# Removal of Pb(II) using the modified lawny grass: Mechanism, kinetics, equilibrium and thermodynamic studies

Dandan Lu[a], Qilin Cao[b], Xiuju Cao[a], Fang Luo[a],*

[a] Key Laboratory of Polyoxometalates Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun 130024, China
[b] Duoluoshan Sapphire Rare Metal Co. Ltd of Zhaoqing, Sihui 526200, PR China

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## ABSTRACT

A series of new chemical-modified lawny grass adsorbents were prepared and the feasibility of absorbents to remove Pb(II) ion from aqueous solution was examined. The absorbents were characterized by FTIR spectra and elemental analysis. Kinetics, equilibrium, thermodynamics, column adsorption and mechanism were studied. The optimum pH is in the range of 5.0–5.8 for all adsorbents. The sorption system follows pseudo-second-order kinetic model and equilibrium time is obtained after 60 min. The maximum adsorption capacities obtained from Langmuir–Freundlich model are 1.55 and 1.26 mol/kg by using 1 CG and 0.6 CG (lawny grass modified by 1 mol/L or 0.6 mol/L citric acid, respectively). Thermodynamic parameters such as $\Delta G$, $\Delta H$ and $\Delta S$ are evaluated for the adsorption process. The results indicates that the adsorption of Pb(II) is spontaneous and endothermic. The breakthrough point is achieved at 100 BV (bed volume) by a column of 0.6 CG. Desorption of Pb(II) and regeneration of the column is achieved by 0.1 mol/L HCl elution. After 3 adsorption/desorption cycles, the breakthrough point remains around 100 BV, which shows that grass adsorbent is regenerated easily and used repeatedly. Above results indicates that lawny grass have a good potential for removal of lead from dilute aqueous solution in the future.

## 1. Introduction

Lead is attracting wide attention of environmentalists as one of the most toxic heavy metals. Lead exists in several industrial and mining wastes, such as chemicals and allied products, lead acid storage batteries, ceramic and glass industries printing, ammunition, lead smelting and mine tailings. In addition, lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain [1,2]. So the disposal of industrial effluents containing lead ions has caused serious societal concern.

Many physical–chemical methods, included chemical reduction, ion exchange, electrochemical treatment, chemical precipitation, membrane separation etc, have been proposed for Pb(II) removal from industrial effluent. However, these methods are often inefficient and/or cost disadvantageous when they are used to remove Pb(II) in low concentration solution, which has led to the investigation of low cost technologies that may be efficiently applied for Pb(II) removal from industrial effluent [3]. For this purpose, numerous biomaterials have been investigated and found useful, such as orange peel [4], marine algae [5,6], rice husk [7], coconut shell [8,9],

wood and bark [10], sugar cane husk and sawdust [11]. Lawny grass principally contains protein, crude fibre, amylum, polysaccharides, pectin, chlorophyll, etc. The rude fibre consists of cellulose, hemi-cellulose and lignin, indicating the feasibility for removing toxic metal ions or enriching trace elements from aqueous solution due to the present of various interesting functional groups on the cellulose; moreover, excess lawny grass is left as solid waste during the process of city beautifying or gardens building. Based on above-mentioned advantages, lawny grass is chosen as the adsorbent for Pb(II) adsorption from aqueous solution.

In this paper, lawny grass as a novel biosorbent was proposed for the removal/recovery of lead from dilute solutions. Its feasibility for Pb(II) removal was assessed by studying the effect of pH, contact time, initial concentration, solid/liquid ratio and temperature on Pb(II) adsorption. In addition, in order to evaluate its practicability of Pb(II) removal by lawny grass, column study was also carried out.

## 2. Experiments

### 2.1. Adsorbents

#### 2.1.1. Raw material

Grass obtained from the lawn of our campus, was washed with water to remove mud, sand and the other contaminants, then

* Corresponding author. Tel.: +86 431 8509 9667 fax: +86 431 8509 9667.
E-mail address: luof746@nenu.edu.cn (F. Luo).

oven-dried at about 60 °C for 12 h. The dried grass was milled with a muller and sieved to a smaller particle by a boult with the diameter of 0.25 mm. 30 g dried grass and 700 mL 20% iso-propyl alcohol were added together into a beaker and stirred for 24 h at room temperature, then filtered and washed with distilled water until the filtrate was colorless. The filter residue was dried in an oven at 60 °C for 12 h, and used in our experiments as raw materials, hereafter abbreviated as RG. Its major chemical constituents are cellulose, hemi-cellulose and lignin.

### 2.1.2. Modified with alkali saponification
6 g RG of was taken in a beaker together with 100 mL 0.1 mol/L NaOH and stirred for 1 h at room temperature. After filtered, this sample was washed with distilled water until pH was neutral. The filter residue was dried in an oven at 60 °C for 24 h. Hereafter abbreviated as SG.

### 2.1.3. Modified with $ZnCl_2$
3 g RG of was soaked in 400 mL $ZnCl_2$ solution with weight ratio of 2:1, then soaked in boiling water for 60 min. After filtered, this sample was washed with distilled water to get rid of excess zinc chloride. The filter residue was dried in an oven at 60 °C for 24 h. Hereafter abbreviated as ZCG.

### 2.1.4. Modified with $CaCl_2$/$MgCl_2$/NaCl mixture
5 g RG of was soaked in 100 mL 0.2 mol/L NaOH and stirred for 6 h at room temperature. After filtered, the filter residue was washed three times with distilled water (each time 100 mL) to remove excess sodium hydroxide and then soaked in 750 mL of $CaCl_2$/$MgCl_2$/NaCl solution with volume ratio of 1:1:1, and stirred for 4 h. The concentrations of $CaCl_2$, $MgCl_2$ and NaCl are 1.0 mol/L, 0.5 mol/L and 0.5 mol/L, respectively. pH was adjusted to 7.0 by 0.1 mol/L NaOH or 0.1 mol/L HCl. After filtered, this sample was washed to remove excess metal ions with distilled water. The filter residue was dried in an oven at 60 °C for 24 h. Hereafter abbreviated as CMNG.

