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Adsorption of Phosphate using Laterite Soil, Black Cotton Soil and Fuller's Earth as Adsorbents

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Abstract - Adsorption technique is one of the most technologies being used for treatment of water and waste water, but the objective of this study is to select the low cost adsorbent. Phosphate is generated by municipal waste water, domestic waste water, agricultural sources, detergents etc. An attempt for naturally available low cost effective adsorbent was made by utilizing Laterite soil, Black cotton soil and Fuller's earth. Kinetics of adsorption was found to follow first order reaction and the adsorption rate of Phosphate are 5.3mg/g, 7.37mg/g and 8.12mg/g by Laterite soil, Black cotton soil and Fuller's earth respectively. Adsorption behavior was found to follow Freundlich and Langmuir isotherm. For Column tracer experiment the values of Freundlich coefficient KF, Freundlich Isotherm constant 1/n, Distribution coefficient KFd and Retardation factor R for Laterite soil are 1.310, 0.831, 1.012, 2.030 and for Black cotton soil are 1.20, 0.946, 1.292, 2.360 and for Fuller's earth are 1.420, 0.890, 1.10, 2.522 respectively. The result of the Column Experiment follows Freundlich Isotherm.

Key Words: Phosphate, Adsorption, Fuller's earth, Kinetics, Isotherms

1. INTRODUCTION

Water is one of the most essential elements on earth. Every living being needs water for its survival. When we look at the water available on earth, we find that a mere 2.5% of fresh water is what is available to humans. While 68.7% of this accounts for glaciers and ice cap, we are left with 30.1% of groundwater and just 1.2% of surface water. The requirement of the fresh water in various sectors such as domestic, irrigation, industry and others increases significantly all over the world. Thus, water liability, both in terms of quality and quantity, has declined to such an extent to the rapid increase in the population and industrialization.

Phosphate is an essential nutrient which is necessary for growth of plants and animal's .Phosphate is most commonly found in industrial waste water and domestic waste water. The amount of Phosphate in water is desirable to certain extent. If it exceeds the limit then it creates a serious issue called Eutrophication. Larger amount of phosphate can cause bone and muscle problems and increase the risk for heart attacks and strokes.

Water pollution by Phosphate is of considerable concern, as this metal is used in a variety of applications including Metal plating industries, Galvanizing industries, Mining operations and Tanneries and are usually present in high concentrations in the liquid wastes which are released directly into the Environment without any pre-treatment.

Phosphate containing wastewater is one of the major pollutants of the environment. If it exceeds the permissible limit then it creates a serious issue called Eutrophication in water bodies and bone and muscle problems and increases the risk for heart attacks and strokes to humans.

1.1 OBJECTIVES

To evaluate a feasible and economical low cost treatment of Phosphate, as present in synthetic sample by Black cotton soil, Laterite soil and Fuller's earth which are naturally available as an adsorbents.

- To study the physical properties of adsorbents like Black cotton soil, Laterite soil and Fuller's earth.
- Adsorbing capacity of Black cotton soil, Red soil and Fullers earth on adsorption of Phosphate as a function of contact time, adsorbent dosage and pH.
- To study Sorption Kinetics
- To study Isothermal patterns
- To study Column experiments

1.2 LITERATURE REVIEW

Mallikarjun. S. D and Dr S. R. Mise (July 2012) have studied the Phosphate Adsorption characteristics on Black cotton soil and Red soil using batch adsorption techniques. Study on Phosphate removal by adsorbent as a function of contact time, adsorbent dosage and pH was carried out and study on sorption kinetics and column experiment and isothermal pattern was also carried out. The obtained results of the batch and column experiments are best fit to Langmuir and Freundlich adsorption isotherms. 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%). 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.

Dr. C. R. Ramakrishnaiah and Vismitha (2012) have studied removal of phosphate from wastewater using low-cost adsorbents like alum sludge, coal ash, class'C' fly ash and ground granulated blast furnace slag (GGBS). The optimum pH, effective dosage and reaction time were studied and Column studies were conducted in order to determine the saturation time by using column Break-through curve. As a result, pH of 5 and dosage of 10gm/100ml was found to be optimized condition for the phosphate removal by alum sludge, class'C'Flyash and GGBS and pH of 7 and 7.5gm/100ml was found to be the optimized condition for the phosphate removal by coal-ash adsorbents. The results obtained on industrial wastewater showed the results were in par with the synthetic sample except for Coal-ash adsorbent.

