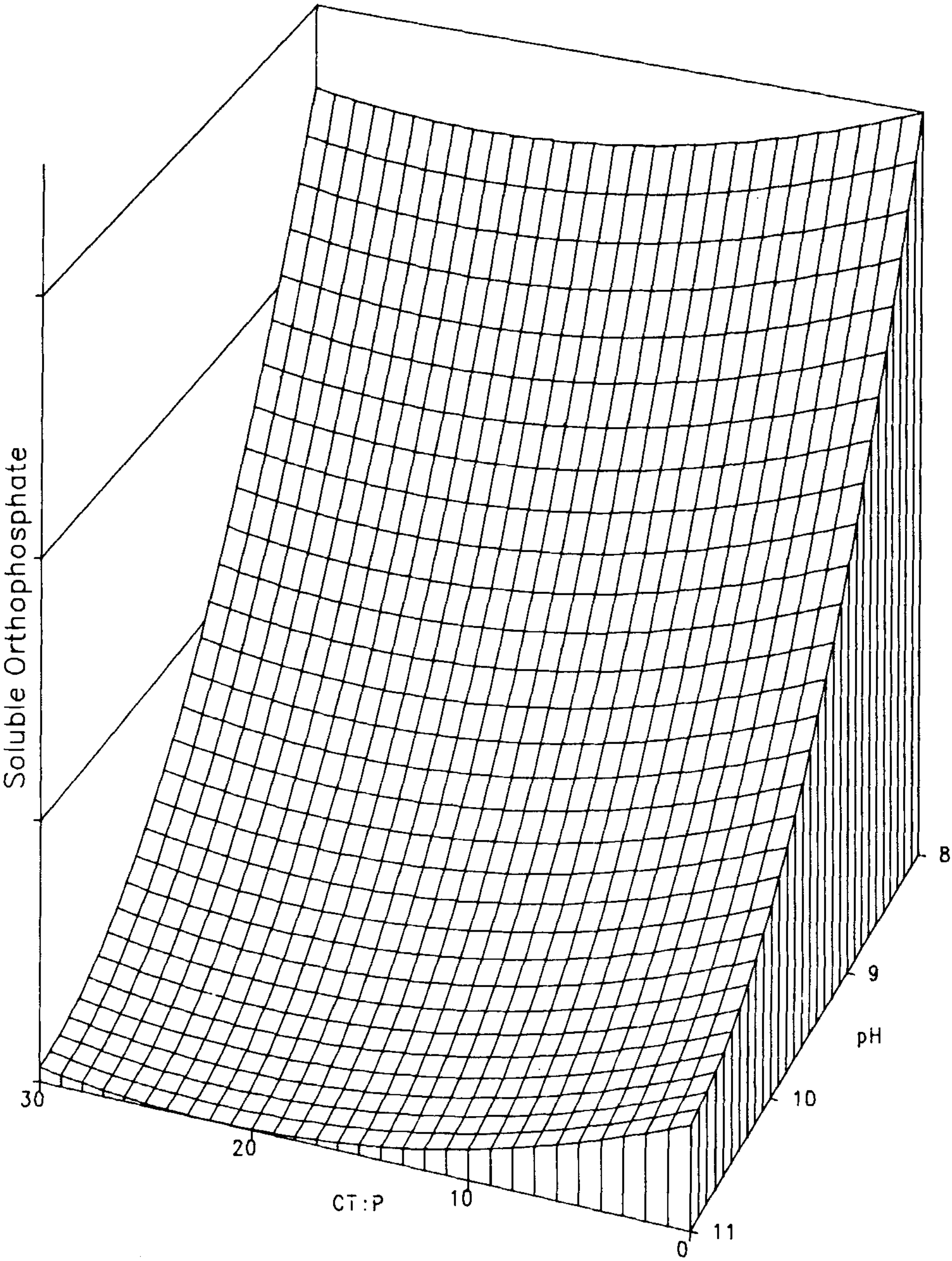

FIG. 6. Surface response plot for residual soluble orthophosphate vs pH and C_T:P molar ratio.

precipitation. This figure represents the relative response of the residual soluble orthophosphate concentration for pH values ranging from 8.0 to 11.0, and C_T:P molar ratios of 0.0 to 30.0, and Mg:P molar ratios of 0.0 to 5.0 based on Eq. (1). The figure shows an almost linear relationship between residual soluble orthophosphate and pH, with residual soluble orthophosphate concentrations decreasing as pH increased. Figure 6 also illustrates the secondary relationship between the C_T:P molar ratio and residual soluble orthophosphate, with the residual soluble orthophosphate concentration decreasing as the C_T:P molar ratio increased.

The surface response plot for residual total orthophosphate concentration versus pH and C_T:P molar ratio are presented in Fig. 7. The figure represents the relative response of the residual total orthophosphate concentration for pH values ranging from 8.0 to 11.0, C_T:P molar ratios of 0.0 to 30.0, and Mg:P molar ratios from 0.0 to 5.0 based on Eq. (2). Figure 7 appears very similar to Fig. 6 as would be expected from the similarity between the two second-order response surface polynomials. The figure also shows the same strong relationship between pH and residual orthophopshate.

Statistically, the fact that there were no significant interaction terms including Mg:P and C_T:P implies that the effects of C_T:P and Mg:P on residual phosphate levels are *independent*. This means that the effect of C_T:P is the same regardless of the Mg:P level. Still, the effect is less noticeable than would be expected based on the findings of Jenkins et al. (*9*). These researchers, however, assessed the magnitude of the effects of magnesium at a pH of 8.0 which is well below the optimum. The response surface polynomials developed in this research do not indicate a large interference by magnesium. Only 0.2% of model sum of squares error was accounted for by the Mg:P molar ratio term in the equation for residual total orthophosphate. In the residual soluble orthophosphate analysis, the Mg:P molar ratio term was not statistically significant and was not included in the equation.

