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# OPTIMIZATION OF PARAMETERS FOR REMOVAL OF PHOSPHATE FROM PHARMACEUTICAL EFFLUENT BY CHEMICAL PRECIPITATION USING $CaCO_3$

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## ABSTRACT
Phosphate is an important nutrient that occurs widely in the environment. It is the key elements necessary for the growth of plants and animals. It is the eleventh most abundant element on the surface of the earth and is most commonly found as phosphate. High phosphate concentration leads to eutrophication and also health problems such as kidney damage, osteoporosis and hyperphosphatemia. Therefore it is necessary to remove phosphate to minimize the health and environmental effects. The present study aimed to investigate effects of different parameters like dosage of CaCO3, time, pH, dosage of alum, dosage of dolomite for the removal of phosphate from the pharmaceutical effluent has been studied.

**KEYWORDS:** Phosphate, Effluent, chemical precipitation, CaCO3, Alum, Dolomite.

## INTRODUCTION
Phosphates are the naturally occurring form of the element phosphorus, found in many phosphate minerals. In mineralogy and geology, phosphate refers to a rock or ore containing phosphate ions. Inorganic phosphates are mined to obtain phosphorus for use in agriculture and industry.A phosphate($PO_4^{3-}$) as an inorganic chemical is a salt of phosphoric acid. In organic chemistry, a phosphate, or organophosphate, is an ester of phosphoric acid. In organic phosphates are mined to obtain phosphorus for use in agriculture and industry. At elevated temperatures in the solid state, phosphates can condense to form pyrophosphates.

Phosphate is an important nutrient that occurs widely in the environment. It is the key elements necessary for the growth of plants and animals. It is the eleventh most abundant element on the surface of the earth and is most commonly found as phosphate. Phosphorus is a pre requisite for microbial growth in the aqueous bodies. The increased concentration of phosphate is the key factor for the eutrophication of surface water. Heavy algal growth occurs when phosphate is present in water and as such is undesirable Phosphates enter waterways from human and animal waste, phosphorous rich bedrock, laundry, cleaning, industrial effluents and fertilizer runoff. These phosphates become detrimental when they pass over fertilize aquatic plants and cause stepped up eutrophication.

Eutrofication is the natural aging process of a body of water such as a river or sea. This process results from the increase of nutrients within the body of water which in turn create plant growth. The plants die more quickly than they can be decomposed. This dead plant matter builds up and together with sediment entering the water, fills in the bed of the bay making it more shallow. Normally this process takes thousands of years. Cultural eutrofication is an unnatural speeding up of this process because of man's addition of phosphates, nitrogen and sediment to the water. Bodies of water are being aged at a much faster rate than geological forces can create new onces.

## CHEMICAL PROPERTIES
Phosphate ($PO_4^{3-}$) as an inorganic chemical is a salt of phosphoric acid. The phosphate ion is a polyatomic ion with the empirical formula $PO_4^{3-}$and a molar mass of 94.97 g/mol. It consists of one central phosphorus atom surrounded by four oxygen atoms in a tetrahedral arrangement. The phosphate ion carries a negative three formal charge and is the conjugate base of the hydrogen phosphate ion $HPO_4^{2-}$ which is the conjugate base of $H_2PO_4^-$ , the dihydrogen phosphate ion which in turn is the conjugate base of $H_3PO_4$, phosphoric acid.A phosphate salt forms when a positively

charged ion attaches to the negatively charged oxygen atoms of the ion, forming an ionic compound. Many phosphates are not soluble in water at standard temperature and pressure. The sodium, potassium, rubidium, caesium and ammonium phosphates are all water soluble. Most other phosphates[5]are only slightly soluble or are insoluble in water. As a rule, the hydrogen and dihydrogen phosphates are slightly more soluble than the corresponding phosphates. The pyrophosphates are mostly water soluble.

