Removal of Phosphate by Modified Lignocellulosic Material

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ABSTRACT

This research work is concerned with preparation, characterization and application of modified lignocellulosic material (Kokko bark) for the removal of phosphate. In the preparation of modified lignocellulosic material, 5 % w/v bleaching powder was the most feasible composition. The removal of phosphate ion by lignocellulosic material (Kokko bark) was determined according to the sorption parameters, pH, initial concentration, contact time, dosage of sorbent and various temperatures by using UV visible spectrometer at wavelength 880 nm. The maximum absorption percent of phosphate was found to be 65.1 % where 10 mg L^{-1} of initial concentration, 1 g / 100 mL of dosage, pH 7 and 1 h of contact time. The effect of temperature was also important role in sorption of phosphate by modified bark. The adsorption capacities increase with increase in temperature for sorbent. The activation energy evaluated by using Arrhenius equation was 9.02 $kJmol^{-1}$. The phosphate sorbed lignocellulosic material was used as nutrient fertilizer for plant growth.

Keywords: lignocellulosic material, Kokko, phosphate, sorbent, sorption

INTRODUCTION

The structural materials that plants produce to form the cell walls, leaves, stems, stalks and woody portions of biomass are called lignocellulose, a composite material of rigid cellulose fibers embedded in a cross- linked matrix of lignin and hemicellulose that bind the fibers. Lignocellulosic material is often a waste material of food processing and forest products industries that may be locally, readily available at low cost (Castro, 1994). Lignocellulose materials exhibit interesting capacities as pollutant sorbents and chemical modification of lignocellulosic materials enhance their sorption capacities for removal of phosphate. The lignocellulosic materials were obtained from Kokko (*Albizzia lebbek* Benth). Wood has a significant proportion of acid hydroxyl groups due to the presence of major structural components, cellulose, hemicellulose and lignins. Wood has a great number of pores and cracks through which a chemical reagent is capable of diffusing inside the interstitial structure (Kamel, 2007). The phosphorus removal processes that occur in natural, domestic and industrial treatment systems are considered to be adsorption, chemical precipitation and biological treatment (Karthikeyan, *et al.*, 2002). The major goal of this study is to prepare modified lignocellulosic material derived from Kokko (bark) to be used as sorbent for minimizing phosphate levels in runoff from agricultural lands. Phosphate in fertilizers, rock, or soil seep into water systems. Natural events such as heavy rainfall will wash agricultural fields of their topsoil and introduce phosphate salts into rivers, lakes and ultimately coastal/oceanic environments, which will increase phosphate concentration causing algal blooms that could lead to kill fish or impact on other organisms. Wastewater released into the environment, that has not been

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properly treated, can potentially contain phosphates from detergents and can cause similar effects that can occur as a result eutrophication (Elena, *et al.*, 2001).

MATERIALS AND METHODS

The chemicals used in this work were the products from British Drug House chemical Ltd., England. The following instruments were used: pH meter, UV-visible Spectrophotometer, pH meter(Jenway 4330, Lab quip, England), Magnetic stirrer (Volts 230, Hz ~ 50, Bibby Sterilini Ltd., United Kingdom), Electric furnace (100-1100°C, Gallenkamp, West Austrialia),Electric shaker (0-200°C, SBS - 30 Bibby, Stuart Scientific shaker Bath, UK), UV - visible Spectrophotometer (Jenway 6305, UK).

Sampling and Preparation of Lignocellulosic Material

The main working sample lignocellulosic material was obtained from Kokko (*Albizzia Lebbek* Benth) tree. It was a locally available collected from Thuwunna, Thingangyun Township, Yangon Region. The sample was separated Kokko bark from Kokko tree. The sample was repeatedly washed with distilled water to remove dust and impurities and dried at sun light. The dried sample was ground and sieved through mesh sieve no.80 (250µm).

Preparation of Modified Lignocellulosic Material

The bleaching powder 5 % (w/v) was dissolved in 100 mL of hot distilled water (55-60°C). The prepared solution was stirred at a constant rate (~ 200 rpm) for about 10 min and then filtered. The sample (1g) was added to the filtrate solution of bleaching powder and stirred for about one hour and kept overnight (24 h). And then filtered, washed with distilled water until the pH of filtrate has to reach about 7. The modified lignocellulosic material was dried at room temperature.

Determination of Physicochemical Properties of Kokko Bark Before and After Modification

The physicochemical properties (moisture content, ash content, solid content, bulk density and pH) of the prepared samples were determined by conventional methods (Table 1).