### 2.1.5. Modified with citric acid
This modified method of citric acid was proposed by Vaughan et al. [12] and Leyva-Ramos et al. [13]. 4 g RG and 100 mL 0.1, 0.6 or 1.0 mol/L citric acid solution were mixed in a beaker, respectively and stirred at 60 °C for 2 h. Then filtered and dried in a convection oven at 60 °C for 12 h, in succession the temperature was increased up to 120 °C for 3 h. After that, the product was washed time and again with distilled water until pH was neutral. Finally, it was dried in oven at 60 °C for 12 h. Hereafter abbreviated as 0.1 CG, 0.6 CG or 1 CG, respectively.

### 2.1.6. Modified with phosphoric acid
Another adsorbent was obtained by above pretreatment with only one change of 0.6 mol/L phosphoric acid instead of citric acid. Hereafter abbreviated as 0.6 PG.

### 2.1.7. Modified with 0.6 mol/L citric acid after saponification with 0.1 mol/L NaOH
This adsorbent was obtained by the same pretreatment process of citric acid modification but only one change of 4 g SG instead of 4 g RG. Hereafter abbreviated as 0.6 SCG.

### 2.2. Reagents and measurements
The stock solution of Pb(II) was prepared by dissolving a weighed quantity of lead chloride in 25 mL 0.1 mol/L NaCl and 10 mL hexamethylene tetramine buffer solution (pH 5.0) and diluting quantitatively to a volume of 250 mL. Before mixing with grass adsorbents, initial pH of each solution was adjusted to an appropriate value by adding 0.1 mol/L HCl or/and NaOH solutions. All the reagents were analytical grade. A pHs-3C model acidity meter (made in China) was used to measure pH values of all solutions. The concentration of Pb(II) was titrated with standard EDTA solution, 0.1% xylenol orange was chosen as indicator and 30% hexamethylene tetramine was used as buffer solution.

### 2.3. Elemental analysis of raw lawny grass
Elemental analysis of raw lawny grass was carried out using GmbH Elementar. The sample was heated in an oven from 25 °C up to 1000 °C at a heating rate of 10 °C /min. The gases generated from heating were analyzed by an electrical conductivity detector.

### 2.4. FTIR spectroscopy
The raw and modified lawny grass adsorbents were analyzed using a Fourier Transform Infrared Spectrometer (Nicolet MagNA-IR 560-spectrophotometer) under ambient conditions. The spectra were recorded from 4000 to 400 cm$^{-1}$ using KBr window.

### 2.5. Determination of active sites
Acidic and basic sites on both raw and chemically modified lawny grass were determined by the acid–base titration method proposed by Boehm [14]. The total acid sites were neutralized using 0.1 mol/L NaOH solution while the basic sites were neutralized with 0.1 mol/L HCl solution. The acidic and basic sites were determined by adding 50 mL of 0.1 mol/L titration solutions and 0.2 g of lawny grass to a 50 mL flask. These flasks were left there for 5 days at room temperature and agitated manually twice a day. Finally, a 10 mL sample was titrated with 0.1 mol/L HCl or NaOH.

### 2.6. Determination of the point of zero charge
Point of zero charge (abbreviated as PZC) of adsorbents was determined by following procedure: 100 mL of distilled water was added to an Erlenmeyer flask, which was then capped with cotton. The distilled water was heated until boiling for 20 min to eliminate $CO_2$ dissolved in water. Once stopped heating, this flask should be capped immediately to prevent $CO_2$ dissolving in water again. On the other hand, 0.2 g of adsorbent was placed in a 25 mL Erlenmeyer flask to which 15 mL of $CO_2$-free water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at room temperature. Then pH of filtrate was measured and this value is point of zero charge. This method has been used satisfactorily by Moreno-Castilla et al. [15] and Leyva-Ramos et al. [13].

### 2.7. Column test
Appropriate 0.6 CG was soaked in distilled water for 6 h. Then it was filled into a glass column with 1.1 cm diameter and 21.5 cm length. Finally, the height of column bed was fixed at 5.0 cm. 0.001 mol/L Pb(II) solution with initial pH 5.1 was pumped downflow through the fix-bed column at a constant volume velocity of 3 mL/min. Effluent was collected regularly and analyzed for the concentration of Pb(II) in this effluent. After saturation, 0.1 mol/L HCl solution was used as eluant for desorption with 3 mL/min flow rate. Elution outlet samples were collected and analyzed by the same procedure used in adsorption experiments. After elution, the column bed was rinsed with distilled water until its pH reached the value of initial Pb(II) solution in the biosorption process. The

regenerated column was reused for the next adsorption–desorption recycle experiments.

## 2.8. Adsorption procedure

The adsorption amount ($q$) and the removal percentage ($E\%$) are calculated according to Eqs. (1) and (2):

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$E\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where $q$ is the adsorption amount of metal ion (mol/kg), $W$ is the weight of adsorbent (g), $V$ is the volume of solution (L), and $C_0$ and $C_e$ are the initial and equilibrium concentrations of Pb(II) in solution, respectively (mol/L).

### 2.8.1. Kinetics models

Pseudo-first-order kinetic model [16,17] is generally expressed as Eq. (3):

$$\ln \frac{q_e - q_t}{q_e} = -K_1 t \tag{3}$$

where $q_t$ and $q_e$ are the amounts of Pb(II) adsorbed (mol/kg) at the time $t$ and equilibrium time, $K_1$ is the pseudo-first-order rate constant (L/min).

Pseudo-second-order kinetic model [18] is expressed as following formulation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where $K_2$ is the pseudo-second-order rate constant (kg/(mol min)).

### 2.8.2. Isotherm models

Langmuir model:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{5}$$

where $q_m$ is the maximum adsorption amount of metal ion per unit weight of adsorbent at $C_e$, $b$ is the affinity constant.

Freundlich model:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where $K_f$ and $n$ are the Freundlich constants.

