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Cd removal from aqueous solution using agricultural wastes

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ABSTRACT

Adsorption processes are widely used by various researchers for the removal of heavy metals from wastewaters and in this type of processes, activated carbon is frequently used as an adsorbent. Despite its extensive usage in water and wastewater treatment industries, activated carbon remains as an expensive material. In recent years, the need for safe and economic methods for elimination of cadmium from contaminated water has directed research interest toward the production of other low-cost adsorbents. Therefore, there is an urgent need to find out all possible sources of agro-based inexpensive adsorbents and also for studying their feasibility for the removal of cadmium. The aim of this study was to investigate the possibility of the utilization of *Phragmites australis* (*P. australis*) and sugarcane straw in microscales as low-cost adsorbent materials for cadmium (Cd) adsorption. In this study, the effects of operation conditions including pH, contact time, adsorbent loading, and initial ion concentrations were examined. The results showed that the optimum pH was equal to 6 and 4 while the equilibrium time was 10 and 30 min for *P. australis* and sugarcane straw, respectively. For two adsorbents, as the adsorbent dose increased from 0.1 to 2 g, the removal percentage became 85.75% at 0.1 g for sugarcane straw and 94.75% at 0.5 g for *P. australis*; however, the other values remained almost constant while adsorbents dosage changed ranging from 0.1 g and 0.5 g to 2 g. With increasing initial cadmium concentration from 0.5 to 5 mg/L, the adsorption capacity of sugarcane straw and *P. australis* increased from 1.7 to 7.78 mg/g and 1.51 to 5.78 mg/g, respectively. The adsorption kinetics of cadmium ions on *P. australis* and sugarcane straw of cadmium ions fitted Freundlich isotherm. The results of the present study indicated that *P. australis* and sugarcane straw can be used to remove cadmium ions during water treatment process. Compared with *P. australis* adsorbent, sugarcane straw showed higher level of capability of cadmium adsorption.

Keyword: *Phragmites australis*; Cadmium removal; Sugarcane straw; Adsorption kinetics; Isotherm model

1. Introduction

Heavy metals are toxic and non-biodegradable and probably have negative effects on health [1,2]. Therefore, treatment of wastewater contaminated by heavy metals is an important environmental concern [3]. Cadmium (Cd) is considered to be an extremely toxic metal without a known biological function [4]. Cd can accumulate in the human body especially in

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kidneys, thus leading to kidney dysfunction. The permissible limit for Cd in drinking water, based on the guideline value recommended by World Health Organization, is 0.005 mg/L. It is of great importance for water treatment processes to develop efficient procedures for the removal of Cd from wastewater [4].

Many conventional methods including oxidation, coagulation, membrane filtration, reverse osmosis, adsorption, ion exchange, and precipitation have been reported in the literature to be used for the removal of cadmium metals from wastewater. These methods may be ineffective or extremely expensive especially when the wastewaters contain relatively low concentration of metal (1–100 mg/L) dissolved in large volume of wastewater [5]. However, adsorption can be considered as one of the most popular methods for the removal of heavy metals from the wastewater due to its low-cost, availability, simplicity of design, and high removal efficiency [6,4].

Activated carbon is a widely used adsorbent, which is commonly applied for controlling wastewater pollution throughout the world and successfully utilized for the removal of metal ions. However, the high-cost of regeneration of activated carbon limits its large scale applications for the removal of metals, and it has encouraged researchers to find out other low-cost adsorbents. The use of agro-wastes as adsorbent is currently receiving wide attention because of their abundant availability and low-cost of production [7]. So far, some researches about Cd, Cr, and pb adsorption have been performed [8–12].

The present study aimed to investigate the adsorption of Cd ions from aqueous solution onto *Phragmites australis* (*P. australis*) and sugarcane straw. To the best of our knowledge, there has been no report on the use of *P. australis* and sugarcane straw as adsorbent in literature. It has also been found that the unique properties of microparticles normally develop high capacities in metal ions. The effects of experimental parameters such as pH, adsorbents dose, initial cadmium concentration, and time on the adsorption process were investigated. The isotherm and kinetic models were tested to identify the potential adsorption process mechanisms.

2. Materials and methods

2.1. Characteristics of adsorbents

The *P. australis* plant and sugarcane straw leaves were obtained from Khuzestan Province, southwest Iran. The collected materials were washed with double distilled water, and then were used as dry *P. australis*. The size of microparticles was examined by sieving with a 200 mesh number sieve.

Surface area and surface morphology of the *P. australis* and sugarcane straw adsorbents were investigated by methylene blue method, scanning electron microscope (SEM), and Fourier transform infrared spectra (FTIR). FTIR study was carried out to understand surface properties and available functional groups involved in adsorption mechanism.

