

Cellulose Powder Functionalized with Phenyl Biguanide: Synthesis, Cross-linking, Metal Adsorption, and Molecular Docking

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A cellulose polymer functionalized with an amine chelating agent was designed and synthesized in a three-step process that involved oxidizing cellulose powder into dialdehyde cellulose, reacting cellulose dialdehyde with phenyl biguanide to create an imine linkage between the two reactants, and reducing the imine linkage to an amine. The cellulose amine polymer was cross-linked with glycerol diglycidyl ether and evaluated as an adsorbent of toxic metal ions from wastewater. The adsorption efficiency of the cross-linked cellulose amine polymer toward Pb(II) and Cu(II) was evaluated as a function of the adsorbent dose, pH, time, temperature, and initial ion concentration. The cross-linked cellulose amine polymer showed an excellent efficiency toward over 15 metal ions present in a real sample of sewage. Thermodynamic analysis showed a spontaneous adsorption of metal ions on the polymer at room temperature. Monte Carlo and Molecular Dynamic simulations showed that the Cu(II) and Pb(II) ions adsorbed onto the cellulose amine polymer surface in a considerable amount, which agreed with the experimental and thermodynamic data. The negative free energy value confirmed the spontaneity of the adsorption process. As such, cross-linked cellulose amine polymers could be a promising alternative to current commercial adsorbents.

Keywords: Cellulose powder; Phenyl biguanide; Molecular dynamic; Monte Carlo; Chelating agent; Adsorption

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INTRODUCTION

The effluents released from various industries, *e.g.*, metal complex dyes, pesticides, fertilizers, fixing agents, mordants, pigments, and bleaching agents, are becoming a present-day threat to creatures (Gupta *et al.* 2009). As such, their removal is becoming mandatory, since these effluents could contain numerous pollutants that include toxic organic and inorganic substances. Among these inorganic pollutants are toxic heavy metals, which can be harmful to all creatures (Clement *et al.* 1995; Renge *et al.* 2004).

As a result of these compounds, there is a constantly increasing demand for highly

efficient metal adsorbents, preferably biobased, to make the industry effluent suitable for reuse as the demand for fresh water is increasing (Milieu 2010). The transition metals of most concern, which can be harmful to plants and animals, and are present in the effluents of various industries, include lead, zinc, copper, arsenic, cadmium, chromium, nickel, and mercury (Sud *et al.* 2008; Gupta *et al.* 2009; Razzouki *et al.* 2015).

Purifying industry effluent from toxic heavy metals is usually performed by various techniques, most of which have been previously reported in the literature (Qaiser *et al.* 2009). The adsorption technique receives the most attention because it is the most efficient and least costly (Saravanan and Ravikumar 2015; Moa *et al.* 2018). Activated carbon is an example of a metal adsorbents and considered as one of the most effective. However, in some cases it could be not the best, as its high processing costs could be a disadvantage (O'Connell *et al.* 2008). Bio-based adsorbents, *e.g.*, cellulose, chitosan, zeolites, and clay, are among the most studied adsorbents for the removal of toxic metal ions from industrial effluents (Chwastowski *et al.* 2017; Uddin 2017; Bo *et al.* 2018; Lin *et al.* 2018). Several cellulosic-based derivatives have been prepared and investigated as an adsorbent for toxic heavy metal ions in multiple studies (Karnitz Jr. *et al.* 2007; Doan *et al.* 2008; Gupta and Babu 2009; Nagy *et al.* 2013; Vieira *et al.* 2014; Carpenter *et al.* 2015; Malik *et al.* 2017; Muhammad *et al.* 2018). Published studies have shown that functionalization of cellulose nanoparticles had high efficiency towards toxic metal ions. Functionalizations have included oxidation, phosphorylation, cationization, *etc.* (Ma *et al.* 2011a,b; Liu *et al.* 2015; Sehaqui *et al.* 2015; Mautner *et al.* 2016; Gopakumar *et al.* 2017).

Despite the rapid progress in creating biobased metal adsorbents, surface-modified cellulose polymers have still not been fully explored, even though they can be unique with high absorbency and turnover.

This work pursues an effective way to create surface modified cellulose powder with a multi-dentate chelating agent as a potential novel adsorbent for toxic metal ions. The cellulose powder was extracted from the solid waste of the olive industry and was functionalized with the polyamine aromatic phenyl biguanide. The synthetic method involved the oxidation of the cellulose powder into dialdehyde, the conversion of the dialdehyde cellulose into cellulose imine, and the reduction of cellulose imine into cellulose amine. The presence of three amino groups per molecule of phenyl biguanide, each with three amines bonded to one carbon and all are bonded to an aromatic ring, leads to a unique structure and the formation of a neat structure with multi coordination sites for metal ions. The prepared cellulose amine polymer (cell-PB) was evaluated as an adsorbent for Pb(II) and Cu(II) from water. The adsorption was also performed on a real sample of wastewater. Thermodynamic, Monte Carlo (MC), and molecular dynamic (MD) analysis were performed on the adsorption process to obtain a detailed insight on the spontaneity and the mechanism of adsorption.

EXPERIMENTAL

Materials

The reagents used in this work were purchased from Sigma-Aldrich (Jerusalem, Israel) and used as received. The primary reagents include phenyl biguanide, sodium periodate, and sodium borohydride. The olive industry solid waste (OISW) used in this study was obtained from an olive factory located in Nablus, Palestine.

Methods

The IR spectra were recorded on a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer connected to a Smart Split Pea micro-ATR accessory (which had a diamond ATR crystal) (Thermo Fisher Scientific, Waltham, MA). The IR spectra were collected at a resolution of 4 cm^{-1} , a spectral range of $600\text{ to }4000\text{ cm}^{-1}$, with 128 scans. Elemental analysis for determining the N content was carried out using a Perkin Elmer 2400 Series II CHNS/O (Waltham, MA).

The polymer surface morphology was scanned *via* scanning electron microscopy (SEM) S-4800 (Hitachi, Tokyo, Japan) at an acceleration of 3.0 kV. The analyzed samples were coated with gold using a Cressington Sputter Coater (Ted Pella, Inc., Redding, CA). The metal ion analysis was carried out using inductively coupled plasma-mass spectrometry (ICP-MS) iCAPTM RQ ICP-MS (Thermo Fisher Scientific, Waltham, MA).

Preparation dialdehyde cellulose (CDA)

A sample of cellulose powder (40.0 g, 247.0 mmol/anhydroglucose unit (AGU)), which was extracted from the olive industry solid waste, was placed in a beaker (2.0 L) and suspended in 0.75 L of deionized water (Hamed *et al.* 2012). The beaker was wrapped with aluminum foil, then sodium periodate (50.1 g, MM = 213.9 g/mol, 0.23 mol) was added to the suspension in one portion. The reaction mixture was heated at a temperature of $45\text{ }^{\circ}\text{C}$ while being mixed *via* a mechanical mixer for approximately 10 h. The produced cellulose dialdehyde was collected *via* suction filtration, washed with a plenty of water ($4 \times 0.5\text{ L}$), and dried at room temperature. The cellulose content of the aldehyde functional group was determined according to a published procedure by Kim *et al.* (2000), which was found to be approximately 1.87/AGU. The oven dried weight of the product was 32.6 g (81.5% yield)

Cellulose-phenyl biguanide polymer (Cell-PB)

Dialdehyde cellulose (5.0 g, 3.1 mmol of AGU) was suspended in ethanol (50.0 mL) in a round bottom flask (100 mL) equipped with a magnetic stir bar and a reflux condenser. Excess phenyl biguanide (1.06 g, 6.0 mmol, MM = 177.2 g/mol) was added to the suspension. The reaction was refluxed for approximately 6 h; afterwards it was cooled down to room temperature, and excess sodium borohydride (0.5 g) was added to the suspension (Abdel-Magid *et al.* 1996). The produced suspension was stirred at room temperature for 12 h. Excess sodium borohydride was decomposed *via* the dropwise addition of a solution of ammonium chloride (1.0%). The cellulose phenyl biguanide (Cell-PB) polymer was collected *via* suction filtration, washed with water, then washed with ethanol, and finally air dried. The yield was quantitative.

