Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.23507

145 (2019) 179–188
March

Environmental remediation of toxic lead ions from aqueous solution using palm tree waste fibers biosorbent

Basma G. Alhogbi, Mohamed Abdel Salam*, Ohowd Ibrahim

Chemistry Department, Faculty of Science, King Abdulaziz University, P.O Box 80200-Jeddah 21589, Saudi Arabia, Tel. +966-500502885, Fax +966-2-6952292, email: alhogbib@gmail.com (B.G. Alhogbi), Tel. +966-541886660, Fax +966-2-6952292, email: masalam16@hotmail.com (M.A. Salam), Tel. +966-556645530, Fax +966-2-6952292, email: iohowd@yahoo.com (O. Ibrahim)

Received 4 April 2018; Accepted 24 November 2018

ABSTRACT

In this study, the low-cost palm tree waste fibers (PTF) biosorbent was used for the removal of the toxic lead ions as an example of heavy metals in water. The XRD pattern showed the major peaks of cellulosic material, and BET specific surface area was 9.0 m^2/g, and total pore volume equals 9.07 × 10^{-3} $cm^3/$ g. The removal process conditions were optimized, and the maximum sorbed amount detected and the percentage removal of lead ions using 0.1 g of natural sorbent at room temperature and 30 min contact time was 86.99%, and the maximum removal capacity obtained was 61.55 mg lead ions/g PTF. The kinetics study showed that lead ion biosorption following pseudo-second-order kinetic model. The adsorption isotherms were studied and the best-fitted isotherm were in order Langmuir ~ Freundlich > Temkin > D-R isotherms. The thermodynamic study showed the adsorption of lead ions was spontaneous, random in nature, and exothermic, as the values of $\Delta H°$, ΔH, and ΔS were –1.2 *kJ/mol*, –10.70 *kJ/mol* and –31.18 *J/mol·K*, respectively. The application of palm tree waste fibers for the removal of lead ions from real environmental water samples was studied and the results showed the high efficiency, feasibility; due to their low-cost, of the fibers and could be as promising biosorbent.

Keywords: Adsorption; Lead ions, Kinetics; Palm tree waste fibers; Thermodynamics; Real water

1. Introduction

Increasing of industrialization and urbanization leading to release of various pollutants into the aquatic environments such as plant nutrients, organic chemicals and inorganic heavy metals producing an undesirable change in the chemical and physical properties of water [1]. Although, heavy metals naturally occurring elements found through earth's crust, their exists in water bodies are extremely harmful to human, animals and, plants because of their accumulation, toxicity even at very low concentration due to their non-biodegradable nature, which cause various diseases and disorders [2]. Lead released to the environment mainly through anthropogenic activities such as metal plating, smelting of ores, battery manufacturing units, combustion of coal and oil, ceramics and glass goods productions, painting and lead solder in food cans [3]. United States Agency for Toxic Substances and Disease Registry (USATSDR), and United States Environmental Protection Agency (USEPA) considered lead ions as one of the non-biodegradable and hazardous heavy metals that pose danger to the living organism [4]. Lead ions are quickly absorbed in the bloodstream and have adverse effects on the central nervous system, cardiovascular system, kidney, immune system, damage cell structures including DNA and inhibit the synthesis of vitamin D besides attacking kidney, liver, and brain [5]. Accordingly, the World Health Organization (WHO), the European Union (EU) Federal-Provincial-Territorial Committee on Drinking Water (CDW) in Canada, the

---

*Corresponding author.

National Health and Medical Research Council (NHMRC) in Australia has set the quality standard for acceptable levels of lead in drinking water to 10 µg/L, whereas 15 µg/L was used as the standard for lead in drinking water by the US Environmental Protection Agency (EPA), and 20 µg/L in Saudi Arabia [6].

There are several techniques used to remove lead ions from the aqueous solution including chemical precipitation, filtration, ion exchange, and membrane technologies. The limitation conventional methods referred to the high cost involved, low efficiency and a large amount of sludge generated [7]. Therefore, adsorption is considered as effective and widely used process technique for wastewater treatment via physisorption or/and chemisorption onto homogenous or heterogeneous solid surface [8,9]. The search for alternative low-cost adsorbents has been the focus of the researcher worldwide [10]. Biosorption has been confirmed a very promising process by using biological materials as biosorbents with different surface functional groups in the removal of heavy metals [11–16], fluoride ions [17–22] from wastewater.

The aim of this study is to explore the biosorption of lead ions using the low-cost natural palm tree waste fibers (PTF). The effect of different experimental conditions on the removal process, such as the contact time, biosorbent mass, solution pH and temperature were explored and optimized. Also, the removal process will be studied kinetically and thermodynamically for a better understanding of the mechanism and spontaneity in order to enhance the efficiency of the removal process.

2. Experiments and methods

2.1. Reagents and materials

PTF was used as the natural biosorbent was collected from several palm trees in the Jeddah region, lead nitrate; $Pb(NO_3)_2$, was obtained from Fluka, sodium hydroxide; NaOH, was obtained from Merkland/Germany, hydrochloric acid; HCl was obtained from Fisher Scientific, nitric acid; HNO_3,was obtained from Panreac. The solution pH was monitored using Mettle Toledo MP220 with 4 digits pH meter, and the sorbent was ground with high-speed cyclone mill (CT 193 Cyclotec™).

2.2. Biosorbent preparation

PTF was collected from several palm trees in Jeddah and were washed several times with tap water to remove dust, then immersed in deionized water overnight and dried at room temperature, the dried fiber were ground and sieved to a different particle size (53–180 µm).

2.3. Preparation of lead solution

The stock solution of 10,000 mg/L prepared by dissolve appropriate amount of $Pb(NO_3)_2$ in 1 L of deionized water, all working solutions prepared by dilution of stock solution with deionized water to 200 mg/L. The concentration of lead ions was measured using Perkin Elmer Optical Emission Spectrophometer (ICP-OES) Optima 8300.

2.4. Biosorption experiments

The biosorption study performed using 53 µm particle size PTF to determine the effect of different parameters on the removal of lead ions from aqueous solution. The experimental procedure performed as following: a series of different concentrations (100–400 mg/L) of 25 mL lead ions solution were prepared, different pH of lead solution was prepared, different sorbent mass (0.02–0.8 g) used, shook each of different parameters separately for a defined period of time at room temperature, contact time (1–60 min) was studied by shaking appropriate mass of PTF with 25 mL of 200 mg/L lead ions solution at different temperature ranging from (25–55°C), at a defined time the solution removed and filtered immediately using Whatman qualitative filter paper of No. 2, the concentration of lead ions remaining in the solution was measured by ICP-OES instrument. The percentage removal of lead ions and the amount of lead ions adsorbed on PTF sorbent were determined by using the following mass balanced equation:

$$\%Removal = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{V\left(C_0 - C_e\right)}{m} \tag{2}$$

where C_0 is initial concentration (mg/L) of lead in solution, C_e is equilibrium concentration of lead (mg/L) in the solution, q_e is sorption capacity of lead ion (mg/g), V is the volume of solution in (L) and m is the sorbent mass in (g).

