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Removal of Phosphate from Aqueous Solution with Modified Sawdust

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Abstract

In the present study, chemically modified Aleppo pine (*Pinus halepensis Miller*) sawdust was used for removal of phosphate from water. The sawdust preparation process included size selection, extraction for surface activation, acid prehydrolysis, and treatment with urea. Sorption of phosphate ions onto the sawdust media was studied using the batch technique. The effect of different parameters such as contact time, adsorbate concentration, and temperature was investigated. The adsorption kinetics data were best described by the pseudo-second order rate equation, and equilibrium was achieved after 40 min. The Langmuir and Freundlich equations for describing adsorption equilibrium were applied to data. The constants and correlation coefficients of these isotherm models were calculated and compared. The adsorption isotherms obey the Freundlich equation. The thermodynamic parameters like free energy, enthalpy and entropy changes for the adsorption of phosphate ions have been evaluated and it has been found that the reaction was spontaneous and endothermic in nature. The low value of activated energy of adsorption, 3.088 Kj/mol indicates that the phosphate ions are easily adsorbed on the sawdust. Results suggest that the prepared chemically modified Aleppo pine sawdust has potential in remediation of contaminated waters by phosphate.

Keywords: Sawdust, Phosphate, Adsorption isotherms, Kinetics, Thermodynamics.

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Nomenclature

C_o Initial solute concentration in the aqueous phase, mg/L

C_e Equilibrium or final solution concentration, mg/L

K_1 Rate constant of the pseudo-first-order equation, min^{-1}

K Rate constant of the pseudo-second-order equation, mg/g/min

K_f Indicator of adsorption capacity, L/g

n   Freundlich constant representing adsorption intensity, g/L

K_L Langmuir equation constant, L/g

K_P Intraparticle diffusion rate constant, $mg/g.min^{1/2}$

q_e Amount of adsorbate at equilibrium, mg/g

Q_{max} Monolayer maximal capacity of adsorption, mg/g

q_t Amount adsorbed at time t, mg/g

R^2 Regression coefficient

t   Contact time, min

T   Experimental temperature, K

R   Universal gas constant, J/ m

K_d Thermodynamic equilibrium constant of the adsorption process

$\Delta G°$ The change in Gibbs free energies, Kj/mol

$\Delta H°$ Enthalpy, Kj/mol

$\Delta S°$ Entropy, J/mol.K

1. Introduction

Phosphorus is an essential nutrient in aquatic environments. The geochemical behaviors of phosphate have been the subject of numerous studies in various disciplines [1-2]. An excessive concentration of this nutrient in water is often responsible for eutrophication leading to short- and long-term environmental and aesthetic problems in lakes and reservoirs, coastal areas, and other confined water bodies, and is a threat to ecological health [3]. Algal blooms causing high economic damage in coastal oceans can be caused by phosphate run-off episode [4]. In many countries, stringent regulations limit phosphorous level to 0,05 mg/L to prevent increased algae growth [5].

Various techniques have been developed for the removal of phosphate from water and wastewater [6]. Which include chemical precipitation [7-8], adsorption using suitable materials [9], biological treatment [10] and crystallization [11]. Adsorption of phosphate onto particulate matter is an important process that affects significantly the mobility and bioavailability of phosphorus in natural environments. In adsorption processes, diverse adsorbents such as red mud, activated alumina, polymeric ligand exchangers, iron/aluminum-coated sand, calcium-based adsorbents, sugarcane bagasse, sawdust, etc have been studied as adsorbents for phosphate removal [12-13].

Lignocellulosic materials exhibit interesting capacities as pollutant adsorbents and by activation process or by chemical surface modification the adsorption capacity of lignocellulosic materials can be increased [14-15]. The activation process enhances the pore volume and hence enlarges the diameter of the pores. During activation the textural properties of materials may change.

The Sawdust Aleppo pine (studied here as biomass for removing ions phosphates) is one of the well known fibre crops [16]. This sawdust suggests a broad potential application to adsorbent production, this is due to the large amount of easily available functional groups such as alcohols, aldehydes existing in the cellulose, hemicelluloses and lignin, which can easily make a series of chemical reactions, such as condensation, etherification and copolymerization.