2.2. Synthetic Cd solution

First, 2 mg/L (8.5×10^{-6} mol/L) of Cd stock solution was prepared by dissolving the required weighed quantities of $CdNO_3$ (Merck Germany) in distilled water. All solutions for the adsorption and subsequent analysis were prepared by diluting the prepared stock solution. The initial pH of the Cd solution was changed by adding 0.1 N HCl or 0.1 N NaOH solutions, as required. For each 40 mL conical flask, 0.1 g of *P. australis,* sugarcane straw, and 40 mL of working solution were mixed and shaken for 6 h at 180 rpm. Then the mixtures were filtered using a filter paper to separate water from the adsorbent. Cd was analyzed by an atomic adsorption spectrophotometer (220 Varian, Australia). All the samples were prepared in triplicate and Cd adsorbed onto adsorbents was determined by equation below:

$$\text{Percentage of removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{2}$$

where q_e is Cd adsorbed on adsorbent (mg/g), m is the adsorbent mass (g), C_0 and C_e are the initial and equilibrium concentrations of Cd in solution (mg/L), and V is solution volume (L).

2.3. Adsorption experiments and analysis method

The adsorption experiments were conducted via batch process. The effects of experimental parameters such as initial pH, equilibrium contact time, adsorbent dosage, and initial Cd ion concentration on the adsorption process were investigated.

2.3.1. pH studies

In order to investigate the effects of pH on Cd adsorption, pH value of 2 mg/L (8.5×10^{-6} mol/L) Cd concentration was adjusted in the ranges of 2, 3, 4, 6, and 8. The initial pH value of solution was adjusted using HCl or NaOH (0.1 N). Then, 0.1 g dried adsorbent was added to the 40 mL $CdNO_3$ solution. The mixtures were shaken for 6 h at 180 rpm. After adsorption, the pH value with a maximum level of Cd removal was determined.

2.3.2. Effect of contact time

At this step, 40 mL Cd solution and 0.1 g adsorbent were agitated at the optimum value of pH. The mixtures were shaken at 180 rpm, and the batch experiments were repeated for different periods of 10, 30, 60, 120, 240, and 360 min until the adsorption equilibrium was obtained.

2.3.3. Effect of adsorbent dosage

The adsorption process was carried out for 2 mg/L (8.5×10^{-6} mol/L) Cd solution in different adsorbent doses of 0.05, 0.1, 0.5, 1, 1.5, and 2.0 g at the optimum values found for pH and contact time.

2.3.4. Effect of initial concentration

The effects of initial concentrations on the adsorption of Cd ions by adsorbents were evaluated for different Cd concentrations of 0.5, 1, 2, 3, and 5 mg/L (2.11×10^{-5} mol/L) at the optimum values of pH, contact time, and adsorbent dosages.

2.4. Equilibrium adsorption isotherm

The equilibrium adsorption data were analyzed using different isotherm models to understand the adsorbate–adsorbent interactions. In order to characterize the adsorption equilibrium of Cd ions by *P. australis* and sugarcane straw adsorbent, the Freundlich, Langmuir, Temkin, Halsey, and Harkins–Jura models were used as follows:

Freundlich equation [13]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

Langmuir equation [14]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}{}^{b}} + \frac{C_e}{q_{\max}} \tag{4}$$

Temkin equation [15]:

$$q_e = b_T \ln K_T + b_T \ln C_e \tag{5}$$

Halsey equation [16]:

$$\ln q_e = \left[\left(\frac{1}{n_H}\right) \ln K_H\right] - \left(\frac{1}{n\mathrm{H}}\right) \ln\left(\frac{1}{C_e}\right) \tag{6}$$

Harkins–Jura model [16]:

$$\frac{1}{q_e{}^2} = \left[\frac{B}{A}\right] - \left[\frac{1}{A}\right] \log C_e \tag{7}$$

where q_e is the amount of adsorbate per gram of the adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate per gram of adsorbent at any time t (mg/g), n is Freundlich constants, b is Langmuir constant (L/mg), $1/n$ is intensity of sorption (mg/g)/(mg/L), C_0 is the initial Cd ion concentration (mg/L), C_e is the Cd equilibrium concentration in solution (mg/L), n_H is Halsey isotherm model constant, A is Harkins–Jura isotherm constant, b_T is Temkin constant, k_H is Halsey isotherm model, and K_T is Temkin isotherm constant. The other parameters represent different isotherm constants that may be determined by regression of the experimental isotherm data.

The dimensionless parameter or separation factor, R_L, after further analysis of the Langmuir equation, may be determined based on following equation [17]:

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

where C_0 (mg/L) is the initial concentration of adsorbed ion, b is the Langmuir constant, and R_L is the separation factor. The parameter of R_L is considered as a more valid indicator of ion adsorption. The value of R_L may be determined for four cases [18]: (i) favorable adsorption, $0 < R_L < 1$, (ii) unfavorable adsorption, $R_L > 1$, (iii) linear adsorption, $R_L = 1$, and (iv) irreversible adsorption, $R_L = 0$.

