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Phosphorus Removal from Water and Waste Water by Chemical Precipitation Using Alum and Calcium Chloride

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Abstract

Phosphorus is usually the limiting nutrient for eutrophication in inland receiving waters; therefore, phosphorus concentrations must be controlled. In the present study, a series of jar test was conducted to evaluate the optimum pH, dosage and performance parameters for coagulants alum and calcium chloride. Phosphorus removal by alum was found to be highly pH dependent with an optimum pH of 5.7-6. At this pH an alum dosage of 80 mg/l removed 83 % of the total phosphorus. Better removal was achieved when the solution was buffered at pH = 6. Phosphorus removal was not affected by varying the slow mixing period; this is due to the fact that the reaction is relatively fast.

The dosage of calcium chloride and pH of solution play an important role in phosphorus removal. The removal efficiency increases with increasing pH, and the optimum dosage of CaCl2 was 60 mg/l. Alum demonstrated much better results in phosphorus removal than CaCl2.

Keywords: Chemical treatment, Phosphorus removal, Alum, Calcium chloride, water treatment, west water treatment

Introduction

Phosphorus present in domestic wastewater is an important macro-nutrient for plant and microorganisms growth. The discharge of large quantities of this nutrient into natural receiving sources raises the growth of algae and results in eutrophication of lakes and streams (Banu, et al., 2008). This can in turn disturb the balance of organisms present in water and affect water quality, mainly through the depletion of oxygen level as the algae decay. Reduced oxygen level can have harmful effects on fish and other aquatic life, causing reduction in biodiversity. The load of phosphorus 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 (Plaza et al., 1997).

Phosphorus removal techniques fall into three main categories; physical, chemical and biological. In a biological treatment plant, it is necessary to transfer phosphate from liquid to the sludge phase, and the removal efficiency usually does not exceed 30%, which means that the remaining phosphate should be removed by other techniques. Chemical precipitation is also widely used for phosphate removal. The precipitation of calcium phosphate from wastewater is an important physiochemical process for phosphorus removal and it becomes increasingly significant for phosphorus recovery, since from the industry's viewpoint, it is far more promising to recover phosphorus as calcium phosphates than other forms because it can be valorized in agriculture as a slightly soluble fertilizer (Hosni, et al., 2007).

Agents used to precipitate dissolved phosphorus are salts of metals, calcium (Ca+2), iron (either Fe+2 or Fe+3), or aluminum (either alum, Al2 (SO4)3. 18H2O or sodium illuminate, Na2Al2O4). The chloride and sulfate salts of Fe+2 and Fe+3 can be used (Droste, 1997).

Basic chemicals for precipitation were lime alone or lime in conjunction with alum, ferric sulfate, burnt magnesia or charcoal, ferric chloride. Precipitation of phosphorus by addition of lime and alum in advanced wastewater treatment technology and different methods to recover aluminum and lime has been described by Clup and Clup

(1971). Kershaw in 1911 mentioned most common precipitants applied in Great Britain including:

- Lime
- Alumino-ferric
- Ferric sulphate
- Sulphuric acid
- Ferrozone
- Lime and ferrous sulphate
- Lime chlorine

Most of these chemicals have been proven to precipitate phosphorus and are in use even today (Rybicki, S., 1997). Since the 1960's major efforts have been made towards phosphorus removal (Jenkins 1971). In general; the degree of phosphorus removal by chemical precipitation is affected by many factors, such as pH, alkalinity, coagulant dose, speed of mixing and other interfering substances (James, et al., 2003). Chemical precipitation or flocculation of biochemically treated wastewater effluents have been investigated by Rudolf (1947), Owen (1953), Lea et al. (1954). These investigations have been discussed by Stumm (1962). In general these investigations had shown that significant amounts of phosphorus can be removed by alum and iron flocculation or lime precipitation (Malhotra, et al., 1964).

The chemistry of phosphate formation is complex because of complexes formed between phosphate and metals and between metals and ligands in the wastewater. Side reactions of the metals with alkalinity to form hydroxide precipitates are another factor to be considered. The common precipitates formed by metals are given in Table (1) along with the optimal pH range for phosphate precipitation (Droste, 1997).

