Effective lead removal from aqueous solutions using cellulose nanofibers obtained from water hyacinth

Sarai Ramos-Vargas, Rafael Huirache-Acuña, José Guadalupe Rutiaga-Quiñones and Raúl Cortés-Martínez

ABSTRACT

In this paper, the removal of Pb(II) ions from aqueous solutions using cellulose nanofibers (NFC) and crystalline nanocellulose (CNC) was studied. These adsorbents were obtained from water hyacinth (Eichhornia crassipes) by the Kraft process. Characterization was carried out to NFC and CNC by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), showing excellent structural properties and high availability of surface functional groups. The influence of different parameters on the adsorption process was evaluated through batch-type adsorption experiments. The results showed effective lead removal reaching adsorption equilibrium at 180 min. Isotherms results showed maximum adsorption capacities ($Q_{\text{max}}$) of 80.02, 84.64, and 87.10 mg/g for NFC at 25, 30 and 45 °C, respectively. Results of Pb(II) adsorption isotherms by CNC showed a $Q_{\text{max}}$ of 17.90, 28.20, and 30.36 mg/g at 25, 30 and 45 °C, respectively. Isotherm data were best described by the Langmuir–Freundlich model for NFC, and the Freundlich model best-described CNC isotherm. Lead adsorption mechanisms were different for both biosorbents. The thermodynamic parameters of the process were calculated. Endothermic reactions were observed for both materials. NFC and CNC materials have great potential as biosorbents for the removal of lead ions from water.

Key words | biosorption, cellulose nanofibers, lead, water hyacinth

HIGHLIGHTS

- Water hyacinth was probed to be a good source for cellulose obtention.
- Simple methods obtained cellulose nanofibers and nanocrystalline cellulose with excellent structural properties.
- Fast lead adsorption was observed for both biosorbents.
- Biosorbents showed high lead adsorption capacities.
- These biosorbents are suitable for cation removal from contaminated waters.

INTRODUCTION

Industrial activities produce wastewaters that are polluted by toxic heavy metals. The mining, metallurgical, electroplating, electronic, nuclear and other industries, are significant causes of water contamination by these type of pollutants (Suopajärvi et al. 2013). Metals are biologically non-degradable and, thus, concentrated in living organisms; thereby, they can move up to the food chain. That can also produce various socio-economic problems by causing multiple human diseases (Kwon et al. 2015).

Lead is one of the most toxic trace metal ions, and human exposure to their inorganic forms is through food and water ingestion, as well as by inhalation (Moyo et al. 2017).
At higher exposure levels, lead causes encephalopathy, cognitive impairment, behavioral disturbances, kidney damage, anemia, and toxicity to the reproductive system (Yu et al. 2015). According to the World Health Organization criteria, the permissible limit of lead in drinking water is 0.01 mg/L (WHO 2017).

In recent years, several methods have been reported for heavy metals removal from wastewaters. Some of these methods include chemical precipitation and reduction, ion exchange, coagulation with lime, membrane filtration, and solvent extraction. In terms of cost and efficiency, adsorption is a promising processing technique for wastewater treatment with low lead concentration (Ren et al. 2016).

The adsorption process has proven to be an efficient and technically feasible method for the removal of heavy metals from water (Hokkanen et al. 2014). Adsorption is a mass transfer process in which a solute (adsorbate) is separated from a solution and concentrated on the surface of solid material (adsorbent). When this material is of biological origin, the process can be called biosorption.

Frequently, metal ions removal in liquid phase adsorption processes have been accomplished utilizing activated carbon as an adsorbent. However, due to the high costs of regeneration of this material and the high consumption of energy for its production, its applications are less economically attractive on an industrial scale (Hokkanen et al. 2014). Therefore, research for wastewater treatment has focused on the search for alternative low-cost adsorbents (Sheikhi et al. 2015). Consequently, low-cost biosorbents derived from renewable resources, agro-industrial byproducts or waste materials have been considered among the most feasible novel alternatives for the removal of this type of metal pollutant (Suopajärvi et al. 2015).

