Utilization of a natural ecosystem bio-waste; leaves of *Arundo donax* reed, as a raw material of low-cost eco-biosorbent for cadmium removal from aqueous phase

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**ABSTRACT**

*Arundo donax* reed grows in a natural ecosystem in Wadi Shueib in Jordan and is also grown in constructed wetlands built for domestic wastewater treatment. The utilization of leaves of excessive *A. donax* reed as an ecosystem bio-waste for the removal of Cd$^{2+}$ from aqueous solutions was investigated. Effects of pH (3.5 to 7.5), contact time (10 to 360 min), adsorbent dose (2.5 and 5 g l$^{-1}$), and adsorbate concentration (5 to 50 mg l$^{-1}$) at an ionic strength of 0.01 M NaNO$_3$ on adsorption efficiency and capacity were studied in batch adsorption experiments. Cadmium removal percentage of 92% occurred in 20 mg l$^{-1}$ Cd solutions at pH 5.5 containing 5 g l$^{-1}$ powdered leaves of *A. donax*. Cadmium removal percentage increased to 97% with decreasing the adsorbent dose to 2.5 g l$^{-1}$. The adsorption process was relatively fast and equilibrium was attained at 120 min contact time. The equilibrium adsorption capacity of *A. donax* leaves increased from 1.96 to 18.80 mg g$^{-1}$ with increasing initial Cd concentration from 5 to 50 mg l$^{-1}$. The kinetic process of Cd$^{2+}$ adsorption onto leaves of *A. donax* obeyed the pseudo-second-order kinetic model ($R^2 > 0.9995$) indicating that chemisorption is the rate-limiting step. Although Freundlich and Langmuir isotherm models described well the experimental data, equilibrium isotherm data were best described by Freundlich model ($R^2$ 0.990 and 0.978, respectively). The monolayer adsorption capacity was 27.9 mg g$^{-1}$. *A. donax* leaves can be potentially used as a raw material of low cost eco-biosorbent for treating Cd-contaminated water systems.

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1. Introduction

The contamination of water systems by toxic heavy metals is still a world-wide environmental problem (Tan and Xiao, 2009). Industrial and municipal wastewaters frequently contain heavy metals and other pollutants. The increase of industrial activities (e.g. the manufacture of cadmium–nickel batteries, fertilizers, pesticides, pigments and dyes, and petroleum refining process and plastic industry) has intensified environmental pollution problems and the deterioration of several ecosystems as well as the accumulation of heavy metals in air, water, and soil (Ghodbane et al., 2008; Chiban et al., 2012). According to the World Health Organization (WHO), cadmium (Cd) is among the metals of immediate concern. Cadmium like other heavy metals can be introduced into water sources in amounts harmful to human health by industrial effluents (Balkaya and Cesur, 2008) and may reach domestic wastewater which can threaten the safety of water supply (Xin et al., 2007). Adsorption method is simple and relatively cost-effective, thus has been widely used. It is generally preferred for the removal of heavy metal ions due to its high efficiency and availability of different adsorbents (Zheng et al., 2008). In addition, biosorption technology is effective when applied to low strength wastes with heavy metal ions concentrations less than 100 mg l$^{-1}$ (Ghodbane et al., 2008). Thus, there is a growing demand to find relatively efficient and low cost eco-(bio)sorbents for the removal of heavy metal ions from contaminated water systems. Many researchers have found that non-living biomaterials (e.g. algae) and waste biomass originated from plants have the ability to adsorb heavy metal ions from environment and can be used as low-cost and environmentally friendly adsorbents (Ahuwalia and Goyal, 2007). The kinetics and maximum adsorption capacity vary with the type of (bio)sorbent as well as the metal ions. Indeed, waste materials as alternative (bio)sorbents for activated carbon have received considerable attention. Among waste materials, natural ecosystems' waste plant biomass deserves a special attention. Chiban et al. (2011a) found that dried *Carpobrotus edulis* plant was efficient in

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removing Cd from aqueous solution and Chiban et al. (2011b) concluded that dried plants can be one alternative source for low cost adsorbents to remove heavy metals from wastewaters.

