

A study of Phosphate Adsorption characteristics on different soils

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ABSTRACT: - In this research, adsorption of Phosphate (p-Adsorption) on Black cotton Soil and Red soil has been studied through using batch adsorption techniques. Main objectives of this study are, to study the physical properties of Black cotton soil and Red soil, detection of Phosphate removal by adsorbent as a function of contact time, adsorbent dosage and pH, to study sorption kinetics, to study column tracer experiment and isothermal pattern. The results of this study showed that the Optimum contact time, dosage and pH for adsorption of Phosphate on Black cotton soil and Red soil reached to equilibrium after 55mins and 60mins, with removal efficiency of (86%), 1000mg and 1200mg (66% and 70%) as optimum dosages. Higher adsorption of Phosphate was observed at higher pH, obtained at pH 8.0 and 8.5, (62.5% and 64%). The rate of adsorption of Phosphate obeys first order rate equation. The obtained results of the batch and column experiments are best fit to Langmuir and Freundlich adsorption isotherms. From the experimental analysis it is concluded that Black cotton soil and Red soil shows good removal efficiency and hence can be used as adsorbents.

Keywords: - P-Adsorption, characteristics, Batch Experiments, Freundlich Isotherm, Langmuir Isotherm, Column tracer experiments

I. INTRODUCTION

For the first time in this entire cultural history, man is facing one of the most horrible ecological crises - the problem of pollution of his environment, which in the past was pure, virgin, undisturbed, uncontaminated, and basically quite hospitable for him ^[1]. Waste disposal from various industries, municipal dumping in the urban areas and increased use of chemical fertilizers, pesticides and irrigation water are of great environmental concern. The residues of fertilizers, pesticides and irrigation water in one hand, increased agricultural production; while, on the other hand, created adverse impact on soil and water bodies ^[1]. Many causes of pollution including sewage and fertilizers contain nutrients such as phosphates. In excess levels, nutrients over stimulate the growth of aquatic plants and algae. Excessive growth of these types of organisms consequently clogs our waterways, use up dissolved oxygen as they decompose, and block light to deeper waters. This, in turn, proves very harmful to aquatic organisms as it affects the respiration ability of fish and other invertebrates that reside in water. The pollution of lakes, rivers and streams with chemical contaminants has become one of the most crucial environmental problems within the 20th century. Waterborne chemical pollution entering rivers and streams cause tremendous amounts of destruction. Pollution is caused when silt and other suspended solids, such as soil, wash off plowed fields, construction and logging sites, urban areas, and eroded river banks when it rains. Under natural conditions, lakes, rivers, and other water bodies undergo Eutrophication, an aging process that slowly fills in the water body with sediment and organic matter. When these sediments enter various bodies of water, fish respiration becomes impaired, plant productivity and water depth become reduced, and aquatic organisms and their environments become suffocated. Pollution in the form of organic material enters waterways in many different forms as sewage, as leaves and grass clippings, or as runoff from livestock feedlots and pastures. When natural bacteria and protozoan in the water break down this organic material, they begin to use up the oxygen dissolved in the water. Many types of fish and bottom-dwelling animals cannot survive when levels of dissolved oxygen drop below two to five parts per million. Animal wastes are high in oxygen demanding material, nitrogen and phosphorus, and they often harbor pathogenic organisms. Wastes from commercial feeders are contained and disposed of on land; their main threat to natural waters, therefore, is from runoff and leaching. ^[2]

The budgeting of phosphorus fertilizer has received less attention than nitrogen fertilizer. The high doses of phosphorus applied to freely draining soil immediately followed by heavy rainfall causes some phosphorus losses through volatilization and leaching processes ^[3]. Phosphorus fertilizer loss is heavily implicated in water course pollution and freshwater Eutrophication. Thus once ecosystems are contaminated by these elements, they become potential threat for many years. Their accumulation reduces soil fertility; soil microbial activity, and plant growth, as well as, the quality of agricultural products ^[1]. It is observed that when an element is applied to soil, some of it may be leached, some may be retained by the soil particles, some may be lost from the soil other than leaching loss, some may be incorporated by soil microorganisms or some may be taken up by plant.

