Research Paper

SOIL – AN ADSORBENT FOR PURIFICATION OF PHOSPHATE CONTAMINATED WATER

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Adsorption characteristics of Kuttanad clay, Laterite and Coastal alluvium were investigated for phosphate removal from aqueous solution employing a batch experimental setup. Various parameters studied include contact time, adsorbent dosage, pH, initial concentration, agitation speed and particle size. Characterization of adsorbents including Point of zero charge, SEM and EDS analysis were done. The results of this study showed that the optimum contact time for adsorption of phosphate on Kuttanad clay, laterite and coastal alluvium reached to equilibrium after 60 min, 120 min and 90 min with removal efficiency of 61.12%, 55.32% and 46.89%, respectively. Optimum adsorbent dosage for adsorption of phosphate on Kuttanad clay, laterite and Coastal alluvium was obtained at 17.5 g/L, 15 g/L and 17.5 g/L with removal efficiency of 77.5%, 68% and 49%, respectively. Higher adsorption of phosphate was observed at lower pH; obtained at pH 3, 2 and 2 with removal efficiency 84.39%, 77.49% and 55.78%, respectively. Adsorption of phosphate on the adsorbents were found to increase with increase in agitation speed and decrease in initial concentration and particle size. In the kinetic study, pseudo 1st order, pseudo 2nd order and intra-particle diffusion models were fitted to the adsorption process. Based on the experimental sorption capacity values compared with model values, the pseudo 1st order fitted more than pseudo 2nd order model. Intra particle diffusion plot shows that adsorption occurs in 3 steps, viz., boundary layer effect, intra-particle diffusion and pore diffusion for the selected adsorbents. In this study, the adsorption characteristic of phosphorus onto soil was investigated with the Langmuir and Freundlich isotherms. Correlation coefficients indicate that the Freundlich isotherm model was applied more effectively than the Langmuir model to phosphate sorption onto the Kuttanad clay, Laterite and Coastal alluvium. Overall, the present study suggests that the selected adsorbents are environmental friendly and low-cost adsorbents, which is useful for the removal of phosphate from aqueous media.

Keywords: Adsorption, Phosphate, Kuttanad clay, Laterite, Coastal alluvium, Kinetics, Isotherm

INTRODUCTION

Among the various known forms of pollution, water pollution is of great concern, since water is the prime necessity of life and extremely

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essential for the survival of all living organisms. Indeed, it is a part of life itself, since the protoplasm of most living cells contains about 80% of water. It is worthy noting that only 0.02% of the total available water on the earth is immediately available for use in the form of rivers, lakes and streams (Amit *et al.*, 2006). However, years of increased industrial, agricultural and domestic activities have resulted in the generation of large amount of wastewater containing a number of toxic pollutants, which are polluting the available fresh water continuously. With the realization that pollutants present in water adversely affect human and animal life, domestic and industrial activities, pollution control and management is now a high priority area. The availability of clean water for various activities is becoming the most challenging task for researchers and practitioners worldwide.

Large-scale wastewater production is an inevitable consequence of contemporary societies. Wastewater is hazardous to human populations and the environment and must be treated prior to disposal into streams, lakes, seas, and land surfaces. Obligatory anaerobic treatment of domestic and agro-industrial wastewater releases large amounts of phosphorus and nitrogen into wastewater. These nutrients are directly responsible for eutrophication (extraordinary growth of algae as a result of excess nutrients in water bodies) of rivers, lakes, and seas worldwide (Lau *et al.*, 1997; Tre´panier *et al.*, 2002). Consequently, disposal of wastewaters produces a constant threat to dwindling fresh water on a global scale (Montaigne and Essick, 2002).

Phosphorus (P) is a naturally occurring element in the environment that can be found in all living organisms as well as in water and soils. It is an essential component for many physiological processes related to proper energy utilization in both plants and animals. Phosphorus can be added to the environment by man's activities as point source discharges or as non-point source runoff. Typical sources include industrial and municipal wastewater discharges or runoff from agricultural lands or urban areas.

