Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.792142

51 (2013) 6798–6807
October

Taylor & Francis
Taylor & Francis Group

Adsorption study of lead(II) onto xanthated date palm trunk: kinetics, isotherm and mechanism

Sunil Kumar Yadav[a], Dhruv Kumar Singh[a,*], Shishir Sinha[b]

[a]*Analytical Research Laboratory, Department of Chemistry, Harcourt Butler Technological Institute, Kanpur 208002, India*
Tel. +91 9450333734; Fax: +91 512 2533812; email: dhruvks123@rediffmail.com
[b]*Department of Chemical Engineering, Indian Institute of Technology, Roorkee, India*

Received 4 April 2012; Accepted 7 February 2013

ABSTRACT

The adsorption of lead(II) onto xanthated date palm trunk (XDPT) from aqueous solutions was studied in a batch adsorption system. Factors influencing lead(II) adsorption such as initial Pb(II) concentration (25.8–207.0 mg/l), pH (1–6), contact time (5–240 min), and adsorbent dosage (0.625–6.0 g/l) were investigated. The adsorption process was relatively fast and equilibrium was established within 120 min. Maximum adsorption of Pb(II) occurred at pH ~ 5. A comparison of the kinetic models on the overall adsorption rate showed that the adsorption system can be best described by the pseudo-second-order kinetics. The adsorption equilibrium data obeyed Langmuir isotherm and the monolayer adsorption capacity of Pb(II) was found to be 53.48 mg/g. The adsorption mechanism has been suggested to be due to the complexation of lead(II) ions with sulfur donors present in XDPT.

Keywords: Adsorption; Lead(II); Xanthated date palm trunk; Batch studies; Adsorption isotherm

1. Introduction

Industrial, agricultural, and domestic activities of human beings have polluted the environmental system, by generation of wastewater containing high levels of carcinogenic metals. Although the heavy metals are necessary in trace amounts for normal development of the biological cycles, most of them become toxic at higher concentrations. It is well documented that lead is one of the contaminants of industrial wastewaters and lead poisoning exists in the wastewater of many industries [1].

Industries, such as battery, printing and pigment manufacturing, metal plating and finishing, ammunition, soldering materials, ceramic and glass industries, and iron and steel manufacturing units, generate large quantities of wastewater contaminated with lead [2–5]. All of these chemicals containing lead are considered as cumulative poisons [6]. Lead poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver, and brain and lead to neonatal deaths [7,8]. In industrial wastewaters, Pb(II) concentrations approach 200–500 mg/l. This value is very high according to water quality standards, and Pb(II) concentration in wastewater should be within a value of 0.1–0.05 mg/l. According to the US Environmental Protection Agency (EPA), the permissible level of lead in drinking water is 0.05 mg/l [9].

---

*Corresponding author.

The various methodologies adopted in wastewater treatment include adsorption chemical precipitation, filtration, ion exchange, solvent extraction, oxidation/reduction, evaporation, and membrane technology. The process of adsorption has been the most versatile and widely used technique for the removal of heavy metal ions from wastewaters in recent years [10–16]. A variety of low-cost agro wastes such as bagasse fly ash [11], tobacco stem [17], imperata cylindrica leaf powder [18], peanut husk [19], sawdust [20], dates stone [21], tree fern [22], and rubber leaf powder [23] have been studied for Pb(II) containing wastewater treatment (adsorption capacity: 2.50–46.73 mg/g). Modified rice husk [24], soda lignin [25], shells (walnut, hazelnut and almond) [26], and rubber leaf powder [27] have been reported as low-cost adsorbents for removal of Cu(II) from wastewater. Removal of Hg(II) and Cr(VI) using wheat straw[28] and wool [29], respectively, have also been reported.

Palm trunk is one of the main agricultural wastes generated by the palm oil industries. Realizing the scale of this waste, several studies were initiated to convert oil palm wood to value added products. Hoi et al. [30] and Lim and Lim [31] reported pyrolyzing oil palm wood charcoal. However, due to friable nature of wood, low calorific value was obtained and it was difficult to control the conversion efficiency as well as the pyrolysis rate. Hence, oil palm wood was suggested unsuitable to be used as charcoal fuel. The use of oil palm wood as raw material for activated carbon was highlighted by Hussein et al. [32], and they showed that the combination of chemical and physical activation methods could be used to produce activated carbon with fairly high surface area. Al-Haidary et al. [33] have studied date palm fibres and palm leaves as adsorbents for Pb(II) ions from its aqueous solution. Issabayeva et al. [34] have studied palm shell activated carbon to remove copper(II) ions from aqueous solutions. Ahmad et al. [35] have reported preparation and characterization of activated carbon from palm wood and its use in methylene blue adsorption. Sulfur as a soft ligand shows strong affinity for a number of metals such as lead, cadmium, copper, etc. which are classified as soft acids. Xanthates are formed by the reaction of an organic hydroxyl-containing substrate with carbon disulfide under basic condition [36]. The main components of date palm fibre and petiole are cellulose 44.17%, hemicelluloses 21.95%, and lipids 0.39% and the loss in ignition is about 14.17% [33]. Many of these contain several hydroxyl groups, which render the date palm trunk as a potential adsorbent by xanthation process.

In this work, we have introduced a xanthate functional group onto the cellulose network of date palm trunk. The xanthate group with a sulfur atom has a greater tendency to form stable complexes with lead(II) ions and lead to the elimination of Pb(II) from aqueous solutions. The purpose of this work is to exploit and utilize xanthated date palm trunk (XDPT) as a new modified agricultural waste for enhanced treatment of wastewater containing lead(II).