*Arundo donax* is a reed native to the Mediterranean basin and Eastern and Southern Asia. In Jordan, it grows in a natural ecosystem in Wadi Shubeib region located in Al-Balqa’ Directorate and is also grown in constructed wetlands built for domestic wastewater treatment. The utilization of an ecosystem waste material; leaves of excessively growing *A. donax* reed for the removal of Cd ions from Cd-contaminated water systems was investigated in this work as a raw material of low cost eco-(bio)sorbent. Structurally, such leaves consist of different biological polymers that enrich these leaves in hydroxyl and phenolic groups. These groups can be used to remove metal ions from aqueous solutions. There are rare reports about the sorption behavior and kinetic studies of heavy metals binding by leaves of a natural ecosystem reed.

For the present work, the removal of Cd ions from aqueous phase by unmodified powdered leaves of *A. donax* was investigated using batch adsorption experiments. Kinetic data and equilibrium isotherms were determined and analyzed. The results of the current study would help in developing or designing cost effective and environmentally compatible technique for the control of pollution by an ecosystem bio-waste; i.e. the removal of Cd from Cd-contaminated water systems.

2. Materials and methods

2.1. Adsorbent

In spring and summer *A. donax* reed grows fast and excessively spreads particularly in the vicinity of water. Leaves of *A. donax* reed were collected in summer, washed, cut into small pieces, and oven-dried. The dried materials were powdered using a mill and sieved through 750 μm sieve to obtain a micro-particle size. The leaf powder was washed repeatedly with distilled water until the electrical conductivity of the washing solutions reached values of 200 to 300 μS cm⁻¹ (i.e. to reduce its content of dissolved substances). Preliminary experiments indicated that the performance of *A. donax* leaf powder was improved after being washed compared to that of unwashed leaf powder (data not shown). The washed powder was dried and used in succeeding experiments. Samples were not subjected to further processing or chemical treatment.

2.2. Characterization of the adsorbent

In order to specify which functional groups were responsible for Cd uptake, the Fourier transform infrared (FTIR) analysis in solid phase before Cd adsorption was performed on the biomass using the Fourier Transform Infrared Spectroscopy (FTIR Prestige-21, Shimadzu, Japan). The FTIR Spectra of *A. donax* leaves before Cd adsorption is shown in *Fig. 1*. In addition, Table 1 presents the FTIR data of *A. donax* leaves before Cd adsorption.

Table 1

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>3452</td>
<td>O-H str.</td>
</tr>
<tr>
<td>2924</td>
<td>C=H str.</td>
</tr>
<tr>
<td>2893</td>
<td>C=H str.</td>
</tr>
<tr>
<td>1743</td>
<td>C=C str.</td>
</tr>
<tr>
<td>1651</td>
<td>C=C str.</td>
</tr>
<tr>
<td>1462</td>
<td>C=C str. (aromatic)</td>
</tr>
<tr>
<td>1265</td>
<td>C=O str.</td>
</tr>
<tr>
<td>1064</td>
<td>C=N str. and C=H bend</td>
</tr>
</tbody>
</table>

To know the surface structure of the adsorbent, morphological analysis was carried out by scanning electron microscopy (SEM) using Environmental Scanning Electron Microscope (ESEM) (QUANTA FEG 450, USA/EEU). *Fig. 2* shows the structure of the adsorbent and indicates that the adsorbent has a porous and heterogeneous structure.

2.3. Preparation of cadmium solutions and analytical methods

A 1000 mg l⁻¹ certified cadmium reference solution (Cd metal in 2% nitric acid) was used to prepare the relevant aqueous solutions with varying concentrations of Cd (5, 10, 20, 30, and 50 mg l⁻¹) and background solutions. All solutions were prepared in pH adjusted 0.01 mol l⁻¹ NaNO₃ (i.e. ionic strength of solutions). The pH of the aqueous solutions was adjusted using diluted NaOH or HNO₃. The cadmium concentration in solutions was analyzed by flame atomic absorption spectrophotometer (AAS).