The aqueous chemistry of alum is extremely complex and when added to water, aluminum enters into a series of complicated reactions. The aluminum ions become hydrated and form monomeric and polymeric species and solid precipitates. Hem et al, 1976, mention that the formation of polynuclear species in dilute solution is a stepwise process involving a deprotonation-dehydration mechanism. Firstly, alum is hydrated. Hydrated aluminum ions are deprotonated and two deprotonated octahedral can then join to form a dimmer. Dimers can join to form a 6-member chain structure by the same deprotonation-dehydration mechanism. These six membered rings may then coalesce further by continued polymerization, resulting in a higher ratio of structural hydroxyl to aluminum.

These steps can be summarized in a very simplified and short manner in Fig. (1) (Georgantas and Grigoropoulou, 2006).

In recent years considerable attention has been paid to the chemistry of alum and mainly in its hydrolyzed products also known as poly-aluminum salts (Boisvert et al., 1997). These salts have shown to offer a number of benefits in comparison to their precursor, alum, such as lower residual soluble Al and lower pre- or post- pH adjustment needed. Therefore, these salts have attracted great interest and extended research has been devoted into its preparation under controlled conditions and characterization (Benschoten and Edzwald, 1990, Sincero, 2003).

The aim of this investigation was to study the feasibility of phosphate removal from aqueous solutions by calcium chloride and alum. The process was examined under different values of pH, the dosage of coagulant and performance parameters.

Table (1) Phosphate precipitates (Jenkins and Hermanowicz, 1991)

Metal	Precipitates	pH range	Comment
Ca^{+2}	Various calcium phosphates, e.g. $Ca_3(PO_4)_2$, $Ca_5(OH)(PO_4)_3$, $CaHPO_4$	≥ 10	Produces lowest residual P concentrations. The alkalinity of the water determines the dose because of formation of $CaCO_3$. Residual P in the range of 1-2 mg/ lit.
	$CaCO_3$	≤ 9.5	
Fe^{+2}	$Fe_3(PO_4)_2$, $Fe_x(OH)_y(PO_4)_3$, $Fe(OH)_2$, $Fe(OH)_3$	6- 8.5	There will be some oxidation of Fe^{+2} to Fe^{+3}.
Fe^{+3}	$Fe_x(OH)_y(PO_4)_z$, $Fe(OH)_3$	6- 8.5	
Al^{+3}	$Al_x(OH)_y(PO_4)_z$. $Al(OH)_3$	6- 8.5	

$$Al(OH_2)_6^{+3} \rightleftharpoons Al(OH)(OH_2)_5^{+2} + H^+$$

$$2Al(OH)(OH_2)_5^{+2} \rightleftharpoons Al_2(OH)_2(OH2)_8^{+4} + 2\,H_2O \rightarrow Al_6(OH)_{12}^{+6}.\,12H_2O \quad Al_6(OH)_{12}^{+6}.\,12H_2O \rightarrow$$

$$Al_{10}(OH)_{22}^{+8}.\,16H_2O \rightarrow Al_{24}(OH)_{60}^{+12}.\,24H_2O$$

$$Al_{32}(OH)_{82}^{+14}.\,28H_2O \rightarrow Al_{54}(OH)_{144}^{+18}.\,36H_2O$$

Fig. 1 Proposed mechanism for alum hydrolysis and polymerization in water

Experimental Work

The coagulation experiments were carried out at laboratory temperature using a Jar-test (Floc tester, Zeitschaltuhr) with a six paddle stirrer. In each of the tests, 1 liter of phosphate solutions prepared from KH_2PO_4 was taken in the jar. The pH was adjusted to the desirable level with the addition of alkali (1N NaOH) or acid (1N HCl). The coagulants (alum and calcium chloride) were added under stirring. Rapid mixing took place for 1 min. at a speed of 200 rpm, followed by slow mixing at 30 rpm for 30 min. The effects of slow mixing on phosphorus removal were carried out at varying times, namely 5, 10, 15, 20, 25, 30, respectively. The settling period lasted for 30 min.

Another experiment was made for the alum addition by buffering the phosphate solutions to pH=6 using few drops of a buffering reagent. The last is prepared by dissolving 136 g sodium acetate ($CH_3COONa.3H_2O$) in water, adding 40 ml 1N acetic acid and diluting to 1 liter.