2. Experimental

2.1. Materials

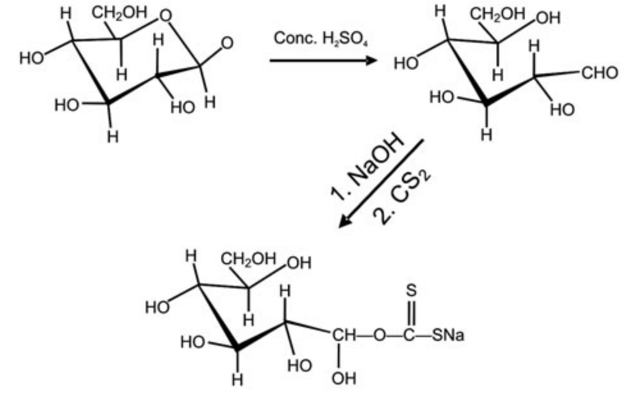
$Pb(NO_3)_2$ (A.R. grade) was purchased from Merck, India. A stock solution of lead(II) (2070 mg/l) was prepared by dissolving $Pb(NO_3)_2$ in demineralized water (DMW) and acidified with concentrate HNO_3 (5 ml) to prevent hydrolysis. The stock solution was diluted with DMW to obtain solutions of desired concentrations. The pH of the solution was adjusted by using buffer solutions viz., HCl/KCl (pH 1–3); CH_3COOH/CH_3COONH_4 (pH 4–6).

2.2. Preparation of XDPT

Date palm trunk (DPT) was obtained from rural areas around Kanpur (India), cut into a length of approximately 1 cm, washed thoroughly with DMW to remove water soluble materials, dried overnight at 100 ± 2°C in a hot air oven, and allowed to cool down to room temperature. It was ground and sieved to obtain an average particle size of 75 μm. Then, the DPT powder (50 g) was stirred with concentrated H_2SO_4 (100 ml) for 60 min and left overnight. The acid treatment of such a biopolymer creates a suitable environment for its ring opening [37,38]. The material was stirred with DMW to remove excess of acid, centrifuged to separate washings, and dried at 70 ± 2°C. Acid-treated DPT (25 g) was treated with NaOH solution (200 ml, 4 M) and shaken for 60 min. Then, CS_2 (25 ml) was added, stirred for 3 h, and allowed to stand for overnight. The product was filtered, washed, centrifuged, and dried at 70 ± 2°C. The material labeled as XDPT was used as an adsorbent. The synthetic route to XDPT is shown in Scheme 1.

2.3. Characterization of XDPT

The specific area of XDPT was measured using a BET surface analyzer (Quanta chrome autosorb). The apparent density was calculated by filling a calibrated cylinder with a given weight of XDPT and tapping the cylinder until a minimum volume was recorded. This density is referred to as the tapping or bulk density of the adsorbent. The pycnometer method was used for



Scheme 1. Synthetic route to XDPT.

Table 1
Properties of XDPT

Bulk density (g/cc)	1.12
Moisture (%)	13.6
Ash content (%)	2.8
Matter soluble in water (%)	0.0
Matter soluble in acid (%)	0.0
pH	7.8
Surface area (m^2/g)	5.33

the measurement of real density wherein a pycnometer was filled with the XDPT and a solvent (methanol) was added to fill the void. The weight was determined at each step. The pH of the XDPT was measured as follows: the suspension was prepared in a ratio of water (10 ml) to XDPT (1 g); this mixture was stirred and pH was measured several times until a constant value was reached. The physicochemical properties of XDPT are presented in Table 1.

2.4. Batch adsorption experiments

For batch adsorption studies, XDPT (0.05 g) was added to a series of Erlenmeyer flasks filled with lead (II) solutions (20 ml; 25.8–207.0 mg/l; pH 1∼6), sealed with parafilm, and then shaken (120 rpm) at room temperature (∼30˚C) in an orbital shaker incubator until the equilibrium was reached (120 min). The sample solution was filtered using Whatman filter paper (No. 4) and the filtrate was analyzed for Pb(II) by spectrophotometric method using 1, 5-diphenyl thiocarbazone in aqueous miceller solutions [39]. The amount of Pb(II) adsorbed (q_e) was calculated using Eq. (1):

$$q_e = \left(\frac{C_i - C_e}{M}\right)V \tag{1}$$

where C_i and C_e (mg/l) are the initial and final Pb(II) concentrations, respectively, V is the solution volume (l), and M is the weight of the adsorbent used (g).

3. Result and discussion

3.1. FT-IR analysis

FT-IR spectra of DPT, H_2SO_4-treated DPT, XDPT, and Pb(II)-loaded XDPT are shown in Fig. 1. In the FT-IR spectrum of DPT, the absorption peaks at 3,396, 2,921, 1,738, and 1247 cm^{-1} are due to –OH, C–H, C=O, and C–O stretching vibrations, respectively. The absorption peaks at 1,730 and 1,207 cm^{-1} in the FT-IR spectrum of H_2SO_4-treated DPT are due to CHO formed during charring process before the modification of DPT. These peaks disappear after modification of DPT into XDPT and intense broad band is observed at 1,587 cm^{-1} corresponding to C=S stretching vibration of the xanthate group. It may be due to –CS_2H deformation suggesting that XDPT has been successfully xanthated. The stretching vibrations of C–S and S–O at 1,193 and 1,038 cm^{-1}, respectively, in the spectrum of XDPT are indicative of the presence of the xanthate group bonded to the charred material. The major absorption bands of the C=S groups lie in the region 1,592–1,035 cm^{-1} [40]. The very weak vibration for C–S is also observed around 615 cm^{-1}. FT-IR spectrum of Pb(II)-loaded XDPT showed that the peaks expected at 3,428, 1,587, 1,193, and 1,038 cm^{-1} have been shifted, respectively, to 3,421, 1,548, 1,193, and 1,027 cm^{-1} due to Pb(II) adsorption. The significant shift of these peaks to lower wave numbers after Pb(II) adsorption indicates chemical interaction between Pb(II) and –OH and C=S groups of XDPT.

3.2. Effect of contact time

Preliminary kinetic experiments were conducted to calculate the time taken for the adsorption equilibrium of Pb(II) onto XDPT (Fig. 2). It is apparent that significant removal of Pb(II) occurred within 30 min and no appreciable change in terms of the removal of Pb(II) ions was observed after 120 min. The high rate of adsorption of Pb(II) in the initial stage is probably due to the availability of larger surface area of XDPT available for the adsorption of Pb(II). Once the surface adsorption sites were exhausted, the rate of adsorption was further controlled by the rate of transport of the adsorbent particles from the exterior to interior sites [41].

