

Factors Affecting Sorption of Pb(II) from Aqueous Solutions Using Sawdust Based Activated Carbon

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Abstract: Pine Sawdust (PSD), agricultural by-product, was used as precursor for preparation of activated carbon by physical activation method using CO₂ at 800°C for 90 min. The obtained activated carbon (PSDC8) was characterized and utilized for sorption of Pb(II) ions from aqueous solution. The effect of pH, initial concentration of lead (II) ions, contact time, and temperature on the adsorption was studied in a batch process mode. The equilibrium sorption data were analyzed by Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm models. The maximum adsorption capacities of PSDC8 obtained from Langmuir were 91.6, 141.0 and 181.0 mg/g at 25°C, 45°C and 65°C, respectively. The kinetic data were found to follow the pseudo-second-order model and that the rate-controlling step was chemical adsorption. Textural analysis was employed in order to determine specific surface area and total pore volume of the prepared activated carbon. Surface structure was characterized by using Fourier transform infrared spectroscopy before and after adsorption of Pb (II). Variations in the ΔH° and ΔS° values showed that the sorption process was spontaneous ($\Delta G^\circ < 0$), endothermic ($\Delta H^\circ > 0$), and had increased entropy ($\Delta S^\circ > 0$).

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1. Introduction

Pollution of the natural environment by heavy metals is a worldwide problem since these metals are non-biodegradable and bio-accumulative, and many of them have toxic effects. Many industrial facilities such as metal plating, petroleum refining, tanneries, batteries, mining operations, electronic and chemical plants, pigments, alloys and fertilizer (Rostamian et al., 2011) discharge heavy metals via their waste effluents. Especially, effluents from extractive industries established over the last century are directly discharged onto surrounding land and surface water bodies constituting point and non-point sources of heavy metals contamination for groundwater. Mining operations are regarded as the significant source of heavy metal contamination of the environment owing to activities such as mineral exploitation, ore transportation, smelting and refining, disposal of the tailings and waste waters around mines. Pb(II) can result in behavioral changes, learning disabilities, reading problems, development defects, language difficulties, mental retardation, and abnormalities in pregnant women (Li and Yangsheng, 2013; Mouni et al., 2011). Hence, it is essential to remove Pb(II) from wastewaters before migration and transformation into environment. The efforts on reducing Pb(II) ion concentration in the effluent wastewaters are motivated by the toxic effects of lead on the aquatic

world and the risk of contamination of water resources designated for human consumption. Current USEPA drinking water standard for Pb(II) is 0.015 mg/l (Li and Wang 2009; Milan et al., 2011). Currently, various physicochemical and biological strategies have been developed for the removal of heavy metals, such as chemical precipitation, electrochemical treatment, ion exchange, solvent extraction, zero-valent metals reaction, membrane separation and adsorption (Matlock et al., 2002; Hunsom et al., 2005; Maturana et al., 2011; Juang and Huang, 2003; Chen et al., 2008; Muthukrishnan and Guha, 2006; Ma et al., 2012; Shin et al., 2011; Sepehrian et al., 2010). Among them, adsorption is found to be cheap, effective and easy to adapt and has been confirmed as one of the most promising technologies for removing heavy metals from wastewaters. Recently, much attention has been paid for investigation of cost efficient sorbents (Wang and Peng, 2010; Huang et al., 2011). Agricultural residues are usually available at low cost. Wood and agricultural-based fibers can be produced from these residues and used as adsorbents to remove various types of contaminants from water. In recent many reports investigated the use of agricultural by-product, such as peanut shell (Ugwekar and Lakhawat, 2012; Oliveira et al., 2010), hazelnut, pine bark, wheat straw, rice husk, Fruit stone, Rice waste and sawdust (Kadirvelu et

al., 2002; Oh and Tshabalala, 2007; Umar et al., 2010; Awwad et al., 2010; Abdelrahman and Mohammed, 2008; Tarun et al., 2011; Fatemeh et al., 2008; Jung-Seok et al., 2010; Gad et al., 2009). Adsorption onto activated carbon was found to be a promising technique as it enables the removal of trace amounts of lead from solutions (Sreejalekshmi et al., 2009). Activated carbon is a porous adsorbent with a high surface area, a great adsorption capacity and an effective regeneration. Carboxylic, carbonylic, lactonic, phenolic, aldehydic, and other organic functional groups are located at the edges of hexagonal carbon layer planes and are responsible for surface reactivity of activated carbon (Aygün et al., 2003). Ionization of these functional groups in solution is pH dependant and leads to a build-up of a charged interface between the solid surface and the bulk of the solution (Yang et al., 2007). The type and quantity of surface functional groups are influenced by the preparation method and by the sort of the precursor (Hassler, 1974). Sawdust is one of the cheapest and abundantly available adsorbent that has the capacity to adsorb and accumulate heavy metals from wastewater. The objective of this research is to investigate the lead removal efficiency of pine sawdust activated carbon (PSDC8) by adsorption from aqueous media. The effects of contact time, initial concentration of Pb (II) ions, pH and temperature were examined. Kinetics and isotherms of Pb (II) ion adsorption on sawdust based activated carbon were studied and described by several models. In addition to this, structural characterization of the prepared adsorbent was performed in order to provide relations of its structure and adsorption capacity of Pb (II) ions.

2. Materials and Methods

2.1. Preparation of Pb (II) solution.

All reagent and chemical used to prepare solutions were of analytical grade. The stock solution of pb(II) (1000 mg/L) is prepared by dissolving a weighed quantity of the respective nitrate salts in double distilled water.

2.2. Preparation of activated carbon.

The pine sawdust (PSD) was collected from a local furniture factory in El-Menoufia Governorate, Egypt. It was washed several times with double distilled water to remove dust and impurities. Then, it was dried at 110°C for 48 h to constant weight and crushed to small particle size. The crushed PSD was used for preparation of adsorbents in different forms as a follow: (i) in the first form, the PSD was used without any treatment. (ii) in the second form, PSD was used for preparation of activated carbon by physical activation. And (iii) in the third form, PSD was

used for preparation of activated carbon by chemical activation.

2.2.1: Preparation of activated carbon by physical activation.

In this experiment, 30 gm of the dry crushed PSD were placed in the tube to be situated in the hot zone of the tubular furnace. The temperature was raised gradually (50°C/15 min) up to 500 °C. Pure carbon dioxide or nitrogen were then introduced through the heated mass, and the temperature was raised gradually (100°C/15 min) up to 800°C and soaked at this temperature for 90 min. After cooling, the product was washed several times with double distilled water, then dried, grinded and sieved to obtain different particles size. The final product was stored in tightly bottles for later use. The obtained activated carbon has a notation of PSDC8 and PSDN8, respectively.

