Competitive sorption of nickel, copper, lead and cadmium on okra leaves (Abelmoschus esculentus)

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Received: 22/02/2016, Accepted: 11/04/2017, Available online: 26/09/2017
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Abstract
In this study, potential of okra leaves for the removal of Ni(II), Cu(II), Pb(II) and Cd(II) from the mixed metal aqueous solution were evaluated. The data were analyzed by Freundlich, Langmuir, D-R, Flory-Huggins and Halsey adsorption models. Pseudo first order rate, Pseudo second order rate, Morris-Weber and Elovich equations were employed to understand the kinetics of the reaction. The characterization of the adsorbent was carried out by EDX and FTIR techniques. The order of maximum metal uptake calculated by D-R isotherm was Cu(II) > Pb(II) > Cd(II) and Ni(II), 453 mg g⁻¹, 81 mg g⁻¹, 13.82 mg g⁻¹ and 1 mg g⁻¹ respectively, with the energy of adsorption in the range of 9-15 for Ni(II) and Cd(II) expected for the ion exchange nature of adsorption and 7-8 for Cu(II) and Pb(II) showing the physical nature of adsorption. The calculated thermodynamic parameters like Gibbs free energy and enthalpy change demonstrate that adsorption process was spontaneous and endothermic in nature. Further it was observed that all four metal ions could be adsorbed at pH 6 with detection limits of 0.04-0.1 µg L⁻¹. The method was successfully applied for the removal of these metal ions from the ground water, tap water and wastewater samples collected from different areas of Pakistan.

Keywords: Okra leaves; Removal; Metals; D-R isotherm; Kinetics

1. Introduction
Ground water contamination with heavy metals wastes is the greatest threat for government agencies, industry and communities (Jaeyoung et al., 2009). Industrial activities and the processing of ore mining are the major sources through which these toxic metals have been introduced into the environment (Fuller et al., 2002). Literature survey indicates that Ni(II), Cu(II), Cd(II) and Pb(II) are some of the potential pollutants of the environment. Cadmium, nickel and lead are known as toxic heavy metals, posing a serious threat to plant, animal, human and environment (Ashenef, 2014). According to W.H.O, maximum contamination levels of copper, cadmium, nickel and lead in drinking water are 2 mg g⁻¹, 0.003 mg g⁻¹, 0.07 mg g⁻¹ and 0.01 mg g⁻¹ respectively (W.H.O, 2011). Lead heads the list of environmental threats because even at extremely low concentrations it causes brain damage in children (Ahmedna et al., 2004). Cadmium is non-essential, non-beneficial and recognized as an occupational health hazard for many decades and increasing number of studies have shown early adverse health effects on the kidney (Kefela et al., 1999; Chandio et al., 2013). Cadmium ions are not biodegradable and easily accumulate in human tissues (Evangelin et al., 2014). The inhalation of nickel and its compounds can lead to serious problems, including respiratory cancer, skin allergies, dermatitis, lung fibrosis, headaches, nausea, vomiting, chest pain, dry cough and shortness of breath (Chandio et al., 2013). The toxic effects of copper are well documented by Sobecka (Sobecka, 2001).

Chemical precipitation, reverse osmosis, ion-exchange, filtration and evaporative recovery are most commonly using methods and effective for the treatment of liquid effluents containing high concentration of metal ions. However, these technologies are usually expensive and become inefficient for treatment of effluents containing metal ions in the range of 100 mg L⁻¹ (Suman et al., 2008). Over the last few years, adsorption has been shown to be an economically and environmentally feasible method for removal of metal ions from ground water and wastewater (Khaskheli et al., 2011). The biggest barrier in the application of this process by the industries is the high cost of adsorbents presently available for commercial use. It is, therefore, important to explore new adsorbents for metals removal and recovery from such effluents, and thus reduce the concentration of these metal ions to the safe levels.

Okra (Abelmoschus esculentus), a flowering plant belongs to mallow family Malvaceae, is a tropical perennial crop growing 3 to 6 feet tall. It is believed to have originated in Ethiopia. In recent years, it has become an important commercial crop, especially in south, where thousands of tons of the pods are grown (Olajide, 2009). In current study an effort has been made to develop an efficient, cheap and environmental friendly method to remove nickel, copper,
lead and cadmium using okra leaves as an adsorbent. Table 1 shows a comparison of the capacities of different sorbent materials with proposed sorbent. It can be shown that okra leaves have comparable capacity values with most of the sorbents reported in the literature. In order to check the practical applicability of a method it has been used for removal of all four metal ions from real water systems.