In most cases, several contaminants are simultaneously released into the environment. Therefore, it is of crucial importance to study in detail the mutual influence of the different minerals in soil retention process. Soil has an important role in Phosphate accumulation, retarding the migration process, which influences further ground- and surface water contamination process.

The retardation factor (R) is one of the coefficients that describe the migration abilities of particular components in groundwater. It shows how many times the migration of the substance subjected to adsorption slower than the actual speed of water flow in pores ^[4]. The retardation factor can be evaluated by laboratory methods, determining the adsorption isotherms of the migrating substances, or by field observations of the speed of substance migration.

Due to availability of water from upper Krishna project irrigation is extensively followed by the farmers, where phosphates pollution is caused due to the use of fertilizers and pesticides. In our area available soils are Red soil, Black cotton soil. The objectives of the work are, to study the retention and leaching of different types of soils available in the area, mainly Red, BLACK COTTON soil. Determining the maximum amount of phosphate adsorbed under mono element condition, and to evaluate the potentials for these mineral to migrate through these soils during groundwater percolation. To perform a set of Batch experiments to obtain Retardation factors for Phosphate for the above mentioned two types of soils by fitting the experimental results to analytical equations given by Langmuir and Freundlich isotherms. To perform Colum Tracer experiments and to study the movement pattern by Break through curves of Phosphate on the two soils.

II. MATERIALS AND METHODS

Soil samples of two different series viz. Red & Black were collected from different locations of Bidar, as they are locally available in Bidar region. All the two soils are moderately acidic in nature. Red and Black Cotton series are developed on medium to moderately fine textured soils.

2.1 Soils Studied

2.1.1 Black soil



Figure 2.1. black cotton soil

Black soils are also known as regur soils. They are black in color as suggested by the name. The color of the soil is black because of the presence of certain salts. However, in some places, presence of humus in the soil imparts its black color. This soil becomes sticky when is wet owing to the high quantity of clay deposition. Black soils are generally thin and sandy in the hilly regions of the country. It does not contain adequate nitrogen but it contains sufficient phosphorus required for the growth of plants as shown in “Fig. 2.1”.

2.1.2 Red and Yellow soils



Figure 2.2 Red and yellow soils

Red and Yellow soils are found in areas, which receive low rainfall. They generally develop on metamorphic rocks. They contain huge concentration of iron oxides that are responsible for giving the reddish or yellow color as shown in “Fig. 2.2” They are less clayey and sandier and are poor in important minerals like lime phosphorous and nitrogen. Red soil is acidic like that of the Lateritic soil. This soil is mainly cultivated during the monsoon rainy season. Red soils also develop in Manipur, Shillong Plateau and Mizoram. [5]

2.2 Soil Characterization

The different soils namely Red, Black generally available in the area are collected and their physical and chemical parameters are determined. pH density and particle size distribution of the soils were determined and listed in “Table 2.1” The top soil of 10-20 cm was cleared and the samples of soil were collected by driving the cores into the soil. The samples were air dried and sieved through a 2.0 mm sieve then mixed thoroughly and stored for further Batch and Tracer column experiments.

Table2.1: Main Soil Characteristics [6]

Sl. No	Characteristics	Black cotton Soil	Red soil	Unit
1	Moisture content	7.39	5.23	%
2	Surface area	650	375	m ² /gm
3	Clay fraction silt fraction	75.64	60.24	-
4	Sand fraction	24.36	39.76	-
5	pH	7.5	7.6	-
6	Specific gravity	2.25	2.96	gm/m ³
7	Bulk density	1.538	1.76	gm/cm ³
8	Porosity	0.5	0.6	-

2.3 Adsorption Isotherms

Adsorption isotherms are developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying amounts of adsorbate. Equations that are often used to describe the experimental isotherm data were developed by Freundlich & Langmuir.

2.3.1. Freundlich Isotherm

Of the above mentioned isotherms Freundlich isotherm is used most commonly to describe the adsorption characteristics, derived empirically in 1912, the Freundlich isotherm is defined as follows in the below “Fig. 2.3”.

