Cellulose with Bidentate Chelating Functionality: An Adsorbent for Metal Ions from Wastewater

Abdalhadi Deghles, a,*, Othman Hamed, b,* Mai Azar, b Bahia Abu Lail, b Khalil Azzaoui, c Ahmad Abu Obied, b and Shehdeh Jodeh b

A cellulose derivative with multiple coordination sites for metals composed of cellulose powder and 1,2-phenylenediamine was synthesized and evaluated as an adsorbent for metal ions from wastewater. The cellulose powder was generated from the solid waste of the olive industry. The adsorption efficiency of the cellulose amine polymer toward Fe(III) and Pb(II) was investigated as a function of adsorbent dose, temperature, pH, and time. The adsorption parameters that lead to excellent adsorption efficiency were determined. In addition, the polymer showed an excellent extraction efficiency toward approximately 20 metal ions present in a sewage sample. The cellulose amine derivative had several coordination sites that included amine, hydroxyl, and aromatic groups. The diversity and frequency of the coordination sites explained the high efficiency of the polymer for metal ions. The thermodynamic analysis results supported the spontaneous adsorption efficiency of the polymer at room temperature. The adsorption process fit well with the Langmuir adsorption isotherm model.

Keywords: Cellulose powder; Metal ion; 1,2-Phenylene diamine; Wastewater; Cellulose aldehyde; Atomic adsorption spectroscopy

Contact information: a: Graduate Studies Department, Al-Istiqlal University, Ariha, Palestinian Territories; b: Department of Chemistry, College of Science, An-Najah National University, Nablus, Palestinian Territories; c: Laboratory of Mineral Solid and Analytical Chemistry LMSAC, Department of Chemistry, Faculty of Sciences, Mohamed 1st University, P.O. Box 717;
* Corresponding authors: ohamed@najah.edu; daghlas2014@pass.ps

INTRODUCTION

There is a constantly increasing demand for more sources of fresh water to cover the growing need for food production and human activities (Milieu 2010). Recycling the wastewater released from both industrial and human activities could be an answer for this demand. Wastewater contains a wide variety of toxic materials, both organic and inorganic, depending on the discharging source (Gupta et al. 2015; Hokkanen et al. 2016). These materials are harmful to plants and animals (Gupta and Babu 2009). The inorganic pollutants include toxic metal ions that are discharged mainly from medical activities, agriculture, plumbing, household chemicals, body care products, and other industrial activities. Some of the toxic metal ions that raise a serious concern are Cd^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+}, Sr^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, and Pb^{2+}ions (Sud et al. 2008).

Purifying the wastewater from toxic heavy metals is performed by several reported methods, and among these, adsorption is the most applicable (Qaiser et al. 2009) and it receives the most attention because it is highly effective and low-cost (Saravanan and Ravikumar 2015). Among the most effective metal adsorbents is activated carbon. However, it is not optimal in some cases due to the high processing costs (O’Connell et al. 2005).
2008). Additionally, natural-based materials, such as clay, zeolites, and peat, are among the most evaluated materials as adsorbents for toxic heavy metal ions from wastewater (Adeyemo et al. 2017; Chwastowski et al. 2017; Uddin 2017; Bo et al. 2018; Lin et al. 2018). They are the most attractive because they are renewable and available at a relatively low cost (Jodeh et al. 2018; Moa et al. 2018). In addition, other natural products, such as cellulose materials, lignin, chitosan, and hemicelluloses, received a lot of attention. Several cellulosic-based adsorbents, such as kenaf, cotton linters, wheat straw, wood sawdust, and rice husk, were prepared and investigated as an adsorbent for toxic heavy metal ions such as those mentioned above (Nada et al. 2002; Acar and Eren 2006; Karnitz, Jr. et al. 2007; Doan et al. 2008; Gupta and Babu 2009; Nagy et al. 2013; Vieira et al. 2014; Muhammad et al. 2018). Cellulose nanoparticles (CNC) are a promising adsorbent for heavy metal ions (Zelić et al. 2018). Despite all of the rapid progress in the study of natural-based metal adsorbents, many natural-based materials and their derivatives have not been explored as an adsorbent for metal ions.

