

Removal of Lead and Cadmium Ions from Aqueous Solution by Adsorption on a Low-Cost Phragmites Biomass

Authors:

Abdulaziz N. Amro, Mohammad K. Abhary, Muhammad Mansoor Shaikh, Samah Ali

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Keywords: kinetic study, Freundlich isotherm, Langmuir isotherm, cadmium, lead, treated phragmites biomass

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Article

Removal of Lead and Cadmium Ions from Aqueous Solution by Adsorption on a Low-Cost *Phragmites* Biomass

Abdulaziz N. Amro ^{1,*}, Mohammad K. Abhary ², Muhammad Mansoor Shaikh ¹ and Samah Ali ^{1,3}

¹ Chemistry Department, Faculty of Science, Taibah University, Al-Madinah Al Munawwarah 30002, Saudi Arabia

² Biology Department, Faculty of Science, Taibah University, Al-Madinah Al Munawwarah 30002, Saudi Arabia

³ The National Organization for Drug Control and Research, Al-Agouzah, Giza 12654, Egypt

* Correspondence: anamro@taibahu.edu.sa; Tel.: +966-5909-90428

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Abstract: In recent years, the interest in waste water treatment increased to preserve the environment. The objective of this study is the removal of lead and cadmium ions from aqueous solution by treated *Phragmites* biomass (TPB). TPB was characterized by using Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray analysis (EDS) which indicates the presence of functional groups that may be responsible of metal adsorption such as hydroxyl, carbonyl, sulfonate and carboxylate. Characterization by scanning electron microscopy (SEM) and surface area analysis using the Brunauer–Emmett–Teller method (BET) illustrated that TPB is nonporous with a small surface area. The influences of various experimental factors were investigated; the proposed method recommended the extraction of Pb^{+2} and Cd^{+2} metal ions by TPB at pH 5.0. A contact time of 60 and 45 min was required for the adsorption 50 mL (50 ppm) Pb^{+2} and Cd^{+2} respectively to reach equilibrium when 0.10 g TPB was used. The optimum TPB dosage was 0.20 g for adsorption both metal ions when adsorbate solution was 50 mL (50 ppm). Particle sizes of 0.125–0.212 mm showed the best metal ion removal of both metal ions. Thermodynamic study illustrated that both metal ions correlate more with Langmuir isotherm. Furthermore, chemisorption of Pb^{+2} and Cd^{+2} on TPB was more likely according to kinetic study data.

Keywords: treated *phragmites* biomass; lead; cadmium; Langmuir isotherm; Freundlich isotherm; kinetic study

1. Introduction

The recent developments of industrial cities along the western coastline of Saudi Arabia have reshaped the socioeconomic environmental status of the area [1,2]. Common reed, *Phragmites australis* (Cav.) Trin. ex Steudel, was recently reported as an invasive species in the area stretching from north [3] to south [4] of the Red Sea shoreline in Saudi Arabia. The reed has a cosmopolitan distribution, occurring in all continents except Antarctica [5] and it is considered a useful model for understanding when and how species become invasive, because of its ability to establish, survive, expand and modify the environment within which it persists [6].

Nowadays, ecosystem pollution with heavy metals is becoming a crucial environmental problem threatening the marine life in the western coastline of Saudi Arabia [2]. Live biomass cultures of *Phragmites australis* has been used in numerous studies for heavy metals water treatment [7,8], because of its ability to accumulate such ions within its tissues [9,10].

Ions of heavy metals are toxic and bio-accumulative, with further biomagnification. Therefore, purification of water from heavy metals is an important issue for human beings [11]. Toxicity of cadmium and lead are well known [12]. Cadmium (Cd) is not an essential metal for human beings, but it has a damaging impact on organs such as the kidneys, liver, and lungs [13]. Lead (Pb) has an unknown biological function and is considered a severe environmental pollutant with hazardous impacts on the human health [14]. Lead ingestion may damage the cardiovascular system and induce undesirable and potentially fatal changes in the body. Exposure to lead was also indicated to interfere with the bio-disposition of calcium in bones [15].

When growing in salt marshes, *P. australis* can alter its physiological responses to the surrounding environment and subsequently promote heavy metal uptake [9], on which occasions the presence of metal ions, such as Cd, was found to stimulate antioxidant activities along with increased levels of glutathione and pyridines [8]. Nevertheless, chemical functional groups such as sulfonate and carboxyl play a key role in binding to heavy metals found in the environment [16]. Therefore, it is expected that *P. australis* biomass that is collected from saline environments has a higher potential in heavy metal removal.

In this work, treated *Phragmites* biomass (TPB) is studied to be used for the first time in the removal of lead and cadmium ions from aqueous solution. After characterization of TPB using several techniques, the parameters impacting the removal of metal ions such as biomass, pH of metal ion solution, TPB dose, and particle size, are investigated. In addition to that thermodynamic isothermal models and kinetic studies have been applied.