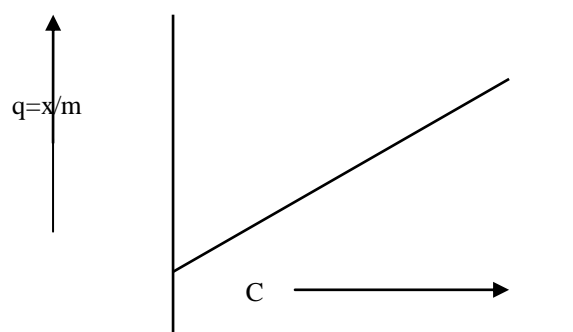


Figure 2.3. Linear form for graphical representation of Freundlich isotherm equation

The general form of Freundlich equation is,

$$q = \left(\frac{x}{m} \right) = KC^{\frac{1}{n}} \quad (1)$$

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 "equation (1)" 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.

$$\log_e (x/m) = \log_e K + 1/n \log_e C \quad (2)$$

As shown in the above, graph is plotted with log (x/m) to log C gives a straight line with a slope 1/n and intercept value (x/m) when C=1. Smaller value of 1/n points out a better adsorption mechanism and formation of relatively stronger between adsorbate and adsorbent. If 1/n<1, bond increases with surface density, if 1/n>1, bond decreases with surface density and if 1/n=1 surface sites are open in order to generate the equilibrium data (mg/L).

2.3.2. Langmuir Isotherm

Langmuir isotherm is based on the assumption that point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site

The Langmuir equation is commonly written as $q = \left(\frac{x}{m} \right) = \frac{abC}{1 + bC} \quad (3)$

$$\frac{C}{x/m} = \frac{1}{ab} + \frac{C}{a} \quad (4)$$

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 'q' 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. This is defined by Webber and Chakarvarthi

$$R = \frac{1}{(1 + a)C_0} \quad (6)$$

Where, a= Langmuir constant, C₀= initial concentration, R=Separation factor

From the above equation Webber and Chakarvarthi given parameter indicating the shape of the isotherm are as follow.

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

2.4 Determination of Phosphate

In acidic condition, orthophosphate reacts with ammonium molybdate to form molybdophosphoric acid. It is further reduced to molybdenum blue by adding reducing agent such as stannous chloride or ANSA. The intensity of the blue colored complex is measured which is directly proportional to the concentration of the phosphate present in the sample.

2.5 Column Tracer Experiments

To observe the retention and leaching of phosphate through soil, Soil columns of length 30 cm was used. For the column, glass column of 4 cm diameter was used. The length of the soil columns were chosen on the basis of soil texture and compaction. At the bottom, a height 6 cm was filled by sand. Outlets were made at the bottom of the column to collect the leachate. First the water was allowed to leach through the column to saturate the soil and then the phosphate solution was passed through the saturated soil, in single flow. The leachate was collected for every 1/2 hours and tested for phosphate concentrations. "Fig. 2.4" shows the column experimental arrangement.



Figure 2.4. Soil column equipment

For the preparation of tracer solution KH_2PO_4 had been used to obtain the following concentrations: 1000 mg/L of P. The column preparation has been based on manual soil compaction methodology^[7].

III. RESULTS AND DISCUSSIONS

A series of Batch and Tracer column experiments have been performed to determine the adsorption of Phosphates on the locally available soils: namely Red and Black cotton Soil. The experimental results obtained are compared to analytical adsorption equations to obtain retardation and adsorption parameter.

3.1 Results of Batch Experiments

The main objective of the batch experiments was to obtain the value of maximum adsorption capacity for each tracer in the locally available soils. For that purpose, and as the aim of the study was to analyze the adsorption phenomena, all batch experiments were done by adding the three tracers solution to each soil in different concentrations. For each soil, the five tracer concentrations have been used to perform the Batch experiments. Following results show the linear relation between $1/Q$ and $1/C$ used to obtain the values of Langmuir constants 'a' and 'k'. The results are also fit to Freundlich power equation to obtain the parameters ' K_f ' and ' C_e '.