The aim of this study was to test the suitability of using the chemically modified sawdust of Aleppo pine (*Pinus halepensis Miller*) as a sorbent for the removal of phosphate ions and to study the effects of initial phosphate ions concentration, contact time, and temperature on sorption process.

2. Materials and Methods

2.1 Materials and general methods

The sawdust of Aleppo pine (*Pinus halepensis Miller*) was used as a sorbent for removal of phosphate ions from aqueous solutions. The species was provided from a foundry in El-Harrach city, Algeria. The sawdust was washed several times with distilled water to remove surface adhered particles and soluble materials.

The oven dried sawdust was sieved and the fraction with particle size between 1.0 and 0.4 mm was extracted in a Soxhlet apparatus containing 300 mL of 2/1 v/v {95% hexane} / ethanol [17].

Extraction is expected to increase the surface energy of the sawdust there by facilitating binding with reactive reagents. At the end of 8 hours, the Soxhlet apparatus were allowed to cool down and the thimble was removed. Then the thimble was air-dried in the ventilation hood overnight, and dried in an oven at approximately 105°C for 6.5 hours.

Thereafter, the thimble was acid prehydrolysed in a 500 ml glass batch reactor, equipped with an internal thermocouple, immersed in a heating oil bath [18]. The prehydrolysis final temperature was 100 °C; 1.8 M H_2SO_4 solutions catalysed the reaction at a liquid-to-solid ratio of 10:1 by mass, and the reaction time was 4 hours. The thimble was cooled to room temperature, removed from the oven, and treated according to the surface chemistry modification schemes outlined below:

To prepare the sawdust modified with urea, the sawdust fraction (10 g) was agitated (140 rpm) in the presence of urea (20 g/L) for 4 h, then rinsed with deionized water and dried in oven (80 °C) overnight.

The stock solution of phosphate was prepared by dissolving $NaH_2PO_4.2H_2O$ salt (analytical reagent grade) in double distilled water (1000 mg/L). The experimental solution was prepared by diluting the stock solution to desired concentration using distilled water. The pH value of the phosphate working solution was adjusted with 1 M HCl and 1M NaOH solutions before adsorption experiments.

2.2 Analytical methods

Phosphate was analyzed by the molybdenum blue method [19]. Molybdenum acid ammonium solution, 2.0 ml, and an L-ascorbic acid solution, 1.0 ml, were added to the sample solution.

After 15 min, the absorbance at a wavelength of 700 nm with UV–visible recording spectrophotometer (UVmini-1240 SHIMADZU) using 10 mm matched quartz cells. The FTIR spectrum of the Sawdust was recorded on a FTIR spectrophotometer (Shimadzu; Model No 8400S). Samples were prepared in KBr disks (2 mg sample in 200 mg KBr). The scanning range was (400 - 4000) cm^{-1} and the resolution was 2 cm^{-1}. Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the adsorbent. SEM images were recorded using JOE-JSM840 field emission SEM. A thin layer of platinum was sputter coated on the samples for charge dissipation during FESEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere. The coated samples were then transferred to the SEM specimen chamber to get the images.

2.3 Adsorption kinetics

Phosphate adsorption kinetics was evaluated at room temperature (25 °C) and an initial PO$_4$ concentration of 300 mg/L.

Portions of 0.5g sawdust were placed into 250 ml Erlenmeyer flasks, and placed it in a temperature controlled orbital shaker to enhance reaction equilibrium at room temperature (25 °C). The pH the solution was maintained at 7.5. The samples were taken in triplicates at the intervals of 0, 10, 20, 25, , 40, , 0, 90, , 180, and 380 min after the start of adsorption reaction and analyzed for residual PO of the solution ow typical kinetic equations i.e. first order and second order were tested.

2.4 Adsorption isotherms

The portions of 0.5 g sawdust samples were stabilized in 250ml Erlenmeyer flasks with solution containing various amounts of KH$_2$PO$_4$ for 120 min. The pH of the solution was adjusted and maintaining at 7.5 with 0.1 M HCl or 0.1 M NaOH. The flasks were capped and shaken at 120 rpm in a temperature controlled orbital shaker to enhance reaction equilibrium at room temperature (25 °C). At end of 120 equilibration period, the suspensions were filtered through a 0.45 μm filter and analyzed for the amount of adsorbed PO$_4^{-3}$. Control samples containing all other reagents except adsorbent were also analyzed. The PO$_4^{-3}$ adsorption data were fitted to the simple Langmuir and Frendlich equations.