Natural waters have a phosphorus concentration of approximately 0.02 mg/L which is a limiting factor for plant growth (Katal and Pahlavanzadeh, 2010). On the other hand, large concentrations of this nutrient can accelerate plant growth. The phosphate determination has grown rapidly in importance in Environmental Engineering and science practice, because of the many ways in which phosphorous compounds affect environmental phenomenon of interest. The inorganic compounds of phosphorous of significance are the phosphates or their molecularly dehydrated forms, usually referred to as polyphosphates or condensed phosphates. Polyphosphates are used in some public water supplies as a means of controlling corrosion. They are also used in some softened waters for stabilization of calcium carbonate to eliminate the need for re-carbonation. Domestic wastewater is relatively rich in phosphorous compounds. Most of the inorganic phosphorous was contributed by human waste as a result of the breakdown of proteins and nucleic acids and elimination of the liberated phosphate in the urine. Many of the synthetic detergents contain 12 to 13% phosphorous or over 50% of polyphosphates.

The use of these materials as a substitute for soap has greatly increased the phosphorous content of domestic wastewater (Irdemez *et al.,* 2006). Phosphate compounds are widely used in steam power plants to control scaling in boilers. If polyphosphates are used, they are rapidly hydrolysed to orthophosphate at the high temperature involved. Control of phosphate levels are accomplished through determinations of orthophosphate (Garg, 1979).

MATERIALS AND METHODS

Removal of phosphate and its various aspects were determined by using soil samples of three different series, viz., Costal alluvium, Kuttanad clay and Laterite as adsorbents. All the three soil samples were collected from different parts of Kerala, India. Chart 1 shows the experimental methodology adopted for the treatment of aqueous solution containing phosphate by adsorption.

Chart 1: Flow Chart for Methodology
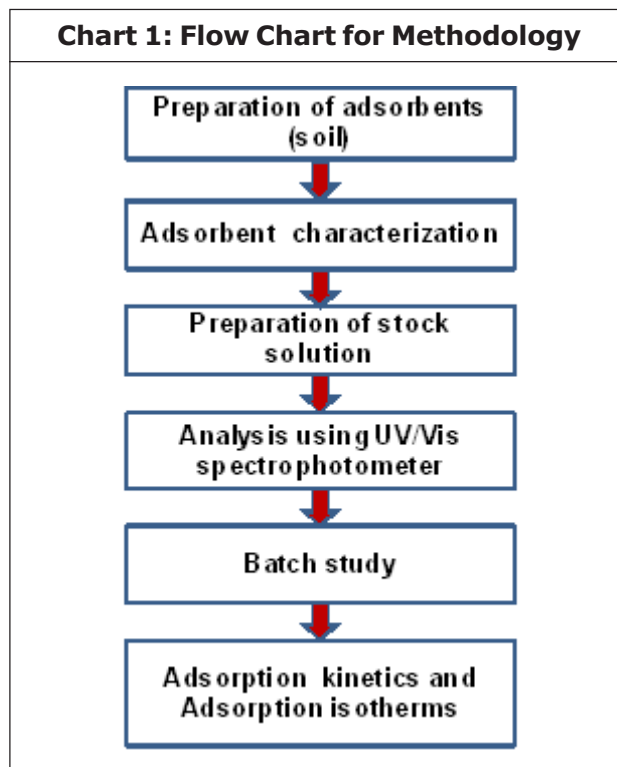
Coastal Alluvium: These soils are seen in Kerala coastal tracts along the west as a narrow belt with an average width of about 10 km. As it has been developed from recent marine deposits, sand is the chief constituent of this type of soil.

Kuttanad Clay (Kuttanad Alluvium/Acid Saline Soil): They occur in the flat lands of large parts of upper Kuttanad and also along the inland stream and rivers in Kerala. Kuttanad region in Kerala is a unique agricultural area in the world which covers about 875 km^2. A good portion of this area lies 1-2 m below MSL and is submerged for major parts of the year. The area is susceptible to seasonal ingress of saline water as a result of tidal inflow from the sea. During the monsoons, the rivers and rivulets pour fresh water into the area. These soils are formed by the transportation activity of rivers.

Laterite: They cover about 65% of the total area of Kerala. Laterite of Kerala is typical kaolinitic weathering products of gneissic and granitic rocks developed under humid tropical conditions.

Specific gravity was found using Pycnometer using the following formulae.

$$\text{Specific gravity} = \frac{(w2-w1)}{(w4-w1)(w3-w2)} \quad ...(1)$$

where

w1 = Empty weight of pycnometer

w2 = Weight of pycnometer with 1/3 of adsorbent

w3 = Weight of pycnometer with 1/3 of adsorbent + water

w4 = Weight of pycnometer filled with water

The Point of Zero Charge (PZC) was determined using the solid addition method (Oladoja *et al.*, 2009). Morphology of bare and phosphate loaded adsorbents were analyzed using Scanning Electronic Microscope (SEM).

