

Removal of lead(II) and nickel(II) ions from aqueous solution via Bermuda grass biomass

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ABSTRACT

Adsorption of lead(II) and nickel(II) ions from aqueous solutions was investigated by Bermuda grass biomass. The adsorption process was studied as a function of pH, initial metal concentration, temperature and time. The experimental data obtained were investigated via Langmuir, Freundlich and Temkin isotherms. The kinetic data were examined by pseudo-second-order and intraparticle diffusion models. The biomass was shown to be highly efficient in the removal of lead and nickel ions with the removal of 99% and 54% for lead and nickel ions, respectively. The results showed that Bermuda grass biomass could be utilized as an available, cheap, biodegradable and efficient adsorbent for the removal of toxic metal ions from aqueous solutions.

Key words | adsorption, Bermuda grass biomass, toxic metal ions, wastewater treatment

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INTRODUCTION

Deterioration of our environment's quality is increasing day by day; one of the most important environmental problems facing humanity is pollution (Begum *et al.* 2009; Sivakumar *et al.* 2014). One major problem is the presence of heavy metal ions, which are extremely toxic even at low concentrations, dumped into the environment by industry (Atia *et al.* 2008; Mahdavi *et al.* 2013). These include lead and nickel, highly toxic even at very low concentrations, and causing dangerous health hazards to the human body and organisms (Song *et al.* 2000; Ma *et al.* 2012; Edris *et al.* 2014). Owing to this, a large number of studies have been concerned with removal of these toxic metal ions and a huge number of regulations have been issued to regulate and prevent the increase of toxic metal ions in the environment (Atia *et al.* 2008; Ma *et al.* 2012; Mahdavi *et al.* 2013; Edris *et al.* 2014).

A wide range of chemical and physical techniques have been employed for the removal of heavy metal ions from water systems, such as sedimentation (Song *et al.* 2000), electrochemical processes (Mao *et al.* 2015), ion exchange, coagulation/flocculation (Fu & Wang 2011), filtration and membrane processes (He *et al.* 2008). Electrodialysis based

on a semi-permeable membrane under the influence of an electric potential, for example, a cation selective-membrane (negatively charged ions) allows positive ions and rejects negatively charged ions (Garcia-Vasquez *et al.* 2016) and adsorption (Inoue *et al.* 1997).

Different types of materials have been used as adsorbents to remove heavy metal ions from water, such as activated carbon, metal oxides, ion exchange resins and biosorbents (Junior *et al.* 2009; Kampalanonwat & Supaphol 2010; Wang *et al.* 2010). The adsorption efficacy has been attributed to the presence of functional groups that chelate with metal ions (Ma *et al.* 2012; Zhu *et al.* 2012). Furthermore, the design and synthesis of adsorbents are considered to be simple, easy to operate, low cost and very suitable for water treatment. As a result, the adsorption process is usually used for the removal of heavy metal ions from various industrial aqueous mediums (Altinkok *et al.* 2011; Zhu *et al.* 2012; Dulcy Evangelin *et al.* 2013). Great efforts are being directed towards the use of natural materials as low cost adsorbents, which are available in large quantities, safe, environmentally friendly and easy to collect and use (Sadeek *et al.* 2015). The uses of natural

or certain waste products from industry or agriculture may have potential as inexpensive adsorbents.

In light of the above discussed and observed results, it has been realized that the development of natural, low cost, available and efficient adsorbents with high performance is required and the absorption capacity needs to be verified. Therefore, in this work, we have developed a new method for the removal of two heavy metal ions, lead(II) and nickel(II), from water samples by using a highly available, low cost, natural, non-toxic medicinal plant called *Cynodon dactylon* belonging to the family Poaceae and also known as Bermuda grass or chayer. It has largely been considered to have fewer side effects and to be a harmless alternative to synthetic pharmaceutical drugs (Ashokkumar *et al.* 2013; Patel *et al.* 2013; Shi *et al.* 2014). This type of grass is native to the warm temperate, tropical regions and is a perennial and prostrate grass; it spreads by scaly rhizomes and flat stolons to form a dense, resilient turf. In this work, lead(II) and nickel(II) ions are chosen as the model pollutants to investigate the sorption activity of the Bermuda grass biomass.