2.2.2. Preparation of activated carbon by chemical activation.

In this phase, one-step of thermal-chemical activation using different acids was used for preparation of activated carbon. Starting with 30 gm of the crushed PSD, it was soaked in 50 ml of pre-diluted acids 80% wt, HCl or H₂SO₄ to cover it completely, slightly agitated to ensure penetration of the solution throughout and left overnight at room temperature. The impregnated mass was dried in an oven at 80°C overnight, then admitted into the tube (ignition tube open from both ends), which was then placed in a tubular electric furnace. The temperature rose by 50°C/ 15min up to 500°C where held for 90 min. After gradual cooling down to room temperature, the final product was repeatedly washed with hot distilled water until the washings showed pH>5. The washed carbon was oven-dried at 110°C for 24 h and finally stored in a desiccator for later use. The prepared activated carbon had a notation PSDC15 and PSDS5, respectively as shown in Table (1).

Table (1) Different types of activated carbons from Pine sawdust

No	Sample notation	Preparation condition
1	PSD	Pine sawdust without any treatment.
2	PSDC8	Carbon dioxide at 800 °C for 90 min.
3	PSDN8	Nitrogen at 800 °C for 90 min.
4	PSDC15	HCl at 500°C for 90 min.
5	PSDS5	H ₂ SO ₄ at 500°C for 90 min.

2.3. Characterization of activated carbon.

The BET surface area measurement of PSDC8 sample was made by nitrogen adsorption at

-196°C using (NOVA 1000e Quantacrome, USA). Before the measurement, the carbon sample was degassed 3 hr at 300°C. CHNS/O elemental analysis was made by Thermofinnigan Elemental Analyzer. Chemical characterization of functional groups on surface of the PSDC8 sample was studied by a Fourier transform infrared spectrometer (FTIR-100, Shimadzu) in the range 4000–500cm⁻¹, using pellets with sample dispersed in KBr. Suspension pH (pH_{SUS}) relates with the overall acidity or basicity of the adsorbent. In the present study, 0.3 g of PSDC8 was suspended into 30 ml of deionized water and equilibrated for 24 h. The resulting pH was denoted as pH_{SUS}. The density, ash and moisture content analysis of PSDC8 was determined.

2. 4. Adsorption experiments

In order to investigate kinetics, the adsorption experiments were carried out by agitating 0.01 gm of PSDC8 with 10 ml of Pb (II) solutions of concentration 60mg/L in the sealed 50 ml Erlenmeyer flasks using water-bath shaker at 25°C for 24 hr. After intervals time, suspensions were filtered through filter paper Whatman 44. Concentrations of Pb (II) ions in the filtrates were determined UV spectroscopy using PAR as an organic chelating agent. For the adsorption isotherm studies, 0.01 g of PSDC8 samples was stirred with Pb (II) solutions of different concentrations until equilibrium was attained. With the goal to examine the influence of solution pH on the mechanism and the capacity of the adsorption, 0.01 g of PSDC8 was stirred for 120 min with 60 mg/l Pb (II) solutions at pH values ranging from 1 to 8. The pH was adjusted by adding a few drops of diluted 0.1N NaOH or 0.1N HCl and measured by using a pH meter (Ecoscan, EUTECH Instruments, Singapore). To investigate the adsorption process at different temperatures (25, 45 and 65 °C) batch techniques was employed. 0.01 g of PSDC8 and contacted with 10 mL of Pb (II) ions of concentration 60 mg/L and agitated using a water-bath shaker. The agitation speed was kept constant at 250 rpm. At predetermined intervals time, solutions were analyzed for the final concentration of Pb (II) ions. Sorption efficiency (%) is considered in percentage as:

$$\% \text{ Sorption} = (C_i - C_e) / C_i \times 100 \quad (1)$$

In all the cases, the adsorption uptake, q (mg/g), was calculated by:

$q = (C_o - C)V/M$ (2), where C_o is the initial concentration of Pb (II) ions, C is the residual concentration of Pb(II) ions at equilibrium or any time t, V is the volume of the solution and M is the mass of activated carbon. The experimental data were fitted to the kinetic and isotherm theoretical

models. The best-fit model indicates the most probable adsorption mechanism.

3. Results and discussion

3.1. Preliminary investigation.

Preliminary test was done to investigate the adsorptive capacity of prepared activated carbon. Fig. (1) illustrates the higher capacity of PSDC8 sample for sorption of Pb(II) than the other prepared activated carbon and the raw material. As seen from the figure, PSDC8 sample has the higher % removal of Pb (II), so it was selected to study its characterization and the factors affecting sorption of Pb (II) from aqueous solution.

3.2. Characterization of prepared activated carbon.

Some of physic-chemical characterizations of prepared adsorbent are summarized in table 2 which indicate to the difference in their properties according to the method of preparation.

Figure 1. % Removal and uptake (mg/g) of Pb(II) using raw material and prepared activated carbons.

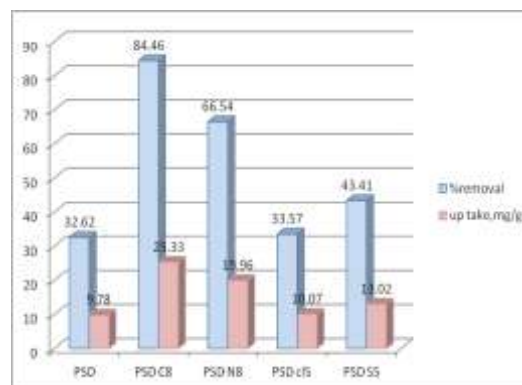


Table 2. Some of physic-chemical characterizations of prepared adsorbent

Samples	Yield %	pH _w	Adsorption %	Density		Elemental analysis					Ash %	
				Apparent	packed	C	H	N	O	C/H		O/C
PSD	100	5.2	10.7	0.16	0.31	48.3	6.5	0.09	45.2	0.62	93.5	1.6
PSDC8	23.65	7.0	4.85	0.34	0.42	78.7	1.1	0.17	19.8	5.96	25.16	4.9
PSDN8	24.33	7.2	6.21	0.37	0.45	65.4	0.9	0.45	32.5	6.06	49.69	7.2
PSDC15	39.25	4.5	8.30	0.25	0.32	73.8	2.6	0.13	23.5	2.37	31.84	10.5
PSDC55	50.0	6.7	9.13	0.54	0.68	60.9	2.1	0.15	36.5	2.42	59.93	15.3

3.2.1. Surface area and pore structure characterization

The surface areas and total pore volume (V_p) of PSDC8 sample were determined by nitrogen adsorption at 77 K on an automatic adsorption instrument. Before the measurement, the carbon sample was out-gassed under a nitrogen atmosphere for 3 hr at 300°C. Table (3) gives the BET surface area (SBET), total pore volume (V_{total}), micropore volume (V_{micro}), micropore surface area (DRmethod and average pore diameter (D_p) of the PSDC8 prepared at the optimum conditions.