2. Experimental Section

2.1. Materials

All reagents used were of analytical grade. All solutions were prepared with fresh deionized water obtained from a Milli-Q water system. Glassware was washed throughout and repeatedly cleaned with Nitric acid then rinsed with Milli-Q water. Nitric acid was bought from Riedel-de'Haën (65%, Puriss, Germany), Cd and Pb elements standards was bought from Panreac (1000 µg mL⁻¹) (Spain). 0.1 M HNO₃ and 0.2 M NaOH are used to adapt the required pH.

2.2. Instrumentation

Metal ion determinations were done using atomic absorption spectroscopy (AAS) Agilent technology (200 series) (Santa Clara, CA, USA). A potentiometric digital pH meter was used to determine the pH of water samples. A digital analytical balance was used for all measurements of samples and chemicals. Fourier transform infrared (FTIR) spectra were conducted at room temperature on a (IR Affinity-1) Shimadzu FTIR spectrometer (Shimadzu, Columbia, MD, USA). Scanning Electron Microscopy (SEM) was performed using NOVA NANO SEM instrument (USA). Elemental analysis was measured using energy-dispersive X-ray spectroscopy (EDS) of Superscan Shimadzu SSX-550 diffractometer with CuKα ($\lambda = 1.54056 \text{ \AA}$) (Shimadzu, Columbia, MD, USA). Surface area was measured by BET (Micromeritics ASAP 2020) (Micromeritics, Norcross, GA, USA).

2.3. Sorption Experiment

The equilibrium sorption of the Pb²⁺ and Cd²⁺ ions by TPB was carried out by contacting 50–300 mg of the adsorbent with different concentrations of adsorbate ions. Each metal ion was studied separately. Each measurement was done in triplicate. The mixture was filtered, and the residual concentration of the filtrated metal ions was analyzed using atomic absorption spectroscopy (Agilent technology (200 series)). Adsorption isotherms of TPB were conducted according to batch experimental procedure: A certain volume of solution (V) and certain concentration (C) of the metal ion solution was shaken with a certain amount of adsorbent (W) for a certain time. After filtration of

the adsorbent, the equilibrium concentration (C_e) of adsorbate in the solution was measured and the adsorbed quantity (Q) was calculated using Equation (1) [17].

$$Q = V \times (C_i - C_e)/W \quad (1)$$

where Q = the quantity of metal ion adsorbed from the solution. V = adsorbate solution volume, C_i = initial concentration of metal ion solution, C_f = the concentration after adsorption and W = adsorbent mass (gram). Metal ion removal efficiency was determined by calculating the sorption percentage using this formula:

$$\% \text{ Sorption} = (C_i - C_e)/C_i \times 100 \quad (2)$$

3. Results and Discussions

3.1. Biomass Characterization

3.1.1. Fourier Transfer Infrared (FTIR)

FTIR characterization of TPB showed the presence of several functional groups, such as hydroxyl, carbonyl, sulfonate and carboxylate groups (Figure 1). An FTIR spectrum discloses the existence of many components like polysaccharides, amino acids, fatty acids and others; such functional groups were reported earlier to have a role in adsorption of metal ions [8,18].

Aliphatic N–H and O–H stretching vibration bands show up at 3405 cm^{-1} , which indicates the presence of amino acids and polysaccharides [19,20]. Aliphatic CH₃ and CH₂ symmetric stretching bands at 2924 and 2841 cm^{-1} assure the existence of Chlorophyll groups [20]. Stretching bands of carbonyl and N=O of pectin esters exhibited at 1724 and 1652 cm^{-1} , and the C=C Stretching band at 1460 cm^{-1} indicate the presence of both pectin and lignin. 1378 , 1247 and 1055 cm^{-1} peaks are stretching bands of S=O related to sulfonamides and lignin C–O–C. C–C band of cellulose ring appears at 1166 cm^{-1} [19]. The presence of 1114 cm^{-1} discloses C–O–C bond of glycosidic ether [19]. Absorption bands observed near 663 and 603 cm^{-1} reveal C–S and C=S stretching vibrations of sulfides [21].

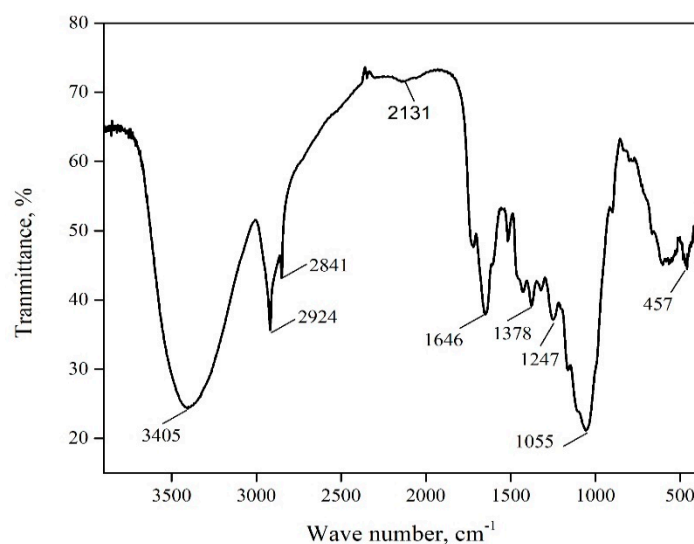


Figure 1. FTIR spectra of treated *phragmites* biomass.