The response surface described by Eq. (3) is given in Fig. 8. Notice that the Al:P molar ratio and not pH had the most significant effect on residual soluble orthophosphate concentration when pH was adjusted after alum addition. This was also evident from data presented in Fig. 2. For instance, at a pH of 6.0, increasing the Al:P molar ratio from 0.0 to 1.5 to 3.0 caused a very dramatic decrease in the residual soluble orthophosphate concentration. Sawyer (*10*) reported a similar result and noted that little removal occurred at low alum dosages but increased rapidly near the optimum or "threshold" dosage and then leveled off at higher alum dosages. However, Lea et al. (*11*) reported that phosphorus removal

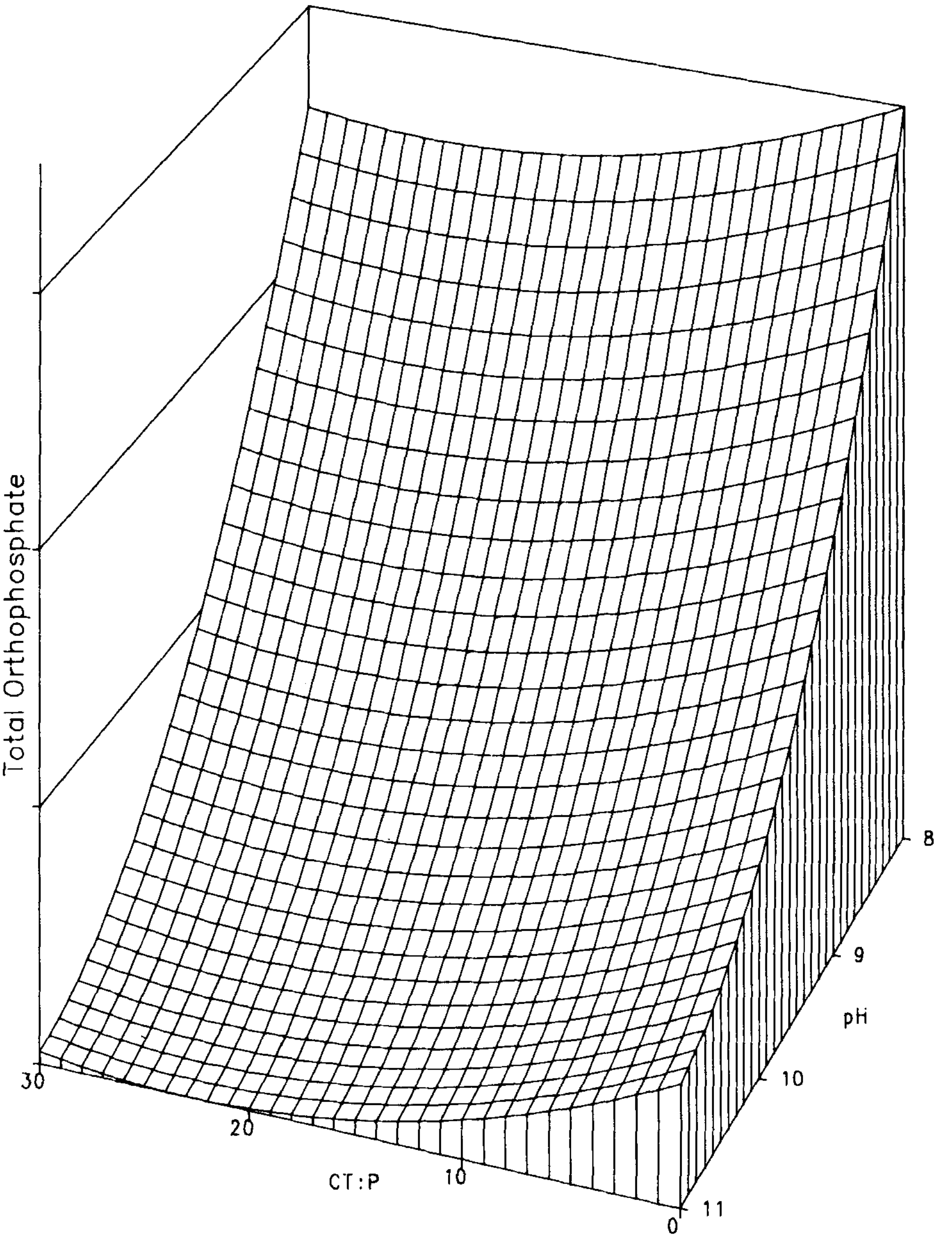

FIG. 7. Surface response plot for residual total orthophosphate vs pH and C_T:P molar ratio.

