Desalination and Water Treatment
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doi: 10/5004/dwt.2012.2244

Taylor & Francis
Taylor & Francis Group

44 (2012) 306–313
June

Adsorptive removal of phosphate from aqueous solution by chemically modified biosorbent

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Received 4 September 2010; Accepted 19 February 2012

ABSTRACT

In the present study, chemically modified biosorbent (*Pinus halepensis Miller*) was used for removal of phosphate from water. Biosorbent preparation process included size fractionation, extraction for surface activation, acid prehydrolysis, and treatment with urea. Sorption of phosphate ions onto biosorbent 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^{-1} 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; Biosorbent; Low cost; Phosphate removal; Adsorption isotherms; Kinetics; Thermodynamics

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 [3,4]. In many countries, stringent regulations limit phosphorus level to 0.05 mg l^{-1} to prevent increased algae growth [5].

Various techniques have been developed for the removal of phosphate from water and wastewater [6], which includes chemical precipitation [7,8], adsorption using suitable materials [9], biological treatment [10] and crystallization [11]. 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 [12–14]. Lignocellulosic materials exhibit interesting capacities as pollutant adsorbents, and by activation process or by

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chemical surface modification the adsorption capacity of lignocellulosic materials can be increased [15,16]. The activation process enhances the pore volume and hence enlarges the diameter of the pores.

The sawdust is one of the well-known fiber crops. This sawdust suggests a broad potential application to adsorbent production [17,18]; 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 [19].

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 hexane/95% ethanol [20]. Extraction is expected to increase the surface energy of the sawdust there by facilitating binding with reactive reagents. At the end of 8 h, the Soxhlet apparatus were allowed to cool down and the sample was removed. Then the sample was air-dried in a ventilation hood overnight, and dried in an oven at approximately 105°C for 6.5 h. Thereafter, the sample was acid prehydrolysed in a 500 ml glass batch reactor, equipped with an internal thermocouple, immersed in a heating oil bath [21]. 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 h. The sample was cooled to room temperature, removed from the oven, and treated according to the surface chemistry modification schemes outlined below:

- To prepare biosorbent modified with urea, the sawdust fraction (10 g) was agitated (140 rpm) in the presence of urea (200 g l^{-1}) for 24 h, then rinsed with deionized water and dried in oven (80°C) overnight.
- The stock solution of phosphate was prepared by dissolving $KH_2PO_4{\cdot}2H_2O$ salt (analytical reagent grade) in double distilled water (1000 mg l^{-1}). 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 1 M NaOH solutions before adsorption experiments.

2.2. Analytical methods

Phosphate was analyzed by the molybdenum blue method [22]. 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^{-3} concentration of 300 mg l^{-1}. Portions of 0.5 g 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 of the solution was maintained at 7.5. The samples were taken in triplicates at the intervals of 0, 10, 20, 25, 30, 40, 60, 80, 90, 120, 180, and 380 min after the start of adsorption reaction and analyzed for residual PO_4^{-3} of the solution. Two typical kinetic equations, that is, pseudo–first order and pseudo–second order were tested.

2.4. Adsorption isotherms

The portions of 0.5 g sawdust samples were stabilized in 250 ml Erlenmeyer flasks with solution containing various amounts of KH_2PO_4 for 80 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 the end of 40 min 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 (20°C, 30°C, 40°C and 60°C) on sawdust mediated phosphate adsorption was investigated at fixed amount of adsorbent and initial phosphorous concentration of 250 mg l^{-1}. Portions of 0.5 g sawdust were placed in 250 ml Erlenmeyer flasks. The pH of the suspension was adjusted to 7.5. The flasks with the content were capped and shaken at 120 rpm in a temperature controlled orbital shaker to enhance reaction equilibrium at room temperature (25°C). At the end of 40 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 FTIR spectra of treated sawdust are shown in Fig. 1. The spectrum shows a broad absorption band around 3300 cm^{-1}, which may be attributed to the OH group. The presence of absorption bands at 3748 and at 2947 cm^{-1} are due to the presence of H-bridges. It also confirms the 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 [23]. Absorption at 1450 cm^{-1} is assigned to methoxy group of lignin in the sawdust [24]. The bands at 1317, 1265 and 1035 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 [25].