Table 3. Surface characterization of PSDC8 prepared sample.

Methods	Parameter	Values	Methods	Parameter	Values
BET	surface area (m ² /g)	538.76	DR	Surface Area	538.76(m ² /g)
	Total pore volume (cm ³ /g)	1.987e-01		Average pore width	36.78 Å
	Average pore radius nm	1.89383 e ⁻¹¹		sorption energy	7.07 kJ/mol
		Micropore volume		0.19 cm ³ /g	
		Micropore surface area		538.76 m ² /g	
Langmuir	surface area(m ² /g)	517.48	BJH	Pore Volume	0.03 cm ³ /g
				Pore Radius	15.6 Å

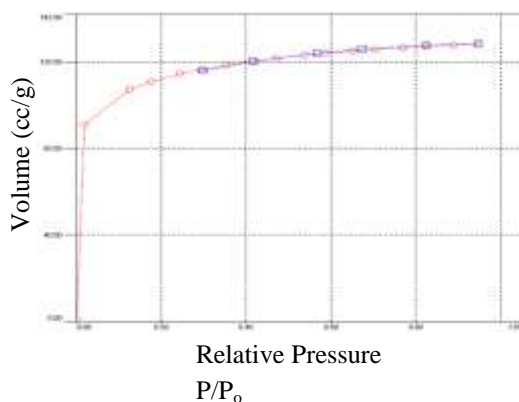


Figure 2. Isotherm linear of adsorption of nitrogen by PSDC8 sample.

3.2.2. Fourier transforms infrared spectroscopy.

To qualitatively characterize surface groups on the PSDC8 carbon, FTIR transmission spectra were collected for the PSD, PSDC8 and PSDC8-loaded with Pb (II) samples in this study (Fig. 3). In the PSD sample, a broad band located around 3419.1 cm⁻¹ is assigned to O–H stretching vibrations of hydrogen bonded hydroxyl groups. This band strongly decreased in the PSDC8 sample due to the dehydration through the preparation of activated carbon and approximately disappeared in

the PSDC8-Pb loaded sample with the presence a strong band at 794.8 cm⁻¹ which attributed to the Pb-C bond or C-O-C bond. The band around 1637.5 cm⁻¹ is usually caused by the stretching vibration of C=O in ketones, aldehydes, lactones, and carboxyl groups (Kunquan et al., 2010); this peak probably suffers minor overlapping with C=C aromatic ring stretching vibration which is usually found at 1580.0 cm⁻¹ (Milan et al., 2011). Aliphatic C–H stretching vibration is found as a peak at 2925.7 cm⁻¹ in the PSD sample while asymmetric vibration of CH₂ group appears at 2995.5 cm⁻¹ in the PSDC8-Pb(II) loaded sample and approximately disappeared in the prepared PSDC8 carbon. The absorption bands at the 2361 to 2336 cm⁻¹ region usually come only from triple bonds and other limited types of functional groups.

The band around 1059.4 cm⁻¹ is attributed to aromatic ring or C-O-C stretching vibration in ethers (Zhao and Sun, 2003; Pei et al., 2007) which becomes more broad with the activation using CO₂ indicating the increase of aromaticity of the PSDC8 carbon yield than the raw PSD and this band disappeared in the PSDC8-Pb(II) loaded sample. The peak at 561.2 cm⁻¹ may be assigned to the stretching bands of C- O- C or C-OH (Reznik et al., 2008). As can be inferred from FTIR analysis, there is presence of surface functional groups containing oxygen like carboxylic, carbonyl, phenolic and lactonic groups on the PSD surface. The bands are strong with PSD, but different or weak with PSDC8 and PSDC8-Pb. This may be due to the condition of preparation and adsorption of Pb(II) suggesting that these functional groups take place in the adsorption of Pb(II).

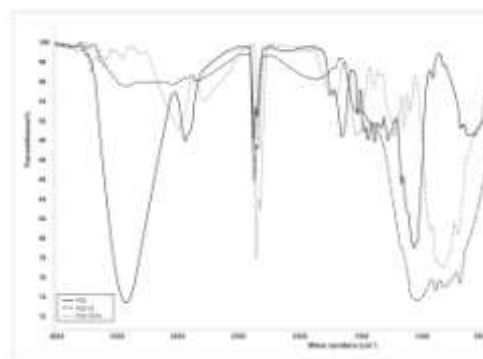


Figure 3. FTIR of the PSD, PSDC8 and PSDC8 sample loaded with Pb(II).

3.3. Factors affecting sorption of Pb(II) using PSDC8 prepared activated carbon.

3.3.1. Effect of pH.

pH of the initial solution is the most important factor affecting of the sorption of heavy

metals or organic compounds from aqueous solution using activated carbons due to the dissociation and ionization of adsorbate and surface functional groups on the adsorbent. The effect of pH on the adsorption of Pb(II) on PSD sample and its modified by different acids was described in Fig. 4. It indicates that the adsorption of Pb(II) on adsorbents are strongly pH dependent, as has been commonly observed for metal ion adsorption on biosorbents (Yu et al., 2001; Taty-Costodes et al., 2005). It is observed that the % removal Pb(II) decreases as pH of the solution decreases for all biosorbents under investigation. With the increase of pH, the negativity of the adsorption sites increases leading to higher % removal of Pb(II) ions. But, at higher pHs, the formation of negatively charged hydrolyzed ion decrease the sorption of Pb(II) ions due to decrease the mobility of hydrolyzed ion in solution and increase the hydrophilicity of hydrolyzed ions to stay in solution than to be adsorbed to the surface of adsorbents. The % removal of Pb (II) takes the following order: PSD < PSDC15 < PSDS5 < PSDN8 < PSDC8. The adsorption of Pb(II) ions onto PSDC8 may be attributed to ion exchange with hydrogen ions at the surface of active carbon. Additionally, a number of anionic ligands such as carboxyl and hydroxyl groups may take part in the complexation with ions at the active carbon surfaces. At a low pH, existence of a relatively large number of hydrogen ions resulted in a depression of the exchange between metal ion and hydrogen ions. Also the complexes formed via interaction between metal ion and acidic functional groups were destabilized at a low pH. Taty-Costodes et al. (2003) have shown the adsorption of Pb(II) and Cu(II) onto sawdust (of *Pinus sylvestris*) increased with the pH and reached a maximum at a 5.5 value. In our work, pH 5.0 was selected as the best pH with highest sorption for the most sorption experiments of Pb(II).

