Removal of phosphorus by metallic coagulation: An experimental aid to dose computations

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Abstract

For the removal of phosphorus from municipal wastewater, dissolved mono-hydrogen phosphates are complexed into suspended particulates through the addition of a metallic coagulant. Complex metal-phosphorus reaction, precipitation kinetics, and hydroxide side reaction render stoichiometric calculations invalid in the determination of the required coagulant dosage. This study describes an experimental investigation using the standard jar-tests to reveal the relationship between phosphorus removal and the required metal-phosphorus molar ratio, under varying pH and initial conditions. The coagulants selected for the study are ferric chloride and aluminum sulfate. Results define a non-linear relationship between percentage removal and turbidity for different molar ratios, with the theoretical values under-estimating the required dosage by a factor of 1.5 to 2.5. Sensitivity to pH levels, the mixing regime, field temperatures, and initial phosphorus levels are discussed in the findings.

1 Introduction

The presence of phosphorus in industrial and municipal effluents presents a major environmental problem to the natural aquatic systems. Increased level of phosphorus in lakes promotes eutrophication, resulting in decreased dissolved oxygen levels, odor problems, excessive algae growth, fish kills, and eventual complete fouling of lakes. A survey carried out by the Ontario Ministry of Environment[1] indicated that the majority of the province's 12,000 to 18,000

industrial plants are directly discharging their waste into municipal sewers. In order to meet the Canadian federal guideline of total phosphorus in the effluent to within 1 mg/L, the removal of phosphorus from our wastewater becomes very important. Furthermore, it has been shown (Gloyna & Eckenfelder[2]) that phosphorus removal is probably the most expensive step in a comprehensive waste treatment facility.
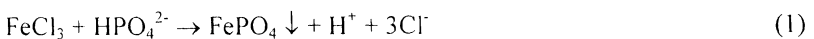
Phosphorus removal from wastewater may be achieved by biological methods, such as trickling filter and activated sludge systems. However, the efficiencies of these methods have been reported (Argentieri & Field[3]) to be quite low, only up to 20 and 40% respectively. A better method is by chemical precipitation, in which dissolved phosphates are complexed into particulates with the addition of a metallic coagulant. Some common coagulants found to be effective include ferric chloride, aluminum sulfate (alum), and lime. The suspended particles are then allowed to settle out from solution, thereby removing the total phosphorus from the effluent. Unfortunately, the exact dosage of coagulant to yield an acceptable removal may not be determined from stoichiometric calculations. This is due to the complex metal-phosphorus reaction and the hydroxide side reaction involved. To overcome this problem, it has been recommended that preliminary information on dosing, mixing, and settling should be obtained from the standard jar-test. In light of this, the following objectives have been defined for this study:
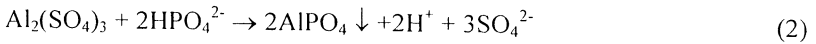
1. To carry out a series of standard jar-tests under controlled laboratory conditions to investigate the process of chemical coagulation on phosphorus removal. The chemicals chosen for the study are ferric chloride ($FeCl_3$) and alum ($Al_2(SO_4)_3$).
2. To study the effect of different field operating conditions, including initial phosphorus levels and pH, on the dosage requirement and removal efficiency.
3. To summarize through graphical presentations the effect of different dosage of coagulants on phosphorus removal and turbidity.

It is envisaged that the results of the study will provide important insight and guidelines to the selection and dosing of chemical coagulants in phosphorus removal. With this information, the amount of time spent in calculation and dosage determination during the operation of the treatment process under different conditions will be greatly reduced. In addition, this will eliminate the application of excessive chemicals during treatment, as was practiced in the past, thereby reducing the associated costs and possible detrimental effects excess chemicals may cause to the environment.