2.5 Effect of temperature

The effect of temperature (, 30, and 60 °C) on Sawdust mediated phosphate adsorption was investigated at fixed amount of adsorbent an initial phosphorous concentration of 250 mg/L. Portions of 0.5 g sawdust were placed in 250 ml Erlenmeyer flasks. The pH the suspension was adjusted to 7.5. The flasks with the content were capped and shaken at 120 rpm a temperature controlled orbital shaker to enhance reaction equilibrium at room temperature (25 °C) at the end of 0 min treatment time, the suspensions were filtered through a 0.45 μm filter and the filtrates were analyzed for residual PO$_4^{-3}$ concentration.

3. Results and Discussion

3.1 Adsorbent characterization

The surface morphologies of unmodified sawdust and that chemically modified was determined using SEM. Fig. 1 Fig. 2 shows the SEM photograph of unmodified sawdust and that chemically modified at 637 times magnifications. SEM images revealed that extraction with hexane-ethanol dissolved the extractive matters, exposed the microfibers and resulted in the development of a porous surface with coarse fibrous texture making the surface more amenable for the attachment of reactive functional groups. Extraction ruffled the bark fiber surface tissue more extensively than the wood fiber. After acid prehydrolysis and urea addition, the presence of ordered string-shaped surface structures and fine particle deposits were observed. The string shaped regions could correspond to the edge of a cell curvature containing a high density of urea accumulation. The results of Fig.1 and Fig.2 also show that chemically modified sawdust has developed more pores than that unmodified, however the adsorption capacity was higher than unmodified sawdust.

This is because adsorption is a surface phenomenon; therefore smaller adsorbent particle size offers a comparatively larger and more accessible surface area (more pores developed) and hence higher adsorption occurs at equilibrium [20].
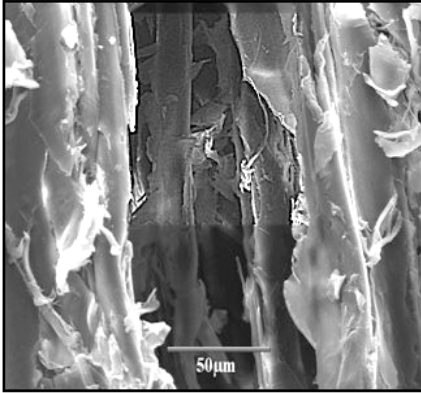

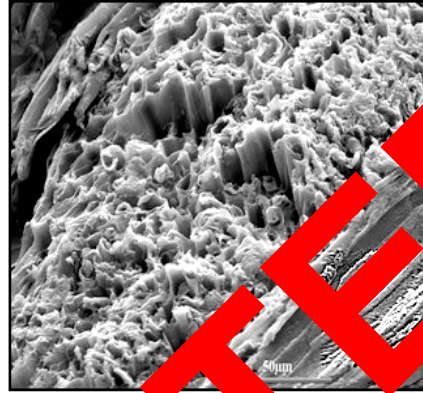Fig. 1. SEM of unmodified sawdust at 637 times magnification; the scale bar corresponds to 50 µm

Fig. 2. SEM of chemically modified sawdust at 637 times magnification; the scale bar corresponds to 50 µm