2.5. Real water samples collection

Two real water samples were collected to investigate the applicability of natural palm fiber as sorbent for lead ions, and their locations are presented in Fig. 1. Sample 1, is a wastewater sample collected from the Membrane Bio-Reactor Technology Waste Water Treatment Plant ((MBR 6000 STP) at King Abdulaziz University (KAUWW), Jeddah City (Latitude deg. North 21.487954, Longitude deg. East 39.236748). Sample 2 is a well water collected from a deep well, Al Jamoom, Makkah Province, Saudi Arabia (Latitude deg. North 21.549194, Longitude deg. East 39.656389). All real water samples were filtered through 45.0 µm Millipore filter paper and kept in Teflon® bottles and stored at 5°C in dark.

3 .Results and discussion

3.1. Characterization of natural palm fiber

SEM image of the natural palm fiber sorbent is presented in Fig.2a, and it is clear that the fiber contains pores with different diameters, which could facilitate the sorption of the lead ions. The XRD pattern of natural palm fiber sorbent is shown in Fig. 2b. It is clear that the major peaks of cellulose similar to JCPDS no 50-2241 XRD patterns at 2θ 15.1, 16.3 and 22.4° corresponding to (101), ($10\bar{1}$), and (002) crystallographic planes. The textural properties for the natural palm fiber sorbent were explored from the nitrogen adsorption/desorption isotherms at 77K, and the results

Fig. 1. Locations of the collected real water samples.

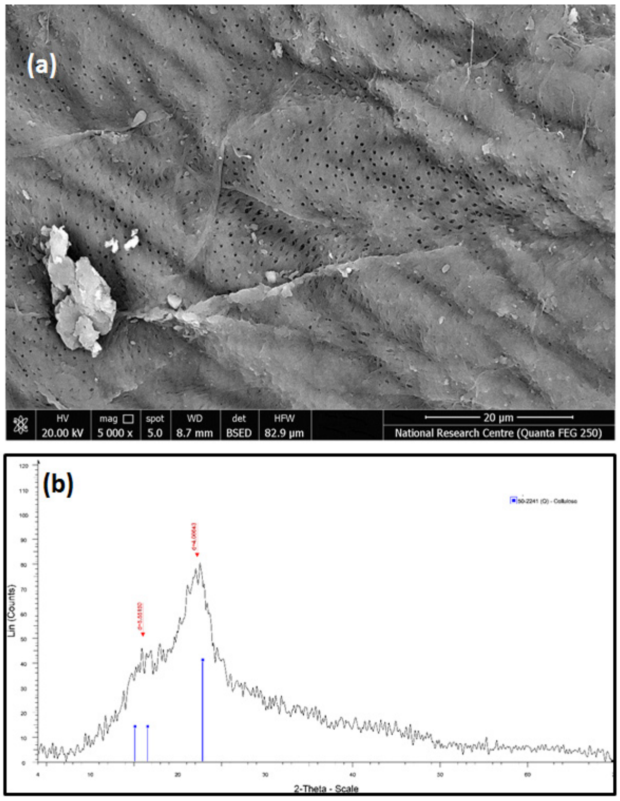

Fig. 2. (a) SEM image and (b) XRD pattern of natural palm fiber sorbent.

showed that the BET specific surface area was 9.0 m^2/g, and total pore volume equals 9.07×10^{-3} $cm^3/$ g.

3.2. Biosorption study

The removal and biosorption ability of different solid adsorbents for environmental pollutants are generally controlled by different operational parameters such as sorbent mass, the concentration of the pollutant, contact time, and the temperature of the solution. Hence, it is very important to study the effect of the above-mentioned parameters on the removal of lead ions from aqueous solution using the low-cost PTF biosorbent.

The PTF was ground to different particle size 180–53 µm, and the effect of the PTF particle size on the removal of lead ions from aqueous solution was studied, and the results are presented in Fig. 3. It is clear from the figure that decreasing the PTF particle size associated with significant increase of the % lead ions removed from solution; 33.84–72.54%. This is due to the great enhancement in the specific surface area of the PTF upon grinding, which create more active sites available for binding lead ions. According, PTF with a particle size of 53 µm was used in the rest of the experiments. Fly ash was used as adsorbent for the removal of Pb^{2+} from water, and the results showed that the percentage removal of Pb^{2+} increased from 88.57% to 90.37% with decreased of fly ash adsorbent size from 120 µm to 52 µm [22]. In another study, the removal efficiency of Pb^{2+} ions was found decreased from 90% to 50% with increasing of date palm fiber adsorbent particle size from 45 µm to 251 µm by shaking 0.5 g adsorbent with 5 mg/L solution concentration for 120 min [23].

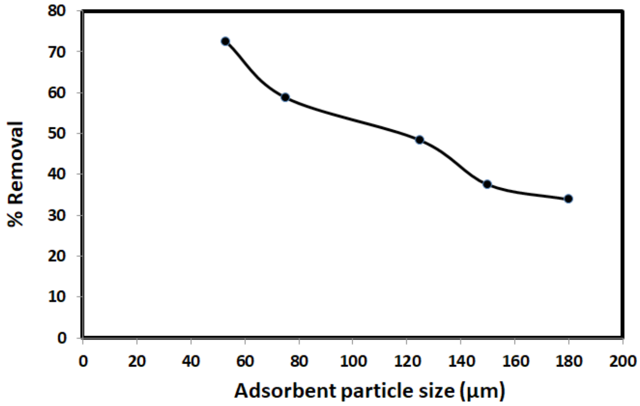

Fig. 3. Effect of PTF particle size on the removal of lead ions from model solution (Experimental conditions: T = 25°C, pH = 6.0, C_o = 200 ppm, mass = 0.3 g, V = 25 mL, shaking time = 120 min).