After the settling period, samples were taken and analyzed for pH and phosphorus. The pH was measured by a digital pH – meter with glass electrode and saturated calomel electrode (Oakton pH 2100 series manufactured by EUTECH instruments, Singapore). A spectrophotometer (Spectro SC, USA) was used for the analysis of phosphate in accordance with the standard methods (vanadomolybdo-phosphoric acid colorimetric method)

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Vanadomolybdo-phosphoric acid colorimetric method

In this method, ammonium molybdate reacts with phosphorus to form molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to phosphate concentration

Vanadate – Molybdate reagent was prepared by weighing (25 gm) of ammonium molybdate and dissolved in 250 ml of distilled water to form solution (A), then (125 gm) of ammonium metavanadate were dissolved in 200 ml of distilled water to prepare a solution to which is added (300 ml)of concentrated HCl to form a solution (B). Solution A and B were mixed together and diluted to a liter volume, thereby forming a standard vanadate-molybdate reagent solution.

Phosphate standards (KH_2PO_4) were prepared from the stock solution (1×10^{-3} M KH_2PO_4):0.1Mm, 0.2Mm, 0.4Mm, 0.6Mm by using 50-cm3 volumetric flasks for construction of a calibration curve. Both samples and phosphate standards then prepared for absorbance measurements at 420 nm using the ammonium molybdate/ ammonium metavanadate color reagent by placing 25 cm3 of diluted sample solution in 50-cm3 volumetric flasks and adding 10 cm3 vanadate-molybdate reagent and diluting with distilled water. A blank was prepared in which 25 cm3 of distilled water was substituted for sample of phosphate standards (Thomas and Burqess, 2007).

Results and Discussion

Phosphorus removal by alum

Effect of alum dosage on removal of phosphorus:

The influence of $Al_2(SO_4)_3.18H_2O$ dosage on the phosphorus removal without pH adjustment is shown in Fig. (2). A rise in alum dosage up to 80 mg/l increases the phosphorus removal. Further addition of alum leads to a decrease in the phosphorus removal efficiency. The decrease in phosphorus removal efficiency after the optimum dosage was due to the restablization of colloidal suspension (Ahmed et al., 2006). This is due to the fact that an increase in the dosage shifts the optimum pH (5.8-6.5) to an unfavorable range for phosphate removal, so the increase in the dosage is meaningless and it actually decreases the performance of the coagulant.

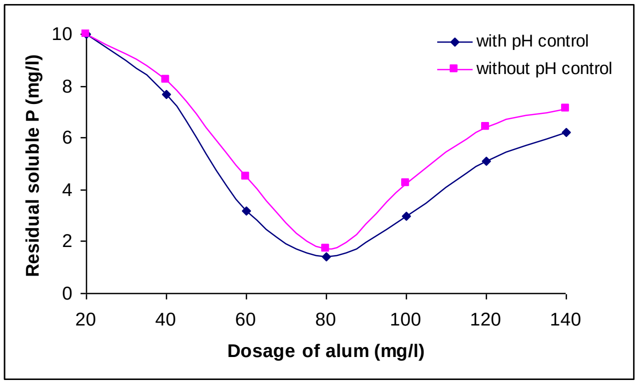

Fig. 2 the influence of alum dosage on phosphorus removal

The influence of pH on phosphorus removal

Phosphate removal as aluminum phosphate highly depends upon the pH of water. After alum was added into water, the pH of solution decreased. This is due to the fact that a part of alum was precipitated as the hydroxide forms and H+ was formed by the following reaction:

$Al^{+3} + 3H_2O \rightarrow Al(OH)_3 \downarrow + 3H^+$

Below a pH range of 5.5 the aluminum ions are soluble and do not participate in the hydration and olation reactions necessary to make alum effective as a coagulant. Also the formation of insoluble $AlPO_4$ according to the scheme:

$Al^{+3}+H_nPO_4^{n-3} \rightleftharpoons AlPO_4+nH^+$

is not possible as $AlPO_4$ is soluble below pH=6 and above pH=8 (Sedlak, 1991). On the other hand, when the pH level of the water is above 8 after the addition of the alum, the aluminum ions again become soluble (Al(OH)4-), and the efficiency of coagulation is decreased (Georgantas and Grigoropoulou, 2006).

After adding coagulant, the pH of water was more important than its initial pH. The effect of the initial pH of sample on the removal of phosphorus is presented in Fig. (3). The data was obtained for total phosphorus removal over a pH range of 3 -11. In these runs an alum dosage of 80 mg/l was used and the initial pH of the sample was adjusted by the addition of NaOH (1N) or HCl (1N).