Crosslinking of the cell-PB and the formation of Cell-X-PB

A mixture of Cell-PB (1.0 g) and glycerol diglycidyl ether (0.1 g, 10 wt.%) was suspended in methanol (20.0 mL). The suspension was placed in an evaporating dish in an oven at a temperature of $80\text{ }^{\circ}\text{C}$ for 1 h. During this period, all the methanol was evaporated, and the cross-linking occurred; the produced solid mass was suspended in methanol to remove unreacted epoxide for 30 min, and then was filtered and dried.

Adsorption study

A batch adsorption process was used in this study. All adsorption runs were performed in 50 mL plastic containers that were placed in a water bath equipped with a

thermostat and a shaker. The effect of various variables, *e.g.*, the adsorbent dosage, metal ion concentration, adsorption time, pH values, and temperature, on the polymer adsorption efficiency for the metal ions Pb(II) and Cu(II) were evaluated. The metal ions analysis was performed on samples that are collected using a syringe connected to a 0.45 μm syringe filter.

The residual metal ions concentration left after the adsorption process was determined using a flame atomic adsorption at 193.7 nm. All adsorption experiments were performed in triplicate, and the mean was reported. The adsorbent efficiency of Cell-X-PB represented by the percent removal was determined according to Eq. 1,

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

where C_0 and C_e are the initial and equilibrium concentrations in ppm of metal ion, respectively.

Wastewater purification

A sample of sewage water was collected from the sewer system in the Palestinian territories and used in this work. The sample was analyzed at the Water Center at the An-Najah National University (Nablus, Palestine) using an ICP-MS, the type of metal ions present in the collected sample and their concentrations (ppb) were determined. A sample of the collected sewage (50 mL) was placed in a plastic container and its pH value was adjusted to 6.5 using a diluted acid solution. The sample was dosed with a 0.01 g of Cell-X-PB. The suspension was shaken at room temperature for 60 min to ensure it reached equilibrium, and then a sample was withdrawn using a syringe and filtered through a 0.45 μm syringe filter, and subjected analysis *via* ICP-MS to determine the residual metal ions

RESULTS AND DISCUSSION

The cellulose powder used in this study was extracted from olive industry solid waste (Hamed *et al.* 2012) The cellulose powder was oxidized to cellulose dialdehyde using the oxidizing agent sodium periodate (Kim *et al.* 2000). The reaction was performed at a temperature of 40 $^{\circ}\text{C}$ for 12 h. The FT-IR spectrum of the produced cellulose dialdehyde is presented in Fig. 1a. The peaks at 1730, 1420, 1378, and 1142 cm^{-1} were assigned to the carbonyl in the C=O of the aldehyde, CH_2 asymmetric bending, C-O stretching, and the C-O-C stretching of the β -glycosidic linkage, respectively. The carbonyl peak appeared as a weak band at 1730 cm^{-1} , which could be attributed to the hydration and formation of acetal (Lázaro-Martínez *et al.* 2010).

Cellulose dialdehyde was reacted with phenyl biguanide in methanol to produce Cell-I-PB. A representative reaction scheme is shown in Fig. 2. Aldehyde carbonyl has an electrophilic carbon and undergoes a nucleophilic addition reaction (condensation) with a nucleophile, *e.g.*, an amine, to form an imine after the loss of a water molecule.

To enhance the stability of the Cell-I-PB samples in an aqueous medium, the imine functionality was reduced to amine *via* sodium borohydride (as shown in Fig. 3).

The reduction of the cellulose imine with sodium borohydride produces cellulose amine, as shown in Fig. 3. The produced amine has multi coordination sites with a high affinity for metals, including amines, imines, hydroxyls, and aromatics. A representative chemical structure of Cell-PB is shown in Fig. 3.

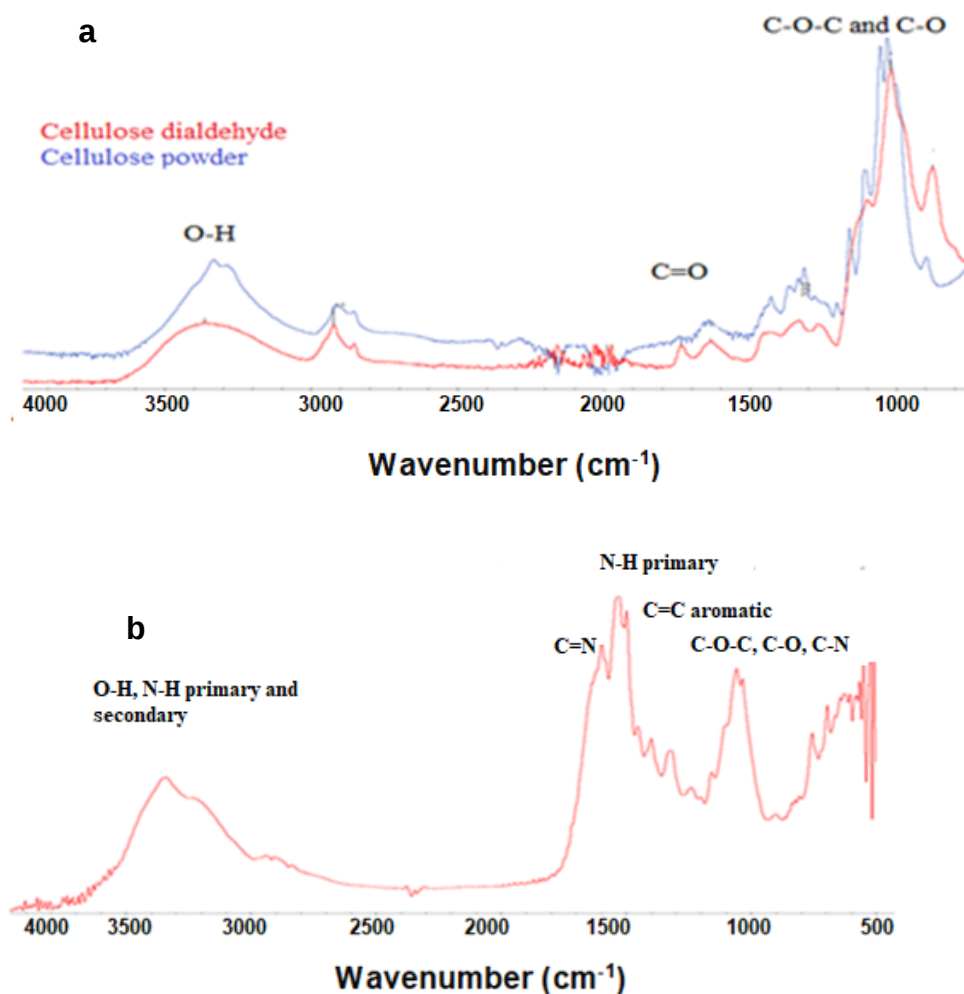


Fig. 1. An overlay of the FT-IR spectra of a) cellulose dialdehyde and cellulose powder; and b) cellulose phenyl biguanide (Cell-PB)

The FT-IR spectrum of the Cell-PB sample (as shown in Fig. 1b) shows multi-fused bands at 3300 cm^{-1} , which corresponded to the O-H and N-H of the primary and secondary amines, respectively. The bands at 1670 cm^{-1} , 1640 cm^{-1} , and 1602 cm^{-1} corresponded to the C=N of the primary amine and the C=C of the aromatic ring, respectively.