MATERIALS AND METHODS

Equipment

Infrared spectra were recorded on a Perkin Elmer 16F PC Fourier transform infrared spectrometer using KBr Pellets in the 500–4,000 cm^{-1} region (FT-IR). ^{13}C -NMR solid state spectra were recorded on a Bruker WB-400 spectrometer with an operating frequency at 100.61 MHz (9.40 T). Samples were packed into 4 mm zirconium oxide rotors at 25 °C. Cross-polarization was used. Pulse delay was 5.0 s and contact time was 2 min in CPMAS experiments. The magic angle spinning rate was 4 KHz. Carbon chemical shifts were referenced to tetramethylsilane using the high frequency isotropic peak of adamantane to 38.56 ppm. Scanning electron microscopy (SEM) images were taken by TESCAN LYRA 3 (Czech Republic) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector model X-Max. The concentration of metal ions was measured by atomic absorption spectroscopy (AAS) ICE 3000 (Thermo Scientific). Thermogravimetric analysis

(TGA) was by utilizing a thermal analyser (STA 429) from Netzsch (Germany). The experimentation was executed in a nitrogen atmosphere from 20 to 800 °C with a warming rate of 10 °C/min and a nitrogen flow rate of 20 cm^3/min .

Plant cultivation and preparation

Cultivated Bermuda grass (*C. dactylon*) plants were directly washed and cleaned with deionized water and dried in air for 2 hours, and then the dried material was soaked in methanol for 24 hours. The remaining material was refluxed for 36 hours in methanol to get rid of all soluble chlorophyll material, filtered and washed with distilled water, dried in an oven for 24 hours and finally ground and passed through mesh size 0.6 mm. The percentage recovery of the biomass was equal to 82%.

Adsorption experiments

Adsorption experiments of Bermuda grass biomass for lead (II) and nickel(II) ion removal were performed. For lead(II) ions the removal experiments were performed as follows: a mixture of Bermuda grass biomass (0.05–0.25 g) in a solution (50 mL) of 10 mg/L aqueous $\text{Pb}(\text{NO}_3)_2$ was stirred at different pH for 24 hours. The biomass was filtered and washed with deionized water. The filtrate was analysed via AAS to determine the amount of lead(II) that remained unabsorbed. The adsorption capacity in mg/g was calculated as follows:

$$q_e = \frac{(C_o - C_f)V}{W} \quad (1)$$

where C_o and C_f are the initial and final concentration of lead(II) ions in mg/L, respectively, W is the weight of the dried biomass (g) and V is the volume of solution (L). Similar experiments were conducted in order to study the adsorption process on nickel(II) ions. The results obtained represent the average of three runs and varied by less than 5% relative standard deviation.

The adsorption isotherms were constructed by changing the concentration of lead(II) ions from 2.0 to 10 mg/L at pH 5 at 298 °K for 24 hours. For adsorption kinetics, Bermuda grass biomass samples were stirred in 50 mL of 10 mg/L

aqueous solutions of lead(II) ions for different times at pH 5. Similar experiments were executed for the removal of nickel ions by the biomass (Akintola *et al.* 2016).

RESULTS AND DISCUSSION

Characterization of Bermuda grass (*C. dactylon*) biomass

The FT-IR spectrum of Bermuda grass biomass (Figure 1) confirmed the presence of functional group characteristics of Bermuda grass biomass. Hydroxyl groups were identified by a broad band attributed to -OH stretching vibration at $\sim 3,400\text{ cm}^{-1}$. Additionally, the aliphatic structure was confirmed by the absorption band attributed to the stretching vibrations of -C-H bonds at $\sim 2,900\text{ cm}^{-1}$, carbonyl groups by the band attributed to stretching vibrations of C=O bonds at $1,750\text{--}1,500\text{ cm}^{-1}$, and the signal at $1,413\text{ cm}^{-1}$ is associated with the stretching vibrations of C-OH groups

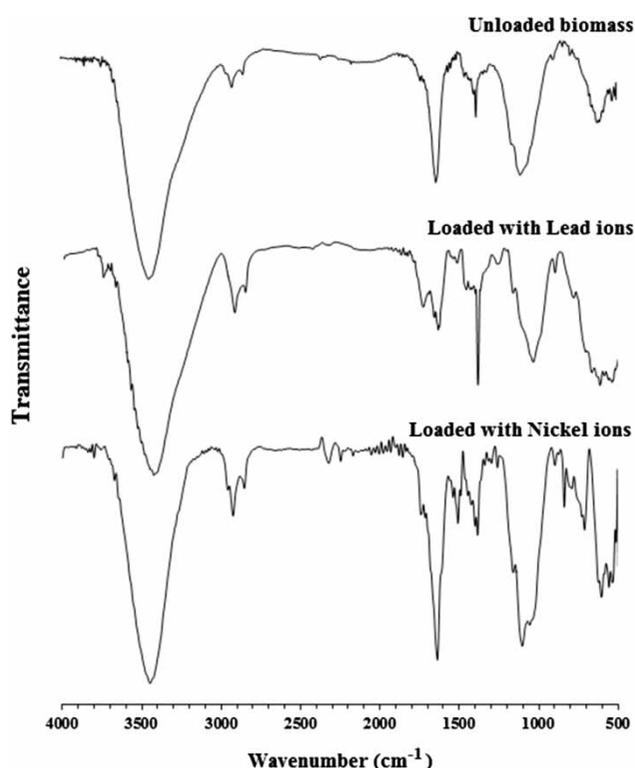


Figure 1 | FT-IR spectra of unloaded and loaded Bermuda grass biomass with lead(II) and nickel(II) ions.