3.1.2. Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDS) and BET (Surface Area)

Measurements using scanning electron microscopy (SEM) were carried out to determine the morphology of the *Phragmites*. Figure 2 displays SEM images of Biomass of *Phragmites*, where all the morphological characteristics were taken at 2000× magnification. Results have showed that the

biomass of *P. australis* has a rough surface due to the presence of fibrous layers. EDS analysis of the biomass is shown in Figure 3, illustrating that the biomass is composed mainly of organic matter, where high concentrations of carbon (37%), oxygen (55%) and nitrogen were found (Table 1). On the other hand, inorganic elements, such as phosphorus, sulfur and fluorine, were also detected. Results showed that *P. australis* biomass had no pores on its surface and the surface area is small ($0.5 \text{ m}^2/\text{g}$), indicating that the adsorption process occurred preferentially on the external surface without any penetration to the bulk.

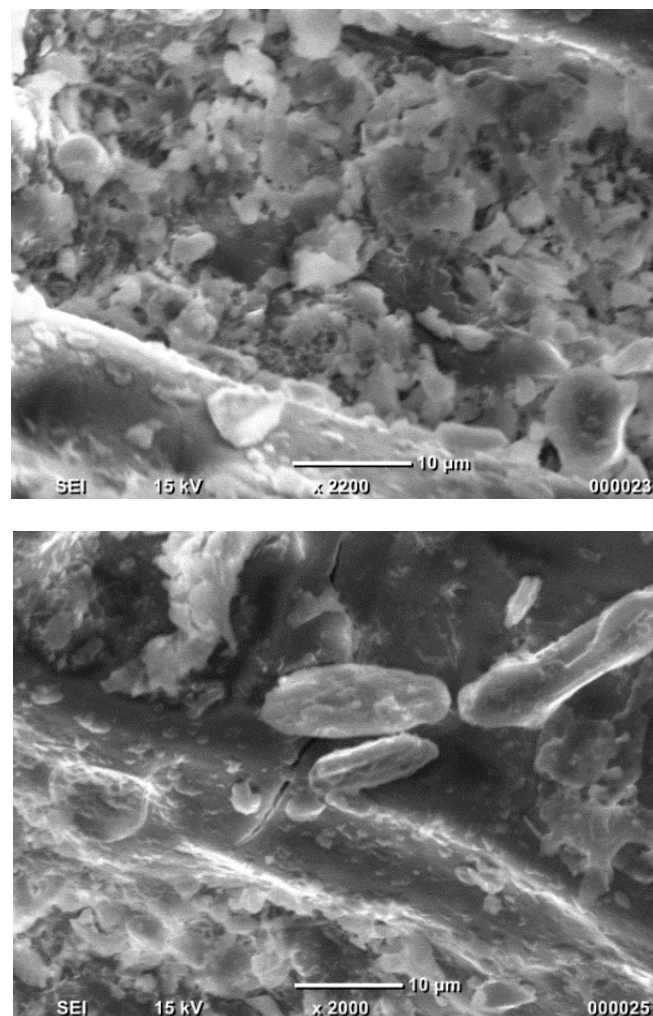


Figure 2. Scanning electron microscope image of the sieved biomass powder of *Phragmites*; scale bar, 10 μm .

Table 1. Energy-dispersive X-ray spectroscopy results of *Phragmites* biomass.

Element	Weight%	Atom%
C	36.96	43.70
N	6.76	6.85
O	55.03	48.84
F	0.15	0.11
P	0.31	0.14
S	0.80	0.36
Total	100.00	100.00

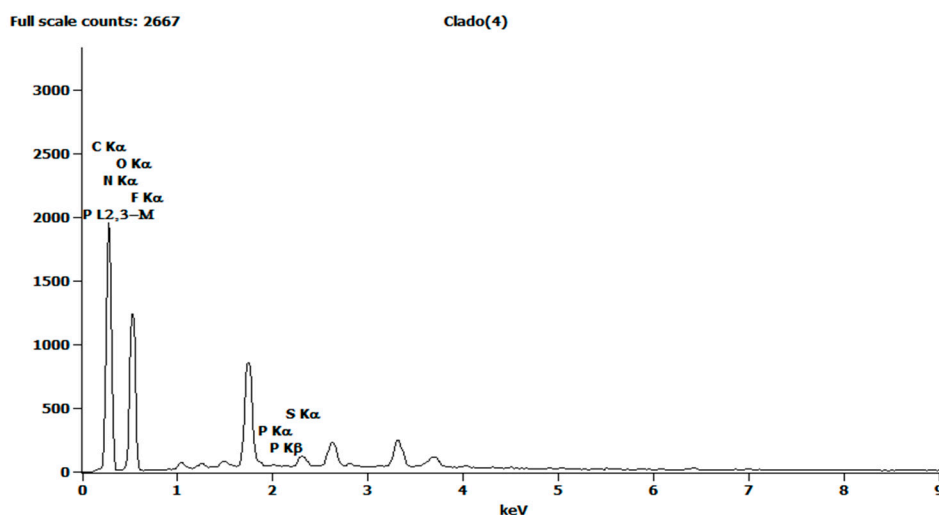


Figure 3. EDS spectra of *phragmites* biomass powder.