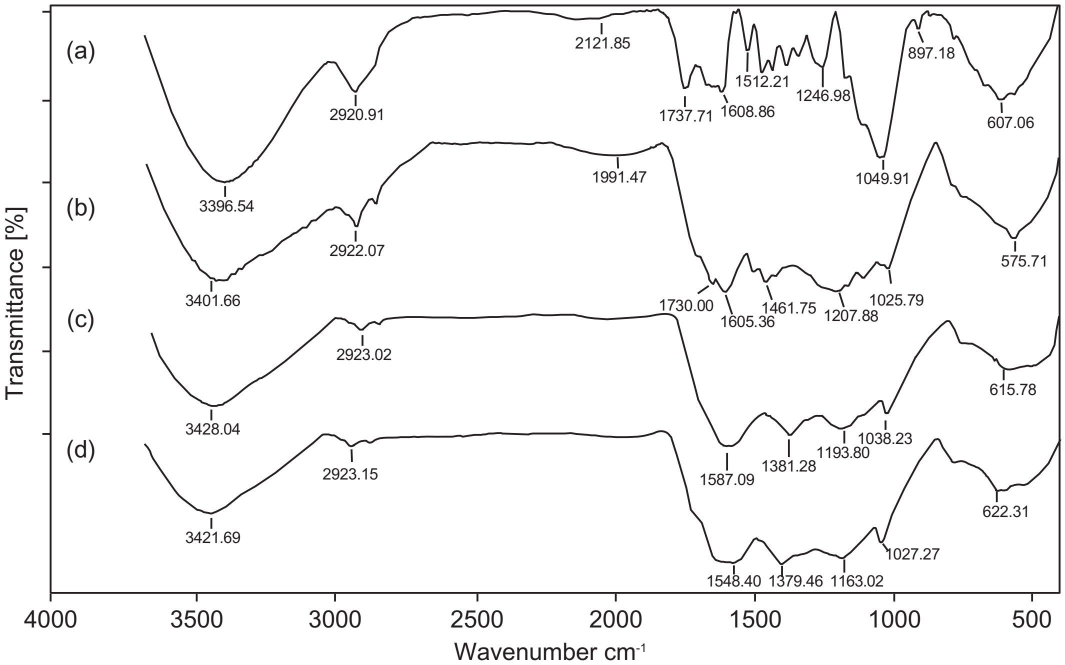


Fig. 1. FT-IR spectra of (a) DPT, (b) H_2SO_4-treated DPT, (c) XDPT, and (d) Pb(II)-loaded XDPT.

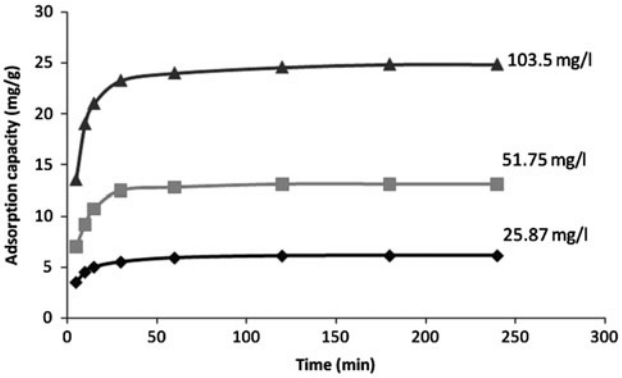


Fig. 2. Effect of contact time on the adsorption of Pb(II) onto XDPT.

3.3. Effect of initial pH of solution

The effect of solution pH (1–6) on the adsorption kinetics of Pb(II) onto XDPT is shown in Fig. 3(a). The experiments were performed for initial Pb(II) concentration (103.5 mg/l), adsorbent dose (2.5 g/l), and temperature (30°C). The results indicate that the maximum uptake of Pb(II) was obtained at pH 5. At $pH < 5$, concentration of H^+ ions is higher and their mobility is also higher compared with Pb(II) ions. Competition between H^+ ions with Pb(II) ions decreased the adsorption of Pb(II) on to XDPT. On the other hand, at $pH \geqslant 5$, adsorption increased due to the low concentration of H^+ ions and a greater number of

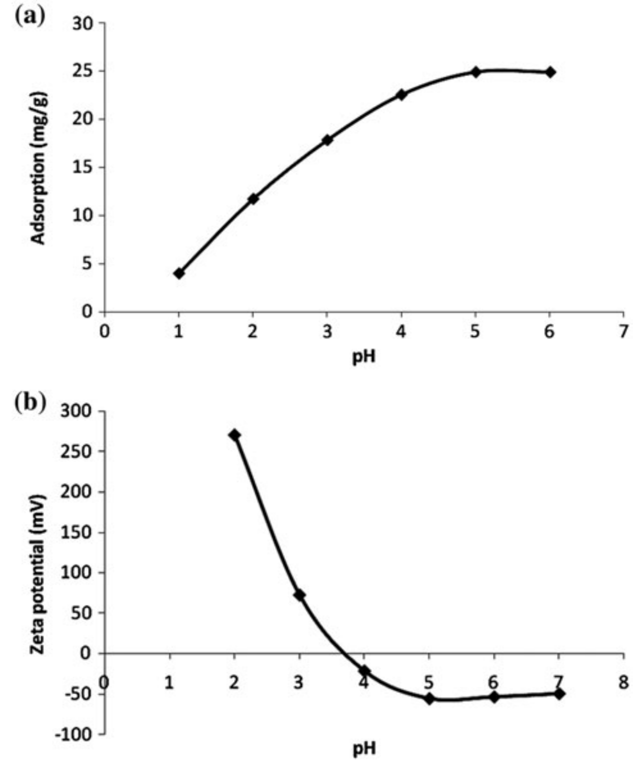


Fig. 3. (a) Effect of pH of solution on the adsorption of Pb (II) onto XDPT. (b) Point of zero charge (pH_{pzc}) curve of XDPT.