2. MATERIALS AND METHODOLOGY

Selection of Suitable Adsorbents

Laterite soil: It is a soil and sedimentary rock type rich in iron and aluminum, and is commonly considered to have formed in hot and wet tropical areas. Nearly all laterites are of rusty-red coloration, because of high iron oxide content. They develop by intensive and long-lasting weathering of the underlying parent rock. Tropical weathering (laterisation) is a prolonged process of chemical weathering which produces a wide variety in the thickness, grade, chemistry and ore mineralogy of the resulting soils. The majority of the land area containing laterites is between the tropics of Cancer and Capricorn.

Black cotton soil: Black soil is also called as Black cotton soil as its colour is black. Black cotton soil is found in the central, western and southern states of India, including Karnataka. Black cotton soil is one of major soil deposits of India. They are very tenacious of moisture and exceedingly sticky, when wet. Due to considerable contraction on drying large and deep cracks are formed. These soils contain abundant iron and high quantities of lime, magnesia and alumina. Black soils are poor in nitrogen, phosphorus and organic matter. The soils are generally rich in montmorillonite and bi elliptic group of clay minerals.

Fuller's earth: It is a clay material that has the capability to decolorize oil or other liquids without chemical treatment. Fuller's earth typically consists of palygorskite (attapulgite) or bentonite. Modern uses of fuller's earth include absorbents for oil, grease, and animal waste (cat litter) and as a carrier for pesticides and fertilizers. Minor uses include filtering, clarifying, and decolorizing; active and inactive ingredient in beauty products; and as filler in paint, plaster, adhesives, and pharmaceuticals.

Preparation of Adsorbent

The adsorbents Laterite soil, Black cotton soil and Fuller's earth are cleaned. Laterite soil, Fuller's earth and Black cotton soil broken into very minute particles in order to make it in powdered form. Adsorbents are washed with distilled water for about 2-3 times to make it free from dissolved and floating organic matter and coloured material. Powder is then oven dried at 105±2°C for about 24Hrs. The adsorbents which are passing through 300 micron sieve and retained on 150 micron sieve are used for batch adsorption studies. Table 1 shows physical characteristics of adsorbents

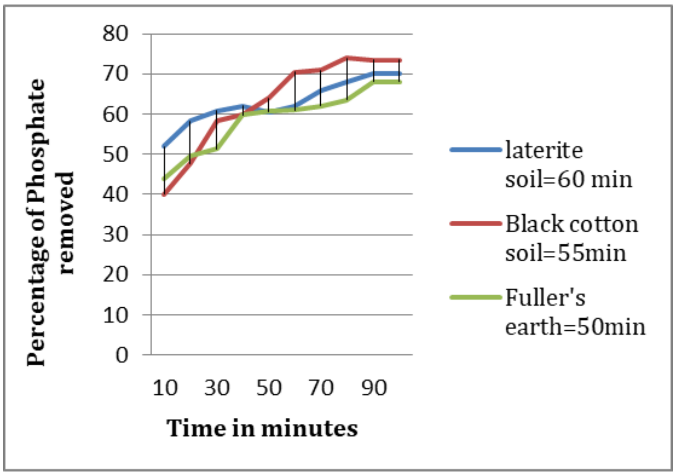
Table -1: Physical characteristics of adsorbents

Sl. NO	characteristics	units	Laterite soil	Black cotton soil	Fuller's earth
01	Moisture content	%	3.44	6.5	8.22
02	pH values	-----	6.9	7.1	7.5
03	Specific gravity	----	2.82	2.12	1.87
04	Bulk density	g/cc	1.38	1.21	0.925
05	Color		Red	Black	Light grey
06	Surface area	m^2/g	495	598	730