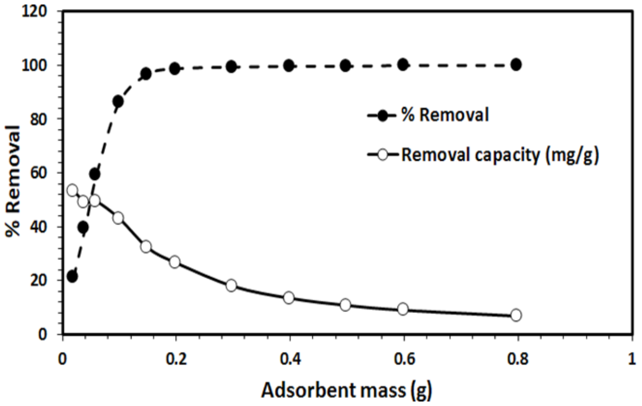

Fig. 4. Effect of natural sorbent mass on the adsorption of lead ions from model solution (Experimental conditions: pH =6.0, C_o = 200 ppm, adsorbent particle size = 53 µm, V = 25 mL, shaking time = 120 min).

The study of sorbent mass is necessary and very useful in order to find the optimum amount of solid adsorbent required. The effect of the PTF mass on the removal of lead ions from aqueous solution was studied, and the results are presented in Fig. 4. The results indicated that the removal percentage of lead ions increased from 21.38% to 86.1%, and the removal capacity decreased from 53.3 mg/g to 43.1 mg/g, with increasing the PTF mass from 0.02 g to 0.10 g. Further increase in the mass of the PTF to 0.15 g was associated with the removal of most of the lead ions from solution 96.5% (32.1 mg/g), and further increase to 0.20 g accompanied with percentage removal of 98.6% (26.5mg/g). The application of more PTF did not change the percentage removal significantly as 0.8 g removed 99.9% (6.71 mg/g) of the lead ions from solution, which may be due to increasing of the available active sites on the adsorbent surface. The PTF mass of 0.1 g was used for the rest of the experiments was to observe the other effects. The removal efficiency of Pb^{2+} ion increased from 20.3% to 96.3% with increasing of dried aquatic plant biosorbent amount from 0.2 g to 4 g [24].

The effect of initial lead ions concentration on the removal percentage of lead ions is shown in Fig. 5 and the experimental results showed that increasing the lead ions concentration from 100 to 400 mg/L cause a drastic decrease in the % removal of lead ions from 99.65 to 37.5% due to the competition of lead ions for the constant number of binding sites. Meanwhile, the number of lead ions adsorbed increased from 25.14 mg/g; with 100 mg/L, to 37.5 mg/g with 150 mg/L, and the further increase in the concentration does not change the removal capacity. Accordingly, the lead ions concentration used for the rest of the experiment was 200 mg/L. The adsorption of Pb^{2+} ion onto raw sawdust was studied the results showed that increasing of initial metal solution of 25, 50 and 100 mg/L leading to increasing the amount adsorbed of Pb^{2+} ion onto raw sawdust as 7.4, 7.8 and 7.9 mg/g [25], and the uptake of Pb^{2+} ion using rapeseed biomass decreased with increasing of initial metal concentration from 5 mg/L to 250 mg/L [26]. Also, the removal of Pb^{2+} ions using Annona squamosa shell was studied and the % removal was decreased with increasing of initial Pb^{2+} ions from 50 mg/L to 200 mg/L and the maximum removal efficiency was 93.08% at initial concentration of 50 mg/L under optimal conditions of adsorbent dosage of 30 mg and 30 min shacking time [27].

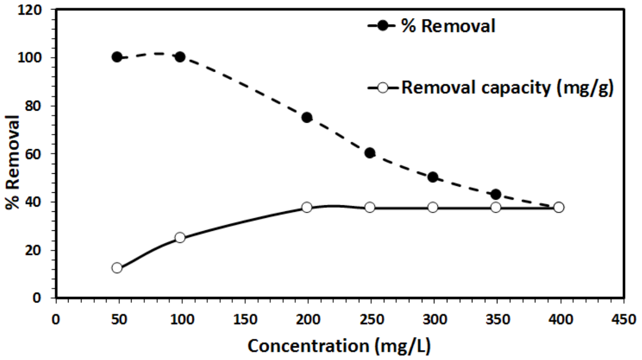

Fig. 5. Effect of initial concentration of solution on lead ion removal from model solution (Experimental conditions: pH = 6.0, T = 25°C, particle size = 53 µm, shacking time = 30 min, mass = 0.1 g, V = 25 ml) mass = 0.1 g, V = 25 mL).

The effect of the contact time on the removal of lead ions from aqueous solution by PTF was studied, and the results are presented in Fig. 6. The results revealed that percentage removal of lead ions increased greatly within the first 5.0 min and reached equilibrium with a % lead ions removal of 85.53%, which did not change significantly after 60 min. The removal of Pb^{2+} ions using Tobacco steams biosorbent was studied, and the results indicated that the equilibrium contact time of the removal was 120 min with 94.37%, 92.10% and 90.43% removal using initial concentrations of 10, 30 and 50 mg/L, respectively [28]. The biosorption capacity of Pb^{2+} ions by Arborvitae leaves increased with increasing of contact time from 0 min to 300 min till reach equilibrium at 120 min with biosorption capacity of 9.25 mg/g [29]. Also, the observed % removal of Pb^{2+} ions by using 3 g/L of raw persimmon leaf was 84.2% at 60 min [30].

The solution pH is one of the principal parameters which controlling the biosorption process, especially for Pb^{2+} ions because it greatly affects by the solution pH. The

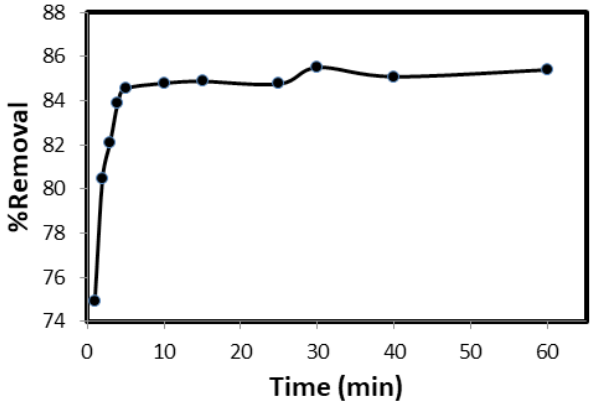

Fig. 6. Effect of contact time on the adsorption of lead ions from model solution (Experimental conditions: pH = 6.0, particle size = 53 µm, C_o = 200 ppm, mass = 2 g, V = 500 mL, T = 25°C).