Wastewater used in the experiments was prepared synthetically by dissolving potassium-di-hydrogen phosphate (KH_2PO_4) of analytical grade in distilled water. 219.5 mg anhydrous KH_2PO_4 in distilled water and diluted to 1000 mL (1.00 mL = 50.0 micro g. PO_4^{3-}-P).

Vanadomolybdophosphoric acid colorimetric method was used for the analysis of phosphate.

Principle: In a dilute orthophosphate solution, ammonium molybdate reacts under acid conditions to form a heteropolyacid, molybdophosphoricacid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the color is proportional to phosphate concentration.

A UV–Vis spectrometer was used for the measurement of phosphate removal. UV–Vis spectra were obtained from samples of raw and treated wastewater using a double beam Perkin-Elmer Lamda 25 spectrophotometer. The scan rate was 960 nms⁻¹ within a 200-270 nm wavelength range. The samples were scanned in quartz cells with a 1 cm optical path. The pH measurements were carried out using Orion EA 940 expandable ion analyzer. An IHC-3280 orbital shaking incubator was used for all adsorption experiments. Supernatant was separated using TC 650 Multiple centrifuge.

RESULTS AND DISCUSSION

Physical Properties of Adsorbents

Following physical properties of the adsorbent were studied and shown in Table 1.

Scanning Electron Micrograph

Scanning Electron Micrograph has depicted the sorption of phosphate onto the sorbent after the phosphate removal process as shown in Figures 1 to 3. SEM images are observed to be irregular clumps and the surface morphological change before and after adsorption indicates phosphate is superficially adsorbed on the surface of adsorbents.

EFFECT OF CONTACT TIME

Effect of contact time studies were conducted to find out the equilibrium time for phosphate uptake by the adsorbents. Phosphate uptake capacity of the adsorbents were studied as a function of the optimum contact time. The

Table 1: Physical Properties of Adsorbents				
S. No.	Properties	Coastal Alluvium	Kuttanad Clay	Laterite
1	Particle size	150-75 µm	150-75 µm	150-75 µm
2	Specific Gravity	2.55	2.3	2.48
3	Water content	1.44%	19.18%	15.15%
4	pH	6.48	4.15	5.35
5	Point of zero charge	6.2	4.625	6.756

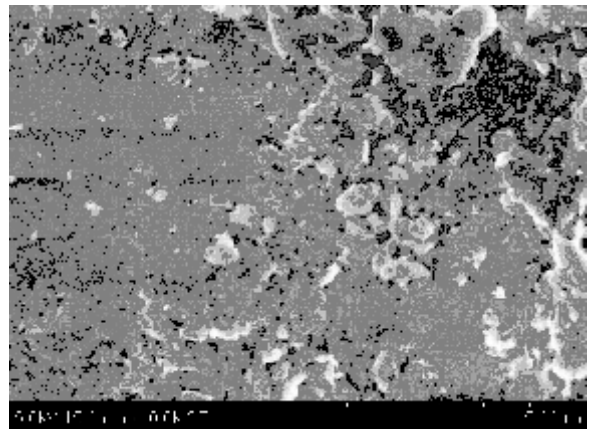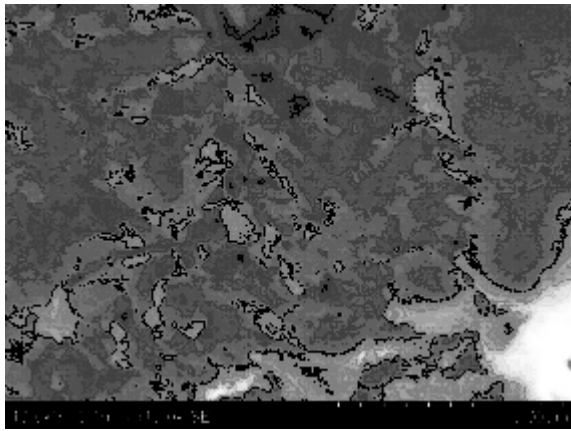**Figure 1: SEM Image of Bare and Phosphate Loaded Kuttanad Clay**

