

A BATCH STUDY OF P HOSPHATE ADSORPTION CHARACTERISTICS ON CLAY SOIL

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Abstract

The research has been carried out on Phosphate (p-Adsorption) on clay soil through batch adsorption techniques. Main objectives of this study are to study the physical properties of clay soils, detection of Phosphate removal by adsorbent as a function of contact time, adsorbent dosage and p^H , to study sorption kinetics. The results of this study shows the optimum contact time, dosage and p^H for adsorption of Phosphate on clay soil reaching the equilibrium condition after 60 minutes with removal efficiency of 86% and 1400 mg as optimum dosage. Higher adsorption of Phosphate was observed at p^H 9.0. The rate of adsorption of Phosphate obeys first order rate equation. The obtained results of the batch experiments are best fit to Langmuir and Freundlich adsorption isotherms. From the experimental analysis it is concluded that clay soil shows good removal efficiency and can be used as good adsorbents.

Keywords: P-Adsorption, characteristics, Batch Experiments, Freundlich Isotherm, Langmuir Isotherm.

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1. INTRODUCTION

The major environmental concerns of 21st century are waste disposal from various industries, municipal dumping in the urban areas and increased use of chemical fertilizers, pesticides and irrigation water. The residues of fertilizers, pesticides and irrigation water created adverse impact on soil and water bodies. The pollutants such as sewage and fertilizers contain nutrients as phosphates and nitrates. If the nutrients are in excess level they over stimulate the growth of aquatic plants and algae. These excessive growths of algae and aquatic plants clogs the water ways, use up dissolved oxygen as they decompose and block light to deeper water affecting the respiration ability of fish and other invertebrates that reside inside the water. Lakes, rivers and other water bodies undergo Eutrophication an aging process in natural condition that slowly fills in the water body with sediment and organic matter. These sediments when enter water bodies fish respiration becomes impaired, plant productivity and water depth becomes reduced and aquatic organisms and their environment becomes suffocated. When the levels of oxygen drops below two-five parts per million many types of fish and bottom dwelling animals cannot survive. When this occurs it leads to the disruptions in the food chain by killing aquatic organisms in large numbers. Oxygen demanding materials such as nitrogen and phosphorous are high in animal wastes and they often harbor pathogenic organisms. Hence some special attention must be given for budgeting of fertilizers; Phosphorous in high doses may be susceptible to drain freely in the soil immediately followed by heavy rainfall causes some phosphorous losses through volatilization and leaching

process. Thus once the ecosystem are contaminated by these elements they become a potential threat for many years. Therefore it is of crucial importance to study the mutual influence of the different minerals in soil retention process whose migration ability of particular component in ground water is explained by the retardation factor(R).Farmers extensively follow the irrigation process due to availability of water from various sources, where phosphate pollution is caused by the use of fertilizers and pesticides. Thus the main objective of this work is to study the leaching and retention of phosphate in the clay soil available in the area used for agricultural process, determining the maximum amount of phosphate adsorbed and to evaluate the potentials of phosphate migrating through the soil during ground water percolation by using a set of batch experiments whose results are fitted to the equations given by Langmuir and Freundlich isotherms.

Ayyaz Mehamood et.al studied, the Understanding of soil phosphorous (P) adsorption chemistry is essential for evolving best fertilizer management practices aimed at enhancing fertilizer P use efficiency and environment quality. Soil chemical parameters which govern P adsorption maxima and binding strength in calcareous and non-calcareous soils were determined. Five soils representing three different parent materials, i.e. mixed mineralogy alluvium, loess and non-calcareous sandstone were sampled at genetic horizons in each profile. Phosphorous adsorption isotherm was developed for each of the 32 soil samples by equilibration of 2gm air dry soil with 0 to 4000 mg l⁻¹(0 to 125 mM) P in 20 ml of 10 mM Kcl are fitted to Langmuir and Freundlich equations. The chemical

parameters i.e. pH, CaCO_3 , total and dissolved organic carbon, exchangeable calcium, dithionite extractable iron (Fe_d) and aluminium (Al_d), oxalate extractable iron (Fe_o) and aluminium (Al_o) and as a test for plant available p extractable with NaHCO_3 were determined. The Freundlich equation, the empirical relation between adsorbed and solution p fitted the adsorption isotherm better than the Langmuir equation which relates adsorption to solid surface coverage by adsorbate.. The Freundlich parameter adsorption exponent which signifies sorption intensity also positively correlated with soil Fe_d , Fe_{cr} and Al_d contents. Phosphorous adsorption at its low concentration in equilibrium solutions seems to be governed by soils iron oxide and precipitation as CA-P is important only at high P concentration which is less frequently achieved in farm fields.