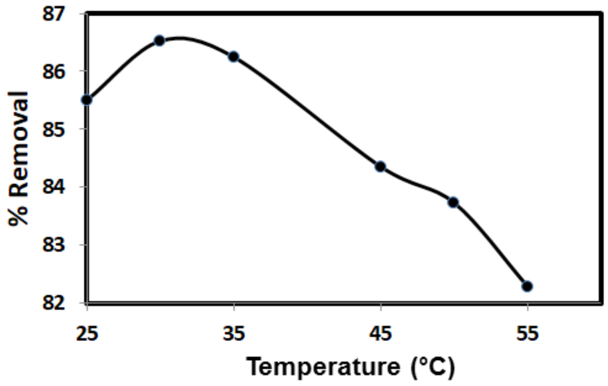

Fig. 7. Effect of solution temperature on the removal of lead ions from model solution (Experimental conditions: pH= 6.0, C_o = 200 mg/L, particle size = 53 µm, shaking time = 30 min, mass = 1 g, V = 250mL).

effect of solution pH on the Pb^{2+} ions by PTF was therefore explored in the pH range 2.0–8.0. The results showed that the percentage removal was increased from 31.7% at pH value of 2.0, to 84.1%, 85.7%, and 99.5%, at pH values of 4.0, 6.0, and 8.0. The low removal percentage at pH 2.0 was mainly due to the high concentration of hydrogen ions (H_3O^+), which have higher mobility and preference to adsorbed on the surface of the PTF, and out-compete with the lead ions for biosorption. At higher pH values of 4.0, and 6.0, there are more binding sites available for the biosorption of lead ions, which increased dramatically to 99.5% at pH value of 8.0. This is basically due to the precipitation lead ions as $Pb(OH)_2$. Accordingly, the solution pH was adjusted to 6.0.

The effect of solution temperature on the removal of lead ions by PTF from aqueous solution was studied and the results shown in Fig. 7, increasing of the removal efficiency of lead ion from 85.53% to 86.60% by raising the solution temperature from 25°C to 30°C, which could be attributed to the high mobility of lead ions toward available binding sites. Meanwhile, the percentage removal of the lead ions decreased from 86.60 to 82.29 % with raising the temperature from 30°C to 55°C, which indicated that the biosorption process; in general, is exothermic in nature. Similar result was found by studying the effect of different temperature on the removal of Pb^{2+} ions onto Otostegiapersica biomass under optimum condition of pH 5.5, adsorbent mass of 1.0 g/L and the results showed decreased of % removal from 81.5 to 76.5% with increase of temperature from 25°C to 45°C indicating the exothermic nature of the process [31].

3.3. Kinetics study

The study of the adsorption kinetics of lead ions in water using PTF is very important to understand the interaction mechanism and pathways. The adsorption experimental data were treated kinetically using Lagergren pseudo-first-order kinetic model [32], and pseudo-second-order kinetic model [33]. Lagergren pseudo-first-order kinetic model is a very common model usually used to describe the adsorption of different adsorbates from an aqueous solution by solid adsorbent:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

where q_e and q_t (mg/g) are sorption capacities at equilibrium and at time t (min) respectively, k_1 (min $^{-1}$) is the pseudo-first-order rate constant determined from the slope of the plotting $\log(q_e - q_t)$ *vs. t*.

The pseudo-second-order equation could be described as the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_2 mg/g min is pseudo-second-order determined from the intercept of the plotting t/q_t *vs. t*.

The goodness of kinetic model fit expressed by the correlation coefficient and chi-square test as the following equation [34]:

$$\chi^2 = \left(q_{e,\exp} - q_{e,cal}\right)^2 / q_{e,cal} \tag{5}$$

where $q_{e,exp}$ and $q_{e,cal}$ are equilibrium and calculated sorption capacities, if the value of χ^2 is small that mean the experimental and calculated sorption capacities are similar but the large value of χ^2 refer to the difference between experimental and calculated adsorption capacities.

From the data represented in Table 1 and Fig. 8 it was observed the linear plot of t/q_t *vs. t* have value of R^2 close to unity and the calculated adsorption capacities of lead ion; $q_{e,cal}$, were in good agreement with experimental adsorption capacities; $q_{e,exp}$, indicating the removal of the lead ions by PTF followed the pseudo-second-order with respect to Lagergren pseudo-first-order, which was confirmed with the low χ^2 obtained by pseudo-second-order model. This result agreed well with the application of persimmon leaf for the adsorption of Pb^{2+} ions, which fitted appropriate the pseudo-second-order with a high value of R^2 and the calculated adsorption capacity much closer to experimental adsorption capacity [30]. Also, the adsorption of Pb^{2+}

Table 1
Kinetics study parameters for sorption of lead ions onto the low-cost PTF biosorbent

Temperature °C	$q_{e,exp}$ (mg/g)	Pseudo-first-order		Pseudo-second-order	
25	39.50	$q_{e,calc}$ (mg/g)	1.075	$q_{e,calc}$ (mg/g)	39.50
		R^2	0.304	R^2	1
		k_1 $(\text{min})^{-1}$	0.0836	k_2 (mg/g min)	0.2137
		χ^2	1373.54	χ^2	2.5141 e^{-7}
30	40.16	$q_{e,calc}$ (mg/g)	1.4447	$q_{e,calc}$ (mg/g)	40.20
		R^2	0.4028	R^2	0.9999
		k_1 $(\text{min})^{-1}$	0.1049	k_2	0.1055
		χ^2	1037.45	χ^2	4.51e^{-5}
35	40.25	$q_{e,calc}$ (mg/g)	1.0333	$q_{e,calc}$ (mg/g)	40.0079
		R^2	0.1256	R^2	0.9997
		k_1 $(\text{min})^{-1}$	0.0576	k_2	0.1406
		χ^2	1488.74	χ^2	0.0015
45	38.37	$q_{e,calc}$ (mg/g)	0.576	$q_{e,calc}$ (mg/g)	38.7792
		R^2	4.00	R^2	0.9999
		k_1 $(\text{min})^{-1}$	–0.0009	k_2	–0.6719
		χ^2	2612.56	χ^2	0.0089
50	38.86	$q_{e,calc}$ (mg/g)	0.3827	$q_{e,calc}$ (mg/g)	38.4825
		R^2	0.0007	R^2	0.9999
		k_1 $(\text{min})^{-1}$	0.0036	k_2	–0.4838
		χ^2	3869.37	χ^2	0.0038
55	38.48	$q_{e,calc}$ (mg/g)	0.3856	$q_{e,calc}$ (mg/g)	37.5471
		R^2	0.0552	R^2	0.9999
		k_1 $(\text{min})^{-1}$	–0.0316	k_2	–0.1743
		χ^2	3763.23	χ^2	0.0232