The Langmuir–Freundlich model [19]:

$$q_e = q_m \frac{b C_e^{1/n}}{1 + b C_e^{1/n}} \tag{7}$$

## 3. Result and discussion

### 3.1. Characters of lawny grass

Elemental analysis results shows that the raw lawny grass is composed of 43.69% carbon, 5.63% hydrogen, 47.04% oxygen and 3.64% nitrogen.

Different chemical reagents are applied to modify lawny grass in order to enhance its adsorption ability. Firstly, 20% iso-propyl alcohol is used to discolor and remove organic compound and organic small molecule. Then filters and washes repeatedly with distilled water in order to remove water-soluble residue, impurity and polarity compound. Finally, RG is obtained, major chemical constituents of which are cellulose, hemi-cellulose and lignin. For enhancing the number of functional groups on cellulose, a series of chemical modifications are further performed. In the modified process, 0.1 mol/L NaOH is utilized to make carboxylic
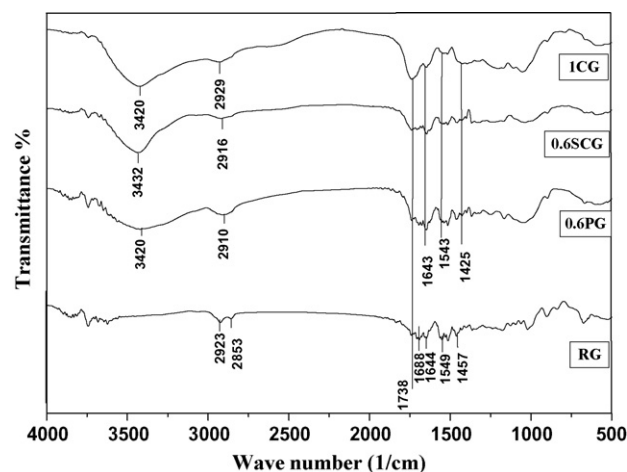


Fig. 1. The FTIR spectra of RG, 0.6 PG, 0.6 SCG and 1 CG.

groups on the surface of cellulose bare and convert H$^+$ type of functional groups into Na$^+$ type so that Pb(II) ions can react with them more easily. ZnCl$_2$ is expected to enhance the amount of micropore, it is equal to expand the surface area of adsorbents which is useful for Pb(II) adsorption. CaCl$_2$/MgCl$_2$/NaCl mixture is selected to exchange H$^+$ type of carboxylic groups to Ca$^{2+}$, Mg$^{2+}$ or Na$^+$ type in order to increase ion-exchange ability. Phosphoric acid can oxidize some groups on cellulose and introduce hydroxyl to the surface of cellulose. Citric acid is chosen to introduce carboxylic groups to cellulose for increasing the amount of surface functional groups upon cellulose. The reactive anhydride is combined with cellulosic hydroxyl groups so as to form an ester linkage and introduce carboxyl groups to the cellulose. The addition of carboxylic function groups increases adsorbents' abilities of binding with positively charged metal ions [20,21]. Finally, a series of chemically modified grass adsorbents are obtained.

FTIR analysis is used to identify some characteristic functional groups and estimate the number ratio of carboxyl before and after chemical modification. It is reported that hydroxyl (–OH) stretching vibration bands is at wave number of 3420 cm$^{-1}$. The doublet peaks at wave number of 2923 cm$^{-1}$ and 2853 cm$^{-1}$ are due to the asymmetric and symmetric stretch of aliphatic chains (–CH) [22]. The absorption band of carbonyl (C=O) stretching and hydroxyl (–OH) deformation vibration of carboxylic groups is at about 1740 and 1644 cm$^{-1}$, respectively [23]. A peak around 1540 cm$^{-1}$ corresponds to the amide [24] and a peak at 1450 cm$^{-1}$ is the symmetric C=O stretching [25]. FTIR spectra as illustrated in Fig. 1 also confirm that the wave number of alkyl (–CH), carbonyl (C=O) and hydroxyl (–OH) of carboxylic groups and amide are 2923 and 2853, 1738 and 1688, 1644, 1549 and 1457 cm$^{-1}$, respectively. For 1 CG, it is observed that the peak at 1738 cm$^{-1}$ stayed in position, but the peak at 1688 cm$^{-1}$ disappear, amide vibration shifts from 1549 to 1543 cm$^{-1}$, hydroxyl (–OH) of carboxylic groups shifts a little from 1644 to 1643 cm$^{-1}$, alkyl (–CH) shifts from 2923 to 2929 cm$^{-1}$ and become a broad peak, hydroxyl (–OH) appear at wave number of 3420 cm$^{-1}$. For 0.6 PG and 0.6 SCG, hydroxyl (–OH) appear at wave number of 3420 and 3432 cm$^{-1}$, respectively. In comparison with hydroxyl (–OH) stretching vibration band of RG, that of 0.6 PG, 0.6 SCG and 1 CG broaden clearly. Moreover, the doublet peaks at wave number 2923 cm$^{-1}$ and 2853 cm$^{-1}$ become a broad peak, which shifts to 2910 cm$^{-1}$ for 0.6 PG and 2916 cm$^{-1}$ for 0.6 SCG. Through appearance and disappearance of different peaks, it indicates that some functional groups (–COOH and –OH) have been successfully introduced into the surface of adsorbents after chemical modification. These functional
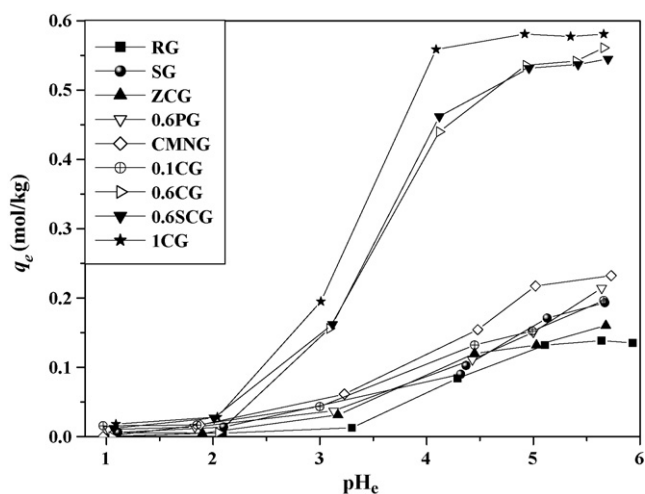
**Fig. 2.** Effect of pH on Pb(II) adsorption by different grass adsorbents (initial lead concentration = 0.001 mol/L; weight of adsorbents = 0.025 g; volume of Pb(II) = 15 mL; contact time = 4 h).