3.2. Factors Affecting Metal Ion Removal Study

3.2.1. Effect of Contact Time

The effect of contact time on the adsorption of metals was investigated here. Figure 4 shows the percentage of the metal ions' removal with respect to time. The effect of shaking time on the extraction of the metal ions was investigated by adding 0.1 g of the TPB to 50 mL (50 ppm) metals ion solution at pH 4. Samples were automatically shaken at different time intervals (0, 5, 10, 25, 45, 60, 90 min). The TPB was separated and the amount of metal ions remaining in the aqueous solution was measured by AAS. The plot in Figure 4 reveals that the rate of metal ions' removal as percentages was higher at the beginning, presumably due to larger surface area of the TPB available at beginning for adsorption. Most metal ion removal was attained after about 60 min of shaking time for both metal ions.

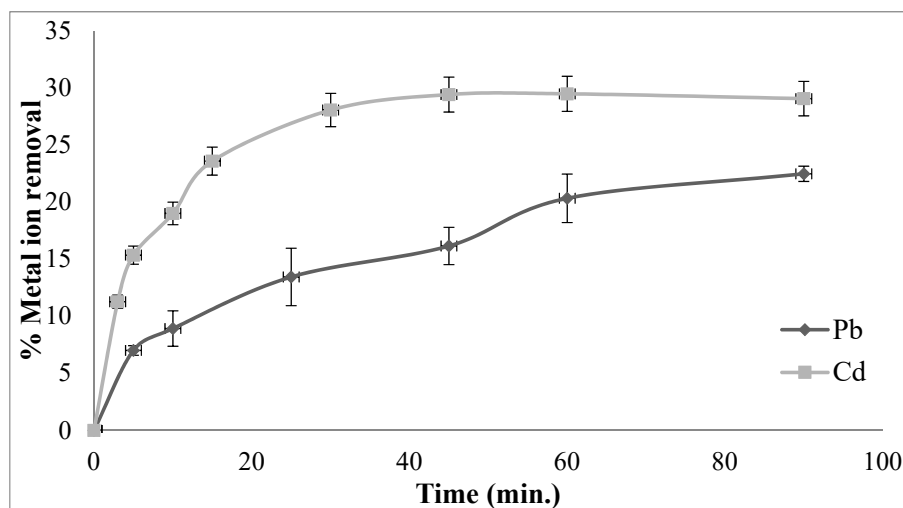


Figure 4. Effect of contact time on metal ion removal (mean \pm RSD) (50 mL, 50 ppm) using *phragmites* powdered biomass (0.1 g, 0.212–0.5 mm) (120 rpm, pH 4, 25 °C). Each measurement has been done in triplicate.

3.2.2. Effect of pH

The pH effect on the TPB sorption was studied using 50 ppm metal ion solutions in pH ranging between 2.0 and 5.0. The results presented in Figure 5 show that the removal efficiency increased with

the increasing of pH from 2 to 5, with a maximum extraction at pH 4.0 and 5.0 for both metal ions, since there is no significant difference between pH 4.0 and 5.0. Low efficiency of metal ion removal at low pH may come from high hydronium ion concentration that competes with metal ion on the adsorbent surface.

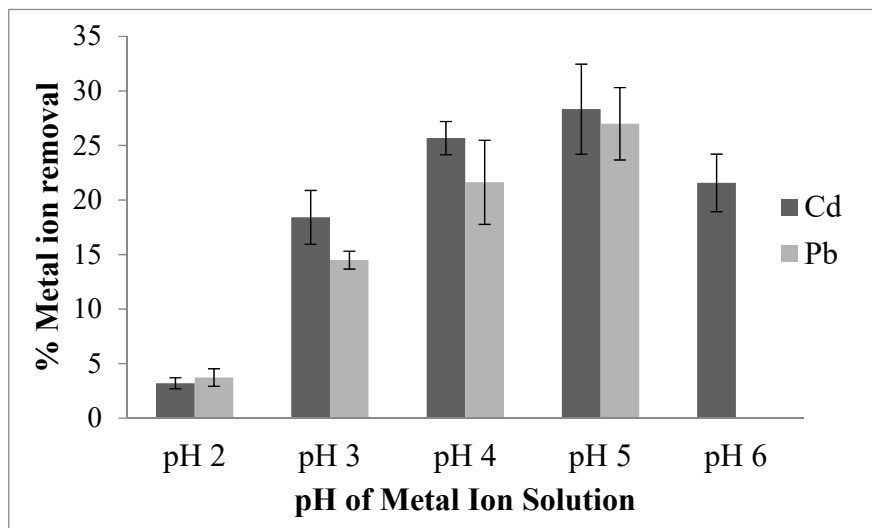


Figure 5. Effect of solution pH on metal ion removal (mean \pm RSD) (50 mL, 50 ppm) using powdered biomass (0.1 g, 0.212–0.5 mm) (120 rpm, 60 min, 25 °C). Each measurement was done in triplicate.