The FTIR spectra of treated sawdust are shown in Fig. 3. The spectra shows a broad absorption band around 3300 cm^{-1}, which may be attributed to the OH group. Presence of absorption bands at 3748 cm^{-1} and at 2947 cm^{-1} are due to the presence of H-bridges. It also confirms formation of carbamide as is evident from bands appeared at 3558 cm^{-1} (N-H stretching). The bands at 1606 and 1510 cm^{-1} reveal the aromatic C-C stretching in the phenyl ring of lignin [21]. Absorption at 1460 cm^{-1} is assigned to methoxy group of lignin in the sawdust [22]. The bands at 1317, 1265 and 1035 cm^{-1} are due to the C=O stretching vibration of primary alcohol. The weak band at 896 cm^{-1} is characteristic of C-H bending vibration in-glucosidic linkage [23].
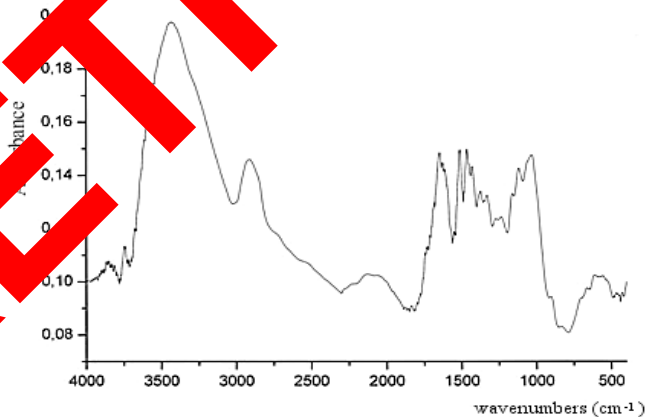

Fig. 3. FTIR spectrum of modified sawdust.

3.2 Effect of Time

The phosphate adsorption results showed that within the first 30 min a rapid uptake of phosphate ions takes place (Fig. 4). After this time, the rate of phosphate ions uptake was reduced as the equilibrium approached. The equilibrium for phosphate ions adsorption onto modified sawdust was reached after 40 min. Therefore, the time of 40 min was chosen for further batch adsorption experiments. The data shown in Fig. 4 were used to determine kinetic parameters in the kinetic models tested.
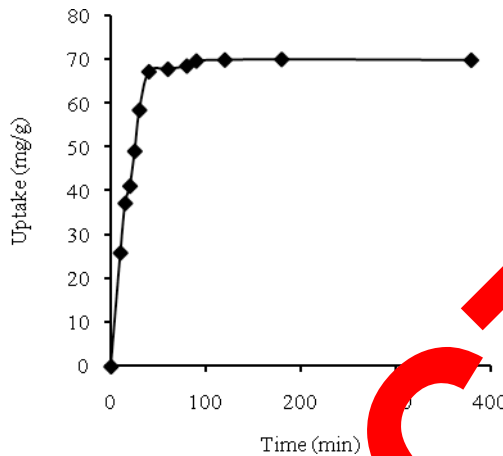

Fig. 4. The kinetic data for PO_4^{-3} adsorption in modified sawdust

3.3 Analysis of kinetic data for sawdust

Mathematical models that can describe the behaviour of a batch sorption process operated under different experimental conditions are very useful for studies or process optimization.

A number of models with varying degrees of complexicity have been developed to describe the kinetics of ions sorption in batch systems. The finally selected kinetic models will be those which not only fit closely the data but also represent reasonable sorption mechanisms. In order to determine which model could properly describe the sorption kinetics, the kinetic equations were used to fit the experimental results.

3.4 Pseudo first order model

A pseudo first order equation for the liquid-solide adsorption due to Lagergren was used by Babu and Gupta [24]:

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \qquad (1)$$

Where q_e and q_t (mg/g) are the amount of phosphates sorbed at equilibrium and at time *t*, respectively and K_1 (min^{-1}) is the rate constant of pseudo first-order adsorption. Equation (1) was integrated with boundary conditions t = 0 to t = t and x = 0 to x = x:

$$\ln\left(\frac{q_e}{(q_e - q_t)}\right) = K_1 t \qquad (2)$$

Equation (2) may be rearranged to the linear form:

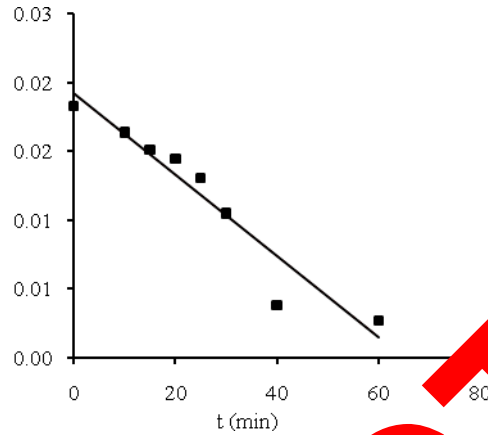$$\log(q_e - q_t) = \log(q_e) - \left(\frac{K_t}{2.303}\right)t \quad (3)$$

