

Development of Modeling Equation and Kinetics of Phosphate Removal from Pharmaceutical Effluent using Obligate Aerobes Derived from Fruit Waste

Kasi Pradgna¹, Sunil Kanamarlapudi², Meena Vangalapati³

M.Tech Student, Department of Chemical Engineering, AUCE (A), Andhra University, A.P, India^{1,2}

Associate Professor, Department of Chemical Engineering, AUCE (A), Andhra University, A.P, India³

Abstract: Phosphorus is usually a limiting element for phytoplankton growth and is thus one of the leading causes of eutrophication. Phosphorus removal from wastewater before discharge has to be considered to protect natural waters from eutrophication [1]. Phosphorus pollution is a major concern for soil and water management. A modeling equation was developed to know the phosphate removal with time. The proposed model equation for the removal of phosphate is $Y_p = -0.0438x + 16.58$ and the model showed good agreement with experimental data and is significantly compared to other methods in the removal of phosphate from pharmaceutical industry. The phosphate removal efficiency from obligate aerobes derived from fruit waste is 94.25%. BOD is reduced from 71 to 29 ppm and COD is reduced from 1056 to 321 ppm. The order of reaction was found out by plotting a graph between $-r_A$ and C_A . From the graph we can say that reaction is of first order and the rate constant is calculated from the values of $-r_A$ and C_A and it is 0.0118 min^{-1} . The time required for the phosphate removal in pharmaceutical effluent was calculated by using batch reactor performance equation and the reaction required is found to be 3.91 hrs from the calculations and 4.2 hrs from the experiments performed. The standard error obtained from the experimental data is ± 0.275 .

Keywords: Phosphate, BOD, COD, Rate equation, Rate constant, Reaction time, Standard error.

I. INTRODUCTION

Removal of phosphate from wastewater by chemical precipitation and advanced biological treatment has been widely investigated. Phosphate discharged into the surface waters stimulates the growth of aquatic micro and macro organisms in nuisance quantities, which in excess can cause eutrophication in stagnant water bodies. Therefore, wastes containing phosphates must meet the discharge limits for phosphates [2]. Water bodies contain certain level of phosphorus in various compounds, which is an important constituent of living organisms [3]. 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 through industrial effluent to waters increases the concentration of phosphate, which leads to the extensive algae growth, these organisms use great amounts of oxygen and prevent sunlight from entering the water [4]. This makes the water fairly unliveable for other organisms. This phenomenon is commonly known as eutrophication. The algae die and decompose high level of organic matter. As a result the water bodies and fish die due to the depletion of available oxygen in water. Eutrophication is also a natural process that typically occurs as lakes age. However, human-caused, accelerated eutrophication (called "cultural eutrophication") occurs more rapidly, and causes problems in the affected water bodies, as described below [5]. It is estimated that 50-70% of all nutrients reaching surface water (principally N and P) originate on agricultural land as fertilizers or animal

waste. Urban and industrial runoff also contributes to eutrophication. Industrial effluent discharges mostly contribute to eutrophication. Too much phosphate can cause health problems, such as kidney damage, osteoporosis and hypophosphatemia. Phosphate should be removed from the effluent according to the standards [6].

II. MATERIALS AND METHODS

Kinetics of phosphate removal using column separation process:

It may be batch or continuous process depending upon the effluent and retention time. Mainly in column separation process adsorbent plays a vital role [7]. Adsorbent usually employed in column are silica, alumina, calcium carbonate, magnesia, starch etc. In this process CaCO_3 is used as adsorbent. Here in this experiment the retention time of CaCO_3 is high, so the process is done in batch.

For removing of phosphate from pharmaceutical effluent we are taking 100 ml of sample in column separation process. The phosphate concentration is estimated for every 10 min. The phosphate concentration is estimated from 10 min to till the sample is over. The phosphate concentration is decreased as the time increases. The below table- and graph explains the decrease in phosphate concentration. In this experiment column is used to know the kinetics of the phosphate removal with respect to time.

Rate equation:

The $-r_a$ versus C_a plot shows that the rate of reaction is low

when concentration phosphate is high. And the rate is high when the concentration of phosphate is low and we can also say that the reaction is of first order ($n = 1$) [8].

Theoretical reaction time required for the removal of phosphate:

The above all experiments are performed in a glass beaker by means of magnetic stirring which means it is a batch reactor. So, we use the batch reactor equation to find out the theoretical reaction time required for the removal of phosphate from the pharmaceutical effluent[9].