## EFFECTS OF PHOSPHATE ON ENVIRONMENT

Phosphate will stimulate the growth of plankton and aquatic plants which provide food for fish. This may cause an increase in the fish population and improve the overall water quality. However. an excess phosphate enters the waterways, algae and aquatic plants will grow wildly and choke up the waterway and uses up large amounts of oxygen. This condition is known as eurtrofication. This rapid growth of aquatic vegetation eventually dies and as it decays it uses up oxygen. This process in turn causes the death of aquatic life because of the lowering of dissolved oxygen levels

## EFFECTS OF PHOSPHATE ON HUMAN BEINGS AND ANIMALS

Phosphates are not toxic to people or animals unless they are present in very high levels. Digestive problems, kidney damage, osteoporosis and hyperphosphatemia could occur from extremely high levels of phosphate. Acute oral exposure to high levels of phosphate in humans is characterized by three stages the first stage consists of gastro intestinal effects, the second stage is symptom-free and lasts about 2 days, the third stage consists of a rapid decline in condition with severe gastro intestinal(vomiting, abdominal cramps and pain), kidney, liver, cardiovascular, and CNS effects. Inhalation exposure has resulted in respiratory tract irritation and coughing in humans. Respiratory, liver and kidney effects have been reported in animals acutely exposed to phosphate smoke via inhalation. Thermal exposure to phosphate in humans may result in severe burns, which are necrotic, yellowish, fluorescent under ultraviolet light, and have a garlic like odor. Animal tests in rats and mice have shown phosphate to have extreme toxicity from oral exposure. Phosphate should be removed[4] from the effluent according to the standards.

## MATERIALS AND METHODS

**Chemicals Required:**

$CaCO_3$, HCl, NaOH, Alum, Dolomite, distilled water

**Equipment Required:**

Magnetic stirrer, pH meter, UV-Visible spectrophotometer

**Experimental Procedure:**

An appropriate amount of $CaCO_3$ was dosed to the pharmaceutical effluent. The $Ca^{2+}$ acts as a precipitating agent with regard to the phosphates. Calcium was introduced in the form of $CaCO_3$ into the solution. In consecutive experiments amount of $CaCO_3$, time of treatment, pH of the solution, alum were changed. Above quantities are changed until optimum conditions are derived.

The pH of the solutions was adjusted by means of NaOH / HCl solutions (A digitally calibrated pH meter 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. The analytical determination of phosphate was carried out with the standard specterophotometric procedure using visible U.V spectrophotometer.

**Treatment Technique- Chemical Precipitation:**

Chemical precipitation was adopted as one of the technique for the removal of phosphates from the pharmaceutical effluent. Chemical precipitation is done with $CaCO_3$.

## RESULTS AND DISCUSSION

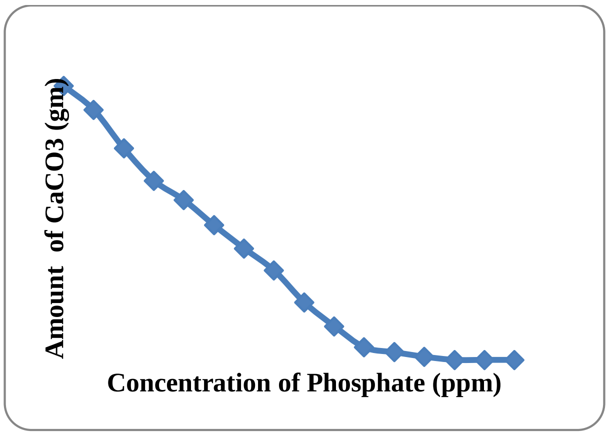
The initial concentration of phosphate in pharmaceutical effluent was 160.0ppm. Considering that concentration dosage of $CaCO_3$, contact time, pH, alum and dolomite dosage are fixed.
The effluent was slightly acidic (pH 5.0).

**Effect of dosage of $CaCO_3$:**

***Table 1: Concentration of phosphate (ppm) with Amount of $CaCO_3$(gm)***

| S.no | Amount of $CaCO_3$, gm | Concentration of phosphate , ppm |
|---|---|---|
| 1. | 0.5 | 60.22 |
| 2. | 1 | 55.61 |
| 3. | 1.5 | 48.24 |
| 4. | 2 | 42.08 |
| 5. | 2.5 | 38.36 |
| 6. | 3 | 33.56 |
| 7. | 3.5 | 29.11 |
| 8. | 4 | 24.87 |
| 9. | 4.5 | 18.79 |
| 10. | 5 | 14.23 |
| 11. | 5.5 | 10.2 |
| 12. | 6 | 9.26 |
| 13. | 6.5 | 8.4 |
| 14. | 7 | 7.8 |
| 15. | 7.5 | 7.8 |
| 16. | 8 | 7.8 |