Figure 2: SEM Image of Bare and Phosphate Loaded Laterite
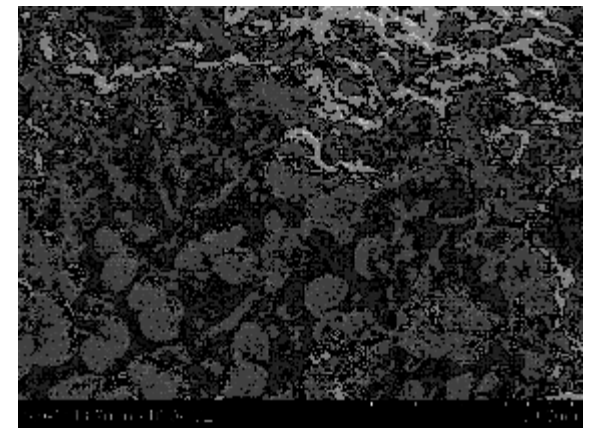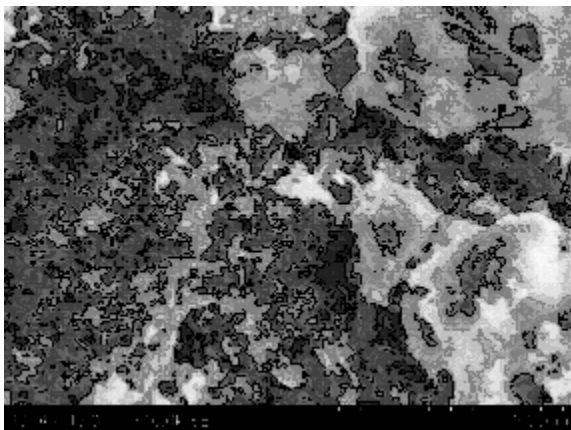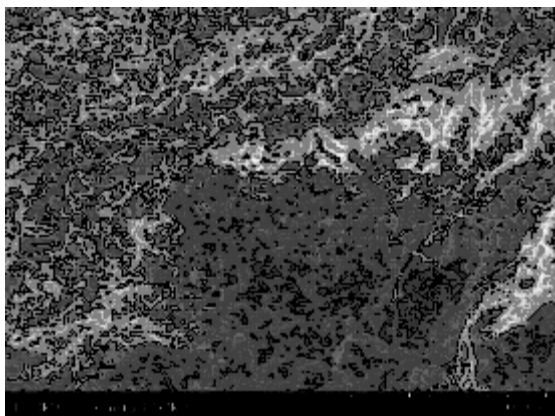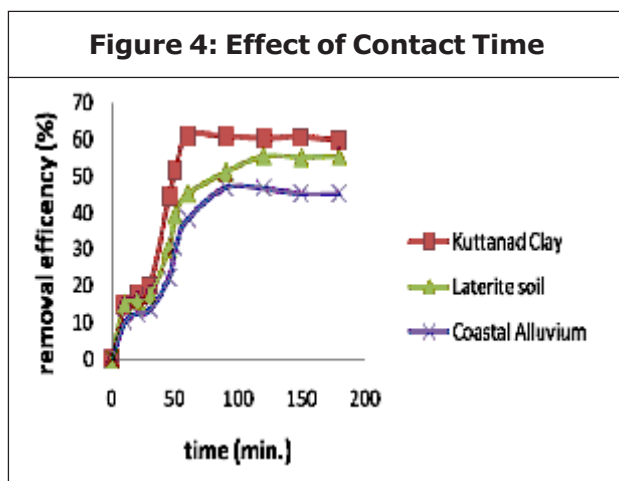

Figure 3: SEM Image of Bare and Phosphate Loaded Coastal Alluvium

uptake capacity was determined by measuring the difference in the concentration of influent and the effluent solution and is expressed as percentage removal. In this study initial concentration of phosphate was taken as 10 mg/L, adsorbent doses were taken as 10 g/L and the adsorbent size was 75-150 µm. The agitation speed was 150 rpm at temperature of 30°C. Figure 4 depicts the effect of the contact time on the removal of phosphate by the selected adsorbents. It was noticed that most of the adsorption occurs in the first 1 h of shaking. Further shaking of 2 h caused only slight increase in the removal efficiency of phosphate for all the three samples. A contact time of 60 min was chosen for the attainment of the equilibrium with Kuttanad Clay as adsorbent, phosphate removal efficiency of 61.12% was obtained at that contact time. A maximum phosphate removal efficiency of 55.32% was observed at 120 min for laterite

Figure 4: Effect of Contact Time

and 46.89% removal efficiency was observed at 90 min for Coastal Alluvium.