2 Literature Review

Phosphorus is typically found as mono-hydrogen phosphate (HPO_4^{2-}) in wastewater. The removal of phosphorus with the addition of ferric chloride and alum may be represented by the following precipitation reactions,

$$FeCl_3 + HPO_4^{2-} \rightarrow FePO_4 \downarrow + H^+ + 3Cl^- \qquad (1)$$

$$Al_2(SO_4)_3 + 2HPO_4^{2-} \rightarrow 2AlPO_4 \downarrow + 2H^+ + 3SO_4^{2-} \tag{2}$$

Although the theoretical amount of chemicals may be calculated from stoichiometric computation, the actual amount depends on many other factors and is usually much higher. These factors may include any side reactions, solubility product limitations, pH, temperature, and daily fluctuations of influent quality. Davis & Cornwell[4] suggested a scale-up factor of 1.5 - 3 for $FeCl_3$, and 1.25 – 2.5 for alum. If the metallic ions of iron and aluminum are represented generally as Me^{3+}, then the hyroxide side reaction may be represented by the simplified equation,

$$Me^{3+} + 3HCO_3^- \rightarrow Me(OH)_3 \downarrow + 3CO_2 \tag{3}$$
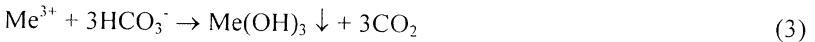
This creates a competition between the hydroxide and phosphate ions for the metallic coagulant, and thus the efficiency of phosphate removal is governed by the relative concentrations of these two ions in solution and is consequently pH-dependent. A decrease in pH favors precipitation of the metal phosphate, but only up to a certain extent. This is because the hydroxides are precipitated as voluminous particles, and as they settle through the liquid they have the tendency to pick up small particles which would otherwise stay in suspension. Therefore, the overall removal of phosphate would also be enhanced if some hydroxides were present.

Many recent references (e.g. Henze[5] and Droste[6]) have described the relationship between the removal efficiency and different parameters; however, relatively little information is available to quantify these effects. In light of the complexity of the process, the recommendation by most (e.g. Droste[6] and Viraraghavan & Cleven[7]) is that the standard jar-test described by Hudson[8] is the most practicable method to evaluate the effects of different operating parameters on the removal efficiency.

3 Experimental Method

Synthetic samples with different phosphorus concentrations and pH are prepared for the experiment. The phosphorus levels are allowed to vary from 2 to 6 mg/L, covering the typical range in municipal wastewater. This is achieved with the addition of anhydrous K_2HPO_4 (APHA[9]) according to the following reaction,

$$K_2HPO_4 \rightarrow 2K^+ + HPO_4^{2-} \tag{4}$$
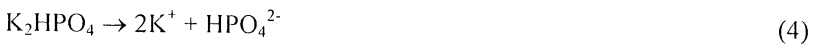
As an example, the addition of 219.5 mg of anhydrous K_2HPO_4 to 1 L of deionized distilled water will yield a solution of 50 mg/L of PO_4^{3-} as P. The pH of the sample is allowed to range from 5 to 8, and is adjusted with the addition of HCl or NaOH. A summary of the experimental parameters for the study is given in Table 1.

Table 1. Experimental parameters for the jar-tests.

Parameter	Values/Range
Initial phosphorus	2, 4, 6 mg/L
Sample pH	5, 6, 7, 8
Coagulant molar ratio	0, 1, 2, 3, 4, 5
Water temperature	15 - 25 °C

For each of the prepared samples, a series of standard jar-tests are carried out with different dosage of ferric chloride (as $FeCl_3 \bullet 6H_2O$) and alum (as $Al_2(SO_4)_3 \bullet 14H_2O$) respectively. The quantity of chemical addition is recorded in dimensionless molar ratios, which represents the number of moles of coagulant per unit mole of initial phosphorus present. The degree and pattern of mixing, selected on the recommendation by Viraraghavan & Cleven[7], are kept consistent throughout the tests. This involves 5 minutes of rapid mixing at 100 rpm to disperse the chemicals, to be followed by 10 minutes of slow agitation at 25 rpm to enhance the chemical precipitation. With the completion of the mixing, the precipitates in the samples are allowed to settle for an hour. All the tests were performed under room temperature, which typically varies from 16 to 20°C, with one exception at 25°C one day when the air conditioner in the laboratory broke down.

The supernatant of the sample is then filtered through 47mm diameter glass-fiber filters, and the filtrate is tested for two parameters. The first is dissolved phosphorus, with the use of a Ultraviolet Spectrophotometer (Unicam model SP1800) and the stannous chloride method according to standard methods (APHA[9]); and the second is turbidity, with a Nephlelometer (Monitek model TA1). Table 2 provides a sample of the data recording sheet of the experiment, which shows the type and dose of coagulant applied, and the different initial phosphorus and pH levels of the samples. Since it may be assumed that sedimentation tanks in treatment plants will remove the precipitates of the reaction, only the dissolved fraction of total phosphorus is measured in the experiment. An illustration of the experimental setup and procedure is provided in Fig. 1.