This work focused on a cellulose powder derivatized with a bidentate chelating agent as a potential new adsorbent for metal ions. The cellulose powder was extracted from solid waste from the olive industry and was reacted with a bifunctional aromatic amine in a three-step process that involved the oxidation of cellulose to aldehyde, the conversion of oxidized cellulose to imine, and the reduction of the imine to an amine. The bifunctional aromatic amine chosen for this purpose is 1,2-phenylenediamine. The positions of the amino groups (ortho) in addition to the presence of other functional groups (hydroxyl, ether, and aromatic in the target cellulose derivative) makes it a novel adsorbent for metal ions. The prepared cellulose amine polymer (cell-o-PDAm) was evaluated as an adsorbent for Fe(III) and Pb(II) from water and other metal ions from a real sample of wastewater. To the best of our knowledge, the cell-o-PDAm presented in this work is the first example in the literature of cellulose polymer with an aromatic amine bidentate ligand.

**EXPERIMENTAL**

**Materials**

All reagents used in this study were purchased from Sigma-Aldrich (Jerusalem, Israel) and used as received. The olive industry solid waste (OISW) used in this work was obtained from an olive factory located in city of Tulkarm, Palestine.

**Cellulose aldehyde**

A solution of sodium hydroxide (8% by weight) was prepared by dissolving 8.0 g of sodium hydroxide in 92.0 mL distilled water. To it was added 6.0 g of cellulose powder. The produced mixture was stirred for 20 min, diluted with water, filtered, and washed several times with distilled water. Then the mixture was neutralized via dropwise addition of the diluted solution of acetic acid (2% by weight) and washed again with water. A sample of the produced activated cellulose (5.0 g, 0.031 mol/anhydroglucose repeat unit (AGU)) was added to a beaker, followed by suspended it in 150.0 mL of distilled water. The flask containing the cellulose suspension was completely wrapped with aluminum foil to isolate it from light. Sodium periodate (12.8 g, molecular mass (MM) = 213.9 g/mol, 0.06 mol) was added to the cellulose suspension in two portions, 6.4 g each at 6 h intervals. The reaction mixture was stirred at 40 °C for approximately 12 h. The produced cellulose aldehyde was collected via filtration and washed with water (3 × 250 mL). Aldehyde
content (1.89/AGU) was determined according to a previously reported procedure (Kim et al. 2000).

Cellulose o-pheneylendiamine polymer

Cellulose aldehyde (2.0 g, 0.012 mmol of AGU) and ethanol (40 mL) were added to a round bottom flask (100-mL) fitted with a magnet stir bar and a reflux condenser. Next, 1,2-diaminobenzene (1.3 g, 12.4 mmol) was added to the suspension. The reaction was refluxed for approximately 3 h. The reaction mixture was cooled to room temperature, and sodium borohydride (0.3 g) was added to the suspension. The reaction mixture was stirred at room temperature for 8 h. It was then treated with a solution of ammonium chloride (0.5%) to destroy excess sodium borohydride. The produced cellulose amine polymer was collected through suction filtration and first washed with water, then ethanol, and then air dried.

Methods

Characterization

The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with the Smart Split Pea™ Hemi Micro ATR accessory (International Crystal Laboratories, Garfield, NJ, USA). The following parameters were used: resolution was 4 cm⁻¹, spectral range was 600 cm⁻¹ to 4000 cm⁻¹, and number of scans was 128. The surface morphology of the cellulose polymer and derivatives were examined using scanning electron microscopy (SEM) (S-4800; Hitachi, Tokyo, Japan) at an acceleration voltage of 3.0 kV after sputter coating the sample with gold (Cressington Sputter Coater; Ted Pella, Inc., Redding, CA, USA). The metal ion analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) via an iCAP™ RQ ICP-MS (Thermo Fisher Scientific, Waltham, MA, USA).

Adsorption study

This work followed a batch adsorption experiment. All experiments were performed in a glass container (50-mL) that was placed in a water bath equipped with a shaker. Different variables on the polymer efficiency for metal adsorption (e.g., metal ion concentration, pH values, adsorbent dosage, adsorption time, and temperature) were examined. The adsorption study was performed on the two metal ions Pb(II) and Fe(III). After each adsorption run, a sample from the mixture was collected via filtration through a 0.45-µm syringe filter and subjected to a flame atomic adsorption analysis at 193.7 nm to determine the residual metal ions concentration. All adsorption experiments were performed in triplicate, and the mean of the three runs was reported. The absorbent efficiency and the amount of metal ions adsorbed by the cell-o-PDAm adsorbent \( q_e \) (mg/g) was determined according to Eqs. 1 and 2, respectively,

\[
R (%) = \frac{C_0 - C_e}{C_0} \quad (1)
\]

\[
Q_e = \frac{C_0 - C_e}{m} V \quad (2)
\]