Degree of substitution determination was performed on the polymer Cell-PB sample, and the N content of the Cell-PB sample was determined *via* elemental analysis. The N content was found to be 5.331%, which was equivalent to approximately 0.27 degrees of substitution (phenyl biguanide / 4 AGU).

The solubility of the Cell-PB sample in water was tested by suspending a 1.00 g sample of Cell-PB in 50.0 mL water. The suspension was stirred for approximately 3.0 h, and then the resulting solid was collected *via* filtration and dried. An approximate 23% reduction in the total mass was observed. The polymer solubility was reduced *via* crosslinking by reacting Cell-PB with glycerol diglycidyl ether (GDGE) to produce Cell-X-PB, as shown in Experimental. The FT-IR spectrum of Cell-X-PB (Fig. 3) shows O-H

and N-H stretching bands at 3314 cm^{-1} . Bands for C=N and C=C were at 1634 cm^{-1} . The spectrum shows a peak at 1041 cm^{-1} that is more intense than that shown in Fig. 1b; this could be due to the presence of more hydroxyl groups and ether linkage due to the crosslinking agent. The crosslinking caused some bands broadening and shift to a lower frequency, as shown in the frequency of C=N and C=O peaks.

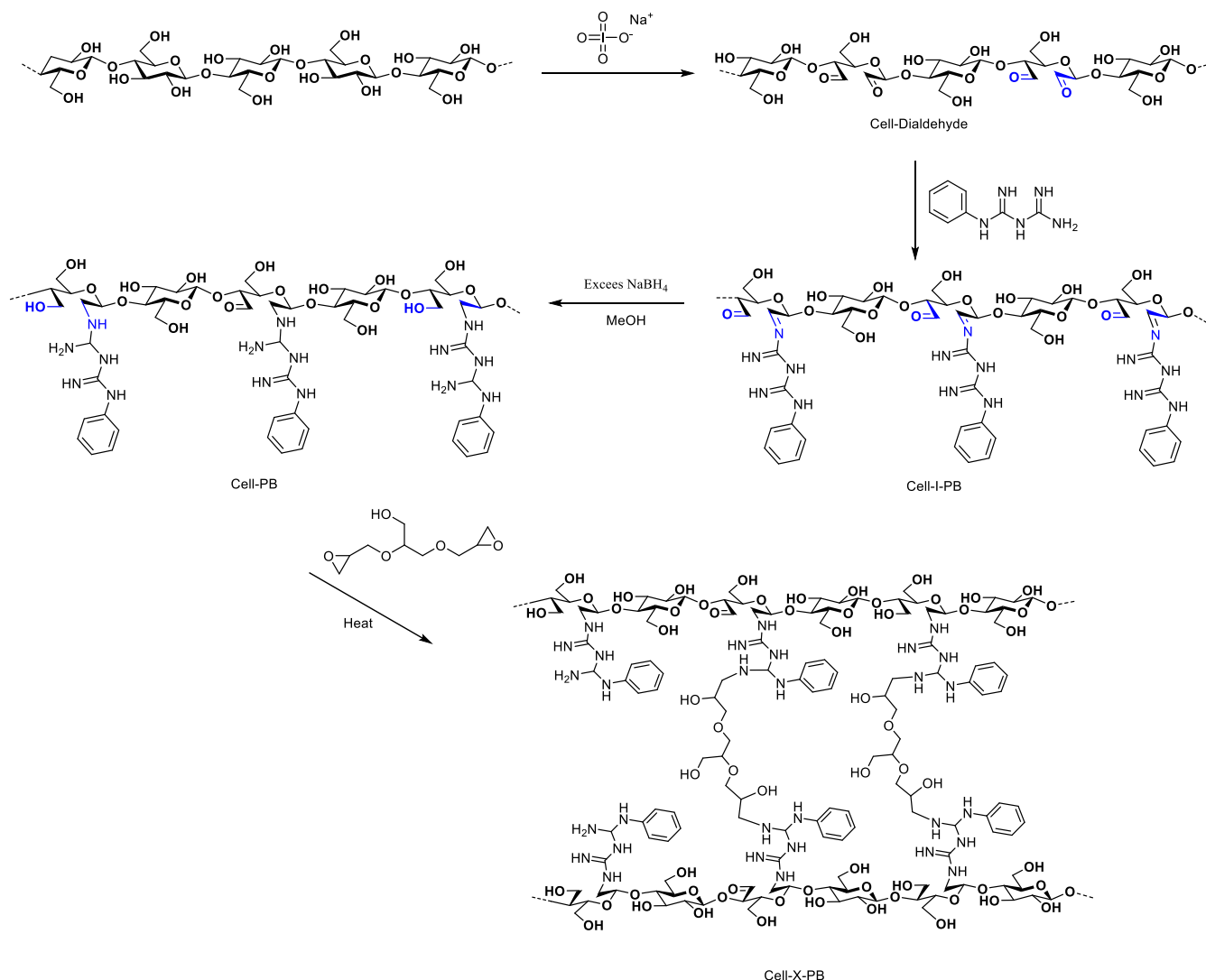


Fig. 2. A schematic drawing showing the formation of Cell-X-PB from cellulose powder

The cellulose dialdehyde SEM image shows the surface morphology with a damaged cell structure. Three images of the Cell-X-PB sample are shown in Fig. 5 at 250x, 1kx and 5kx; the images show a porous spongy structure. This structure makes it suitable for use in as an adsorbent.