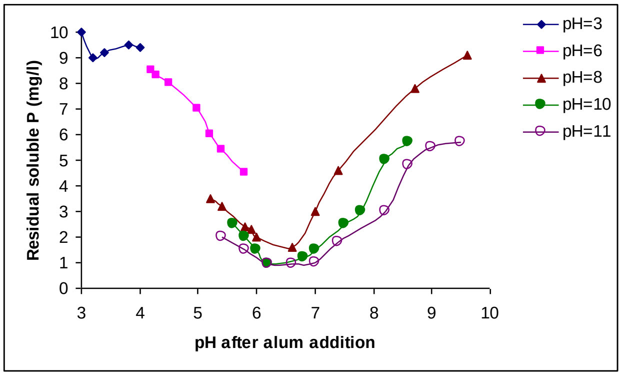

Fig. 3 Effect of pH on the removal of phosphorus.

In the case of pH=3, it did not play any role in the phosphorus removal, whereas at pH=6, the phosphorus removal was high at low dosage when compared to that of remaining pH. The increase in the dosage resulted in a decrease in the phosphorus removal for pH=6 rather than others. This is due to the rapid shifting of pH by alum dosage. In the pH 8, 10 and 11 the residual phosphorus decreases in the pH range of 5.7 to 6 which are similar to the findings of Georgants and Grigropolou (2006) and Denham (2007).

Fig.(2) also shows that significantly better removal were achieved when the solution was buffered at pH=6, because when alum is added in the solution, pH drops rapidly at about pH= 4. At this pH the produced aluminum phosphate is redissolved releasing phosphate again. On the contrary, at pH= 6, aluminum phosphate is actually undissolved.

Effect of slow mixing time (kinetics) on phosphorus removal

Fig.(4) shows the effect of slow mixing time on the phosphorus removal for alum dosage of 40,60 and 80 mg/l. It is evident from Fig.(4) that phosphorus removal was not affected by slow mixing time. The reason may be due to the fact that the phosphorus removal is relatively fast and equilibrium had been reached in less than 5 minutes. A similar behavior was observed by Szabo et al., (2008) and Georgantas and Grigoropoulou, (2003).

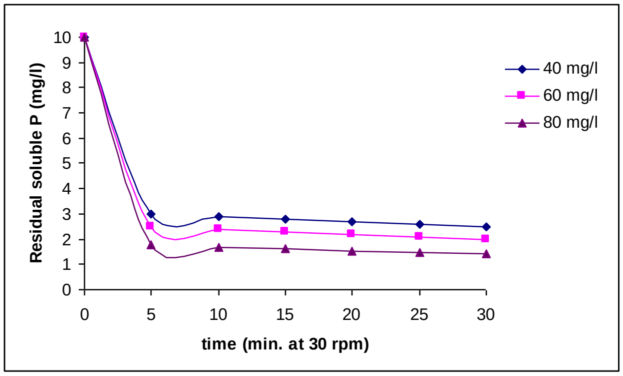

Fig. (4): kinetics of phosphorus removal using alum.

Removal of phosphorus by calcium chloride

Effect of pH and $CaCl_2$ dosage on phosphorus removal

Variation of the phosphorus removal efficiency as a function of initial pH at different CaCl2 dosage is shown in Fig.(5). It shows that pH and CaCl2 dosage play an important role in PO4-3 removal. Phosphate removal increases with increasing pH and CaCl2 dosage, at pH= 11 the residual phosphorus passes from (5 to 3 mg/l) when CaCl2 dosage passes from 40 to 60 mg/l. The pH effect can be explained by the change of orthophosphate compounds with pH (i.e. conversion of H3PO4 $\rightleftharpoons$ H2PO4- $\rightleftharpoons$ HPO4-2 $\rightleftharpoons$ PO4-3 with increasing pH) (Jenkins et al., 1971 and Hosni et al., 2007). However CaCl2 dosage larger than 60 mg/l has nearly no effect on phosphorus removal.