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations (ppm) of metal ion in solution, respectively, \( Q_e \) is the equilibrium adsorption capacity (ppm), \( m \) is the mass of cell-o-PDAm (mg), and \( V \) is the volume of the solution (L).
Wastewater purification

A sample of sewage water was collected from the sewage system (Nablus, Palestine) and used in this study. The sample was subject to analysis using ICP-MS (performed by the Water Center at An-Najah National University, Nablus, Palestine) to determine the metals’ content and their concentrations. A 50.0 mL sample of the sewage water was placed in an Erlenmeyer flask and its pH values were adjusted to 6.3. Each sample received 0.1 g of cell-o-PDAm. The mixture was shaken at room temperature for 30 min. A sample was withdrawn from the mixture with a syringe, pushed through a 0.45-µm syringe filter, and subjected to ICP-MS analysis for any residual metal ions concentrations.

RESULTS AND DISCUSSION

Product Analysis

The cellulose powder was extracted from olive industry solid waste following a process of pulping and bleaching, as reported in previous studies (Hamed et al. 2012, 2014). The produced cellulose powder was oxidized to cellulose aldehyde by reacting it with sodium periodate, following a published procedure (Kim et al. 2000). The reaction was performed under neutral conditions at 40 °C for 12 h. The FTIR spectrum of the oxidized cellulosics is shown in Fig. 1a. The most noticeable peaks for cellulose dialdehyde (CDA) were observed at 1732 cm\(^{-1}\), 1425, 1375, and 1140 cm\(^{-1}\), assigned to C=O (aldehyde), CH\(_2\) asymmetric bending, C-O stretching of ether and alcohol, and C-O-C stretching of β-glycosidic linkage, respectively. The weak band at 1732 cm\(^{-1}\) was due to the hydration and acetal formation (Lázaro-Martínez et al. 2010; Algarra et al. 2019). The mechanism is depicted in Fig. 1b.
The X-ray diffraction (XRD, D8 Advance; Bruker, Hamburg, Germany) patterns of cellulose aldehyde and cell-o-PDAm are shown in Fig. 1S. The intensity of the crystalline peaks at $2\theta = 16^\circ$ and $2\theta = 32^\circ$ in cellulose aldehyde broadened with some shift in their values. This could indicate a loss of crystallinity. The loss of crystallinity was attributed to the ring opening of glucopyranose, which causes a disruption and loss of H-bonding, and consequently, a loss of crystallinity (Kim et al. 2000; Heinze and Liebert 2001). The XRD of cell-o-PDAm showed that the cellulose crystallinity completely changed as the new compound emerged.

The aldehyde carbonyl group had an electrophilic carbon, therefore undergoing a condensation reaction with a nucleophile, such as amine, to form an imine after the loss of a water molecule. Reduction of the cellulose imine with sodium borohydride produces cellulose amine, as shown in Fig. 2. The produced amine had several coordination sites for
metal ions, including amines, hydroxyl, and aromatic functionalities. A representative molecular structure of cell-o-PDAm is shown in Fig. 2.

The FT-IR spectra of cell-o-PDAm (Fig. 1a) showed two peaks at 1635 cm$^{-1}$ and 1610 cm$^{-1}$, corresponding to a primary amine and an aromatic C=C, respectively. The broad adsorption peak at approximately 3350 cm$^{-1}$ was composed of several peaks originating from O-H or N-H stretching vibrations of primary and secondary amines. Additionally, the IR spectrum showed a peak at 2930 cm$^{-1}$ that could have been attributed to the symmetric and asymmetric stretching vibration of the C-H bond. The peak at 750 cm$^{-1}$ could be related to ortho substitution of phenylene diamine.

The SEM images of cellulose aldehyde, and the cell-o-PDAm prepared from it, are shown in Fig. 3.

![Fig. 3. SEM images of (a) cellulose aldehyde and (b) cell-o-PDAm at magnifications of 250x and 50x, respectively](image)

The cellulose aldehyde image showed that the cell structure had been damaged. The morphology of cell-o-PDAm as shown in its image was a highly porous spongy type. The solubility of cell-o-PDAm in water was evaluated by suspending a known weight (1.00 g)
of cell-o-PDAm in water (50 mL) for approximately 12 h before being filtered and dried. It showed minimal weight loss within the experimental error.