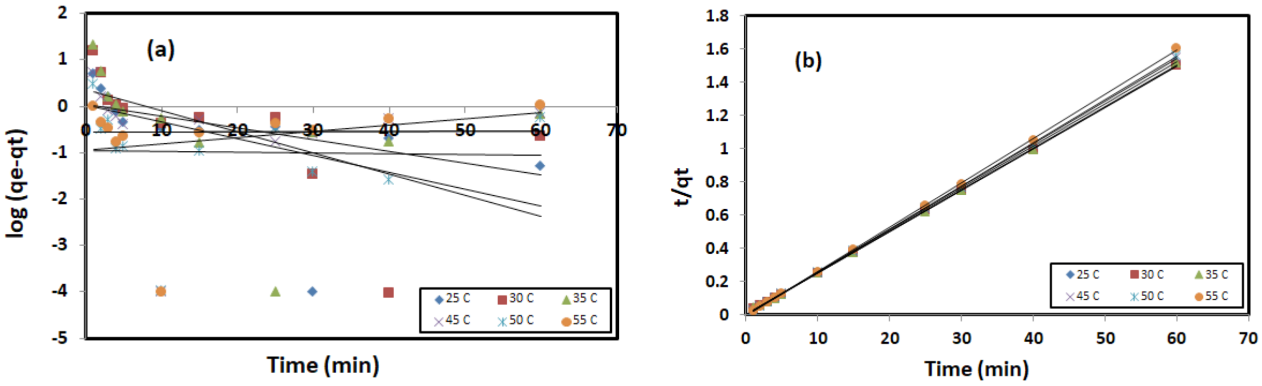

Fig. 8. The application of Lagergren pseudo-first-order kinetic model (a), pseudo-second-order kinetic model (b) for lead ions removed from an aqueous solution by PTF.

ions onto corn straw and municipal sludge derived biochar adsorbent was best-fitted pseudo-second-order [35].

3.4. Isotherm study

The fundamental concept of adsorption isotherm is to describe the interaction between lead ions and the active sites of PTF adsorbent at a constant temperature. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were used to describe the equilibrium and mechanism of the lead sorption using PTF [36].

Langmuir isotherm model expressed as:

$$C_e / q_e = C_e / q_m + 1 / k_L q_m \tag{6}$$

where q_m is monolayer adsorption capacity (mg/g) and k_L is the Langmuir adsorption constant (L/mg). The separation factor determined as:

$$R_L = \frac{1}{1+(K_L C_o)} \tag{7}$$

The value of R_L indicate the mode of adsorption; the adsorption process is unfavorable if $R_L > 1$, the process is linear if $R_L = 1$, the adsorption process is favorable if $0 > R_L > 1$, and the process is irreversible if $R_L = 0$. From Fig. 9a and Table 2, the linear plot of (C_e/q_e) *vs.* C_e has R^2 of 0.994 indicated that the experimental data best fitted with Langmuir isotherm model with q_m of 61.77 mg/g and suggested the adsorption of lead ion take place onto the homogeneous surface with R_L ranged from 0.85 to 0.53 confirmed the favorable monolayer with the limited number of active sits.

Freundlich isotherm model could be expressed as the following:

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{8}$$

where k_F is Freundlich constant related to adsorption capacity, $1/n$ describe sorption intensity, if $n = 1$ then the adsorption is linear, $n < 1$ referred to chemisorption process but if $n > 1$ referred to physisorption process. From Fig. 9b and Table 2, the indicated R^2 of 0.994 showed the Freundlich model confirmed multilayer onto the heterogeneous surface with sorption capacity k_F of 29.19 mg/g, the sorption intensity $0 < 1/n < 1$ and $n > 1$ suggesting favorable physisorption onto the heterogeneous surface.

Temkin isotherm model could be expressed as:

$$q_e = (R\,T/b)\ln k_T + (R\,T/b)\ln C_e \tag{9}$$

$$B = R\,T/b \tag{10}$$

where b is the Temkin constant and kT is binding constant (L/g) determined from the slope and intercept of the plotting of q_e *vs.* lnC_e respectively, B is constant related to the heat of sorption (J/mol). From the data represented in Fig. 9c and Table 3, the R^2 value of 0.9861 and B value of 5.25 J/mol confirmed the physisorption nature of the adsorption of lead ions by PTF from solution.

Dubnin-Radushkevich isotherm model describe the adsorption mechanism onto the heterogeneous surface, and its equation could expressed as the following:

$$\ln q_e = \ln q_d - \beta\,\varepsilon^2 \tag{11}$$

where β is the activity coefficient related to sorption mean free energy (mol²/J²) and ε is Polanyi potential represent as the following equation [37]:

$$\varepsilon = R\,T\,ln(1+1/Ce) \tag{12}$$

The sorption mean free energy E (kJ/mol) [37] is described as:

$$E = 1/\surd -2\beta \tag{13}$$

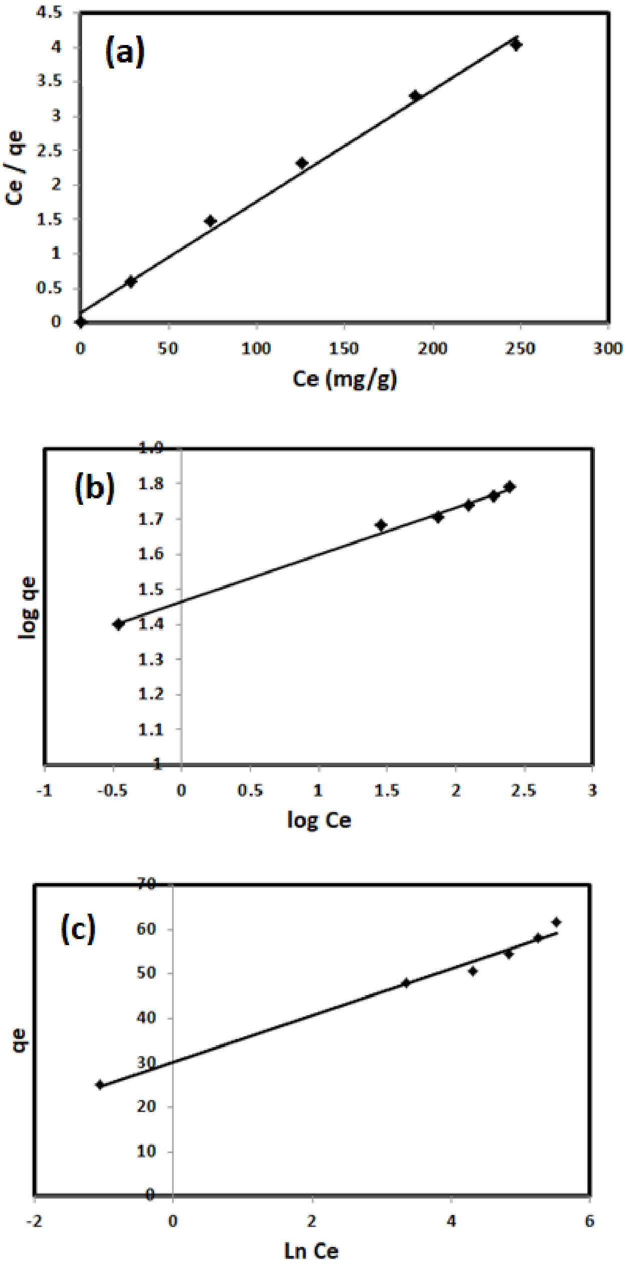

Fig. 9. The application of a) Langmuir, b) Freundlich and c) Temkin Isotherms for lead ions removed from an aqueous solution by PTF.