**Table 1**
Concentration of active sites and point of zero charge (PZC).

| Sorbents type | Acidic sites (mol/kg) | Basic sites (mol/kg) | PZC |
|---|---|---|---|
| 0.1 CG | 1.6 | 2.8 | 5.0 |
| 0.6 CG | 5.2 | 2.5 | 3.8 |
| 1 CG | 6.2 | 1.7 | 3.6 |
| 0.6 SCG | 4.8 | 2.4 | 3.7 |
| 0.6 PG | 3.3 | 2.6 | 4.8 |
| ZCG | 2.0 | 2.6 | 5.7 |
| SG | 2.7 | 3.7 | 7.0 |
| CMNG | 2.0 | 3.5 | 7.6 |

groups are very effective in capturing Pb(II) ion from aqueous solution.

### 3.2. Effect of pH on Pb(II) adsorption

Acidity of a solution has two effects on metal sorption. Firstly, protons in acid solution can protonate binding sites of chelating molecules. Secondly, hydroxide in basic solution may be complex and precipitate many metals. Therefore, pH of a solution is the first parameter to be optimized [26].

For obtaining an optimum pH for Pb(II) adsorption by our modified grass adsorbents, a series of experiments were investigated at different $pH_e$. Fig. 2 illustrates a relationship between lead uptake and equilibrium $pH_e$ by different adsorbents. It is observed that higher $pH_e$ values leads to higher lead uptake.

When $pH_e < 2$, hydrogen proton may compete with lead ions for active binding sites on the surface of grass, which leads to fewer binding sites being available to bind lead ions, so the adsorption amount of Pb(II) is very little. As $pH_e$ increases there are fewer hydrogen proton in solution, this means that there is less competition for binding sites and more binding sites are released, which results in the increase of adsorption amount of Pb(II). In Pb(II) adsorptive process a sharply increase occurs at $pH_e = 3.5$ and the maximum Pb(II) adsorption amount are obtained in $pH_e$ range of 5.0–5.8. In this $pH_e$ range, Pb(II) removal efficiencies of RG is about 22%, 0.6 PG, 0.1 CG, CMNG, SG and ZCG are little higher effect than RG, all of them are around 30%. But 0.6 CG, 0.6 SCG and 1 CG exhibits an outstanding adsorption ability, Pb(II) removal efficiencies of 0.6 CG and 0.6 SCG are more than 90%, and that of 1 CG is almost 100%. The adsorption capacities of Pb(II) with different adsorbents decreases in this order: 1 CG > 0.6 CG ≈ 0.6 SCG > CMNG ≈ 0.6 PG ≈ 0.1 CG ≈ SG ≈ ZCG > RG. At higher $pH_e$, the formation of lead hydroxide decreases the concentration of free Pb(II) ions, thereby the adsorption capacity of Pb(II) is decreased. Herein the optimum pH range is chosen to be 5.0–5.8. The solution pH diminishes after adsorption, which indicates that ion-exchange mechanism is involved in the adsorption process.

Active sites and points of zero charge (PZC) of different adsorbents were determined and the results were shown in Table 1. It can be seen that concentrations of acidic sites are different due to different chemical modification, the order is 1 CG > 0.6 CG > 0.6 SCG > 0.6 PG ≈ SG CMNG ≈ 0.1 CG ≈ ZCG. It is

same with the adsorbed amount of Pb(II) shown in above section. PZC shown in Table 1 also can be used to explain the effect of pH on Pb(II) adsorption. At pH = PZC, the surface charge of adsorbents is neutral, it is negligible of the electrostatic force between Pb(II) and surface of adsorbents. When pH > or < PZC, this balance is broken. At pH < PZC, the surface charge of adsorbents is positive, so adsorbents have a positive surface. There is an electrostatic repulsion between Pb(II) and this positive surface, which results in low lead sorption. At pH > PZC, the surface charge of adsorbents is negative, the surface of adsorbents is negative, too, so Pb(II) ions in solution are attracted to this surface. The lower PZC is, the more Pb(II) ions are attracted to this surface, this is attributed to the surface of adsorbents becoming more negative [13]. Maximum sorption is likely to occur at pH values greater than PZC when adsorbents have a net negative charge [27]. The rule of PZC agrees with the adsorption behaviors of adsorbents for Pb(II). As can be seen from Table 1, PZC of 1 CG is 3.6, which is the lowest PZC, so it has the maximum adsorbed amount for Pb(II). PZC of other adsorbents is high, especially some adsorbents such as CMNG and SG, their PZC are higher than the optimal pH, so they have lower adsorbed amount of Pb(II). The adsorbents 1 CG, 0.6 CG and 0.1 CG are chosen to investigate effect of concentrations of citric acid on modifying lawny grass. With increasing concentration of citric acid, more surface functional groups are gained. This finding is also supported by determination of active sites and PZC. The concentrations of active sites for 1 CG, 0.6 CG and 0.1 CG are 6.2, 5.2 and 1.6 mol/kg and PZC of 1 CG, 0.6 CG and 0.1 CG is 3.6, 3.8 and 5.0, respectively, so the order for Pb(II) adsorption is 1 CG > 0.6 CG > 0.1 CG. After consideration of removal efficiency and economic benefit, 1 CG, 0.6 CG and 0.6 SCG are chosen as primary adsorbents to adsorb lead ions in next study.