Determination Of Biological Oxygen Demand (Bod)

The BOD in a water sample is directly related to the extent of pollution by sewage or other oxygen demanding waste. If the oxygen in water is less than Biological Oxygen Demand, the decomposition of microorganisms takes place anaerobically (in absence of oxygen) and hence produces highly objectionable end products including H_2S , NH_3 and CH_4 .

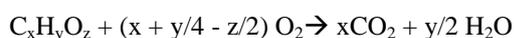
Therefore sufficient oxygen must be present or supplied externally to maintain aerobic conditions so that organic matter decomposes into acceptable products. To know the amount to oxygen required by the given sample, the determination of BOD is necessary[15].

Polluted waters will continue to absorb oxygen for many months, till the oxidation gets completed and hence it is not practical to determine this ultimate oxygen demand which would require an extended period of time. As a result, it has become standard practice to simply measure the oxygen over a shorter period of 5 days [11]. This is known as 5-day BOD test. BOD_5 is the total amount of oxygen consumed by microorganisms during the first five days of biodegradation.

Chemical Oxygen Demand (Cod)

The chemical oxygen demand is defined as the amount of oxygen used while oxidizing the organic matter content of a sample with a strong chemical oxidant under acidic conditions.

A known amount of $K_2Cr_2O_7$ is added to the measured amount of the sample and mixture is boiled with concentrated sulphuric acid [12]. The organic matter gets completely oxidized to produce CO_2 and H_2O .



The excess of $K_2Cr_2O_7$ remained after the reaction is titrated against standard Mohr's salt solution using Ferrion as indicator [13]. The dichromate consumed is calculated which gives oxygen required for the oxidation of organic matter.

III. RESULTS AND DISCUSSIONS

Kinetics of phosphate removal using column separation process:

It is batch process, depending upon the effluent and retention time. Mainly in column separation process adsorbent play vital role. Adsorbent usually employed in column are silica, alumina, fruit waste, magnesia, starch etc. In this process fruit waste is used as an adsorbent.

Here in this experiment, the retention time of fruit waste is high, so the process is done in batch [14].

For removal of phosphate from pharmaceutical effluent, we have taken 100 ml of sample and subjected to column separation process. The phosphate concentration was estimated for every 10min. The phosphate concentration was estimated from 10 min. to till the end of sample volume. The phosphate concentration was decreased as the time progress. The below Figure 1 depicts the decrease in phosphate concentration. In this experiment, column is used to know the kinetics of the phosphate removal with respect to time.

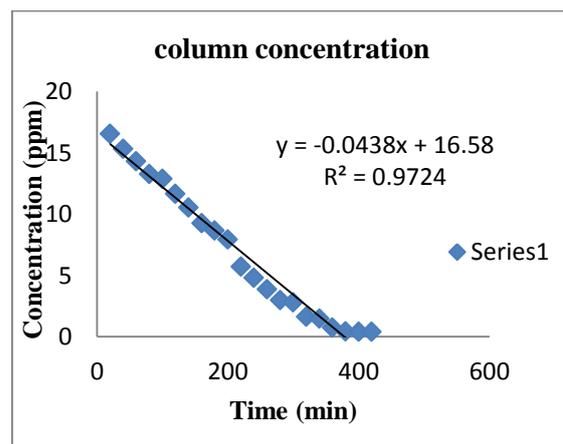


Figure-1: Concentration of Phosphate versus Time

Modeling of phosphate removal by using column separation process:

To describe the removal of phosphate in effluent using chemical precipitation process, a modeling equation was developed. The highest percentage removal of phosphate was found to be 97.45 % from the optimized conditions. The final form of the proposed model equation for the removal of phosphate is

$$Y_p = -0.843t + 160.3$$

Where, Y_p = Concentration of phosphate, ppm
 t = Time, min

The model showed good agreement with experimental data by R^2 value of about 0.962 in removal of phosphate from pharmaceutical effluent using chemical precipitation

Removal efficiency:

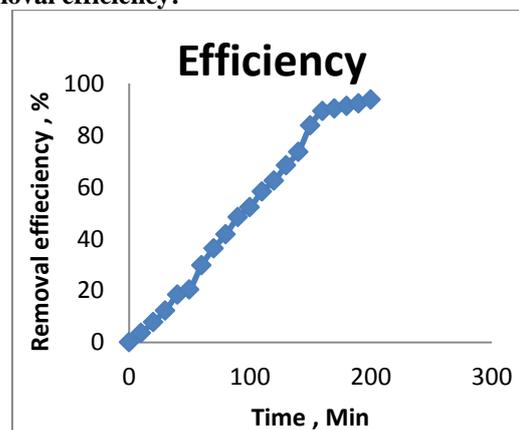


Figure-2: Removal efficiency of phosphate versus Time

As the time proceeds, the phosphate concentration in the effluent decreased and removal efficiency increased. Removal efficiency is calculated by taking the ratio of difference concentration to the initial concentration. From the optimized conditions, the percentage removal of phosphate was found to be 94.45% and it remained constant. The results are shown in Figure 2.