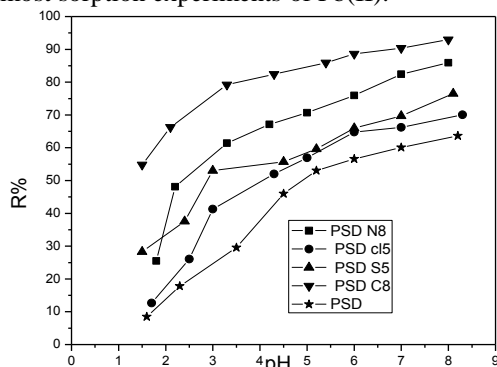


Figure 4. Effect of pH on the adsorption of Pb(II) onto PSD and its modification .

3.3.2. Effect of contact time.

To investigate the effect of shaking time on the sorption of Pb(II) using the PSDC8 sample, aliquots of 10 ml of 60 mg/L of Pb(II) solution adjusted to pH 5 were shaken with 0.01 gm of the PSDC8 sample for different intervals time. The obtained results are presented in Figure 5. The rate of adsorption was relatively fast in the initial stage, showing approximately 78% within 40 min. This result indicate that adsorption of Pb(II) in this stage may be occurring at the surface of the PSDC8 sample. After this stage, the rate of adsorption became slower, and this may be due to the inter and intra-particle diffusion of the Pb(II) ion into active site on the surface and pores of PSDC8 sample. Finally, as shown from the figure the equilibrium state was reached at 2 hr. Therefore, 2 hr was selected for other experiments of this work.

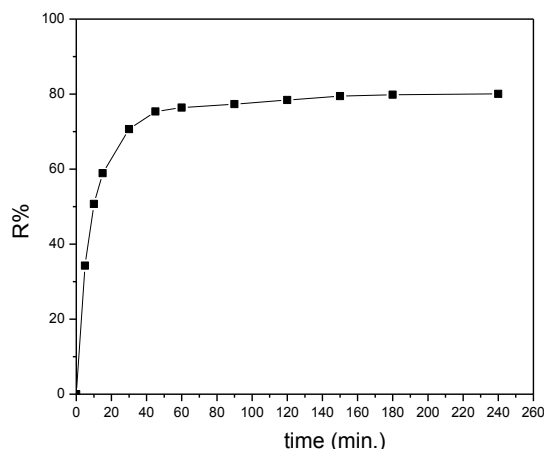


Figure 5. Effect of contact time on the removal of Pb(II) onto PSDC8.

3.3.3. Sorption Dynamics.

A kinetic study of adsorption is necessary as it provides the information about the adsorption mechanism, which is crucial for the practicality of the process. In our case, three different kinetic models were applied in order to establish which of them shows the best fit with experimentally obtained data. The pseudo-first-order kinetic model is frequently used in kinetic studies (Hameed et al., 2007). It is expressed by the following equation:

$$\text{Log}(q_e - q) = \text{log } q_e - (K_1 / 2.303) t \quad (3)$$

Where q and q_e are the amount of Pb(II) (mg/g) at time t (min) and at equilibrium respectively. The rate constant, K_1 can be obtained from the slope of $\text{log}(q_e - q)$ vs. time as shown in Fig. (6). The values of K_1 and R^2 are calculated and summarized in Table 4.

Table 4. Three kinetic models for Pb(II) ions adsorbed by PSDC8.

First-order rate constants		Second-order rate constants		intra-particle diffusion rate constants	
$q_{e, exp} (mg/g)$	48.1	$h (mg/g \cdot min)$	9.0	$K_p (mg/g \cdot min^{0.5})$	8.0
$K_1 (min^{-1})$	0.04	$K_2 (mg/g \cdot min)$	3.6×10^{-3}		
$q_{e, cal} (mg/g)$	21.5	$q_{e, cal} (mg/g)$	49.3	R^2	0.963
R^2	0.899	R^2	0.999		

The pseudo-second-order model for adsorption kinetics is expressed as (Franca et al., 2009):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where K_2 (g/mg · min) is the second-order rate constant determined from the plot of t/q_t vs. t , as shown in Fig, (6). The second-order rate constant is used to calculate the initial sorption rate, given by:

$$h = K_2 q_e^2 \quad (5)$$

The values of K_2 , h and R^2 are calculated and represented in Table 4. The correlation coefficients are higher compared to the results obtained from the first-order kinetic model. Also, the theoretical and experimental q_e values are in a good accordance with each other. So, it is possible to suggest that the sorption of Pb(II) onto PSDC8 followed the pseudo second- order kinetic model. It is a general understanding that pseudo-second order kinetic model provide best fits to the experimental data for the sorption systems where chemisorption seems significant in the rate controlling step (Helffersh, 1964). Therefore, second-order chemical reaction kinetics would be expected to be followed in the sorption processes and it is possible to state that chemisorption is the rate determining step.

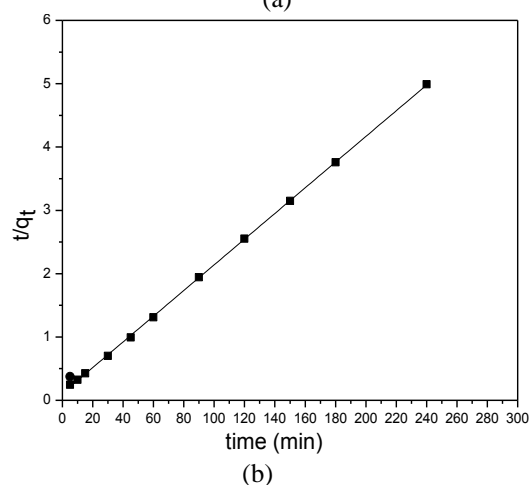
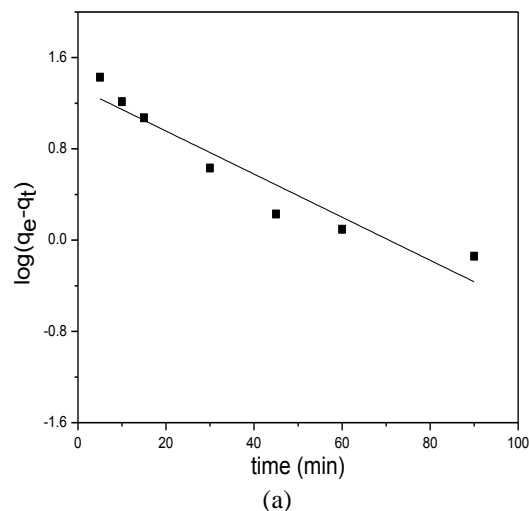


Figure 6. Kinetic models for adsorption of Pb(II) onto PSDC8: (a) Pseudo-first-order model (b) Pseudo-second-order model.