Preparation of standard stock solution

Standard Stock solution containing 100 mg L^{-1} was prepared by dissolving potassium dihydrogen phosphate. In the preparation of series of phosphate solutions, (concentrations ranging from 0.1 ppm to 2 ppm) distilled water was used as the dilutent. Analyses were carried out by colormeteric method using UV-visible spectrophotometer and calibration curves of phosphate solution was plotted at wavelength 880 nm.

Effect of pH, initial concentration, contact time, dosage and temperature on phosphate ion removal

The model solutions of potassium dihydrogen phosphate (5 mg L^{-1} to 20 mg L^{-1}) were prepared and the ranges of pH (4 - 9) were adjusted by the adding of 0.1M sodium hydroxide and 0.1M hydrochloric acid. Each 10 mL of phosphate solution was mixed 0.1g of sample in the flasks. The flasks were shaken with electric shaker at room temperature for 1 h. At the end of the equilibrium time, each of the solution was filtered. The filtrates were analyzed by UV - visible spectrophotometer at 880 nm. The removal percent of phosphate ions are described in Table 2 and Figure 1.

In the contact time experiment, the sample (0.1 g) was placed into a 10 mL of phosphate solution (10 mg L^{-1}) at pH 7. The solutions were shaken by an electric shaker. After the contact time (5, 10, 15, 20, 30, 40, 50, 60, 70 min), each solution was filtered and the filtrates were analyzed by UV- visible spectrophotometer. The removal percent of phosphate ions are described in Table 3 and Figure 2.

The accurately weighed different samples of 0.5 g to 3.0 g were taken into a conical flask. A constant concentration of phosphate solution (10 mg L^{-1}, pH 7) 100 mL is added to each conical flask and shaken by electric shaker at room temperature for 1 h. After this contact time, each of the solution was filtered. The filtrates were analyzed by UV - visible spectrophotometer at 880 nm. The resulting data are shown in Table 4 and Figure 3. Langmuir, Freundlich and Temkin isotherms of phosphate ions on the sorbent is plotted by dosage method.

RESULTS AND DISCUSSION

Table 1 shows that the physicochemical properties (moisture content, ash content, bulk density, and pH) of Kokko bark before and after modification.

Table 1 Determination of the Physicochemical Properties of Kokko Bark Before and After Modification

No.	Physicochemical Properties	Kokko Bark	Modified Kokko Bark
	Moisture content (%)	15.87	16.87
	Ash content (%)	1.35	2.56
3.	Bulk density (g mL^{-1})	0.219	0.259
	pH	6.8	7.3

Effect of pH on the adsorption of phosphate ion

The dependence of adsorption of phosphate on pH of the aqueous dispersion for modified bark is shown in Table 2 and Figure 1.The adsorption of phosphate on sorbent, was examined at various pH values ranging from 4 to 9 with an initial phosphate concentration ranging from 5 mg L^{-1} to 20 mg L^{-1} at room temperature. From the resulting data, as pH increases, the percent removal also increases until it reaches an optimum condition of pH 7. Beyond the optimum pH of 7, the percent removal of phosphate ions markedly begins to decrease to low values up to pH 9.The maximum percent removal of phosphate for 10 mg L^{-1} initial concentration was 65 % at pH 7.

The effect of initial concentration on the percent removal of phosphate by bark was also studied at different initial concentrations ranging from 5mg L^{-1} to 20 mg L^{-1} by keeping all other parameters such as adsorbent dose 1g / 100 mL and contact time 60 min at room temperature. It was noticed that with increase in initial phosphate concentration, the percentage removal of phosphate decrease. At higher adsorbate concentration, the binding capacity of adsorbent approaches saturation resulting in decrease in overall percent removal. in Table 2 and Figure 1.

Table 2 Effect of pH on the Removal of Phosphate by Modified Kokko Bark

Initial concentration (mgL^{-1})	Percent removal (%)					
	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
5	70.2	70.6	71.8	72.3	67.0	64.7
10	64.3	64.5	64.8	65.1	61.5	58.4
20	52.2	52.9	53.9	54.2	50.1	47.8