2.4. Batch experiments

Briefly, batch adsorption experiments were carried out in acid washed PE-bottle (Alemany and Lennartz, 2009) at laboratory ambient temperature (approximately 25 ± 1 °C) in 50 ml pH adjusted solutions of 20 mg l⁻¹ Cd containing 5 g l⁻¹ (i.e. 250 mg 50 ml⁻¹) powdered *A. donax* leaves at 0.01 mol l⁻¹ NaNO₃. Cadmium sorption to PE-bottle walls was not detected. The pH values of the aqueous solutions were adjusted to the desired levels (pH 3.5, 5.5, and 7.5). The *A. donax* leaves-Cd aqueous solution mixtures were shaken on an orbit shaker at 200 rpm for varying durations (10, 30, 60, 120, 240, and 360 min; i.e. contact time). The pH at which maximum Cd adsorption (i.e. maximum removal efficiency) occurred was selected to further investigate the influence of other contributing parameters on the adsorption process. The effect of different amounts of unmodified powdered *A. donax* leaves (2.5 vs. 5 g l⁻¹ adsorbent dose; i.e. 125 vs. 250 mg 50 ml⁻¹, respectively) was investigated by adding these doses to pH 5.5 adjusted 50 ml aqueous solutions of 20 mg l⁻¹ Cd. The *A. donax* leaves-Cd aqueous solution mixtures were shaken for varying durations as mentioned above. The adsorbent dose at which maximum Cd adsorption (i.e. maximum removal efficiency) occurred was selected to further investigate the influence of various initial Cd concentrations. The favorable adsorbent dose was added to pH 5.5 adjusted 50 ml aqueous solutions of 5, 10, 20, 30, and 50 mg l⁻¹ Cd. The *A. donax* leaves-Cd aqueous solution mixtures were shaken for varying durations as mentioned above. After specified contact times, solutions were filtered through 0.45 μm filters and the filtrates were analyzed for residual Cd concentration using flame AAS for adsorption efficiency assessment and adsorption isotherm and kinetics analyses. Samples were sacrificed for each time point. The equilibrium time was determined as the contact time required for the concentration of cadmium in the solution to reach equilibrium. Adsorption efficiency was expressed as a percentage of adsorbed metal compared to initial metal concentration, whereas adsorption capacity was expressed as amount of Cd adsorbed per mass unit of powdered *A. donax* leaves using the following equations:

\[
q (\text{mg g}^{-1}) = \frac{(C_i - C_f) \times V}{m}
\]

where \(C_i\) and \(C_f\) are the initial and residual (\(C_f\)) or equilibrium (\(C_e\)) concentrations of Cd in (mg l⁻¹), \(q\) is the adsorption capacity in (mg g⁻¹) at time \(t (q_t)\) or at equilibrium (\(q_e\)), \(V\) is the volume of Cd solution in l, and \(m\) is the adsorbent mass in g.
2.5. Adsorption isotherm models

Cadmium adsorption data are usually described, analyzed and modeled using adsorption isotherms which relate the metal uptake per unit mass of the adsorbent to the equilibrium metal concentration in the bulk phase (Abu Al-Rub et al., 2004). Adsorption isotherms are important to describe the adsorption mechanism of a solute on adsorbent surface thus aid in optimizing the design of a specific adsorption process. In the current study, the equilibrium data obtained for Cd removal using powdered A. donax leaves was tested with two isotherm models available in the literature to reveal the best fitting isotherm. Adopted isotherm models were Langmuir and Freundlich isotherm equations. Isotherm adjustable variables and coefficients of determination ($R^2$) were computed from linearized equations of these isotherms.