4 Results

The results of $FeCl_3$ for samples with initial phosphorus of 2, 4, and 6 mg/L respectively are given in Fig. 2. As observed from the graphs, the removal of phosphorus is substantially achieved after a certain dosage regardless of initial phosphorus levels, and any excess chemicals added beyond that point does not improve the removal. The effect of pH is also consistently reflected in all three graphs – with improved performance for lower pH range, and this effect is more

Table 2. Sample data recording sheet.

Initial Phosphorus	2 mg/L
Initial pH	8

Metallic Precipitant		Period	Start Time	Stop Time
Mixing	Fast, 100rpm	5 min.	1:40 p.m.	1:45 p.m.
	Slow, 25rpm	10 min.	1:45 p.m.	1:55 p.m.
	Settlement	60 min.	1:55 p.m.	2:55 p.m.

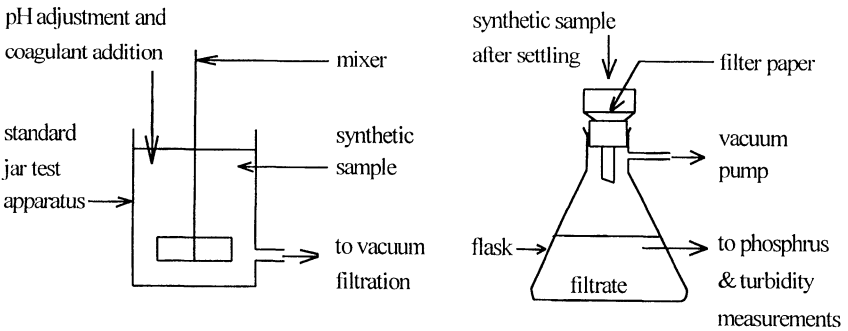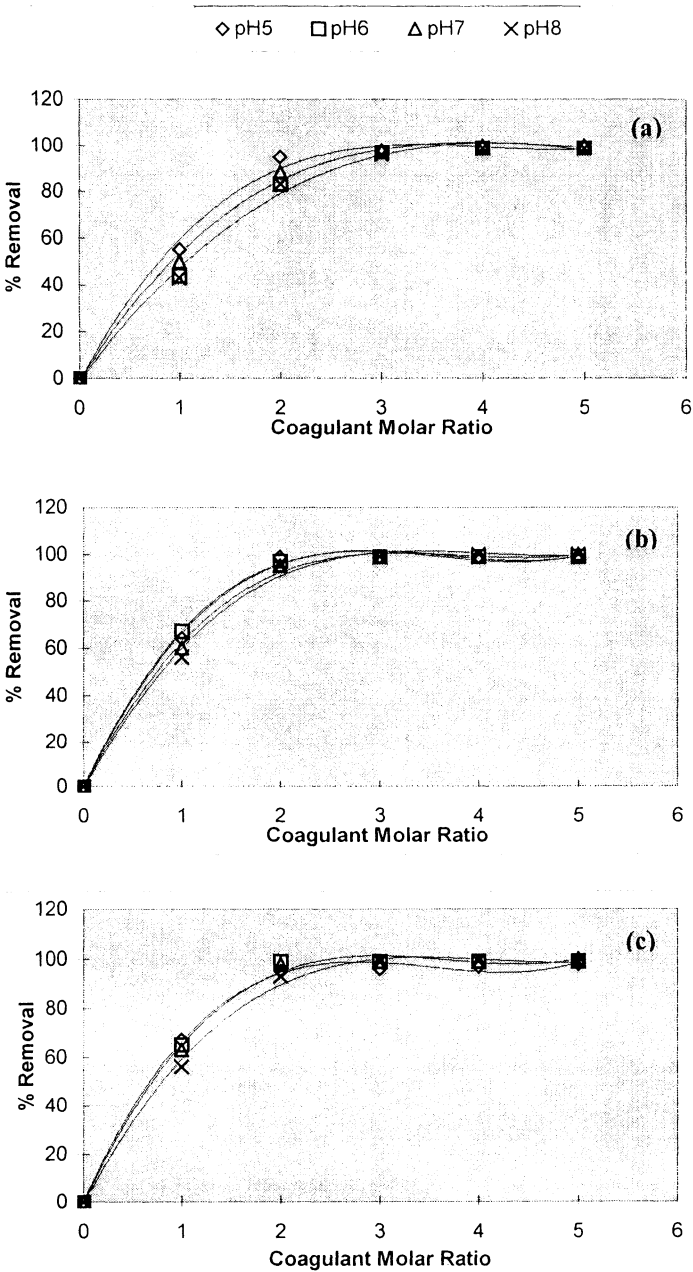| Jar	MR	Final pH	Turbidity	Absorption	Final - P	% Removal
1	0	7.2	0	1.43	2.00	0.0
2	1	7.0	1	0.93	1.17	41.5
3	2	6.7	2	0.34	0.35	82.5
4	3	6.5	2	0.09	0.09	95.5
5	4	6.2	4	0.02	0.02	99.0
6	5	6.1	9	0.02	0.02	99.0