Dosage = 1 g /100 mL
Time = 1 h

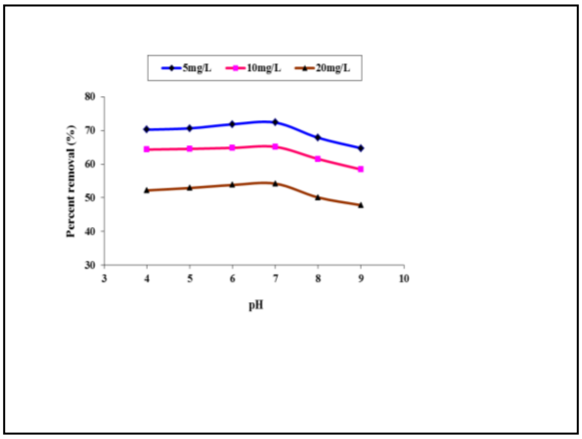


Figure 1. Effect of pH on the removal of phosphate by modified Kokko bark

Effect of contact time on the adsorption of phosphate ion

The effect of contact time on the removal of phosphate (using initial concentration 10mg L^{-1}) by modified bark is shown in Table 3 and Figure 2. It can be seen from the profiles as shown in Figure 2.The extent of adsorption increases with time and attained equilibrium for sorbent at 60 min.

After this equilibrium period, the amount of phosphate adsorbed did not change significantly with time. The amount of phosphate adsorbed versus time curves are smooth and continuous. The changes in the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the phosphate uptake rate by adsorbent had decreased significantly, due to the decrease in number of adsorption sites. Decreased removal rate, particularly, towards the end of experiment, indicates the possible monolayer of phosphate ions on the outer surface, pores of both the adsorbents and pore diffusion onto inner surface of adsorbent particles through the film due to continuous shaking maintained during the experiment.

Table 3 Effect of Contact Time on the Removal of Phosphate Ion by Modified Kokko Bark

Contact time (min)	Percent removal (%)
5	39.1
10	41.9
15	44.6
20	46.9
30	49.3
40	53.3
50	57.3
60	65.1
70	65.2

Initial concentration = 10 mg L^{-1}
Dosage = 1g /100 mL
pH = 7

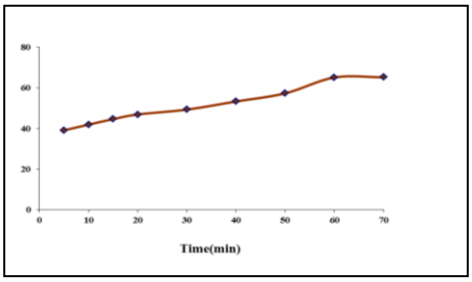


Figure 2 Effect of contact time on the removal of phosphate ion by modified Kokko bark

Effect of dosage on the adsorption of phosphate ion

Table 4 shows the removal of phosphate from a constant initial concentration 10mg L^{-1} at pH 7 by the amount of sorbents in range from 0.5 g to 3.0 g in 100 mL potassium dihydrogen phosphate solution. Figure 3 shows the corresponding data in terms of percent removal with respect to sorbent dose. It can be seen that as the percent removal of phosphate increases with an increase in sorbent dose. At the dose of 3.0 g in 100 mL, it was found that after 60 min agitation time, the amount of phosphate being adsorbed were 88.3 % for modified bark. The higher percent removal capacity may be attributed to the greater quantity of sorbent dose being used. This is due to increase in adsorbent dosage attributed to increase in surface area and availability of adsorption site.

Table 4 Effect of Dosage on the Removal of Phosphate Ion by Modified Kokko Bark

Dosage (g/100mL)	Percent removal (%)
0.5	37.8
1.0	65.1
1.5	73.3
2.0	82.0
2.5	85.4
3.0	88.3

Initial concentration = 10 mg L^{-1}
pH = 7
Time = 1 h

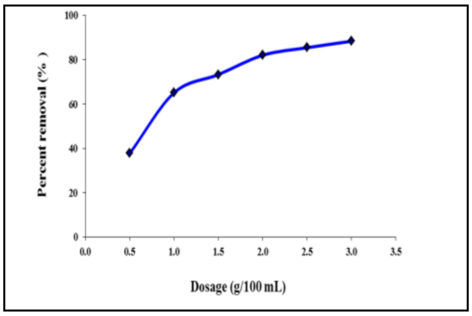


Figure 3 Effect of dosage on the removal of phosphate ion by modified Kokko bark

Effect of temperature on the adsorption of phosphate ion

Temperature experiments show that there is an apparent direct relation between extent of removal of phosphate and temperature at which sorption is affected. Table 5 and Figure 4 show the results of sorption capacity with respect to time at different temperatures for the removal of phosphate ion (using initial concentration 10mg L^{-1}) on bark (1g/100 mL dose). The rate of removal of phosphate ion is increased by an increase in temperature of the solution for sorbent.