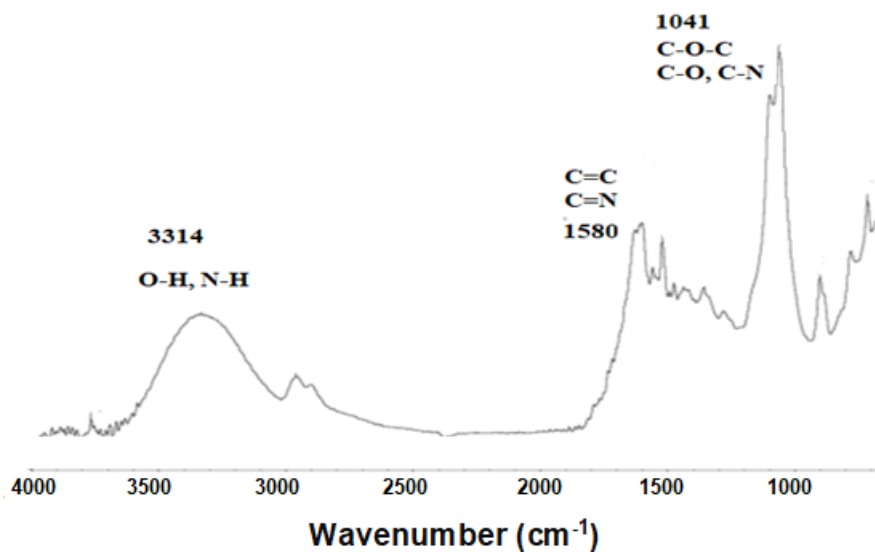


Fig. 3. The FT-IR spectra of Cell-X-PB

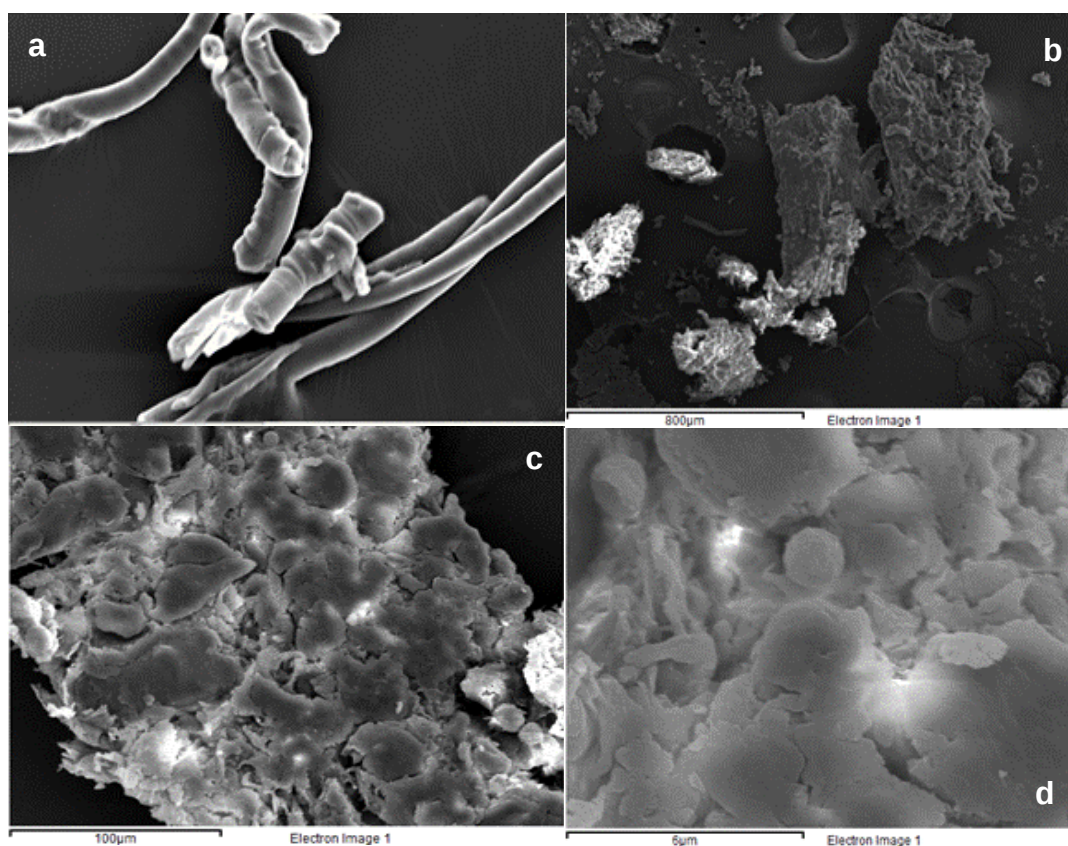


Fig. 4. The SEM images of a) cellulose dialdehyde; b) Cell-X-BP at a magnification of 250x; c) Cell-X-BP at a magnification of 1kx; and d) Cell-X-BP at a magnification of 5kx

Adsorption Study

Extraction of lead(II) and copper(II)

The extraction was conducted using a batch adsorption process. During this process, a solution with known weight concentrations of Pb(II) and Cu(II) were prepared and dosed with a known mass of Cell-X-PB, and then filtered and analyzed. The filtrate was subjected to analysis to determine the concentration of the residual ions. The effect of variables, *e.g.*, polymer dosage, time, temperature, and solution pH value, were evaluated to determine the optimal extraction conditions that lead to the highest adsorption efficiency.