in the structure of Bermuda grass biomass. The presence of the ether group was manifested by the band attributed to stretching vibrations of -C-O bonds at $\sim 1,000\text{ cm}^{-1}$ to $\sim 1,250\text{ cm}^{-1}$, aromatic ring groups by the band attributed to stretching vibrations of C=C bonds at $\sim 1,600\text{ cm}^{-1}$ and -C-H aromatic stretching vibrations at $\sim 650\text{ cm}^{-1}$ (Parparita *et al.* 2014). The loaded Bermuda grass biomass revealed an increase in the intensity of carbonyl and hydroxyl peaks due to chelation with the nickel and lead ions; the appearance of a new peak at $1,384\text{ cm}^{-1}$ revealed the adsorption of the negative nitrate ions, which enables the biomass to adsorb negative ions (Al Hamouz 2016).

Solid state C^{13} -NMR is considered to be a powerful tool for characterizing cross-linked materials due to their insolubility, such as Bermuda grass biomass. The C^{13} -NMR spectra (Figure 2) revealed the presence of aliphatic - CH_2 - at $\sim 22\text{ ppm}$, -CH- at $\sim 33\text{ ppm}$, - OCH_3 for lignin at $\sim 55\text{ ppm}$, strong peaks at ~ 65 to $\sim 75\text{ ppm}$ due to oxygenated aliphatic carbons from carbohydrates. There was a strong peak at $\sim 107\text{ ppm}$ due to anomeric carbon (-O-C-O-), two weak peaks at ~ 130 and $\sim 150\text{ ppm}$ due to olefinic/aromatic and oxygenated aromatic carbons, respectively, and a weak peak at $\sim 175\text{ ppm}$ due to carboxyl/carboxylate/amide groups, which could be attributed to hemicellulose and partially associated proteins and peptides (De la Rosa *et al.* 2008; Li *et al.* 2015).

The TGA curve (Figure 3) of Bermuda grass biomass revealed two thermal patterns: first, from 0 to 100°C the curve showed the loss of water molecules; second, at $\sim 230^\circ\text{C}$ the thermogram revealed thermal degradation of the biomass up to $\sim 340^\circ\text{C}$ due to decomposition of the lignocellulosic structure of the biomass material (Valente Nabais *et al.* 2013).

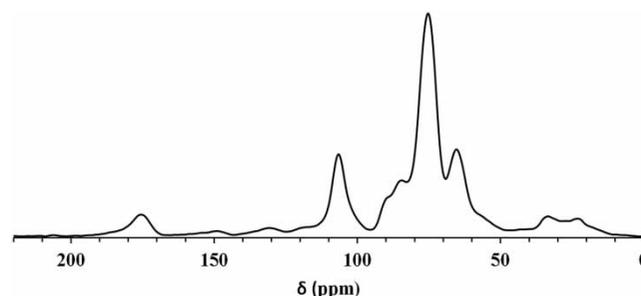


Figure 2 | C^{13} -NMR spectra of Bermuda grass biomass.

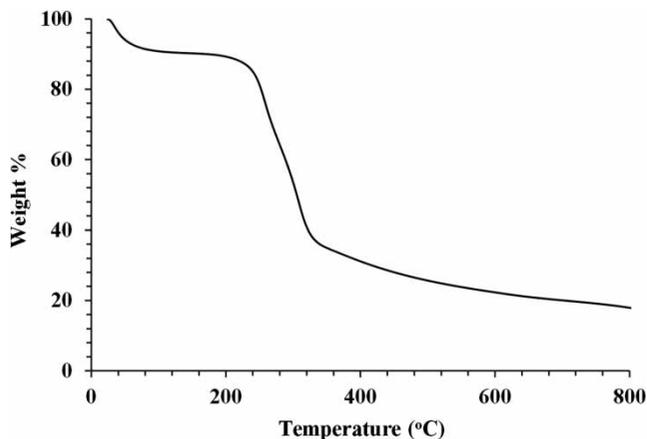


Figure 3 | TGA of Bermuda grass biomass.

Adsorption properties of Bermuda grass biomass

The efficient removal of lead(II) and nickel(II) ions by the biomass could be attributed to the presence of the hydroxyl groups (-OH) and their affinity toward the metal ions. The presence of lignin with aromatic groups functionalized with hydroxyl and ether groups attributes to the high tendency to coordinate with metal ions, forming stable complexes, and leads to the higher efficiency of the Bermuda grass biomass. Another factor is the presence of hydroxyl groups found in cellulose and hemicellulose chemical structures that enhance the adsorption capacity of the biomass (Sadeek *et al.* 2015).