2.5.1. Langmuir isotherm model

The Langmuir model adequately describes cadmium adsorption as the equilibrium concentration of cadmium ($C_e$) becomes large (Essington, 2004). In addition, the Langmuir equation assumes that (i) the number of surface adsorption sites are fixed; (ii) adsorption includes a single monolayer; (iii) adsorption behavior is independent of surface coverage; (iv) all adsorption sites are represented by similar types of functional groups; and (v) the isotherm displays L-type behavior (Evangelou, 1998; Huang et al., 2007). According to Essington (2004), the L-type isotherm indicates that the adsorbate has a relatively high affinity for the surface of the adsorbent at low surface coverage; however, as coverage increases, the affinity of the adsorbate for the surface of the adsorbent decreases. Langmuir equation can be described as:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$$

where $K_L$ (l mg$^{-1}$ of adsorbent) is the adsorption equilibrium constant, which is a measure of the intensity of the adsorption isotherm (Essington, 2004), $q_e$ (mg g$^{-1}$) is the amount of adsorbed cadmium at equilibrium and $q_m$ (mg g$^{-1}$) is the saturated monolayer sorption capacity, which represents a practical limiting adsorption capacity when the surface is fully covered with Cd. Langmuir equation can be described by the linearized form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} \times C_e$$

By plotting $C_e/q_e$ versus $C_e$, $K_L$ and $q_m$ can be determined when a straight line is obtained. $q_m$ and $K_L$ values will be calculated from the slope and intercept of the graphed line, respectively. The Langmuir parameters can be used to predict the affinity between the
adsorbate and adsorbent using the dimensionless separation factor \( R_L \) defined by Hall et al. (1966) as:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \( K_L \) is defined above and \( C_0 \) is the initial concentration of Cd (mg l\(^{-1}\)). For a favorable adsorption, the value of \( R_L \) should be \( 0 < R_L < 1 \), \( R_L = 1 \) indicates unfavorable adsorption, \( R_L = 1 \) indicates linear adsorption and \( R_L = 0 \) indicates irreversible adsorption (Gupta and Babu, 2008).

2.5.2. Freundlich isotherm model

The Freundlich model adequately describes the adsorption data over the entire range of \( C_e \) studied (Essington, 2004). In addition, the Freundlich model is an empirical equation based on adsorption on a heterogeneous surface. It was chosen to estimate the adsorption intensity of Cd toward powdered A. donax leaves. It is given as:

\[
q_e = K_F C_e^{1/n}
\]

where \( K_F \) and \( n \) are the Freundlich constants of the system, indicating the sorption capacity (i.e. the number of adsorptive sites on the adsorbent surfaces Mustafa et al. (2004)) and sorption intensity, respectively. This equation can be linearized in logarithmic form as follows:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

The Freundlich constants can be determined by plotting \( \log q_e \) versus \( \log C_e \).

2.6. Adsorption kinetics

The process of pollutant removal from an aqueous phase by any adsorbent can be explained using kinetic models and examining the rate-controlling mechanism of the adsorption process (Semerjian, 2010). The knowledge of adsorption velocity is important information for designing batch adsorption systems. The kinetics of adsorption was studied by using pseudo-second order model, which takes into account the adsorbed quantities that will enable engineers to determine the reactor volume (Azouaou et al., 2010). It has been reported that most adsorption systems follow a pseudo-second-order kinetic model (Vadivelan and Kumar, 2005). Pseudo-second-order kinetic equation can be described as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( k_2 \) is the second-order adsorption rate constant in g mg\(^{-1}\) min\(^{-1}\) computed from the linear plot of \( t/q_t \) versus \( t \). The rate constant and the initial adsorption rate (g mg\(^{-1}\) min\(^{-1}\)) are calculated as follows:

\[
k_2 = \frac{1}{\text{intercept} \times q_e^2}
\]

Initial adsorption rate \( = k_2 \times q_e^2 \).

Additionally, the possibility of intra-particle diffusion was explored using the intra-particle diffusion model (Dogan et al., 2004). The intra-particle diffusion equation can be described as:

\[
q_t = k_d t^{1/2}
\]

where \( k_{id} \) is the rate constant for intra-particle diffusion estimated from plotting \( q_t \) versus \( t^{1/2} \).