One potential bio-based nano-adsorbent material is nanocellulose, which can be obtained from different renewable resources. It has a high surface area morphology that has the potential for environmental and health applications (Siró & Plackett 2010; Abhishek et al. 2013) and remediation of toxic metals from water bodies. This nanostructure has attracted attention for application in several different areas because of its excellent physical properties, biodegradability, biocompatibility, and low cytotoxicity (Nascimento et al. 2015). Besides, the low genotoxicity and high biodegradability of cellulose nanofibrils distinguish them from inorganic nano-adsorbents (Sheikhi et al. 2015).

Cellulose is the most abundant and renewable polymeric resource available worldwide. It is composed of β-1,4-linked anhydro-D-glucose units and, thus, the hydroxyl groups (–OH) present in these structures enable cellulose to establish hydrogen bonds with other molecules. The OH groups of C4 and C1 carbon atoms provide hydrophilicity, chirality, and reactivity properties in the structure of cellulose (Abhishek et al. 2013).

Cellulose can be classified as a semi-crystalline fibrillar material since it has both an amorphous region and a crystalline structure (Yu et al. 2015). There are two general classes of cellulose nanomaterials (CNs) that can be extracted from different resources such as plant or bacterial. These types of nano-cellulose materials can be called cellulose nanofibrils (NFC) or cellulose nanocrystals (CNC), which have also been reported as cellulose nanowhiskers (CNW). Depending on the size and method of extraction, NFC can also be referred to as micro-fibrillated cellulose (MFC) (Kumar et al. 2014). The NFCs can be obtained by mechanical fibrillation (homogenization, micro-fluidization or ultrafine grinding) of cellulose biomass (Liu 2015), depending on the source of cellulose and its previous treatments. Also, shorter cellulose nanocrystals (CNC) can be obtained by acid hydrolysis or oxidative treatment of natural fibers (Sirviö et al. 2016).

The water hyacinth is a hydrophyte plant that can be abundantly present in bodies of water with high levels of nutrients. Due to its quite dense foliage, it can be used in the extraction of cellulose. The abundant aquatic weed species *Eichhornia crassipes* (water hyacinth) in tropical weather conditions is a major problem in open water bodies for its different uses like power generation, irrigation, and boating. Thus, high amounts are being spent worldwide to remove the weed selectively. The plant is rich in fiber content and has no significant differences in the percentage of cellulose content in the shoot and root (Sundari & Ramesh 2012).

Therefore, the present work aimed to extract CNC and NFC from *Eichhornia crassipes* by acid hydrolysis (H2SO4) and mechanical disintegration and to evaluate the adsorption behavior of these biosorbents on the removal of lead from aqueous solution.
MATERIALS AND METHODS

Materials

Analytically pure grade chemical reagents were used in all experiments carried out in this work. Lead (Pb) solutions were prepared by dissolving Pb(NO₃)₂ in deionized water. The pH of lead solutions was adjusted with 0.1 M NaOH and 0.1 M HCl solutions, as required. A standard Pb solution (1,000 mg/L) was used to calibrate the Inductively coupled plasma optical emission spectrometry (ICP-OES) which was used to analyze solutions samples.

Preparation of cellulose materials

Eichhornia crassipes live plants were collected from a lake at Cuitzeo, Michoacán, México, they were washed with tap water followed by double-distilled water to eliminate the sediments and impurities, and then they were dried at room temperature for two weeks. Later, dried biomass was fibrillated and homogenized. The Kraft pulping method was used to obtain cellulose fibrils. Demineralization was carried out with 2% H₂SO₄ solution at 90–95°C for 2 h. The fibers were bleached with MgSO₄.7H₂O 0.1% under oxygen condition at pH 12 for 1 h at 110°C. After that, a treatment with ClO₂ for 2 h at 60°C pH 2–3 was made. This process was repeated twice, washed with double-distilled water until neutral pH, and the white tissues were obtained. A sodium hydroxide solution was used to remove hemicelluloses from the tissues by treating them with this solution at 25°C for 2 h. Between each of the steps, the samples were centrifuged and washed with double-distilled water.

