

Removal of Phosphates from Industrial Waste Water by Chemical Precipitation.

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Abstract – Phosphorus pollution is a major concern for soil and water management. Phosphorus in water is found in the form of phosphate. The objective of this study is to remove phosphates from industrial waste water by chemical precipitation to convert the soluble phosphates into other compounds can be utilized in fertilizer industry. Metallic salts were used in this study such as calcium oxide, aluminum sulfate, iron sulfates and a mixture of iron sulfates and calcium oxide. The removal of phosphates compounds was investigated in terms of various parameters namely: pH, and dosage concentration of each precipitating agent. The study revealed that the optimum conditions for the removal of phosphates compounds were achieved with percentage removal of 90% with CaO concentration of 40 mg/l at pH value of (8.5-10).with aluminum sulphate the percentage removal was (85%) at pH value of 4, but with iron sulphates the best removal was 80% at pH range of (8.5-10).The mixture of the two salts mentioned above has no effect on increasing the percentage removal of phosphates .All experiments were done at room temperature.

Keywords-Phosphorus removal; Chemical precipitation; Calcium oxide; Aluminum sulphate.

I. INTRODUCTION

Surface waters contain certain level of phosphorus in various compounds, which is an important constituent of living organisms. In natural conditions the phosphate concentration in water is balanced i.e. accessible mass of this constituent is close to the requirements of the ecological system. When the input of phosphorus to waters is higher than it can be assimilated by a population of living organisms the problem of excess phosphorus content occurs[1].The excess content of phosphorus in receiving waters leads to extensive algae growth (eutrophication). The phenomenon of eutrophication usually decreases the water quality and as a result it may increase significantly the cost of water treatment at treatment plants for surface water. The load of phosphates discharged to receiving waters comes from various groups of sources of which the main sources are agricultural use of fertilizers, domestic and industrial wastewater, and atmospheric

deposition [2, 3]. Phosphorus removal techniques are chemical treatments like adsorption [4-6], chemical precipitation [7], ion exchange, electro dialysis hybrid systems containing fly-ash adsorption , membrane filtration[8] and electrocoagulation [9-11].Chemical precipitation for phosphates removal is a reliable, time-tested, wastewater treatment method that has not drastically changed over the years. To achieve removal, various coagulant aids are added to wastewater where they react with soluble phosphates to form precipitates. The precipitates are removed using a solids separation process, most commonly settling (clarification). Chemical precipitation is typically accomplished using either lime or a metal salt such as aluminum sulfate (alum) or ferric chloride. The addition of polymers and other substances can further enhance floc formation and solids settling. Operators can use existing secondary clarifiers or retrofit primary clarifiers for their specific purposes. Phosphorus removal by chemical precipitation is at present the best known process of those mentioned above and is widely used despite its relatively high costs. Transformation of phosphorus ions into the solid state takes place in three stages. These stages are: core formation of a solid matter, storage of a precipitate, start of crystal growing crystal maturation [12]. Orthophosphates are the most common group of phosphorus compounds and theoretical papers mostly focus on these compounds. Trivalent metal salts are used for removal of phosphorus from municipal wastewater. The most common are: Aluminum sulfate, Ferric chloride, Ferrous (bivalent) and ferric sulfates. Lime which previously was one of the main chemicals used for phosphorus removal now plays only a minor role. This change is due to, a substantial increase in the sludge mass, and problems with maintenance and operation of lime handling and dosage facilities. Precipitants mentioned above: Fe (III), Fe (II), Al (III) and Ca salts form in the presence of aqueous solutions of orthophosphates precipitates. The following equations represent the reactions of precipitation [13], Lime which previously was one of the main chemicals used for phosphorus removal, now plays only a minor role. This change is due to, a

substantial increase in the sludge mass, and problems with maintenance and operation of lime handling and dosage facilities. Precipitants mentioned above: Fe (III), Fe (II), Al (III) and Ca salts form in the presence of aqueous solutions of orthophosphates precipitates. The following equations represent the reactions of precipitation:

Aluminum ions combine with phosphate ions as shown by reaction:



So the weight ratio of the reaction is 0.87: 1 of Al : P.