surface ligands of XDPT with negative charges. The optimum pH of the solution can be explained on the basis of pH_{pzc} (Point of zero charge). The pH_{pzc} is defined as the pH at which the net charge of adsorbent surface becomes zero. The point of zero charge for XDPT was found to be 3.8 as shown in Fig. 3(b). Below pH_{pzc} ($pH < 3.8$), the surface charge was positive and above pH_{pzc} ($pH > 3.8$), the surface charge of the xanthated adsorbent was negative. Hence, at $pH > 3.8$, the adsorption of the Pb(II) ions increased while the adsorption of Pb(II) ions decreased at $pH < 3.8$. The amount of adsorption increased above pH_{pzc} due to interaction of Pb(II) ions and $Pb(OH)^+$ with a negatively charged adsorbent surface. However, at the point of zero charge, the change in adsorption rate was not similar (Fig. 3(a)). Probably, H^+ ions (competing ions) are responsible for the adsorption rate below pH 5. At low pH, particularly below pH_{pzc}, the positively charged Pb^{+2} and $Pb(OH)^+$ species may repel with the positively charged adsorbent surface having an identical charge and there by decreases the Pb(II) adsorption.

3.4. Effect of adsorbent dose

The amount of adsorbent dose was varied (0.625–6.0 g/l) and all of the other experimental variables were fixed (pH 5.0, initial concentration; 103.5 mg/l, contact time; 120 min agitation speed/rpm; 125). A plot of adsorbent dose vs. % removal of Pb(II) adsorption is presented in Fig. 4. The Pb(II) removal increased from 33.9–99.4% with an increase in the amount of adsorbent dose (0.625–5.0 g/l). This may be due to an increased adsorbent surface area and availability of more adsorption sites or more functional groups resulting from the increased dose of the adsorbent [42]. At higher adsorbent doses (>5.0 g/l), the incremental Pb(II) removal was very low due to equilibrium between the surface Pb(II) concentration and the solution Pb(II) concentration.

3.5. Effect of initial concentration of Pb(II)

A plot of adsorption capacity vs. concentration (Fig. 5) shows that adsorption capacity increases (6.9–36.2 mg/g) with the increasing initial Pb(II) concentration (25.8–207.0 mg/l). This seems to be due to the increase in the driving force of the concentration gradient with an increase in the Pb(II) initial concentration.

3.6. Adsorption isotherms

Initial Pb(II) concentrations were varied and the adsorbent mass in each experiment was kept constant. The Langmuir model [43] takes the form of equation:

$$\frac{C_e}{q_e} = \frac{1}{bK_L} + \frac{C_e}{b} \tag{2}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount of Pb(II) ions adsorbed per specified amount of the adsorbent (mg/g), K_L (l/mg) is the Langmuir equilibrium constant, and b (mg/g) is the amount of adsorbate required to form a monolayer. Hence, a plot of C_e/q_e vs. C_e should be a straight line with a slope $(1/b)$ and an intercept $(1/bK_L)$ as shown in Fig. 6. The Langmuir constant and its correlation coefficient evaluated from the adsorption for Pb(II) are given in Table 2. The high value of Langmuir coefficient ($R^2 = 0.99$) confirms that the Langmuir isotherm is the best fit for the adsorption of Pb(II) onto XDPT.

The essential characteristics of the Langmuir isotherm can be expressed by a dimension less constant called the equilibrium parameter (R_L) as expressed by equation:

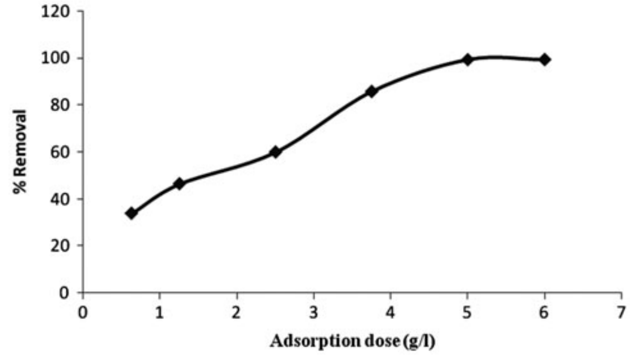


Fig. 4. Effect of adsorbent dose on the adsorption of Pb(II) onto XDPT.

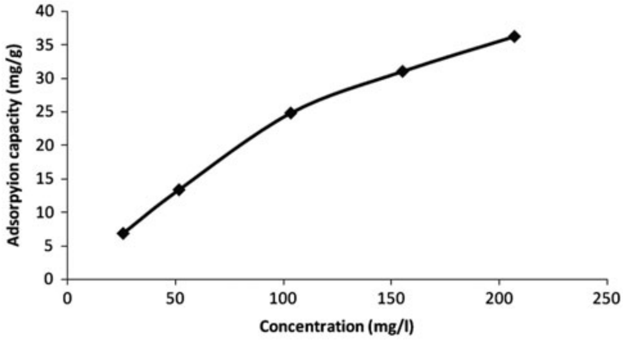


Fig. 5. Effect of concentration on the adsorption of Pb(II) onto XDPT.

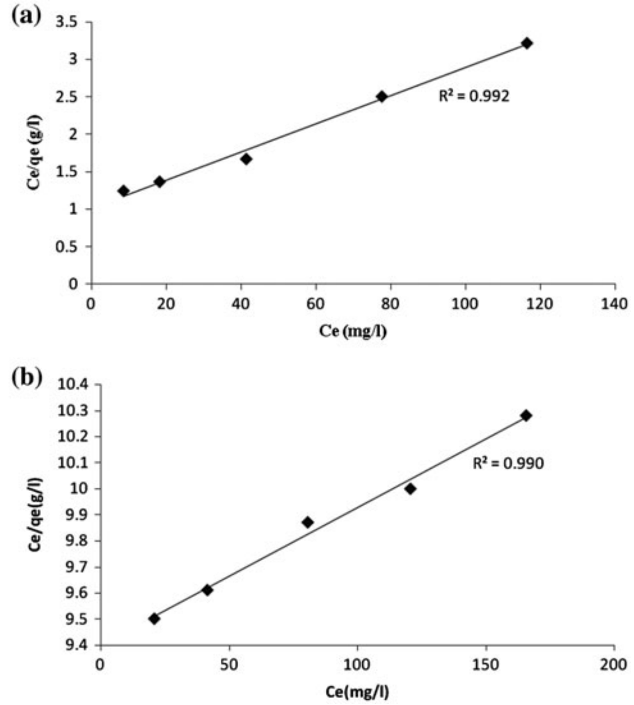


Fig. 6. Langmuir isotherms for adsorption of Pb(II) onto (a)XDPT and (b) raw-DPT.