**Table 1. Comparison of sorption capacities of various sorbents for Cu(II), Cd(II), Ni(II) and Pb(II)**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Capacity (mg g⁻¹) Based on Langmuir isotherm</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat bran</td>
<td>5.5</td>
<td>Pb(II) 62.0, Cd(II) 21.0, Cu(II) 15.0, Ni(II) 12.0</td>
<td>Not applied</td>
<td>Farajzadeh and Monji, 2004</td>
</tr>
<tr>
<td>Barley straw</td>
<td>6.6</td>
<td>Pb(II) 23.2, Cd(II) - , Cu(II) 4.64, Ni(II) -</td>
<td>Not applied</td>
<td>Pehlivan et al., 2009</td>
</tr>
<tr>
<td>Tartaric acid modified</td>
<td>-</td>
<td>Ni(II) 108, Cd(II) - , Cu(II) 29.0, Ni(II) -</td>
<td>Not applied</td>
<td>Wong et al., 2003</td>
</tr>
<tr>
<td>rice husk</td>
<td>-</td>
<td>Ni(II) 68.5, Cd(II) 7.5, Cu(II) - , Ni(II) -</td>
<td>Not applied</td>
<td>Oliveira et al., 2008</td>
</tr>
<tr>
<td>Waste black tea</td>
<td>-</td>
<td>Ni(II) 90.9, Cd(II) - , Cu(II) - , Ni(II) -</td>
<td>Wastewater</td>
<td>Malakakhmad et al., 2016</td>
</tr>
<tr>
<td>HCl treated oak sawdust</td>
<td>7.7</td>
<td>Ni(II) 149, Cd(II) 66.7, Cu(II) - , Ni(II) -</td>
<td>Waste water</td>
<td>Argun et al., 2007</td>
</tr>
<tr>
<td>Dairy sludge</td>
<td>-</td>
<td>Ni(II) - , Cd(II) - , Cu(II) - , Ni(II) -</td>
<td>Not applied</td>
<td>Sassi et al., 2010</td>
</tr>
<tr>
<td>Treated Geobacillus</td>
<td>4.5</td>
<td>Cd(II) 32.3, Cu(II) 42.9, Ni(II) 50, Pb(II) -</td>
<td>Industrial waste water</td>
<td>Chatterjee et al., 2010</td>
</tr>
<tr>
<td>marine algae</td>
<td>6.6</td>
<td>Cu(II) 232.6, Ni(II) 88.5, Pb(II) 92.6, Cd(II) -</td>
<td>Waste water</td>
<td>Feng and Aldrich, 2004</td>
</tr>
<tr>
<td>Functionalized HLS biomass</td>
<td>-</td>
<td>Cu(II) 52.8, Ni(II) - , Pb(II) 23.6, Cd(II) -</td>
<td>Not applied</td>
<td>Panda et al., 2008</td>
</tr>
<tr>
<td>Pristine biomass</td>
<td>-</td>
<td>Ni(II) 35.0, Cd(II) - , Cu(II) 15.7, Ni(II) -</td>
<td>Not applied</td>
<td>Li et al., 2008</td>
</tr>
<tr>
<td>Orange peel cellulose</td>
<td>5.7</td>
<td>Ni(II) 55.1, Cd(II) - , Cu(II) 27.0, Ni(II) -</td>
<td>Not applied</td>
<td>Martinez et al., 2006</td>
</tr>
<tr>
<td>Unmodified</td>
<td>-</td>
<td>Ni(II) - , Cd(II) - , Cu(II) - , Ni(II) -</td>
<td>Not applied</td>
<td>Bulut and Tez, 2007</td>
</tr>
<tr>
<td>Grape stalk waste</td>
<td>5.5</td>
<td>Ni(II) 49.9, Cd(II) 27.9, Cu(II) - , Ni(II) -</td>
<td>Not applied</td>
<td>Bulut and Tez, 2007</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>-</td>
<td>Ni(II) 16.23, Cd(II) 5.42, Cu(II) - , Ni(II) -</td>
<td>Not applied</td>
<td>Bulut and Tez, 2007</td>
</tr>
<tr>
<td>Almond shell</td>
<td>-</td>
<td>Ni(II) 3.43, Cd(II) 3.18, Cu(II) - , Ni(II) -</td>
<td>Not applied</td>
<td>Bulut and Tez, 2007</td>
</tr>
<tr>
<td>Holly oak(stem)</td>
<td>-</td>
<td>Ni(II) 0.75, Cd(II) 0.36, Cu(II) 0.21, Ni(II) 0.58</td>
<td>Not applied</td>
<td>Parsad and Freitas, 2000</td>
</tr>
<tr>
<td>Brewery biomass</td>
<td>5.5</td>
<td>Ni(II) 96.4, Cd(II) 14.3, Cu(II) 48.9, Ni(II) -</td>
<td>Waste water</td>
<td>Kim et al., 2005</td>
</tr>
<tr>
<td>Sawdust of walnut</td>
<td>-</td>
<td>Ni(II) 6.66, Cd(II) 4.90, Cu(II) - , Ni(II) 2.79</td>
<td>Mine water, Electroplating water, metal industry</td>
<td>Bulut and Tez, 2007</td>
</tr>
<tr>
<td>Sawdust of deciduous trees</td>
<td>3.5</td>
<td>Ni(II) 3.50, Cd(II) 9.90, Cu(II) 4.60, Ni(II) -</td>
<td>Not applied</td>
<td>Bozic et al., 2009</td>
</tr>
<tr>
<td>Phaseolus aureus hull carbon</td>
<td>6</td>
<td>Ni(II) 21.8, Cd(II) 15.7, Cu(II) 19.5, Ni(II) -</td>
<td>Not applied</td>
<td>Rao et al., 2009</td>
</tr>
<tr>
<td>Olive stone waste</td>
<td>5.5</td>
<td>Ni(II) 9.26, Cd(II) 7.73, Cu(II) 2.02, Ni(II) 1.23</td>
<td>Not applied</td>
<td>Fiol et al., 2006</td>
</tr>
<tr>
<td>NaOH treated Reed biomass</td>
<td>4</td>
<td>Ni(II) 0.083, Cd(II) 0.019, Cu(II) 0.156, Ni(II) 0.135</td>
<td>Not applied</td>
<td>Southichak et al., 2006</td>
</tr>
<tr>
<td>'Okra leave (present work)</td>
<td>6</td>
<td>Ni(II) 81.0, Cd(II) 18.8, Cu(II) 453, Ni(II) 2.16</td>
<td>Drinking and waste water</td>
<td>This study</td>
</tr>
</tbody>
</table>