The reaction of ferric ions can be illustrated by:



The stoichiometric weight ratio of this reaction is 1.8:1.

The phosphate precipitation by the metal salts leads to the formation of large quantities of sludge. They have a potential fertilizing value, although the investigations concerning the biological accessibility of phosphorus bonded in them for plants still remain unconvincing [14]. In chemical dephosphatation of waste water, the application of calcium compounds plays a very important role. Depending on the wastewater composition, pH, the molar ratio of $\text{Ca}^{2+}:\text{PO}_4^{-3}$, concentration of phosphate solution and reaction temperature [15]. In this study the examination of different chemical precipitating agents which are used on precipitating phosphorous at different pH values.

II. MATERIAL AND METHODS

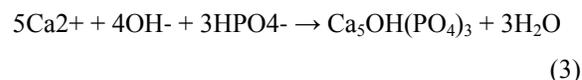
A stock solution of phosphate was prepared by using an analytical grade of sodium tri phosphate as a source of phosphate in the samples and dissolving it in distilled water. Experimental solutions of the desired concentrations were obtained by successive dilution with distillate water. Different precipitating agents of the desired concentrations were prepared (calcium oxide, ferrous sulfates, aluminum sulfate) by successive dilution with distillate water. The analytical determination of phosphate was carried out with the standard spectrophotometric procedure [16] using visible U.V spectrophotometer [UNICO, Model U.V.2100]. The pH of the solutions was adjusted by means of NaOH / HCl solutions (A digitally calibrated pH meter (HANNA, Model pH211) used to measure the pH of samples before and after treatment. At the end of each experiment, the treated solutions were filtered by using filter paper no.5 before the analysis.

III. RESULTS AND DISCUSSION

A. Effect of calcium oxide as precipitating agent:

Lime (CaO , $\text{Ca}(\text{OH})_2$): recently more common due to low cost and low problems with sludge dewatering. But its disadvantages are low solubility in water (1.65 g/L at 20 o C) which is 220 lower than alum's and 550 lower than ferric chloride's solubility [17]. It has recently been considered more often because of its ability to reduce phosphorus to very low levels when combined with effluent. When lime is added to wastewater, as the pH increases to more than 10, excess

Calcium ions will react with phosphate to precipitate hydroxylapatite [$\text{Ca}_5(\text{OH})(\text{PO}_4)_3$]. The typical reaction between calcium compounds and phosphorus is represented below:



The effect of (CaO) on the percentage removal and on the residual concentration of phosphorous at different pH is shown in "Fig. 1. and Fig. 2". It was found that an increase in CaO concentration increases the percentage removal of phosphorous and reduces the residual concentration at higher pH values. This is ascribed to the fact that the higher the concentration of Calcium oxide (CaO) the higher the ability of Calcium ions to form the complex with phosphate and precipitate it in the solution at pH range from (8.5-10) [18,19].

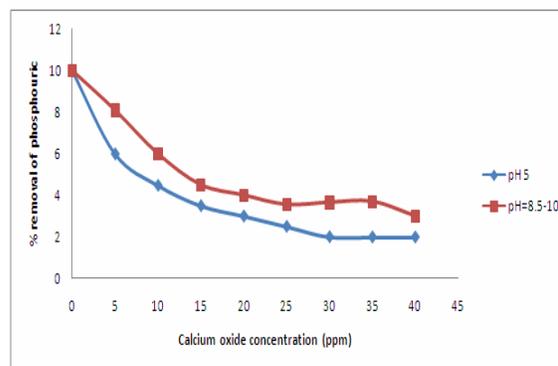


Figure1. Effect of pH and calcium oxide dosage on residual concentration of phosphate. ($\text{PO}_4=10\text{mg/l}$, $\text{Temp}=25^\circ\text{C}$).