***Figure 1: Amount of $CaCO_3$ (gm) versus Concentration of Phosphate (ppm)***




Dosage of chemical plays a vital role in every chemical process. It is very important in chemical treatment process. The amount of $CaCO_3$ required for phosphate removal is estimated by taking 100 ml of sample in a conical flask and keep it for stirring at 100RPM. The phosphate concentration is estimated after one hour of treatment with $CaCO_3$. From 0.5gm to 7.0gms the phosphate concentration is decreased gradually and it is stable at 7.5 & 8.0gms. Continuously the phosphate concentration decreased from 0.5gm to 7.0gms and then it becomes stable even further adding of $CaCO_3$ which means that increase in the dosage of chemical does not have effect on the phosphate. In this process the removal of phosphate or concentration of phosphate with respect to amount of $CaCO_3$ is shown in the above table-1 and figure-1. Hence the optimum amount of $CaCO_3$ required for the removal of phosphate in this process is found as 7.0gms.

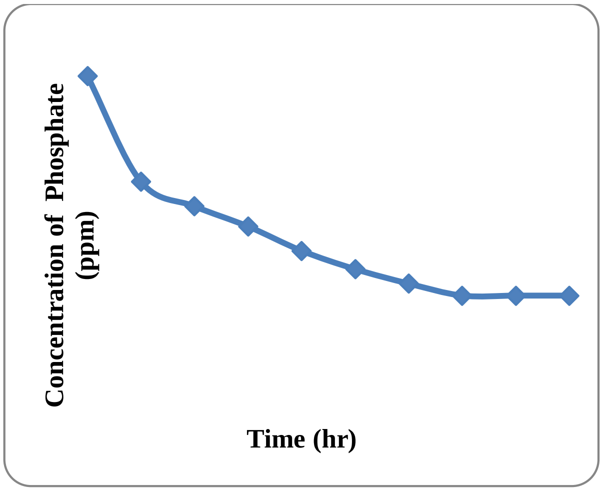
**Effect of time:**

***Table 2: Concentration of phosphate (ppm) with time (hr)***

| S.no | Time, hr | Concentration of phosphate , ppm |
|---|---|---|
| 1. | 0.5 | 10.8 |
| 2. | 1 | 7.8 |
| 3. | 1.5 | 7.1 |
| 4. | 2 | 6.53 |
| 5. | 2.5 | 5.84 |
| 6. | 3 | 5.32 |

| | | |
|---|---|---|
| 7. | 3.5 | 4.91 |
| 8. | 4 | 4.57 |
| 9. | 4.5 | 4.57 |
| 10. | 5.0 | 4.57 |

***Figure 2: Concentration of Phosphate (ppm) versus Time (hr)***



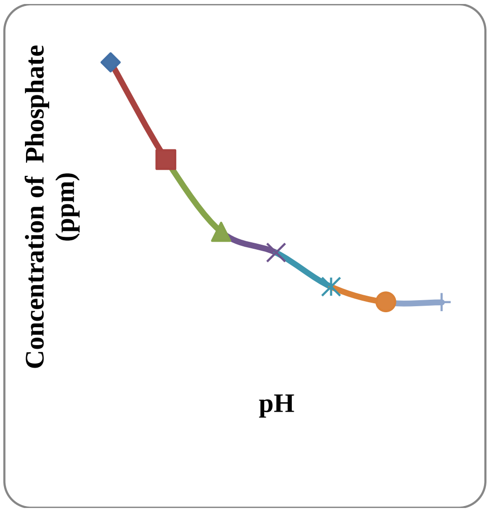

Time places a vital role in every process. It is very important in chemical treatment processes. The time required for reducing phosphate concentration in the pharmaceutical effluent is estimated by taking 100 ml of sample in a conical flask and add 7.0gms of $CaCO_3$ to the sample and keep it for stirring at 100RPM. The phosphate concentration is estimated for every half an hour. The phosphate concentration is estimated from half an hour to till it comes stable. From 0.5 hr to 4.0 hr the phosphate concentration is decreased gradually and it is stable at 4.5hr. Continuously the phosphate concentration decreased from 0.5 hr to 4.0 hr and then it becomes stable even though the process continues further there is no change in the phosphate concentration, which means that increase in the time of treatment with $CaCO_3$ does not have effect on the phosphate. In this process the removal of phosphate or concentration of phosphate with respect to time is shown in the above table-2 and figure-2. Hence the optimum time required for the removal of phosphate in this process is found as 4.0 hrs.