Fig. 5. Pseudo–first order plot for the adsorption of PO_4^{-3} into modified sawdust

3.5 Pseudo-second-order model

Adsorption data were also evaluated according to the pseudo-second-order reaction kinetic was used by previously proposed [24]:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (4)$$

Where K_2 is the second-order reaction constant. If Equation (4) is integrated, the following expression is obtained:

$$\frac{1}{(q_e - q_t)} = K_2 t + C \quad (5)$$

In Equation (5), C is the integration constant of the second-order reaction kinetic. With an algorithmic arrangement, the following statement is formed:

Fig. 6. Pseudo–second order plot for the adsorption of PO_4^{-3} into modified sawdust

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e}\right) + \frac{t}{q_e} \quad (6)$$

The constants K_2 and q_e were calculated from the linear plot of $\log(q_e - q_t)$ vs. t (Fig. 5) for pseudo-first-order model and plot of $\frac{t}{q_t}$ vs. t. (Fig. 6) for Pseudo-second-order model.

The adsorption constant values of each model (K_1 and K_2), the correlation coefficients, R^2, and the predicted and experimental q_e values for all tested combinations are given in Table 1. Observing globally the correlation coefficients of each used model and the comparison between the predicted and experimental sorption capacity, the best fitting is achieved using the pseudo-second-order kinetic model ($R^2 = 0.92$) suggested that the chemisorption process could be a rate-limiting step [25].

Table 1. A comparison of pseudo-first-order, and pseudo-second-order kinetic model rate constants obtained from PO_4^{-3} adsorption into modified sawdust.

Kinetic model	Equations	Parameters	Modified sawdust
Pseudo–first order	$Log(q_e - q_t) = Log(q_m) - K_1 \dfrac{t}{2.303}$	R^2	0.920
		K_1 (min^{-1})	0.066
		q_e (mg g^{-1})	82.60
Pseudo–second order	$\dfrac{t}{q_t} = \dfrac{1}{q_e^2 K_2} + \dfrac{t}{q_e}$	R^2	0
		K_2 (min^{-1})	576.10^{-4}
		q_e (mg g^{-1})	

The variation in the amount of adsorption with time may be processed further for evaluating the role of diffusion in the adsorption of phosphate ions on sawdust. Adsorption is a multi-step process involving transport of the solute ions from the aqueous phase to the surface of the solid particulates and then diffusion of the solute Ions into the interior of the pores which is likely to be a slow process and is therefore, rate determining. The intra-particle diffusion rate constant (k_p) is given by the equation [26]:

$$q_t = K_p . t^{1/2} + C$$

Where, K_p is the diffusion rate constant (mg/g.min) and value of C (mg/g) is proportional to boundary layer thickness [27]. It has been reported that the adsorption capacity increases when the thickness of boundary layer decreases [28]. The initial rates of intra-particle diffusion are obtained from the Equation (7) from the plots of q_t vs. $t^{1/2}$ (Figure 7). If the plot of adsorption capacity versus the square root of time is linear, the intra particle diffusion is involved. If the line passes through the origin diffusion in the sorbent is the only controlling step. However, plot presented in Fig. 7 shows relevant linearity ($r^2 = 0.837$) and the intercept (C) has higher value than zero (9.583), and the slopes (K_P) was found be 7.53 mg/g.min$^{1/2}$. Therefore, some boundary layer control must be involved and intraparticle diffusion is not the rate limiting factor.
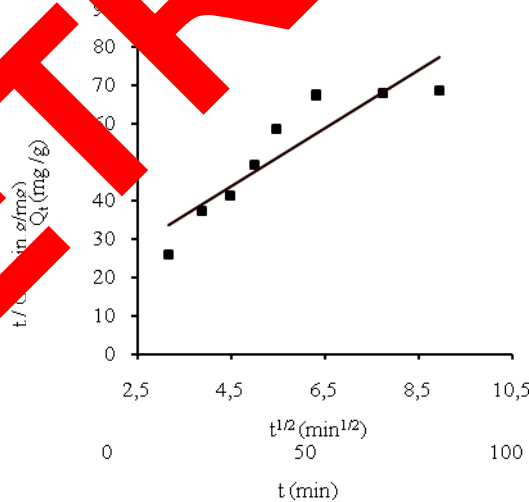