Preparation of CNC and NFC

The CNCs were obtained dispersing the pulp fibers in concentrated sulfuric acid. The proportion of the pulp fibers to acid was 1:6. Then, the suspension was maintained inside a convection oven at 60°C for 2 h. Afterward, the addition of a double-distilled water aliquot, of the same volume of suspension, was carried out. Excess of water and acid was removed from the dispersion with a centrifuge for 10 min at 10,000 rpm. Subsequently, dialysis of this dispersion containing the precipitate was performed for one week with double-distilled water; the effluent of the dialysis procedure was checked for pH neutrality. After that, the recovery of CNCs fibers from the dialyzed suspension was carried out by a freeze-drying process.

The fibers were frozen and crushed in liquid nitrogen. A powder consisting of crystalline nanofibrils was obtained as a result of the high shear forces and impact that acted on the CNCs. Cryo-crushed fibers can then be used for further experiments (Sundari & Ramesh 2015). NFCs were obtained by the same cryo-crushing method but without acid treatment of the pulp fibers.

Scanning electron microscopy (SEM)

To determine the morphology and elemental microanalysis of the NFC and CNC samples, a scanning electron microscope FEG JSM-7600F was used, with a 50 kV acceleration voltage. To carry out such analyses, the samples of both biosorbents were coated with copper and then were placed on a carbon grid by placing a drop of a suspension of each type of sample on the grid and evaporating the liquid (Vázquez-Guerrero et al. 2016). Also, NFC and CNC samples were put in contact with a 1,000 mg/L lead solution for 180 min to achieve adsorption equilibrium. Then, samples were dried and stored in a desiccator until elemental microanalysis (EDS) was carried out.

Transmission electron microscopy (TEM)

TEM images were obtained using a transmission electron microscope JEM-2100 operated at 120 kV. For TEM sample preparation, the nanocellulose biosorbents were prepared by putting 10 μL of a copper-coated NFC and CNC suspensions supernatant, separately, on a carbon-coated square mesh copper grid.

Zeta potential measurements

To determine the zeta potential and to establish the point of zero charge (PZC) of both materials, electrophoretic curves were obtained as a function of pH. These
parameters were determined to NFC and CNC fibers using a dynamic light scattering spectrophotometer (Zetasizer instrument, Malvern Co., UK). In order to obtain such curves, 2 mg of each biosorbent was dispersed in 30 mL of double-distilled water, separately, and they were treated in an ultrasonic bath before the measurement. The pH of the colloidal suspensions was adjusted as mentioned above.

Fourier transform infrared spectroscopy (FTIR)

The FTIR studies were carried out in an Agilent 660 FTIR spectrophotometer to determine the functional groups present in the structure of both biosorbents, as well as to establish the interaction between the adsorbate and the groups involved in its removal. To perform these measurements, approximately 20 mg of the finely ground and dried sample was placed in a sample holder. The determination of the FTIR spectra was carried out at room temperature, adjusting the resolution of the equipment to 4 cm\(^{-1}\).

Kinetic experiments

Batch-type tests were performed to determine the effect of contact time on the biosorption of lead with the two types of biosorbents: CNC and NFC. 0.05 g of each type of nanocellulose biosorbent was put in contact, separately, with 10 mL of a 20 mg/L Pb(II) metal solution in vials. Later, the vials were placed on an orbital shaker at 250 rpm and 25 °C ± 2. The solution pH was adjusted at 5.5 for Pb(II) solutions. Solutions were kept in contact at different contact times for 8 h. After the contact time was achieved, the samples were centrifuged and filtered with a Whatman filter paper 0.2 μm pore size, and the supernatant was placed in vials for later analysis of lead by ICP-OES. A control experiment was also set up with no biosorbent addition in order to determine analyte loss by a different process than adsorption. The tests were carried out in triplicate check reproducibility, and the mean values were considered.

