

Optimum phosphorus and organic matter removal by combining different types of coagulants

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Abstract

The effects of combining simple metal salts and pre-polymerised Al-salts were examined in lab-scale. The optimal feeding of simple trivalent metal ions (Al^{3+} , Fe^{3+}) as coagulants for suspended organic matter removal can provide so effective ortho-phosphate precipitation that may deteriorate the AS processes. Non-polymerised salts are utilised primarily in precipitating ortho-phosphate, especially at small doses. Due to the different dominance of P removal processes, pre-polymerised metal salts are less effective in $\text{PO}_4\text{-P}$ precipitation; however they provide significant organic matter removal and small pH decrease. It was aimed to find out how it is possible to reach the maximum removal of organic matters by the combined feeding of simple and pre-polymerised metal salts, while the remaining $\text{PO}_4\text{-P}$ concentration is 1 mg/L at the same coagulant dose. It could be concluded that the above mentioned objectives of the chemical pre-treatment - set up considering the subsequent biological treatment steps - can be reached by combining the different types of coagulants.

Keywords: phosphate precipitation; pre-polymerised metal salts; organic matter; optimisation; trivalent metal salts

INTRODUCTION

Chemical wastewater treatment by simple aluminium or ferric salts involves parallel processes taking place within a very short period of time (Fettig et al., 1990). The key of chemical P-precipitation is to transform soluble phosphate ion into weakly water soluble precipitate (containing phosphate, metal and hydroxide) using the ability of ferric/aluminium ions to establish chemical bond with phosphate ions. Simultaneously, the applied metal ions take part in step-wise hydrolysis reactions and produce metal-hydroxides that are able to coagulate/flocculate the suspended solids of the wastewater. Positively charged intermediate hydrolysis products can also form chemical bond with phosphate ions. Moreover, adsorption of different compounds (ranging from macromolecules to simple ions such as PO_4^{3-}) on metal-hydroxides can take place.

Considering that large portion of the organic pollutants in the sewage is connected to SS, up to 50-85% of the organic matter (measured as COD or BOD_5) can be removed in the coagulation-flocculation and the subsequent sedimentation processes (Szabó and Licskó, 2005). In chemical pre-treatment as a consequence of organic matter removal in the primary settling tank, the downstream biological stage receives a lower organic load, present mostly in dissolved form. The biological reactor can operate with higher efficiency, and nitrification can occur where ammonium conversion would not be possible without chemical pre-treatment due to the high organic load (Henze and Harremoës, 1992). However, as nitrifying microorganisms are sensitive to pH change, one limitation of coagulant feeding prior to the biological processes is its pH decreasing effect. Furthermore, efficient removal of organic matter often requires higher coagulant dose than the one required for precipitating $\text{PO}_4\text{-P}$. Applying the higher doses, very small (<0.02 mg/L) $\text{PO}_4\text{-P}$ concentrations can be reached that may also deteriorate the performance of bacteria.

While pre-polymerised metal salts show similar organic removal rates to simple trivalent metal salts, they are less effective in precipitating phosphate ions. At the same time, they cause smaller pH change. The above considerations suggest that by the appropriate combination of simple and pre-polymerised coagulants optimal organic matter and phosphate removal can be reached, while the pH of the treated water is still acceptable from the point of view of the subsequent biological treatment. In the experiments on the combination of coagulants it was aimed to find out how it is possible to reach the maximum removal of organic matters in the chemical treatment process, while the remaining PO₄-P concentration is 1 mg/L at the same coagulant dose.

METHODS

Coagulation-flocculation Jar tests were carried out with phosphate solutions and raw wastewater. All experiments were performed in 1-litre glass cylinders with a KEMIRA flocculator device (KEMIRA, 1990). Coagulants were mixed with wastewater for 1 minute with a propeller speed of 350 rpm. Coagulation was carried out in 10 minutes with a propeller speed of 20 rpm. Samples were allowed to settle for 20 minutes. Different iron(III) and aluminium salts [Prefloc (iron(III)-sulphate), Bopac (poly-aluminium-chloride), FeCl₃·6H₂O, ferric nitrate and Al₂(SO₄)₃·18H₂O] were used as coagulants. Alkalinity, pH; chemical oxygen demand (COD_{Cr}); ortho-phosphate (PO₄-P); biochemical oxygen demand (BOD₅) were analysed before and after the coagulation. PO₄-P values were measured in the filtrate of 0.45 µm pore size membrane filter. Model solutions were prepared from distilled water and tap water by the addition of KH₂PO₄. pH in phosphate solutions was adjusted by HCl or NaOH prior to coagulant addition. To provide the adequate alkalinity of the solution NaHCO₃ was added. Experiments with raw wastewater were carried out at original pH and alkalinity. Raw wastewater was taken from different municipal wastewater treatment plants.