[^D-R capacity]: Not applied

### 2. Experimental

#### 2.1. Materials and methods

All chemicals used were of analytical grade and supplied by Merck (Darmstadt, Germany). A stock standard solution of all four metal ions was prepared by dissolving the appropriate amount of their salts in deionized water (conductivity <0.5 S cm⁻¹). Buffer solutions of pH 1–3, 4–6 and 7–9 were prepared by mixing appropriate ratios of 0.1M HCl and KCl, 0.5M acetic acid and sodium acetate and 0.5M ammonia and NH₄Cl solutions respectively.

#### 2.2. Chemical analysis

Perkins-Elmer Atomic Absorption Spectrophotometer (AA-800) was used to quantify metal ions using recommended conditions. All pH measurements were carried out by Thermo Scientific Orion 5 Star (pH. ISE. Cond. DO Benchtop, 81028NULWP; Made in USA) PH-meter. Shaking Incubator Model 1-40000 Irmeco GmbH (Geesthacht/Germany) was used for batch experiments. Peristaltic pump (Gilson, Made in France) was used for column study.

#### 2.3. Batch sorption study of Ni(II), Cu(II), Cd(II) and Pb(II)

A weighed amount of Okra leaves was equilibrated with 20 mL solution containing 10 mg mL⁻¹ of each Ni(II), Cu(II), Cd(II) and Pb(II) at pH 6 and ionic strength (0.001 mol L⁻¹) at 25±1°C. The sorbent was filtered and the equilibrium concentration was determined.

#### 2.4. Sorption of metal ions (Ni (II), Cu(II), Cd(II) and Pb(II)) by column method

A fixed bed study was carried out in a glass column made up of glass. A glass column of 18 cm length and 1.2 cm diameter was selected for the study. Small amount of glass wool was placed in the bottom to avoid the wastage of sorbent from the lower end of the column. Then slurry in water of 0.5 g of sorbent was poured and column filled up to the 2.5 cm. pH 6 maintained metals ion solution was
pumped through the embedded column by peristaltic pump controlling the flow rate 1-6 mL min⁻¹. The passing of the solution at an optimized flow rate, continued till no sorption of metal ion occurred or biomass in the column was fully saturated with metal ions means breakthrough was achieved. Then a suitable amount of leaching agent (H₂SO₄) was eluted through the column having metal loaded sorbent. Consequently, metal analysis of eluted sample solutions collected at regular intervals of time after sorption and desorption were done with an Atomic Absorption spectrometer. Column studies were conducted at room temperature (25 °C). Finally, breakthrough curves were drawn from the observed results.