### 3.3. Effects of contact time on Pb(II) adsorption

Fig. 3 shows contact time profiles of the modified grass adsorbents on Pb(II) adsorption (0.001 mol/L). A very rapid increasing trend is observed during initial 40 min, and thereafter, the rate of Pb(II) adsorption decreases, after about 60 min, no significant change in Pb(II) removal is obtained. During initial stage of sorption, a large number of vacant surface sites are available for Pb(II) adsorption. After lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces from lead ions adsorbed on adsorbents surface. Here, the active external sites get almost saturated. Thereafter, lead ions have to traverse farther and deeper into the active intra-particular sites encountering much larger resistance. This slows down the rate of Pb(II) adsorption during later period of adsorption. During adsorption process, the rate of Pb(II) adsorption using 1 CG is faster than that using 0.6 CG and 0.6 SCG. It may be due to the difference on the amount of available active sites on the surface of adsorbents.

Experimental data are processed by pseudo-first and second-order kinetic models and the results are presented in Table 2. As

**Table 2**
The parameters of pseudo-first and second-order kinetics models.

| Sorbent type | The pseudo-first-order model | | | The pseudo-second-order model | | |
|---|---|---|---|---|---|---|
| | $R^2$ | $q_e$ (mol/kg) | $K_1$ (L/min) | $R^2$ | $q_e$ (mol/kg) | $K_2$ (kg/(mol min)) |
| 0.6 CG | 0.90 | 0.42 | 0.10 | 0.96 | 0.47 | 0.31 |
| 1 CG | 0.92 | 0.46 | 0.23 | 0.98 | 0.49 | 0.76 |
| 0.6 SCG | 0.97 | 0.41 | 0.097 | 0.99 | 0.46 | 0.28 |

shown in Table 2, pseudo-second-order kinetic model provides much better $R^2$ values (0.96, 0.98 and 0.99) than that of pseudo-first-order kinetic model (0.90, 0.92 and 0.97), which indicates that pseudo-second-order kinetic model have a better agreement with experimental data for all sorbents than that of pseudo-first-order kinetic model. Pseudo-second-order kinetic rate constants $K_2$ are 0.76 kg/(mol min) for 1 CG, 0.31 kg/(mol min) for 0.6 CG and 0.28 kg/(mol min) for 0.6 SCG, respectively.

Besides adsorption at external surface of biosorbents, there is a possibility of intraparticle diffusion from the external surface into the pore of biosorbents[28], this possibility is explored by plotting of $q_t$ versus $t^{1/2}$, according to Weber–Morris model, $q_t = K_{id} t^{1/2}$ [29], where $K_{id}$ is the intraparticle diffusion coefficient. The plots are shown in Fig. 4. It can be seen that these plots are multi linear curves with three distinct regions. The initial curve stage relates the adsorption of external surface. The second region corresponds to the gradual uptake, which reflects intraparticle diffusion as the rate limiting step. Final plateau region indicates equilibrium uptake. It shows that the intraparticle diffusion is not the only rate controlling step [30].

### 3.4. Effects of the initial concentration of Pb(II) on adsorption

The effect of initial concentration on Pb(II) removal by the modified grass adsorbents is investigated and illustrated in Fig. 5. It can be seen that the curve has a steep increase when concentration of lead ions rises from 0.0005 to 0.002 mol/L, then the curve becomes mild, when concentration of lead ions is about 0.003 mol/L, the curve leans to a beeline, which denotes the adsorption amount of Pb(II) do not increase. At lower Pb(II) concentrations, sufficient adsorption sites are available for adsorbing Pb(II). However, the numbers of Pb(II) are relatively higher as compared to availability of binding sites at higher Pb(II) concentrations. Due to restriction
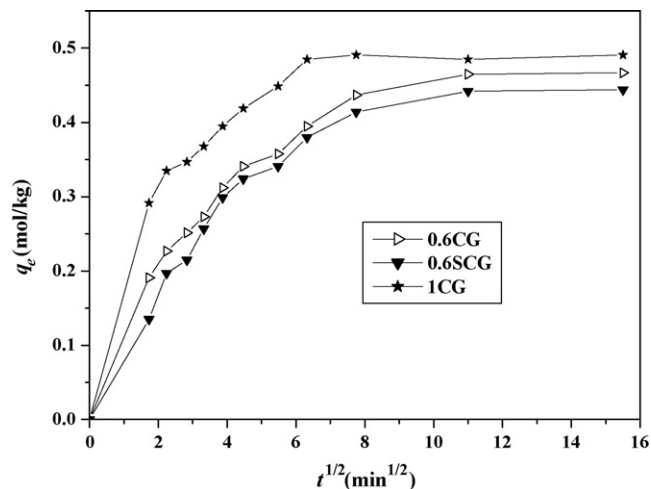


**Fig. 4.** Intraparticle diffusion plots on Pb(II) adsorption by different grass adsorbents (initial lead concentration = 0.001 mol/L; weight of adsorbents = 0.025 g; volume of Pb(II) = 15 mL; initial pH 5.1).

of binding sites present on the surface of grass, adsorbents become saturated at higher Pb(II) concentration.

Langmuir, Freundlich and Langmuir–Freundlich models are applied to describe equilibrium sorption isotherm, and parameters of these models are given in Table 3. For Pb(II) adsorption, the correlation coefficient $R^2$ for Langmuir and Langmuir–Freundlich are all higher than 0.95, for Freundlich $R^2$ are higher than 0.90. This indicates that all models fits the experimental data well. A comparison of different isotherm models reveals that Langmuir–Freundlich model fits the experimental data best. Values of $q_m$ calculates from Langmuir–Freundlich model are 1.55, 1.26 and 1.08 mol/kg for 1 CG, 0.6 CG and 0.6 SCG, respectively. The Langmuir affinity constant $b$ is related to an affinity between adsorbent and adsorbate. The larger values of $b$ are, the higher this affinity is. Adsorbents with the highest possible $q_m$ and a high value of $b$ are the most desirable of the
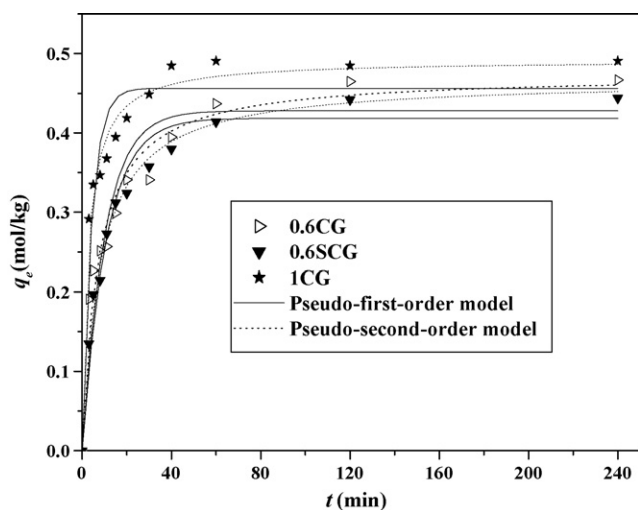