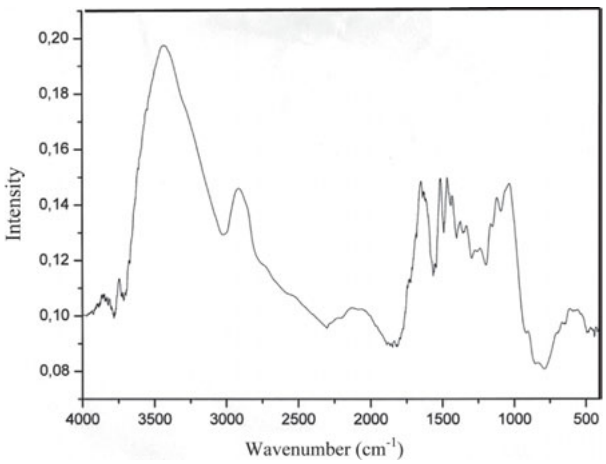

Fig. 1. FTIR spectrum of modified sawdust.

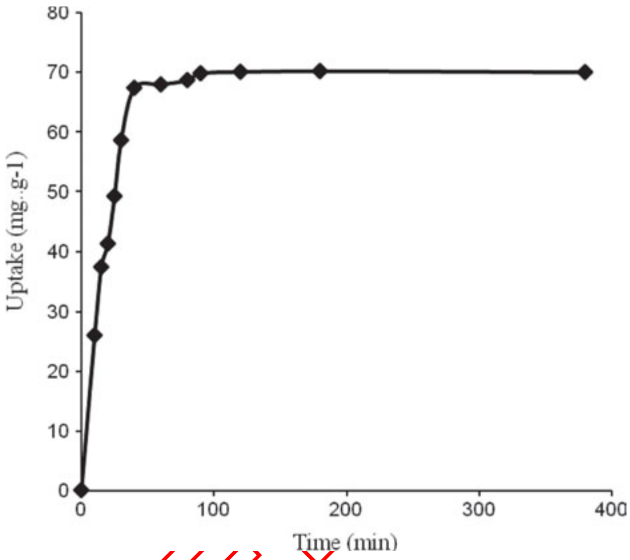

Fig. 2. The kinetic data for PO_4^{-3} adsorption into modified sawdust.

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. 2). 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. 2 were used to determine kinetic parameters in the kinetic models tested.

3.3. Analysis of kinetic data for sawdust

Mathematical models that can describe the behavior of a batch sorption process operated under different experimental conditions are very useful for scale-up studies or process optimization. A number of models with varying degrees of complexity 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, two kinetic equations were used to fit the experimental results.

3.4. Pseudo–first-order equation

A simple pseudo–first-order equation for the liquid–solid adsorption due to Lagergren was used by Babu and Gupta [26]:

$$\frac{dq_t}{dt} = K_1 \left(q_e - q_t \right) \tag{1}$$

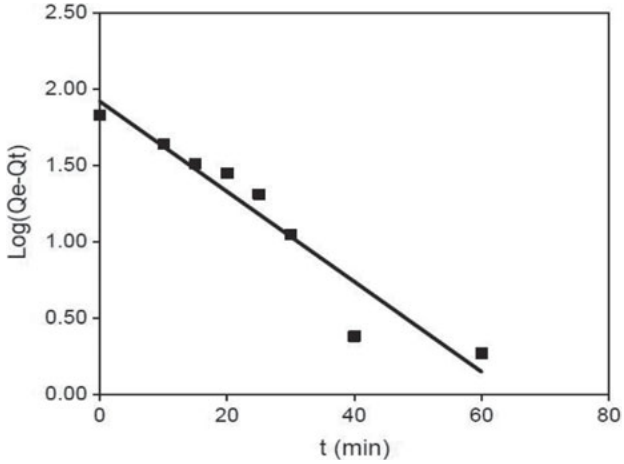

Fig. 3. Pseudo–first-order plot for the adsorption of PO_4^{-3} into modified sawdust.

where q_e and q_t (mg·g^{-1}) 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. Eq. (1) was integrated with boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$:

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

3.5. Pseudo–second-order equation

Adsorption data were also evaluated according to the pseudo–second-order reaction kinetic [26]:

$$\frac{dq_t}{dt} = K_2\left(q_e - q_t\right)^2 \tag{3}$$

where K_2 is the second-order reaction constant. If Eq. (3) is integrated, the following expression is obtained:

$$\frac{1}{(q_e - q_t)} = K_2 t + C \tag{4}$$

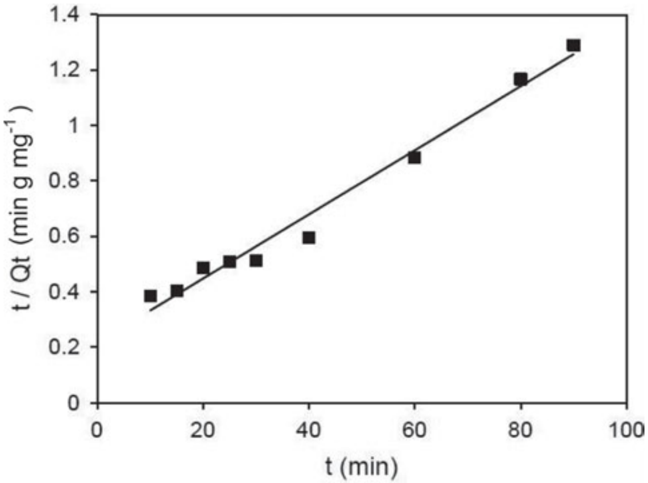

Fig. 4. Pseudo–second-order plot for the adsorption of PO_4^{-3} into modified sawdust.

The constants K and q_e were calculated from the linear plot of $\log(q_e - q_t)$ versus t (Fig. 3) for pseudo–first-order model and plot of t/q_t versus t. (Fig. 4) 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 ($R^2 = 0.981$), an indication of chemisorption mechanism [27].

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 into 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 [28]:

$$q_t = k_p{\cdot}t^{1/2} + C \tag{5}$$

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	$\log(q_e - q_t) = \log(q_{th}) - K_1\dfrac{t}{2303}$	R^2	0.920
		K_1 (min^{-1})	0.066
		q_e (mg g^{-1})	82.60
Pseudo–second order	$\dfrac{t}{q_t} = \dfrac{1}{q^2{}_eK_2} + \dfrac{t}{q_e}$	R^2	0.981
		K_2 (min^{-1})	5.576 10^{-4}
		q_e (mg g^{-1})	90.91

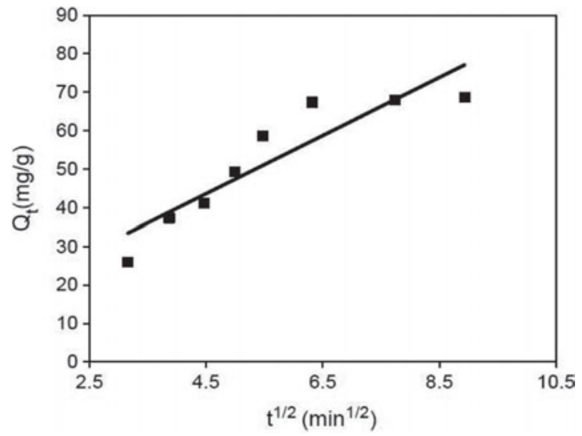

Fig. 5. Intraparticle diffusion plot for adsorption of PO_4^{-3} into modified sawdust.

where, K_p is the diffusion rate constant (mg g^{-1} $min^{-0.5}$) and value of C (mg g^{-1}) is proportional to boundary layer thickness [29]. It has been reported that the adsorption capacity decreases when the thickness of boundary layer decreases [30]. The initial rates of intra-particle diffusion are obtained from the Eq. (5) from the plots of q_t versus $t^{1/2}$ (Fig. 5). If the plot of adsorption capacity (q_t) 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. 5 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 to be 7.552 mg g^{-1} $min^{-0.5}$. Therefore, some boundary layer control must be involved and intraparticle diffusion is not the rate limiting factor.

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 [Eq. (6)] 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, all sites are equivalent, and no interaction between adsorbed molecules:

$$q_e = \frac{(q_{max} K_L C_e)}{(1 + K_L C_e)} \tag{6}$$

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^{-1}) and K_L is a constant related to the affinity of binding sites with the phosphate ions (g mg^{-1}). 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 [Eq. (7)] is the most important multi-site sorption 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:

$$Q_e = K_f C_e^{1/n} \tag{7}$$

where K_f is the adsorption constant, which is a comparative measure of the adsorption capacity of the adsorbent, and n indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity (dimensionless).