Fig. 7. Intraparticle diffusion plot for adsorption of PO_4^{-3} into modified sawdust

3.6 Adsorption isotherms

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. Classical adsorption models, such as the Langmuir and Freundlich models have been extensively used to describe the equilibrium established between adsorbed phosphate ions on the sawdust (q_e) and phosphate ions remaining in solution (C_e) at a constant temperature. The Langmuir equation {Equation (8)} is the most important model for mono-layer adsorption. It is based on the assumptions: adsorption can only occur at a fixed number of definite localized sites, each site can hold only one adsorbate molecule, and all sites are equivalent and no interaction between adsorbed molecules:

$$q_e = \frac{(q_{max} K_L C_e)}{(1 + K_L C_e)} \qquad (8)$$

Where q_{max} is the maximum quantity of phosphate ions per unit weight of sawdust to form a complete monolayer on the surface (mg/g) and K_L is a constant related to the affinity of binding sites with the phosphate ions (L/mg). It should be noted that q_{max} represents a practical limiting adsorption capacity corresponding to the surface of sorbent fully covered by sorbate ions. This quantity is particularly useful in the assessment of the adsorption performance, especially in cases where the sorbent does not reach its full saturation as it enables the indirect comparison between different sorbents.

The Freundlich model Equation (9) is the most important multi-site adsorption isotherm for heterogeneous surfaces. Even though the model originates from empirical expressions, it has also been derived by assuming an exponential decay energy distribution function:

$$Q_e = K_f C_e^{1/n}$$

Where K_f is an indicator of adsorption capacity (mg/g) and *n* indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity (dimensionless).

Experimental adsorption isotherms of phosphate are obtained with room temperature (25 °C), the initial phosphate concentration was varied from 0 to 300 mg/L and stirred with 2.5 g/L of adsorbent at the pH value of 7.5. The results are shown in Fig. 7. According to the slope of initial portion of the curve, as seen from Fig. 8, the adsorption isotherm may be classified in H-type of Gilles' classification [29]. The H-type isotherms are the most common and correspond to high affinity of adsorbate for a given adsorbent. The plot of PO_4^{-3} amount adsorbed against equilibrium concentration (Fig. 8) indicated that adsorption increased initially with PO_4^{-3} concentration in equilibrium solution, but the increase diminished upon further increasing PO_4^{-3} loading, possibly due to less available active phosphorus adsorption sites.
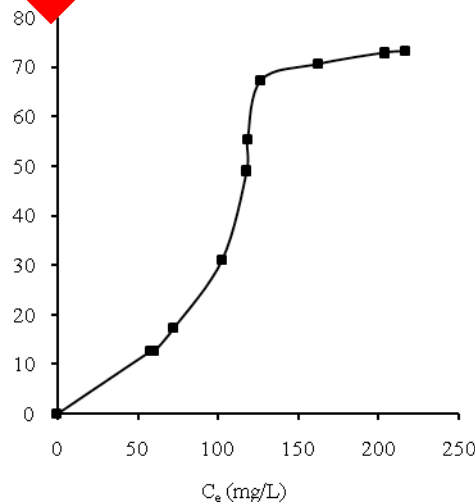

Fig. 8. Adsorption isotherms for PO_4^{-3} onto modified sawdust

The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients (R^2) are presented in Table 2. According to the coefficients of Table 2, the R^2 values obtained for the Freundlich and Langmuir isotherms were 0.968 and 0.225 respectively. The Freundlich isotherm model gave a better fit than the Langmuir isotherm model as shown by the higher R^2 value. The constant *n* refers to the interaction between exchange sites in the adsorbent and phosphate ions. A high value for *n*>1 indicates favorable adsorption. The adsorption capacity (K_f) was 0.889 mg/g. Similar results have been reported for the adsorption of phosphate by juniper (*Juniperus monosperma*) [30], and oven dried sludge and cement kiln dust [31].