**Fig. 3.** Effect of contact time on Pb(II) uptakes by different grass adsorbents (weight of adsorbents = 0.025 g; volume of Pb(II) = 15 mL; initial lead concentration = 0.001 mol/L; initial pH 5.1).
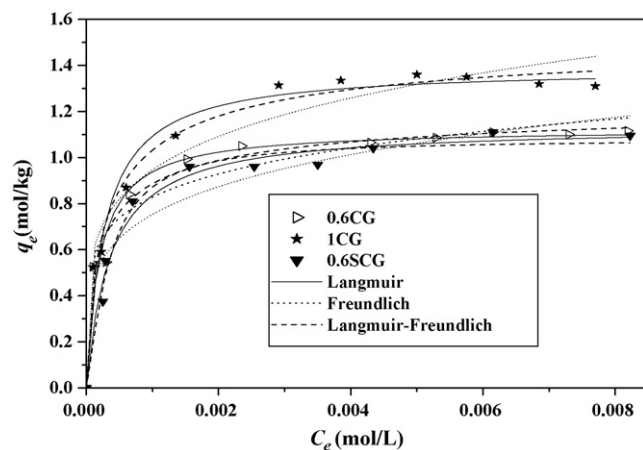


**Fig. 5.** Adsorption isotherms of Pb(II) by different grass adsorbents (initial pH 4.85; weight of adsorbents = 0.025 g; volume of Pb(II) = 15 mL; contact time = 4 h).

**Table 3**
Langmuir, Freundlich and L–F models parameters for Pb(II) adsorption equilibrium.

| Sorbent type | $q_m$ (mol/kg) | $b$ | $K$ | $n$ | $R^2$ | Sorption model |
|---|---|---|---|---|---|---|
| | 1.13 | 5.01 | | | 0.97 | Langmuir |
| 0.6 CG | | | 2.59 | 6.06 | 0.96 | Freundlich |
| | 1.26 | 0.167 | | 1.63 | 0.98 | L–F |
| | 1.39 | 3.68 | | | 0.98 | Langmuir |
| 1 CG | | | 3.91 | 4.87 | 0.96 | Freundlich |
| | 1.55 | 0.219 | | 1.47 | 0.99 | L–F |
| | 1.14 | 2.80 | | | 0.98 | Langmuir |
| 0.6 SCG | | | 3.30 | 4.68 | 0.94 | Freundlich |
| | 1.08 | 32.9 | | 0.770 | 0.98 | L–F |

**Table 4**
Maximum adsorption capacities of different lignocellulosic adsorbents and 1 CG for Pb(II).

| Adsorbent | | Adsorption capacity (mg/g) | Reference |
|---|---|---|---|
| Sugar beet pulp | | 73.8 | [31,32] |
| Wheat bran | | 62.1 | [33] |
| Lignocellulosic agrowastes | Sugar beet pulp | 60 | |
| | Rice husk | 108 | |
| | Rice husk | 45 | [34] |
| | Rice husk | 11.4 | |
| Lawny grass-1 CG | | 320.9 | Present study |

three of adsorbents, 1 CG shows the best Pb(II) adsorption performance compared with 0.6 CG and 0.6 SCG. Adsorption capacities of different lignocellulosic adsorbents collected from the references are listed in Table 4 along with the values corresponding to 1 CG for comparison. From Table 4, 1 CG exhibits higher adsorption capacity compared with other adsorbents.

Fig. 6 presents adsorption isotherms of Pb(II) by 1 CG at various equilibrium pH values. It can be seen that the trend of these curves is similar to that of Fig. 5. All isotherms in Fig. 6 are fitted to Langmuir model with high correlation coefficient $R^2$. Similar results have been reported by other researchers, e.g. for uptake of copper and cadmium by *Sphaerotilus natans* [35], and for biosorption of cadmium and zinc onto the aquatic moss *Fontinalis antipyretica* [36]. As the increase of equilibrium pH, it is also increased for deprotonation of functional groups on the surfaces of adsorbents, This result in increasing of Pb(II) adsorption, which suggests that the adsorption process of Pb(II) occurs primarily via electrostatic interactions between positive charged Pb(II) and the negative surfaces of adsorbents.
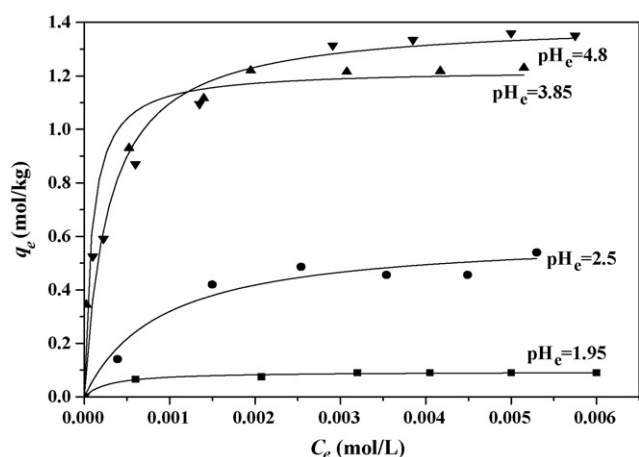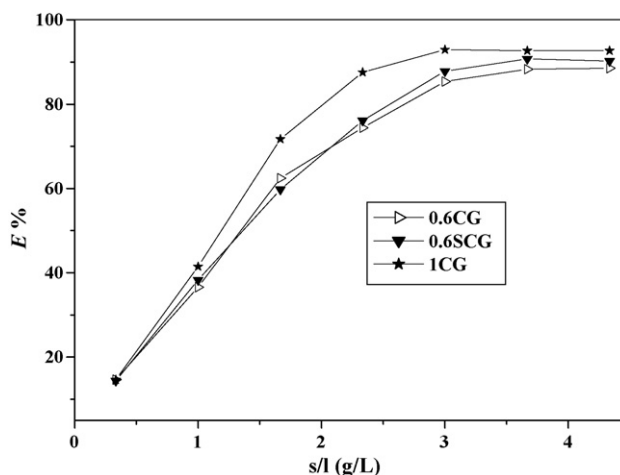