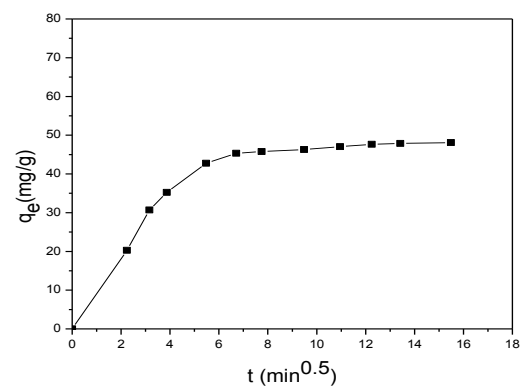


Figure 7. Intra-particle diffusion plot for Pb(II) adsorption onto PSDC8.

3.3.4. Adsorption isotherms

The adsorption isotherm indicates how molecules of adsorbate are partitioned between the

adsorbent and liquid phase at equilibrium as a function of adsorbate concentration.

In this study, the sorption of Pb(II) onto PSDC8 sample as a function of their concentration was studied at different temperatures (25°C, 45°C, 65°C) by varying the metal concentration from 60 to 360 mg/L, while keeping all other parameters constant. The result is shown in Fig.(8). The amount of ion increased with the increase in temperature thereby indicating the process to be endothermic. The equilibrium data obtained for the adsorption of lead(II) ions onto PSDC8 were analyzed by considering the Langmuir, Freundlich and R-D isotherm models.

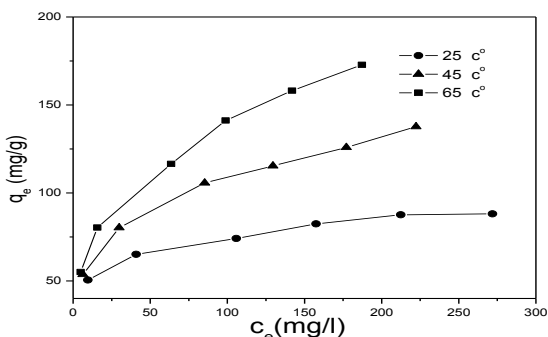


Figure 8. Adsorption isotherm of Pb(II) onto PSDC8

Freundlich isotherm model

Freundlich isotherm is purely empirical and it best describes the adsorption on heterogeneous surfaces (Ng et al., 2002). Freundlich isotherm equation is shown below in its linear form:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (7)$$

Where, q_e is the amount of metal ions adsorbed per unit weight of PSDC8 (mg/g), C_e is the equilibrium concentration of the metal ion in the equilibrium solution (mg/L), K_F is constant indicative of the relative adsorption capacity of PSDC8 and $1/n$ is the constant indicative of the intensity of the sorption process. The pictorial illustration of $\log q_e$ vs. $\log C_e$ is shown in Fig.(9), which suggests that the sorption of Pb(II) ions onto PSDC8 obeys Freundlich isotherm over the entire range of sorption concentration studied. The numerical values of the constants $1/n$ and K_F are computed from the slope and the intercepts, by means of a linear least square fitting method, and given in Table (5). The $1/n$ value is usually dependent on the nature and strength of sorption process as well as on the distribution of active sites (Unninathan and Anirudhan, 2001).

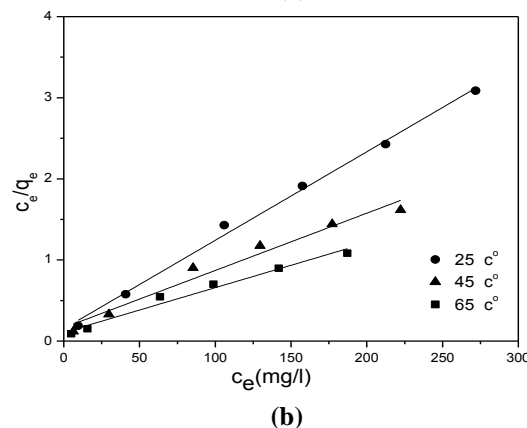
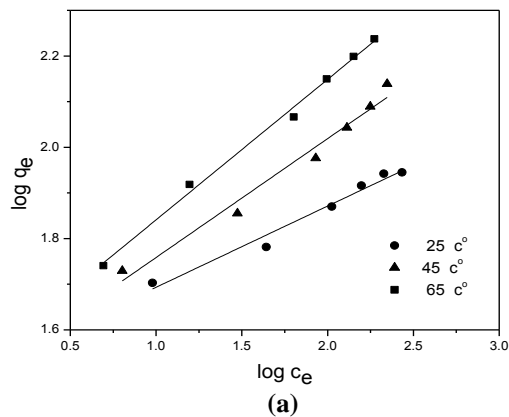


Figure 9. Freundlich (a) and Langmuir (b) plots of Pb(II) adsorption on PSDC8 at different temperature.

Langmuir isotherm model

The results of the adsorption studies of Pb(II) onto PSDC8 were well fitted in the rearranged Langmuir equation:

$$C_e/q_e = (1/Q_0)b + C_e/Q_0 \quad (8)$$

Where C_e is the equilibrium concentration (mg/l), q_e is the amount of Pb(II) adsorbed at equilibrium time (mg/g) and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption (Wang et al., 2005), which can be calculated from the C_e/q_e vs. C_e plot. The linearized Langmuir plot is shown in Fig. (10). The Langmuir parameters were calculated at different temperatures and listed in Table 5.

Dubinin-radushkevich (D-R) isotherm model

D-R isotherm describes sorption on a single type of uniform pores. In this respect, the D-R isotherm is an analogue of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential. The D-R isotherm is given with the following equation:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (9)$$

Where, q_m is the maximum amount of ion that can be adsorbed onto unit weight of PSDC8. i.e., sorption capacity (mg/g), β is a constant related to the sorption energy (mol^2/kJ^2); and ϵ is the Polanyi potential = $RT \ln(1 + 1/C_e)$, where R is the gas constant (kJ/mol.K), and T is the absolute temperature. The mean free energy of sorption is the free energy change when one mole of ions is transferred to the surface of the PSDC8 from infinity in the solution, and it is calculated from:

$$E = (-2\beta)^{-1/2} \quad (10)$$

The magnitude of E can be related to the reaction mechanism. If E is in the range of 8-16 kJ/mole, sorption is governed by ion exchange. In case of $E < 8$ kJ/mole, physical forces may affect the sorption mechanism. The D-R plots of $\ln q_e$ versus ϵ^2 at different temperatures are given in Fig. (10).

Linear regression analysis using paired of $\ln q_e$ and ϵ^2 resulted in derivation of q_m , β , E and the correlation factor (R^2). The correlation factor is a statistical measure of how well the data points fit the regression line. These D-R parameters, evaluated at different temperatures, are presented in Table (5). The values of the mean free energy, E, are in the range of 8-16 kJ/mol, which are within the energy ranges of ion exchange reaction.

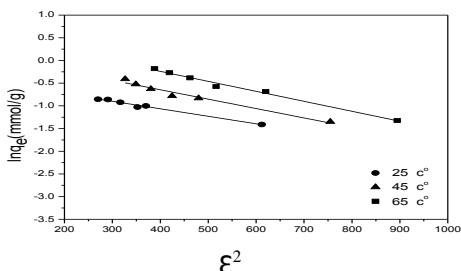


Figure 10. D-R plots for Pb(II) sorption onto PSDC8 at different temperatures.