**Metal Ions Extraction**

The extraction was completed using a batch adsorption process. During this process, a known weight (ranging from 0.5 mg/mL to 5.0 mg/mL metal solution) of cell-o-PDAm was suspended in an aqueous solution of metal ions, filtered, and analyzed. The analysis was performed on the filtrate to determine the concentration of the extracted ions. The effects of several variables (e.g., adsorbent dosage, extraction time, temperature, and pH) were evaluated to determine the best conditions for the highest adsorption efficiency. The adsorption study was performed on lead (Pb) and iron (Fe) ions.

**Optimum Adsorbent Dosage**

The dosage that provided the lowest residual concentration of metal ions was chosen as the optimal dosage. This was achieved by performing the experiment with 50 mL each of Fe(III) and Pb(II), with a concentration of 30 ppm, pH value of 6.3, adsorption time of 30 min, and performed at room temperature. The effect of the adsorbent dosage on the removal of Fe(III) and Pb(II) ions is shown in Fig. 4a. As shown in the figure, the amount of metal extracted increased when increasing the polymer dosage. Metal ion removal reached approximately 67.8% and 88.1% for Pb(II) and Fe(III), respectively, at a 2.0 mg/mL dose of cell-o-PDAm. At dosages higher than 2.0 mg/mL, it became nearly constant. This was because the adsorption process was controlled by two mechanisms, diffusion and surface coordination. An increase in the dosage resulted in the number of available binding sites increasing, and thus the ion removal increased. When all sites on the surface were occupied, the diffusion process began. It is controlled by osmosis; when the concentration of the metal ions adsorbed by the polymer are equal to that of the solution, the adsorption stops (Abdel-Ghani et al. 2007).

**Effect of Initial Ion Concentration**

The effect of the initial ion concentration on the adsorption efficiency was evaluated under the following adsorption conditions: adsorption time was 30 min, adsorbent dose was 2.0 mg/mL, and pH was 6.3. The amines’ functional groups were in Lewis base form at this pH value. As shown in Fig. 4b, the highest removal was at the concentration of 10 ppm. At this concentration, the percent of ions removed reached 88.3% and 83.2% for Fe(III) and Pb(II), respectively. At concentrations higher than 10 ppm, the removal started to gradually decline. The results indicated that at low concentrations of metal ions, the driving force for adsorption was controlled by the ion diffusion (Sahmoune et al. 2011). At high concentrations, the availability of the binding sites was the limiting factor, and the number of available sites was governed by the adsorbent dosage. According to the obtained results, at a concentration of approximately 10 ppm, the binding sites were almost saturated for this reason. However, concentrations higher than 10 ppm resulted in the rate of metal removal decreasing.
Effect of Contact Time

Adsorption of the metal ions Pb(II) and Fe(III) by cell-o-PDAm as a function of time was evaluated under the conditions: pH 6.3, initial ion concentration of 20 ppm, adsorption temperature of 25 °C, and the adsorbent dose was 2.0 mg/mL. As shown in Figs. 4c and 4d, the adsorbed metal ions rapidly increased for the first 40 min due to the availability of the binding sites. Then, the adsorption rate became almost constant for the next 20 min and reached equilibrium after 40 min. The results indicated that at this period, almost all the coordination sites are occupied (Liu et al. 2013). A contact time of 40 min was chosen as the optimal contact time. The two ions showed nearly similar adsorption behavior with time.
Effect of Temperature
The effect of temperature on the adsorption of metal was evaluated under the conditions: pH 6.3, initial metal ion concentration of 30 ppm, adsorption time of 40 min, and the adsorbent dose was 2.0 mg/mL (Fig. 4e). The adsorption efficiency showed no dependence on the temperature. Up to approximately 60 °C, the adsorption efficiency was almost constant.

Effect of pH
The effect of the adsorption efficiency as a function of the pH value is shown in Fig. 4f. The pH value was a critical factor in metal adsorption because the pH value could control the surface charge of the polymer. At low pH values (≤3.0), the amine is in the salt form (-NR₂H⁺). For this reason, the adsorption efficiency was the minimum (approximately 20%). However, at pH values higher than 3.0, the lone pair of electrons on amine N became more available, causing the amine group to behave as a metal binding agent. The highest efficiency was observed at pH 8.6. At higher pH values, the adsorption efficiency started to decline. The formation of metal oxides and metal hydroxides at pH higher than 9.0 could be the reason for the decreasing adsorption efficiency.