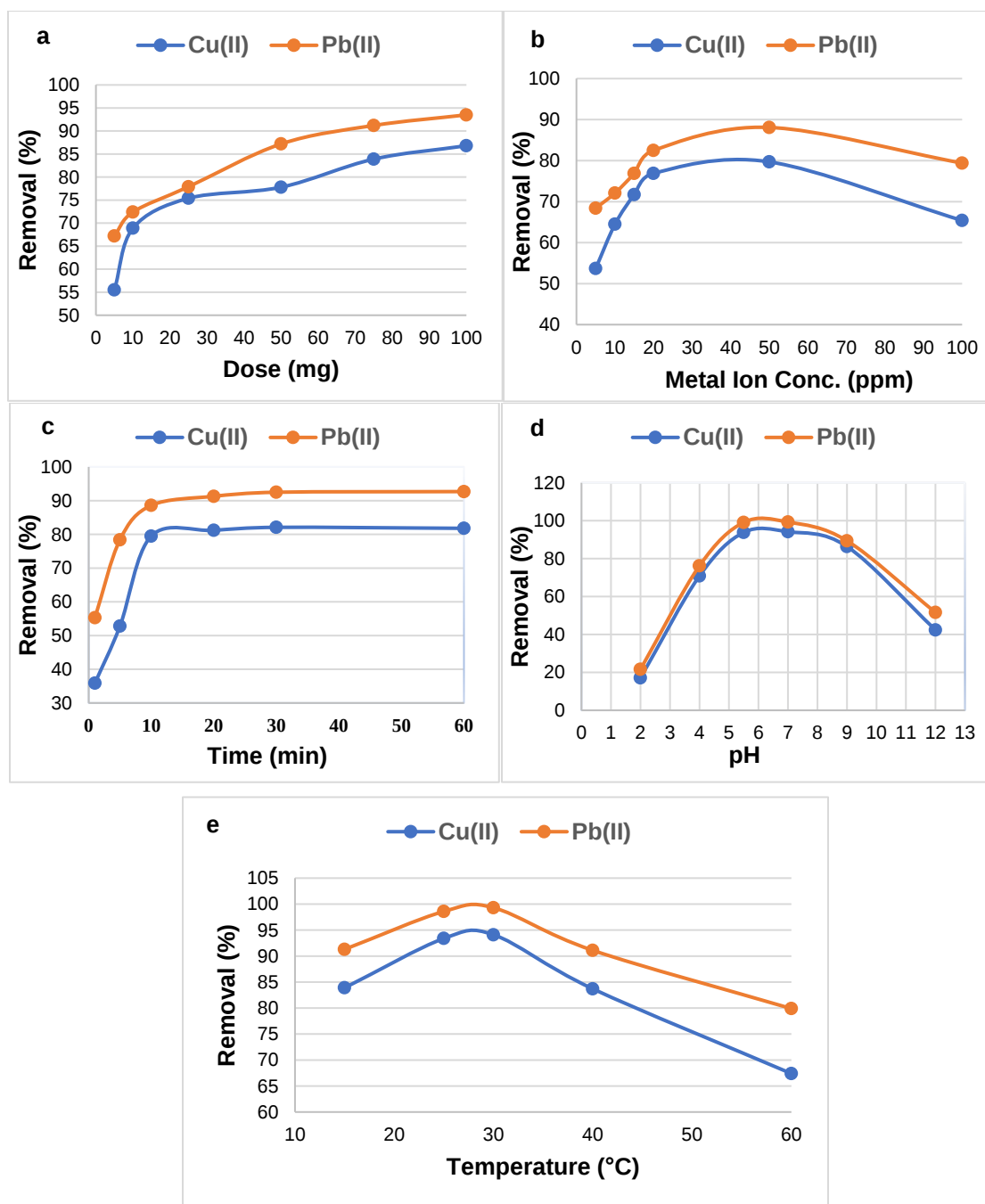


Fig. 5. The effect of the a) adsorbent dose; (b) initial ion concentration; (c) adsorption time; d) pH; and e) temperature on the removal of Cu(II) and Pb(II) via Cell-X-PB

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 Cu(II) and Pb(II) (at an initial concentration of 50 ppm), at a pH value of 4.0, an adsorption time of 20 min, and at room temperature. The removal of the Cu(II) and Pb(II) ions as a function of the adsorbent dosage is shown in Fig. 5a. The percent removal reached approximately 77.8% and 87.2% for Cu(II) and Pb(II), respectively, when using 50.0 mg of Cell-X-PB. At an adsorbent dose greater than 75.0 mg, the percent removal started to level off. The results could be related to the mechanism of adsorption, which is controlled by diffusion and surface coordination. As the amount of added adsorbent increases, the number of available amine sites increases; thus, the percent removal increases. As the coordination sites become saturated, another adsorption process becomes the dominant factor, *i.e.*, the diffusion process, which is primarily controlled by the concentration of the metal ions on the polymer surface and the free metal ions; when these two concentrations become equal, adsorption ends (Abdel-Ghani *et al.* 2007). The results summarized in Fig. 6a showed that the optimum adsorbent dosage was approximately 50.0 mg.

Initial ion concentration

The optimum initial ion concentration was determined while the other variables were kept constant. The constant parameters were as follows: the time was set at 20 min, the adsorbent dose was 50 mg, and the pH was kept at 4.0. As shown in Fig. 5b, the highest percent removal occurred at an initial concentration ranging from 20 to 50 ppm.

At this concentration, the highest percent of ions removed reached 88.3% and 80.0% for Pb(II) and Cu(II), respectively at an initial concentration of 50 ppm of both ions. At a concentration higher than 50 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 20 ppm, the binding sites were almost saturated.

Contact time

The effect of the contact time on the adsorption of Pb(II) and Cu(II) *via* Cell-X-PB was studied while the other variables, *i.e.*, ion initial concentration, temperature, pH, and adsorbent dose, were kept at 20 ppm, 4.0, 25 °C, and 50 mg, respectively. The effect of the constant time is presented in Fig. 5c; the produced graph shows rapid adsorption in the first 10 min, then it became constant and reached equilibrium in approximately 10 min. These results indicated that the binding sites were initially available, then, almost all the coordination sites became occupied (Liu *et al.* 2013). A contact time of 20 min was selected as the optimal adsorption time. The two ions (Pb(II) and Cu(II)) showed nearly similar adsorption manners with time.

pH value

The effect of the pH value on the ion removal rate is presented in Fig. 5d. The solution pH is a critical factor in terms of metal adsorption *via* Cell-X-PB due to the presence of an amine functional group, which is highly affected by the solution pH. At a pH value of less than three, the amine presents in a protonated form (-NRH_3^+) and the lone

pair is not available on the N atom. This explains the low ion removal rate (17% for Cu(II) and 21.6% for Pb(II)) at a low pH value. At a pH of 4.0 or greater, the amine N becomes free and starts to behave as a metal binding site. The highest rate of removal was observed at a pH value of 6.2, which becomes quantitative. At a pH value greater than 7.2, the ion removal rate started to decrease, which could be attributed to the formation of metal oxides and hydroxides.

Temperature

The optimal adsorption temperature was determined under the following adsorption conditions: a pH of 6.3, an initial metal ion concentration of 20 ppm, a contact time of 20 min, and an adsorbent dose of 50 mg. The effects of a temperature up to 60 °C were evaluated, and the results are depicted in Fig. 6e. The ion removal rate showed a slight dependence on temperature up to 30 °C, but it started to decrease as the temperature continued to increase. The results indicated a spontaneous adsorption at room temperature. Therefore, a temperature of 25 °C was selected as the optimal adsorption temperature.

Wastewater purification from metals

A sample of wastewater was collected from a sewer system and was treated with Cell-X-PB. The metal content of the sample before and after purification are presented in Table 1. The high affinity of Cell-X-PB for over 16 metals can be clearly seen from the results presented in Table 1. The high affinity could be attributed to the variety and the high number of binding sites in Cell-X-PB (as shown in Fig. 6). The binding sites are di- and trivalent chelating with the end groups NH and OH.

Table 1. Percent Removal of the Ions Present in a Sewage Sample Using the Adsorbent Cell-X-PB ^a

Metal	Initial Conc. (ppb)	Final Conc. (ppb)	Removal (%)
Al	4680.0	16.058	99.66
Ag	38.2	0.873	97.71
Ga	2.4	0.083	96.54
Sr	609.0	84.201	86.17
Cd	0.31	0.051	83.55
Cr	523.0	21.268	95.93
Co	12.5	0.496	96.03
Cu	103.0	3.554	96.55
Fe	8160.0	68.081	99.17
Pb	5840.0	1.082	99.98
Mn	167.0	5.674	96.60
Ni	430.0	2.652	99.38
Se	609.0	0.61	99.90
Li	6.8	0.0	100.00
V	17.0	1.097	93.55
Zn	696.0	40.36	94.20
Al	4680.0	16.058	99.66

^a The adsorption experiment was run in triplicate, the value presented in the table is an average of three runs.

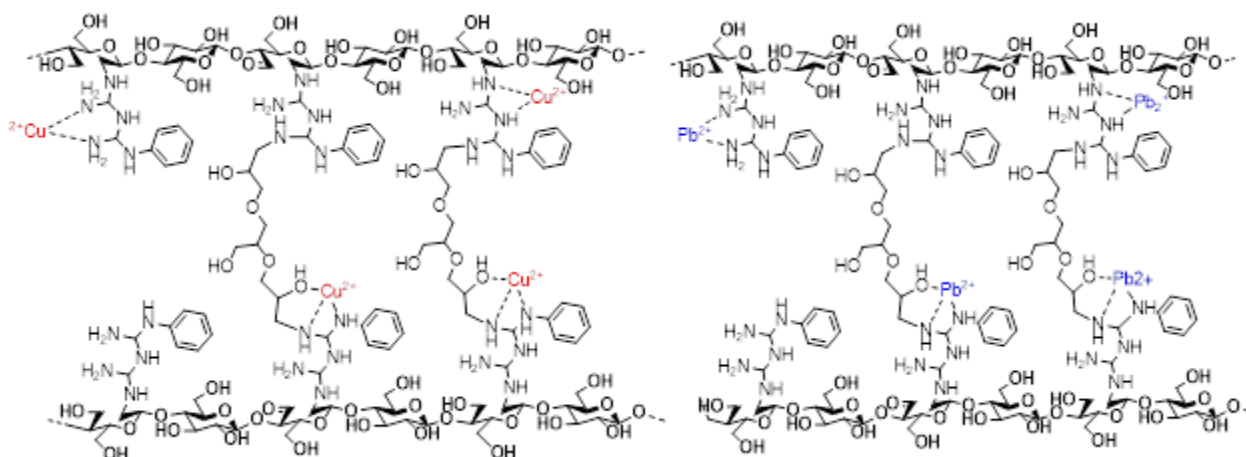


Fig. 6. Schematic drawing showing the binding sites in Cell-X-PB for Pb(II) and Cu(II)