**Effect of pH:**

***Table 3: Concentration of phosphate (ppm) with pH***

| S.no | pH | Concentration of phosphate , ppm |
|---|---|---|
| 1. | 3 | 5.77 |
| 2. | 4 | 5.08 |
| 3. | 5 | 4.57 |
| 4. | 6 | 4.42 |
| 5. | 7 | 4.18 |
| 6. | 8 | 4.07 |
| 7. | 9 | 4.07 |

*Figure 3: Concentration of Phosphate (ppm) versus pH*



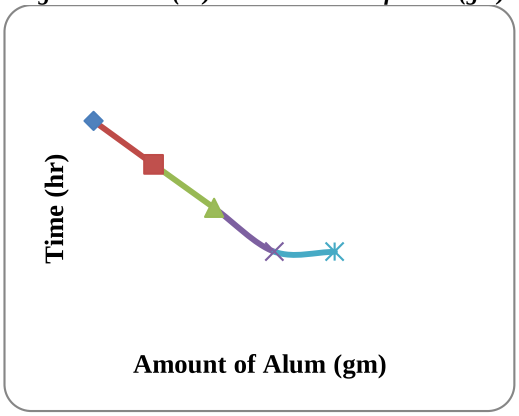

The pH required for reducing phosphate concentration in the pharmaceutical effluent is estimated by taking 100 ml of sample in a conical flask and add 7.0gms of $CaCO_3$ to the sample and keep it for stirring at 100RPM for four hours. The phosphate concentration is estimated at different pH for four hours. The phosphate concentration is estimated from pH 3to till it comes stable. At pH 3 and 4 the concentration of phosphate after the treatment is high when compared initial pH of the effluent (pH 5). From pH 5 to 8 the phosphate concentration is decreased gradually and it is stable at pH 9. Continuously the phosphate concentration decreased from pH 5 to 8 and then it becomes stable even though the process continues further there is no change in the phosphate concentration, which means that change in the pH of the effluent does not have effect on the phosphate. In this process the removal of phosphate or concentration of phosphate with respect to pH is shown in the above table-3 and figure-3. Hence the optimum pH required for the removal of phosphate in this process is found as pH-8 and concentration of phosphate is 4.07ppm.

**Effect of dosage of alum:**

*Table 4: Amount of Alum (gm) with time (hr)*

| S.no | Amount of Alum, gm | Time, hr |
|---|---|---|
| 1. | 0.02 | 4 |
| 2. | 0.04 | 3.5 |
| 3. | 0.06 | 3 |
| 4. | 0.08 | 2.5 |
| 5. | 0.1 | 2.5 |

*Figure 4: Time (hr) versus Amount of Alum (gm)*



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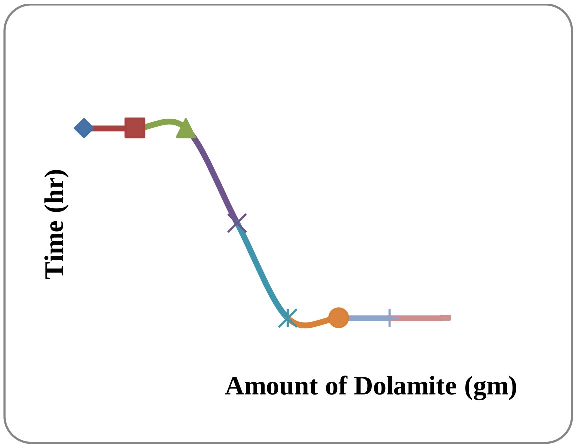
Alum is added because of its specific property of developing the attractive forces between the particles which leads to the increase in chemical precipitation and which intend decreases the time required for the treatment. The increase in the concentration of alum increases the chemical precipitation and decreases the phosphate concentration. The amount of alum required for reducing the phosphate concentration in the pharmaceutical effluent is estimated by taking 100 ml of sample in a conical flask which is at the pH 8 and add 7.0gms of $CaCO_3$ to the sample and keep it for stirring at 100RPM for four hours. The phosphate concentration is estimated at different amounts of alum for every half an hour. The phosphate concentration is estimated from half an hour to till it comes stable. The phosphate concentration is estimated from 0.02gm of alum to till it comes to stable. At 0.02 gm of alum, no change in phosphate concentration is observed with respect to time, which means removal of phosphate is same as without alum. After further increase in alum dosage there is a change in phosphate concentration with respect to time. From 0.04 gm to 0.08 gm the time required for reducing the phosphate concentration is decreased gradually and it is stable at 0.1gm.Continuously the time required for reducing the phosphate concentration decreased from 4.0 hr to 2.5 hr and then it becomes stable even though the process continues further there is no change in the phosphate concentration, which means that increase in the dosage of alum does not have effect on the phosphate. In this process the time required for removal of phosphate or concentration of phosphate with respect to alum is shown in the above table-4 and figure-4. Hence the optimum amount of alum required for the removal of phosphate in this process is found as 0.08gm and removal is done at 2.5hrs.