The amounts of lead adsorbed in NFC and CNC were calculated from the initial concentration of the solution and the concentration of Pb at equilibrium, according to Equation (1):

\[
q = \frac{V(C_0 - C_e)}{M}, \quad (1)
\]

% Removal = \( \frac{(C_0 - C_e)}{C_0} \times 100 \) \( \quad (2) \)

where \( q \) is the sorption measured per unit weight of the solid (mg/g); \( v \) is the volume of the solution used for the tests (L); \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of Pb (mg/L), respectively, and \( M \) is the dry weight of the biosorbent (g). The removal percentage was determined using Equation (2).

Effect of amount of biosorbent

Biosorption experiments were performed to ascertain the effect of the biosorbent amount on Pb(II) removal. These experiments consisted of putting in contact 5 mL of a 20 mg/L Pb(NO\(_3\))\(_2\) solution in vials with different quantities of NFC and CNC biosorbents, separately, ranging from 0.01 to 0.1 g. The vials were then placed on an orbital shaker until the equilibrium time for each system was achieved, and then the solutions were centrifuged and filtered as mentioned above. Then, supernatants were analyzed for lead by ICP-OES.

Effect of pH on Pb biosorption

Effect of pH on Pb ions biosorption for both NFC and CNC-Pb systems was studied. For this purpose, biosorption experiments were performed at varying pH (from 3 to 8). 5 mL of a 20 mg/L Pb(NO\(_3\))\(_2\) were added to different vials with 0.06 g of each sorbent, separately. The initial pH of Pb solutions was adjusted as mentioned above, as required. The vials were then placed on an orbital shaker at 250 rpm at 25 °C until the equilibrium time was attained. At the end of contact time for each adsorption system, the solution was centrifuged and filtered, and the supernatant was placed in vials for later analysis of lead by ICP-OES.

Isotherms

To obtain the biosorption isotherms of the NFC-Pb and CNC-Pb systems, batch adsorption experiments were carried out by placing 0.04 g of NFC and CNC, separately,
with 5 mL of lead solutions in a concentration range from 5 to 1,750 mg/L, at 25, 30 and 40 °C, on an orbital stirrer at 250 rpm for 180 min. Different temperatures were chosen to determine the effects of the system’s adsorption behavior, as well as to determine the thermodynamic parameters of the process. The specific temperature values were selected to simulate the conditions that the adsorbate-biosorbent system could face in the treatment of real industrial wastewaters. Once the biosorption equilibrium was reached in each system, the suspension was filtered and the lead solution analyzed by ICP-OES. The experimental data obtained from these tests were fitted to three well-known adsorption isotherm models, which described the equilibrium relationships between the Pb(II) ions and the NFC and CNC biosorbents at the different temperatures.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

The study conducted by SEM allows us to understand the morphological aspects of microscopic areas of the materials used in this work, as well as the processing and analysis of the images obtained to relate the mechanism of adsorption of Pb(II) in NFC and CNC biosorbents. To know the morphology of the material, samples of NFC and CNC were analyzed by SEM to determine differences in their structure due to the different synthesis processes to which both biosorbents were subjected. In the case of CNC (Figure 1(a)), well-defined nanocellulose fibers with different sizes and some agglomeration of fibers can be observed. The grain size of the agglomerates for both biosorbents was about 0.5 mm. According to Othman et al. (2015), agglomeration is generally due to the Van der Waals attraction forces between nanoparticles. Moreover, it can be seen that the diameter of the nanocellulose fiber (CNC) was 97.9 nm (Figure 1(b)). According to the report by Kumar et al. (2012), agglomeration is generally due to the Van der Waals attraction forces between nanoparticles. Moreover, it can be seen that the diameter of the nanocellulose fiber (CNC) was 97.9 nm (Figure 1(b)). According to the report by Kumar et al. (2014), the diameter of nanofibers may vary between 20 and 80 nanometers. Interestingly, the diameter of the nanocellulose obtained in this study was similar to those produced by acid hydrolysis from different sources such as bamboo fiber (30–80 nm) (Chen et al. 2011) and rubberwood (10–90 nm) (Jonoobi et al. 2011). In Figure 1(c), the presence of a porous open structure of cross-linked fibers in the surface of CNC can be observed;

![SEM micrographs of CNC samples (a and c), CNC isolated fiber (b), and NFC samples (d and e).](image-url)
however, this effect is due to a large number of non-isolated nanofibers that have contact with each other at certain points in their structure.