Table 2
Langmuir and Freundlich adsorption isotherm constants for adsorption of Pb(II) on XDPT and on raw-DPT

Isotherm	Constants	XDPT	Raw-DPT
Langmuir	b (mg/g)	53.48	19.2
	K_L (l/mg)	0.175	0.055
	R^2	0.992	0.990
Freundlich	K_F (mg/g)	1.949	1.231
	n	1.578	1.25
	R^2	0.968	0.966

$$R_L = \frac{1}{1 + K_L C_i} \tag{3}$$

where K_L is the Langmuir constant and C_i is the initial Pb(II) concentration. R_L values represent the type of isotherm and its value between 0 and 1 indicates favorable adsorption. The R_L values evaluated (data not given) from the b values for Pb(II) ions at various concentrations were found to be between 0 and 1, further supporting the Langmuir model [44].

The Freundlich model [45] can be easily linearized by the Freundlich equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

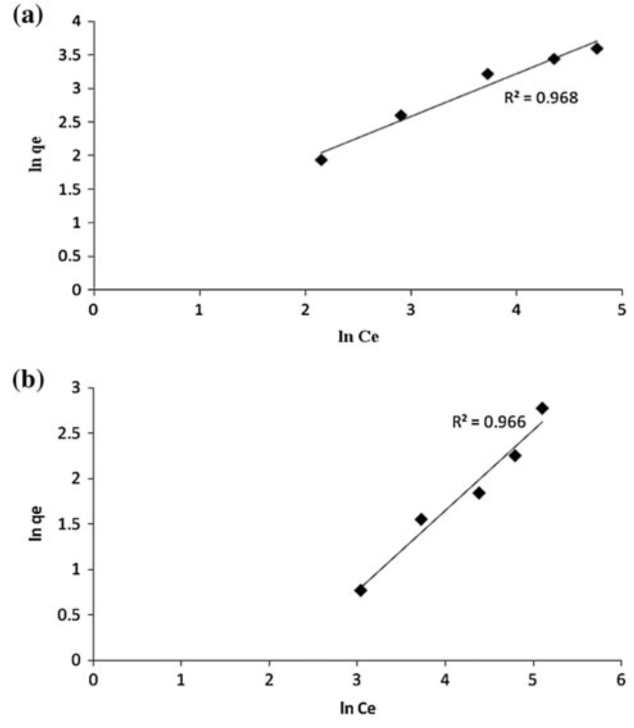


Fig. 7. Fruendlich isotherms for adsorption of Pb(II) onto (a) XDPT and (b) raw-DPT.

where q_e is the amount of Pb(II) adsorbed (mg/g) and C_e is the equilibrium concentration of Pb(II) solution (mg/l). K_F and n are the Freundlich constants which indicate the capacity and the intensity of the adsorption, respectively. Thus, a plot of ln q_e vs. ln C_e should be a straight line with a slope of 1/n and an intercept of ln K_F as shown in Fig. 7. The value of the Freundlich constant (n) was 1.578 for XDPT (Table 2) showing that the adsorption process may be favorable. R^2 value (<0.99) obtained from Freundlich isotherm indicated that Freundlich model is not suitable. (Fig. 7, Table 2).

The Langmuir and Freundlich adsorption isotherms of raw-DPT are compared in Figs. 6(b) and 7(b) and the adsorption data are given in Table 2. On the whole, the Langmuir isotherm displays a higher regression coefficient (R^2) compared to the Freundlich isotherm for both raw-DPT and XDPT and the adsorption data fit better with the Langmuir adsorption isotherm model.

3.7. Adsorption kinetics study

The transient behavior of the batch adsorption process at different Pb(II) concentrations is analyzed using the pseudo-first-order and pseudo-second-order models.

3.7.1. Pseudo-first-order model

The pseudo-first-order rate model of Lagergren [46] is based on solid adsorbent capacity and generally expressed as follows:

$$\log(q_e - q_t) = (\log q_e) - \left(\frac{k_1}{2.303}\right)t \qquad (5)$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of solute adsorbed at any time (mg/g), and k_1 (min^{-1}) is the adsorption rate constant. Values of k_1 calculated from the plots of log ($q_e - q_t$) vs. t (Fig. 8) at different initial concentrations are summarized in Table 3. The rate constant k_1 ranges between 1.5×10^{-2} to 2.2×10^{-2} min^{-1}. Boudrahem et al. [47] have reported K_1 values 4.3×10^{-2}, 2.7×10^{-2}, 3.5×10^{-2}, 5.1×10^{-2}, and 3.7×10^{-2} for the initial Pb (II) concentrations of 10, 30, 50, 70, and 90 mg/l, respectively. As shown in Table 3, the coefficient of linear regression (R^2) of Eq. (2) is low, ranging from 0.874 to 0.932 and q_e (cal) values do not agree with q_e (exp.) data. These results suggest that the pseudo-first-order model does not describe the adsorption kinetics of Pb(II) onto XDPT.

3.7.2. Pseudo-second-order model

The pseudo-second-order model [48] can be expressed as:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \qquad (6)$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-order equation, q_e (mg/g) is the maximum adsorption capacity, and q_t (mg/g) is the amount of adsorption at time t (min). The plot of t/q_t vs. t (Fig. 9) shows a linear relationship. The value of q_e (mg/g) and k_2 (g/mg min) are determined from the slope and intercept of the plot. The results are summarized in Table 3 for each initial concentration. It can be seen that the calculated coefficient of determination (R^2) is very close to unity and that q_e (cal) values agree with the experimental values. These results suggest that the pseudo-second-order model describes the adsorption kinetics of the present system. It can be understood from Table 3 that k_2 values decreased with the increased initial Pb(II) concentration. This decrease in k_2 values at higher concentrations seems to be due to the repulsion effect between the adsorbed and the nonadsorbed Pb(II) ions.