Effect of pH

The effect of pH was investigated for the uptake of lead(II) and nickel(II) ions at a fixed concentration of 10 mg/L for 24 hours, in a pH range of 3 to 7. The pH of the metal ion solution was adjusted by nitric acid ($\text{HNO}_3 = 0.1 \text{ M}$) and sodium hydroxide ($\text{NaOH} = 0.1 \text{ M}$). The results of the uptake of metal ions with pH are shown in Figure 4. The optimum pH was found to be 5. At the higher pH range, competition between adsorption by biomass and metal hydrolysis could occur. At lower pH levels, the concentration of H^+ increases and competes with metal ions toward active sites on the surface of the biomass, leading to lower adsorption capacity (Wang *et al.* 2010).

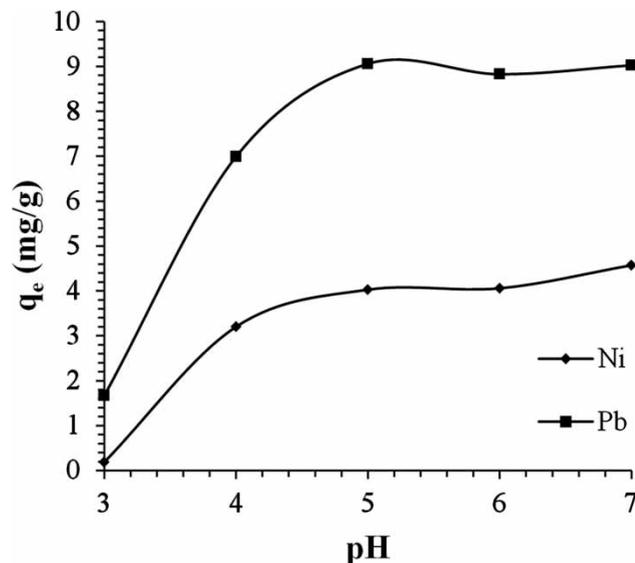


Figure 4 | Effect of pH on the adsorption capacity of lead(II) and nickel(II) ions by Bermuda grass biomass.

Effect of dosage

The effect of biomass dosage on the adsorption of lead(II) and nickel(II) ions was investigated using different biomass concentrations (from 0.05 g/50 mL to 0.25 g/50 mL). The adsorption process was studied by stirring the desired concentration of biomass with a fixed metal ion concentration for 24 hours. Figure 5(a) shows the removal efficiency increased as the dosage of biomass increased, which could be attributed to the higher availability of active sites to bind to metal ions. Figure 5(b) shows the decrease in the adsorption capacity as the mass of biomass increases; this could be explained by the high amount of unsaturated active sites compared to the metal ion concentration.

Effect of initial concentration and isotherm models

As shown in Figure 6(a), the adsorption capacity of Bermuda grass biomass increases with the increase in the initial concentration. To further investigate the phenomena of adsorption, three isotherm models were studied: Langmuir, Freundlich and Temkin isotherm models.

The Langmuir isotherm model describes the adsorption process to be homogeneous in nature, and each metal ion is adsorbed to one active site assuming monolayer adsorption. All adsorption sites possess equal affinity toward metal

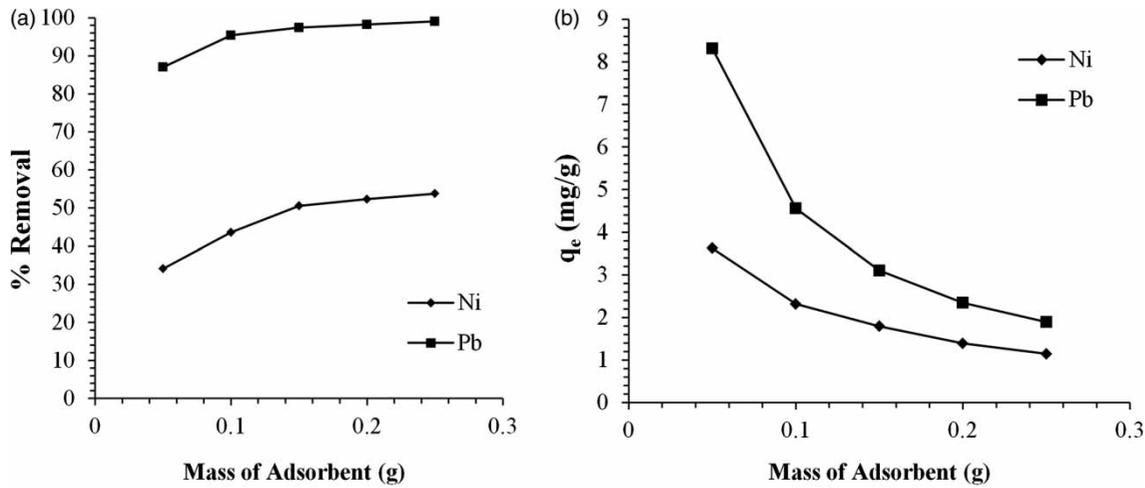


Figure 5 | (a) Effect of Bermuda grass biomass dosage on the per cent removal; (b) effect of Bermuda grass biomass on the adsorption capacity.