In some experiments instead of feeding metal salts to phosphate solutions, first the metal salt was added to tap water. After 1 minute of intensive stirring, (350 rpm) phosphate solution was added and fast stirring continued to 1 more minute. After that slow mixing was applied. Samples were taken in different times. Mixing conditions (length and propeller speed) after metal addition were varied.

RESULTS AND DISCUSSION

Non-polymerised metal salts effectively precipitate ortho-phosphate at small doses. When applying P-precipitation prior to the biological treatment it is aimed to leave a certain amount of soluble phosphate necessary for bacterial growth. It is assumed that decreasing PO₄-P concentration to 1 mg/L shall not deteriorate bacterial processes (Andersson et al., 1992). According to raw wastewater experiments 1 mg/L residual PO₄-P can often be reached by the addition of aluminium-sulphate (or other non-polymerised metal salts) in a dose smaller than 0.2 mmol Me³⁺/L. In the same wastewater the maximum removal (i.e. minimum residual concentration) of organic matter can be reached with significantly higher doses (Figure 1.).

With higher doses the resulting pH can be lower than the optimum range for bacteria, especially in wastewaters with low buffering capacity. Pre-polymerised metal salts are often used instead of simple Fe or Al-salts. Because part of the hydrolysis reactions occurs already during the production of pre-polymerised metal salts, they have a much smaller effect on pH. As the different metal-hydroxides are efficient in the coagulation-flocculation process, the organic removal rates are similar in the case of simple and pre-polymerised metal salt feeding. However, pre-polymerised salts (e.g. Bopac) do not precipitate phosphate ions as effectively as trivalent metal salts (Figure 2.).

After the addition of simple trivalent metal salts, metal ions form mixed metal-hydroxide-phosphate precipitates and different metal-hydroxides. When applying pre-polymerised metal salts, phosphate ions get in contact with the already formed metal-hydroxides and can be build in the precipitated hydroxide to a smaller extent.

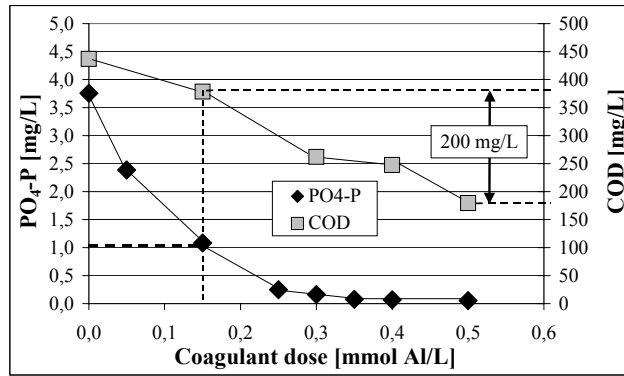


Figure 1. Residual PO₄-P and COD concentration (raw ww)

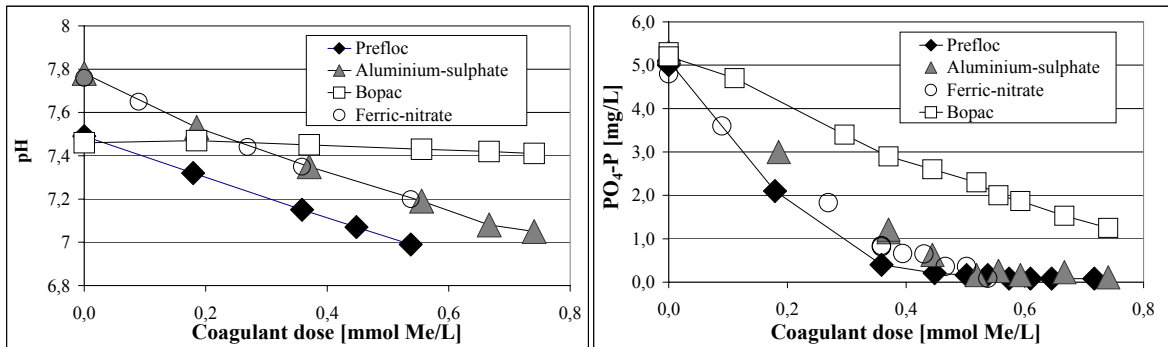


Figure 2. Effect of different metal salts on pH and on residual PO₄-P concentration (raw ww)