3. Results and discussion

3.1. Influence of solution pH and contact time on Cd removal efficiency of unmodified A. donax leaves

The pH of aqueous solutions has a dramatic effect on the adsorption of metal ions onto the adsorbent due to its effect on the degree of ionization, speciation of the metal ions and the surface charge of the adsorbent (Elliott and Huang, 1981). Thus, there is a favorable pH range for the adsorption of every metal on a specific adsorbent (Gupta and Babu, 2008; Azouaou et al., 2010). To characterize the influence of pH on Cd ions adsorption using unmodified powdered A. donax leaves, batch equilibrium adsorption experiments were carried out modifying the solution pH from 3.5 to 7.5. These experiments were conducted in solution of 20 mg l\(^{-1}\) Cd containing 5 g l\(^{-1}\) powdered A. donax leaves at 0.01 M NaNO\(_3\) ionic strength. The A. donax leaves–Cd solutions were agitated for a period of time ranging from 10 to 360 min. Fig. 3 shows that the maximum Cd removal efficiency of 78%, 92%, and 85% occurred, respectively, at pH 3.5, 5.5, and 7.5 at contact times ≥ 120 min. Thus, the favorable pH for high Cd adsorption by A. donax leaves was 5.5 and all the experiments other than on pH effects were conducted at pH of 5.5 to further investigate the influence of other contributing parameters on the adsorption process. These results are in good agreement with those of previous studies for different types of adsorbents. Rao et al. (2011) reported that Cd adsorption by Ficus religiosa leaf powder increased from 1.4 to 77.5% with the increase in pH from 2 to 5.5.

According to Srivastava et al. (2006), hydrogen ions themselves are strong competing adsorbates (mainly at low pH) and partly that the solution pH influences the chemical speciation of Cd ions. For the actual experimental solution composition as estimated by Visual MINTEQ, the chemical species of Cd as a percentage of total Cd concentration is shown in Fig. 4A. Under the current experimental conditions (i.e. pH 5.5, 0.01 M NaNO\(_3\), and 5–50 mg l\(^{-1}\) Cd concentrations); Cd\(^{2+}\) species formed more than 97% of the total Cd concentration. Moreover, Fig. 4B showed that decrease in Cd soluble concentration was not expected at the solution pH levels investigated in the current study (i.e. 3.5, 5.5, and 7.5). According to Snoeyink and Jenkins (1980), at pH ≈ 10.0, the solubility of M(OH)\(_2\)(S) becomes much smaller and, therefore, at such pH, precipitation plays the main role in the removal of the Cd(II) ions.
Moreover, Srivastava et al. (2006) reported that there are two possible mechanisms for the effect of pH on adsorption of metal ions on any adsorbent: (a) electrostatic interaction between the protonated groups of the adsorbent and cations, and (b) the chemical reaction between the metal ions and the adsorbent. Indeed, Cd(II) ions adsorption at lower pH (pH 3.5) is lower than that at higher pH (5.5) as shown in Fig. 3. In addition to the possible competition between Cd\textsuperscript{2+} and H\textsuperscript{+} ions, this might also be due to that the surface charge developed at low pH is not favorable to adsorption. A negatively charged surface site on the adsorbent favors the adsorption of metal ions due to electrostatic attraction (Srivastava et al., 2006). However, the force of electrostatic attraction will be weakened because of the increasing fraction of Cd(OH)\textsuperscript{+} with the rise in pH. According to the speciation diagram of Cd(II) ions in deionized water presented by Srivastava et al. (2006), for pH > 6 the fraction of Cd(OH)\textsuperscript{+} increases and that of Cd\textsuperscript{2+} ions decreases. Indeed, Cd(II) ions adsorption at higher pH (pH 7.5) is lower than that at pH 5.5 as shown in Fig. 3.