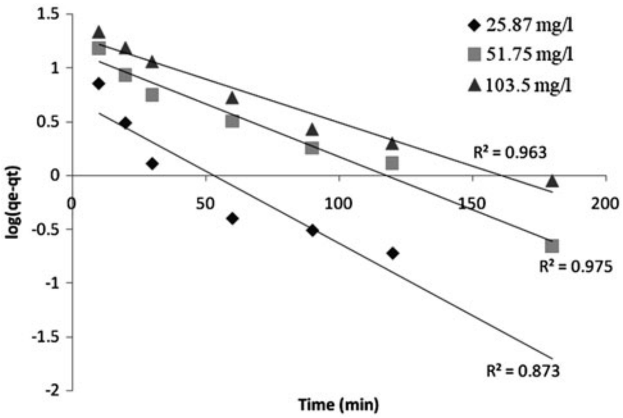


Fig. 8. Pseudo-first-order kinetic plot for adsorption of Pb(II) onto XDPT.

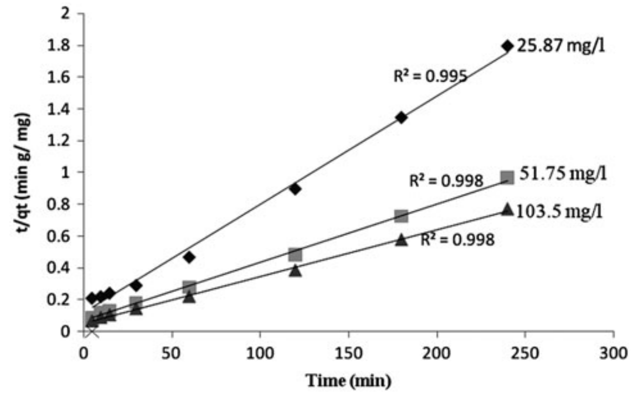
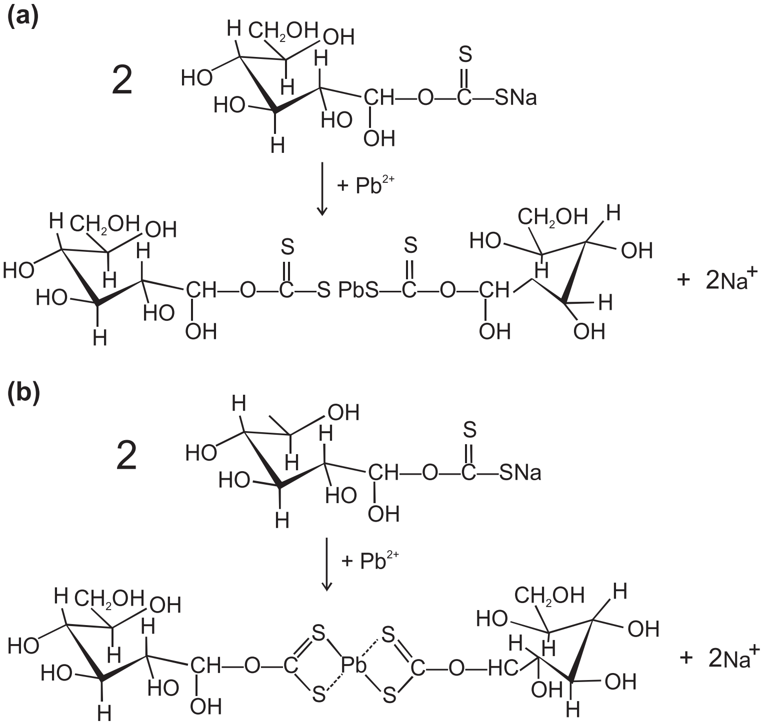


Fig. 9. Pseudo-second-order kinetic plot for adsorption of Pb(II) onto XDPT.

Table 3
Pseudo-first-order and pseudo-second-order models for adsorption of Pb(II) on XDPT

Initial concentration (mg/l)	$q_{e \cdot exp.}$(mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	$q_{e\ (cal)}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e\ (cal)}$ (mg/g)	R^2
25.87	6.12	0.015	2.981	0.874	0.039	6.28	0.995
51.75	13.09	0.019	6.321	0.932	0.016	13.12	0.998
103.5	24.84	0.022	8.935	0.864	0.010	25.49	0.998



Scheme 2. Proposed adsorption mechanism: (a) ion exchange and (b) complexation.

3.8. Adsorption mechanism

The adsorption of Pb(II) was found to be maximum at optimum pH ~ 5 and decreased below the pH point of zero charge (pH_{pzc} 3.8). The adsorption sites on XDPT for the adsorption of Pb(II) ions are sulfur atoms of the xanthate groups. The xanthate groups are not protonated above pH 1.5 and have a net negative charge and hence the adsorption of Pb(II) ions on XDPT started above pH 2.

Since the XDPT has a very low specific surface area (~5.83 m^2/g), physical adsorption alone cannot contribute to the higher Pb(II) uptake values. The probable adsorption mechanism between Pb(II)–XDPT interaction could be ion exchange, complexation, or combination of both processes. The cation (Na^+) from the xanthated group contained in the monomeric unit has been exchanged by the Pb(II) ions present in the solution. A schematic representation of the ion exchange and complexation mechanisms of Pb(II) ions with the xanthate groups is shown in Scheme 2. In ion exchange process, two negatively charged sulfur atoms participate in capturing one divalent lead ion (Scheme 2(a)). However, complexation occurs between four sulfur atoms and one divalent lead ion (Scheme 2(b)). Because lead belongs to post-transition metals, which have empty orbitals that can be occupied by electrons to form complex, and considering steric hindrance, complexation mechanism is the most possible adsorption process.