3.2 Batch Sorption Experiments

3.2.1 Effect of contact time

Contact time has great influence on the adsorption process. The effects of contact time on the adsorption of phosphate on Black cotton soil & Red soil were shown in "Fig 3.1" respectively. 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 Black cotton soil is 55mins and Red soil is 60mins.

Initial concentration of phosphate $C_0=5\text{mg/L}$

Dosage=1000mg, 1200mg, Temperature= $32^\circ\pm 1^\circ$

pH=8.0, 8.5

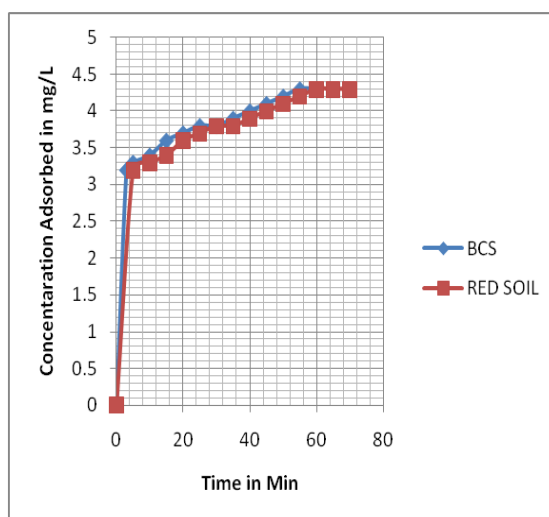


Figure 3.1. Effect of contact time of phosphate on black cotton soil & red soil

3.2.2 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 3.2 from the graph it is observed that, as the dose of Black cotton soil and Red soil increases, amount of residual phosphate decreases sharply and attains minimum. The point where maximum removal is attained is taken as optimum dosage. After this, not much change in adsorption is observed even after increase in the amount of different soil. Initial concentration of phosphate $C_0=5\text{mg/L}$, Dosage=1000mg, Contact Time=55min, 60min & pH=8.0,8.5 ,Temperature= $32^\circ\pm 1^\circ\text{c}$

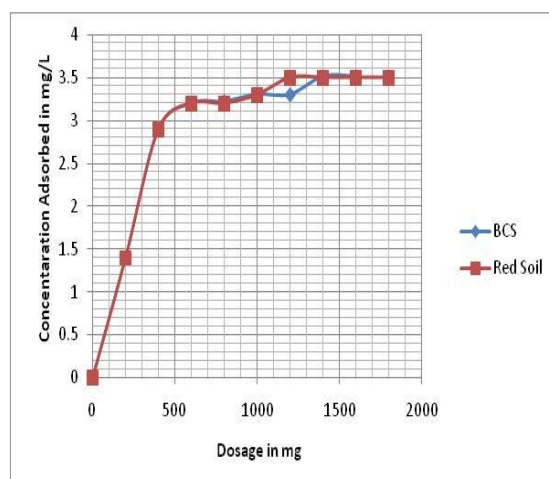


Figure 3.2. Effect of optimum dosage of phosphate on black cotton soil & red soil

3.2.3 Effect of pH

The impact of phosphate removal is depends on pH of the medium. The graph of pH against phosphate removal at constant time and dosage is shown in "Fig 3.3", it is observed from the graph that, phosphate removal is not only depends on surface area, time and dosage but also depends on pH. Initial concentration of phosphate $C_0=5\text{mg/L}$, Dosage=1000mg/L, 1200mg/L Temperature= $32^\circ\pm 1^\circ\text{c}$ & Contact time=55minutes, 60minutes.