The Freundlich isotherm is based on an empirical equation, where the adsorption takes place on a heterogene surface of the adsorbent. The Freundlich isotherm constants n and K_f are experimental parameters that vary with the degree of heterogeneity and are related to adsorption capacity. The values of n should lie between 1 and 10 for the desired adsorption process. Halsey isotherm model was used to explain the multilayer adsorption system for Cd ion.

Temkin isotherm model was applied to evaluate the adsorption potentials of adsorbents for adsorbates, i.e. Cd ion from aqueous solution. Harkins isotherm model suggested the multilayer adsorption as well as heterogeneous pore distribution in the adsorbents surface.

2.5. Kinetic study

The adsorption rate of cadmium was studied at different time intervals for 360 min using 2 mg/L initial concentrations and at the optimum value of pH. The modeling of Cd adsorption kinetics for *P. australis* and sugarcane straw were checked by four common models, Eqs. (9)–(12), as explained below:

Pseudo-first-order equation [19]:

$$\log\,(q_{\mathrm{e}} - q_t) = \log\,q_{\mathrm{e}} - \frac{k_1}{2.303}t \tag{9}$$

Pseudo-second-order equation [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{1}{q_{\mathrm{e}}}t \tag{10}$$

Pore diffusion, intraparticle diffusion model [21]:

$$q_t = k_{\mathrm{i}} t^{0.5} + C \tag{11}$$

Power equation:

$$q_t = a t^b \tag{12}$$

where q_t is the amount of Cd adsorbed during time t (mg/g), q_{e} is the amount of Cd adsorbed at equilibrium state, and k_1, k_2, a, b, and C are constants.

Pseudo-first-order and second-order kinetic models were based on the assumption of physisorption and chemisorption process, respectively. Intraparticle diffusion in liquid-porous solid was explained by surface diffusion, pore volume diffusion, or both the processes. Diffusion models were also employed to explain the Cd adsorption process. Three main steps are involved in the solid–liquid sorption process occurred between the metal ions and the adsorbent (a) the metal ions are transferred from the bulk solution to the external surface of the adsorbent; this is known as film diffusion, (b) the metal ions are transferred within the pores of the adsorbent; this is known as intraparticle diffusion, occurring either as pore diffusion or as a solid surface diffusion mechanism, (c) the active sites on the surface of the adsorbent capture the metal ions [22].

In this study, the best fit between experimental data and model-estimated data was evaluated by R^2 and the RMSE, as follow:

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} (q_{\mathrm{e}} - q_{\mathrm{c}})^2}{n}} \tag{13}$$

where q_{e} and q_{c} are the measured and model estimated amounts of Cd adsorbed, respectively, and n is the number of measurements. A lower RMSE value and higher R^2 value show the best fit of agreement between the measured and estimated Cd adsorbed data.

3. Results and discussion

Surface area of *P. australis* and sugarcane straw was 23.5 and 35.5 m^2/g, indicating that sugarcane straw had a pore size distribution larger than *P. australis*, hence sugarcane straw was more effective in Cd adsorption.

3.1. SEM and FTIR study

The results of SEM measurements on *P. australis* and sugarcane straw are shown in Fig. 1. Fig. 1 shows that the surface of *P. australis* had many holes and looked rough. Also, sugarcane straw had softer surface and deeper pores than *P. australis*. Considering the results of SEM analysis, it is expected that sugarcane straw would be more effective than *P. australis* absorbent in the cadmium adsorption.

The FTIR study of fresh adsorbent was carried out to identify the function groups effective in the adsorption process. Fig. 2 indicates the wave numbers for different functional groups present in adsorbents. Aliphatic C–H and C–O stretching may be responsible for Cd adsorption onto *P. australis* and sugarcane straw as wave number shifts from 2,918.55 to 2,913.74 cm^{-1} and 1,058.08 to 1,035.36 cm^{-1}, respectively. The Aliphatic C–H and C–O can show cadmium adsorption ability by studied adsorbents. Hence, considering the results of FTIR, it is expected that *P. australis* and sugarcane straw play a major role in Cd absorption.

3.2. Adsorption experiment

3.2.1. Effect of initial pH

Changing the pH of metal solution from 2 to 8, the effect of pH on cadmium adsorption was tested. Fig. 3