EFFECT OF ADSORBENT DOSAGE
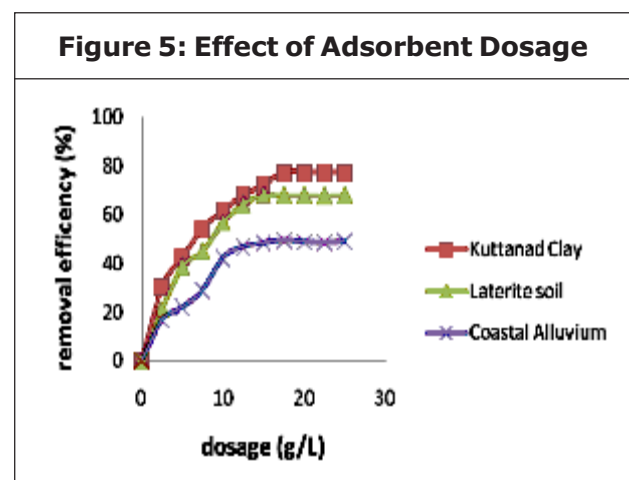
The percentage removal of phosphate for the selected adsorbents at different dosages was analyzed for a aqueous phosphate solution with working volume of 100 mL. The effect of the adsorbent dose was studied at room temperature (29-30°C) by varying the sorbent amounts from 2.5 to 25 g/L. For all the trials, initial concentration of phosphate was fixed as 10 mg/L and the agitation speed was 150 rpm at optimum conditions. It was observed that the percentage removal of phosphate increased with respect to the increased sorbent dosage. This was because of the increase in the number of active sites as the dosage increases (Mourabet *et al.*, 2011). Maximum phosphate uptake was found to be 77.5% for 17.5 g/L of Kuttanad Clay dose at 30°C and 150 rpm. And for laterite, it was 68% with a dose of 15 g/L. Phosphate removal efficiency of 49% was obtained for Coastal Alluvium with a dose of 17.5 g/L. Figure 5 shows the effect of adsorbent dosage on the removal of phosphate. Thereafter no significant increase was observed. At low adsorbent dose the phosphate uptake capacity is high, because of the better utilization of the available active sites and at high adsorbent dose, too many sites are available for limited

**Figure 5: Effect of Adsorbent Dosage**

quantity of adsorbate. The significant increase in uptake was observed when the dose was increased from a range of 2.5-5 g/L to 15-17.5 g/L. Any further addition of the adsorbent beyond the optimum dosage, did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Patil and Raut, 2013)

EFFECT OF pH

The removal of phosphate ions from aqueous phosphate solution was highly dependent on the solution pH in many cases, as it alters the surface charge on the adsorbents. The effect of pH on the adsorption percentage of phosphate ions was investigated at room temperature (29-30°C) by different pH ranging from 2 to 12. For all the trials, initial concentration of phosphate was fixed as 10 mg/L and the agitation speed was 150 rpm at optimum conditions. Adsorption potential of all the three adsorbents for phosphate were seen to increase with increase in solution pH. Since, anion adsorption is associated with a release of OH-ion or water molecules, so phosphate adsorption on the adsorbents surface is probably more feasible at low pH of solution. Further, PZC of Kuttanad Clay is 4.625, 6.756 for Laterite and 6.2 for Coastal Alluvium. pH range below PZC results in net positive surface charge. So negatively charged phosphate species adsorb easily by electrostatic attraction force. In the pH range > PZC, phosphate adsorption decreases rapidly due to electrostatic repulsion between net negatively charged adsorbent surface and negatively charged phosphate ions (Maiti *et al.*, 2011). Maximum phosphate removal efficiency of 84.39% was obtained at pH 3 for Kuttanad Clay. 77.49% removal efficiency was

achieved at pH 2 for Laterite and 55.78% efficiency was obtained at pH 2 for Coastal Alluvium. The increase in phosphate uptake above pH 9 for Kuttanad Clay suggest a possibility of phosphate precipitation as calcium phosphate (Kamiyango *et al.*, 2007). Figure 6 shows the effect of pH on phosphate removal efficiency of the selected adsorbents.