In the experiments combined addition of simple and pre-polymerised coagulants were tested in order to optimise phosphate and organic matter removal. The aim of feeding simple metal salts was to reach 1.0-2.5 mg/L PO₄-P concentration after chemical pre-treatment and the subsequent solid-liquid phase separation. These simple salts were able to remove a significant portion of the organic matter as well. By feeding pre-polymerised Al-salt at the same time (in combination with simple salts), significant further decrease of the organic matter concentration was performed, while the desired 1.0 mg/L residual PO₄-P concentration was not exceeded (Figure 3-4.). It was proved that depending on the raw wastewater quality it is possible to find the appropriate combination of these salts to fulfil the requirement and add relatively small amount of coagulant.

As an example, PO₄-P can be reached by the addition of 0.2 mmol Al/L Aluminium-sulphate, while 0.5 mmol Al/L is needed for the same residual ortho-phosphate concentration when feeding poly-aluminium-chloride (Figure 3.; Table 1.). Residual COD and BOD₅ are 230 and 205 mg/L respectively in the first case; 200 and 165 mg/L in the second case. By the addition of higher coagulant doses, organic matter content can further be decreased. When testing the optimal combination, 0.05; 0.10 and 0.15 mmol Al/L was applied as Aluminium-sulphate which was completed by Bopac feeding (0.05-0.6 mmol Al/L). The desired 1 mg/L residual ortho-P can be reached by different combinations: (a) 0.05 mmol/L Alum + 0.35 mmol/L Bopac; (b) 0.10 mmol/L Alum + 0.20 mmol/L Bopac; (c) 0.15 mmol/L Alum + 0.05 mmol/L Bopac. At the same time residual COD was (a) 195 mg/L; (b) 195 mg/L; (c) 210 mg/L; and BOD₅ was about 175 mg/L in all

the three cases. In combination (a) and (b) small amount of total coagulant (expressed as mmol Me/L) was used, therefore both fulfil the set requirements.

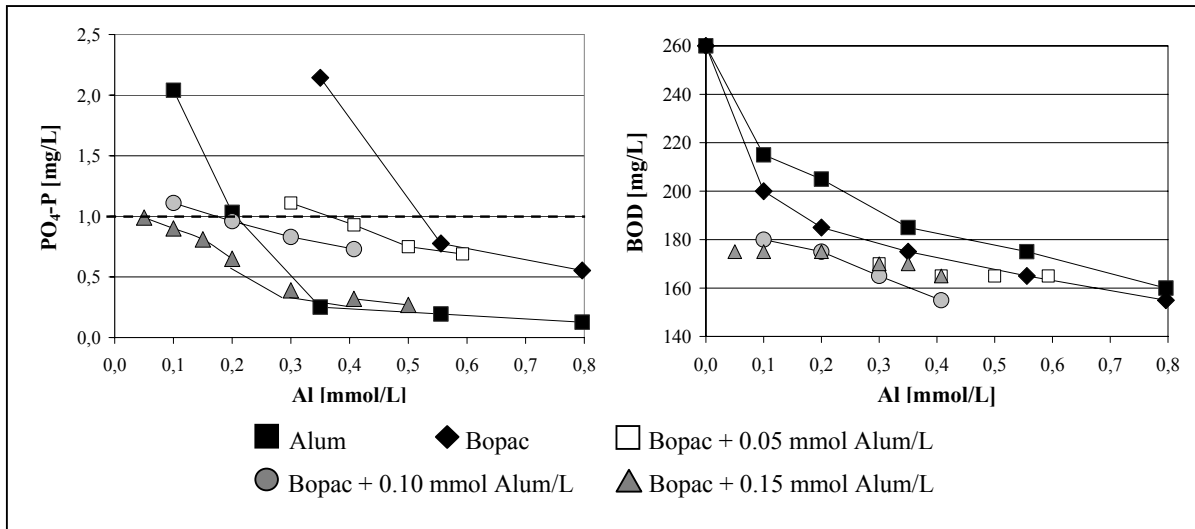


Figure 3. PO₄-P and BOD removal by combined Aluminium-sulphate and Bopac feeding (raw ww)