Data manipulation

The percent sorption of all four metal ions was determined using the following equation: \[ \% \text{Sorption} = \frac{C_0 - C_f}{C_0} \] (Bazrafshan et al., 2012).

Where

\( C_0 = \) Concentration of solution before sorption (mol L⁻¹)
\( C_f = \) Concentration of solution after sorption (mol L⁻¹)

3. Results and discussion

3.1. Characterization of sorbent

3.1.1. Energy Dispersive X-ray Analysis (EDX) of metal loaded okra leaves

The surface study of okra leaves before and after the sorption of metal ions was carried out. Both figures Fig. 1a and Fig. 1b show the elemental analysis of okra leaves before and after the sorption respectively. In Fig. 1a okra leaves sorbent contains a number of elements including carbon, oxygen, sodium, aluminum and calcium. While peaks of Cu(II), Cd(II), Ni(II) and Pb(II) appeared in the EDX spectrum of okra leaves (Fig. 1b) shows the retention of these metal ions.

3.1.1. Fourier Transform infrared spectroscopy (FT-IR) analysis

In order to understand the mechanism of interaction between functional groups present in the okra leaves...
sorbent and metal ions, the FT-IR analysis technique was employed (Silverstein and Webster, 1998). The spectra of the unloaded and metal ions loaded sorbents were taken in the range of 500-4000 cm\(^{-1}\) wave number. The spectra of okra leaves sorbent before and after the metal ions sorption are shown in Fig. 2. The bands at 2847-2921 cm\(^{-1}\), 1589-1634 cm\(^{-1}\), 1409-1421 cm\(^{-1}\), 1303-1319 cm\(^{-1}\), 1000-1237 cm\(^{-1}\) and 699 cm\(^{-1}\) were attributed to H-C-H asymmetric and symmetric stretching (alkane), C=N stretching (oxime), O-H bending (carboxylic acid), N=O bending (nitro group), C-O-C stretching (ethers) and C-H bending (alkenes).

The shift of peaks for copper at (2913 cm\(^{-1}\), 1605 cm\(^{-1}\), 1413 cm\(^{-1}\), 1311 cm\(^{-1}\)& 1225 cm\(^{-1}\)), cadmium (2913 cm\(^{-1}\), 1413 cm\(^{-1}\)& 1225 cm\(^{-1}\)), nickel (2847 cm\(^{-1}\), 1605 cm\(^{-1}\), 1413 cm\(^{-1}\), & 1311 cm\(^{-1}\)) and lead (2913 cm\(^{-1}\), 2847 cm\(^{-1}\), 1605 cm\(^{-1}\), 1413 cm\(^{-1}\), 1311 cm\(^{-1}\)& 1225 cm\(^{-1}\)) were observed. The disappearance of peak at 996 cm\(^{-1}\) and emergence of new peak at 1000-1012 cm\(^{-1}\) in Fig. 2 was also analyzed. These changes in vibrational frequencies and appearance and disappearance of peaks indicate that C-H (alkane), N-H (amide), O-H (carboxylic acid), N=O (nitro group), C-O-C (ether) and C-H (alkene) functional groups are involved in the metal ions binding.

3.2 Effect of pH

The pH of the metal ion solution can affect the surface charges of the sorbent, degree of ionization of pollutants and dissociation of functional groups at active sites (Bazrafshan et al., 2013). The study of pH identifies binding sites and the type and amount of species sorbed onto the surface okra leave sorbent. The effect of pH (Fig. 3) of Ni(II), Cu(II), Cd(II) and Pb(II) ions solution was optimized with respect to the amount of metal ions loaded onto the sorbent surface.

The initial increase in sorption of all four metal ions was observed with increasing pH up to 3. Copper and lead showed a similar behavior after pH 3 and their sorption remains constant up to pH 6. Both metals showed a little decrease at pH 7 and then increases at pH 8-9. Whereas the sorption of nickel was constant up to pH 7 and then increased drastically at pH 8-9. Cadmium showed completely different behavior than rest of three metals. There was a continuous increase in percent sorption with increasing pH. The different behavior of sorption of metal ions may be due to the formation of different species at different pH values.