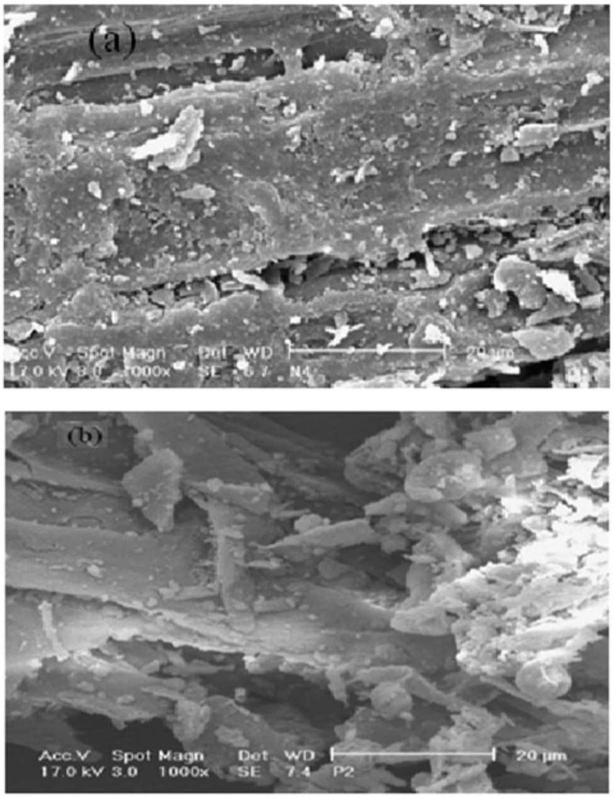

Fig. 1. SEM image (scale 1,000×) of *P. australis* (a) and sugarcane straw (b).

shows variations in the removal percentage as a function of initial pH values for Cd ion.

According to Fig. 3, the minimum adsorption efficiency for *P. australis* adsorbent was observed at pH 2. The increase in hydrogen ions at pH 2 resulted in greater competition of H^+ with solved cations and instead of cadmium, H^+ was adsorbed onto the adsorbent, consequently the adsorption of cadmium decreased; these same results have been observed in other studies [22]. With gradual increase in pH, due to the increased amount of OH^-, cadmium adsorption further increased. For *P. australis*, the removal percentage of Cd(II) showed a rapid increase from 55.2 to 91.85 in a pH range of 2–6, but it changed a little when pH was greater than 6.

The lowest adsorption efficiency for sugarcane straw was also observed in pH 2. With gradual increase in pH range of 2–4, the adsorption efficiency showed a rapid increase from 78.9 to 96.15. At pH levels greater than 4, the removal percentage increased to 96.35, which changed a little. Similar results are obtained by other researchers which report in the acidic pH the adsorption capacity decreases and with increasing pH, the adsorption is enhanced [4]. Thus, the optimal pH for adsorption of cadmium was found to be 6 for *P. australis* absorbent and 4 for sugarcane straw.

3.2.2. Effect of contact time

Fig. 4 shows the changes in the removal percentage of cadmium with different contact times in the optimum pHs of 6 and 4, with the initial concentration of 2 mg/L (8.5×10^{-6} mol/L) of cadmium and 0.1 g of *P. australis* and sugarcane straw. In order to determine the equilibrium time, tests were performed for different contact times of 10, 30, 60, 120, 240, and 360 min. As observed in Fig. 4, for *P. australis* adsorbent, the adsorption speed was high at the initial time of the process so that at the first 10 min 86% of the cadmium concentration was adsorbed from the solution. In time range of 10–60 min, the removal percentage increased (87%); however, the change was little. After 60 min the adsorption has reached equilibrium. Therefore, it was found that the equilibrium time for the optimum cadmium adsorption using *P. australis* was 10 min. Putting the cadmium in contact with the adsorbent after the equilibrium time, it had a little effect on adsorption. These same results have been observed in other studies using other adsorbents [4].

For the sugarcane straw, the increase in contract time from 10 to 30 min led to a rapid increase in the adsorption efficiency from 93.7 to 95.3%. In time range of 30–60 min, removal percentage changed a little and after 60 min adsorption had become approximately constant. Accordingly, cadmium adsorption equilibrium time for sugarcane straw was found to be 30 min. According to the results, the cadmium removal percentage of sugarcane straw was more than that of *P. australis*. In sugarcane straw, the increase in contact time between adsorbent and solution increased the level of adsorption because it increased the chance of contact between ions with functional groups existing in adsorbent structure (adsorption sites); additionally, the adsorption specific surface area of sugarcane straw was larger than that of *P. australis* (based on methylene blue method).

3.2.3. Effect of adsorbent dosage

Another factor which can affect removal percentage is the amount of adsorbent. At this stage of the experiments, the adsorption efficiency was measured using different amounts of adsorbent (0.05, 0.1, 0.3, 0.5, 1, and 2 g, dissolved in 40 mL solution), with an initial concentration of 2 mg/L of cadmium, equilibrium time of 10 min, pH 6 for *P. australis*, and