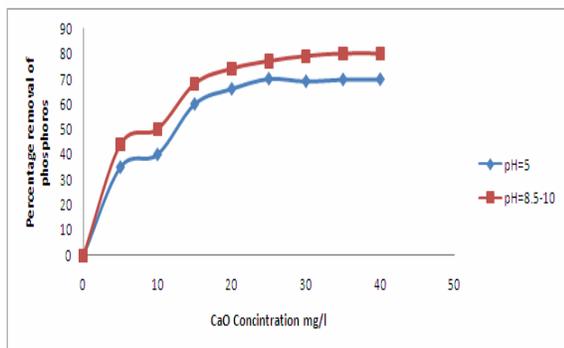
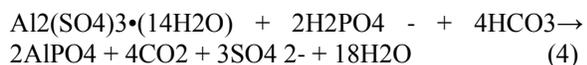


Figure 2. Effect of pH and calcium oxide dosage on Percentage removal of phosphate.($PO_4=10\text{mg/l}$,Temp= 25°C)

B. Effect of Aluminum sulfate:

Alum and ferric or ferrous salts are commonly used as coagulant and settling aids in both the water and wastewater industry. They are less corrosive, create less sludge, and are more popular with operators compared to lime.

The typical reaction between aluminum compounds and phosphorus is represented below:



“Fig. 3 and Fig. 4” show the effect of pH and Aluminum sulfate dosage on Percentage removal and residual concentration of phosphate solution. It was obviously shown that at lower pH values the percentage removal increase this is due to the fact that the solubility of aluminum salts is a function of pH. The optimum solubility for alum was previously reported to occur at a pH range of 5.5 to 6.5, significantly lower than most influent wastewater. Recent studies (Szabo et al., 2008) showed that the range alum is between 3.5 and 7.5 with the highest efficiency between pH 4 and 6 [20].

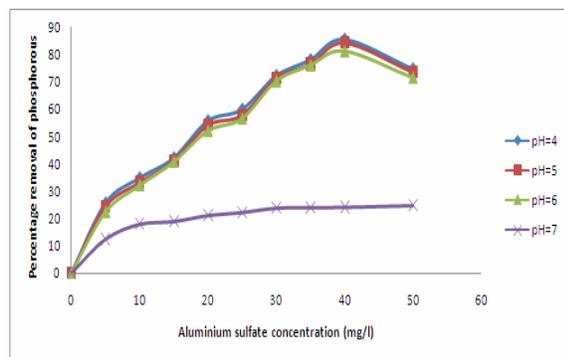


Figure 3. Effect of pH and Aluminum sulfate dosage on Percentage removal of phosphate.($PO_4=10\text{mg/l}$,Temp= 25°C)

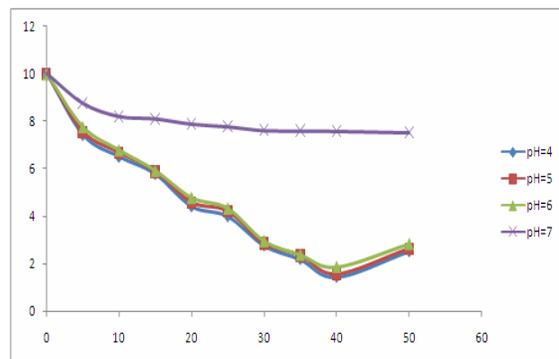


Figure 4. Effect of pH and Aluminum sulfate dosage on residual concentration of phosphate.($PO_4=10\text{mg/l}$,Temp= 25°C).

C. Effect of ferric sulfate:

ferric sulfate $<Fe_2(SO_4)_3 \cdot 9H_2O>$:supplied as a bulk or liquid, produced by oxidation of ferrous sulfate or Alluminate. **Another iron salt** widely used for precipitation of phosphorus is a ferrous sulfate ($FeSO_4 \cdot 7H_2O$), usually known as copperas. It is a cheap byproduct in the steel industry which can be successfully applied in simultaneous precipitation processes. Two unit processes should be considered while discussing precipitation with ferric salts. Hydrolysis of iron compounds and precipitation of phosphorus compounds. **A hydrolysis** of trivalent iron compounds (ferric) was described [21]. Iron hydroxide Comparing it to precipitation with alum, the solubility of $FePO_4$ is 10 times higher than that of $AlPO_4$. Minimum solubility of $FePO_4$ occurs at pH=5. Ferric ions create strong complexes with pyro- and tripoliphosphates [11].