The main specie of Ni(II) at pH 8 is Ni\(^{2+}\) and at pH 10 the dominant species of Ni(II) ions would be Ni(OH)\(_2\) (60%),...
Ni\(^{2+}\) (18%), Ni(OH)\(^+\) (11%) and Ni(OH)\(^3−\) (10%). At pH 9 the dominant species of Cu(II) would be Cu\(_2\)OH\(_2\) (60%), Cu(OH)\(^+\) (25%), Cu(OH)\(^-\) (10%) and Cu\(^2+\) (4%) which would change to Cu(OH)\(^2+\) (40%), Cu(OH)\(^+\) (37%), Cu(OH)\(^-\) (12%), Cu(OH)\(^2−\) (10%) and Cu(OH)\(^4−\) (5%) at pH 10 (Memon et al., 2007).

Up to pH 7 the main species of Pb(II) is Pb\(^{2+}\) (>80%) and at pH 8 the dominant species of Pb(II) ions would be Pb\(^{2+}\) (~50%), Pb(OH)\(^+\) (~5%), Pb\(_2\)O\(_3\)\(^{2+}\) (~3%), and Pb(OH)\(_2\) (~1%) (Memon et al., 2005). Cadmium is the metal having ~100% of Cd as Cd\(^{2+}\) (~100) up to pH 8 (Memon et al., 2007) this may explain the reason for its different behavior from all three metal ions. Keeping in view the hydroxyl species of metal ions, pH 6 has been selected as a medium of sorption. Therefore, the hydroxide retention mechanism can be avoided.

**Figure 3.** Effect of pH on removal of Cu(II), Cd(II), Ni(II) and Pb(II) on okra leaves

### 3.3. Amount of sorbent

In sorption process the dosage of sorbent considerably affect the sorption efficiency of the sorbent. The amount of sorbent determines the uptake capacity of okra sorbent for the competitive sorption of various metal ions. The trend of sorption of copper, cadmium, nickel and lead was similar. Initially as amount of sorbent was increased, 30-80% sorption was increased at 0.1 mg per 10 mL and then smaller decrease or nearly constant sorption was observed as amount of sorbent was increased. The increase in sorption was due to the availability of the more active sites for the sorption of Cu(II), Cd(II), Ni(II) and Pb(II), while the decrease in sorption may be attributed to the accumulation of sorbent. Accumulation decreases the sorption active sites (Rojas et al., 2005).

### 3.4. Uptake of Ni(II), Cu(II), Cd(II) and Pb(II) as a function of time

The contact time between sorbate and sorbent is one of the most important design parameters that affect the performance of adsorption process (Bazrafshan et al., 2016). The effect of equilibration time on the amount adsorbed was optimized at pH 6. Results are shown in Fig. 4.

**Figure 4.** Uptake of Cu(II), Cd(II), Ni(II) and Pb(II) on okra leaves as a function of time

All four metal ions have nearly same trend of equilibration. All four metal ions attained equilibration within 60 minutes and after 60 minutes the sorption remains nearly constant. The kinetic data were evaluated by first order, second order rate equations (Khaskheli et al., 2014) as well as Elovich and Morris-Weber equations in order to understand the mechanism of adsorption. Following linearized equations were used:

\[
\log(q_e-q_t) = \log q_e - \frac{k_1t}{2.303} \\
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \\
q_t = R_d\sqrt{t} \\
\frac{1}{q_t} = \ln\alpha + \frac{\ln t}{\beta} \\
\alpha = \frac{k_2}{\beta} \\
\beta = \frac{1}{k_2q_e^2} \\
\]

Where \(k_1\) is the pseudo first and \(k_2\) second order rate constant, \(q_e\) is the amount of metal ions sorbed at equilibrium (mg g\(^{-1}\)), and \(q_t\) is amount of metal ions on the okra leaves at specified time (mg g\(^{-1}\)). \(R_d\) is rate constant for intra particle diffusion. \(\alpha\) is the initial sorption rate (mg g\(^{-1}\) min\(^{-1}\)) and \(\beta\) is desorption constant (mg g\(^{-1}\) min\(^{-1}\)) during any one experiment.