2. EXPERIMENTAL SET UP AND PROPERTIES OF MATERIALS USED

Phosphate retention characteristic of selected soil were measured by laboratory batch experiments. In this experiment different concentration of adsorbate used for the soil of same quantity and maximum phosphate adsorption capacities (Q) are calculated using Langmuir and Freundlich isotherm models.

2.1 Test Set Up

The typical batch test set up typically consists of the following process: 10 gram of soil sample has been put into 250 ml conical flask and then, 100 ml of a solution has been added into the flask. All the 4 concentrations used for tracers were 5, 10, 15 & 20 mg/L. intermediate phosphate solution has been used. The soil suspension has been shaken for 12 hours at constant temperature and left without shaking for additional 24 hours. The suspension was then filtrated through a wattman No.1 filter and the effluent was analyzed. The adsorbed amount, Q was calculated

$$Q = \frac{v\Delta C}{M} \quad \text{-----} \quad (1)$$

Where
 Q = adsorbed amount (mg/kg)
 ΔC = difference in metal concentration before and after the experiment (mg/L)
 V = volume of solution 100 ml.
 M = mass of soil 0.01kg.

2.2 Properties of Materials Used

Phosphate retention characteristic of selected soil were measured by laboratory Batch experiments. In this experiment an adsorbate of different concentrations were used for the soil of same quantity and kept in contact for a particular time and maximum phosphate adsorption capacities (Q) are calculated using Langmuir and Freundlich isotherm models.

Clay soil samples were collected from different locations of available region. The samples are moderately acidic in nature.

Table 1: Properties of materials used

Characteristics	Clay soil
p ^H	9
Silt & Clay fraction (%)	88.66
Sand fraction	11.34
Gravel fraction	0
Soil bulk density (kg/m ³)	1173.3
Porosity	0.4
Soil texture	Clay

2.3 Batch Sorption Experiment

A predetermined amount of adsorbent is mixed with the sample in a batch experiment. For a given contact period the sample is agitated on a rotary shaker and subsequently separated by filtration. For the batch type contact process powdered adsorbent is more suitable. Phosphate removal affinity of clay soil is determined by batch experiments such as contact time, dosage of the adsorbent, p^H, and kinetics of phosphate removal.

2.4 Selection of Optimum Contact Time

The contact time strongly influences the adsorption, for this study an 100 ml phosphate solution of 5mg/L was mixed with 1000gm of soil sample and stirred for different period of contact time i.e. for 1hr and time interval varies as 3,5,10,15.....60min .This is filtered and analyzed for phosphate concentration using spectrophotometer method.

2.5 Determination of Optimum Dosage of Adsorbent

Adsorbents were added to the conical flask containing known concentration of phosphate solution (5mg/L) to determine the optimum dosage of adsorbent. The solution in the conical flask was subjected to stirring for optimum contact time and the dosage varies from 200, 400, 600.....1400mg/L. Filtered and analyzed for residual and removal of phosphate concentration. The dosage which gives minimum residual concentration is chosen as optimum dosage.

2.6 Determination of Optimum p^H

A series of conical flasks were taken with 100ml of 5mg/L phosphate solution to determine the optimum p^H. Optimum dosage of soil (5mg/100ml) is added .The p^H of the flasks was adjusted ranging from 4.0 to 10.0. The flasks were shaken on a rotary shaker for optimum contact time. After stirring the samples are filtered and analyzed for the residual phosphate concentration. The flask which gives minimum residual concentration is selected as the optimum p^H.

2.7 Sorption Kinetics

The beakers containing 100ml of phosphate solution of concentration 5mg/l and known amount of soil sample were stirred. The samples were withdrawn at different time intervals and filtered supernatant were analyzed.

2.8 Langmuir and Freundlich Isotherms

Adsorption isotherms are developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying amounts of adsorbate. The general form of Freundlich equation is shown Eqn. 2.

$$q = \left(\frac{x}{m}\right) = K C^{\frac{1}{n}} \tag{2}$$

Where

(x / m) = Amount of solute adsorbed per unit mass of adsorbent in mg/g.

C = Equilibrium concentration of adsorbate in solution after adsorption in mg/l.

K = Freundlich capacity factor and

(1/n) = Freundlich intensity factor.

The constants K and n in the Eqn. 2 can be evaluated by plotting amount of solute adsorbed per unit mass of adsorbent versus equilibrium concentration of adsorbate in solution after adsorption on a double logarithmic graph. The Freundlich equation is basically empirical but is often useful as means for data description. Data are usually fitted to the logarithmic form of equation.

$$\log_e (x/m) = \log_e K + 1/n \log_e C \tag{3}$$

The Langmuir equation is commonly written as shown in Eqn. 4.

$$q = \left(\frac{x}{m}\right) = \frac{abc}{1+bc} \text{ (Or) } \frac{c}{x/m} = \frac{1}{ab} + \frac{c}{a} \tag{4}$$

Where

q = Amount of solute adsorbed per unit mass of adsorbent in mg/g.