Figure 1(d) and 1(e) show SEM micrographs of a dilute suspension of natural NFC samples. Well-defined fibers with diameters ranging from 0.5 to 1 μm can be observed; these fibers are bigger than those of CNC biosorbent. Due to the process of synthesis which this material was subjected, lignin and hemicelluloses were not eliminated from the fibers; therefore, the NFC samples have surface capes with a high content of extractable compounds (wax, pectin, oil) (Kumar et al. 2014). Comparing the morphology of NFC and CNC in the micrograph, it can be observed that, after the delignification, CNC it has a surface free of impurities, due to the alkaline treatment and to the acid hydrolysis of the fibers. The diameter and the size of the CNC fibers were reduced significantly due to the elimination of the amorphous region present in the NFC. In a few occasions, it is possible to observe twisted thin segments in CNC; these are representative of the nanofibers (NFC) proving that their natural structure was preserved in them (Usov et al. 2015).

To study the presence of lead in the adsorbent after the contact with Pb(II) elemental microanalysis (EDS) was carried out. Figure 2(a) shows an EDS micrograph of CNC after adsorption of lead where small bright particles of lead in the form of elongated cylinders can be observed, with no arrangement pattern, indicating the presence of lead retained in the adsorbent. In the case of NFC, Figure 2(b)–2(d) shows the presence of lead particles forming cylinders interacting with NFC fibers directly. The presence of lead particles was found in well-defined fibers of NFC and CNC as well as in the amorphous structures formed by the agglomeration of the fibers with the remaining lignin and hemicelluloses in NFC.

According to the elemental analysis of the CNC, it has a percentage of lead of approximately 2.30% (Figure 2(a)), while other points on the surface of CNC showed higher Pb concentrations near 80%. In Figure 2(c) and 2(d), two NFC-Pb micrographs at ×5,000 are presented. In Figure 2(c), four zones (indicated by numbers) with a different morphology are marked. Zone 1 denotes a smooth structure; it could not be defined as fiber. Zone 2 is a defined fiber, where a white color stands out in large part of its area.

Figure 2 | SEM micrographs of (a) CNC/Pb and (b), (c), (d) NFC/Pb.
Zone 3 is a fiber of approximately 1 μm without finding any contrast in color; and zone 4 that belongs to several defined fibers where small clusters of amorphous particles on the surface can be seen. An EDS analysis was carried out on these zones to confirm the presence of lead, obtaining in zone 2 an approximate lead concentration of 45.4%; in zone 3, 18% and in the zone 4, 4.25% (Figure 2(c)). It can be said that the adsorption of lead in NFC is not homogenous, concentrating in different proportions on the surface of the material.

Transmission electron microscopy (TEM)

The geometrical characteristics of the nanocellulose depend on the origin of the cellulose microfibers and the conditions of the acid hydrolysis process, such as time, temperature and purity of the materials. The morphological and physicochemical characterization of nanocylinders, nanocrystals and nanofibers are essential for its potential uses as a nano-composite (Nascimento et al. 2015); however, it is widely accepted that the raw material is the most critical factor. In Figure 3, TEM micrographs from a diluted suspension of CNC are shown. Longitudinal cutting of these microfibrils can be done by submitting the biomass to hydrolysis treatment with a strong acid, which allows the dissolution of the amorphous domains. The resulting nanoparticles are produced as nanocrystals or whiskers (Kalia et al. 2011). In Figure 3(a) and 3(b), cellulose nanocrystals (CNC) are observed in the form of small needles with a diameter between 8 and 10 nm and with a variable length between 20 and 80 nm. Agglomerated and individual crystals were also noticed in TEM micrographs. The long-wide ratio (L/D) is unusually low, ranging from 2.5 to 8, which is not similar to those reported in the literature for different cellulose nanocrystals.

Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) is an essential method to define the functional groups present in the nanofibers and crystalline cellulose as well as to determine the changes in the chemical structures by observing such functional groups in FTIR spectra after the biosorption process has occurred. Cellulose, hemicellulose, and lignin are mainly composed by alkanes, esters, ketones, alcohols and aromatic rings with different functional groups. The FTIR spectra of the biosorbents NFC and CNC are shown in Figure 4(a). The broad bands around 1,637 cm\(^{-1}\) are characteristic of C=O double bonds, the bands located between 1,027 and 1,060 cm\(^{-1}\) represent –OH groups. In the case of NFC, bands at 1,102 cm\(^{-1}\) were found indicating the presence of secondary –OH groups. The peaks present at 900 cm\(^{-1}\) are related to C-H groups, these groups imply the β-glycosidic linkages between the anhydroglucose units in cellulose. Bands between 1,575 and 1,480 cm\(^{-1}\) are typical for deformation modes of hydrogen in NH\(_2\) group attached to the –OH functions residues of the cellulosic substrate (Hokkanen et al. 2014). It can also be observed in this spectrum (Figure 4(a)) that the bands present in the wave number at 1,590 cm\(^{-1}\) can be related to the bending vibrations of the CH and CO groups, which are characteristic of aromatic rings that define the structure of the
polysaccharides present in this type of biomaterial (Anirudhan & Rejeena 2013). Likewise, the peak position assigned at around 2,900 cm$^{-1}$ is related to the stretching vibration of the aliphatic C-H group, whose presence is frequent in compounds such as cellulose, hemicellulose, and lignin (Nguyen et al. 2013). The stretching vibrations of OH groups, related to aromatic and aliphatic structures present in the biomaterial, predominate in the broad band that appeared at 3,443 cm$^{-1}$ wavenumber. The strong peak at 1,649 cm$^{-1}$ is attributed to amide or carboxyl structures due to the stretching of C=O bonds. Bending of N–H bonds was also located at the band at 1,535 cm$^{-1}$. The peak position at around 1,646 cm$^{-1}$ can explain the absorption of water by cellulose treated fibers. The reaction of the hydroxyl groups, existing in this cellulosic biomaterial, with the sodium hydroxide and the consequent formation of water molecules can explain the occurrence of this peak in the NFC and CNC spectra. Despite the NFCs and CNCs fibers were dried in an oven, as mentioned before, water was difficult to extract in this procedure due to the strong interaction between molecules of cellulose and H$_2$O (Lani et al. 2013). There are several differences between NFC and CNC bands, which shows that there are changes and differences in the chemical structure of these two materials. For instance, it was not found a band at 1,520 cm$^{-1}$ on CNC, but it appeared on NFC, and this was attributed to the effective removal of lignin during the treatment (Nuruddin et al. 2011; Nguyen et al. 2013). The band at 610 cm$^{-1}$ in CNC corresponds to the stretching of the bonds C-O-S, this is typical of obtaining nanocellulose by acid hydrolysis with sulfuric acid as reported by Bolio-López et al. (2011). It was also found that the main characteristics of the NFC maintained and they were not affected significantly by acid hydrolysis to which CNC was subjected (Pérez et al. 2003).