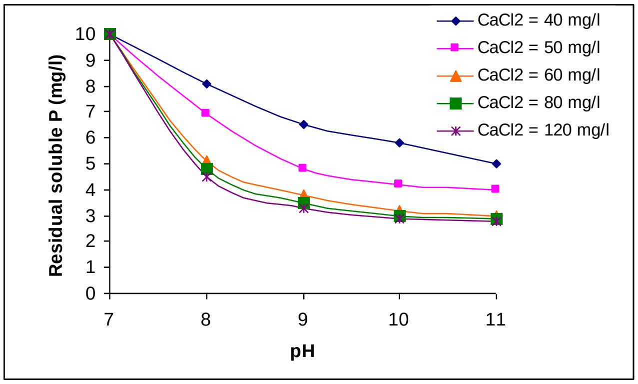

Fig. 5 Phosphorus removal as a function of pH for various $CaCl_2$ dosages.

Comparison between alum and calcium chloride regarding their efficiency to remove phosphorus

Fig.(6) shows the phosphorus versus pH for alum and CaCl2 dosage of 80 mg/l. Alum demonstrated much better results in phosphorus removal, being up to approximately 2 times better than CaCl2 for the same dosage.

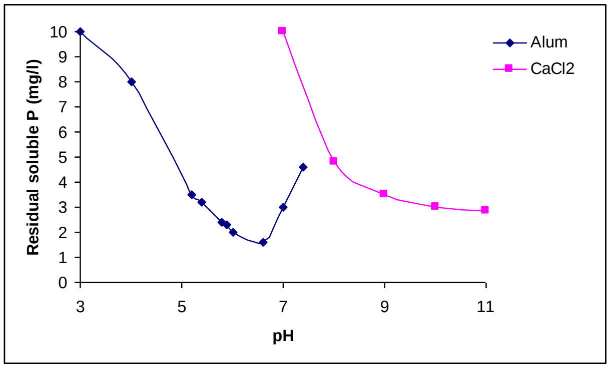

Fig.6 Comparison between alum and calcium chloride regarding their efficiency to remove phosphorus.

Conclusions

The phosphorus removal by alum was found to be highly pH dependent with an optimum pH of 5.7 to 6. At this pH an alum dosage of 80 mg/l removed 83 % of the total phosphorus. Better phosphorus removal was achieved when the solution was buffered at pH = 6. Phosphorus removal was not affected by varying slow mixing period; this is due to the fact that phosphorus removal is relatively fast.

The dosage of CaCl2 and pH play an important role in phosphorus removal, the removal efficiency increases with increasing pH, and the optimum dose of CaCl2 was 60 mg/l. Alum demonstrated much better results in phosphorus removal being 2 times better than CaCl2 for the same dosage.

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ازالة الفسفور من المياه بطريقة الترسيب الكيمياوي باستخدام كبريتات الالمونيوم المائية(الشب) وكلوريد الكالسيوم

سوسن عبد مسلم و حيدر عباس شنشول
قسم الهندسة الكيمياوية – كلية الهندسة - جامعة بغداد- بغداد- العراق

الخلاصة:

يعتبر الفسفور من المواد الملوثة للماء و التي تؤدي الى عملية التحول في الحياة المائية(Eutrophication) ولهذا فمن الضروري السيطرة على تركيزه في الماء. في هذه الدراسة تم اجراء سلسلة من التجارب باستخدام جهاز (jar test) لايجاد افضل قيمة للرقم الهيدروجيني وكمية المادة الكيمياوية المضافة.لقد وجد ان افضل قيمة للرقم الهيدروجيني في حالة استخدام الشب هو من 5.5 – 6 وافضل كمية مستخدمة هي 80 ملغم/ لتروالتي تعمل على ازالة 83% من كمية الفسفور الذائب في الماء وكانت عملية الازالة افضل عندما تمت السيطرة على قيمة الرقم الهيدروجيني على قيمة 6.لم تتاثر كفاءة الازالة بتغيير الزمن اللازم للتحريك البطئ وذلك لكون التفاعل سريع.

اما في حالة ازالة الفسفور باستخدام كلوريد الكالسيوم فان كمية الكلوريد المضاف والرقم الهيدروجيني للمحلول كان لها دور مهم في عملية الترسيب وان افضل قيمة للرقم تالهيدروجيني هو 11وافضل قيمة لكمية الكلوريد هي 60 ملغم/لتر. دلت النتائج على ان الشب اعطى كفاءة افضل في عملية ترسيب الفسفور بالمقارنة مع كلوريد الكالسيوم.