Thermodynamics Study

A thermodynamic study was conducted to check the spontaneity of the adsorption process. The parameters, *i.e.*, the standard free energy, standard enthalpy, and standard entropy, were calculated according to Eqs. 2 through 4, respectively,

$$K_c = \frac{C_{ads}}{C_e} \quad (2)$$

$$\Delta G^\circ = RT \ln K_c \quad (3)$$

$$\ln K_s = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

where K_c is the apparent constant of the thermodynamics, C_{ads} is the amount adsorbed at equilibrium (mg/L), C_e is the concentration of metal ion in the solution (mg/L), R is the universal gas constant (8.314 J/mol K), and T is the mixture temperature ($^\circ\text{C}$) (Guo *et al.* 2008). The $\ln K_s$ vs. $1/T$ plot is shown in Fig. 7a; the slopes and crossings were utilized to determine the standard free energy, standard enthalpy, and standard entropy results (as summarized in Table 2). The values of the ΔS° and ΔH° were positive, whereas the entropy increased at the solid/solution interface induced as a result of the adsorption process. The free energies values of adsorption *via* Cell-X-PB were negative, which indicated a spontaneous process of adsorption at various temperatures.

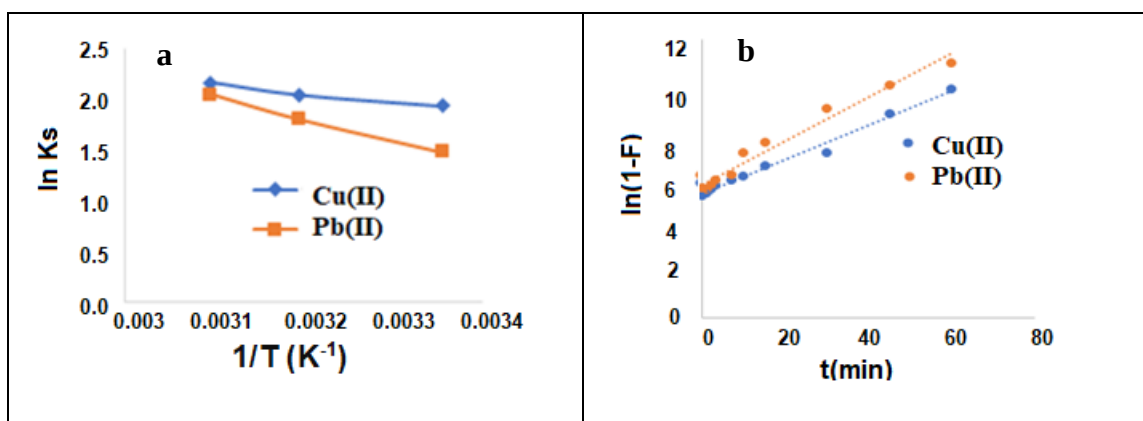


Fig. 7. The plot shows a) the relationship between $\ln K_s$ vs. $1/T$; and b) the liquid film diffusion model plots for the adsorption *via* Cell-X-PB

Table 2. Thermodynamic Parameters for the Adsorption of Cu²⁺ and Pb²⁺ Ions via Cell-X-PB

T(K)	Cu ²⁺		
	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/K.mol)
298	-18.2541	10.3214	62.3214
313	-18.241		
323	-19.1025		

The metal adsorption process generally occurs *via* a two-stage process. The first stage involves the migration of metal ions from the solution toward the Cell-X-PB surface, which then diffuse across the boundary-layer to the outer surface of Cell-X-PB and then bind at the active sites. The second stage involves intra-particle diffusion through the polymer body structure. The adsorption mechanism was investigated using the liquid film and the intra-particle diffusion models.

The film diffusion models imply that the travel of the adsorbate through a liquid film around the solid adsorbent is the controlling stage in the adsorption process, *i.e.*, the rate determining stage the kinetics of the velocity processes. The liquid film diffusion model is described by Eq. 5,

$$\ln(1 - F) = k_{fd}t \quad (5)$$

where F is the ratio of q_t to q_e at equilibrium, and k_{fd} (min^{-1}) is the film-diffusion coefficient. A linear plot of $\ln(1 - F)$ versus t at a zero intercept, demonstrates that the kinetics of the adsorption process were controlled by the diffusion across the liquid barrier enclosing the Cell-PB, where q_e is the adsorption capacity at equilibrium ($\text{mg} \cdot \text{g}^{-1}$). Figure 7b shows that applying the liquid film diffusion model to the obtained Cu²⁺ and Pb²⁺ adsorption results *via* Cell-PB from an aqueous solution at various temperatures did not display linear lines crossing the zero point. In addition, the values of the correlation coefficients were not high (0.1876 and 0.1578 for Cu²⁺ and Pb²⁺, respectively). This suggested that the diffusion of Cu²⁺ and Pb²⁺ through the liquid barrier around the Cell-X-PB sample was not the rate-determining step. However, applying the film diffusion model showed improved coefficient of regression values (0.9735 and 0.9873 for Cu²⁺ and Pb²⁺, respectively). The results indicated that diffusion through the liquid film is not the slowest step, but it still could affect the adsorption process.

Monte Carlo (MC) and Molecular Dynamic (MD) Simulation

A large number of randomized Monte Carlo steps were used to explore the interaction between the Cell-B surface and the heavy metal ions (2,000,000 configurations). The MD computations based on the MC approach provided the lowest energy posture. The geometry was optimized using the Forcite module built-in to the Biovia software (using a tolerance for energy convergence of $1 \cdot 10^{-5}$ kcal/mol and an atom-based summation method was used for both the electrostatic and van der Waals interactions with a cutoff distance of 15.5, a spline width of 1, and a 0.5 buffer) prior to the MD stage. Molecular dynamic simulation was performed at a temperature of 25 °C using the constant volume/constant temperature (NVT) canonical ensemble with a simulation time of 1 ns (using a 1fs time step) (Hsissou *et al.* 2019; Dagdag *et al.* 2020a; Dagdag *et al.* 2020b; Hsissou *et al.* 2020a; Hsissou *et al.* 2020b; Thaçi *et al.* 2020).

A Berendsen thermostat maintained the T control. The calculations for the MC and MD simulations were performed using the universal force field (Rappé *et al.* 1992).