Table 2. Isotherms used for description of PO_4^{-3} adsorption onto modified sawdust, including the coefficients calculated and correlation coefficients

Isotherme type	Equation	Coefficients	Modified sawdust
Freundlich	$Lnq_e = LnK_F + \frac{1}{n}LnC_e$	R^2	0.968
		K_f	0.889
		N	1.27
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	R^2	0.225
		K_L	0.021
		q_m	0.65

3.7 Adsorption thermodynamics

The thermodynamic equilibrium constants (K_d) of the adsorption process, i.e. the constants for phosphate distribution between the solid and liquid phases at equilibrium, were computed using the method of Lyubchik et al. [32] by plotting $\ln\left(\frac{q_e}{C_e}\right)$ versus q_e and extrapolating to zero. The change in Gibbs free energies (ΔG) was then calculated with Equation (10). ΔH and ΔS were calculated from the slope and intercept of the plot of ln K_d versus $\frac{1}{T}$ using Van't Hoff Equation (11), and which is shown in Fig 9 with a correlation coefficient (R^2) of 0.95.

$$\Delta G = -RT \ln K_d \qquad (10)$$

$$\ln K_d = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \qquad (11)$$

Where R is the universal gas constant (8.31441 J/mol.K).

All the thermodynamic parameters are listed in Table 3. The negative values of ΔG and positive values of ΔH indicate that the adsorption of phosphate onto sawdust is spontaneous and endothermic. The values of ΔG decreased from -77 to -3 J/mol in the temperature range of 293, 333 K. The endothermic adsorption of phosphate onto sawdust was induced by an increase in temperature. The values of ΔH are high enough to ensure strong interaction between the phosphate and the adsorbents. The positive values of ΔS state clearly that the randomness increased at the solution interface during the phosphate adsorption onto the sawdust, and shows that some structural exchange may occur among the active sites of the sorbent and the ions [33]. The increase in adsorption capacity of sawdust at higher temperatures may be caused by the enlargement of pore size and/or activation of the adsorbent surface [34].
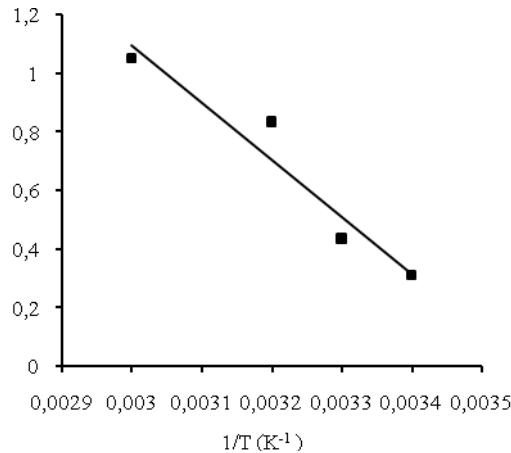
Fig. 9. A plot of $\ln K_d$ against $1/T$ for PO_4^{-3} adsorption by modified sawdust

Table 3. Thermodynamic parameters for adsorption of PO_4^{-3} onto modified sawdust

	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol.K)	$\Delta G°$ (j/mol) Temperature (K)			
			293	303	313	333
Modified sawdust	16195.67	57.71			-1930.16	-3088.36

4. Conclusions

The present investigation evaluated that the chemically modified sawdust of *Pinus halepensis* can be used as an effective adsorbent for the removal of phosphorus from synthetic waste water. The SEM photographs clearly show that after chemical treatment a lot of pores were produced. That sawdust modified was shown to be capable of adsorbing phosphate ions from aqueous solution. Phosphate ions binding were rapid, indicating its probable sorption to the cell walls of the sawdust. High temperature favours the sorption of phosphate ions on sawdust. The biosorption equilibrium data obeyed Freundlich models in the concentration ranges studied. The kinetics of sorption follows the pseudo-second-order model indicated that the adsorption was controlled by chemisorption process which was found to be endothermic and spontaneous.

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