RESULTS AND DISCUSSION

Effect of optimum contact time

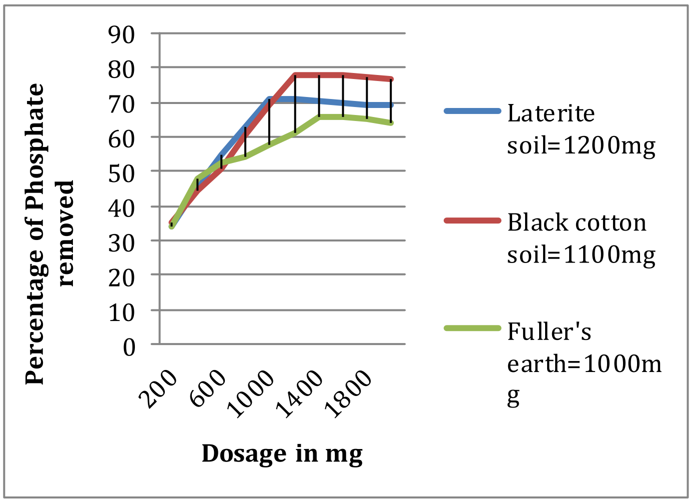
The adsorption is strongly influenced by the contact time, for the study of effect of contact time 100mL of 10mg/L Phosphate solution is mixed with 1gm of adsorbents and stirred on Gyro shaker for various time intervals. The samples are filtered and analysed for Phosphate concentrations using UV spectrophotometer and Atomic absorption spectrophotometer respectively. The removal efficiency of phosphate by Laterite soil, Black cotton soil and fullers earth is found to be 86%, 66%, and 70% with optimum contact time of 60minutes, 55 minutes, 50 minutes respectively as shown in graph 1.



Graph-1 Effect of Contact Time on phosphate removal by Laterite soil, Black cotton soil and Fuller's earth.

Effect of optimum dosage

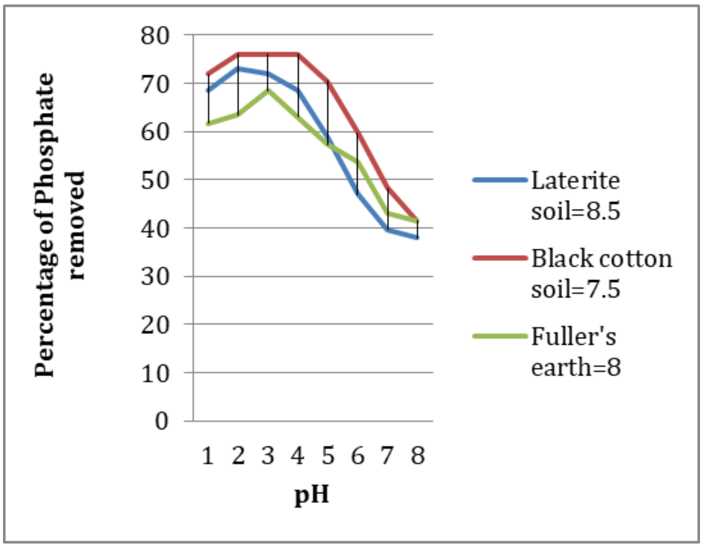
To determine the optimum dosage of adsorbent, various dosages of adsorbents are added to 100mL of 10mg/L concentration of Phosphate solutions to the conical flasks. The solution in the conical flask was subjected to stirring for optimum contact time and then samples are filtered and analysed for residual concentration Phosphate. The dosage which gives minimum residual concentration is chosen as optimum dosage. The optimum dosage for phosphate removal by Laterite soil, Black cotton soil and fullers earth are 1200mg, 1000mg and 1000mg with the removal efficiency of 70%, 66% and 68% respectively as shown in graph 2.



Graph-2 Effect of Adsorbent Dosage on Phosphate removal by Laterite soil, Black cotton soil and Fuller's earth.

Effect of optimum pH

To determine the optimum pH 100 mL of 10mg/L Phosphate solutions is taken in the conical flask. Optimum dosages of adsorbents are added. The pH of the flask is adjusted; the flask is shaken for optimum contact time. After stirring, the samples are filtered and analysed for the residual Phosphate concentration. The pH which gives minimum residual concentration is chosen as optimum pH. The optimum pH for phosphate removal by Laterite soil, Black cotton soil and Fullers earth are 8.0, 8.5&8.0 with removal efficiency of 62.5%, 64% and 66% respectively as shown in graph 3



Graph-3 Effect of pH on phosphate Removal by Laterite soil, Black cotton soil and Fuller's earth.

The results of optimum contact time, optimum dosage, and optimum pH are shown in table 2

Table -2: Optimum Contact Time, Optimum Dosage and Optimum pH for phosphate by Naturally Available Adsorbents

Parameters	**Laterite soil**	**Black cotton soil**	**FULLERS EARTH**
OPTIMUM CONTACT TIME(in minutes)	60	55	50
OPTIMUM DOSAGE(in mg)	1200	1100	1000
OPTIMUM pH	8.5	7.5	8.0

Sorption Kinetics

The kinetics of Phosphate removal was performed at ambient temperature at different time interval of adsorption. The batch sorption kinetic data for the adsorption of the Phosphate was tested for the first order reaction. The rate constants K are as shown in table 3 for all the adsorbents. The rate equation for the first order reaction is given by levenspiel.