$E < 8k$ J/mol referred to physisorption, $E < 8k$ J/mol $< E < 16$ kJ/mol referred to ion exchange and $E > 8$kJ/mol referred to diffusion [36]. According to the data represented in Fig. 9c and Table 2, the R^2 value of 0.94 and E value of 2.697 kJ/mol indicated that the removal process is physisorption in-nature. The maximum adsorption capacity obtained from Langmuir isotherm model indicated that palm fiber sorbent was more efficient material for removal of Pb^{2+} ions than Moringa stenopetala seed powder with maximum adsorption capacity of 16.13 mg/g [38]. In another study, Langmuir and Freundlich isotherm models were best fitted the adsorption of Pb^{2+} ions onto date palm fiber and petiole with maximum adsorption capacity of 18.622 mg/g and 20.04 mg/g, respectively [39]. Also, the sorption energy from D-R isotherm model referred to physisorption of Pb^{2+}

Table 2
Isotherm models parameters for sorption of lead ions using PTF

Isotherm model	Parameter	Value
Langmuir	q_m (mg/g)	61.77
	k_L (L/g)	0.0018
	R^2	0.9943
Freundlich	k_F (mg/g)	29.19
	$1/n$	0.133
	R^2	0.9935
Temkin	k_T (mg/g)	313.87
	B (J/mol)	5.2514
	R^2	0.9861

Table 3
Thermodynamic parameters for sorption of lead ions using PTF

Temperature (K)	Thermodynamic parameters		
	ΔH (*kJ/mol*)	ΔS (*J/K·mol*)	ΔG (*kJ/mol*)
298	–10.70	–31.18	–1.40
303			–1.25
308			–1.09
318			–0.780
323			–0.624
328			–0.468

ions by using luffa actangula adsorbent with higher adsorption capacity of 48.09, 50.97 and 49.34 mg/g at 30, 40 and 50°C, respectively [40], which agreed well the adsorption of Pb^{2+} ions onto menthapiperita carbon follow the Freundlich and Temkin isotherm models [41]. Based on Langmuir isotherm, the palm fiber showed maximum adsorption capacity greater than the maximum adsorption capacity of 37.037 mg/g obtained from the removal of Pb^{2+} ions by using coffee husk adsorbent [42].

3.5. Thermodynamics study

In general, the solution temperature greatly affects the kinetic rate and solubility of metal ions and the interaction between metal ions and solid adsorbent surface active sites. In order to investigate the biosorption mechanism of lead ion by PTF adsorbent, the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of the biosorption process were estimated to explain the spontaneity, randomness and thermal nature of the process as the following thermodynamics equations [43].

$$\Delta G = -R\ T\ lnK_D \tag{14}$$

where ΔG is the Gibbs free energy change (kJ/mol), R is the ideal gas constant (8,314 J/mol·K) and T is temperature (°K)

$$k_D = q_e / C_e \tag{15}$$

$$\Delta G = \Delta H - \Delta S \tag{16}$$

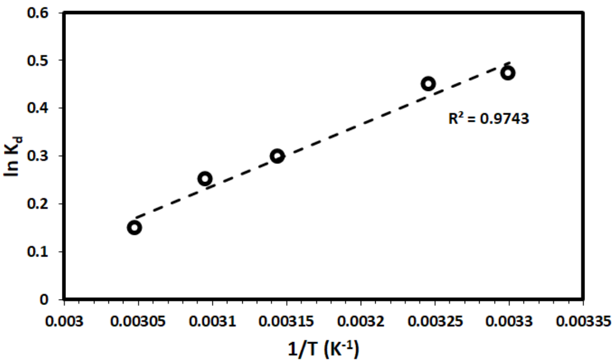

Fig. 10. Thermodynamics for lead ions sorption using PTF sorbent.

The slope of linear plotting lnK_D against $1/T$ will give the value of ΔS and the intercept gives the value of ΔH as it is presented in Fig. 10, and the thermodynamic parameters were calculated and presented in Table 3. The ΔG value was negative, and its magnitude decreased with rising the solution temperature indicating that the biosorption of lead ion onto PTF was a spontaneous process and the spontaneity of the process decreased with increasing the temperature. The values of ΔH and ΔS were –10.70 *kJ/mol* and –31.18 *J/mol·K* confirmed the exothermic physisorption nature of the biosorption process and the decrease in the degree of freedom at the solid–liquid interface due to the immobilization of lead ions on the PTF surface. Accordingly, the negative values of ΔG, ΔH, and ΔS suggested that the removal of lead ions on the PTF from aqueous solution is a spontaneous enthalpy-driven process. These results agreed well with the removal of Pb^{2+} ions onto mixed waste (paper, plastic and palm wastes) activated carbon, where the negative value of ΔG and positive values of both ΔS and ΔH with the magnitude of 9.3 kJ/mol indicated the spontaneous, more disorder and endothermic physisorption process [44]. Moreover, the biosorption of Pb^{2+} ions using peat adsorbent was more spontaneous at a higher temperature, more disorder and endothermic in nature due to the negative value of ΔG and the positive values of both ΔS and ΔH [45].