3.2.3. Effect of TPB Dosage

The influence of TPB amount was tested by shaking 50 mL solution containing 50 ppm of Pb and Cd ions with variable amount of TPB in the range of 50–300 mg for 1 h. The sorption increased with increasing the amount of TPB, and reached to a maximum value of 51%, and 41% for Cd (II), and Pb (II) ions, respectively. Results in Figure 6 show no significant difference in the removal of both metal ions between a 200 and 300 mg TPB dose; these results demonstrate that 200 mg is the optimum dose for every 50 mL of 50 ppm metal ion solution.

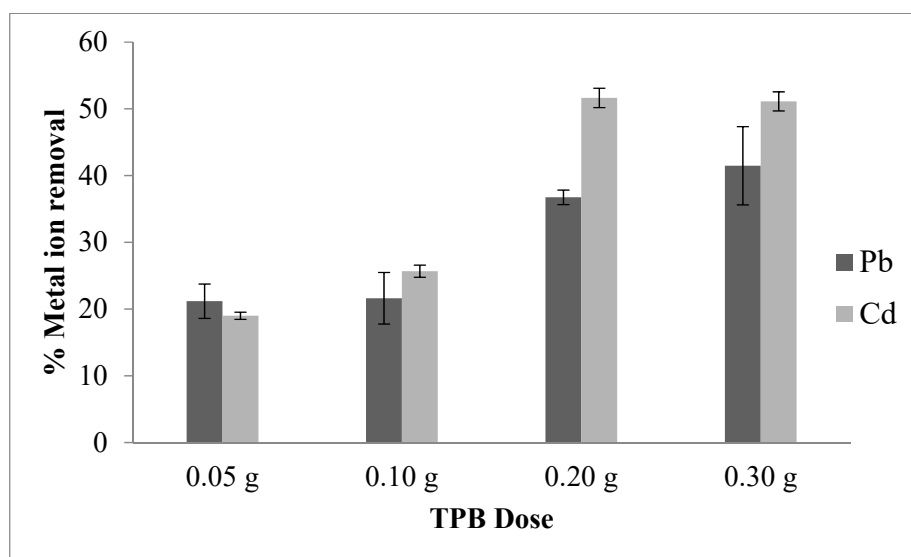


Figure 6. Effect of powdered biomass dose (0.212–0.50 mm) on metal ion removal (mean \pm RSD) (50 mL, 50 ppm, pH 4) (120 rpm, 60 min, 25 °C). Each measurement has been done in triplicate.

3.2.4. Effect of *Phragmites* Biomass Particle Size

Different particle sizes of TPB were used as absorbent material to investigate the best size for removal efficiency. Results in Figure 7 show the effect of TPB particle size, which represents the relationship between removal efficiency and particle size of TPB. It is observed that the decrease of particle size increases the removal efficiency of lead and cadmium ions, which indicates the highest removal efficiency would occur when particle size of 0.125–0.212 mm is used. That demonstrates that larger surface area confers higher metal ion removal ability.

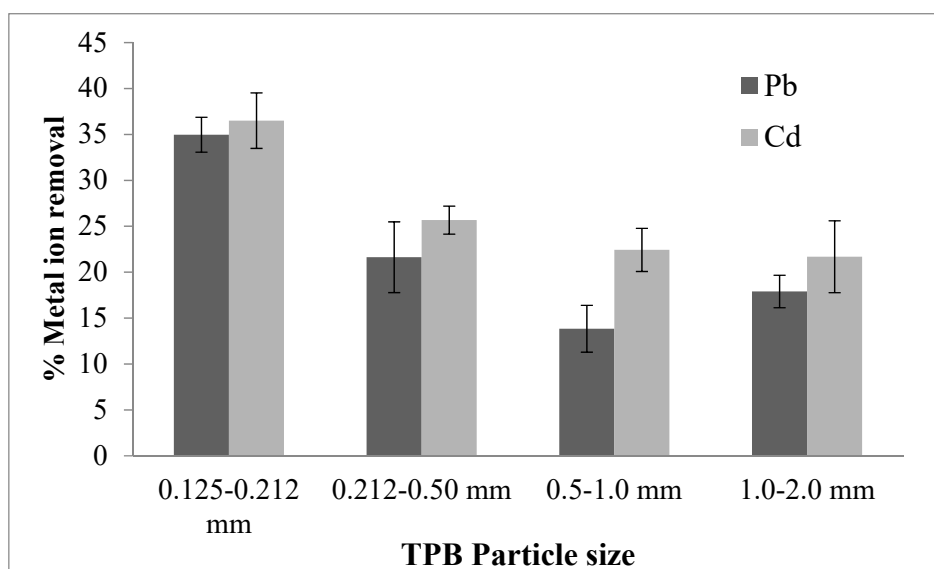


Figure 7. Effect of particle size (0.10 g) on metal ion removal (mean \pm RSD) (50 mL, 50 ppm, pH 4) (120 rpm, 60 min, 25 °C). Each measurement has been done in triplicate.