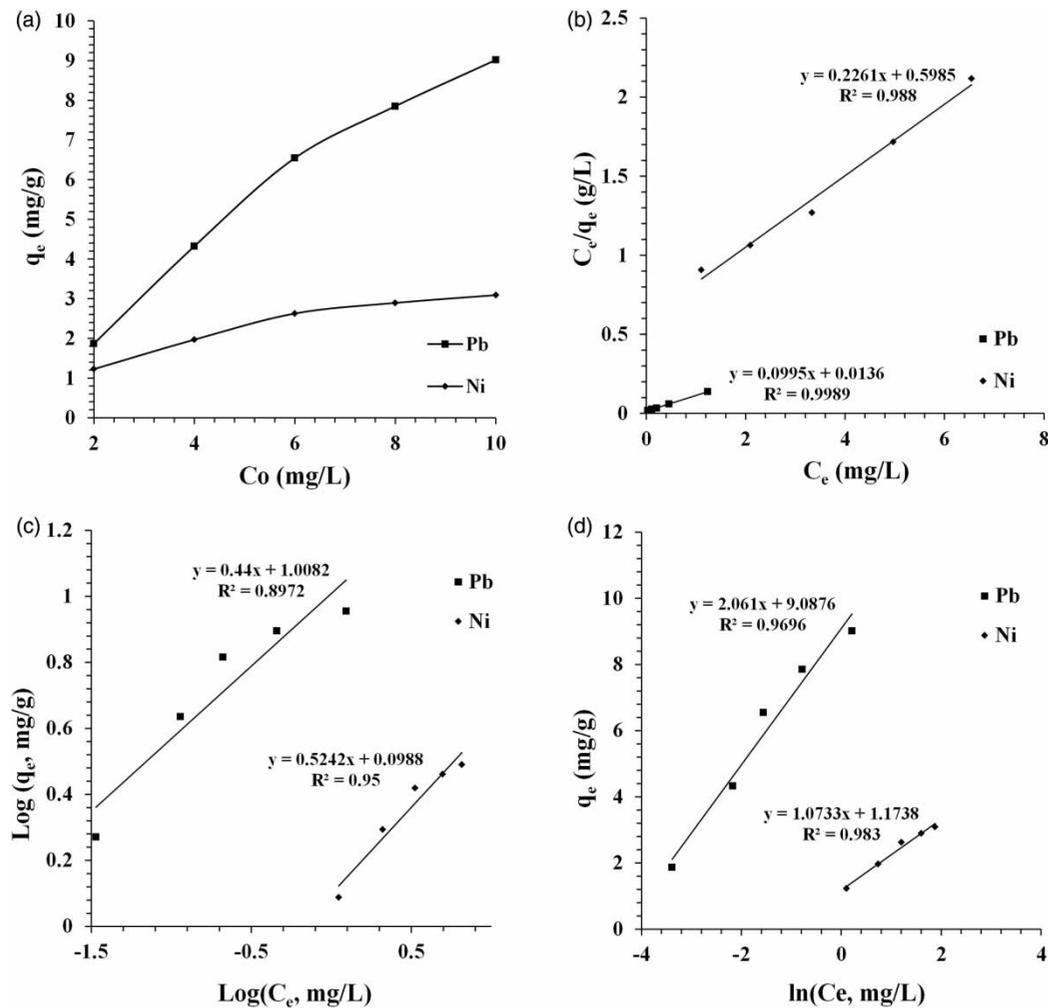


Figure 6 | (a) Effect of initial metal ion concentration on the adsorption capacity of Bermuda grass biomass; (b) Langmuir isotherm model; (c) Freundlich isotherm model; (d) Temkin isotherm model.

ions (Wang *et al.* 2009). The linear expression can be described as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (2)$$

where C_e and q_e are the concentration of metal ions (mg/L) and adsorption capacity (mg/g) at equilibrium, respectively. Q_m and b represent the maximum adsorption capacity (mg/g) and Langmuir isotherm constant (L^3/mg), respectively. The linear expression of the isotherm model is presented in Figure 6(b) (Table 1). As can be seen from Figure 6(b), the experimental data fit the Langmuir model with good regression (R^2) values of 0.9989 and 0.988 for lead(II) and nickel(II) ions, respectively. The good regression values assume that the adsorption process is a monolayer with Q_m values of 73.5 and 10.1 mg/g for the adsorption of lead(II) and nickel(II) ions, respectively.