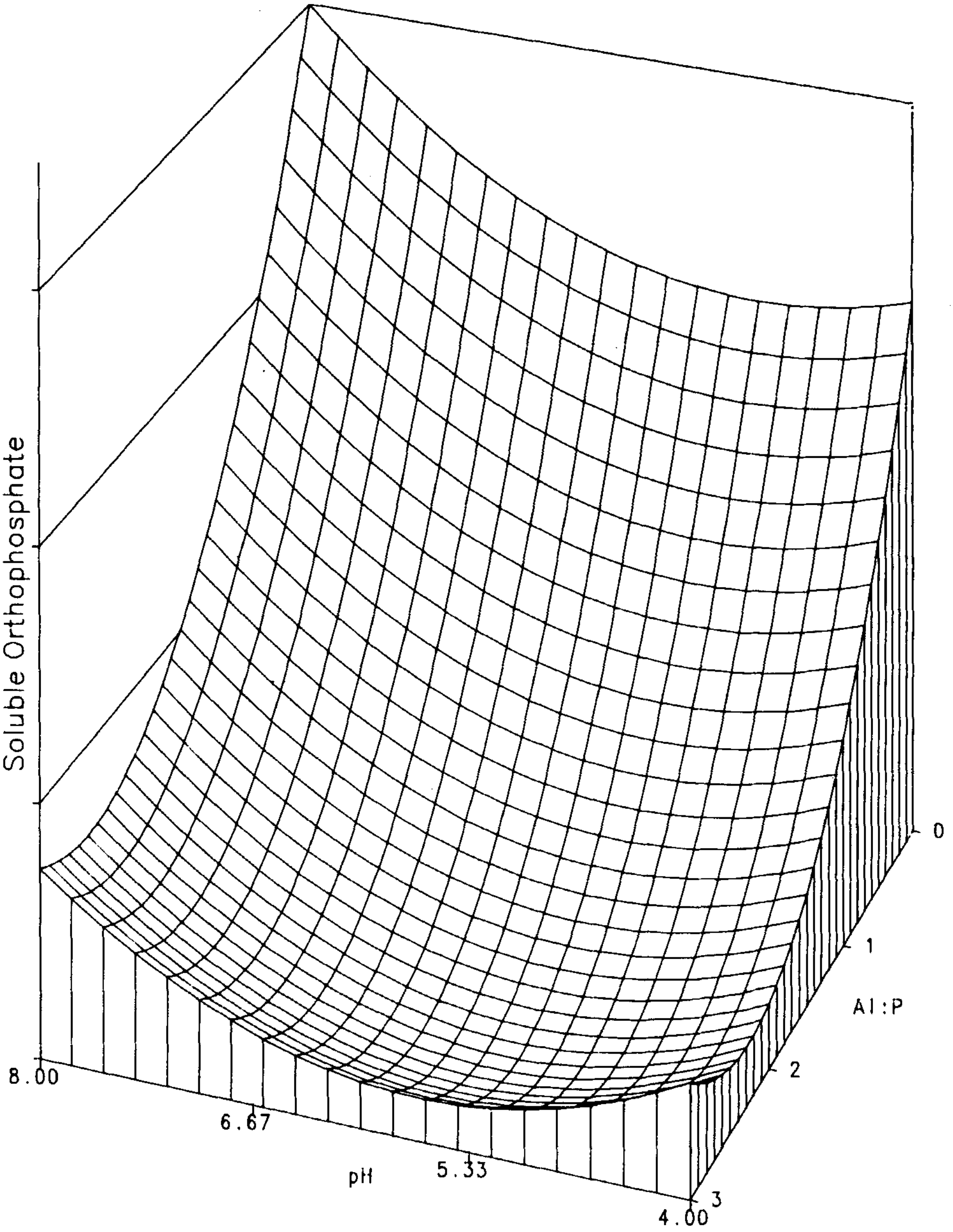

FIG. 8. Surface response plot for residual soluble orthophosphate vs Al:P molar ratio and pH when pH was adjusted after alum addition.

was nearly linear with alum dose for low dosages and very high removals occurred at very high alum dosage.

Figure 9 shows the surface response plot described by Eq. (5). Although the first-order Al:P molar ratio term was still the dominant term in the equation, the first- and second-order pH terms were more significant when pH was adjusted before and during alum addition. A comparison of Figs. 8 and 9 shows the larger impact of pH when pH was adjusted before and during alum addition. Figure 8 indicates that removal begins to level off near an Al:P molar ratio of 3.0. Since pH was not maintained during alum addition, this would be the case. However, if pH is held constant during alum addition, the residual orthophosphate concentration should continue to decline for a given pH as the Al:P molar ratio is increased until some limiting value is reached. Figure 9 shows that the residual soluble orthophosphate did continue to decline as expected.

The response surface plot described by Eq. (4) is presented in Fig. 10. Notice that the figure is very similar to the plot for residual soluble orthophosphate for the case when pH was adjusted after alum addition. Also, pH was more significant in the equation for residual total orthophosphate concentration. This would be expected since the precipitation reactions occur very quickly and are largely influenced by pH.

Figure 11 shows the surface response plot described by Eq. (6). The increased significance of pH was again apparent. The surface response plots for residual soluble and residual total orthophosphate are not as similar in the case where pH was adjusted before and during alum addition as they were when pH was adjusted only after alum addition. This again relates to the importance of pH in the precipitation reactions.

The lack of fit error term was statistically significant for both treatment schemes for both residual soluble and residual total orthophosphate. This indicates that the relationships should contain higher order terms for pH, Al:P molar ratio, and/or interaction terms. On the basis of the lack of fit error, it was not possible to conclude definitely which treatment scheme was the most effective. However, based on the findings previously discussed, there was some evidence supporting the findings of Ferguson and King (7) suggesting that pH adjustment should occur before and/or during alum addition. A comparison of Figs. 8 and 9 also indicates that orthophosphate removal was somewhat more efficient when pH was adjusted before and during alum addition although the difference was not as great as would be expected based on the findings of Ferguson and King (7).

The surface response plot described by Eq. (7) is illustrated in Fig. 12. The plot is very similar to the surface response for residual soluble