According to the "HSAB" theory by Pearson, xanthate is a soft base and it tends to form stable complexes with soft acids like heavy metal ions [49]. The Pb(II) ions are larger in size and more polarizable and the ligands of XDPT will have a much higher affinity towards the Pb(II) ions and hence the adsorption capacity was found to be higher than its raw biomass. The precipitate formation constant (K_s) indicates the strength of lead and XDPT complex. It also shows that the lead complexation with sulfur is stronger than the formation of lead hydroxide complex [50]; [$Pb(OH)_2$; $K_s = 10^{15.2}$ and PbS $K_s = 10^{27.5}$]. This strong affinity between sulfur and lead may result in a high affinity constant.

3.9. Desorption studies

Desorption studies were carried out by batch method. Eluting using EDTA (0.01 M) –HNO_3 (0.1 M) resulted ~95% desorption of Pb(II) ions. The loss in the adsorption capacity after three cycles of operation was found to be ~18%.

4. Conclusions

A new adsorbent XDPT was prepared by the treatment of DPT with CS_2 under basic condition. The adsorption of Pb(II) ions on the XDPT was found to be dependent on Pb(II) concentration, pH, time, and adsorbent dosage. Adsorption process revealed that the initial uptake of Pb(II) was rapid and equilibrium was achieved within 120 min. The optimum pH for maximum adsorption was found to be 5. An adsorbent dosage of 5 g/l was required to remove ∼99.4% Pb(II) from a solution of initial concentration, 103.5 mg/l. Experimental results indicate that the adsorption process follows a pseudo-second-order reaction kinetics. The isotherm studies show that the adsorption data correlate well with the Langmuir isotherm model. The adsorption process of Pb(II) ions on XDPT is mainly due to the complexation of lead(II) ions with the sulfur donors of XDPT. This study demonstrate that the XDPT could be used as a potential adsorbent for the treatment of wastewater containing Pb(II) ions.

Acknowledgement

The authors are thankful to Director, HBTI, Kanpur, for providing necessary research facilities.

References

[1] M. Sekar, V. Sakthi, S. Rengaraj, Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell, J. Colloid Interface Sci. 279 (2004) 307–313.

[2] I. Fisher, D.J. Pain, V.A. Thomas, Review of lead poisioing from ammunition sources in terrestrial birds, Conserv. Biol. 131 (2006) 421–432.

[3] H. Cheng, Y. Hu, Lead (Pb) isotropic finger printing and its application in lead pollution studies in China: A Review, Environ. Pollut. 58 (2010) 1134–1146.

[4] M.A.H. Bhuiyan, L. Parvez, M.A. Islam, S.B. Dampare, S. Suzuki, Heavy metal pollution of coal mine-affected agricultural soils in the Northern part of Bangladesh, J. Hazard. Mater. 173 (2010) 384–392.

[5] E. Katsou, S. Malamis, K.J. Haralambous, Industrial wastewater pre-treatment for heavy metal reduction by employing a sorbent-assisted ultra filtration system, Chemosphere 82 (2011) 557–564.

[6] M. Nadeema, A. Mahmood, Shahid, S.S. Shah, A.M. Khalid, G. McKay, Sorption of lead from aqueous solution by chemically modified carbon adsorbents, J. Hazard. Mater. 138 (2006) 604–613.

[7] S. Bhattacharjee, S. Chakrabarty, S. Maity, S. Kar, P. Thakur, G. Bhattacharyya, Removal of lead from contaminated water bodies using sea nodule as an adsorbent, Water Res. 37 (2003) 3954–3966.

[8] S. Tunali, T. Akar, A. Safa Ozcan, I. Kiran, A. Ozcan, Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by *Cephalosporium aphidicola*, Sep. Purif. Technol. 47 (2006) 105–112.

[9] I.S.I. Tolerance limits for industrial effluents prescribed by Indian Standards Institution. IS: 2490 (Part II), New Delhi, India, 1982.

[10] B. Sen Gupta, M. Curran, H. Shameem, T.K. Ghosh, Adsorption characteristics of Cu and Ni on *Irish Peat Moss*, J. Environ. Manage. 90 (2009) 954–960.

[11] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using baggase fly ash a sugar industry waste, J. Colloid Interface Sci. 271 (2004) 321–328.

[12] S. Khatoon, J. Anwar, M. Hassan, R. Farooqm, H.B. Fatima, H.N. Khalid, Removal of chromium (VI) by biosorption of eucalyptus bark, World Appl. Sci. J. 6 (2009) 1638–1643.

[13] D. Park, S.R. Lim, Y.S. Yun, J.M. Park, Development of a new Cr(VI) biosorbent from agricultural biowaste, Bioresour. Technol. 99 (2008) 8810–8818.

[14] R. Salim, M. Al-Subu, E. Dawod, Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency, J. Environ. Manage. 87 (2008) 521–532.

[15] M.A.M. Lara, I.L.R. Rico, I.C.A. Vicente, G.B.G. , M.C. Hoces, Modification of the sorptive characteristics of sugarcane bagasse for removing lead from aqueous solutions, Desalination 256 (2010) 58–63.

[16] L. Semerjian, Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust, J. Hazard. Mater. 173 (2010) 236–242.

[17] W. Li, L. Zhang, J. Peng, N. Li, S. Zhang, S. Guo, Tobacco stem as a low cost adsorbent for the removal of Pb(II) from wastewater: Equilibrium and kinetic studies, Ind. Crops Prod. 28 (2008) 294–302.

[18] M.A.K.M. Hanafia, S.C. Ibrahim, M.Z.A. Yahya, Equilibrium adsorption study of lead ions onto sodium hydroxide modified lalang (*Imperata cylindrica*) leaf powder, J. Appl. Sci. Res. 2 (2006) 1169–1174.

[19] Q. Li, J. Zhai, W. Zhang, M. Wang, J. Zhou, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk, J. Hazard. Mater. 141 (2006) 163–167.

[20] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of copper (II), chromium (III), nickel (II), and lead (II) ions from aqueous solutions by meranti sawdust, J. Hazard. Mater. 170 (2009) 969–977.

[21] L. Mouni, D. Merabet, A. Bouzaza, L. Belkhiri, Removal of Pb(II) and Zn(II) from the aqueous solutions by activated carbon prepared from dates stone, Desalin. Water Treat. 16 (2010) 66–73.