Wastewater Purification from Metals
A sample of wastewater was collected from a sewer system and was treated with cell-o-PDAm. A photograph of the wastewater sample before and after its treatment is shown in Fig. S2. The metal content of the sample before and after purification is summarized in Table 1.

Table 1. Metal Concentration of Wastewater before and after Treatment, pH 6.8

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Before (ppm)</th>
<th>After (ppm)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>38.1</td>
<td>0.635</td>
<td>98.3</td>
</tr>
<tr>
<td>Al</td>
<td>4680</td>
<td>52.2</td>
<td>98.9</td>
</tr>
<tr>
<td>Pb</td>
<td>12.5</td>
<td>1.6</td>
<td>98.7</td>
</tr>
<tr>
<td>Cu</td>
<td>103</td>
<td>0.644</td>
<td>62.1</td>
</tr>
<tr>
<td>Cd</td>
<td>0.67</td>
<td>0.07</td>
<td>89.6</td>
</tr>
<tr>
<td>Cr</td>
<td>523</td>
<td>43.1</td>
<td>91.8</td>
</tr>
<tr>
<td>Co</td>
<td>12.5</td>
<td>1.07</td>
<td>91.4</td>
</tr>
<tr>
<td>Fe</td>
<td>8156</td>
<td>383</td>
<td>95.3</td>
</tr>
<tr>
<td>Ga</td>
<td>2.4</td>
<td>0.48</td>
<td>80</td>
</tr>
<tr>
<td>Rb</td>
<td>35.4</td>
<td>20.7</td>
<td>41.5</td>
</tr>
<tr>
<td>Li</td>
<td>6.7</td>
<td>5.3</td>
<td>21</td>
</tr>
<tr>
<td>Mn</td>
<td>167</td>
<td>25.3</td>
<td>85</td>
</tr>
<tr>
<td>Mo</td>
<td>9.7</td>
<td>2.4</td>
<td>75.3</td>
</tr>
<tr>
<td>Ni</td>
<td>43</td>
<td>11</td>
<td>74.7</td>
</tr>
<tr>
<td>Sr</td>
<td>609</td>
<td>231</td>
<td>62</td>
</tr>
<tr>
<td>Cs</td>
<td>0.31</td>
<td>0.13</td>
<td>58.1</td>
</tr>
<tr>
<td>V</td>
<td>16</td>
<td>1.4</td>
<td>92</td>
</tr>
<tr>
<td>Zn</td>
<td>696</td>
<td>19.3</td>
<td>98</td>
</tr>
</tbody>
</table>
The results showed that the cell-o-PDA polymer had excellent efficiency toward most of the metals present in the wastewater sample, i.e., the removal exceeded 90% for several of them.

The high efficiency of the cellulose amine polymer toward the metal ions was possibly related to the unique structure that was composed of several coordination sites that include amine, hydroxyl, and aromatic groups.

**Adsorption Analysis**

The Langmuir (Eq. 3) and Freundlich isotherm (Eq. 4) methods were used to evaluate the distribution of metal ions on the surface of cell-o-PDAm after reaching the equilibrium at a constant temperature (Limousin et al. 2007; Azzaoui and Mejdoubi 2014). The Langmuir model assumes the formation of a monolayer of adsorbate on a homogeneous surface of an adsorbent (Brdar et al. 2012). However, the Freundlich model describes the adsorption between the adsorbate molecule and the adsorbent with a heterogeneous surface. Below is Eq. 3,

**Langmuir isotherm model:**

\[
\frac{C_e}{Q_e} = \frac{1}{q_{\text{max}}} C_e + \frac{1}{q_{\text{max}} K_L}
\]

where \( C_e \) is the equilibrium concentration of metal ion (ppm), \( Q_e \) is the amount of adsorbate adsorbed per unit mass of cellulose amine at equilibrium (mg/g), \( Q_{\text{max}} \) is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g), and \( K_L \) is the Langmuir isotherm constant related to the adsorption energy (L/mg). Equation 4 is as follows,

**Freundlich isotherm model:**

\[
\ln(Q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)
\]

where \( K_F \) and \( \frac{1}{n} \) are empirical constants that indicate the relative adsorption capacity and intensity related to the affinity of the metal, respectively.