**Effect of dosage of dolomite:**

***Table 5: Amount of Dolomite (gm) with time (hr)***

| S.no | Amount of Dolomite, gm | Time, hr |
|---|---|---|
| 1. | 0.02 | 4 |
| 2. | 0.04 | 4 |
| 3. | 0.06 | 4 |
| 4. | 0.08 | 3.5 |
| 5. | 0.1 | 3 |
| 6. | 0.12 | 3 |
| 7. | 0.14 | 3 |
| 8. | 0.16 | 3 |

***Figure 5: Time (hr) versus Amount of Dolomite (gm)***




Dolomite is added because of its specific property similar to alum like developing the attractive forces between the particles which leads to the increase in chemical precipitation and which intend decreases the time required for the treatment. The increase in the concentration of dolomite increases the chemical precipitation and decreases the phosphate concentration. The amount of dolomite required for reducing the phosphate concentration in the pharmaceutical effluent is estimated by taking 100 ml of sample in a conical flask which is at the pH 8 and add 7.0gms of $CaCO_3$ to the sample and keep it for stirring at 100RPM for four hours. The phosphate concentration is estimated at different amounts of dolomite for every half an hour. The phosphate concentration is estimated from half an hour to till it comes stable. The phosphate concentration is estimated from 0.02gm of dolomite to till it comes to stable. At 0.02 gm, 0.04gm, 0.06gm of dolomite, no change in phosphate concentration is observed with respect to time, which means removal of phosphate is same as without dolomite. After further increase in dolomite dosage there is a change in phosphate concentration with respect to time. From 0.08 gm and 0.10 gm the time required for reducing the phosphate concentration is decreased gradually and it is stable at 0.12gm.Continuously the time required for reducing the phosphate concentration decreased from 4.0 hr to 3.0 hr and then it becomes stable even though the process continues further there is no change in the phosphate concentration, which means that increase in the dosage of dolomite does not have effect on the phosphate. In this process the time required for removal of phosphate or concentration of phosphate with respect to dolomite is shown in the above table-5 and figure-5. Hence the optimum amount of dolomite required for the removal of phosphate in this process is found as 0.10 gm and removal is done at 3.0hrs.

## CONCLUSION

There are wide range of technologies to remove the phosphate from effluents by using various methods like chemical precipitation, coagulation, electro coagulation method, electro dialysis method, electro dialysis method, adsorption and biological treatment methods. Among these methods chemical precipitation is the best suitable method for the removal phosphate because it is cost effective and high removal of phosphate has been observed.

The present study aimed to investigate the chemical precipitation using $CaCO_3$. In studies the effective dosage of $CaCO_3$, reaction time, optimum pH, effective dosage of alum and effective dosage of dolomite were optimized. As a result dosage of $CaCO_3$ 7.0gm/100ml, reaction time of 4hr, pH of 8, by adding the alum to the effluent the reaction time is reduced from 4 to 2.5hr and also by adding the dolomite to the effluent the reaction time is reduced from 4 to 3hr under optimized conditions.

The phosphate concentration is decreased from 160ppm to 4.07ppm in 2.5hrs at optimum conditions using alum.

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