The increase in the initial rate of removal of phosphate from solution at the higher temperatures also reduces the time required to attain equilibrium conditions. For example, the contact time required to reach equilibrium at 30 °C for the removal of phosphate ion on all sorbents were found to be nearly 60 min and at 80 °C the contact time required was at about 20 min.

In this adsorption, increase in temperature leads to increase both in adsorption rate and the amount of adsorbed material, thus, adsorption of phosphate ion is possibly a chemical adsorption process. The enhancement in the adsorption capacity may be due to the chemical interaction between adsorbent and adsorbate, creation of some new adsorption sites or the increased rate of intraparticle diffusion of phosphate ions into the pores of the adsorbent at higher temperatures.

Table 5 Effect of Temperature on the Removal of Phosphate by Modified Bark at Different Contact Times

Contact time (min)	Percent removal (%)			
	30 °C	40 °C	60 °C	80 °C
5	39.1	50.2	55.1	65.8
10	41.9	56.1	67.4	76.2
15	44.6	62.5	77.4	79.3
20	46.9	65.2	80.8	81.2
25	48.1	67.3	81.3	81.5
30	49.3	68.1	81.7	81.8
35	51.4	70.0	82.1	82.4
40	53.3	71.2	82.2	82.4
45	55.2	72.3	82.2	82.4
50	57.3	72.5	82.2	82.4
55	61.8	73.4	82.2	82.4
60	65.1	73.9	82.2	82.4

Initial concentration = 10 mg L^{-1}
Dosage = 1 g /100 mL, pH = 7

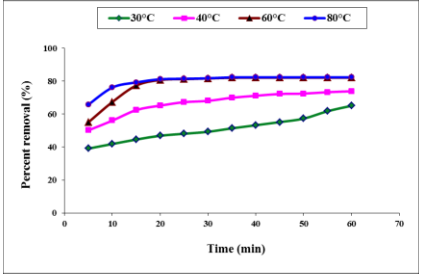


Figure 4 Effect of temperature on the removal of phosphate by modified Kokko bark at different contact times

Adsorption Isotherm Studies

The adsorption of phosphate by modified Kokko bark was based on dosage method. The dosage method is the practical method of assessing the sorption capacity of a sorbent towards an adsorbate. The dosage method involves the use of different masses of sorbent but a constant initial concentration 10 mg L^{-1} by the amount of sorbent in range from 0.5 g to 3.0 g at a fixed temperature.

In a two component system (solid-liquid system), a graph of the sorption capacities x/m (mg g^{-1}) can be plotted as a function of the solute concentration in the liquid phase C_e (mg L^{-1}) at equilibrium. The sorption capacities versus the equilibrium concentration, by non linear regression method were presented in Table 6, Figures 5, 6 and 7 for the isotherms of phosphate sorption on modified bark.

In this type of isotherm, the initial portion provides information about the availability of the active sites to the adsorbate and the plateau signifies the monolayer formation. The initial curvature indicates that a large amount of phosphate is adsorbed at a lower concentration as more active sites of sorbents are available. As the concentration increases, it becomes difficult for a phosphate molecule to find vacant sites and so monolayer formation occurs.

Langmuir Isotherm

Table 6 represent the data and Figure 5 showed the Langmuir isotherms pertaining to Langmuir sorption equation for the sorption of phosphate ion by the sorbent.The Langmuir sorption equation was used to fit the experiment sorption data.

Freundlich Isotherm

The Freundlich isotherm is regarded as an empirical isotherm. It indicates the surface heterogeneity of the sorbent. Table 6 corresponding Figure 6 showed the sorption data for the Freundlich isotherm of the sorption of phosphate ion by the sorbent.

Temkin Isotherm

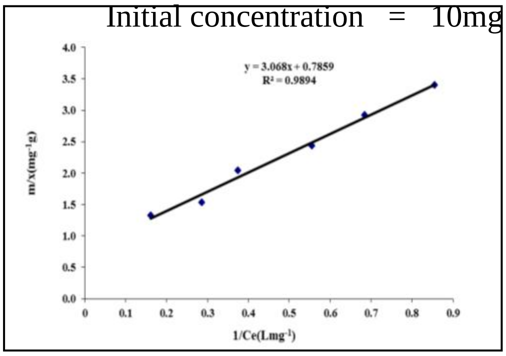
Temkin model is more general than those of Langmuir and Freundlich. They do not assume an energetically homogeneous surface and propose a non-homogeneous distribution of sorption sites.Temkin parameters ‘a’ and ‘b’ can be determined from slope and intercept (See Figure 7).