3.2.5. Adsorption Isotherm

The Langmuir model was applied to interpret adsorption of Cd^{+2} and Pb^{+2} on TPB. The adsorption capacities of TPB for Cd^{+2} and Pb^{+2} obtained from the experiment fit to Langmuir adsorption isotherm model (Figure 8). The curve could be illustrated by the equation below [22]:

$$\frac{C_e}{Q_e} = \frac{1}{X_m K} + \frac{1}{X_m} C_e \quad (3)$$

where Q_e is the quantity of metal ions adsorbed per gram of sorbent and C_e is the amount of metal ions persist in the solution at equilibrium (mg L^{-1}). The X_m is the maximum sorption capacity (mg g^{-1}) and K is the Langmuir constant. Values of X_m and K were determined from the figure and were found to be 5.46 mg/g and 0.1625 L/mg for Pb^{+2} ions, while Cd^{+2} ions values of X_m and K were found to be 6.40 mg/g and 0.0395 L/mg , respectively (Table 2). It was found that the isotherm data fits the Langmuir equation well with good correlation coefficients: $R^2 = 0.936$ and 0.918 for Pb^{+2} and Cd^{+2} ions, respectively, showing that the sorption data correlates more to Langmuir Isotherm model. In order to confirm the adsorption efficiency, the dimensionless separation factor (R_L) could be calculated according to the following equation [23]:

$$R_L = 1/(1 + bC_0) \quad (4)$$

where b is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration of metal ions (mg L^{-1}). While $0 < R_L < 1$ denotes favourable adsorption, $R_L > 1$ is an indication of unfavourable adsorption. Values for R_L were calculated at metal ions initial concentration 50 mg L^{-1} . The value of R_L was found to be 0.110 and 0.336 for Pb (II) and Cd (II) ions, respectively, which is in the favourable range 0–1,

indicating a tendency for the metal ions' adsorption by treated biomass. Freundlich proposed an isothermal model characteristic of heterogeneous surfaces. The quantity of metal ions adsorbed, Q_e , is related to the concentration of metal ions persisting in the solution C_e , as mentioned in the equation below [24]:

$$\text{Log } Q_e = \log KF + (1/n) \log C_e \quad (5)$$

where KF and n are Freundlich constants which can be calculated from the plot of $\log Q_e$ vs. $\log C_e$.

A linear relation with correlation coefficient was observed ($R^2 = 0.724$ for Cd^{+2} and 0.743 for Pb^{+2}). By comparing the correlation coefficients (R^2) for both isothermal models, it's clear that adsorption is better correlated to the Langmuir model than the Freundlich model, meaning that adsorbates form a homogenous monolayer is on the adsorbent surface.