Results

The lowest energy configurations for binding Cu(II) or Pb(II) ions to the Cell-X-PB surface are presented in Fig. 8. The quantifiable verdict of the interaction between the heavy metal ions and the Cell-B surface is implemented over the calculation of the adsorption energies, as shown in Eq. 6,

$$E_{ads} = E_{total} - [E_{Cu(II) \text{ or } Pb(II)ions} + E_{Cell-B}] \quad (6)$$

where E_{total} is the total energy of the system as a result of the Cell-B surface and the heavy metal ions interaction, and $E_{Cu(II) \text{ or } Pb(II)ions}$ and E_{Cell-B} is the system energy in the absence and presence of heavy metal ions, respectively.

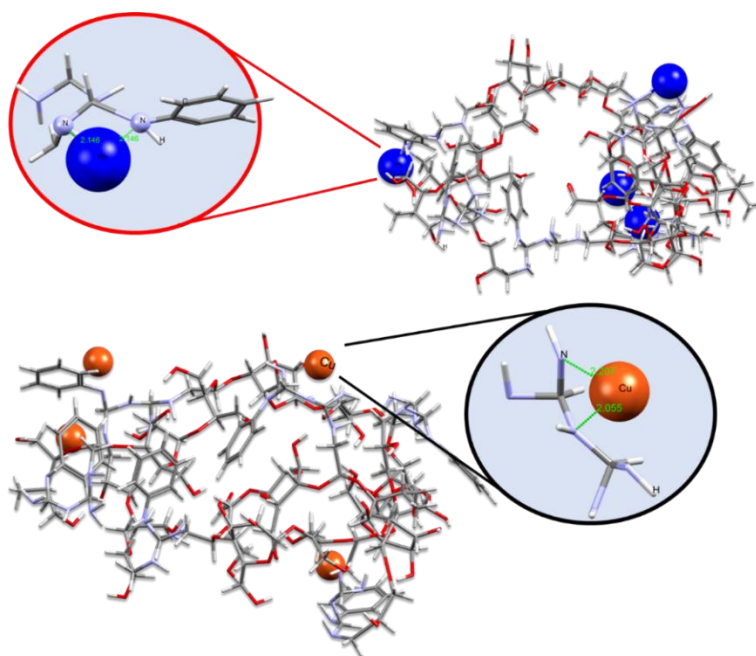


Fig. 8. Monte Carlo pose of the lowest adsorption configurations for the Cu(II) and Pb(II) ions onto the Cell-X-PB surface

The lowest energy pose from the MC calculations was obtained over an enormous number of randomized configurations. The clues for attaining the lowest energy pose are shown in Fig. 9 (the average energy that remains properly unaffected).

The Monte Carlo simulations (Fig. 10) show that the Cu(II) and Pb(II) ions have a considerable adsorption amount onto the Cell-B surface, which agrees with the experimental data. The negative adsorption value confirms the spontaneity of the adsorption process when using this adsorbent (Mehmeti and Berisha 2017; Hsissou *et al.* 2019, 2020a,b; Khalaf *et al.* 2021)

The distribution of the adsorption energies (as shown in Fig. 10) were in the following ranges: a) Cu(II) 30 kcal/mol to -738 kcal/mol; b) Pb(II) 39.6 kcal/mol to -597.2 kcal/mol. Distribution of the adsorption energies for the Cu(II) and Pb(II) ions on the Cell-X-PB, as shown by MC, indicates that Cell-X-PB has higher toward Cu(II) and the adsorption process for both ions is spontaneous and exothermic.

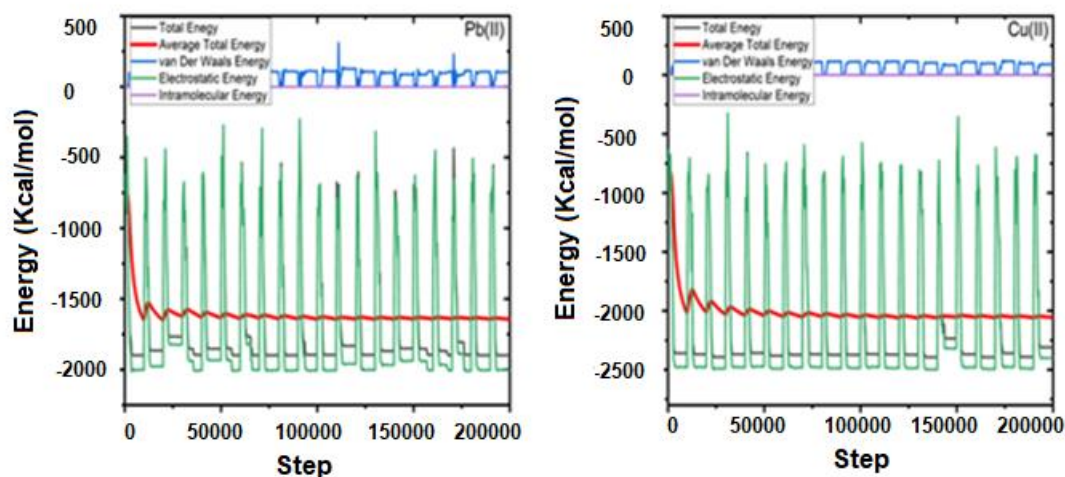


Fig. 9. Energy terms during the search for the MC pose of the lowest adsorption configurations for the heavy metal ions onto the Cell-X-PB surface

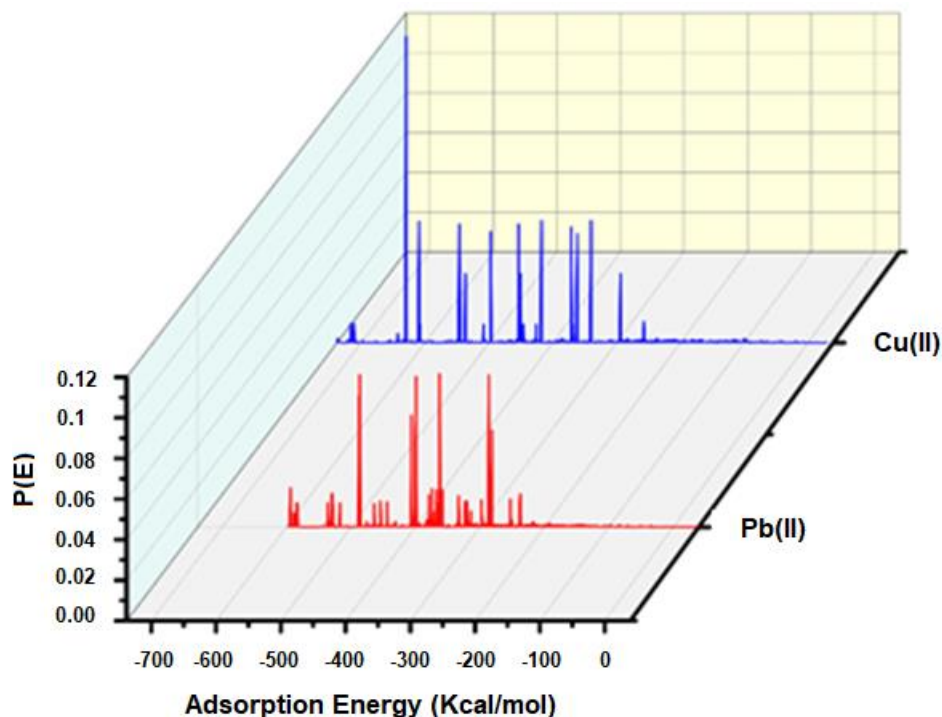


Fig. 10. Distribution of the adsorption energies for the Cu(II) and Pb(II) ions on the Cell-X-PB surface obtained by MC

Molecular dynamic simulation is more reliant on monitoring and recording the dynamics of the process in general. The equilibrium configuration was reached, as demonstrated by the modest temperature drift in the graph shown in Fig. 11.