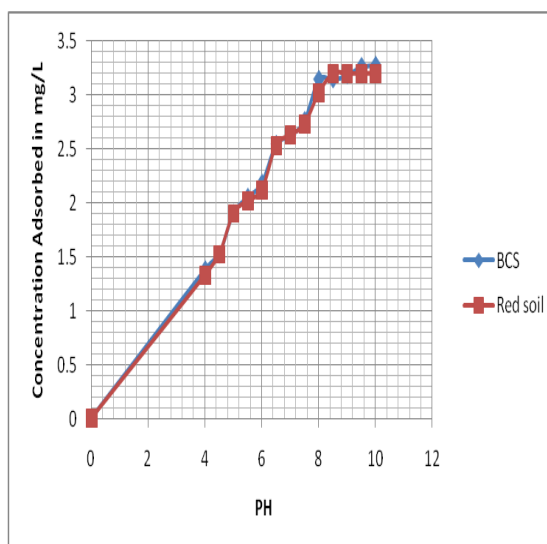


Figure 3.3. Effect of ph of phosphate on black cotton soil & red soil

3.3. Sorption Kinetics

The kinetics of Phosphate removal was performed at constant temperature (*i.e.* $32 \pm 1^\circ\text{C}$) at different time interval of adsorption. The batch kinetic data for the adsorption of Phosphate was tested for the first order reaction. The rate for the first order reaction is given by Levenspiel.

$$\ln C_0/C_t = kt$$

$$\text{Or } 2.303 \log a/(a-x) = kt$$

$$\text{Or } \log a/(a-x) = k/2.303t$$

$$\text{Or } k = 2.303/t \log a/(a-x)$$

Where, X=Amount of Phosphate adsorbed at any time t, (a-x)=Residual amount of Phosphate & k=Rate constant

This is equation of the type $y = mx$, Where, $y = \log a/(a-x)$, and $x = t$

This produces a straight line graph with slope $k/2.303$. From the values of graphical and calculated “k” values, it is observed that adsorption of Phosphate follows first order rate equation. The resulting graph is as shown in the “Fig 3.4”.

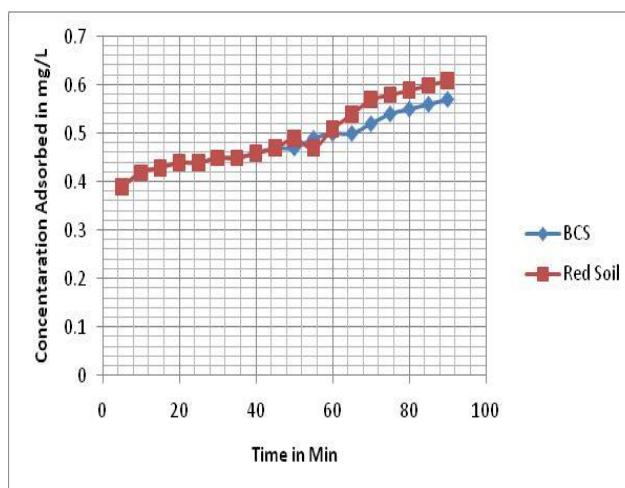


Figure 3.4. Reaction rate constant of phosphate adsorption by black cotton soil & red soil

3.4. Single Adsorption of Phosphate

3.4.1 Black Cotton soil

The batch experiments were carried out on Black cotton soil of the properties given in “Table 3.1”, with the tracer concentrations of 5, 10, 15 and 20 mg/L respectively.

Table 3.1. Retardation Factor for Tracer Experiment Using Freundlich and Langmuir Isotherm

Black Cotton Soil		
Phosphate	Langmuir	Freundlic
	a=12.777	K=0.544
	b=0.031	1/n=4.66
	R=0.014	n=0.214
Red Soil		
Phosphate	a=30.00	K=0.477
	b=0.00416	1/n=1
	R=0.00645	n=1

The results of the Phosphate test on Black cotton soil to fit the results to the Langmuir isotherm. The results are plotted as shown in “Fig 3.5” and are fit to “equation (5)” which gives: $\frac{1}{Q} = 0.029 \frac{1}{C} + 0.0049$, where the regression coefficient $R=0.014$; from the fit we obtained maximum adsorption and Langmuir constants, ‘a’=12.77 and ‘b’=0.031.