[22] Y.S. Ho, W.T. Chiu, C.S. Hsu, C.T. Huang, Sorption of lead ions from aqueous solution using tree fern as a sorbent, Hydrometallurgy (2004) 55–61.

[23] M.A.K.M. Hanafiah, W.S.W. Ngah, S.C. Ibrahim, H. Zakaria, W.A.H.W. Ilias, Kinetics and thermodynamic study of lead adsorption onto Rubber (*Hevea brasiliensis*) leaf powder, J. Appl. Sci. 6 (2006) 2762–2767.

[24] H. Jaman, D. Chakraborty, P. Saha, A study of the thermodynamics and kinetics of copper adsorption using chemically modified rice husk, Clean-soil Air Water 37 (2009) 704–711.

[25] M.N.M. Ibrahim, W.S.W. Ngah, M.S. Norliyana, W.R.W. Daud, Copper (II) biosorption on soda lignin from oil palm empty fruit bunches (EFB), Clean-soil Air Water 37 (2009) 80–85.

[26] T. Altun, E. Pehlivan, Removal of copper (II) ions from aqueous solutions by walnut hazelnut-, and almond-shells, Clean-soil Air Water 35 (2007) 601–606.

[27] M.A.K.M. Hanafiah, W.S.W. Ngah, Preparation, characterization and adsorption mechanism of Cu(II) onto protonated rubber leaf powder, Clean-soil Air Water 37 (2009) 696–703.

[28] R. Gong, W. Cai, N. Li, J. Chen, J. Liang, J. Cao, Preparation and application of thiol wheat straw as sorbent for removing mercury ions from aqueous solution, Desalin. Water Treat. 21 (2010) 274–279.

[29] N. Balkaya, N. Bektas, Chromium (VI) sorption from dilute aqueous solutions using wool, Desalin. Water Treat. 3 (2009) 43–49.

[30] W.K. Hoi, P.F. Akmar, Solid and liquid fuels, in: K. Shari, K. C. Khoo, A.R. Mohammad (Eds.), Oil Palm Stem Utilization: Review of Research, Forest Research Institute, Kuala Lumpur, vol. 107, 1991, pp. 87–97.

[31] K.O. Lim, K.S. Lim, Caronization of oil palm trunks at modrate temperatures, Bioresour. Technol. 40 (1992) 215–219.

[32] M.Z. Hussein, Z. Zulkarnain, K.H. Khor, M. Barbri, The prepration of activated carbon from chips of oil palm trunk catalysed by Zn_2Cl_2/CO_2 surface area and porosity studies, J. Chem. Technol. Biotechnol. 64 (1995) 34–40.

[33] A.M.A. Al-Haidary, F.H.H. Zanganah, S.R.F. Al-azawi, F.I. Khalili and A.H. Al-Dujaili, A study on using date palm fibres and leaf base of palm as adsorbents for Pb(II) ions from its aqueous solution, Water Air Soil Pollut. 214 (2011) 73–82.

[34] G. Issabayeva, M.K. Arova, N.M. Sulaiman, Study on palm shell activated carbon adsorption capacity to remove copper ions from aqueous solutions, Desalination 262 (2010) 94–98.

[35] A.I. Ahmad, M.M. Loh, J.A. Aziz, Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption, Dyes Pigments 75 (2007) 263–272.

[36] S. Liang, X. Guo, N. Feng, Q. Tian, Application of orange peel xanthate for the adsorption of Pb^{2+} from aqueous solutions, J. Hazard. Mater. 170 (2009) 425–429.

[37] R.T. Morrison, R.N. Boyd, Organic Chemistry, sixth ed., Prentice Hall, New Delhi, 1994, pp. 1200–1201.

[38] P.L. Homogai, K.N. Ghimire, K. Inove, Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse, Bioresour. Technol. 10 (2010) 2067–2069.

[39] H. Khan, M.J. Ahmed, M.I. Bhanger, A rapid spectrophotometric method for determination of trace level using 1,5-diphenyl thiocarbazone in aqueous micellar solutions, Anal. Sci. 23 (2007) 193–199.

[40] P.L. Homogai, K.N. Ghimire, K. Inove, Preparation and characterization of charred xanthated sugarcane bagasse for the separation of heavy metals from aqueous solutions, Sep. Sci. Technol. 46 (2011) 330–339.

[41] Y. Wu, S. Zhang, X. Guo, H. Huang, Adsorption of chromium (III) on lignin, Bioresour. Technol. 99 (2008) 7709–7715.

[42] S.S. Baral, N. Das, G.R. Chaudhary, S.N. Das, A preliminary study on adsorptive removal of Cr(VI) using seaweed, *Hydrilla verticillata*, J. Hazard. Mater. 171 (2009) 358–369.

[43] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40(9) (1918) 1361–1403.

[44] M.H. Nasir, R. Nadeem, K. Akhtar, M.A. Hanif, A.M. Khalid, Efficacy of modified distillation sludge of rose (*Rosa centifolia*) petals for lead(II) and zinc(II) removal from aqueous solutions, J. Hazard. Mater. 147 (2007) 1006–1014.

[45] H. Freundlich, Ueber dye adsorption in loesungen, Z. Phys. Chem. 57 (1907) 385–470.

[46] S. Lagergren, About the theory of so called adsorption of soluble substances, kungliga svenska vetenskap sakademiens, Handlingar 24(04) (1898) 1–39.

[47] F. Boudrahem, F. Aissani-Benissad, A. Soualah, Adsorption of lead(II) from aqueous solution by using leaves of date trees as an adsorbent, J. Chem. Eng. Data 56 (2011) 1804–1812.

[48] H. Kim, K. Lee, Application of cellulose xanthate for the removal of nickel ion from aqueous solution, J. Korean Soc. Eng. 20 (1998) 247–254.

[49] M.J. Winter, D-Block Chemistry, Oxford University Press, New York, NY, 1994.

[50] A. Hulanicki, Complexation reaction of dithiocarbamates, Talanta 14 (1967) 1371–1392.