Table 5. Langmuir, Freundlich, and D-R parameters for adsorption of Pb(II) on PSDC8

Temp. °C	Langmuir			Freundlich			Dubinin-Rudshkevich			
	Q^* mg/g	b l/g	R^2	K mg/g	n	R^2	q_m mg/g	B mol^2/kJ^2	E kJ/mol	R^2
25	91.6	0.072	0.989	32.7	5.6	0.995	138	1.6×10^{-2}	17.4	0.985
45	141	0.042	0.938	31.4	3.8	0.995	248	2×10^{-2}	15.5	0.965
65	181	0.051	0.987	34.1	3.2	0.980	293	2.2×10^{-2}	15.0	0.987

Graphic presentations of Pb(II) adsorption onto the PSDC8 at the experimental temperature of 25, 45, and 65°C are shown in Fig. 11. It was found that the equilibrium adsorption amount q_e

increased with increasing temperature, indicating that the adsorption was an endothermic process. As we know, the physical adsorption is generally exothermic reaction. Hence, logical cause of the observation is that the adsorption should include some endothermic chemical reactions. This is also supported by the positive values of enthalpy change (ΔH°).

Temperature has two major effects on adsorption processes. Increasing temperature is known to increase the rate diffusion of the adsorbate ions or molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in velocity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (Abd El-Rahman et al., 2006).

Thermodynamic parameters of Pb(II) adsorption on the PSDC8 can be evaluated from the variation of the thermodynamic equilibrium constant K_C at different temperature. The adsorption standard enthalpy change and the standard entropy change (ΔS°) can be calculated plotting of $\ln K_C$ versus $1/T$ according to Eq. (11).

$$\ln K_C = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (11)$$

Plot of $\ln K_C$ versus $1/T$ for the adsorption of Pb(II) onto PSDC8 is shown in Fig. 11. The obtained thermodynamic parameters are listed in Table 6. It is well known that these parameters can evaluate the orientation and feasibility of the physicochemical adsorptive reaction (Kunquan et al., 2010).

The adsorption standard free energy changes (ΔG°), can be calculated according to Eq. (12).

$$\Delta G^\circ = -RT \ln K_C \quad (12)$$

Where R refers to the universal gas constant, T denotes the different adsorptive Kelvin temperatures.

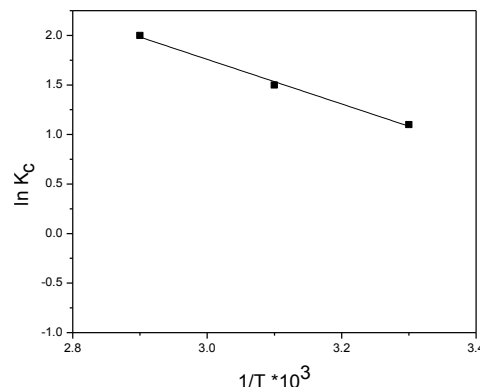


Figure 11. Plot of $\ln K_c$ versus $1/T$ for sorption of Pb(II) onto (PSDC8)

The negative adsorption standard free energy changes (ΔG°) at all temperatures indicated that the adsorption reaction was a general spontaneous process.

Table 6. Thermodynamic Parameters of Pb(II) adsorption onto PSDC8 at different temperature

Temperature K	K^o (/g)	ΔG° (KJ/mol)	ΔH° J/mol.k	ΔS° J/mol.k
298	3.0	-2.887		
318	4.5	-4.203	18.765	70.731
338	7.3	-5.620		

The positive value of enthalpy indicated that the adsorption was endothermic, which is consistent with the observation that the adsorption amount increased with increasing temperature. The positive standard entropy changes (ΔS°) indicated the increased randomness at the solid liquid interface during the adsorption process, and also suggested the process was entropy driven and not enthalpy driven.

3.3.6. Effect of interfering ions.

Effect of interfering ions such as Ca^{+2} , Na^+ and K^+ was studied. For this purpose, 10 mL of the test solution containing 60 mg/L of the Pb(II) ion and the same concentrations of interfering ions were shaken with 0.01 gm of PSDC8 under optimum conditions. The amount of Pb(II) ion extracted was determined and the results were summarized in Table 7.

Table 7. Effect of interfering ions on sorption of Pb(II) using PSDC8.

Type of cations (60 mg/L)	Uptake q_e (mg/g)	% Removal	Type of anions (60 mg/L)	Uptake q_e (mg/g)	% Removal
Pb^{2+}	48.0	80.00	PO_4^{3-}	55	91.67
Ca^{2+}	43.0	71.66	CO_3^{2-}	41.5	69.17
Na^+	46.1	76.80	HCO_3^-	44.2	73.7
K^+	47.5	79.19	Cl^-	46	76.66
--	--	--	SO_4^{2-}	46.9	78.16

It was noticed that Pb(II) removal efficiency was reduced by 10.42%, 3.92% and 1.04% in the presence of Ca^{+2} , Na^+ and K^+ , respectively. Effect of interfering anions such as CO_3^{2-} , HCO_3^- , Cl^- and SO_4^{2-} was also studied. It was noticed that the sorption efficiency of Pb(II) was reduced by 13.54%, 7.92%, 4.17% and 2.29%

in the presence of CO_3^{2-} , HCO_3^- , Cl^- and SO_4^{2-} , respectively. This means that the presence of anions or cations decrease the sorption capacity of PSDC8 for the removal of Pb(II) as shown in table (7). The presence of PO_4^{3-} is the only exception of the studied anions and cations because its presence increases the sorption capacity of PSDC8 by 14.58%. Therefore, the PO_4^{3-} could be added through the sorption of Pb(II) to increase the sorption capacity of prepared PSDC8.