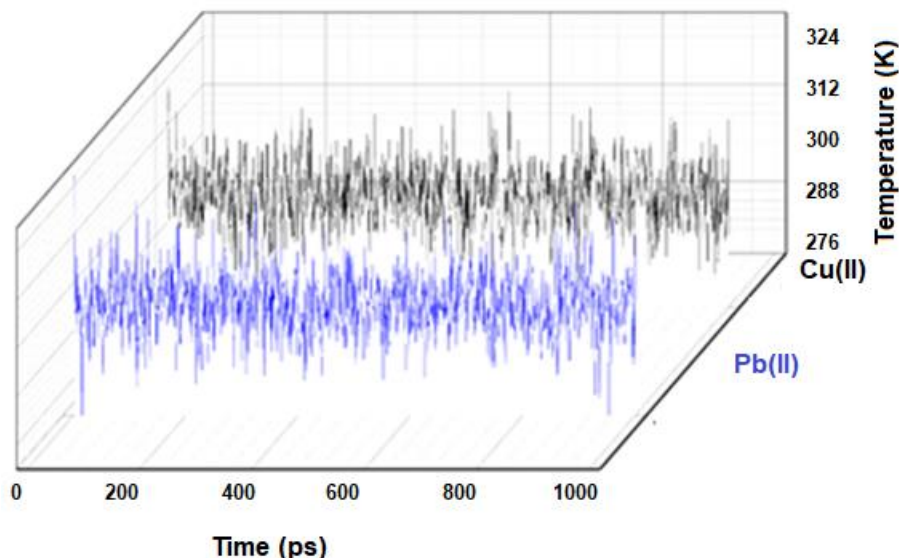


Fig. 11. Graph of the temperature control from the MD simulation during the interaction of the difenoconazole molecule onto (Cell-X-PB) surface

Figure 12 shows the lowest equilibrium energy structure for the interaction of the Cu(II) and Pb(II) ions with the Cell-X-PB surface, obtained from the MD simulation.

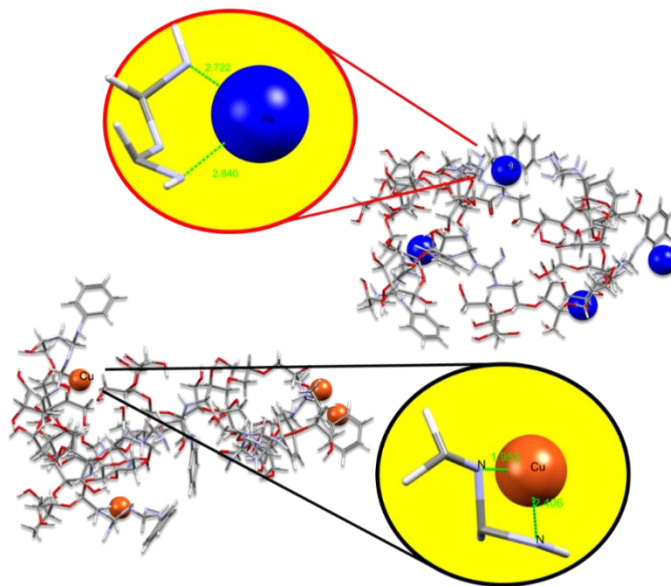


Fig. 12. Lowest energy configurations of the interaction of the Cu(II) and Pb(II) ions onto the Cell-X-PB surface obtained via the MD simulation

As can be seen from Figs. 8 and 12, both of the heavy metal ions interacted with the Cell-X-PB surface through the complexation by N-H groups. The interaction (adsorption) energy during the MD simulation was assessed at each time elapse and is presented in Fig. 13, and the descriptive statistics are shown in Table 3.

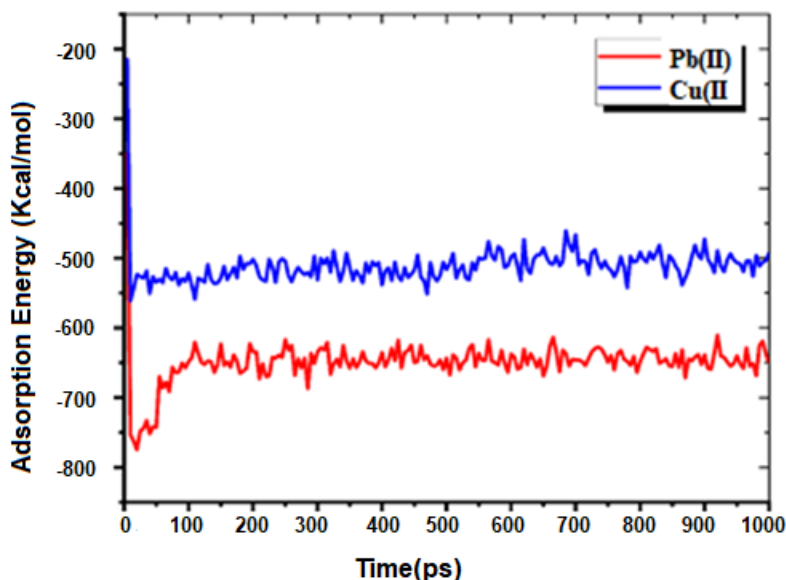


Fig. 13. Interaction energy of the heavy metal ions on the Cell-X-PB surface during MD simulation

Relative high adsorption energies are consistent with the experimental findings. The negative values of the adsorption energies indicated the spontaneity of the adsorption process.

Table 3. Statistics of the Interaction Energy of the Pb(II) and Cu(II) Ions onto the Cell-PB Surface During the MD Simulation

Metal Ion	Mean (kcal/mol)	Minimum (kcal/mol)	Median (kcal/mol)	Maximum (kcal/mol)
Pb(II)	-649.29	-350.05	-647.71	-774.70
Cu(II)	-511.45	-215.12	-511.91	-561.03

CONCLUSIONS

1. Cellulose powder was extracted from olive industry solid waste and functionalized with the chelating agent phenyl biguanide to produce a cellulose-based amine (Cell-PB) with multi-binding sites for metal ions. The solubility of the Cell-PB in water was reduced *via* crosslinking with glycerol diglycidyl ether to produce Cell-X-PB.
2. The efficiency of the prepared Cell-X-PB sample in terms of extracting metal ions from wastewater was evaluated. The effect of various parameters, *i.e.*, the adsorbent dose, temperature, pH, metal ion initial concentration, and time, on the adsorption efficiency was evaluated, and the optimal extraction conditions were determined.
3. The cellulose-based amine polymer (Cell-X-PB) showed excellent efficiency toward all metal ions present in the sample wastewater.
4. The thermodynamic study showed a free energy with a negative value, which indicated a spontaneous metal binding at various temperatures.
5. The high efficacy and spontaneous adsorption process were confirmed *via* theoretical

calculations and molecular modeling using Monte Carlo (MC) and molecular dynamic (MD) simulations.

6. The polymer could be a promising commercial alternative for existing metal ion adsorbents.

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