3.6. Application to real samples

Finally, the PTF was used for the removal of lead ion from different environmental samples; wastewater and well water, collected from various areas of Saudi Arabia. The concentration of the lead ions was measured in all water samples, and the results showed that the concentrations were below the detection limit of the ICP-OES. Therefore, the samples were spiked by a concentrated lead ions solution to obtain a final concentration of 200 mg/L. As shown in Fig. 11, the high removal percentage, and removal capacity, 26.5 mg/g of lead ion from wastewater and well water confirmed the high efficiency of PTF as promising solid adsorbent for removal of lead ions from real polluted water samples. The obtained results were excellent compared with % removal of Pb^{2+} ion from the effluent of Siloam waste stabilization ponds of 95.8% and 96.4% for both initial concentrations of 10 mg/L and 12 mg/L respectively

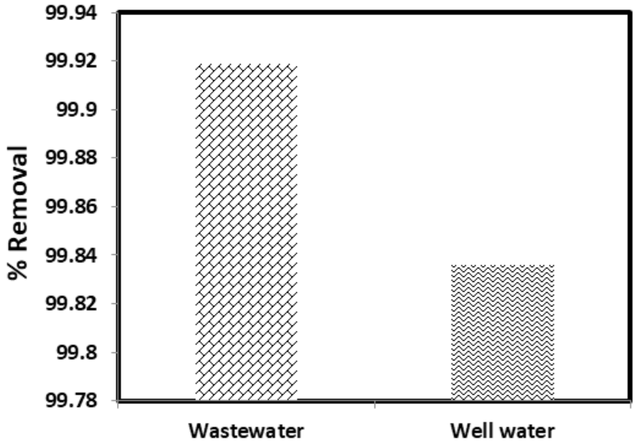

Fig. 11. Efficiency of PTF sorbent to removal of lead ions from real water samples.

using mucilaginous leaves from Diceriocaryum eriocarpum plant [46].

4. Conclusions

The presented work describes the efficiency of palm tree waste fibers as economic and environmental friendly bioadsorbent material for the removal of the toxic lead ions from a model solution, and real water samples. It was observed that grinding the PTF to small particle size greatly enhanced their removal efficiency, and the most suitable adsorbent particle size was 53µm. The biosorption of lead ion using PTF followed pseudo-second-order and the best-fitted isotherm were in order Langmuir ~Freundlich > Temkin > D-R isotherms. The thermodynamic study showed that the biosorption of lead ions was spontaneous; due to the negative value of ΔG, random in nature; due to the negative value of ΔS, and exothermic; due to amount adsorbed decrease with increasing of solution temperature. Finally, the PTF was used for the removal of the toxic lead ions from different real environmental water samples and the results showed the high efficiency of the PTF for the removal of the toxic lead ions. These results showed that PTF could be used efficiently as low-cost biosorbent for the removal of pollutants from the polluted aquatic environment.

Acknowledgment

This Project was funded by the Deanship of Scientific Research (DSR) at King Abdulaziz University, Jeddah, under grant No. (G-372-247-37). The authors, therefore, acknowledge with thanks DSR for technical and financial support.

References

[1] S.A. Alrumman, A.F. El-kott, S.M.A.S. Keshk, Water Pollution: Source & Treatment, Am. J. Environ. Eng., 6 (2016) 88–98.

[2] P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla, D.J. Sutton, Heavy metals toxicity and the environment, J. Mol. Clin. Environ. Toxicol., 101 (2012) 133–164.

[3] A. Carocci, A. Catalano, G. Lauria, M.S. Sinicropi, G. Genchi, Lead toxicity, antioxidant defense and environment, J. Rev. Environ. Contam. Toxicol., 238 (2016) 45–67.

[4] D.H.K. Reddy, K. Seshaiah, A.V.R. Reddy, M.M. Rao, M.C. Wang Biosorption of Pb^{2+} from aqueous solutions by Moringa oleifera bark: equilibrium and kinetic studies, J. Hazard. Mater., 174 (2010) 831–838.

[5] A.L. Wani, A. Ara, J.A. Usmani, Lead toxicity: A review, J. Interdiscip. Toxicol., 8 (2015) 55–64.

[6] http://www.leadfreewater.com/world-standards/

[7] R.K. Gautam, A. Mudhoo, G. Lofrano, M.C. Chattopadhyaya, Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration, J. Environ. Chem. Eng., 2 (2014) 239–259.

[8] J.C. Igwe, A review of potentially low cost sorbents for heavy metal removal and recovery, J. Terr. Aquat. Environ.Toxicol., 1 (2007) 60–69.

[9] M. Grassi, G. Kaykioglu, V. Belgiorno, G. Lofrano, Emerging compounds removal from wastewater, J. Green Chem. Sustain., 2 (2012) 15–38.

[10] S. Hokkanen, E. Repo, T. Suopajärvi, H. Liimatainen, J. Niinimaa, M. Sillanpää, Adsorption of Ni(II), Cu(II) and Cd(II) from aqueous solutions by amino modified nanostructured microfibrillated cellulose, J. Cellul., 21 (2014) 1471–1487.

[11] M. Khorsand, S. Dobaradaran, E. Kouhgardi, Cadmium removal from aqueous solutions using Moringa oleifera seed pod as a biosorbent, Desal. Water Treat., 71 (2017) 327–333.

[12] F.F. Ghasemi, S. Dobaradaran, A. Raeisi, A. Esmaili, M.J. Mohammadi, M. Keshtkar, S.G. Nasab, F. Soleimani, Data on Fe (II) biosorption onto Sargassum hystrix algae obtained from the Persian Gulf in Bushehr Port, Iran. Data Brief, 9 (2016) 823–827.

[13] S. Dobaradaran, I. Nabipour, M. Keshtkar, F.F. Ghasemi, T. Nazarialamdarloo, F. Khalifeh, M. Poorhosein, M. Abtahi, R. Saeedi, Self-purification of marine environments for heavy metals: A study on removal of lead (II) and copper (II) by cuttlebone, Water Sci. Technol., 75 (2017) 474–481.

[14] S. Saini, I. Kaur, J.K. Katnoria, Potential of Saccharomyces cerevisiae flocculent strain to biosorb copper and cadmium metal ions from aqueous solution, Desal. Water Treat., 83 (2017) 111–122.

[15] K. Nithya, Asha Sathish, P. Senthil Kumar, T. Ramachandran, Biosorption of hexavalent chromium from aqueous solution using raw and acid-treated biosorbent prepared from Lantana camara fruit, Desal. Water Treat., 57 (2016) 25097–25113.

[16] S. Mirani, N.S. Langeroodi, A. Goudarzi, P. Ebrahimi, Mn^{2+} ions retention onto agriculture waste: a statistical design analysis, estimation of equilibrium and kinetic parameters, Desal. Water Treat., 72 (2017) 52–60.

[17] S. Dobaradaran, M.A. Zazuli, M. Keshtkar, S. Noshadi, M. Khorsand, Biosorption of fluoride from aqueous phase onto Padina sanctaecrucis algae: Evaluation of biosorption kinetics and isotherms, Desal. Water Treat., 57 (2016) 28405–28416.

[18] S. Dobaradaran, M. Kakuee, I. Nabipour, A. Pazira, M.A. Zazouli, M. Keshtkar, M. Khorsand, Fluoride removal from aqueous solutions using Moringa Oleifera seed ash as an environmental friendly and cheap biosorbent, Fresenius Environ. Bull., 24 (2015) 1269–1274.