Concerning the influence of the contact time, the initial uptake rate of Cd varied with the contact time as shown in Fig. 3. Adsorption process was relatively fast and equilibrium was attained at 120 min and there was no interaction between solution pH and contact time (Fig. 3). Salim et al. (2008) reported that the time required to reach maximum removal of Cd (i.e. equilibrium time) varies highly from one type of leaves to another. The equilibrium time ranged from 30 min for dried plants (Chiban et al., 2011b) to 190 h for oak leaves (Salim et al., 2008). Generally, the initial high adsorption rate is due to the abundance of free binding sites. According to Wang et al. (2010), the meso-pores become almost saturated with Cd\textsuperscript{2+} as well as Cd(OH)\textsuperscript{+} ions during the initial stage of adsorption process. Subsequently, the Cd ions have to traverse farther and deeper into the micro-pores encountering much larger resistance, thus leading to decrease driving force and adsorption rate. Additional explanation might be that large sized metal ions such as Cd(II) (1.71 Å) have easier accessibility to the surface and meso-pores than to micro-pores.

3.2. Influence of adsorbent dose and contact time on Cd removal efficiency and adsorption capacity of unmodified A. donax leaves

Results showed that the residual Cd concentration decreased while Cd removal efficiency increased with decreasing the dose of A. donax leaves from 5 to 2.5 g l\textsuperscript{-1} at almost all contact times (except for 10 min contact time) as shown in Fig. 5A and B. As can be seen, the maximum Cd removal efficiency increased from 92% to 97% for 5 and 2.5 g l\textsuperscript{-1}, respectively. After 120 min no further increase in Cd removal was observed (Fig. 5B). At the shorter contact times, the observed increase in the percentage of Cd removal can be attributed to increased adsorbent's surface area and availability of more active sites. The amount of cadmium adsorbed per unit mass of A. donax leaves decreased with increasing the adsorbent dose (Fig. 5A). According to Ghodbane et al. (2008), at higher A. donax to solute concentration ratios, there is a very fast superficial adsorption onto the adsorbent surface that produces a lower solute concentration in the solution than when the A. donax to solute concentration ratio is lower. The decrease in amount of Cd adsorbed with increasing the adsorbent mass is, thus, due to the split in the flux or the concentration gradient between solute concentration.
in the solution and the solute concentration in the surface of the adsorbent. Therefore, with increasing adsorbent mass, the amount of Cd adsorbed onto unit weight of adsorbent gets reduced, thus causing a decrease in adsorption capacity with increasing adsorbent mass concentration. Another reason may be due to the particle interaction, such as aggregation, resulting from high adsorbent concentration. Such aggregation would lead to decreases in total surface area of the adsorbent and an increase in diffusion path length (Rao et al., 2008). The current results were in good agreement with previously reported studies. Semerjian (2010) reported that almost complete Cd removal was achieved in the presence of 10 g l⁻¹ untreated Pinus halpensis sawdust compared to higher adsorbent does. Gutiérrez-Segura et al. (2012) reported that the adsorption capacities of Cd decreased with increasing the dosage adsorbent (Na and Fe modified zeolitic tuffs and carbonaceous material from pyrolyzed sewage sludge). On the other hand, the Cd removal efficiency of A. donax leaves was higher than that of Withania frutescens plant (92–93%) recently reported by Chiban et al. (2012). For all subsequent experiments 2.5 g l⁻¹ A. donax leaves was used for adsorption of metal ions.