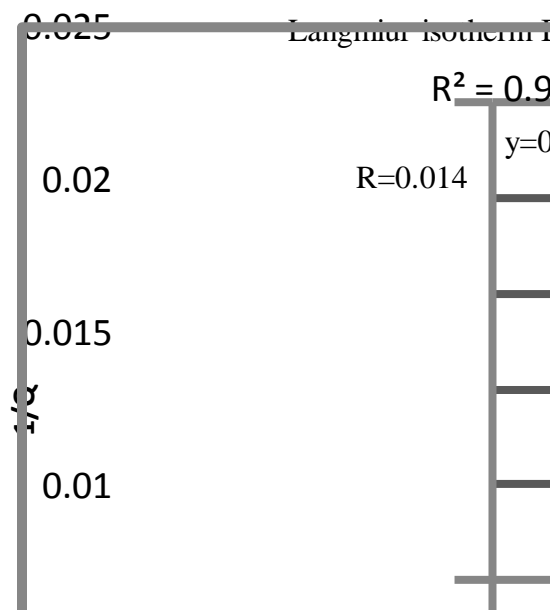


Figure 3.5. Single adsorption of phosphate on black soil

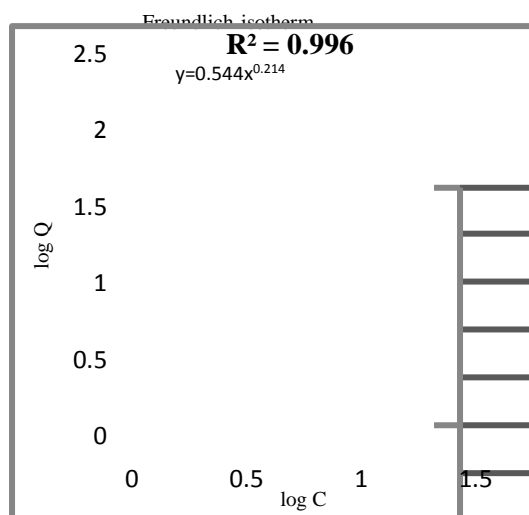


Figure 3.6. Single adsorption of phosphate on black soil

The same experimental results are fit to Freundlich power equation given by “equation 2”, by plotting ‘Q’ vs. ‘C’ as shown in above “Fig 3.6” and fitting we obtain ‘ $qe' = 0.554 C_e^{0.214}$ ’ Which gives $(1/n) = 4.66$ and ‘ $K_F = 0.544$ ’

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, & Freundlich capacity factor and $1/n$ = Freundlich intensity factor.

In this equation $1/n > 1$, therefore bond decreases with surface density. Similarly the graphs are plotted for Red soil respectively.

3.5. Column Tracer Experiments

A series of column tracer experiments as explained in “section 2.5” have been performed with Phosphates on the three different soils considered to obtain the breakthrough curves and retardation coefficients. Results obtained by Column tracer method were interpreted using Freundlich, and Langmuir linear formulas describing the adsorption isotherms. In all cases of phosphate adsorption, the best fit was obtained for the Freundlich isotherm, described by the formulae:

$$C_{ads} = K^F \times C_{aq}^{1/n} \quad \text{----- (7)}$$

Where, C_{ads} = balance concentration of the studied compound in the ground, C_{aq} = balance concentration of the studied compound in the water & ‘ K^F ’ and ‘ n ’ = coefficients of the Freundlich adsorption isotherm.

Substitute distribution coefficient (determined using the Freundlich isotherm) K_d^F for a given value of balance concentration of ion adsorbed in the solution equals

$$K_d^F = \frac{K^F C_{aq}^{1/n}}{C_{aq}} = K^F C_{aq}^{(1/n-1)} \quad \text{----- (8)}$$

For the distribution coefficient determined on the basis of the adsorption isotherm, the retardation has been

$$\text{defined } R = 1 + \frac{\rho_d}{n} K_d^F \quad \text{----- (9)}$$

3.6 Single Adsorption of Phosphate

3.6.1 Black Cotton Soil

A series of column tracer experiments have been performed on Black cotton soil and the “Fig. 3.7” shows tracer breakthrough curve for 2 mg/L of initial concentration. The results obtained with different concentrations are fit to Adsorption isotherms as follows.

Similar experiments were performed for concentrations of 5 and 10 mg/L, the results of the tracer experiment are fit to Freundlich and Langmuir isotherms as shown in below “Fig 3.8, 3.9” and the results are analyzed. Similarly the graphs are plotted & the results are analyzed for red soil respectively.