[19] S. Dobaradaran, I. Nabipour, A.H. Mahvi, M. Keshtkar, F. Elmi, F. Amanollahzad, M. Khorsand, Fluoride removal from aqueous solutions using Shirmp shell waste as a cheap biosorbent, Fluoride, 47(3) (2014) 253–257.

[20] M. Keshtkar, S. Dobaradaran, I. Nabipour, A. Mahvi, F.F. Ghasemi, Z. Ahmadi, M. Heydari, Isotherm and kinetic studies on fluoride biosorption from aqueous solution by using cuttlebone obtained from the persian gulf, Fluoride, 49 (2016) 343–351.

[21] S. Dobaradaran, A.A. Babaei, I. Nabipour, S. Tajbakhsh, S. Noshadi, M. Keshtkar, M. Khorsand, N.M. Esfahani, Determination of fluoride biosorption from aqueous solutions using Sargassum hystrix algae, Desal. Water Treat., 63 (2017) 87–95.

[22] S. Vani, Y.V. Sridevi, M.V.V.C. Lakshmi, Adsorption performance of fly ash for the removal of lead, Inter. J. Eng. Res. Technol., 1 (2012) 1–7.

[23] M. Amin, A. Alazba, M. Amin, Absorption behaviours of copper, lead, and arsenic in aqueous solution using date palm fibres and orange peel: kinetics and thermodynamics, Pol. J. Environ. Stud., 26 (2017) 543–557.

[24] Y. Tang, L. Chen, X. Wei, Q. Yao, T. Li, Removal of lead ions from aqueous solution by the dried aquatic plant, Lemna perpusilla Torr., J. Hazard. Mater., 244–245 (2013) 603–612.

[25] S. Jellali, E. Diamantopoulos, K. Haddad, M. Anane, W. Durner, A. Mlayah, Lead removal from aqueous solutions by raw sawdust and magnesium pretreated biochar: Experimental investigations and numerical modelling, J. Environ. Manag., 180 (2016) 439–449.

[26] I. Morosanu, C. Teodosiu, C. Paduraru, D. Ibanescu, L. Tofan, Biosorption of lead ions from aqueous effluents by rapeseed biomass, J. New Biotechnol., 39 (2017) 110–124.

[27] C. Prince, J. Isaac, A. Sivakumar, Removal of lead and cadmium ions from water using Annona squamosa shell : kinetic and equilibrium studies squamosa shell: kinetic and equilibrium studies, Desal. Water Treat., 51 (2013) 7700–7709.

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

[29] J. Shi, Z. Fang, Z. Zhao, T. Sun, Z. Liang, Comparative study on Pb(II), Cu(II), and Co(II) ions adsorption from aqueous solutions by arborvitae leaves, Desal. Water Treat., 57 (2015) 4732–4739.

[30] S.Y. Lee, H.J. Choi, Persimmon leaf bio-waste for adsorptive removal of heavy metals from aqueous solution, J. Environ. Manage., 209 (2018) 382–392.

[31] S.A. Alavi, H. Zilouei, A. Asadinezhad, Otostegia persica biomass as a new biosorbent for the removal of lead from aqueous solutions, Intern. J. Environ. Sci. Technol., 12 (2014) 489–498.

[32] S.Y. Lagergren, ZurTheorie der sogenannten Adsorption gelösterStoffe. Kungliga Svenska Vetenskapsakad. Handlingar 24 (1898) 1–39.

[33] W. Plazinski, W. Rudzinski, Kinetics of adsorption at solid/solution interfaces controlled by intraparticle diffusion: A theoretical analysis, J. Phy. Chem. C, 113 (2009) 12495–12501.

[34] V.B. Bagdonavicius, M.S. Nikulin, Chi-squared goodness-of-fit test for right censored data, Inter. J. Appl. Math. Stat., 24 (2011) 30–50.

[35] S. Wang, W. Guo, F. Gao, R. Yang, Characterization and Pb (II) removal potential of corn straw- and municipal sludge-derived biochars, R. Soc. Open Sci., 4 (2017) 170402.

[36] A.R. Kaveeshwar, S.K. Ponnusamy, E.D. Revellame, D.D. Gang, M.E. Zappi, R. Subramaniam, Pecan shell based activated carbon for removal of iron(II) from fracking wastewater: Adsorption kinetics, isotherm and thermodynamic studies, J. Process Saf. Environ. Prot., 114 (2018) 107–122.

[37] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J., 156 (2010) 2–10.

[38] T.G. Kebede, A.A. Mengistie, S. Dube, T.T.I. Nkambule, M.M. Nindi, Study on adsorption of some common metal ions present in industrial effluents by Moringa stenopetala seed powder, J. Environtal Chem. Eng., 6 (2018) 1378–1389.

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

[40] R. Ahmad, S. Haseeb, Kinetic, isotherm and thermodynamic studies for the removal of Pb^{2+} ion by a novel adsorbent Luffa acutangula (LAPR), Desal. Water Treat., 57 (2016) 17826–17835.

[41] R. Ahmad, S. Haseeb, Adsorption of Pb (II) on Mentha piperita carbon (MTC) in single and quaternary systems, Arab. J. Chem., 10 (2017) 5412–5421.

[42] B.G. Alhogbi, Potential of coffee husk biomass waste for the adsorption of Pb(II) ion from aqueous solutions, J. Sustain. Chem. Pharma., 6 (2017) 21–25.

[43] Z. Yi, J. Yao, M. Zhu, H. Chen, F. Wang, X. Liu, Kinetics, equilibrium, and thermodynamics investigation on the adsorption of lead(II) by coal-based activated carbon, Plus, 5 (2016) 1–12.

[44] Z.A. ALOthman, M.A. Habila, N.H. Al-Shalan, S.M. Alfadul, R. Alil, I.G.A. Rashed, B. Alfarhan, Adsorptive removal of Cu(II) and Pb(II) onto mixed-waste activated carbon: kinetic, thermodynamic, and competitive studies and application to real wastewater samples, Arab. J. Geosci., 9 (2016) 315.

[45] T. Zehra, L.B.L. Lim, N. Priyantha, Removal behavior of peat collected from Brunei Darussalam for Pb (II) ions from aqueous solution: equilibrium isotherm, thermodynamics, kinetics and regeneration studies, J. Environ. Earth Sci., 74 (2015) 2541–2551.

[46] J.N. Edokpayi, J.O. Odiyo, T.A.M. Msagati, E.O. Popoola, A novel approach for the removal of lead(II) ion from wastewater using mucilaginous leaves of Diceriocaryum eriocarpum plant, J. Sustain., 7 (2015) 14026–14041.