The Freundlich isotherm model describes non-ideal adsorption; it can be utilized to describe the adsorption process as heterogeneous in nature. The model assumes that the adsorption is multilayer and the affinity toward metal ions is non-uniform, where the binding affinity is maximum at first occupation, and then decreases gradually as the active sites are completely consumed (Shen *et al.* 2011). The linear expression can be described as follows:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (3)$$

Table 1 | Langmuir, Freundlich and Temkin isotherm model constants for lead(II) and nickel(II) ion adsorption

Langmuir isotherm model			
Metal ion	Q_m (mg/g)	b (L/mg)	R^2
Pb(II)	73.52941	1	0.988
Ni(II)	10.05025	0.166249	0.9989
Freundlich isotherm model			
Metal ion	k_f ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$)	$1/n$	R^2
Pb(II)	10.1906	0.44	0.8972
Ni(II)	1.25545	0.5242	0.95
Temkin isotherm model			
Metal ion	B (J/mol)	A (L/g)	R^2
Pb(II)	2.061	82.15	0.9696
Ni(II)	1.0733	2.985	0.983

where k_f and n are Freundlich constants, as can be seen from Figure 6(c) (Table 1). The regression values (R^2) are not good with values of 0.95 and 0.8972 for the adsorption of lead(II) and nickel(II) ions, respectively, indicating that the adsorption process does not follow the Freundlich isotherm model. The values of $1/n$ are lower than 1, as seen in Table 1, indicating that the adsorption process is favourable (Tay *et al.* 2009).

The Temkin isotherm model assumes that the heat of adsorption decreases linearly with increased binding of metal ions with the active sites (Vijayaraghavan *et al.* 2006). The linear expression of the model can be described as follows:

$$q_e = B \ln A + B \ln C_e \quad (4)$$

where B and A are constants related to the heat of adsorption and equilibrium binding constant (L/g), respectively. As can be seen from Figure 6(d) and Table 1, the regression values are good with values of 0.9696 and 0.983 for lead(II) and nickel(II) ions adsorption, respectively. The values of constant A , which is related to the binding energy, indicates that lead ions have higher affinity toward the biomass ($A = 82.15$) compared to nickel ($A = 2.985$) ions. This is also shown from the experimental values, which indicates that the adsorption of lead ions is much more preferred than nickel ions (Boparai *et al.* 2011).

Effect of temperature, contact time and kinetic models

As can be seen from Figure 7, the adsorption capacity increased with increasing temperature up to 308 °K, which could be attributed to the expansion of the biomass pores leading to the diffusion of metal ions through the pores of biomass. At higher temperatures of ~323 °K, the adsorption capacity decreased, which could be attributed to weak interaction between the biomass and metal ions, which favours the physisorption process (Vinod & Anirudhan 2001). Another explanation could be that the biomass at 308 °K reached maximum capacity (Aksu & Kutsal 1991).

Experimental kinetic data provide valuable information about the adsorption rate and mechanism in order to design highly efficient material for the removal of toxic metal ions from water. Two isotherm models, pseudo-second-order and intraparticle diffusion, were used to analyse the

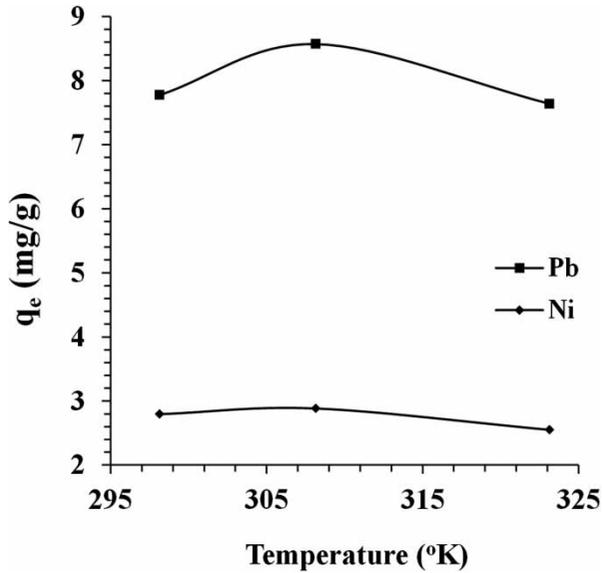


Figure 7 | Effect of temperature on the Bermuda grass biomass adsorption capacity (the initial concentration of each metal ion was 10 ppm at pH 5).

experimental data obtained for the adsorption of lead(II) and nickel(II) ions from Bermuda grass biomass. As seen from Figure 8(a) and 8(d), the adsorption capacity increased with time (Boparai *et al.* 2011; Sadeek *et al.* 2015).