The calculated results of the Langmuir, Freundlich and Temkin isotherm constants are presents in Table 7. From three isotherms, the correlation coefficient (R^2) are nearly 0.9 for modified bark. The adsorption of phosphate ion on the sorbent was found to agree with Langmuir, Freundlich and Temkin models. Adsorption Parameters for Sorbent is presented in Table 7.

Table 6 Data Treatment for Langmuir, Freundlich and Temkin Isotherm (Adsorption of phosphate by Modified Kokko Bark)

Dosage (g/ 100 mL)	Ce (mg L^{-1})	x/m (mg g^{-1})	1/e (L mg^{-1})	1/(x/m) (g mg^{-1})	Log Ce	Log x/m
0.5	6.22	0.756	0.161	1.323	0.794	-0.121
1.0	3.49	0.651	0.286	1.536	0.543	-0.186
1.5	2.67	0.489	0.375	2.045	0.427	-0.311
2.0	1.80	0.410	0.556	2.439	0.255	-0.387
2.5	1.46	0.342	0.685	2.924	0.164	-0.466
3.0	1.17	0.294	0.855	3.401	0.068	-0.532

Initial concentration = 10mg L^{-1} Contact time = 1 h pH = 7



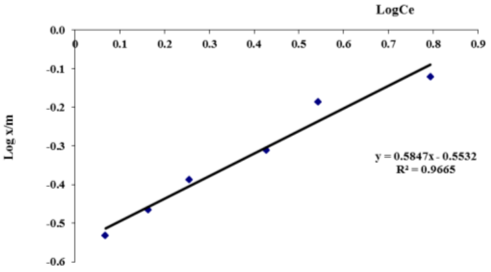


Figure 5 Langmuir isotherm for sorption Figure 6 Freundlich isotherm for
sorptionof phosphate on modified Kokko bark of phosphate on modified Kokko bark

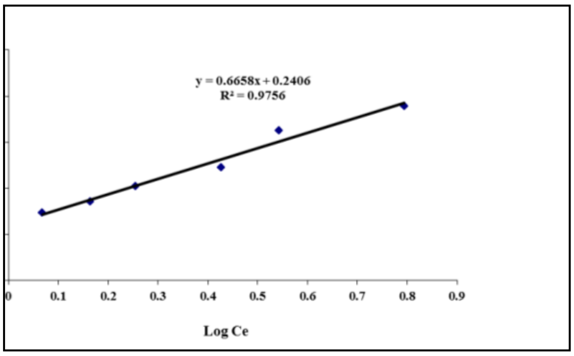


Figure 7 Temkin isotherm for sorption of phosphate on modified Kokko bark

Table 7 Adsorption Parameters for Sorbent

Sorbent	Langmuir Model				Freundlich Model			Temkin Model		
	X_m (mg g^{-1})	b (L mg^{-1})	R^2	R_L	K (mg g^{-1})	1/n (Lmg^{-1})	R^2	a (mg g^{-1})	b (L mg^{-1})	R^2
Bark	1.272	0.256	0.989	0.281	0.279	0.584	0.966	0.241	0.289	0.975

Sorption Kinetics

The typical experimental results of phosphate adsorption on the sorbent versus adsorption time of different temperature are shown in Table 8 and Figure 8.The value of rate constant, k, were found to slightly increase for an increase in solution temperature. The k values were plotted as a function of the reciprocal of the Kelvin temperature. Linear variations were observed as shown in Figure 9. Therefore, the sorption rate constant may be expressed as a solution function of temperature by the Arrhenius relationship:

$k = k_o \exp (-E_a / RT)$

where k is the rate constant of sorption (mgg^{-1} $min^{-0.5}$); k_o is the temperature independent factor (mg g^{-1} $min^{-0.5}$) , E_a is the activation energy of sorption ($kJmol^{-1}$),R is the gas constant (8.314 J $mol^{-1}K^{-1}$), T is solution temperature (K). The linear equation $\log k = \log k_0 - E_a/ 2.303 RT$.

From Arrhenius equation,the activation energies computed from the slope of the plot, activation energy of modified bark is 9.02 $kJmol^{-1}$ (See Table 9).

Removal efficiency of phosphate ion from wastewater by modified Kokko bark is presented in Table 10.