Figure 6: Effect of pH
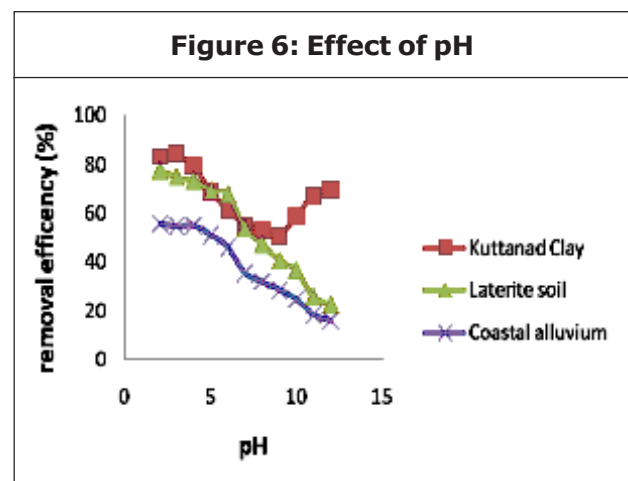
EFFECT OF INITIAL CONCENTRATION

In this study, initial phosphate concentration was varied ranging from 2, 5, 10, 15, 20 ppm (Figure 7) in optimum conditions. Removal efficiency decreased with the increment in the concentration with higher removal efficiency being attained at 2 ppm with all other parameters constant for all the three samples. Because, At low phosphate concentration, the ratio of surface active sites to total phosphate is high and therefore the interaction of adsorbate with the active sites on adsorbent surface was sufficient for efficient phosphate removal (Thakre *et al.,* 2010). At initial phosphate concentration >10 mg/L there was a rapid decrease in removal efficiency. This was because, at high concentration the available sites of adsorption become fewer,

and hence the percentage removal of phosphate is dependent upon the initial concentration (Hema and Arivoli, 2007).

Figure 7: Effect of Initial Concentration
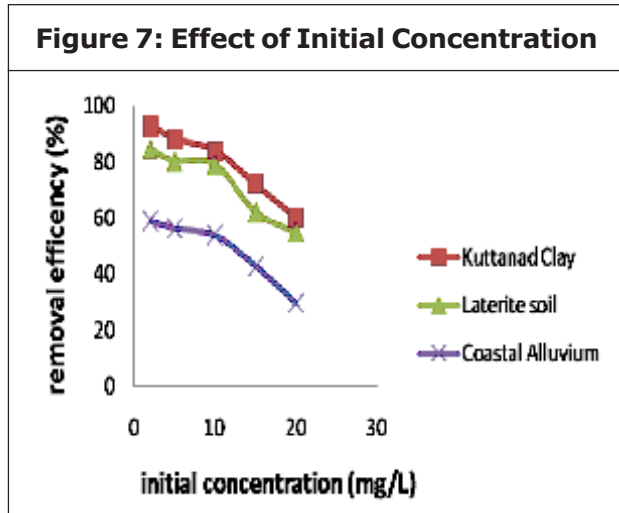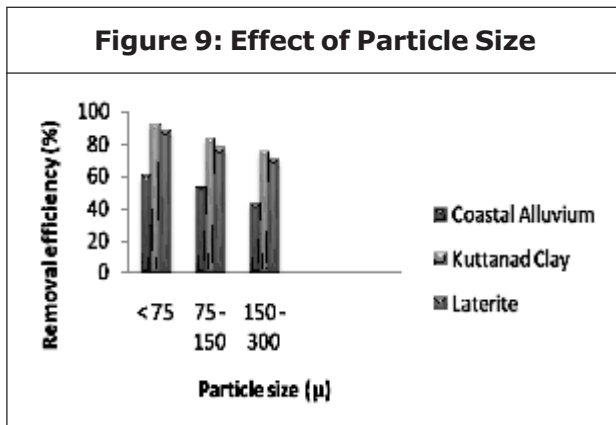

EFFECT OF AGITATION SPEED

In the batch adsorption systems, agitation speed plays a significant role in affecting the external boundary film and the distribution of the solute in the bulk solution (Crini *et al.*, 2007). Effect of agitation speed was studied by varying the speed in the range of 100 rpm, 150 rpm and 200 rpm in optimum conditions. Samples were collected and centrifuged for analysis. Removal efficiency was found to increase with increase in agitation speed as shown in Figure 8 . Higher removal was achieved at an agitation speed of 200 rpm in optimum conditions for all the three adsorbents. It was because; with increase in the agitation speed, the rate of diffusion of adsorbate molecules from bulk liquid to the liquid boundary layer surrounding the particle become higher because of an enhancement of turbulence and a decrease of thickness of the liquid boundary layer (Patil *et al.,* 2011)*.* Due to this, the adsorbate is forced towards

the adsorbent surface. This leads to the increase in the diffusion of adsorbate into the surface of the adsorbent.