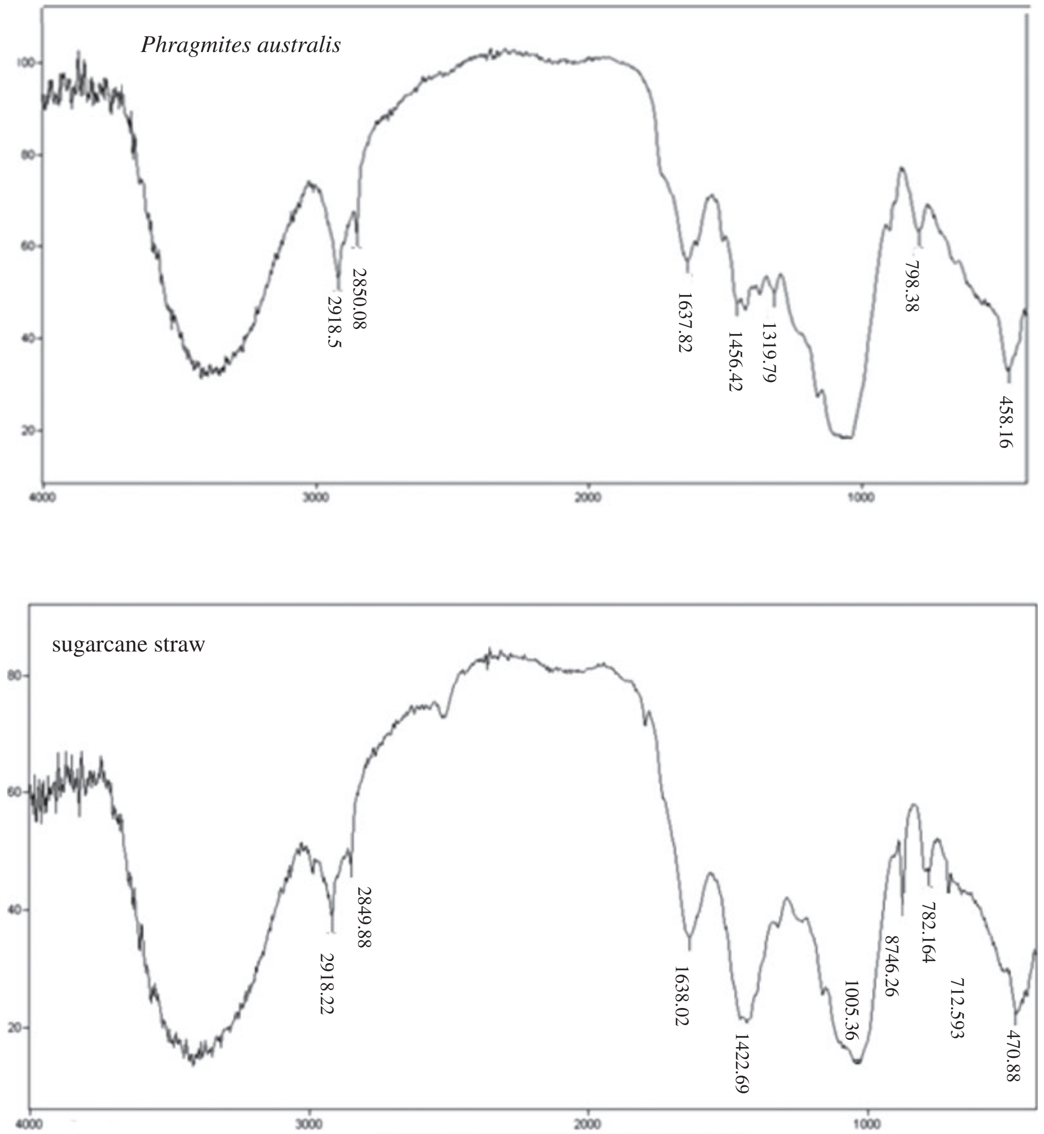

Fig. 2. FTIR spectra of raw *P. australis* and sugarcane straw.

equilibrium time of 30 min and pH 4 for the sugarcane straw. Fig. 5 shows the effect of adsorbent mass on cadmium removal using *P. australis* and sugarcane straw adsorbent. As Fig. 5 shows, the minimum adsorption (65.66%) was in a mass of 0.05 g. With an increase of adsorbent dosage from 0.05 to 0.1 g, removal percentage rapidly increased to 85.75%. Further increase in adsorbent mass from 0.1 to 2 g did not significantly affect on cadmium removal percentage; it might be due to the saturation of adsorption sites of *P. australis* by cadmium and the concentration of cadmium in the *P. australis* adsorbent which became equal to its concentration in the solution and it reached equilibrium.

Considering the sugarcane straw, with an increase in adsorbent mass from 0.05 to 0.5 g, the removal percentage increased from 70.21 to 94.75%, because it increased the surface area available for adsorption and also increased the adsorption sites. However, increasing the adsorbent mass from 0.5 to 2 g, the adsorption efficiency changed a little (94.75 to 95%). Hence, 0.5 g of sugarcane straw was enough for the removal of cadmium at a concentration of 2 mg/L (8.5×10^{-6} mol/L).

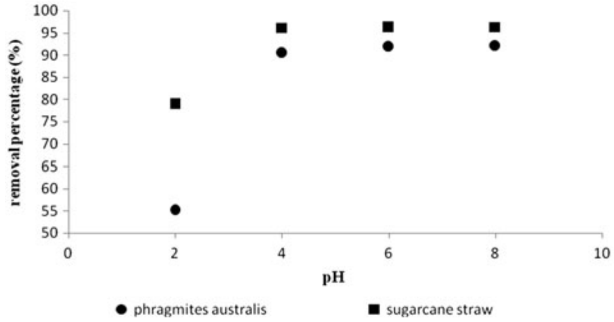

Fig. 3. Effect of pH on the adsorption of Cd ion by *P. australis* (Cd initial concentration: 2 mg/L, adsorbent loading: 0.1 g, adsorption time: 6 h).