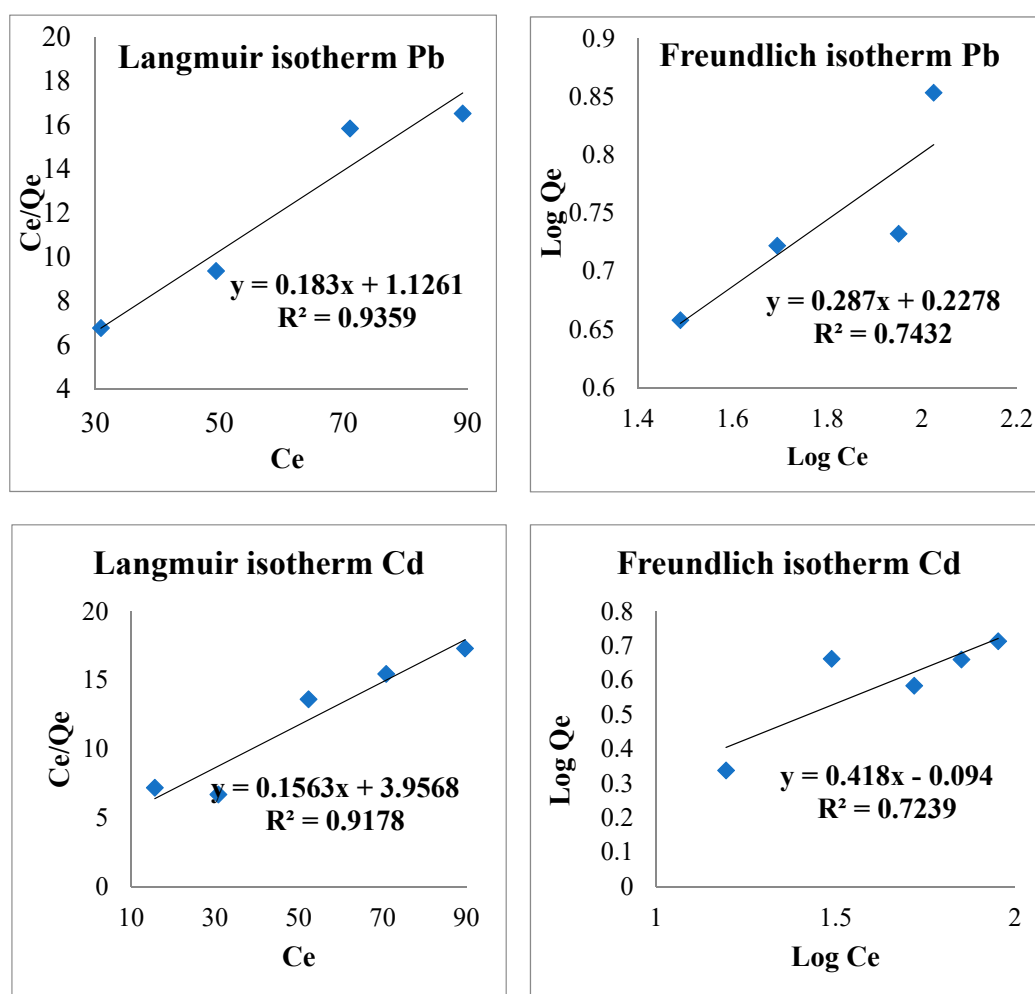


Figure 8. Langmuir and Freundlich isotherms of Pb and Cd ions, 0.10 g *Phragmites* powdered biomass, and 20–120 mg L^{−1} initial concentrations (50 mL, pH 4, 120 rpm, 60 min, 25 °C).

Table 2. Langmuir and Freundlich isotherm model constants for the adsorption of Pb (II) and Cd (II) ions.

	Langmuir Isotherm			Freundlich Isotherm		
	X_m (mg/g)	K (L/mg)	R^2	KF	$1/n$	R^2
Pb	5.46	0.1625	0.936	1.689	0.287	0.743
Cd	6.40	0.0395	0.918	0.805	0.418	0.724

3.2.6. Sorption Kinetics

In order to analyze the adsorption kinetics of Pb^{2+} and Cd^{2+} on TPB surface, correlations between adsorbed amounts and time were studied by testing different mathematical expressions corresponding to various models. Pseudo first and second order kinetic models were applied to study the adsorption of metal ions on the surface of *Phragmites* biomass.

Pseudo first order kinetic models have often been applied on experimental adsorption kinetic results to study whether the adsorption of metal ions dominated by a physical or chemical sorption mechanism. The Kinetics of the studied *Phragmites* were subjected to the linearized forms of the Pseudo first order equation [25,26] and a linear fit of $\log (Q_e - Q_t)$ versus time (t) is observed in Figure 9b:

$$\text{Log } (Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303} \quad (6)$$

where Q_e , Q_t is the sorbed amount of *Phragmites* (mg g^{-1}) at equilibrium and at any time (t), respectively, and k_1 is the first order rate constant of sorption.