Figure 8: Effect of Agitation Speed
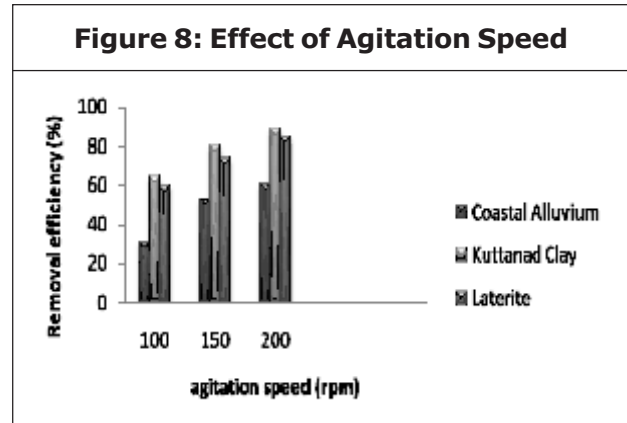
EFFECT OF PARTICLE SIZE

Three set of experiments were performed (<75 µm, 75-150 µm and 150-300 µm) keeping the other parameters constant. The removal efficiency increased as the particle size decreased as shown in Figure 9 for all the three samples. This is due to the larger surface area associated with smaller particles. The presence of large number of smaller particles provides the sorption system with a larger surface area available for phosphate ion removal and it also reduces the external mass transfer resistance (Jamode *et al.*, 2004). This can be attributed to the fact that the smaller adsorbent particles have shortened diffusion paths and increased total surface area, and therefore the ability to penetrate all internal pore structures of adsorbent is very high (Gupta *et al.*, 2009). For larger particles, the diffusion resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently, the amount of phosphate adsorbed is small.

Figure 9: Effect of Particle Size

ADSORPTION KINETICS

To understand the sorption mechanism, such as mass transfer and chemical reaction processes, two types of models, viz., reaction-based and diffusion-based models, were applied, to test the fitness of the experimental data (Sivasankar *et al.*, 2010)

Reaction Based Models

Reaction based models, viz., pseudo-first order and pseudo second order model were plotted. Based on the experimental and theoretically calculated q_e values related to kinetic plots, it was found that pseudo first order model fitted better than pseudo second order model. Kinetic coefficient values for pseudo first order and pseudo second order were given in Table 3.

Diffusion Based Models

In adsorption studies, it is necessary to determine the rate-limiting step. Since the particles were vigorously agitated during the experiment, it is reasonable to assume that the mass transfer from the bulk liquid to the particle external surface did not limit the rate (Yadav *et al.*, 2006). Therefore, the results obtained from the experiments were used to

ADSORPTION ISOTHERMS

Equilibrium studies were performed to get the maximum phosphate adsorption capacities of the adsorbents in the concentration range of 10 mg/L at 30°C and 150 rpm for 60 min in the case of Kuttanad clay, 120 min in the case of laterite and 90 min for Coastal alluvium. The adsorption data were analyzed by the regression analysis to fit the Langmuir and Freundlich isotherm models. The constant values of all the above described isotherms are given in Table 2. R_L values calculated for the Langmuir isotherm from the present study was found to be 0.97 for Kuttanad clay, 0.799 for Laterite and 0.96 for Coastal alluvium, which indicate a favorable adsorption process as the values lies between 0 and 1.

Table 2: Isotherm Constants for 10 mg/l Phosphate Solution				
Isotherm Models	**Adsorbent**	**Regression Values (R^2)**	**Constants**	
Langumuir	Kuttanad Clay	0.891	q_{max} = 52.63 mg/g	b = 0.0031 l/mg
	Laterite	0.829	q_{max} = 5.37 mg/g	b = 0.025 l/mg
	Coastal alluvium	0.792	q_{max} = 12.5 mg/g	b = .00457 l/mg
Freundlich	Kuttanad Clay	0.942	k_f = 0.166 mg/g	n = 1.02
	Laterite	0.876	k_f = 0.154 mg/g	n = 1.18
	Coastal alluvium	0.808	k_f = -0.0160 mg/g	n = 0.590