The Langmuir isotherm model also can distinguish whether the adsorption was favorable or not by using the dimensionless constant separation factor shown in Eq. 5,

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

where \( K_L \) is the Langmuir constant and \( C_0 \) is the initial adsorbate concentration. The adsorption is unfavorable if the \( R_L \) value is greater than 1. However, if the value of \( R_L \) is between 1 and 0, then the adsorption is favorable. The adsorption is linear if \( R_L = 1 \).

All fitting parameters obtained from Fig. 5 are summarized in Table 2. The coefficients of determination for the Langmuir isotherm model (Table 2) were much higher than those for the Freundlich isotherm model, indicating that the adsorption of Pb(II) and Fe(III) ions followed the Langmuir isotherm model (Eq. 4) because the Pb and Fe ions were equally and homogeneously spread over the cell-o-PDAm porous surfaces. The separation factor \( R_L \), which was calculated for various amounts of adsorbents for cell-o-PDAm, was \( 0 < R_L < 1 \) (Table 2).

The \( R \) values were much smaller than 1, indicating a high affinity of cell-o-PDAm for Pb(II) and Fe(III).

**Table 2.** Langmuir and Freundlich Parameters for the Adsorption of Pb(II) and Fe(III) Ions by cell-o-PDAm

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Fe(III)</th>
<th>Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298</td>
<td>313</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q^0$ (mg/g)</td>
<td>2.3792</td>
<td>2.7137</td>
</tr>
<tr>
<td>$K_L$ (L/mg)</td>
<td>0.1540</td>
<td>0.1259</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.01282</td>
<td>0.01563</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.8705</td>
<td>0.9176</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9507</td>
<td>0.995</td>
</tr>
</tbody>
</table>

**Kinetics Adsorption**

The two kinetic models, pseudo-first-order (Eq. 7) and pseudo-second-order (Eq. 8), were used to describe the kinetics of the adsorption process, comprising the adsorption rates and adsorption mechanism of the metal ions Pb(II) and Fe(III) onto the surface of cell-o-PDAm (Zhao et al. 2014; Jodeh et al. 2016):

\[
\ln(q_e - q_t) = \ln q_e - K_1 t
\]

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

Fig. 5. Langmuir of (a) Pb(II) and (b) Fe(III); Freundlich adsorption model of (c) Pb(II) and (d) Fe(III) ions on cell-o-PDAm at various temperatures.
In addition, the intraparticle diffusion model (Eq. 9) was used to determine the rate-determining step during the metal ion adsorption,

\[ Q_t = K_{id}t^{1/2} + Z \]  

(9)

where \( Q_e \) and \( Q_t \) are the adsorption capacities at equilibrium (mg/g), \( t \) is the various times (min), \( K_1 \) is the pseudo-first-order rate constant (1/min), \( K_2 \) is the pseudo-second-order rate constant (g/mg min), \( K_{id} \) is the intraparticle diffusion rate constant (mg/gmin\(^{1/2}\)), and \( Z \) (mg/g) was used to conclude the thickness of the boundary layer.

Additionally, the liquid film diffusion model (Eq. 10) was employed to investigate whether the transport of metal ions from the liquid phase to the solid phase boundary plays a role in the adsorption process,

\[ \ln(1 - F) = -K_fdt \]  

(10)

where \( F \) is the fractional attainment of equilibrium \( (F = q_t/q_e) \), \( q_e \) is the adsorption capacity of the sorbent at equilibrium (mg\( \times \)g\(^{-1}\)), and \( K_1 \) is the liquid film diffusion constant. A linear plot of \( \ln(1 - F) \) versus \( t \) with zero intercept would suggest that the kinetics of the adsorption process was controlled by diffusion from the liquid surrounding the solid sorbent.

The values of all the parameters shown in the above equations are summarized in Table 3 and Fig. 5.