**Fig. 7.** Effect of s/l ratio on Pb(II) adsorption by different grass adsorbents (initial pH 5.1; initial lead concentration = 0.002 mol/L; contact time = 4 h).

### 3.5. Effects of solid/liquid ratio on Pb(II) adsorption

The influence of solid/liquid ratio (abbreviated as s/l) on Pb(II) adsorption is investigated and represented in Fig. 7. In a batch system experiments, various s/l ratios are tested to evaluate optimum adsorbent weight per unit solution volume, while the concentration of Pb(II) is fixed at 0.002 mol/L. It is to be noted from the results that, initially, the removal efficiency of Pb(II) increases with the increase of s/l ratio, then changes a little when s/l ratio reaches some value. The maximum removal percent obtained is almost 90% when s/l is after 3.67 g/L. In terms of high removal percent and cost effect, optimum s/l ratio is pitched on 3.67 g/L.

### 3.6. Effects of temperature on Pb(II) adsorption

Temperature may play an important role in the process of Pb(II) removal. So batch experiments are performed under different temperatures from 278 K to 328 K to examine the effect of temperature on Pb(II) adsorption by the modified grass adsorbents. The results are presented in Fig. 8, which is the plot of $1/T$ versus $\ln K_d$. $K_d$ is the distribution coefficient and can be calculated from the following



**Fig. 6.** Effect of pH on Pb(II) adsorption by 1 CG at different initial concentration of Pb(II).
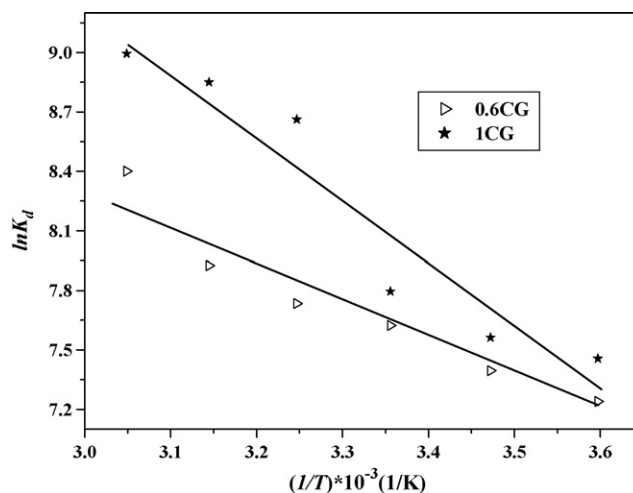


**Fig. 8.** Plots of $1/T$ vs. $\ln K_d$ on Pb(II) uptake by 0.6 CG and 1 CG (initial pH 5.1; weight of adsorbents = 0.025 g; volume of Pb(II) = 15 mL; contact time = 30 min; initial lead concentration = 0.001 mol/L).

**Table 5**
Thermodynamic parameters for Pb(II) adsorption.

| Sorbent type | $\Delta H$ (kJ/mol) | $\Delta S$ (kJ/(mol K)) | $\Delta G$ (kJ/mol) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 278 K | 288 K | 298 K | 308 K | 318 K | 328 K |
| 0.6 CG | 0.016 | 0.12 | −33.34 | −34.54 | −35.74 | −36.94 | −38.14 | −39.34 |
| 1 CG | 0.027 | 0.16 | −44.45 | −46.05 | −47.65 | −49.25 | −50.85 | −52.45 |

equation:

$$K_d = \frac{(C_0 - C_e)V}{C_e W} \tag{8}$$

With the increase of temperature, the adsorbed amount of Pb(II) increases from 0.45 to 0.60 mol/kg by 1 CG and 0.42 to 0.53 mol/kg by 0.6 CG, indicating this sorption process is endothermic in nature. That may be attributed to either change in pore size of the adsorbent causing intra particle diffusion within the pores or enhancement in the chemical affinity of lead ions to the surface of adsorbent leading to some chemical interaction to take place during adsorption process [37]. And with the increase of temperature, an important driving force is provided to overcome mass transfer resistance of Pb(II) between aqueous and surface of the adsorbents, leading to diffusion rate of Pb(II) in external mass transport process increases, so greater adsorption is observed. Further, above results are confirmed by various thermodynamic parameters evaluated for adsorption.

Thermodynamic parameters namely free energy $\Delta G$, enthalpy changes $\Delta H$ and entropy change $\Delta S$ are calculated from slopes and intercepts of linear variation plot of $1/T$ versus $\ln K_d$ according to following equations [38] and the results are shown in Table 5.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{9}$$

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

where $R$ is the gas constant (8.314 J/mol K), $T$ is the temperature (K).