3.3.7. Regeneration and Recovery of PSDC8 and Pb(II).

For successful applications of any biosorbent, the regeneration and subsequent reuse of biosorbent is of utmost importance. The desorption process should yield the contaminants in a concentrated form and restore the biosorbent close to the original form for effective reuse with undiminished pollutant uptake and no physical change or damage (Vijayaraghavan et al., 2011). Recovery of the biosorbed Pb(II) on PSDC8 was carried out using various eluting agents containing organic acids (acetic, oxalic) and salt solution ($NaHCO_3$, Na_2CO_3) mineral acids (H_2SO_4 , HNO_3 and HCl) and distilled water. As seen from table (8), HNO_3 was found to be the most efficient desorbent agent in case of Pb(II) - PSDC8 system. These reagents could alter the chemical form of the adsorbed species and/or destroy the bonding between the adsorbate and the adsorbent. Thus, metal ion is released from the surface of the carbon. The elution studies with various concentrations of HNO_3 (up to 5M) on desorption efficiency was also studied. It was found that Pb(II) reached its maximum desorption efficiency from the PSDC8 by using 3M HNO_3 . From table (8), there is no desorption by using the distilled water and oxalic acid but by using the acetic acid the desorption process is weak and improved by using of sodium carbonate and bicarbonate. Since the major mechanism for Pb(II) sorption is ion exchange, positively charged ions are required to replace Pb^{2+} in carboxyl binding sites. Even though, Na^+ can bind with carboxyl sites, it is a soft ion and its affinity towards carboxyl group is least compared to other metal ions. On the other hand, the performance of 3.0 M HNO_3 , H_2SO_4 and HCl in desorbing Pb(II) ion from the biosorbent is superior, with elution efficiencies over 99.16, 91.2 and 83.2 % respectively for Pb(II). This superior performance is due to the presence of excess of H^+ ions in strong acidic environment, which successfully eliminates Pb^{2+} ions from carboxyl sites. Since PSDC8 is known for its rigidity, highly acidic desorbent medium had no influence on the

physical structure of biomass with biosorbent weight loss of less than 5%.

Table 8. desorption of Pb(II) using different desorbing agents.

No	desorption		Effect of conc. HNO ₃		Effect of conc. H ₂ SO ₄		Effect of conc. HCl	
	Reagents (M)	Desorption (%)	conc. (M)	Desorption (%)	conc. (M)	Desorption (%)	conc. (M)	Desorption (%)
1	Hydro acid	36.16	0.1	15	0.1	63.3	0.1	30
2	Sulphuric acid	35.2	0.5	83.3	0.5	78	0.5	38.4
3	Hydrochloric acid	85.2	1	91.67	1	81.7	1	65
4	Sodium sulphate	30.3	2	85	2	88.3	2	75
5	Sodium hydroxide	71.3	3	89.16	3	91.2	3	83.2
6	acetic acid	36.77						
7	oxalic acid	-						
8	tartaric acid	-						

Conclusions

The following are the major conclusions of the present study,

- Sawdust can be used for preparation of new adsorbent by different treatment methods leading to different characterization and behaviors.
- From the characterization of the prepared PSDC8 sample, the FTIR proved that this sample contains different functional groups which can be take part and increase the adsorption capacity of adsorption of Pb(II) from aqueous solution. And the examined PSDC8, showed a very good capability to biosorb Pb(II) ion from aqueous solutions.
- Experiments performed as a function of equilibrium pH revealed that Pb(II) biosorption was found to be highest at pH 5, under examined conditions. Isotherm experiments conducted at this pH value were well described by Langmuir equation, with a constant interaction factor.
- Kinetic experimental results showed that PSDC8 has a considerable potential for the rapid uptake of Pb(II) ions within 60 min, followed by relatively slow attainment of equilibrium.
- From the effect of temperature it was concluded that; the negative adsorption standard free energy changes (ΔG°) at all temperatures indicated that the adsorption reaction was a general spontaneous process, the positive value of enthalpy indicated that the adsorption was endothermic, which is consistent with the observation that the adsorption amount increased with increasing temperature and the positive standard entropy changes (ΔS°) indicated the increased randomness at the solid liquid interface during the adsorption process, and also suggested the

process was entropy driven and not enthalpy driven.

- Interfering ions experimental results showed that the presence of anions or cations decrease the sorption capacity of PSDC8 for the removal of Pb(II). The presence of PO_4^{-3} is the only exception of the studied anions and cations because its presence increases the sorption capacity of PSDC8 by 14.58%. Therefore, the PO_4^{-3} could be added through the sorption of Pb(II) to increase the sorption capacity of prepared PSDC8.
- Desorption and subsequent reuse of PSDC8 adsorbent was possible with 3.0 M HNO_3 , which performed well with elution efficiencies greater than 99.12 %.
- Thus, the present study indicates that the PSDC8 has promising applications for removal and separation of Pb(II) ions from aqueous effluents.

References

1. Rostamian R, Najafi M, Rafati A.A. Synthesis and characterization of thiolfunctionalized silica nano hollow sphere as a novel adsorbent for removal of poisonous heavy metal ions from water: kinetics, isotherms and error analysis, Chem. Eng. J. 2011; 171: 1004–1011.
2. Li Yuan, Yangsheng Liu, Removal of Pb(II) and Zn(II) from aqueous solution by ceramisite prepared by sintering bentonite, iron powder and activated carbon, Chemical Engineering Journal 2013; 215–216: 432–439.
3. Mouni L, Merabet D, Bouzaza A, Belkhir L. Adsorption of Pb(II) from aqueous solutions using activated carbon developed from Apricot stone, Desalination 2011;276: 148–153.
4. Li K., Wang X., Adsorptive removal of Pb (II) by activated carbon prepared from *Spartina alterniflora*: equilibrium, kinetics and thermodynamics, Bioresour. Technol. 2009; 100:2810–2815.
5. Milan Momčilović, Milovan Purenović, Aleksandar Bojić, Aleksandra Zarubica, Marjan Randelović, Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon, Desalination 2011; 276: 53–59.
6. Matlock MM, Howerton BS, Atwood DA. Chemical precipitation of heavy metals from acid mine drainage, Water Res. 2002; 36: 4757–4764.