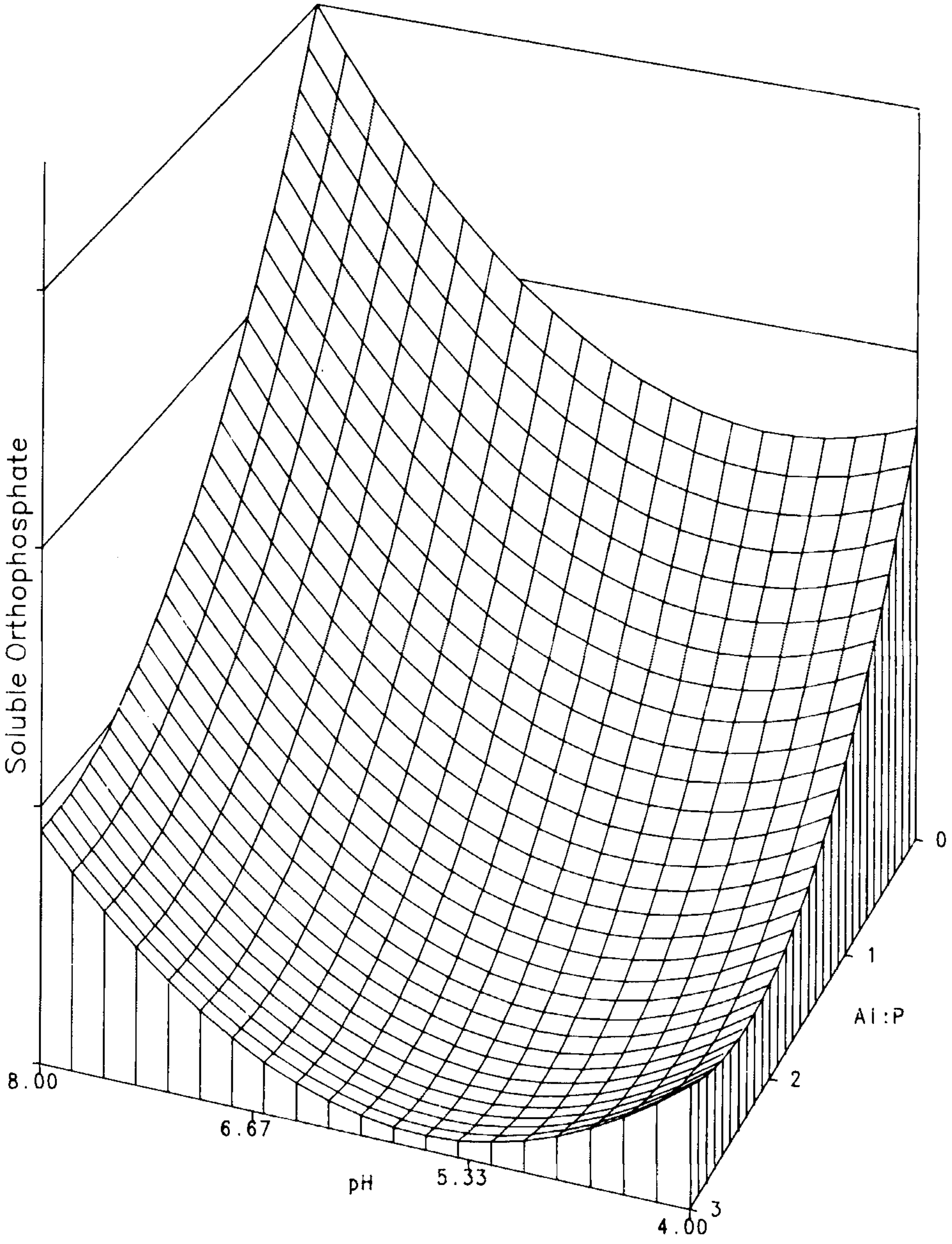

FIG. 9. Surface response plot for residual soluble orthophosphate vs Al:P molar ratio and pH when pH was adjusted before and during alum addition.

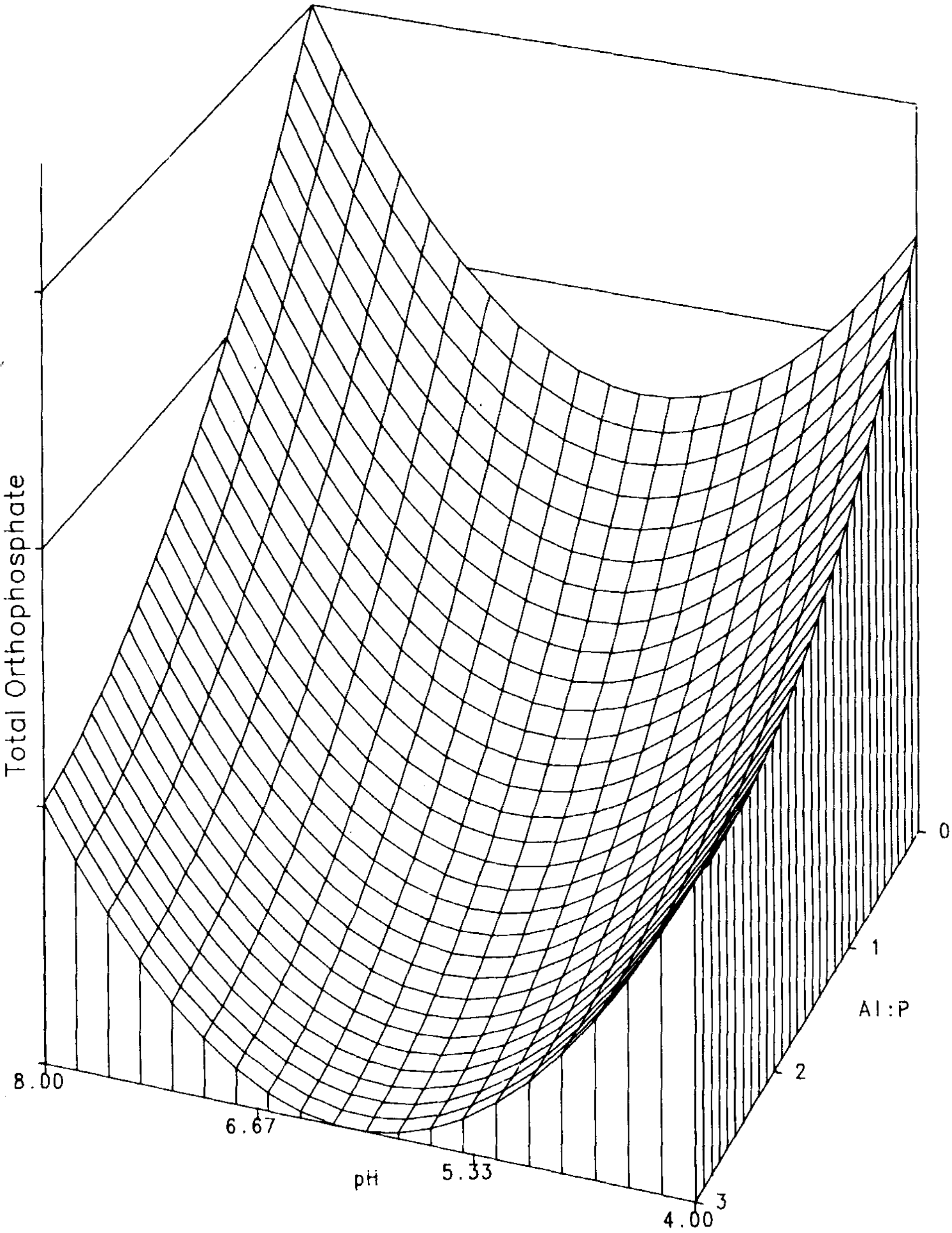

FIG. 10. Surface response plot for residual total orthophosphate vs Al:P ratio and pH when pH was adjusted after alum addition.