The pseudo-second-order kinetic model has been applied for the analysis of chemisorption kinetics from liquid solutions; the adsorption of lead(II) and nickel(II) ions with Bermuda grass biomass could be explained by the electrostatic interaction between the oxygen lone pairs with the positive metal ions. The linear expression can be described as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_2 and q_t are the second-order rate constant (g mg/h) and adsorption capacity (mg/g) at time t . As seen from Figure 8(b) and 8(e) (Table 2), the regression values for the

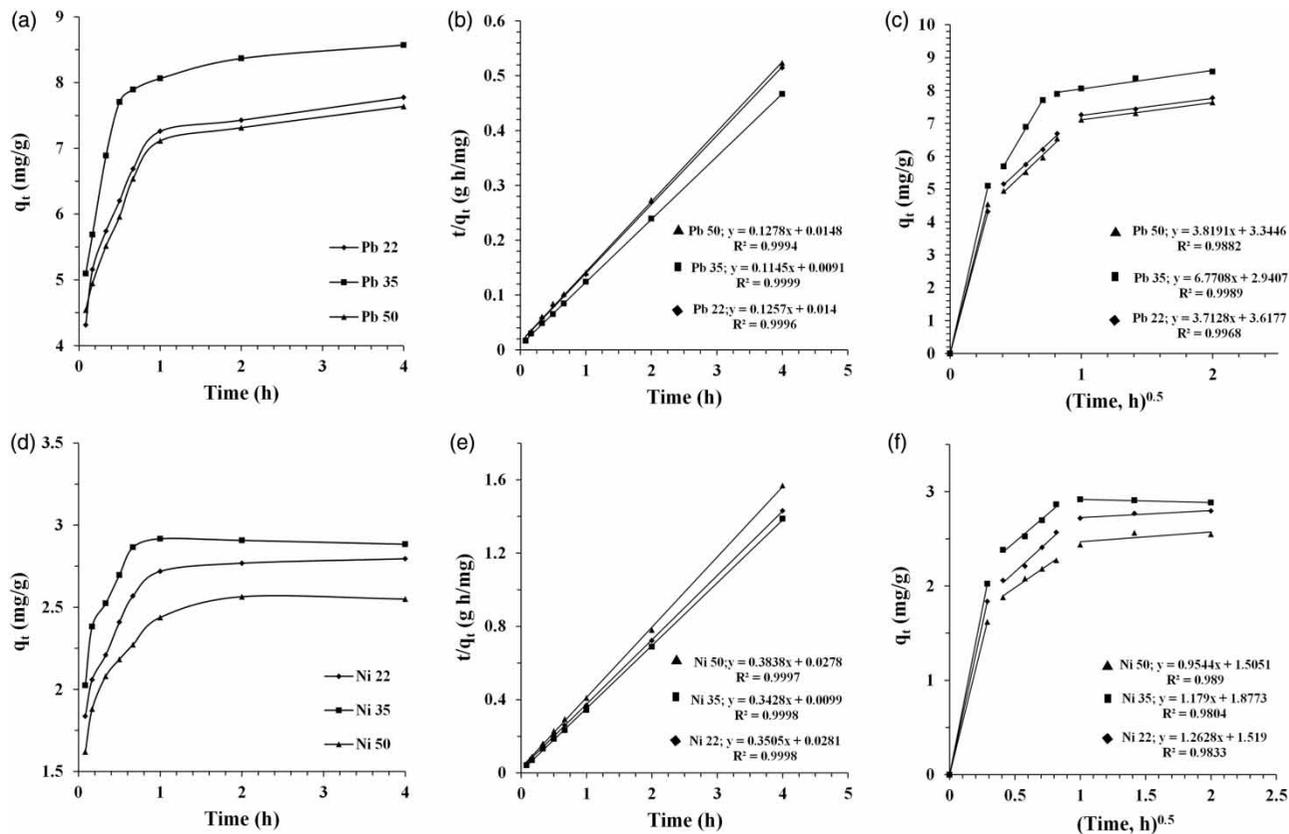


Figure 8 | (a) Effect of time on the adsorption capacity of lead(II) ions of biomass; (b) pseudo-second-order kinetic model for lead(II) ion adsorption of biomass; (c) intraparticle diffusion model for lead(II) adsorption of biomass; (d) effect of time on the adsorption capacity of nickel(II) ions of biomass; (e) pseudo-second-order kinetic model for nickel(II) ion adsorption of biomass; (f) intraparticle diffusion model for nickel(II) ion adsorption by biomass.

adsorption of lead(II) and nickel(II) ions ($R^2 > 0.999$) indicate that the experimental data fit with the model, assuming the role of chemisorption in the adsorption process. The rate constant k_2 values show that the rate of adsorption of nickel ions is faster than for lead ions, which could be due to a lower ionic radius (0.72 \AA nickel ions, 1.19 \AA lead ions) (Bohli *et al.* 2013).