Table 2 shows the kinetic parameters calculated by all four equations. As clear from Table 2 Ni(II) and Cd(II) followed second order rate equation; whereas kinetic data of Pb(II) and Cu(II) followed first order rate equation. From these results it can be concluded that the mechanism of sorption of Ni(II) and Cd(II) is ion-exchange or chemisorption (Kumar et al., 2010) whereas, Pb(II) and Cu(II) follow the physical nature of sorption (Ranjan et al., 2009; Chen et al., 2008; Urik et al., 2009; Ho, 2006).

In case of Morris–Weber equation the straight lines of Ni(II), Cd(II) and Pb(II) did not pass through their origins which demonstrated that intra particle diffusion was not only the rate controlling step but other mechanisms were also involved in the rate determining step.

Elovich equation which was followed by Ni(II) and Cd(II), supported the chemisorption nature of the sorption reaction.

**Table 2.** Kinetic parameters for the sorption of Ni(II), Cu(II), Cd(II) and Pb(II) on okra leaves

<table>
<thead>
<tr>
<th>Metal</th>
<th>Elovich</th>
<th>Morris-web</th>
<th>first order eq.</th>
<th>second order eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.5. Sorption Isotherm studies

Isotherm study demonstrates the relationship between the amounts of metal ions present in solution and adsorbed on the surface of sorbent when equilibrium was established between these two phases. The affect of concentration on the amount of metal sorbed onto the surface was calculated and the data were evaluated using Langmuir, Freundlich (Khaskheli et al., 2016), D-R, Flory-Huggins and Halsey isotherm equations (Basar, 2006; Vijayaraghavan et al., 2006). All equations were analyzed in following linearized form:

\[ \frac{C_e}{q_e} = \frac{1}{K} + \frac{1}{C_s} \quad \text{Langmuir} \]

\[ \log q_e = \log K_N + \frac{1}{n} \log C_e \quad \text{Freundlich} \]

\[ \log q_e = \log K_d + \beta \log C_e \quad \text{D-R} \]

\[ \log \frac{q_e}{C_i} = \log K_f + n_F \log (1-\theta) \quad \text{Flory-Huggins} \]

\[ \theta = 1 - \frac{C_e}{C_i} \]

\[ \log q_e = \frac{\log K_i}{n_H} - \frac{\log C_e}{n_H} \quad \text{Halsey} \]

Where \( C_e \) is the equilibrium concentration of metal ions in solution (mol L\(^{-1}\)), \( q_e \) is the amount of metal ions on surface (mol g\(^{-1}\)), \( C_s \) is the maximum amount of ions sorbed, \( K_s \) is the Langmuir constant related to the binding energy of solute, \( K_d \) and \( 1/n \) are Freundlich constants representing sorption capacity and sorption intensity, respectively; \( e \) is polanyi potential and equal to \( RT/(1+C_e) \), \( T \) is temperature and \( R \) is general gas constant; \( \beta \) is related to the mean free energy of sorption per mole of the sorbent when it is transferred from infinite distance in the solution to the surface of the solid by equation:

\[ E = \frac{1}{\sqrt{2\beta}} \]

\( \theta \) is degree of surface coverage, \( n_H \) is the Flory-Huggins model exponent represents the number of metal ions of solute occupy active sites of sorbent, \( K_i \) is the Flory-Huggins model equilibrium constant is used to calculate the Gibbs free energy of spontaneity (\( \Delta G^o \)) by following relationship.

\[
\Delta G^o = -RT \ln K_i
\]

\( K_i \) is the Halsey constant and \( n_H \) is the exponent.

As shown in Table 3 Langmuir adsorption isotherm was nickel and cadmium envisages that all sites on sorbent are equal and uniform, there is no attraction between sorbed molecules and there is no steric hindrance between sorbed molecules and incoming ions and monolayer is formed at the maximum sorption capacity.

Copper and lead experimental data were fitted to Freundlich adsorption isotherm (Table 3). This isotherm describes the heterogeneity of the surface and formation of multilayers sorbed ions on the surface of the sorbent.

D-R sorption isotherm on the basis calculated energy values define the nature of sorption of metal ions. In table 3, energy of sorption range 8-15 for Ni(II) and Cd(II) demonstrates the ion exchange nature of sorption, while energy less than 8 for Pb(II) and Cu(II) shows the physical nature of sorption (Ranjana et al., 2009). The order of maximum metal uptakes calculated by D-R isotherm was Cu\(^{2+}\) > Pb\(^{2+}\) > Cd\(^{2+}\) and Ni\(^{2+}\), 453 mg g\(^{-1}\), 81 mg g\(^{-1}\), 13.82 mg g\(^{-1}\) and 1 mg g\(^{-1}\) respectively.