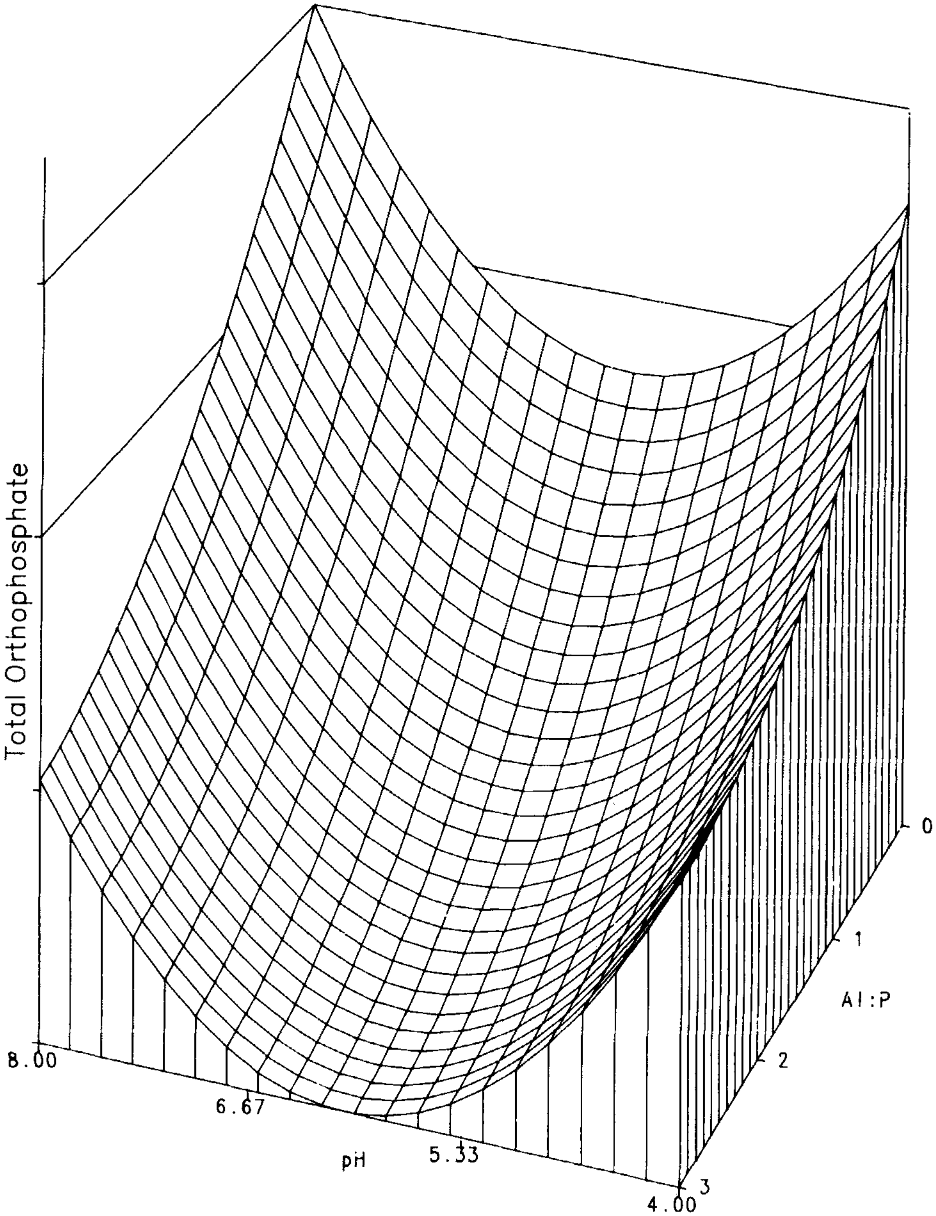

FIG. 11. Surface response plot for residual total orthophosphate vs Al:P molar ratio and pH when pH was adjusted before and during alum addition.

