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Development of Modeling Equation and Kinetics of Phosphate Removal from Pharmaceutical Effluent

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Abstract- Phosphates are the naturally occurring form of the element phosphorus, found in many phosphate minerals. 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. A modeling equation was developed to known the phosphate removal with time. The proposed model equation for the removal of phosphate is $Y_P = -0.843t + 160.3$ and the model showed good agreement with experimental data (chemical precipitation method) and is significant compared to other methods in the removal of phosphate from pharmaceutical industry using chemical precipitation process. And the phosphate removal efficiency was with $CaCO_3$ is 97.45%. BOD is reduced from 74 to 28 ppm and COD is reduced from 1045 to 279ppm. 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 0.0303min^{-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 2.03hrs from the calculations and 2.5hrs from the experiments performed. The standard error obtained from the experimental data is ± 0.235.
Keywords: Phosphate, BOD, COD, Rate equation, Rate constant, Reaction time, Standard error.

I. INTRODUCTION

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 (CHEN Xuechu et al.,2009). 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(Dr. Ehssan Nassef, 2012). 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 once. In testing for cultural eutrofication, one should expect to find an algal bloom or scum on the water accompanied by a fishy smell to the water and low dissolved oxygen content.
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.

Removal of phosphate has been largely studied, at present chemical precipitation is used for removal (Sawsan A. M. Mohammed, 2009)(J.M. Chimenos et al., 2003).

II. EXPERIMENTAL PROCEDURE FOR KINETICS OF REMOVAL OF PHOSPHATE BY USING COLUMN STUDIES

An appropriate quantity of cotton was kept at bottom of the column to reduce the loss of $CaCO_3$. Here we use a batch process because the settling time of $CaCO_3$ is fast, so in batch process itself we got results. In the column, adsorbent used is $CaCO_3$ and it

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was done under optimized conditions (Michael J. Baker et al., 1998).

Initially 100ml of pharmaceutical effluent is taken into the column as batch process. In the column constant flow rate is maintained, for every ten minutes sample is collected and collected sample is taken to calculate phosphate concentration and % removal of phosphate. The removal of phosphate was done under optimized conditions. The parameters we optimized are dosage of $CaCO_3$ - 7.0gm, pH- 8.0, dosage of Alum -0.8gm are maintained for knowing the kinetics of the phosphate removal.

III. MODELING OF PHOSPHATE REMOVAL

In order to describe the phosphate removal from the effluent water the following hypothesis were used. The removal of phosphate is done under atmospheric conditions. The final form of modeling equation was obtained from the kinetics of phosphate removal

$$Y_P = m\,t + c$$

Where,

Y_P = Concentration of phosphate, ppm

t = Time, min

m = Slope and

c = Intercept

IV. RESULTS AND DISCUSSION

A. *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, calcium carbonate, magnesia, starch etc. In this process $CaCO_3$ is used as an adsorbent. Here in this experiment, the retention time of $CaCO_3$ is high, so the process is done in batch.

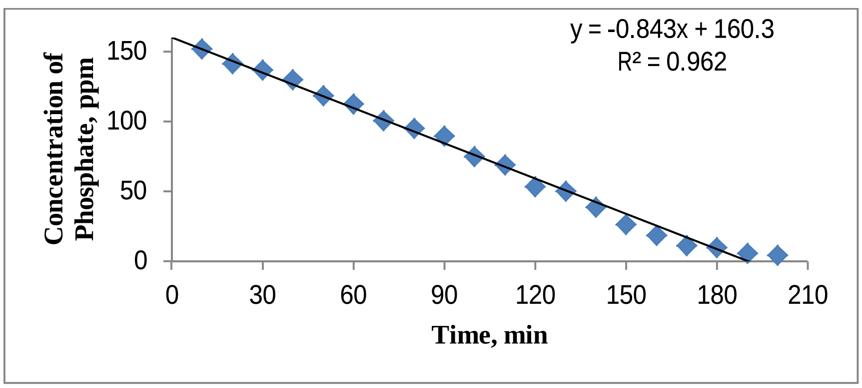

Figure-1: Concentration of Phosphate versus Time

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 above 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.

B. *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

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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.

C. Removal Efficiency

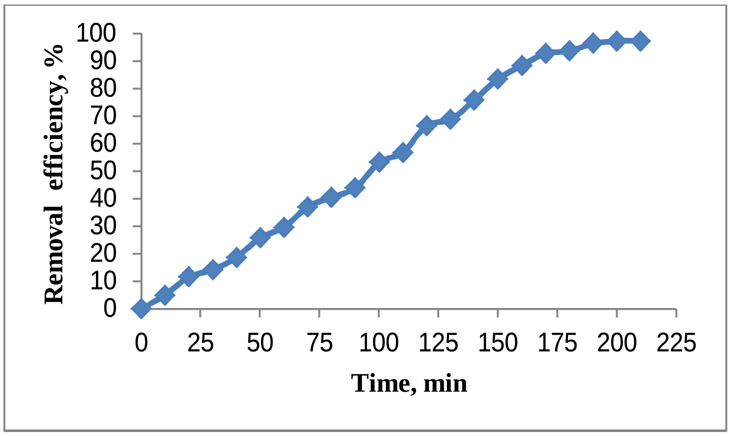

Figure-2: Removal efficiency of phosphate versus Time

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 97.45% and it remained constant. The results are shown in above Figure 2.

D. Rate Equation

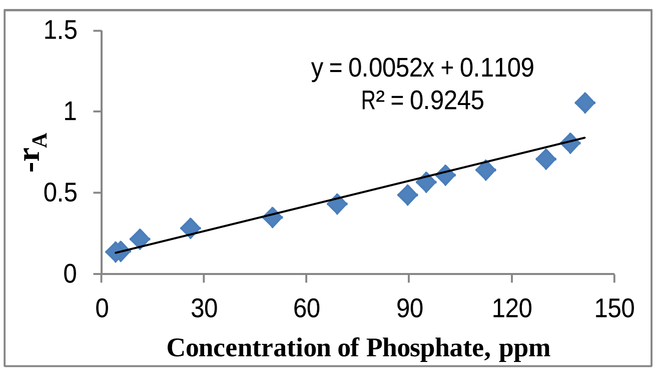

Figure-3: $-r_A$ versus Concentration of phosphate

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 above Figure 3.

E. 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

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reactor equation to find out the reaction time required for the removal of phosphate from the pharmaceutical effluent.

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_{Ao} 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,

$$k = \frac{0.713 - 1.058}{129.96 - 141.31}$$

$$K = 0.0303 min^{-1}$$

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

$$\ln\frac{160.01}{4.07} = 0.0303t$$

$$t = 122.386\ min$$

$$t = 2.03 hrs$$

Therefore, the reaction time required for the phosphate removal from the pharmaceutical effluent was found to be 2.03 hrs from the above calculations and 2.5 hrs from the experiments performed. The standard error obtained from the experimental data is ± 0.235.

F. 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	74	1045
Final	28	279

V. 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 $Y_P = -0.843t + 160.3$ and the model showed good agreement with experimental data (chemical precipitation method) and is significant compared to other methods in the removal of phosphate from pharmaceutical industry. And the phosphate removal efficiency with $CaCO_3$ observed was 97.45% 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 74 ppm and 1045 ppm respectively. After the phosphate removal, the parameters obtained were 28 ppm and 279 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 $0.0303 min^{-1}$. 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 2.03 hrs from the above calculations and 2.5 hrs from the experiments performed. The standard error obtained from the experimental data is ± 0.235.

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