Table 8. Sorption Capacities of Modified Kokko Bark on Phosphate with respect to Square Root of Time at Different Temperatures

Initial concentration = 10 mg L^{-1}

Time (min)	Time $^{0.5}$ (min)	Sorption capacity (mgg^{-1})			
		30 ºC	40 ºC	60 ºC	80 ºC
5	2.2	0.391	0.502	0.551	0.658
10	3.2	0.419	0.561	0.674	0.762
15	3.9	0.446	0.625	0.774	0.793
20	4.5	0.469	0.652	0.808	0.812
25	5.0	0.481	0.673	0.813	0.815
30	5.5	0.493	0.681	0.817	0.818
35	5.9	0.514	0.700	0.821	0.824
40	6.3	0.533	0.712	0.822	0.824
45	6.7	0.552	0.723	0.822	0.824
50	7.1	0.573	0.725	0.822	0.824
55	7.4	0.618	0.734	0.822	0.824
60	7.8	0.651	0.739	0.822	0.824

Dosage = 1 g /100 mL pH = 7

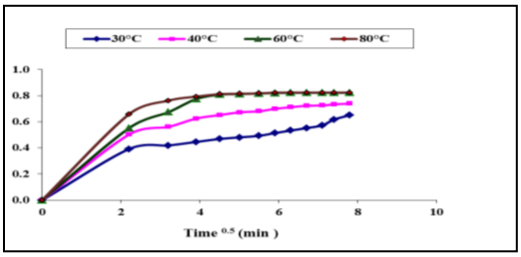


Figure 8 Sorption capacities of modified Kokko bark on phosphate with respect to square root of time at different temperatures

Table 9 Arrhenius Relation for Phosphate Adsorption on Modified Kokko Bark at Different Temperatures

Sorbents	Temperature (K)	1/T(10^{-3}) (K^{-1})	Rate constant (k) ($mgg^{-1}min^{-1}$)	Log k	Activation Energy (E_a) ($kJmol^{-1}$)
Bark	303	3.30	0.18	-0.744	9.02
	313	3.19	0.24	-0.619	
	333	3.00	0.26	-0.585	
	353	2.83	0.30	-0.523	

Initial concentration = 10 mg L^{-1} Dosage = 1 g /100 mL pH = 7

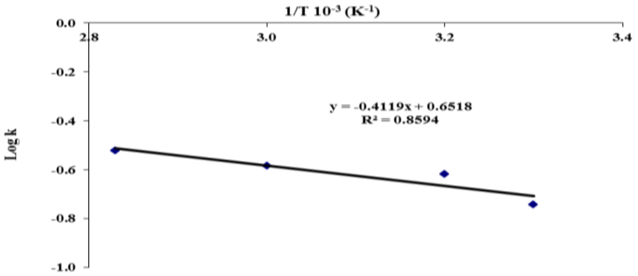


Figure 9 Log rate constant vs reciprocal absolute temperature for removal of phosphate by modified Kokko bark

The removal percent of phosphate by modified Kokko bark is shown in Table 9.

Table 10 Phosphate Removal Efficiency in Wastewater by Modified Kokko Bark

Sorbent	Colour residual (absorbance)	Colour removal (absorbance)	Removal efficiency (%)
Bark	0.542	1.179	70.24

Initial concentration of wastewater solution = 1.721 (absorbance)
Dosage = 1 g /100 mL
Contact time = 1 h , pH = 7

CONCLUSION

Lignocellulosic material (Kokko bark) was modified by using bleaching powder. The prepared modified lignocellulosic materials (Kokko bark) for the removal of phosphate were investigated. The removal of phosphate by sorbent was determined according to the sorption parameters; pH, initial concentration of phosphate ions, contact time, dosage of sorbents and temperature At the optimum pH 7, the percent removal of phosphate by bark is 65.1% corresponding to a contact time of 60 min and initial concentration of 10 mg L^{-1} were observed. In the effect of temperature, the removal of phosphate by sorbent, the rate of adsorption increase by an increase in temperature. On the basis of dosage method, the resulting data were found to fit the Langmuir, Freundlich and Temkin isotherms. Sorption kinetics study using relevant equation corresponded Arrhenius equation was applied and sorption rate constant ‘k’ was evaluated. The activation energy computed from the Arrhenius plot was 9.02 $kJmol^{-1}$. The removal of phosphate ion from wastewater by modified Kokko bark was observed as 70.24%. On the context, the modified lignocellulosic material (kokko bark) is effective and efficient sorbent for the removal of phosphate ion was observed.

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