Flory-Huggins model of isotherm discuss the mature of sorbent. Table 3 shows that there are number of metal ions (\( n_H \)) occupying sorption sites [copper (3.19), cadmium (1.87), lead (1.56) and nickel (1.3)] are present on the surface of the sorbent.

In case of Halsey isotherm high value of correlation coefficient (\( r = 0.94-0.99 \)) indicates that data are well fitted to the isotherm and attests the heteroporous (macropores and micropores) nature of the sorbent (Oladoja et al., 2009).

3.6. Thermodynamic Study

The estimation of the feasibility and nature of the sorption process is evaluated by the calculation of thermodynamic parameters (Iftikhar et al., 2009). Thermodynamic parameters (Gibbs free energy, enthalpy change and entropy change) were calculated by using following equations.

\[
\Delta G^o = -RT \ln K_i
\]

\[
\ln K_i = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

The graph plotted \( \ln K_i \) against \( 1/T \) gives linear curve. Entropy change (\( \Delta S \)) and enthalpy change (\( \Delta H \)) are determined from intercept and slope respectively.

### Table 3. Regression parameters for the Langmuir, Freundlich, D-R Flory-Huggins and Halsey sorption isotherms by using okra leaves as sorbent

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Cu(II)</th>
<th>Cd(II)</th>
<th>Ni(II)</th>
<th>Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α (mg g(^{-1}) min(^{-1}))</td>
<td>0.92</td>
<td>0.75</td>
<td>0.94</td>
<td>7.34</td>
</tr>
<tr>
<td>β (g mg(^{-1}))</td>
<td>35.96</td>
<td>2.07</td>
<td>0.98</td>
<td>1.36</td>
</tr>
<tr>
<td>Re (μmol g(^{-1}) min(^{-1}))</td>
<td>0.96</td>
<td></td>
<td></td>
<td>0.0072</td>
</tr>
<tr>
<td>r</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4 shows that Gibbs free energy ($\Delta G$) values of all metals are negative, means sorption reaction of metal ions on okra leaves sorbent was spontaneous (i.e. sorption forces are quite strong to overcome the potential barrier). Increase of negative value with the increase of temperature favour the sorption process (Khaskheli et al., 2016). In other words it can be said that the degree of spontaneity increases with increasing the temperature (Thajeel, 2013). Positive values of entropy ($\Delta S$) for Ni(II), Cd(II), Pb(II) and Cu(II) show that there was randomness of metal ions on the surface of sorbent during the process. These values also reflect the affinity of sorbent for particular metal ions. Positive values of enthalpy change $\Delta H$ for all metals indicate that sorption process was an endothermic. These results support that sorption capacity of the adsorbent increases with the increasing of temperature (Surchi, 2011).

### Table 4. Thermodynamic constants for the sorption of Ni(II), Cd(II), Pb(II) and Cu(II) on okra leaves at various temperatures

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Temp. (K)</th>
<th>$\ln k_c$ (mg g$^{-1}$)</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (kJ mol$^{-1}$ K$^{-1}$)</th>
<th>$R$ (kJ mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td>293</td>
<td>1.21</td>
<td>-3.46</td>
<td>17.09</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.37</td>
<td>-3.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.65</td>
<td>-4.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>1.58</td>
<td>-3.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(II)</td>
<td>293</td>
<td>1.72</td>
<td>-4.33</td>
<td>8.77</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.72</td>
<td>-4.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.82</td>
<td>-4.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>1.73</td>
<td>-4.22</td>
<td></td>
<td></td>
<td>8.3143 x 10$^{-3}$</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>293</td>
<td>1.99</td>
<td>-5.02</td>
<td>22.04</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>2.31</td>
<td>-6.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>2.31</td>
<td>-6.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>303</td>
<td>2.44</td>
<td>-6.15</td>
<td>40.43</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.06</td>
<td>-7.95</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.7. Column sorption studies of Cu(II), Cd(II), Ni(II) and Pb(II) ions

For the evaluation of sorbent efficiency of okra leaves for the sorption of Cu(II), Cd(II), Ni(II) and Pb(II) ions was analyzed by employing the flow method containing column experiments.