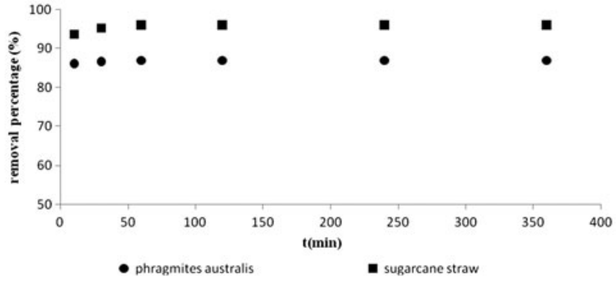

Fig. 4. Effect of contact time on the adsorption of Cd ion by *P. australis* and sugarcane straw (Cd initial concentration: 2 mg/L (8.5×10^{-6} mol/L), adsorbent dosage: 0.1 g, pH 6, 4).

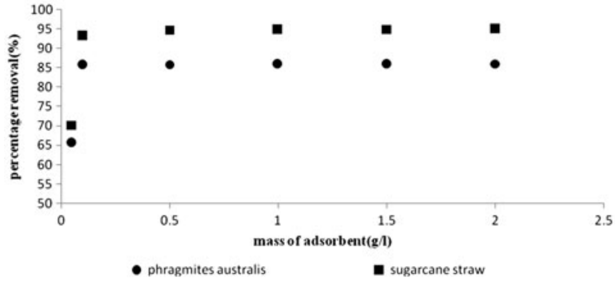

Fig. 5. Effect of adsorbent dosage on removal of Cd by *P. australis* and sugarcane straw (Cd initial concentration: 2 mg/L (8.5×10^{-6} mol/L), pH 6, 4).

Other studies had also reported a decreased adsorption per unit of adsorbent mass [23], which could be due to two different reasons: (1) higher amounts of adsorbent significantly decrease the number of nonsaturated adsorption sites and the number of sites per unit of mass decreases and consequently leads to lower amounts of adsorption in the presence of high amounts of adsorbent; (2) high amounts of adsorbent leads to the formation of massive particles that reduce the total area and decreases the length of distribution line, both of which reduces the level of adsorption rate per mass unit of the adsorbent [23,24].

In another research [25] adsorption capacity of Cr and Cu by rose waste was 15 and 18 mg/g at 0.1 g adsorbent, but in this research adsorption capacity of Cd by *P. australis* absorbent was 5.78 mg/g at 0.1 g adsorbent and adsorption capacity of cd by sugarcane straw was 8.78 mg/g at 0.5 g adsorbent.

According to the results, with an increase in the amount of *P. australis* absorbent and sugarcane straw, the adsorption rate did not increase in the same proportion. It might be due to the fact that by increasing the absorbent, some of the absorbents are conjoined and a large number of holes are eliminated [26].

3.2.4. Effect of initial concentration

Fig. 6 shows the effect of initial cadmium concentration on adsorption capacity by *P. australis* and sugarcane straw absorbents. Initial concentrations of 0.5, 1, 2, 3, and 5 mg/L, using 0.1 and 0.5 g of *P. australis* and sugarcane straw at pH 6 and 4, respectively. Usually for all absorbents, in case of increasing the amount of pollutant concentrations, the adsorption rate increases and removal percentage decreases; however, the rate of change is different for various pollutants [27,28].

According to Fig. 6, considering *P. australis* absorbent, for *P. australis* with an increase in initial cadmium concentration from 0.5 to 5 mg/L, the adsorption capacity increased from 1.51 to 5.78 mg/g. At low concentrations of cadmium, specific surface area and adsorption sites were high and cadmium ions were able to interact with the adsorption sites

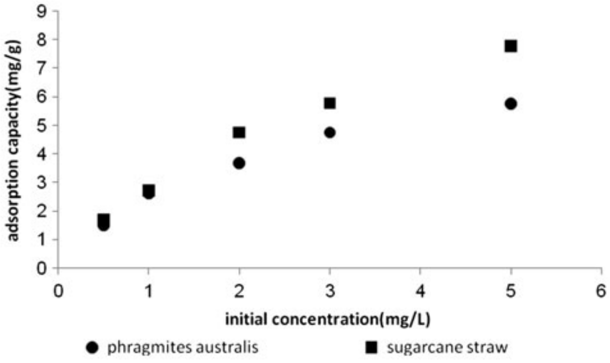

Fig. 6. Effect of initial concentration on the removal of Cd by *P. australis* and sugarcane straw (adsorbent dosage: 0.1 g, 0.5 g, pH 6, 4).

existing on the adsorbent surface area, consequently adsorption efficiency increased. With increasing initial concentrations, the weighted amount of absorbent and the adsorption capacity increased. Therefore, due to the stability of the amount of adsorbent (0.1 g), with increasing Cd concentration, the adsorption percentage increased [26]. This result is supported by the findings of another researcher [29].