The intraparticle diffusion model explains the adsorption process in three steps: film diffusion or fast adsorption, intraparticle diffusion or the diffusion of metal ions through the pores of the adsorbent, and finally, the equilibrium step where adsorption and desorption occurs between the active sites and the metal ions (Wu *et al.* 2009; Boparai *et al.* 2011). The linear expression of the model is described as follows:

$$q_t = k_p t^{0.5} + x \quad (6)$$

where x and k_p are the boundary layer thickness and the rate constant of the intraparticle diffusion process, respectively. As can be seen from Figure 8(c) and 8(f) (Table 3), the adsorption process goes through three steps, indicating that the adsorption process is not only controlled by intraparticle diffusion.

SEM-EDX analysis of biomass

Loaded biomass samples with lead(II) and nickel(II) ions were analysed by SEM-EDX to confirm the adsorption of lead(II) and nickel(II) ions on the biomass, as can be seen from Figure 9. The results revealed that lead(II) and nickel(II) ions were adsorbed in and on the surface of the biomass.

Table 2 | Pseudo-second-order kinetic model for the adsorption of lead(II) and nickel(II) ions by Bermuda grass biomass

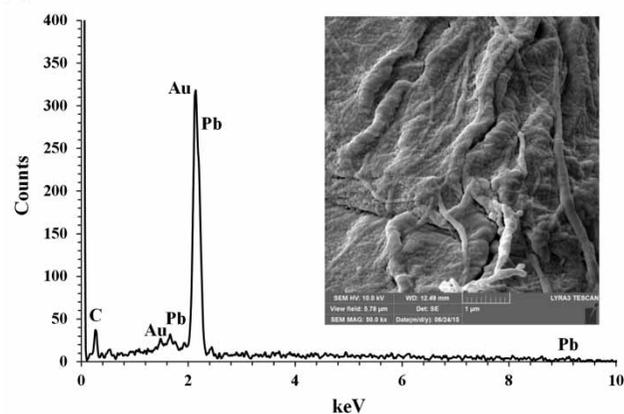
Metal ion	Temperature (K)	$q_{e, \text{exp}}$ (mg g^{-1})	$q_{e, \text{cal}}$ (mg g^{-1})	k_2 ($\text{h}^{-1} \text{g mg}^{-1}$)	h^a ($\text{h}^{-1} \text{g}^{-1} \text{mg}$)	R^2
Pb(II)	295	7.78	7.955	1.129	71.42	0.9996
	308	8.57	8.734	1.441	109.9	0.9999
	323	7.64	7.825	1.103	67.57	0.9994
Ni(II)	295	2.80	2.853	4.372	35.59	0.9998
	308	2.91	2.920	11.85	101.0	0.9998
	323	2.55	2.610	5.280	35.97	0.9997

^aInitial adsorption rate $h = k_2 q_e^2$.

Table 3 | The intraparticle diffusion model constants

Metal ion	Temperature (K)	x	k_p ($\text{mg h}^{0.5}/\text{g}$)	R^2
Pb(II)	295	3.618	3.713	0.9968
	308	2.941	6.771	0.9989
	323	3.345	3.819	0.9882
Ni(II)	295	1.519	1.263	0.9833
	308	1.877	1.179	0.9804
	323	1.505	0.954	0.9890

(a) Adsorbent loaded with Pb ions.



(b) Adsorbent loaded with Ni ions

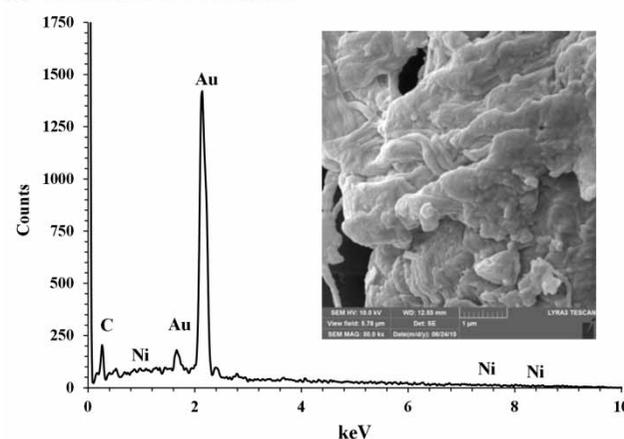


Figure 9 | SEM-EDX for the adsorption of lead(II) and nickel(II) ions by Bermuda grass biomass.

CONCLUSIONS

The physicochemical characteristics of Bermuda grass biomass confirmed that it is a very interesting material containing functional groups in its structure that can easily adsorb positively charged metal ions. The adsorption process was determined by different parameters, such as pH

of the reaction system, biomass dosage, temperature and contact time. The results proved that Bermuda grass biomass has the potential to be a natural adsorbent for the removal of lead(II) and nickel(II) ions from aqueous solutions. Furthermore, the undoubted advantages of this material include its availability, low cost, biodegradability and efficiency in its application in the purification of aqueous solutions containing different types of metal ions.

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