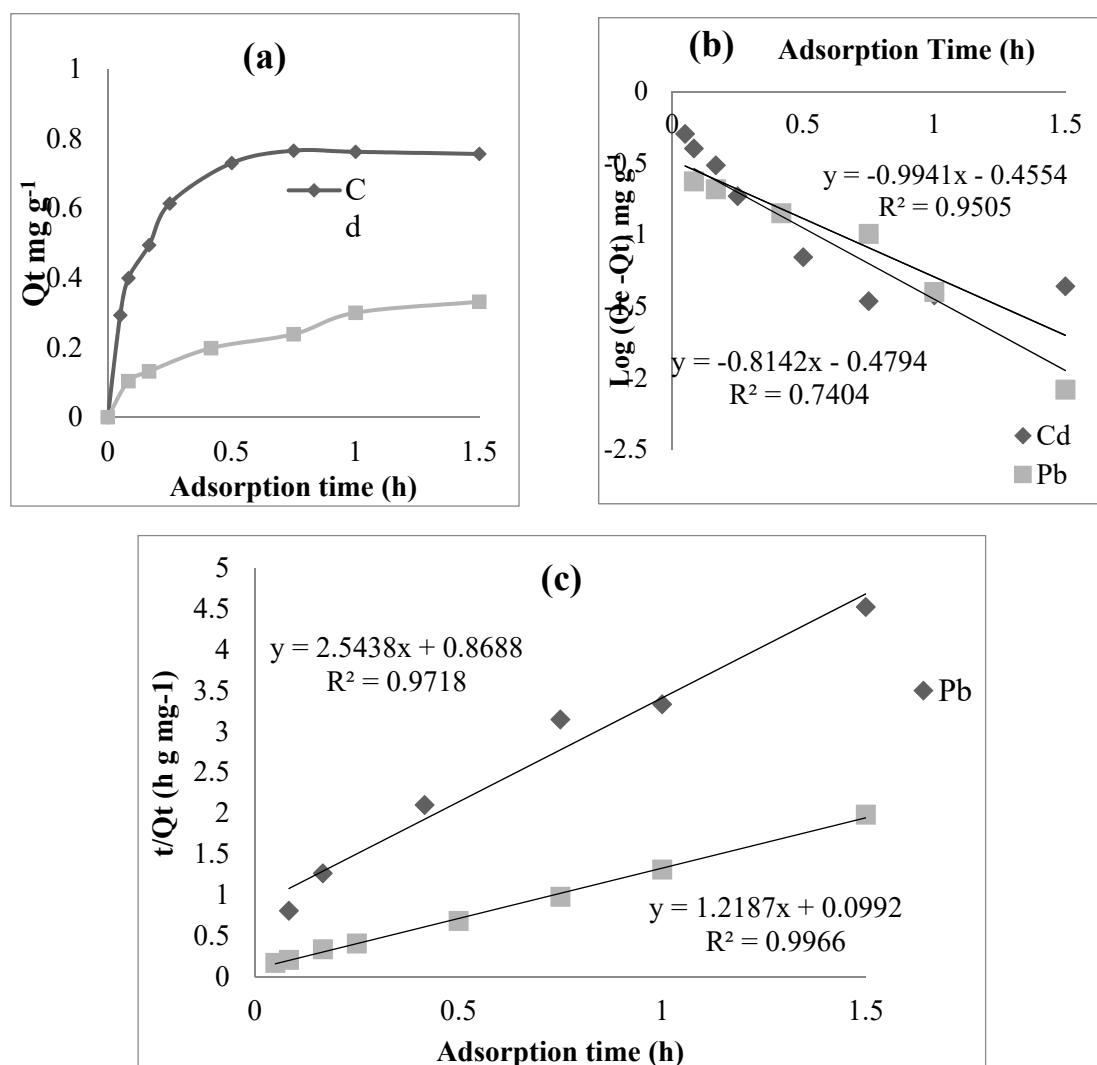


Figure 9. (a) Effect of time on the adsorption capacity of Cd and Pb ions on powdered biomass, (b) Pseudo first-order kinetic model, (c) Pseudo second-order kinetic model.

The second order kinetic equation:

$$t/Q_t = 1/(K_2 Q_e^2) + (t/Q_e) \quad (7)$$

K_2 is the second order rate constant of adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$). The plot t/Q_t versus time (t) should give a straight line if pseudo second order kinetics is applicable and both Q_e , K_2 is simply determined from the slope and intercept of the above equation plot in Figure 9c.

Kinetic models are tested to fit the experimental data for sorption of Cd^{+2} and Pb^{+2} . (Figure 9) and Table 3 shows a significantly higher correlation coefficient R^2 value of pseudo second order kinetic model compared with first one for both metal ions. Furthermore, Table 3 shows a lower difference between Q_e calc and Q_e Exp for pseudo second order model compared to first one. The fitness of the data to the pseudo second-order kinetic model could be interpreted by chemisorption of Pb and Cd ions by *Phragmites* biomass.

Table 3. Pseudo first-order and pseudo second-order kinetic models for the adsorption of Pb and Cd ions on powdered biomass.

Metal Ion		Pseudo First Order Kinetic Model		
	$Q_{e, \text{exp}} (\text{mg g}^{-1})$	$Q_{e, \text{calc}} (\text{mg g}^{-1})$	$k_1 (\text{h}^{-1})$	R^2
Pb	0.335	0.101	1.048	0.9505
Cd	0.765	0.153	1.104	0.7404
Metal Ion		Pseudo Second Order Kinetic Model		
	$Q_{e, \text{exp}} (\text{mg g}^{-1})$	$Q_{e, \text{calc}} (\text{mg g}^{-1})$	$k_2 (\text{g mg}^{-1} \text{ h}^{-1})$	R^2
Pb	0.335	0.393	7.452	0.9718
Cd	0.765	0.821	14.96	0.9966

Table 4 shows a comparison between *Phragmites* biomass and other bio-adsorbent ability for removal Pb and Cd ions from aqueous solution. It can be concluded that *Phragmites* biomass has a comparable adsorption capacity for both metal ions.

Table 4. A comparison of various bio-adsorbents used to adsorb lead and cadmium ions from aqueous solutions.

Bio-Adsorbent	Pb Maximum Capacity mg/g	Cd Maximum Capacity mg/g	Reference
<i>Leucaena leucocephala</i> Residues	25.51	14.79	[27]
<i>Hydrodictyon reticulatum</i>	-	7.03	[28]
agriculture wastes of ramie stalk	-	10.33	[29]
<i>Cladophora</i> biomass	20.65	12.07	[30]
activated carbon originating from cow bone	50.10	-	[31]
Fungal Biomass	2.971	-	[32]
<i>Phragmites</i> biomass	5.46	6.40	Present study

4. Conclusions

In this study low coast is locally available; *Phragmites australis* has been collected from salt marshes and treated to be used as alternative biomass adsorbent to remove metal ions from aqueous solution. Even though TPB has a low surface area, it is considered a good adsorbent of metal ions from aqueous solution, when considering the abundance of low-cost raw materials used for its preparation.

Several techniques have been applied to characterize TPB in this study. Optimization of adsorption parameters for metal ions on TPB have been illustrated in this study. It can be concluded from thermodynamic and kinetic investigations that adsorption of metal ions on TPB fit Langmuir homogenous monolayer chemisorption. Further studies are recommended on TPB for the removal of other metals and organic pollutants.

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