Considering sugarcane straw, with increasing initial cadmium concentration from 0.5 to 5 mg/L, the adsorption capacity increased from 1.7 to 7.78 mg/g. According to Fig. 6, at the initial concentration of 0.5 mg/L of cadmium, the adsorption capacity of both absorbents was similar and at the initial concentration of 5 mg /L, the adsorption capacity of *P. australis* and sugarcane straw was 5.78 and 7.78 mg/g, respectively. Thus, according to the obtained results, sugarcane straw had larger specific surface area and adsorption sites than *P. australis*. Additionally, with increasing the initial cadmium concentration, its adsorption capacity was increased by sugarcane straw adsorbent with steeper slope which might be due to the absorbent's high capacity for cadmium adsorption.

3.3. Adsorption isotherm study

Adsorption isotherms characterize the equilibrium relationship between the amounts of adsorbed ions by adsorbents and its equilibrium concentration in the solution [30]. The applicability of the isotherm models was confirmed by evaluating the value of statistical parameters. In this study, adsorption isotherms data obtained for *P. australis* and sugarcane straw were fitted to the Freundlich, Langmuir, Halsey, Temkin, and Harkins models. The estimated model parameters including R^2 and RMSE for the different models are presented in Table 1.

One of the important parameters in Langmuir equation is R_L. Fig. 7 shows that R_L value approaches zero as C_0 value increases, indicating that at high concentrations of Cd there are lower rates of adsorption of Cd ion onto sugarcane straw and *P. australis*. Therefore, Langmuier equation cannot explain Cd adsorption well [31].

In Langmuier isotherm, the maximum monolayer adsorption capacity was 8 and 5.41 mg/g for sugarcane straw and *P. australis*, respectively. The constant of $1/n$ for the Freundlich isotherm ranges from 0 to 1 and is a measure of adsorption intensity or surface heterogeneity with a value of $1/n$ smaller than 1 that indicates favorable removal conditions [32]. In this study, the value of $1/n$ (Freundlich constant) was 0.73 and 0.89 for sugarcane straw and *P. australis*, respectively (Table 1), suggesting that the adsorption conditions were actually favorable.

Table 1
Different isotherm models for Cd adsorption

Model	Sugarcane straw	*P. australis*
Freundlich		
k	4.73	3.44
$1/n$	0.73	0.89
R^2	0.99	0.97
RMSE	0.42	0.53
Langmuir		
q_m (mg/g)	8	5.41
b (L/mg)	0.78	2.42
R^2	0.96	0.96
RMSE	0.29	0.92
Temkin		
bt	0.656	0.2
kt	31.97	26.05
R^2	0.94	0.94
RMSE	0.42	0.92
Halsey		
k_h	5.38	2.44
n_h	1.08	0.72
R^2	0.95	0.95
RMSE	0.62	0.93
Harkins		
B	−0.62	−0.81
A	0.041	0.001
R^2	0.95	0.90
RMSE	0.27	0.62

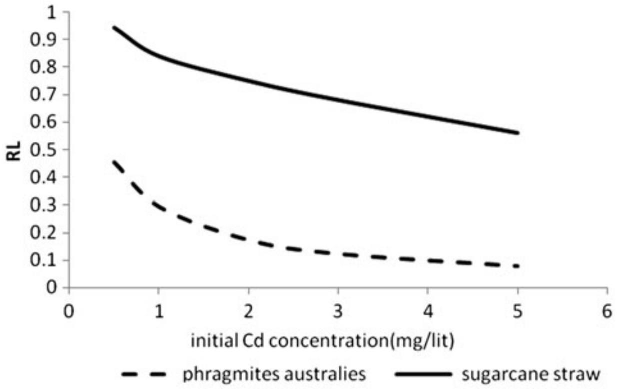

Fig. 7. Variation of separation factor (R_L) as a function of initial Cd concentration for *P. australis* and sugarcane straw.

Concerning sugarcane straw, the R^2 values for Temkin, Halsey, and Harkins model showed good fits of 0.94, 0.95, and 0.95 and RMSE values of 0.42, 0.62, and 0.27, respectively. Concerning *P. australis* the R^2

values for Temkin, Halsey and Harkins model showed good fits of 0.94, 0.95, and 0.90 and RMSE values of 0.92, 0.93, and 0.62, respectively. The results in Table 2 show that the Freundlich models provided better fits with respect to R^2 (0.99, 0.97) and RMSE (0.42, 0.53) for sugarcane straw and *P. australis*, compared with other isotherms. This result is supported by the findings of other researcher [32].