Experimental adsorption isotherms of phosphate anions are obtained with room temperature (25°C), the initial phosphate concentration was varied from 80 to 400 mg l^{-1} and stirred with 2.5 g l^{-1} of adsorbent at the pH value of 7.5.The results are presented in Fig. 6. According to the slope of initial portion of the curve, as seen from Fig. 6 the adsorption isotherm may be classified as H-type of the Giles' classification [31]. 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. 6) indicated that adsorption increased initially with PO_4^{-3} concentration in

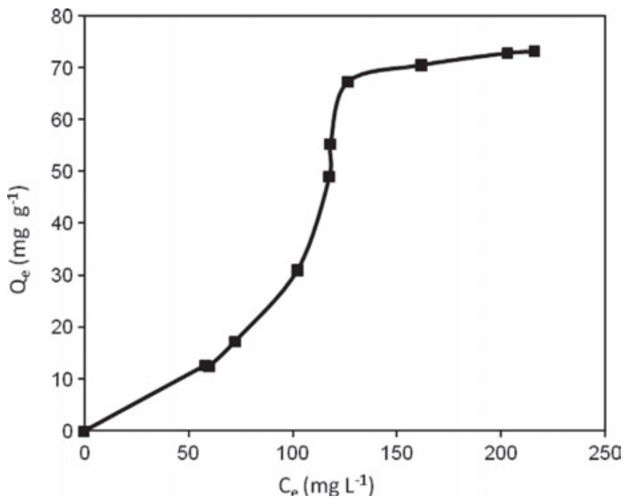

Fig. 6. Adsorption isotherms for PO_4^{-3} onto modified sawdust.

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	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	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	116.25

equilibrium solution, but the increase diminished upon further increasing PO_4^{-3} loading, possibly due to less available active phosphorus adsorbing sites.

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^{-1}. Similar results have been reported for the adsorption of phosphate by juniper (*Juniperus monosperma*) [32], and oven dried sludge and cement kiln dust [33].

3.7. Adsorption thermodynamics

The thermodynamic equilibrium constants (K_d) of the adsorption process,that is the constants for phosphate distribution between the solid and liquid phases at equilibrium, were computed using the method of Lyubchik et al. [34] by plotting ln (q_e/C_e) versus q_e and extrapolating q_e to zero. The change in Gibbs free energies (ΔG) was then calculated with Eq. (8). ΔH and ΔS were calculated from the slope and intercept of the plot of ln K_d versus $1/T$ using Van't Hoff equation (9), and

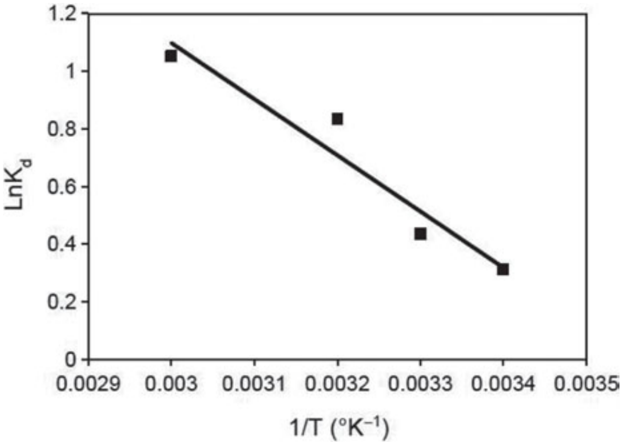

Fig. 7. A plot of ln K_d against $1/T$ for PO_4^{-3} adsorption by modified sawdust.

which is shown in Fig. 7 with a correlation coefficient (R^2) of 0.95.

$$\Delta G = -RT \ \ln \ K_d \tag{8}$$

$$\ln \ K_d = \left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \tag{9}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

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 −771.96 to −3088.36 J mol^{-1} in the temperature range of 293–333 K. The value of ΔG becomes more negative with increasing temperature. This shows that an increase in temperature favors the removal process. 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 solid–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 [35]. 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 [36].

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

	ΔH°(J mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (J mol^{-1})			
			Temperature (K)			
			293	303	313	333
Modified sawdust	16,195.67	57.71	–771.96	–1351.06	–1930.16	–3088.36

4. Conclusions

The present investigation shows that the chemically modified sawdust of *Pinus halepensis* can be used as an effective adsorbent for the removal of phosphate ions from synthetic waste water. That biosorbent 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.