7. Hunsom M, Pruksathorn K., Damronglerd S., Vergnes H, Duverneuil P. Electrochemical treatment of heavy metals (Cu^{2+} , Cr^{6+} , Ni^{2+}) from industrial effluent and modeling of copper reduction, *Water Res.* 2005;39: 610–616.
8. Maturana HA, Peric IM, Rivas BL, Pooley S.A. Interaction of heavy metal ions with an ion exchange resin obtained from a natural polyelectrolyte, *Polym. Bull.* 2011; 67: 669–676.
9. Juang R.S, Huang H.L. Mechanistic analysis of solvent extraction of heavy metals in membrane contactors, *J. Membrane Sci.* 2003;213: 125–135.
10. Chen S.Y, Chen W.H, Shih C.J. Heavy metal removal from wastewater using zero-valent iron nanoparticles, *Water Sci. Technol.* 2008; 58: 1947–1954.
11. Muthukrishnan M, Guha B.K.. Heavy metal separation by using surface modified nanofiltration membrane, *Desalination* 2002; 006: 351–353.
12. Ma X.M, Li LP, Yang L, Su C.Y., Wang K., Yuan S.B., Zhou J.G. Adsorption of heavy metal ions using hierarchical CaCO_3 -maltose meso/macroporous hybrid materials: adsorption isotherms and kinetic studies, *J. Hazard. Mater.* 2012; 209: 467–477.
13. Shin K.Y., Hong J.Y., Jang J., Heavy metal ion adsorption behavior in nitrogendoped magnetic carbon nanoparticles: isotherms and kinetic study, *J. Hazard. Mater.* 2011; 190: 36–44.
14. Sepehrian H, Ahmadi S.J, Waqif-Husain S, Faghihian H., Alighanbari H. Adsorption studies of heavy metal ions on mesoporous aluminosilicate novel cation exchanger, *J. Hazard. Mater.* 2010; 176: 252–256.
15. Wang SB., Peng Y.L. Natural zeolites as effective adsorbents in water and wastewater treatment, *Chem. Eng. J.* 2010;156: 11–24.
16. Huang L, Xiao C.M., Chen B.X. A novel starch-based adsorbent for removing toxic $\text{Hg}(\text{II})$ and $\text{Pb}(\text{II})$ ions from aqueous solution, *J. Hazard. Mater.* 2011; 192: 832–836.
17. Ugwekar R.P, Lakhawat, G.P. Recovery of Heavy Metal by Adsorption Using Peanut Hull *International Journal of Advanced Engineering Technology*, 2012; 3 (3): 39-43.
18. Oliveira F.D, Soares, A.C. Freitas O.M. Figueiredo S.A. Copper, nickel and zinc removal by peanut hulls: Batch and column studies in mono, tri component systems and with real effluent, *Global NEST Journal*, 2010; 12 (2): 206-214.
19. Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., Pattabhi, S., "Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. *Biores. Technology* 2002; 87(3): 291-293.
20. Oh, M, Tshabalala, M pelletized ponderosa pine bark for adsorption of toxic heavy metals from water." *J. Bioresources* 2007; 2(1) : 66-81.
21. Umar Farooq, Janusz A. Kozinski, Misbahul Ain Khan, Makshoof Athar Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature" *J. Biores. Technolog*, 2010; 101 (14): 5043-5053.
22. Awwad N.S., Gad H.M.H., Ahmad M.I., Aly H.F. Sorption of lanthanum and erbium from aqueous solution by activated carbon prepared from rice husk, *Colloids and Surfaces B: Biointerfaces* 2010; 81 : 593–599.
23. Abdelrahman, .B Fadhil, Mohammed M.Deyab, Conversion of Some Fruit Stones and Shells Into Activated Carbons, *The Arabian Journal for Sci. and Eng.*, 2008; 33(2A): 175-184.
24. Tarun Kumar Naiya1, Biswajit Singha, Sudip Kumar Das. FTIR Study for the Cr(VI) Removal from Aqueous Solution Using Rice Waste *International Conference on Chemistry and Chemical Process IPCBEE* 2011;10: 114-119, IACSIT Press, Singapore.
25. Fatemeh Asadi, Hossien Shariatmadari, Noorallah Mirghaffari, "Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater. *J. Hazard. Mater.* 2008;154: 451-458.
26. Jung-Seok Yang, Young-Tae Park, Kitae Baek, Jaeyoung Choi Removal of Metal Ions From Aqueous Solutions Using Sawdust Modified with Citric Acid or Tartaric Acid "*Separation Science and Technology* 2010;145(12-13): 1963-1974.
27. Gad, H M H, El-Mouthy N A, Aly H F. Separation Science and Technology, 2009; 44: 681–711.

28. Sreejalekshmi K.G, Anoop Krishnan K., Anirudhan TS. Adsorption of Pb(II) and Pb (II)-citric acid on sawdust activated carbon: kinetic and equilibrium isotherm studies, *J. Hazard. Mater.* 2009; 161: 1506–1513.
29. Aygun A., Yenisooy-Karakas S., Duman I., Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, *Microporous Mesoporous Mater.* 2003; 66: 189–195.
30. Yang Yin C, Kheireddine Aroua M, Mohd Ashri Wan Daud W. Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, *Sep. Purif. Technol.* 2007; 52: 403–415.
31. Hassler JW. *Activated Carbon*, Chemical Publishing, New York, 1974.
32. Kunquan Li, Zheng Zheng, Ye Li, Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one-step H₃PO₄ activation. *Journal of Hazardous Materials* 2010; 181: 440–447
33. Zhao YX, Sun XY. *The Spectrographical Identification of Organic Molecular Structure*, Science Press, Beijing, 2003.
34. Pei Z.G., Shan X.Q., Liu T. Effect of lead on the sorption of 2,4,6-trichlorophenol on soil and peat, *Environ. Pollut.* 2007; 147: 764–770.
35. Reznik SG, Katz I, Dosoretz CG. Removal of dissolved organic matter by granular-activated carbon adsorption as a pretreatment to reverse osmosis of membrane bioreactor effluents, *Water Res.* 2008; 42: 1595–1605.
36. Yu, B., Zhang, Y. Shukla, A., Shukla, S.S. and Dorris, K.L. "Removal of heavy metals from aqueous solutions by sawdust adsorption-removal of lead and comparison of its adsorption with copper, *J. Hazard. Mater.* 2001; 84: 83-94.
37. Taty-Costodes, V.C, Fauduet H, Porte C, Ho YS. Removal of lead(II) ions from synthetic and real effluent using immobilized pinus sylvestris sawdust: Adsorption on a fixed-bed column, *J. Hazard. Mater.* 2005; (B123): 135-144.
38. Taty-Costodes, V.C, Fauduet H, Porte C, Delacroix A. Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of pinus sylvestris *J. Hazard. Mater* 2003; 105: 121-142.
39. Hameed BH, Ahmad AL, Latiff K.NA. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, *Dyes Pigm.* 2007; 75: 143–149.
40. Franca AS, Oliveira LS, Ferreira ME. Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds, *Desalination* 2009; 249: 267–272.
41. Helfferish F.: *Ion Exchange*, Mc Graw-Hill, New York 1964.
42. Ng C, Losso JN, Marshall WE, Rao RM. Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin–water system, *Bioresour. Technol.* 2002; 85: 131–135.
43. Unnathan, M.R. Anirudhan, T.S The kinetics and thermodynamics of sorption of Cr(VI) onto the Fe(III) complex of a poly acrylamide-grafted saw dust, *Ind. Eng. Chem. Res.* 2001; 40: 2693–2701.
44. Wang S, Boyjoo Y, Choueib A. A comparative study of dye removal using fly ash treated by different methods. *Chemosphere* 2005; 60(10): 1401–1407.
45. Abd El-Rahman K.M, El-Kamash AM, El-Sourougy MR, Abdel-Moniem N M. Thermodynamic modeling for the removal of Cs⁺, Sr²⁺, Ca²⁺ and Mg²⁺ ions from aqueous waste solution using zeolite A. *Radioanal. Nucl. Chem.* 2006; 268: 221-230.
46. Vijayaraghavan K., Sathishkumar M., Balasubramanian R. Interaction of rare earth elements with a brown marine alga in multi-component solutions, *Desalination* 2011; 265: 54–59.

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