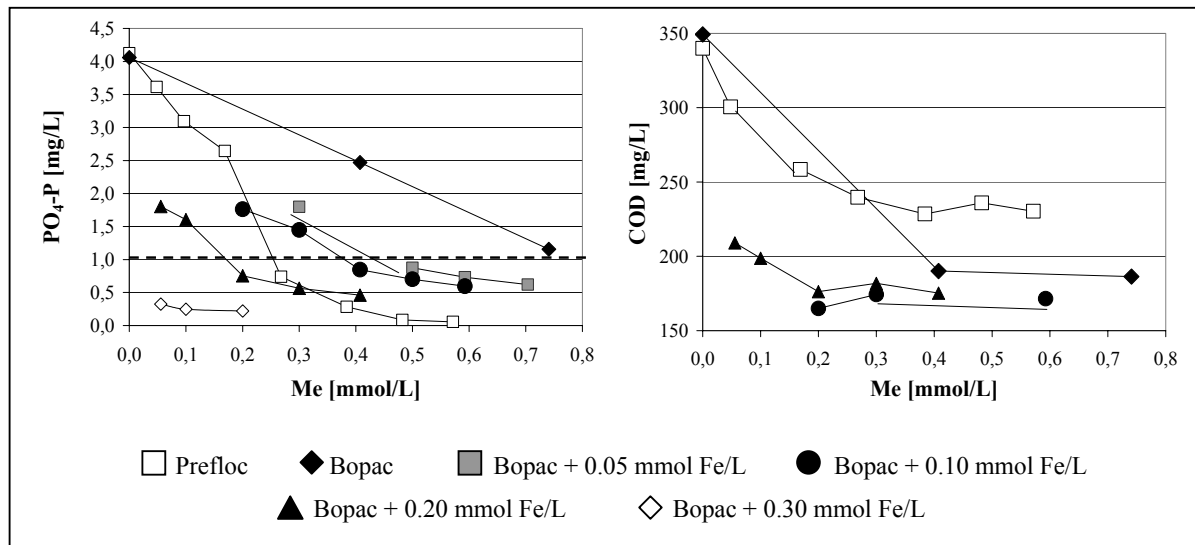


Figure 4. PO₄-P and COD removal by combined Prefloc and Bopac feeding (raw ww)

Table 1. Treated wastewater parameters at combined coagulant addition

	Prefloc or Alum mmol Me/L	Bopac mmol Me/L	ΣMe mmol Me/L	pH	PO ₄ -P mg/L	TP mg/L	COD mg/L	BOD mg/L
Experiment 1.	0.00	0.50	0.50	7.6	1.15	1.3	200	165
Aluminium- sulphate + Bopac	0.20	0.00	0.20	7.4	1.00	2.4	230	205
	0.15	0.05	0.20	7.4	1.00	1.7	195	175
	0.10	0.15	0.25	7.5	1.00	1.4	195	175
	0.05	0.35	0.40	7.6	1.00	1.4	210	175
	Experiment 2.	0.00	0.75	0.75	7.8	1.15	1.2	190
Prefloc + Bopac	0.25	0.00	0.25	7.5	1.10	2.0	240	185
	0.20	0.15	0.35	7.6	1.15	1.5	190	150
	0.10	0.35	0.45	7.7	1.15	1.4	175	145
	0.05	0.45	0.50	7.8	1.10	1.5	-	145

It is assumed that ortho-phosphate precipitation can have a priority compared to the hydroxide formation, coagulation, and other reactions in the case of simple trivalent ion feeding. On the basis of our lab experiments it was concluded that up to 60-90% of the applied coagulant is used in the precipitation reaction at doses smaller than 0.2 mmol Me³⁺/L. This ratio is independent of the water source (tap water or wastewater); however original pH (outside of the 6-7.5 pH range) and alkalinity; PO₄-P, TSS and COD concentration of raw wastewater can play a significant role. When applying pre-polymerised metal salts, the major portion of the coagulant takes part in the coagulation-flocculation reactions and only 8-25% of the added coagulant is consumed on phosphate removal (Figure 5.). This suggests that in the case of simple metal salts the development of mixed metal-phosphate-hydroxide prevails, while formation of chemical bond with the intermediate hydrolysis products and adsorption on metal-hydroxides can have a more pronounced role in phosphate removal in the case of pre-polymerised metal salts.