Symbols

C_o — initial solute concentration in the aqueous phase, mg l^{-1}
C_e — equilibrium or final solution concentration, mg l^{-1}
K_1 — rate constant of the pseudo–first-order equation, min^{-1}
K_2 — rate constant of the pseudo–second-order equation, mg g^{-1} min^{-1}
K_f — indicator of adsorption capacity, mg g^{-1}
n — Freundlich constant representing adsorption intensity
K_L — Langmuir equation constant, l mg^{-1}
K_p — intraparticle diffusion rate constant, mg g^{-1} $min^{-0.5}$
q_e — amount of adsorbate at equilibrium, mg g^{-1}
Q_{max} — monolayer maximal capacity of adsorption, mg g^{-1}
q_t — amount adsorbed at time *t*, mg g^{-1}
R^2 — regression coefficient
t — contact time, min
T — experimental temperature, °K
R — universal gas constant, 8.314 J mol^{-1} K^{-1}
K_d — thermodynamic equilibrium constants of the adsorption process
$\Delta G°$ — the change in Gibbs free energies, kJ mol^{-1}
$\Delta H°$ — enthalpy, kJ mol^{-1}
$\Delta S°$ — entropy, kJ mol^{-1} K^{-1}

References

[1] L.J. Puckett, Identifying the major sources of nutrient water pollution, Environ. Sci. Technol., 29(9) (1995) 408A–414A.
[2] L .Borgninoa, M.J. Avenab and C.P. De Pauli, Synthesis and characterization of Fe(III)-montmorillonites for phosphate Adsorption, Colloids Surf. A, 341 (2009) 46–52.
[3] E.N. Pelek and E.A. Deliyanni, Adsorptive removal of phosphates from aqueous solutions, Desalination, 245 (2009) 357–371.
[4] H.D. Ruan and R.J. Gilkes, Phosphorus accumulation in farm ponds and dams in Southwestern Australia, J. Environ. Qual., 29(6) (2000) 1875–1881.
[5] H. Behrendt, D. Opitz and M. Klein, Zielvorgaben für die Berliner Gewässer aus gewässerökologischer Sicht, Arch. Nat. Conserv, Landscape Res., 35 (1997) 329–334.
[6] R. Camarillo, I. Asencio and J. Rincón, Micellar enhanced ultrafiltration for phosphorus removal in domestic wastewaters, Desalin. Water Treat., 6 (2009) 211–216.
[7] R.G. Penetra, M.A.P. Reali, E. Foresti and J.R. Campos, Post-treatment of effluents from anaerobic reactor treating domestic sewage by dissolved-air flotation, Water Sci. Technol., 40 (1999) 137–143.
[8] T. Nir, E. Arkhangelsky, I. Levitsky and V. Gitis, Removal of phosphorus from secondary effluents by coagulation and ultrafiltration, Desalin. Water Treat., 8 (2009) 24–30.
[9] R. Chitrakar, R. Tezuka, A. Sonoda, K. Sakane, K. Ooi and T. Hirotsu, Selective adsorption of phosphate from seawater and wastewater by amorphous zirconium hydroxide, J. Colloid Interface Sci., 297(2) (2006) 426–433.
[10] A. Gieseke, P. Arnz, R. Amann and A. Schramm, Simultaneous P and N removal in a sequencing batch biofilm reactor: insights from reactor and microscale investigations, Water Res., 36(2) (2002) 501–509.
[11] E. Eggers, A.H. Dirkzwager and H. Van Der Honing, Full-scale experiences with phosphate crystallisation in a crystalactor, Water Sci. Technol., 24 (1991) 333–334.
[12] G.M. Ayoub, B. Koopman and N. Pandya, Iron and aluminum hydroxy (oxide) coated filter media for low-concentration phosphorus removal, Water Environ. Res., 73(4) (2001) 478–485.
[13] M.A. Camargo Valeroa (Columbia), M. Johnson, T. Mather and D.D. Marab (UK), Enhanced phosphorus removal in a waste stabilization pond system with blast furnace slag filters, Desalin. Water Treat., 4 (2009) 122–127.
[14] M. Del Bubba, C.A. Arias and H. Brix, Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm, Water Res., 37 (2003) 3390–3400.
[15] M.M. Abd El-Latif and A.M. Ibrahim, Adsorption, kinetic and equilibrium studies on removal of basic dye from aqueous solutions using hydrolyzed oak sawdust, Desalin. Water Treat., 6 (2009) 252–268.
[16] M.C. Basso, E.G. Cerrella and A.L. Cukierman, Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater, Ind. Eng. Chem. Res., 41 (2002) 3580–3585.
[17] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal and S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J., 137 (2008) 529–541.
[18] T.K. Naiya, P. Chowdhury, A.K. Bhattacharya and S.K. Das, Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions, Chem. Eng. J., 148 (2009) 68–79.
[19] T.S. Anirudhan, S. Rijith and C.D. Bringle, Iron(III) complex of an amino-functionalized poly(acrylamide)-grafted lignocellulosic residue as a potential adsorbent for the removal of chromium(VI) from water and industry effluents, Desalin. Water Treat., 12 (2009) 3–15.
[20] A.V. Abolonskay, V.P. Chegolev, G.L. Akim, N.L. Kossovich and I.Z. Emelianova, Handbook for Practical Work in the Chemistry of Wood and Cellulose. Edited by Lisnaya promichlinoste, Moscow, 1965.
[21] D.K. Sidiras and E.G. Koukios, Acid hydrolysis of ball milled straw, Biomass, 19 (4) (1989) 289–306.
[22] K.A. Krishnan, Adsorption of nitrilotriacetic acid onto activated carbon prepared by steam pyrolysis of sawdust: kinetic and isotherm studies, Colloids Surf. A, 317 (2008) 344–351.
[23] X. Guo, S. Zhang and X. Shan, Adsorption of metal ions on lignin, J. Hazard. Mater., 151 (2008) 134–142.