C = Equilibrium concentration of adsorbate in solution after adsorption in mg/l and a and b are Langmuir constants related to capacity and energy of adsorption respectively. Plot of C/(x/m) Vs C would give the value of constants. A dimensionless equilibrium parameter called separation factor, R is use to study the applicability of Langmuir adsorption isotherm.

$$R = \frac{1}{(1+a) C_0} \tag{5}$$

Where

a = Langmuir constant

C₀ = Initial concentration.

From the above equation Webber and Chakarvarthi given parameter indicating the shape of the isotherm are as follows:

Values of R	Type of isotherm
R>1	unfavorable
R=1	linear
0<R<1	favorable
R=0	irreversible

3. RESULTS AND DISCUSSIONS

3.1 Effect of Contact Time

Contact time has great influence on the adsorption process. The effects of contact time on the adsorption of phosphate were shown in Fig. 2. From the graph it is observed that the extent of phosphate adsorption increases with increase in time and attain equilibrium at particular time. The adsorption curves are characterized by sharp rise initial stage and decrease near equilibrium. From the graph after equilibrium further increase in time adsorption is not changing hence the optimum contact time for clay soil is 60 mins.

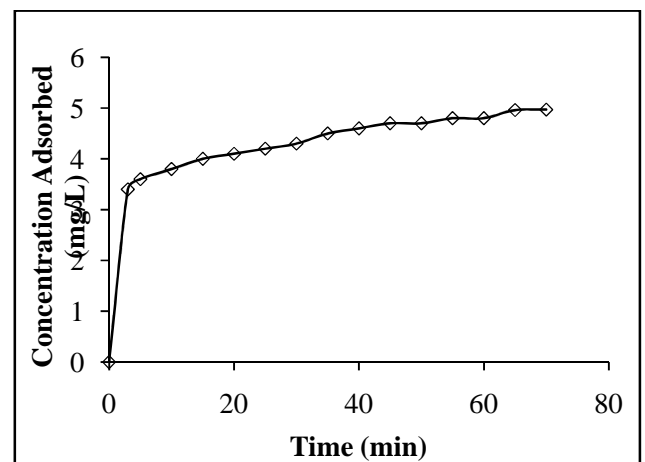


Fig. 2 Effect of contact time of phosphate on clay soil

3.2 Effect of Adsorbent Dosage

Adsorption is a process in which there is continuous transfer of solute from solution to adsorbent until residual concentration of solution maintains equilibrium with that adsorbed by the surface of adsorbent at constant contact time. Effect of adsorbent dosage is studied and graph of phosphate removal verses dosage is plotted as shown in Fig. 3. From the graph it is observed that, as the dose of clay soil increases, amount of residual phosphate decreases sharply and attains minimum. The point where maximum removal is attained is taken as optimum dosage i.e. 1400mg/L. After this, not much change in adsorption is observed even after increase in the amount of different soil.

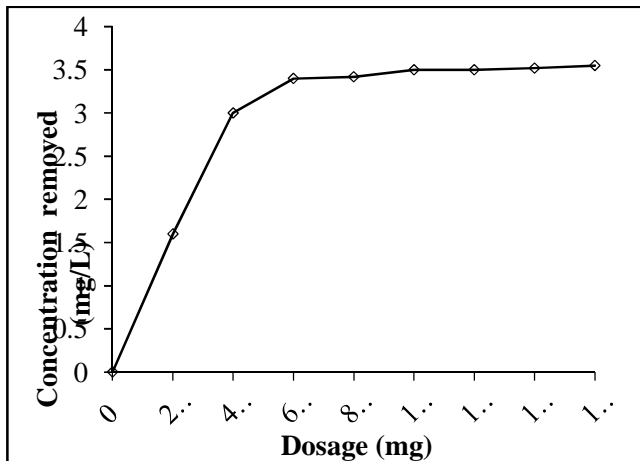


Fig. 3 Adsorbent dosage of phosphate on clay soil

3.3 Effect of pH

The impact of phosphate removal depends on pH of the medium. The graph of pH against phosphate removal at constant time and dosage is shown in Fig. 4, the values of pH and corresponding phosphate adsorbed are shown from the graph, phosphate removal not only depends on surface area, time and dosage but also depends on pH and the pH attains equilibrium at 9.0 therein no increase or decrease takes place.