#### 3.7.1. Effect of flow rate of sample

At optimum pH, the effect of flow rate in the range 1-3 mL min$^{-1}$ for the sorption of Cu(II), Cd(II), Ni(II) and Pb(II) ions was analyzed. Fig. 5 shows that maximum sorption was obtained at 2 mL min$^{-1}$ and then decreased. The decrease in sorption at higher flow rate may be attributed to the short contact time between sample ions and sorbent present in the column. As a result equilibrium did not properly establish at high flow rate.
3.7.2. Regeneration/Desorption Study

To make sorption method more economical, it is necessary to desorb the adsorbed metals ions. Desorption process yields metals in concentrated form; facilitate their disposal and restore sorbent for effective reuse (Ladeira and Ciminelii, 2004). For the regeneration of sorbent and recovery of metal ions, different mineral acids and bases were employed. The efficiency of leaching agents was evaluated with different concentrations (0.1-1M) and volumes (1-5 mL). The results indicated that 5 mL of 1M H2SO4 recovered 95-99% of metal ions.

3.7.3. Limit of preconcentration and preconcentration factor

The determination of preconcentration limit was based on the principle that the amount of metal ions was maintained constant (10 µg) and volume of solution increased. Cu(II), Cd(II), Ni(II) and Pb(II) ions were quantitatively collected from the solutions having concentrations in the range of 0.04-0.1µg mL⁻¹. The calculations revealed that preconcentration factor for Cu(II), Cd(II), Ni(II) and Pb(II) ions were 40, 20, 50 and 40 respectively.

3.7.4. Breakthrough study (Total sorption capacity)

Breakthrough study is related to the concentration of the effluent of column. Generally, when the effluent concentration reaches to 3-5% of influent is treated as breakthrough point. Solutions of Cu(II) 7.9 × 10⁻⁵ mol L⁻¹, Cd(II) 4.4 × 10⁻⁵ mol L⁻¹, Ni(II) 8.5 × 10⁻⁵ mol L⁻¹ and Pb(II) 2.4 × 10⁻⁴ mol L⁻¹ were passed through columns. Fig. 6 shows that breakthrough curve is obtained at 75 mL for Cu(II), 110 mL for Cd(II), 130 mL for Ni(II) and 220 mL for Pb(II). Sharp jump in the percent sorption nearly in all metal ions favors the equilibrium.

Table 5. Actual concentrations of Ni(II), Cu(II), Cd(II) and Pb(II) in different water samples

<table>
<thead>
<tr>
<th>Metal</th>
<th>Conc: present in * (S1) mg L⁻¹</th>
<th>Conc: present in * (S2) mg L⁻¹</th>
<th>Conc: present in * (S3) mg L⁻¹</th>
<th>Conc: present in * (S4) mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>0.26</td>
<td>0.29</td>
<td>0.300</td>
<td>0.25</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>0.29</td>
<td>0.01</td>
<td>0.007</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.25</td>
<td>0.08</td>
<td>0.360</td>
<td>0.10</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>2.58</td>
<td>2.74</td>
<td>1.100</td>
<td>2.39</td>
</tr>
</tbody>
</table>

*S1: Hand pump water (Choudhary Mohammad Sadiq Chak 147, Taluka Sadiqabad, Distt: Rahimyar Khan), *S2: Hand pump water (Basic Health Unit Manthar, Taluka Sadiqabad, Distt: Rahimyar Khan), *S3: Tap water (Institute For Advanced Research Studies in Chemical Sciences, University Of Sindh, Jamshoro), *S4: Hand Pump (Madarssa Dar-ul-uloom Manthar Taluka Sadiqabad Distt: Rahimyar Khan)

Table 6. Removal of Ni(II), Cu(II) Cd(II) and Pb(II) from drinking water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount added (mg L⁻¹)</th>
<th>Total concentration (mg L⁻¹)</th>
<th>% Removal</th>
<th>Residual Concentration (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>Cd</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>2.45</td>
<td>2.39</td>
</tr>
</tbody>
</table>
6. Conclusion

Present work explores the competitive sorption of Ni(II), Cu(II), Cd(II) and Pb(II) from aqueous solutions. It has been found that the okra leaves can efficiently be used for the removal of all four metal ions simultaneously. Kinetic, equilibrium and thermodynamic studies favour the adsorption of all metal ions on okra leaves sorbent. EDX analysis confirms the presence of four metal ions on the surface of metal sorbed okra leaves. At the flow rate of 2 mL min⁻¹, about 75-220 mL of metal ions having concentration 0.04-0.1µg mL⁻¹ can be passed through the column. Further, low values of COD and BOD of treated contaminated water encourage the application of the method. It can be concluded that okra leaves can be used as a replacement to existing expensive sorbents.

References


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