Figure 1: Experimental setup.

Figure 2: Removal of phosphorus with ferric chloride for initial
phosphorus levels of (a) 2 mg/L; (b) 4 mg/L and (c) 6 mg/L.

pronounced in samples with low phosphorus levels. This is consistent with the "hydroxide competition" theory suggested in Section 2. In addition, the higher is the original phosphorus, the more $FeCl_3$ is required, but the molar ratio remains more or less constant throughout. Finally, even for very low phosphorus levels, the addition of $FeCl_3$ still proves to be beneficial, and it is entirely possible to maintain effluent phosphorus to within the 1 mg/L guideline with chemical precipitation.

Some of the alum results are tabulated in Table 3, from which similar observations are drawn. The only exception is the effect of pH: for some reasons the removal efficiency trails off for all samples with pH of 5 at high molar ratios. It seems that the presence of some alkalinity in the sample, at pH>6, is necessary for phosphorus precipitation with alum. This may be explained by the fact that the alum-phosphate flocs have very poor settling properties, and could only be removed if larger alum-hydroxide flocs are present. This further substantiates the point that the reaction is so complex and governed by so many factors that the jar test becomes an indispensable tool for reliable data.

The performance of the two coagulants is compared in Fig. 3, which was prepared for the sample with initial pH of 7. From this figure, it is apparent that alum is more effective in phosphorus removal. For example, a molar ratio of 1.4 for $FeCl_3$ and 0.6 for alum is required for 80% phosphorus removal from samples with 4 mg/L. This is consistent with the reactions in Eqns. (1) and (2). Furthermore, when the theoretical quantities are calculated from these chemical reactions, and superimposed onto Fig. 3, it may be seen that the actual chemical requirement is 2.0 times for $FeCl_3$ and 1.5 times for alum. These values are well within the range suggested by Davis & Cornwell[4], but provide much better guidelines than before.

The turbidity values for all samples are acceptable with the 1-hour settling time. In most cases, however, a minimum turbidity is achieved at particular combination of initial pH, concentrations and dosage. Therefore, the results of the jar tests should be consulted for estimating the final clarity of the treated effluent.

Table 3. Summary of removal rates using alum, for sample pH = 7.

Initial P (mg/L)	Alum	Molar	Ratio			
	0	1	2	3	4	5
2	0	50	88	98	100	100
4	0	60	95	99	100	100
6	0	63	97	99	100	100