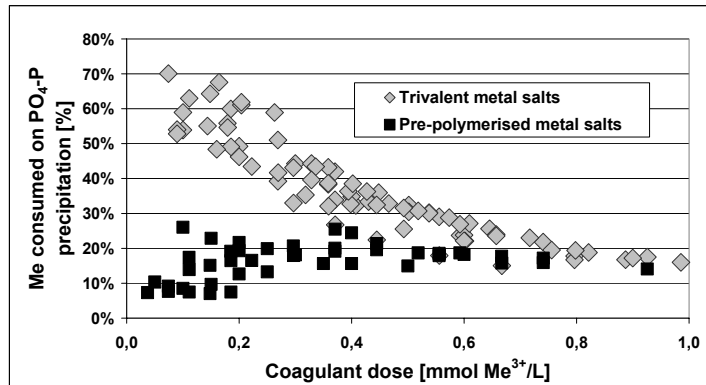


Figure 5. Portion of coagulant consumed on P precipitation (raw ww)

Phosphate removal is much more efficient when metal-hydroxides are formed in the presence of phosphate (Figure 6.). The very effective removal is due to direct metal-phosphate precipitation and co-precipitation of metal-hydroxide-phosphates. Results show that in the case of pre-formed metal hydroxides there are two different processes in phosphate removal: one is very fast (takes place within 30 seconds), and another has a slow reaction rate, continuing even after 1 day. The fast process (which is responsible for the majority of P-removal) is thought to be chemical binding of phosphate ions to the positively charged metal-hydroxides (pseudo-precipitation). The slow process is supposed to be adsorption of ortho-phosphate on metal-hydroxides.

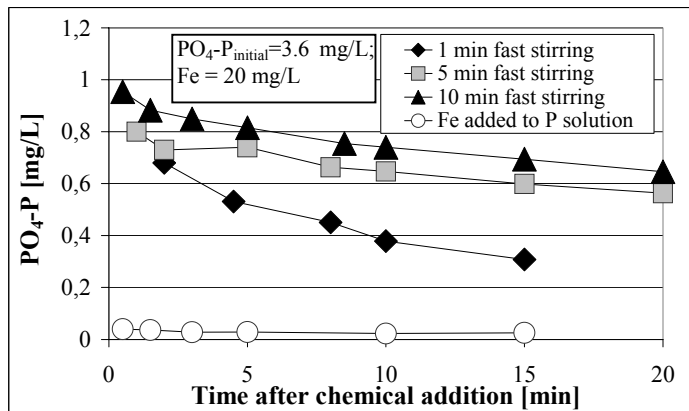


Figure 6. PO₄-P removal by Fe³⁺ and pre-formed Fe-hydroxides

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CONCLUSION

It is well-known that for the proper operation of bacteria used in the activated sludge treatment process certain quantity of ortho-phosphate ion is needed. Different information is available on the minimal required $\text{PO}_4\text{-P}$ concentration, therefore it was aimed to have 1 mg/L residual $\text{PO}_4\text{-P}$ after chemical pre-treatment, assuming that this amount of dissolved P is definitely sufficient for bacterial growth. However, in several cases the coagulant dose needed for the maximal removal of organic matter provides ortho-phosphate precipitation exceeding its desired level. Lab experiments aimed to reach maximum organic removal while assuring the necessary residual $\text{PO}_4\text{-P}$ concentration. The common trivalent aluminium and ferric salts can efficiently be applied in precipitating ortho-phosphate as well as in coagulating inorganic and organic suspended solids. Pre-polymerised aluminium salts are also effective concerning coagulation processes, but they are considerably less efficient in phosphate precipitation. In trivalent metal salt addition direct precipitation and co-precipitation are the dominant P removal processes, while pseudo-precipitation (chemical binding of PO_4^{3-} to the positively charged metal hydroxides) and adsorption prevail in the case of pre-polymerised metal salts.

During our laboratory experiments we developed a combined coagulant and precipitant application for maximum organic removal while the necessary ortho-phosphate level could be maintained. By this application the high efficiency of suspended matter removal, furthermore the removal of total phosphorus and required residual level of ortho-phosphate can be harmonised. Feeding of trivalent metal salts approaches the required precipitation of $\text{PO}_4\text{-P}$ (rough control) and starts the coagulation of suspended matters while the pre-polymerised metal salts complete the precipitation (fine control) and significantly enhances coagulation of organic matter. The developed combined feeding of simple and pre-polymerised metal salts provides a possibility to minimize the pH decrease occurring due to hydrolysis reactions if necessary.

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