[24] M.A. Khan, S.M. Ashraf and V.P. Malhotra, Development and characterization of a wood adhesive using bagasse lignin, Int. J. Adhes., 24 (2004) 485–493.

[25] A.K. Rana, R.K. Basak, B.C. Mitra, M. Lawther and A.N. Banerjee, Studies of acetylation of jute using simplified procedure and its characterization, J. Appl. Polym. Sci., 64(8) (1997) 1517–1523.

[26] B.V. Babu and S. Gubta, Adsorption of Cr(VI) using activated neem leaves: kinetic studies, Adsorption, 14 (2008) 85–92.

[27] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and nonlinear methods, Water Res., 40(1) (2006) 119–125.

[28] W.J. Weber and J.C. Morris, Kinetics of adsorption on carbon solution, J. San. Eng. Div. ASCE, 89 (1963) 31–59.

[29] N. Kannan and M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons: a comparative study, Dyes Pigm., 51(1) (2001) 25–40.

[30] Z. Aksu, Equilibrium and kinetic modeling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, Sep. Purif. Technol., 21(3) (2001) 285–294.

[31] C.H. Giles and D.A. Smith, General treatment and classification of the solute sorption Isotherms, J. Colloid Interface Sci., 47 (1974) 755–765.

[32] J.S. Hane, P.N. Hur, B. Choi and S.H. Min, Removal of phosphorus using chemically modified lignocellulosic materials. 6th Inter-Regional Conference on Environment- Water Land and Water Use Planning and Management, Albacete, Spain, September 3–5, 2003.

[33] M. Mortul, M. Gubbons and G.A. Gagnon, Phosphorus adsorption by naturally-occuring materials and industrial by-products, J. Environ. Eng. Sci., 6 (2007) 157–164.

[34] S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca and S.B. Lyubchik, Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes, Colloids Surf. A, 242 (2004) 51–158.

[35] H. Rehman, A.I. Shakirullah and S.S. Hameedullah, Sorption studies of nickel ions onto swdust of Dalbergia sissoo, J. Chin. Chem. Soc., 53 (2006) 1045–1052.

[36] L.G. Yana, Y.Y. Xub, H.Q. Yub, X.D. Xina, Q. Weib and B. Dua, Adsorption of phosphate from aqueous solution by hydroxy-aluminum,hydroxy-iron and hydroxy-iron–aluminum pillared bentonites, J. Hazard. Mater., 179 (2010) 244–250.