**Table 3A.** The Pseudo-second-order Model for Adsorption of Pb(II) and Fe(III) ions by Cell-o-PDAm

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>298</th>
<th>( K_2 ) (g/mg ( \times )min)</th>
<th>( Q_{cal} ) (mg/g)</th>
<th>( R^2 )</th>
<th>313</th>
<th>( K_2 ) (g/mg ( \times )min)</th>
<th>( Q_{cal} ) (mg/g)</th>
<th>( R^2 )</th>
<th>323</th>
<th>( K_2 ) (g/mg ( \times )min)</th>
<th>( Q_{cal} ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)</td>
<td>0.3568</td>
<td>416.5</td>
<td>0.9868</td>
<td>0.3911</td>
<td>533.5</td>
<td>0.9745</td>
<td>0.3814</td>
<td>622.8</td>
<td>0.9845</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(II)</td>
<td>0.3568</td>
<td>152.9</td>
<td>0.9866</td>
<td>0.3907</td>
<td>196.3</td>
<td>0.9748</td>
<td>0.3813</td>
<td>230.7</td>
<td>0.9836</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3B.** The Intraparticle Diffusion Parameters of Pb(II) and Fe(III) Ions onto Cell-o-PDAm

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>298</th>
<th>( K_{id} )</th>
<th>( Z )</th>
<th>( R^2 )</th>
<th>313</th>
<th>( K_{id} )</th>
<th>( Z )</th>
<th>( R^2 )</th>
<th>323</th>
<th>( K_{id} )</th>
<th>( Z )</th>
<th>( R^2 )</th>
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<tbody>
<tr>
<td>Fe(III)</td>
<td>1.041</td>
<td>1.92</td>
<td>0.931</td>
<td>1.126</td>
<td>1.851</td>
<td>0.905</td>
<td>1.333</td>
<td>1.689</td>
<td>0.944</td>
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<tr>
<td>Pb(II)</td>
<td>0.905</td>
<td>1.08</td>
<td>0.934</td>
<td>1.036</td>
<td>0.871</td>
<td>0.942</td>
<td>1.083</td>
<td>0.96</td>
<td>0.963</td>
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</table>

The value of \( K_1 \) was obtained by plotting \( \ln(q_e - q_t) \) vs. \( t \) (Fig. S3a), while the \( K_2 \) values and the adsorption capacity \( q_e \) were calculated from the slope and the intercept of plotting \( t/q_t \) vs. \( t \) (Fig. S3b). The values for \( K_{id} \) and \( Z \) were obtained from plotting \( q_t \) vs. \( t^{1/2} \) (Fig. S3c). When the experimental data was plotted for both the pseudo-first-order and the second-pseudo-order kinetics, the coefficients of determination (\( R^2 \)) for the pseudo-second-order (0.91 to 0.973) were higher than the pseudo-first-order (0.891). The
calculated $q_e$ values (2.675 mg/g, 15.252 mg/g, and 20.856 mg/g) for the pseudo-second-order (see Table 3 and Fig. S3c) were close to the experimental $q_e$ values (2.133 mg/g, 13.91 mg/g, and 18.786 mg/g), indicating that the adsorption process of metal ions on the surfaces of cell-o-PDAm followed the pseudo-second-order.

All plots shown in Fig. S3 did not pass through the origin, indicating the presence of more than one rate-determining step in the absorption processes. From the initial linearity of the graphs shown in Fig. S3c, the adsorption process of Pb(II) and Fe(III) ions occurred first via an instant adsorption stage (on the exterior surface of cell-o-PDAm), which may have resulted in a chemical complexation between the metal ions, amines, and other functionalities (Guo et al. 2008). Additionally, the rest of the stages were linear, indicating the gradual adsorption and the intraparticle diffusion rate limiting step of Pb(II) and Fe(III) ions. The values of Z in Table 3 indicate an expansion in the surface layer and a diminished external mass transfer while the potential for internal mass transfer increased.

The mechanism for the removal of metals via adsorption occurred in several steps. In the first step, the metal ions migrate from the solution to the external surface of the adsorbent. This was followed by the diffusion through the boundary layer to the active sites. Finally, intraparticle diffusion and the adsorption of metal ions in the inner part of the polymer occurred. The valid mechanism in this work was examined by the two models: the liquid-film model and the intraparticle-diffusion model. The liquid-film diffusion model (Eq. 10) assumed that the flow of the adsorbate molecules through a liquid film surrounding the adsorbent was the rate-determining step. According to Eq. 10, a linear plot of $-\ln(1 - F)$ vs. $t$ (Fig. 6) with a zero intercept suggested that the kinetics of the adsorption process were controlled by diffusion through the surrounding liquid film. As shown in Fig. 6, the experimental adsorption data of the metals by cell-o-PDAm from an aqueous solution at different temperatures did not provide straight lines that passed through the origin, and had coefficients of determination 0.1876 and 0.1578 for Fe(III) and Pb(II) (Table 5), respectively. This indicated that the diffusion of the metals through the liquid film around the cellulose-amine was not the rate-determining step, but may contribute to the adsorption process, especially at the beginning of the adsorption as shown in Table 3.