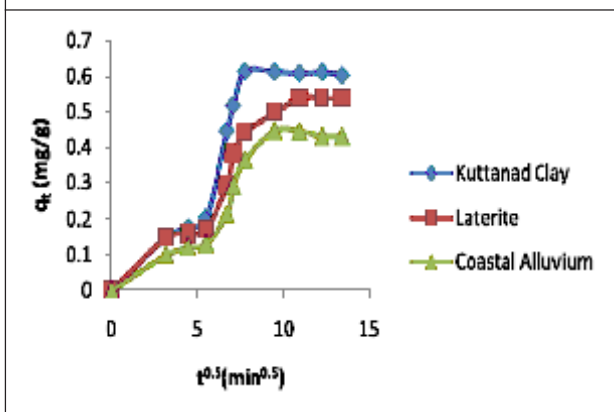| Table 3: Kinetic Coefficient Values for Phosphate Concentration of 10 mg/l							
Adsorbent	Theoretical q_e(mg/g)	Pseudo First Order Kinetic Model			Pseudo Second Order Kinetic Model		
		q_e	k_1	R^2	q_e	k_2	R^2
Kuttanad Clay	0.614	0.738	0.032	0.850	0.837	0.023	0.865
Laterite	0.543	0.646	0.028	0.938	0.777	0.020	0.895
Coastal alluvium	0.445	0.5081	0.023	0.832	0.6702	0.019	0.834

study the rate-limiting step by plotting intra-particle diffusion model as shown in Figure 10.

The intraparticle diffusion plot shows that the adsorption occurs in three steps.

· The first linear portion is attributed to the diffusion of phosphate towards adsorbent.

· The second linear portion is a delay process that corresponds to intra-particle diffusion but the intra-particle diffusion rate increases with initial phosphate concentration.

· The third stage is the diffusion through small pores and is followed by the establishment of equilibrium (Vaghetti *et al.*, 2009).

Figure 10: Intra-Particle Diffusion Model

CONCLUSION

The following were the conclusions drawn from the study.

· It is evident from the results that Kuttanad clay and Laterite are good adsorbent for removing Phosphate and these adsorbents are easily and cheaply available.

· Kuttanad clay has shown maximum Phosphate removal efficiency compared to Laterite soil. Coastal alluvium has shown only moderate removal efficiency when compared to Kuttanad clay and Laterite.

· The optimum contact time was found to be 60 min with the removal efficiency of about 61.12% for Kuttanad clay, 120 min with a removal efficiency of 55.32 % for laterite and 90 min with a removal efficiency of 46.89% for Coastal alluvium; at an adsorbent dose of 10 g/L for 10 mg/L aqueous phosphate solution at 30°C and at 150 rpm for a particle size of 75-150 μm

· From the effect of adsorbent dosage, it can be concluded that the removal efficiency increased with increase in adsorbent concentration. This can be attributed to the fact that the number of available adsorption sites increased by an increase in the adsorbent dose and this resulted in an increase in removal efficiency. A maximum removal efficiency of 77.5% was observed at a dosage of 17.5 g/L for Kuttanad clay, 68% removal efficiency was obtained with

15 g/L of Laterite and 49% removal efficiency with 17.5 g/L of Coastal alluvium

- All the three adsorbents showed more adsorption at lesser pH range. A maximum removal efficiency of 84.39% was obtained at a pH of 3 for Kuttanad clay, 77.49% removal efficiency was observed at a pH of 2 for Laterite and 55.78% removal efficiency at a pH of 2 for Coastal alluvium.

- The removal efficiency increased with the increase in the agitation speed for all the three adsorbent samples as increase in agitation speed decreases the boundary layer resistance for the transfer of adsorbate molecules from the bulk solution to the adsorbent surface.

- Percentage removal of phosphate molecule decreased with increase in initial concentration. This is because of presence of limited number of binding sites in the adsorbent.

- Percentage removal increased with the decrease in the particle size from 150-300 μm to a size <75 μm for all the three samples. This can be attributed to the fact that larger particles have small surface area and most of the internal surface areas of the larger particles are not utilized for adsorption.

- In the kinetic study, pseudo 1st and 2nd order models were fitted. Based on the experimental sorption capacity values compared with model values, it can be concluded that pseudo 1st order fitted more than pseudo 2nd order model. R^2 value was found to be higher for all the three samples.

- Intra particle diffusion plot shows that adsorption occurs in 3 steps, viz., boundary layer effect, intra-particle diffusion and pore diffusion for the selected adsorbents.

- From the isotherms study, it was found that the data fits well for Langmuir and Freundlich isotherm.

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