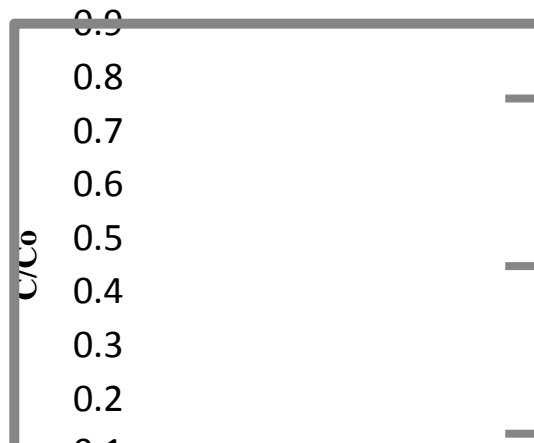


Figure 3.7. Break through curve for single adsorption of phosphate on black soil

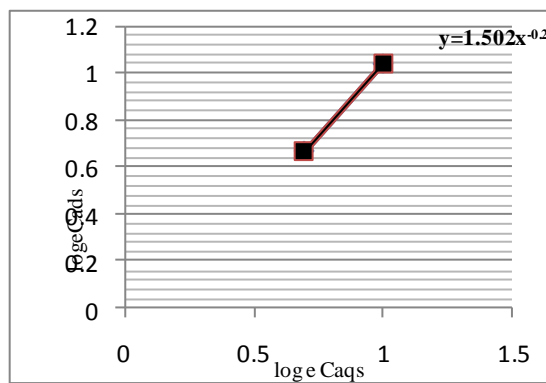


Figure 3.8. Freundlich isotherm of single adsorption of phosphate on black soil

Where $y = 1.502x^{-0.2}$ which is of the form $C_{ads} = K^F \times C_{aq}^{1/n}$ Where from “equation (4.1)” we get $K^F = 1.502$ and $1/n = -0.2$ and from “equation 8” we get $K_d^F = 0.995$ from “equation (9)” we get retardation value as: $R = 2.892$

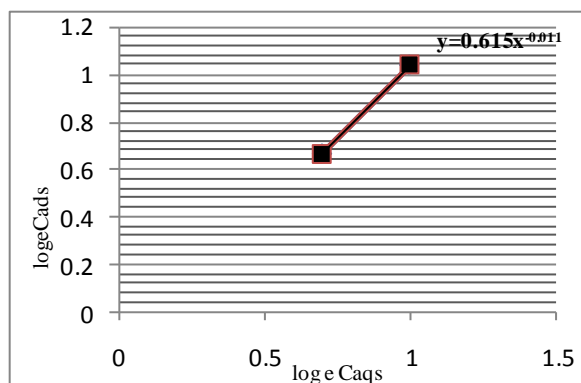


Figure 3.9. Langmuir isotherm of single adsorption of phosphate on black soil

Table 3.2. Single adsorption of phosphate for selected concentrations and soils to fit langmuir isotherm

Initial conc.	Black cotton soil mg/L	Red soil in mg/L
1/C	1/Q	1/Q
0.2	0.0212	0.0128
0.1	0.0118	0.00525

Table 3.3. Single adsorption of phosphate for selected concentrations and soils to fit Freundlich isotherm

Initial conc. mg/L C_{aq}	Black cotton soil mg/L C_{ads}	Red soil mg/L C_{ads}
5.0	4.2	4.2
10.0	9.998	9.997

IV. CONCLUSION

A series of Batch and Soil column tracer experiments have been performed in the laboratory for adsorption of Phosphate in Red & Black cotton soils and the results are fit with analytical isotherms. The conclusions from the study can be summarized as follows:

It's evident from the characteristics properties that Black cotton soil and Red Soil are 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. The rate of adsorption of Phosphate obeys first order rate equation. 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 a different behavior in the two studied adsorbents. In this Black cotton Soil has shown maximum adsorption for Phosphate compared to Red Soil. It was observed that the maximum amount of Phosphate was leached through Black cotton Soil followed by Red Soil. In column tracer experiments results of Langmuir isotherm and Freundlich isotherm holds good, because when we fit the results to isotherms it gives equilibrium parameter $R < 1$ and $1/n < 1$ respectively.

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