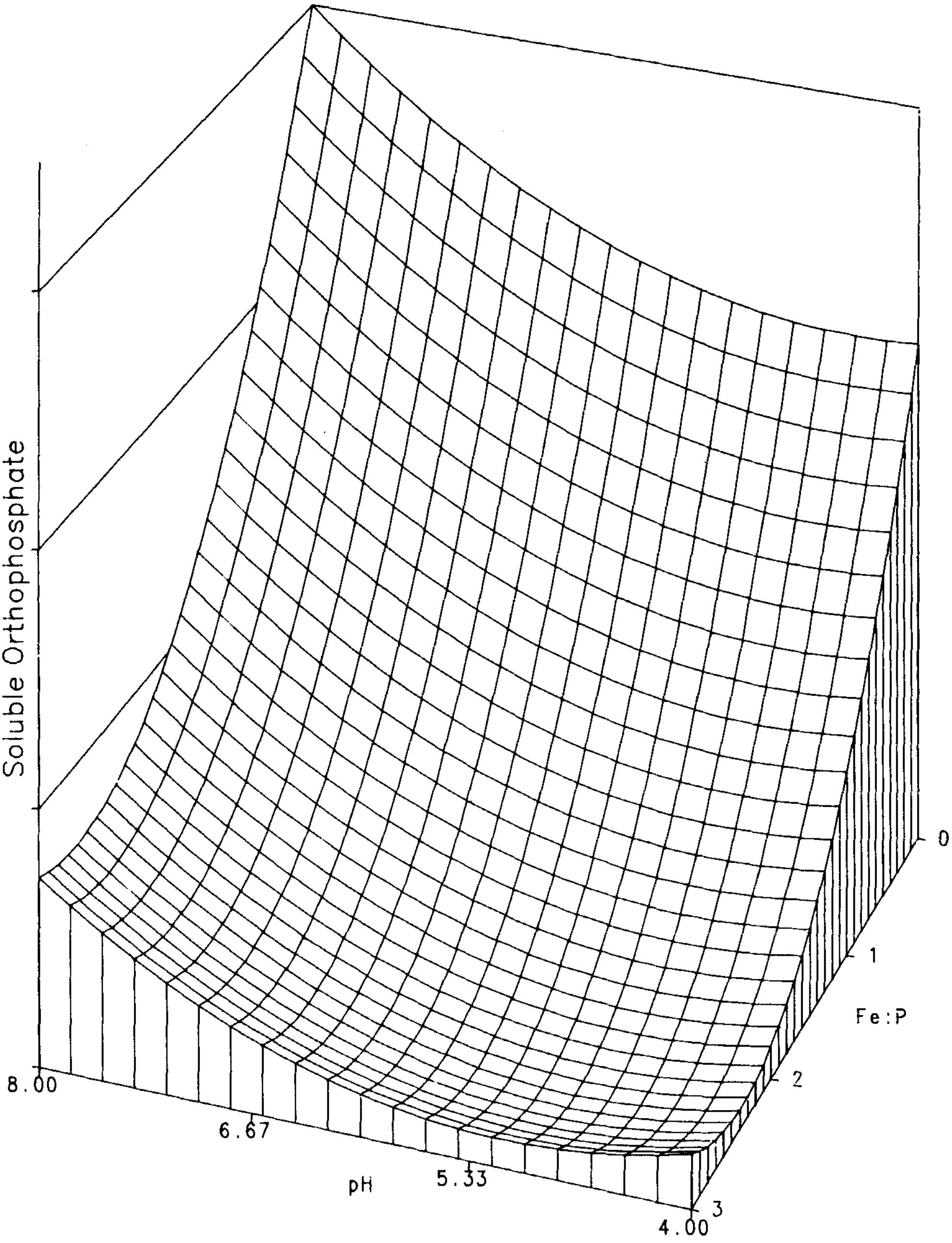

FIG. 12. Surface response plot for residual soluble orthophosphate vs Fe:P molar ratio and pH when pH was adjusted after iron addition.

orthophosphate obtained using alum and adjusting the pH after alum addition. Notice that the optimum pH is not well defined.

The response surface described by Eq. (9) is given in Fig. 13. The increased significance of pH in the equation is evident when the surface response plots for the two treatment schemes are compared. The surface response plot shown in Fig. 13 has a more clearly defined optimum pH range between pH 5.0 and pH 6.0.

The surface response plot described by Eq. (8) is shown in Fig. 14. A comparison of Figs. 12 and 14 shows that, as expected, the surface response plots for residual soluble and residual total orthophosphate were very similar when pH was adjusted after iron addition.

Figure 15 shows the surface response plot described by Eq. (10). There is a distinct difference between the shape of the surface compared to the surfaces developed thus far. The increased significance of the lack of fit error and, thus, the lower regression coefficient for Eq. (10) compared to Eq. (8) indicated that the relationship was more complex than the model assumed; therefore it is best to adjust pH after iron addition.

Another difference was also noted between the two treatment schemes. When pH was adjusted after iron addition, larger flocs were formed. Overdosing the solution with iron and driving the pH below the optimum range for precipitation resulted in a solution saturated with iron. When the pH was adjusted and passed through the optimum range for precipitation, solid formation occurred almost immediately. When pH was adjusted before and during iron addition, smaller flocs were formed. This difference was not as noticeable when alum was used. One possible explanation may have been suggested by Hsu (*12*) who noted that Fe^{3+} has a stronger affinity for phosphate and a stronger hydrolyzing power than Al^{3+}.

SUMMARY AND CONCLUSIONS

The results of this study indicate that orthophosphate removal from synthetic wastewater with calcium phosphate precipitation was most efficient at pH 11.0 and a C_T:P molar ratio of 15.0 where the residual total orthophosphate concentration was 0.12 mg/L-P. The Mg:P molar ratio was 2.5 but had little effect on orthophosphate removal.

The addition of alum was effective in removing orthophosphate from the synthetic wastewaters at a pH of about 6.0 and an Al:P molar ratio of 3.0. Also, soluble orthophosphate removal efficiency was slightly improved when pH adjustment occurred before and during alum addition. However, whether pH adjustment occurred before or after alum addition