(Note : numbers in table represent the percent removal of phosphorus)
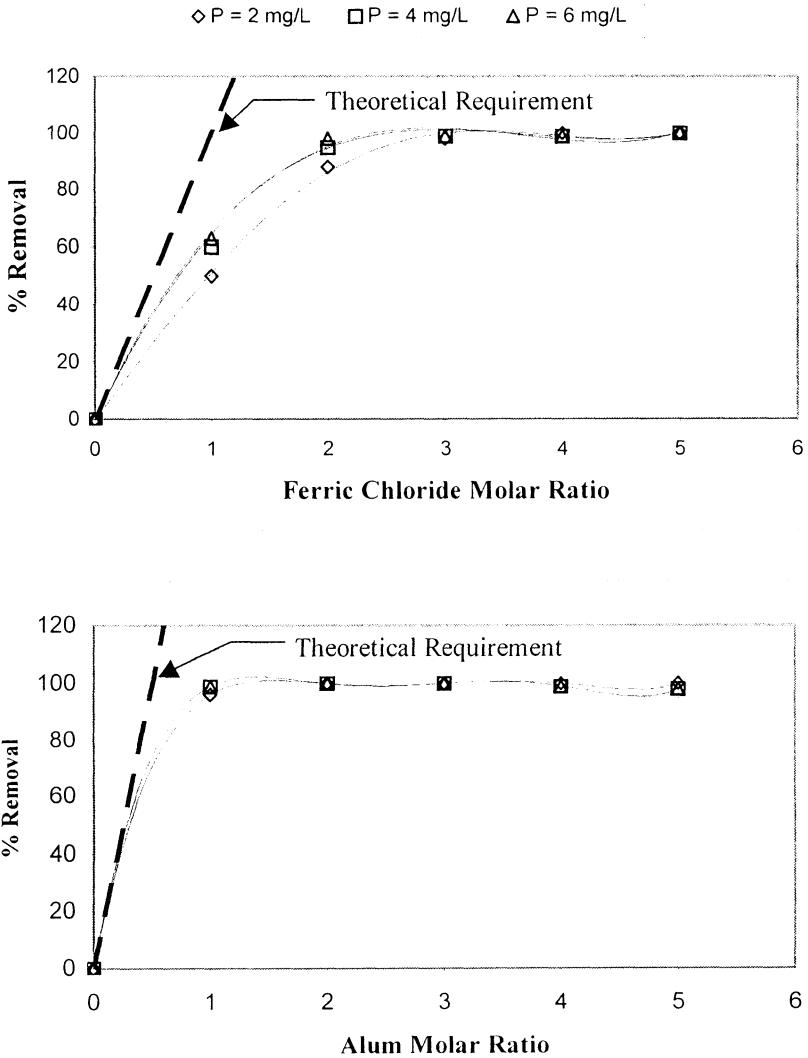
Figure 3: Comparison of the performance between the two coagulants at sample pH = 7 for ferric chloride (top) and alum (bottom).

5 Discussion and Conclusions

The following conclusions may be drawn from the study:

1. It was found that both $FeCl_3$ and alum are acceptable for phosphorus removal at typical wastewater conditions, but alum appears to be more effective.
2. The theoretical dosages computed from stoichiometric relations are found to be grossly understated, and much more accurate solution on dosage requirements may be obtained from the jar-tests.
3. The minimum dosage required for acceptable phosphorus removal may be obtained from the graphs; and provided proper mixing, flocculation and settling are maintained, it will not be necessary or even beneficial to overdose the operation.
4. The mixing regime employed in the jar-test is found to be sufficient, and this may best be reproduced in treatment plants with the use of a rapid mixing basin and flocculation tank ahead of the final sedimentation tanks.
5. $FeCl_3$ functions better in a lower pH environment, whereas alum does not even work with pH<6, after this point the effect of pH is less noticeable.
6. The optimal point for turbidity removal is often different from that of phosphorus removal. Therefore if clarity of effluent is a concern after achieving a certain phosphorus removal, it may be necessary to allow for extra settling time.

Although every effort is made to produce testing conditions similar to real life treatment plants, many practical limitations to the study still exist. For example, the temperature was kept at room temperature for the experiment, but they would vary for the plant. Since the solubility product and side reactions are all temperature-sensitive, the results of the experiment are not directly transferable. Also, artificial samples were used in the experiment, and these are very different in composition than municipal wastewater. Since the test samples have no organic contents, the effects of biological process on phosphorus removal cannot be studied. This and other reactions omitted from the study are difficult to be quantified, but the overall effects may be significant. Therefore, it is strongly suggested that a pilot study be carried out at the plant to verify these results before actual application. In addition, it should be noted that proper sedimentation and detention times are important on the removal efficiency, and a well-designed sedimentation tank must be incorporated into the operation. Otherwise, even though the dissolved phosphorus is removed from solution, the precipitated form and hence the total phosphorus still remain in the effluent. Finally, the study only concentrates on typical phosphorus ranges in municipal wastewater, and the experimental results should not be expanded to cover other types of discharges with phosphorus outside this range.

6 Acknowledgements

7 References

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