3.3. Adsorption isotherm study

Adsorption isotherms are characterized by specific constants that express the surface properties and affinity of adsorbent toward the adsorbed metal ions. The amount of cadmium adsorbed per unit mass of A. donax leaves at equilibrium increased with an increasing Cd(II) concentration of the solution from 5 to 50 mg l⁻¹ (Table 2). This is in agreement with the findings from various studies (Kula et al., 2008; El-Said et al., 2010; Semerjian, 2010). The increase in adsorbed Cd ions with increasing initial Cd concentrations is due to that more Cd²⁺ ions were available in the liquid phase at higher concentrations and, thus, the solute concentration gradient (mass transfer driving force) became greater. This is supported by the higher initial adsorption rate that increased from 0.26 to 204 mg g⁻¹ min⁻¹ for 5 and 50 mg l⁻¹ Cd²⁺, respectively (Table 2). Though, the adsorbed Cd: dissolved Cd²⁺ ratio (q_C/d_C) decreased with increasing initial Cd concentration (data not shown) taking into account that the used adsorbent mass (dose) was 2.5 g l⁻¹ at all Cd concentrations. This can be attributed to the decrease in Cd removal efficiency from 98% to 94% at 5 and 50 mg l⁻¹ Cd²⁺, respectively. According to Azouaou et al. (2010), for a given adsorbent dose the total number of available active sites on the surface of the adsorbent is fixed thereby adsorbing almost the same amount of Cd; thus resulting in a decrease in the Cd removal corresponding to an increase in initial Cd concentration. Indeed, increasing the initial Cd concentration from 5 to 50 mg l⁻¹ resulted in 9.6 times higher adsorbed Cd (q_e) and 30 times higher equilibrium Cd²⁺ concentration (d_C). Whereas, increasing the initial Cd concentration from 30 to 50 mg l⁻¹ resulted in only 1.6 times higher q_e and 2.4 times higher d_C. This is typical for the L-type isotherm, which indicates that the adsorbate has a relatively high affinity for the surface of the adsorbent at low surface coverage; however, as coverage increases, the affinity of the adsorbate for the surface of the adsorbent decreases.

Analysis of the relationship between the adsorption capacity of A. donax leaves and different Cd initial concentrations was performed using the isotherm equations mentioned previously. The linearized Freundlich and Langmuir isotherms and the coefficients of determination (R²) are shown in Figs 6 and 7. Although Freundlich and Langmuir isotherm models described well the experimental data, equilibrium isotherm data were best described by Freundlich model (R² 0.990 and 0.978, respectively). High coefficients of determination indicate a good agreement between the experimental values and isotherm parameters. According to Gutiérrez-Segura et al. (2012), the values of 0.1 < 1/n < 1 show favorable adsorption of Cd ions onto adsorbents; i.e. adsorption intensity. The 1/n value (0.674) was >0.1 and <1 indicating favorable adsorption of Cd on powdered A. donax leaves, as new sites could be available and the adsorption capacity would be increased. However, since Cd was the only metal ion in solutions, it is not possible to compare the affinity of the adsorbent sites of A. donax leaves to Cd with that to other metal ions. The values of 1/n obtained in this work are close to the values obtained in previous works on the removal of cadmium by plant leaves (Salim and Abu-El-Halawa, 2002; Salim et al., 2008). The parameter KF is related to the distribution coefficient, and consequently to the degree of Cd affinity and mobility to the adsorbent. The value of the parameter KF is 9.725 g⁻¹, which is higher than that reported by Abu Al-Rub et al. (2004), Srivastava et al. (2006), Azouaou et al. (2010), Wasewar et al. (2010) for immobilized dead algal cells, rice husk ash, untreated coffee grounds, and granular activated carbon, respectively. This reflects
the remarkable cadmium affinity of A. donax leaves compared to other adsorbents.

The Langmuir constant, $q_{\text{max}}$, which is a measure of monolayer adsorption capacity of A. donax leaves is calculated as 27.9 mg g$^{-1}$ and the Langmuir constant, $K_L$, which denotes the affinity of Cd to binding sites of the adsorbent (Gutiérrez-Segura et al. 2012) or retention intensity, is calculated as 0.6481 mg$^{-1}$. The $K_L$ value obtained in the present work is also higher than that reported by Abu Al-Rub et al. (2004), Srivastava et al. (2006), Tan and Xiao (2009), Azouaou et al. (2010), Wasewar et al. (2010) for immobilized dead algal cells, rice husk ash, ground wheat stems, untreated coffee grounds, and granular activated carbon, respectively, which indicates significant differences in the retention intensity among these adsorbents; i.e., a large value of $K_L$ implies the strong bonding of Cd(II) ions to A. donax leaves. The value of the dimensionless parameter $R_L$ confirms that the adsorption is favorable (0 < $R_L$ < 1) over the entire range of Cd concentration (5–50 mg l$^{-1}$) as shown in Fig. 7B.