![Fig. 6. Liquid film diffusion model plots for the adsorption of composite based of cellulose](image-url)
Table 4. Liquid Film Diffusion Model Parameters

<table>
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<th>$K_{df}$</th>
<th>$R^2$</th>
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</thead>
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<tr>
<td>Fe(II)</td>
<td>0.1876</td>
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<tr>
<td>Pb(II)</td>
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Adsorption Thermodynamics

The Gibbs free energy ($\Delta G_0$), enthalpy ($\Delta H_0$), and entropy ($\Delta S_0$) were calculated according to the following equations and the results are summarized in Table 5. These are important when evaluating the behavior of the adsorption of Pb(II) and Fe(III) ions on cell-o-PDAm. The equations are as follows,

$$K_c = \frac{C_{ads}}{C_e}$$  \hspace{1cm} (11)

$$\Delta G^0 = -RT \ln K_c$$ \hspace{1cm} (12)

$$\ln K_s = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$ \hspace{1cm} (13)

where $K_c$ is an apparent constant of the thermodynamics, $C_{ads}$ is the amount adsorbed at equilibrium (mg/L), $C_e$ is the equilibrium concentration in an aqueous solution of metal ion (mg/L), $R$ is the gas constant (J/mol $\times$ K), and $T$ is the ions solution temperature (K) (Azzaoui and Mejdoubi 2014).

Table 5. Thermodynamic Parameters for the Adsorption of Pb(II) and Fe(III) ions onto Cell-o-PDAm

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\Delta G^0$ (KJ/mol)</th>
<th>$\Delta H^0$ (KJ/mol)</th>
<th>$\Delta S^0$ (KJ/mol)</th>
<th>$\Delta G^0$ (KJ/mol)</th>
<th>$\Delta H^0$ (KJ/mol)</th>
<th>$\Delta S^0$ (KJ/mol)</th>
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<td>298</td>
<td>-17.144</td>
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<td>57.5627</td>
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<tr>
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<td>-18.5832</td>
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</tbody>
</table>

Fig. 7. Adsorption thermodynamics of Pb(II) and Fe(III) ions by cell-o-PDAm
The $K_c$ value was calculated according to the Van’t Hoff equation (Eq. 11) (Zhang et al. 2010). The standard Gibbs free energy ($\Delta G_0$) (Jmol$^{-1}$) was calculated using Eq. 12. The $\ln(K_s)$ versus $1/T$ was plotted as shown in Fig. 7. The slopes and the intercept were used to calculate various thermodynamics parameters; results are shown in Table 5. The obtained values of $\Delta S_0$ and $\Delta H_0$ were positive, while the entropy increased at the solid/solution interface, driven by the adsorption process. The free energies were negative, indicating a spontaneous adsorption process at the tested temperatures.

CONCLUSIONS

1. Cellulose powder derivatized with an aromatic amine chelating agent (cell-o-PDAm) was successfully prepared from cellulose powder extracted from olive industry solid waste.

2. The efficiency of the prepared cell-o-PDAm toward adsorbing the metal ions Fe(III) and Pb(II) was studied as a function of adsorbent dose, temperature, pH, metal ion initial concentration, and time.

3. The cell-o-PDAm polymer showed an excellent efficiency toward both metals, the highest absorbency was observed at a pH of approximately 8.0 and at room temperature.

4. The polymer showed excellent efficiency for metal ions present in a real sample of sewage.

5. The kinetic study revealed that the metal ion adsorption by cell-o-PDAm was pseudo-second-order and followed the Langmuir isotherm model.

6. The thermodynamic analysis showed a negative free energy, indicating a spontaneous adsorption process at different temperatures.

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APPENDIX

Supplementary Information

**Fig. S1.** XRD spectra of cellulose aldehyde and cell-o-PDAM

**Fig. S2.** Images of wastewater sample before and after treatment with cell-o-PDAM
Fig. S3. A) Pseudo-first-order model for the adsorption of Pb(II) and Fe(III); B) Pseudo-second-order model for the adsorption of Pb(II) and Fe(II) ions by cell-o-PDAm; C) Intraparticle diffusion model for the adsorption of Pb(II) and Fe(III) ions by cell-o-PDAm polymer at various concentrations.