Rate equation:

The $-r_A$ versus C_A plot shows that the rate of reaction is low when concentration of phosphate is high. And the rate is high when the concentration of phosphate is low and we can also say that the reaction is of first order ($n = 1$). The plot and the values are shown in the below Figure 3.

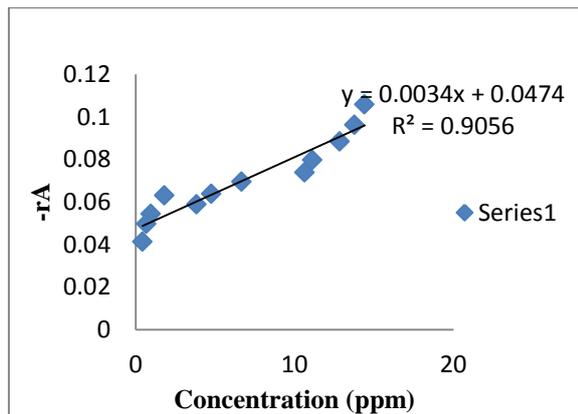


Figure-3: $-r_A$ versus Concentration of phosphate

Reaction time required for the removal of phosphate:

The above all experiments were performed in a glass beaker by means of magnetic stirring as a batch reactor. So, we use the batch reactor equation to find out the reaction time required for the removal of phosphate from the pharmaceutical effluent [14].

For the first order reaction the rate equation is $-r_A = k C_A$

The performance equation for the batch reactor is $\ln \frac{C_{A0}}{C_A} = k t$

Where, C_{A0} is the initial concentration of phosphate, ppm
 C_A is the final concentration of phosphate, ppm
 k is the rate constant, min^{-1}
 t is theoretical reaction time, min

We can get the k value from slope of the $-r_A$ versus C_A plot and we get,

$$k = \frac{0.0884 - 0.1059}{12.96 - 14.31}$$

$$K = 0.01185 \text{ min}^{-1}$$

Substituting the above k value in the performance equation gives the time required for the phosphate removal,

$$\ln \frac{16.54}{0.413} = 0.01185t$$

$$t = 234.64 \text{ min}$$

$$t = 3.91 \text{ hrs}$$

Therefore, the reaction time required for the phosphate removal from the pharmaceutical effluent was

found to be 3.91 hrs from the above calculations and 4.2 hrs from the experiments performed. The standard error obtained from the experimental data is ± 0.275 .

Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD):

In this process the BOD and COD test is conducted to effluent water in the starting of the process and after the completion of the process. The results are shown in Table 1 in this process the BOD is reduced from 52 ppm to 28 ppm and COD is reduced from 1045 ppm to 279 ppm

Table-1: Effect of BOD and COD

Pharmaceutical Effluent	BOD, ppm	COD, ppm
Initial	71	1056
Final	29	321

IV. CONCLUSION

For the removal of phosphate, a modeling equation is developed to know the phosphate removal with respect to time. The proposed model equation for the removal of phosphate is $Y_P = -0.0438x + 16.58$ and the model showed good agreement with experimental data and is significant compared to other methods in the removal of phosphate from pharmaceutical industry. And the phosphate removal efficiency from obligate aerobes derived from fruit waste was 94.45% under optimized conditions.

At the same time, the water quality parameters Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were also estimated and were found to be initial effluent water was 71 ppm and 1056 ppm respectively. After the phosphate removal, the parameters obtained were 29 ppm and 321 ppm respectively.

From the $-r_A$ versus C_A plot we found that the reaction is a first order reaction ($n=1$) and the rate constant, k is 0.01185min^{-1} . The time for the removal of phosphate is calculated by using the batch reactor performance equation and the reaction time required for the phosphate removal from the pharmaceutical effluent is found to be 3.91 hrs from the above calculations and 4.2hrs from the experiments performed. The standard error obtained from the experimental data is ± 0.275 .