Ln Ca/Co = K*T

K = rate constant

Adsorption isotherm studies

Modelling the equilibrium data is a fundamental for the industrial application of adsorption since it gives information for designing and optimizing operating procedure. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent qe and the solute concentration for the solution at equilibrium Ce.

In order to successively represent the equilibrium adsorptive behaviour, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Two kinds of isotherms equations were tested to fit the experimental data, The Isotherm constants are presented in table 3.

Langmuir equation: Ce /qe = (Ce /qmax) + [1/ (qmaxb)]

Freundlich equation: log qe = log KF + (1/n) log Ce

Where qe is the amount adsorbed at equilibrium (mg/g) and Ce is the equilibrium concentration of metal ions in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation, qmax (mg/g) is the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on a sorbate surface.

Table -3: Parameters of Freundlich and Langmuir isotherm models

	Freundlich Isotherm		Langmuir Isotherm		
	1/n	K	a	b	R
Laterite Soil	0.9	0.477	29.00	0.00416	0.00545
Black cotton soil	1.66	0.544	11.777	0.041	0.015
Fuller's earth	0.24	0.05	16.223	0.045	0.011

From the table 3, it is clear that Laterite soil and Fuller's earth follows Freundlich isotherm and proves to be a favorable adsorption as 1/n values are less than unity. All soil obeys Langmuir isotherm as separation factor 'R' is lesser than 1 and greater than 0 ($0<R<1$).

Column Tracer Experiments

To observe the retention and leaching of Phosphate through respective adsorbent column, Perspex plastic columns of 5.5cm diameter were used. The length of the adsorbent filled in the columns is chosen based on texture and compaction. A series of column tracer experiments have been performed with Phosphate on different adsorbents obtaining retardation coefficients. Results obtained by Column tracer method are interpreted using Freundlich isotherm formulae describing the adsorption isotherms. For all adsorbents of Phosphate adsorption, the best fit is obtained for the Freundlich isotherm and it is described by the formula:

Cads = KF x$Caq1/n$

Where,

Cads = balance concentration of the studied compound in the carbon bed;

Caq = balance concentration of the studied compound in the water;

KF and n = coefficients of the Freundlich adsorption isotherm.

Substitute distribution coefficient (determined using the Freundlich isotherm)

KdF for a given value of balance concentration of ion adsorbed in the solution equals

K_d^F = KF$Caq1/n$ /Caq = $K^F C_{aq}(1/n-1)$

For the distribution coefficient determined on the basis of the adsorption isotherm, the retardation has been defined as R=1 +ρ d/n K_d^F

The Freundlich constants are presented in table 4.

Table -4: Data Showing the Values of Freundlich Coefficients on phosphate Adsorption

Adsorbent	KF(Coefficient of Freundlich Isotherm)	1/n (Coefficient of Freundlich Isotherm)	KFd Distribution coefficient	R(Retardation coefficient)
Laterite soil	1.210	0.931	1.032	2.070
Black cotton soil	1.10	0.966	1.192	2.560
Fuller's earth	1.420	0.890	1.10	2.522

From the table 4, it is clear that follows Freundlich isotherm and proves to be a favorable adsorption as 1/n values are less than unity.

3. CONCLUSIONS

- From the kinetic study rate of reaction follows first order and the adsorption rate of Phosphate are 5.3mg/g, 7.37mg/g and 8.12mg/g Laterite soil, Black cotton soil and Fuller's earth respectively.
- From the study, the optimum contact time, optimum dosage and optimum pH for laterite soil are 60, 1200 and 8.5and for black cotton soil are 55, 1100, 7.5 and for Fuller's earth are 50, 1000, 8.0 respectively.
- From the Isotherm constants it is concluded that adsorption process obeys Freundlich and Langmuir isotherms.
- For Column experiment the values of Freundlich coefficient K_F, Freundlich Isotherm constant 1/n, Distribution coefficient K_{Fd} and Retardation factor R for Laterite soil are 1.310, 0.831, 1.012, 2.030 and for Black cotton soil are 1.20, 0.946, 1.292, 2.360 and for Fuller's earth are 1.420, 0.890, 1.10, 2.522 respectively.
- The result of the Column Experiment follows Freundlich Isotherm as $1/n<1$.

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