3.4. Adsorption kinetics study

The mechanism of adsorption process depends on physical and chemical characteristics of solute and structure of the adsorbent. In present study, adsorption kinetics data obtained for *P. australis* and sugarcane straw were fitted to pseudo-first-order, pseudo-second-order, power function, and intraparticle model. The value of rate constants and statistical parameters for each model are shown in Table 2. In pseudo-first-order model, the predicted q_e values of 1.34 and 1.02 mg/g were lower than the experimentally observed values of 1.84 and 1.35 mg/g for sugarcane straw and *P. australis*, respectively. However, in pseudo-second-order the predicted q_e values were 2.78 and 2.62 mg/g. Therefore, pseudo-second-order model accurately predicted the adsorption kinetics throughout the experiments. The highest RMSE values obtained for the pseudo-first-order model were 1.91 and 1.78. Therefore, this model could not be used to predict the kinetics of adsorption of Cd for two adsorbents. The Power function model satisfactorily explains the adsorbed Cd with RMSEs of 1.34, 1.62, R^2: 0.88, 0.87, for sugarcane straw and *P. australis*, respectively (see Table 2).

The intraparticle diffusion plots of the experimental results, q_t versus $t^{0.5}$ for different adsorbents are shown in Fig. 8. The values of K_i and correlation coefficients (R^2) obtained from intraparticle diffusion plots are given in Table 2. The intraparticle model determines the amount of Cd removed by sugarcane straw and *P. australis* with RMSEs of 1.34, 0.62, and R^2: 0.73, 0.77, respectively. The values of C were 1.783 and 0.378 for sugarcane straw and *P. australis*. The values of C obtained from intraparticle diffusion model indicated that intraparticle diffusion might not be the controlling factor in determining the kinetics of the process and film diffusion controls the initial rate of the adsorption, it also indicates the thickness of the boundary layer.

As shown by the statistical parameters, for two adsorbents, pseudo-second-order model is more applicable for the Cd adsorption process, i.e. correlation coefficient (R^2) and RMSE of pseudo-second-order model were 0.96, 0.93, 0.36, and 0.62, respectively.

Table 2
Different kinetic models for Cd adsorption

Model	Sugarcane straw	*P. australies*
Pseudo-first-order equation		
q_{exp}	1.84	1.35
k_1	0.023	0.02
q_e	1.34	1.02
R^2	0.68	0.64
RMSE	1.91	1.78
pseudo-second-order equation		
K_2	−0.48	−2.27
q_e	2.78	2.62
R^2	0.96	0.93
RMSE	0.36	0.62
Power function		
a	1.736	0.376
b	0.008	0.002
R^2	0.88	0.87
RMSE	0.34	0.62
intraparticle		
k_i	0.001	0.0002
c	1.783	0.378
R^2	0.73	0.77
RMSE	1.34	0.62

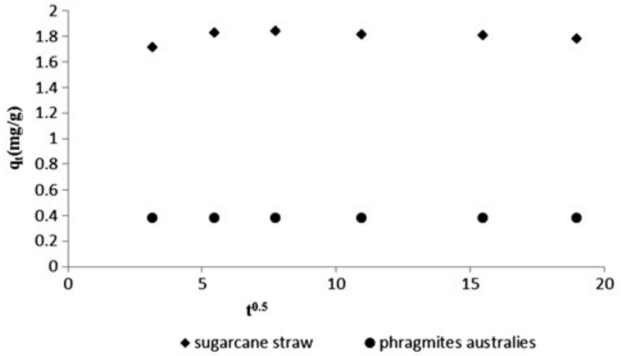

Fig. 8. Intraparticle diffusion plots for the removal of Cd ions onto sugarcane straw and *P. australis.*

Hence, the rate constant of the adsorption process appears to be controlled by the chemical adsorption process. The results showed that the pseudo-first-order, power model, and intraparticle expression were not valid to be used in the studied systems (see Table 2). The calculated and experimental equilibrium adsorption values fit well to pseudo-second-order.

It was also found that the fitting to pseudo-second-order model gave a higher level of determination coefficients (R^2), and had lower RMSE than the other models under the study. Therefore, pseudo-second-order model may be used to predict the kinetics of cadmium adsorption. The results are in agreement with those obtained by other researchers [33]. By comparing *P. australis* and sugarcane straw, one can infer that the sugarcane straw has more extended surface area, softer surface, and adsorbs Cd quickly.

4. Conclusion

The results of this study showed that the cadmium adsorption was optimal at pH 6 and 4 for *P. australis* and sugarcane straw, respectively. The equilibrium times were found to be 10 and 30 min for *P. australis* and sugarcane straw, respectively. With increase in initial concentrations of cadmium, adsorption capacity increased. As the adsorbent dose increased, the removal of cadmium increased while the adsorption capacity decreased. Adsorption kinetics of cadmium ions onto *P. australis* and sugarcane straw may be most successfully explained by the pseudo-second-order model. The adsorption behavior of cadmium ions followed Freundlich isotherm. The results help us to conclude that *P. australis* and sugarcane straw are two promising adsorbents for the removal of cadmium ions from aqueous solutions. According to the results of this research, sugarcane straw developed higher capacities of particles for the adsorption of cadmium, and it showed higher capability of adsorbing cadmium as compared to *P. australis* adsorbent.

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