As illuminated in Table 5, values of $\Delta H$ and $\Delta S$ are 0.016 kJ/mol and 0.12 kJ/(mol K) for 0.6 CG, and 0.027 kJ/mol and 0.16 kJ/(mol K) for 1 CG, respectively. The positive value of $\Delta H$ indicated endothermic nature of adsorption process. The positive value of $\Delta S$ shows an affinity of these adsorbents and the increasing randomness at the solid–solution interface during adsorption process of Pb(II). The negative value of $\Delta G$ indicates a feasibility and spontaneous nature of this adsorption process. The values of $\Delta G$ are found to increase as temperature increased, indicating more driving force and hence resulting in higher adsorption capacity.
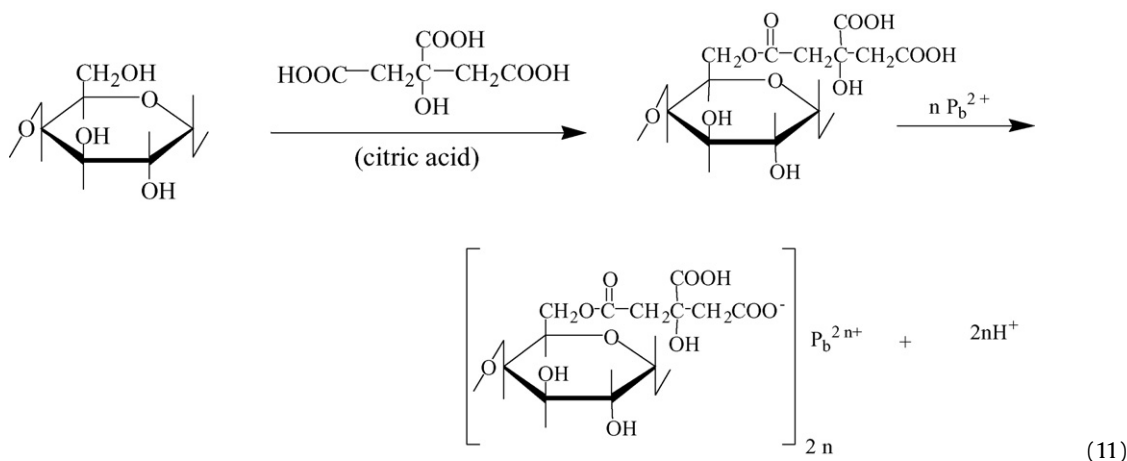
### 3.7. Column study

Based on the batch experimental results shown earlier, column study is also performed. The experimental breakthrough curves are used to calculate the column capacity at complete exhaustion, which is usually greater than in the batch experiments. The experimental breakthrough curves of Pb(II) are presented in Fig. 9a. It can be seen that the breakthrough begins at 100 BV (bed volume) and the bed is completely saturated at 280 BV. Here, BV is defined as a volume ratio of metal solution which passes through the column (cm³) to the packed biosorbent−0.6 CG (cm³). The higher column capacity may be due to the fact that a continuously large concentration occurs at the interface as it passes through the column, while the concentration gradient decreases with time in the batch experiment [39]. Above-mentioned content indicates that Pb(II) can be greatly concentrated by a column of 0.6 CG.

Pb(II) adsorbed onto the column bed can be easily regenerated by a small amount of 0.1 mol/L HCl. Elution curve is shown in Fig. 9b. It shows that the elution is completed within 20 BV of 0.1 mol/L HCl. For obtaining the reusability of the adsorption column, the adsorption/desorption cycle is repeated three times, the adsorption behavior of the regenerated adsorption column is similar to that of the new column. These results indicates that grass adsorbents have a good potential for removal of Pb(II) from dilute aqueous solutions.

### 3.8. Adsorption mechanism

The Pb(II) adsorption by these lawny grass adsorbents occurs through ion-exchange reaction. Functional groups such as –COOH and –OH of cellulose can react with Pb(II) to form complexes by releasing protons. The reaction equation can be described as:



$$\tag{11}$$

One Pb(II) can form a complex through two oxygen donor atoms by releasing hydrogen from the carboxylic functional groups. It shows that ion change reaction increases acidity of solution. This is further supported by the fact that pH of metal solution decreases after adsorption.
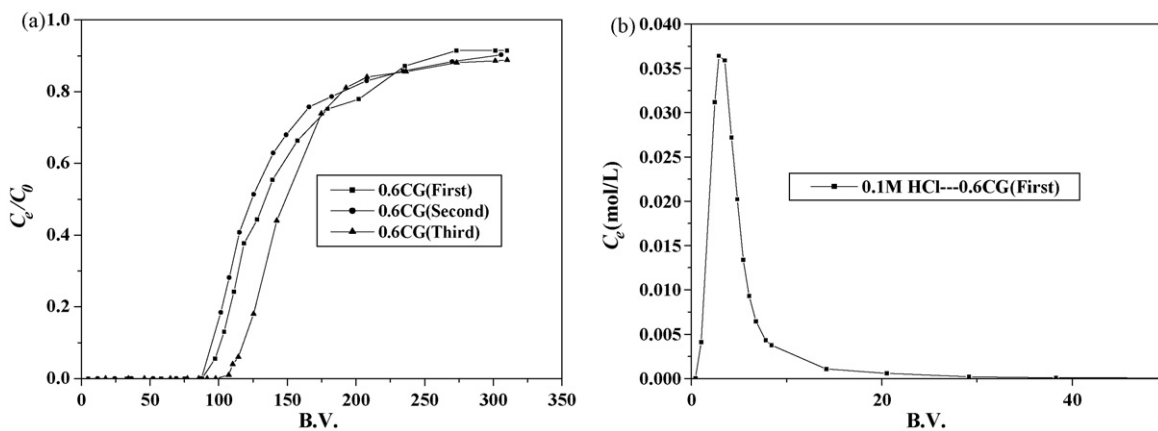
**Fig. 9.** Breakthrough (a) and Elution (b) curves of Pb(II) by column filled with 0.6 CG (initial lead concentration = 0.001 mol/L; initial pH 5.1).

## 4. Conclusion

Lawny grass is a familiar and abundant waste during the process of city beautifying or gardens building. Simple pretreatment, high-sorption performances under low concentration condition, easy desorption and high regeneration are further demonstrated in this paper. All of these appropriate features shows that it is feasible for this plant material as a novel biosorbent for Pb(II) removal in the future.

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