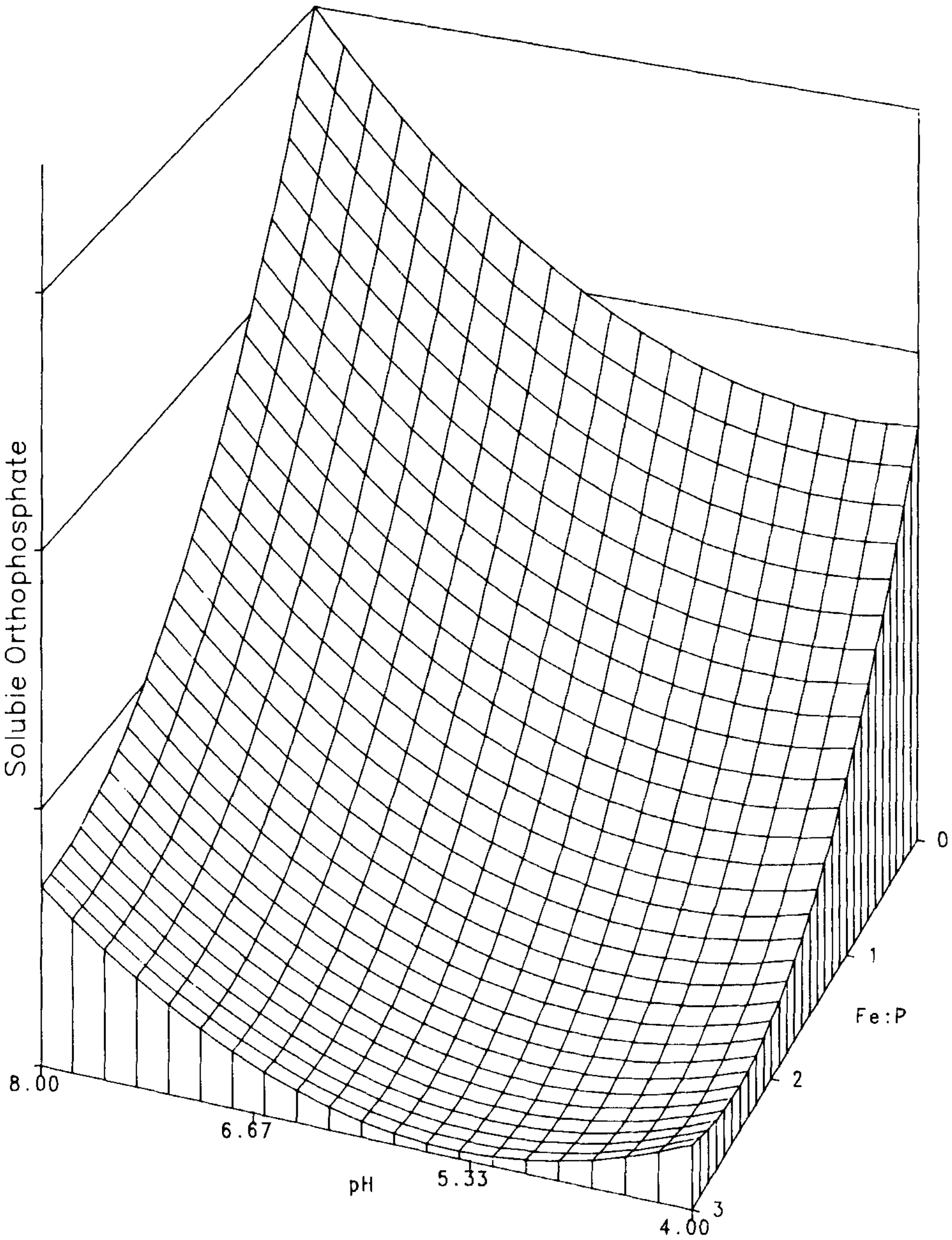

FIG. 13. Surface response plot for residual soluble orthophosphate vs Fe:P molar ratio and pH when pH was adjusted before and during iron addition.