The comparison of adsorption capacity of unmodified A. donax leaves with that of various adsorbents is shown in Table 3. A comparison of these values with that obtained in the current study showed that unmodified A. donax leaves exhibited a considerable capacity for cadmium adsorption from aqueous solutions.

**Table 3**

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$q$ (mg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial activated carbon</td>
<td>8.21</td>
</tr>
<tr>
<td>Oxidized granular activated carbon</td>
<td>5.73</td>
</tr>
<tr>
<td>Untreated P. halepensis sawdust</td>
<td>0.11–5.36</td>
</tr>
<tr>
<td>Areca (food waste)</td>
<td>1.12</td>
</tr>
<tr>
<td>Corn cob</td>
<td>5.06</td>
</tr>
<tr>
<td>Rice husk ash</td>
<td>3.03</td>
</tr>
<tr>
<td>Withania frutescens plant</td>
<td>0.002</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>11.75</td>
</tr>
<tr>
<td>Activated clay</td>
<td>8.72</td>
</tr>
<tr>
<td>Ground wheat stems</td>
<td>11.60</td>
</tr>
<tr>
<td>Immobilized dead algal cells</td>
<td>31.3</td>
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<tr>
<td>Untreated coffee grounds</td>
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<tr>
<td>Eucalyptus bark</td>
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<td>S. anthophorum plant</td>
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<td>L. arboreseus plant</td>
<td>11.50</td>
</tr>
<tr>
<td>Cuprotron edulis</td>
<td>28</td>
</tr>
<tr>
<td>A. donax leaves (present work)</td>
<td>27.90</td>
</tr>
</tbody>
</table>

*Sources: Azouaou et al. (2010),
Semerjian (2010),
Zheng et al. (2008),
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3.4. Adsorption kinetics study

Cadmium adsorption kinetics onto unmodified A. donax leaves was tested with the pseudo-second-order kinetic model by plotting $t/q_t$ versus $t$ and the intra-particle diffusion model by plotting $q_t$ versus $t^{1/2}$ as shown in Fig. 8A and B. The conformity between experimental data and the model predicted values was expressed by the coefficients of determination ($R^2$ values close or equal to 1). A relatively high $R^2$ value indicates that the model successfully describes the kinetics of the adsorption. Excellent fits ($R^2 > 0.9995$) for A. donax leaves indicate that the pseudo-second-order kinetic model is the only applicable kinetic model. The applicability of this model implies that the rate limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between A. donax leaves and Cd ions (Ho and McKay, 1999). From the plot shown in Fig. 8A, the estimated equilibrium capacity, $q_e$, was calculated for the initial Cd concentrations ranging from 5 to 50 mg l$^{-1}$ as summarized in Table 2. The calculated $q_e$ values show a very good agreement with the experimental values with $R^2$ values
4. Conclusions

This study concludes that unmodified Arundo donax leaves have significant adsorption capacity for cadmium. The Cd removal efficiency was found to be dependent on pH, contact time and adsorbent dose. Although Freundlich and Langmuir isotherm models described well the experimental data, equilibrium isotherm data were best described by Freundlich isotherm model. Kinetic study obeyed pseudo-second-order model, which indicates chemisorption as the rate limiting step in the adsorption process. Based on the results, Arundo donax leaves can be potentially used as a new raw material of low cost eco-(bio)sorbent for Cd removal from Cd-contaminated water systems. Results of the present work can be used to design batch adsorption systems for Cd removal for small and medium-scale industries where disposing industrial wastewater imposes environmental hazard.

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