In a process of phosphorus precipitation in raw wastewater these complexes can be absorbed at ferric hydroxyphosphates surfaces. Competition between hydroxy ions and phosphates for ferric ions when ferric salt ions are added causes a situation where the actual dose of ferric salts is higher than calculated by stoichiometric equations. Reactions in hydrolysis and precipitation of phosphorus compounds (as represented by phosphates) reacting with trivalent iron salts can be summarized as in following equation at higher pH:



Then percentage removal increased by increasing the pH value of the solution and this is the same results obtained in this study as shown in “Fig. 5 and Fig. 6”

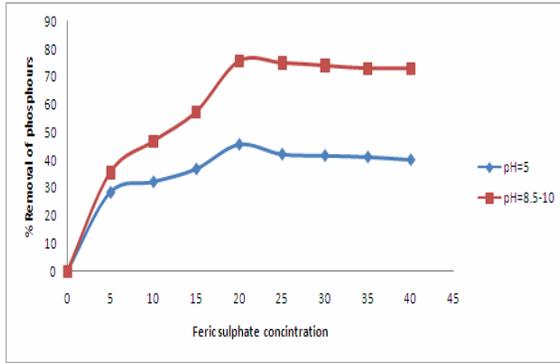


Figure 5. Effect of pH and iron sulfate dosage on Percentage removal of phosphate.($PO_4=10\text{mg/l}$,Temp= 25°C)

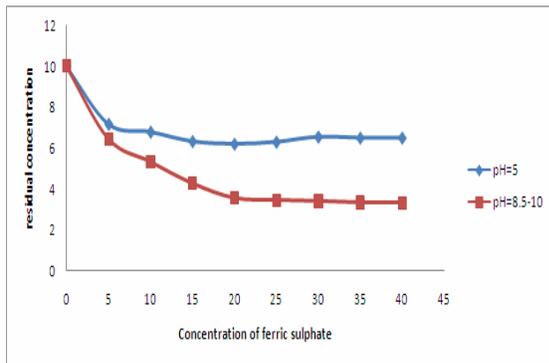


Figure 6. Effect of pH and iron sulfate dosage on residual concentration of phosphate.($PO_4=10\text{mg/l}$,Temp= 25°C.

D. Effect of Calcium Oxide and Aluminum Sulfate as a mixture

“Fig. 7”. Shows the effect of combining two metal salts on the percentage removal of phosphorus it was found that as increasing aluminium sulfates concentration with addition of CaO has no increasing effect on the percentage removal of phosphates.

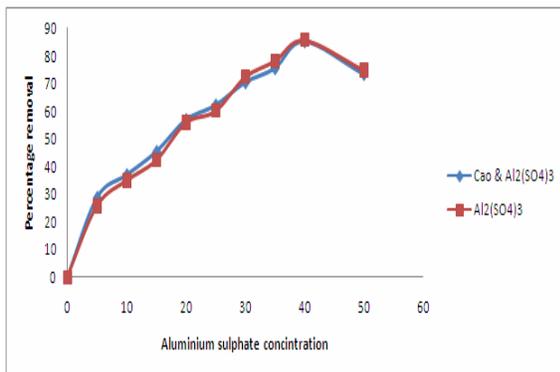


Fig.7. Effect of Calcium Oxide and Aluminum Sulfate as a mixture on % removal of.($PO_4=10\text{mg/l}$,CaO=10 mg/l,Temp= 25°.)

IV. CONCLUSION

Phosphorus must be removed from wastewater as too high concentration may lead to an eutrophication effect and rapidly deteriorating water quality .Chemical precipitation is today a well-established technology for phosphorus removal from municipal wastewaters. Removing phosphorus with lime is a function of pH that is largely independent of phosphorus concentration, making lime an attractive option if phosphorus concentration is high. Removing phosphorus with lime creates far more sludge than aluminum or iron salts;Lime is typically easy to handle and more maintenance intensive

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