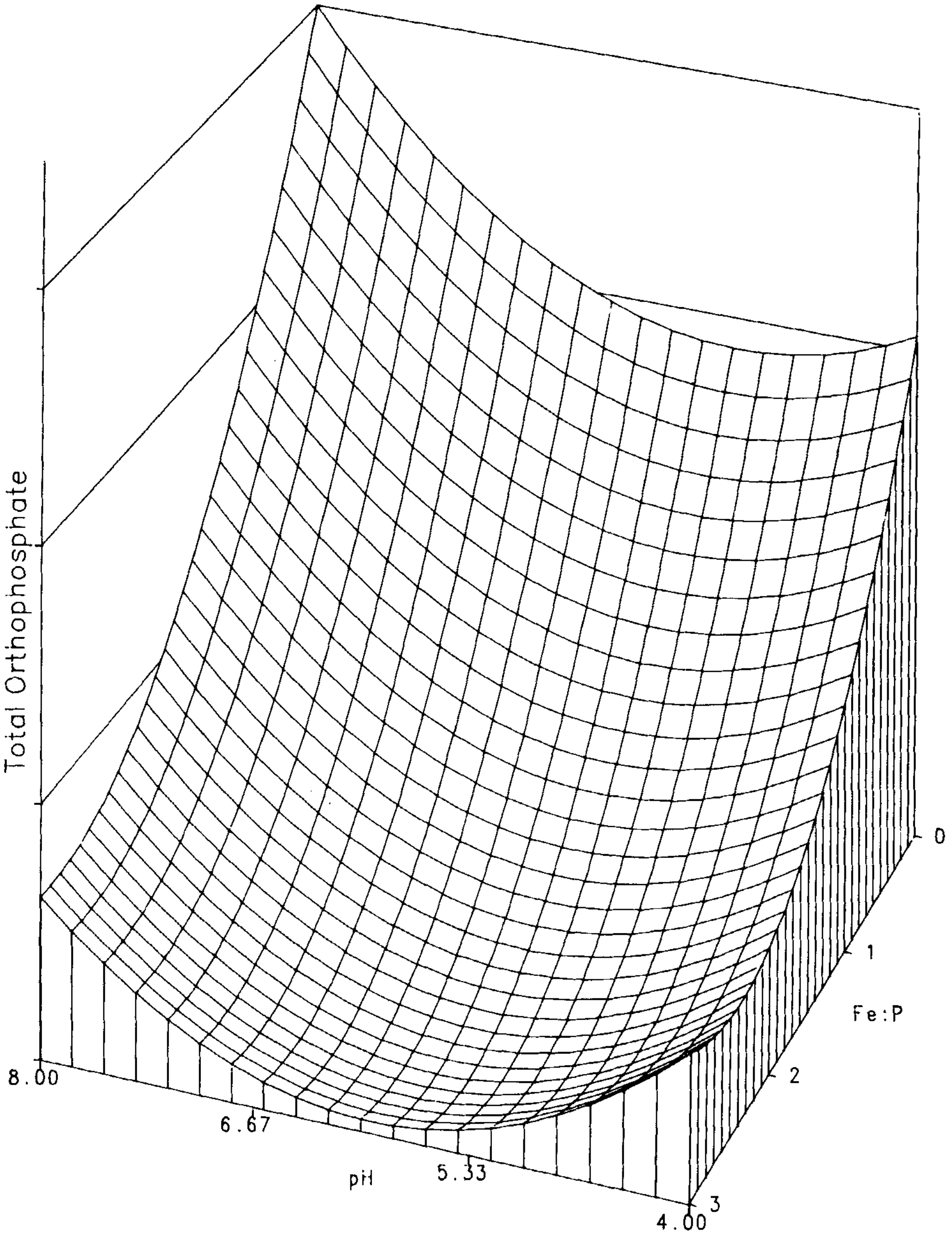

FIG. 14. Surface response plot for residual total orthophosphate vs Fe:P molar ratio and pH when pH was adjusted after iron addition.

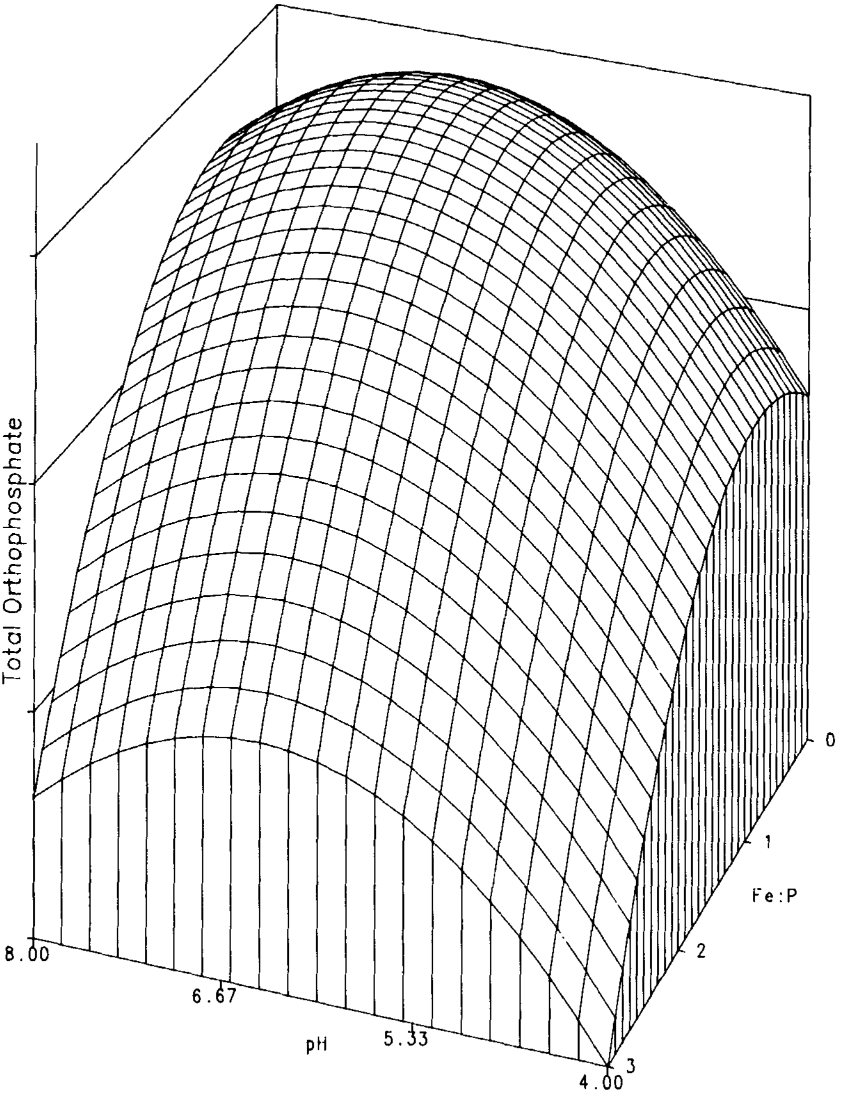

FIG. 15. Surface response plot for residual total orthophosphate vs Fe:P molar ratio and pH when pH was adjusted before and during iron addition.

seemed to have little effect on total orthophosphate removal. The residual total orthophosphate concentration in the synthetic wastewater was 0.21 mg/L-P for an Al:P molar ratio of 3.0, and a pH of 6.0 produced a residual total orthophosphate concentration of 0.19 mg/L-P in the synthetic wastewater when pH was adjusted before and during iron addition.

The efficiency of ferric chloride in removing total orthophosphate was very similar to that of alum when pH was adjusted after chemical addition. The response surfaces for the two treatments appeared very similar except that the response surface for aluminum phosphate had a more defined minimum solubility point than the one for iron phosphate. The larger impact of the ferric chloride solution on pH may have been partially responsible.

The multiple regression analysis for the synthetic wastewater produced mathematical relationships which can be used to predict residual orthophosphate concentrations. Each of the models (except the iron phosphate model for residual total orthophosphate when pH was adjusted before and during iron addition) contained a lack of fit error and, therefore, did not totally describe the system response. However, reducing the lack of fit error would not produce large changes in the general shape of the response surfaces. The models are not applicable to conditions in which the molar ratios and pH values are outside the ranges used to construct the models. However, within the range of the models, the predicted and actual values for residual orthophosphate concentration should show good agreement.

Further study is needed to evaluate various control systems for chemical addition and pH control. Since pH was a major factor in all of the situations studied, better pH control could result in more efficient and less expensive treatment. Many modern wastewater treatment facilities now use computerized control systems for monitoring the various plant processes. Such a system would be very helpful in monitoring and controlling pH and chemical addition to achieve the maximum phosphate removal.

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