REFERENCES

1. CHEN Xuechu, Kong Hainan, Wu Deyi, Wang Xinze, Lin Yongyong, "Phosphate removal and recovery through crystallization of hydroxyapatite using xonotlite as seed crystal" in *Journal Environmental Sciences*, vol. 21, pp 575–580, 2009.
2. Dr. EhssanNassef, "Removal of Phosphates from Industrial Waste Water by Chemical Precipitation" in *Iracst – Engineering Science and Technology: An International Journal (Estij)*, vol. 2, no. 3, 2012.
3. Sawsan A. M. Mohammed and Haider Abbas Shanshool, "Phosphorus Removal from Water and Waste Water by Chemical Precipitation Using Alum and Calcium Chloride" in *Iraqi Journal of Chemical And Petroleum Engineering*, vol. 10, no. 2, pp 35-42, 2009.
4. J.M. Chimenos, A.I. Fernandez, G. Villalba, M. Segarraa, A. Urruticoechea, B. Artaza, F. Espiell, "Removal of ammonium and phosphates from wastewaterresulting from the process of cochineal extraction using MgO-containing by-product" in *Journal of Water Research*, vol. 37, pp 1601–1607, 2003.

5. Michael J. Baker, David W. Blowes and Carol J. Ptacek, "Laboratory Development of Permeable Reactive Mixtures for the Removal of Phosphorus from Onsite Wastewater Disposal Systems" in *Journal Of Environmental Science Technology*, vol. 32, pp 2308-2316,1998.
6. Barbara Grzmil, Jaroslaw Wronkowski, "Removal of phosphates and flourides from industrial waste water" in *Journal of Desalination*, vol. 189, pp 261-268,2006.
7. MbarkaGouider, MongiFeki and Sami Sayadi, "Treatment of Wastewaters from Phosphate Fertilizer Industry" in *Journal of Environmental Progress & Sustainable Energy*, vol. 33, no. 2, 2014.
8. Maya R. Unnithan, V. P. Vinod, T. S.Anirudhan, "Ability of Iron(III)-Loaded Carboxylated Polyacrylamide-Grafted Sawdust to Remove Phosphate Ions from Aqueous Solution and Fertilizer Industry Wastewater: Adsorption Kinetics and Isotherm Studies" in *Journal of Applied Polymer Science*, vol. 84, pp 2541–2553, 2002.
9. E. Klimiuk, U. Filipkowska, B. Libecki, "Coagulation of Wastewater Containing Reactive Dyes with the Use of Polyaluminium Chloride (PAC)" *Polish Journal of Environmental Studies*, vol. 8, no. 2, pp 81-88, 1999.
10. A.H. El-Shazly, M.A. Daous, "Kinetics and Performance of Phosphate Removal from Hot Industrial Effluents Using a Continuous Flow Electrocoagulation Reactor", in *INT. J. ELECTROCHEM. SCI.*, VOL. 8, pp 184 – 194, 2013.
11. Safaa M. Ragheb, "Phosphate removal from aqueous solution using slag and fly ash" in *Hbrc Journal*, vol. 9, pp 270–275, 2013.
12. A. Negrea, L. Lupa, P. Negrea, M. Ciopec and C. Muntean, "Simultaneous Removal of Ammonium and Phosphate Ions from Wastewaters and Characterization of the resulting Product" in *Journal of Chemical Bulletin of Politehnica University of Timisoara, Romania Series of Chemistry And Environmental Engineering*, vol. 55, no. 69, 2010.
13. Jing Chen and Zhaokun Luan, "Enhancing phosphate removal by coagulation using polyelectrolytes and red mud" in *Journal of Fresenius Environmental Bulletin*, vol. 19, no. 10, 2010.
14. Zhipan Wen, Yalei Zhang, ChaomengDaib, "Removal of phosphate from aqueous solution using nanoscalezerovalent iron (nZVI)" in *Journal of Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 457, pp 433–440, 2014.
15. KeXu, Tong Deng, Juntan Liu, WeigongPeng, "Study on the phosphate removal from aqueous solution using modified fly ash" in *Fuel*, vol. 89, pp 3668–3674, 2010.

BIOGRAPHIES



Kasi Pradgna M.Tech., Department of Chemical Engineering, Andhra University College of Engineering (A), Andhra University, Visakhapatnam, Andhra Pradesh, India. She published 3 more Papers published in National and International Reputed

Journals.



Sunil Kanamarlapudi, M.Tech, Department of Chemical Engineering, Andhra University College of Engineering (A), Andhra University, Visakhapatnam, Andhra Pradesh, India. he published 3 more Papers published in National and International Reputed Journals



Meena Vangalapati M.Tech., Ph.D, Associate Professor, Department of Chemical Engineering, Andhra University College of Engineering (A), Andhra University, Visakhapatnam, Andhra Pradesh, India. She has 14 years of teaching experience and published 75 more Papers published in

National and International Reputed Journals, published 10 monographs/Books and also published 3 patents.