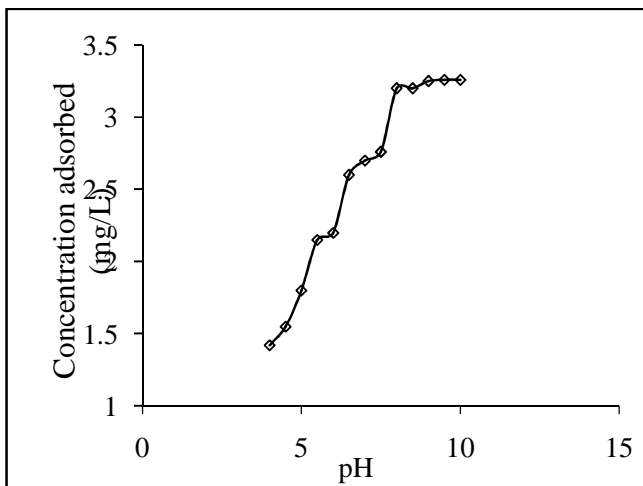


Fig. 4 Effect of pH of phosphate on clay soil

3.4 Single Adsorption of Phosphate Clay Soil

The batch experiments were carried out on clay soil with the tracer concentrations of 5, 10, 15 and 20 mg/L respectively. Table 2 shows the results of the Phosphate test on clay soil to fit the results to the Langmuir isotherm. The results are plotted as shown in Fig 5 and are fit to Eqn (4) which gives

$\frac{1}{Q} = 0.095 \frac{1}{C} + 0.001$, where the regression coefficient $R=0.993$; from the fit we obtained maximum adsorption and Langmuir constants, $a = 12.80$ and $b = 0.035$.

Table 2: Single adsorption of Phosphate on clay Soil

C mg/L	Q mg/kg	1/C	1/Q
5.0	49.0	0.2	0.02040
10.0	90.4	0.1	0.01106
15.0	119.2	0.066667	0.00838
20.0	182.4	0.05	0.00548

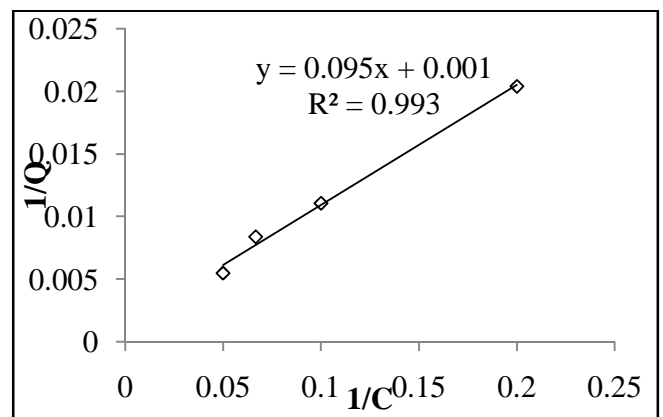


Fig.5 Single adsorption of Phosphate on clay Soil for Langmuir isotherm

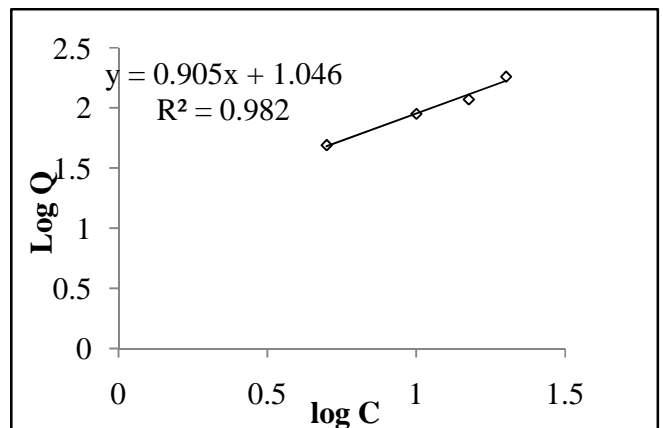


Fig.6 Single adsorption of Phosphate on clay Soil for Freundlich isotherm

The same experimental results (Table 2) are fit to Freundlich power equation given by Eqn 2, by plotting 'Q' vs. 'C' as shown in above Fig. 6 and fitting we obtain $(1/n) = 4.66$ and $K_F=0.91$.

Where, $q_e = (x/m)$ = Amount of solute adsorbed per unit mass of adsorbent in mg/kg,

C_e = Equilibrium concentration of adsorbate in solution after adsorption in mg/L,

K_f = Freundlich capacity factor and $1/n$ = Freundlich intensity factor.

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CONCLUSIONS

In the laboratory a series of batch experiments have been performed for adsorption of Phosphate in clay soil whose results are fit with analytical isotherms. The conclusions from the study can be summarized as follows:

It's evident from the characteristics properties that clay soil is a good adsorbent for removing Phosphate and these adsorbents are easily and cheaply available. Kinetic study indicated that adsorption of Phosphate is very rapid up to and decrease while approaching equilibrium. In batch experiments studies adsorption of Phosphate follows Freundlich and Langmuir isotherms indicating single adsorption of Phosphate and proves to be a favorable adsorption. Batch experiment results have clearly shown that clay soil has shown maximum adsorption for Phosphate.

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