Figure 4(b) shows the changes in the FTIR spectrum of the NFC material after lead adsorption. Changes in some of the bands that suggest an interaction of the representative functional groups were noticed. The bands involved are those corresponding to the following vibrations: 3,500 cm$^{-1}$ and 1,102 cm$^{-1}$, 1,649 cm$^{-1}$, which correspond to the stretching vibration in the alcohol groups and -COO stretching vibrations, respectively. These changes suggest that these groups are involved in the adsorption of Pb.
Since it is not probable that lead is bound to a carbon atom, such shifts and decreases in the band intensities indicate that the O atoms in the OH groups present in the NFC biosorbent were directly involved in Pb(II) ions adsorption. Moreover, changes in band intensity at 1,520 cm\(^{-1}\) wavenumber can be attributed to the NH\(_2\) stretching vibration. Therefore, it can be established that amine groups in NFC play an essential role in lead biosorption on this biomaterial, by sharing one electron pair of the nitrogen atom with the Pb ions. Thus, FTIR spectra analyses disclose that amine, carboxyl, and hydroxyl functional groups, as well as phosphate present on the NFC biosorbent structure, are involved in lead adsorption. On the other hand, the results of FTIR for the CNC biosorbent after contact with Pb(II) solutions are shown in Figure 4(c) where changes on the bands of typical functional groups of this material can be observed. The peaks at 3,391 cm\(^{-1}\), 1,064 cm\(^{-1}\), 1,116 cm\(^{-1}\) can be assigned to the stretching vibration in –OH groups. Therefore, it can be established that Pb(II) ions adsorption onto CNC includes an ion exchange mechanism involving –OH surface groups; this fact was confirmed by a rise in pH of the solution after biosorption of lead on this biosorbent. Bands at 1,446 cm\(^{-1}\) and 1,370 cm\(^{-1}\) were assigned to –CH groups present in the material. Peaks at 607 cm\(^{-1}\) and 800 cm\(^{-1}\) are referred to sulfur groups (–SO\(_x\)). Sulfur groups are present on CNCs due to the acid hydrolysis that was applied to this material, which confers additional negatively charged groups to the sorbent structure; this would favor the adsorption of metal cations in solution, such as Pb(II) ions.

### Zeta potential

The zeta potentials were determined to examine the nanocellulose colloidal stability and charge (Nascimento et al. 2015). The change in the zeta-potential against pH for NFC and the CNC can be observed in Figure 5. The NFC had a PZC around 3.53 and became negative above pH 4. The value of the PZC for CNC is 2.98. At pH values lower than PZC, the material gets a positive surface charge due to the presence of H\(^+\) in solution; therefore, the concentration of protons that could compete with metal ions for the active sites is higher. The adsorbent surface is charged positively, which causes the metal ions with a positive charge to have difficulty in approaching the functional groups in the surface of the biosorbent due to electrostatic repulsion (Abdel-Ghani et al. 2007). Because of this, lower Pb(II) adsorption capacities were found at low pH values of the solution. With increasing pH (pH > PZC), the proton concentration decreases and the surface charge of the adsorbent becomes negative. Therefore, it increases the electrostatic attraction between the metal ions and the adsorbent, which leads to higher capacity adsorption (Yu et al. 2013). The PZC of CNC is lower than that observed for NFC due to oxidation with H\(_2\)SO\(_4\), indicating an increase in oxygen-containing surface groups (Song et al. 2010).

### Adsorption kinetics

The effect of contact time on Pb(II) ions adsorption in aqueous solution is presented in Figure 6. The adsorption rates of Pb(II) ions on CNC and NFC were significantly fast. The adsorption capacity increased rapidly at the first 15 min, where practically 90% of the total lead removal was achieved in both materials; this is due to the phenomenon of surface adsorption, where the transport process and adsorbate diffusion takes place between the film and the adsorbent. The second phase is characterized by a slower rate of adsorption due to slow diffusion of lead ions and surface phenomena; this suggests that the rate-limiting step in this systems is film diffusion. Equilibrium time was selected after 180 min of contact on CNC and NFC to ensure that the adsorption equilibrium is reached in
further experiments. The maximum Pb removal efficiencies were 13% and 95%, for CNC and NFC, respectively. The equilibrium time can be defined as the time interval in which a system reaches a chemical equilibrium and the instance at which the concentration of the product and the reactants cease to change with time (Akinbiyi 2000). If both Pb biosorption kinetic curves are compared (Figure 6), it can also be noticed that the elimination of lead from aqueous solution is fast in the first minutes of contact for both NFC and CNC materials and that equilibrium was achieved relatively fast. Two main steps control adsorption kinetics, according to intraparticular diffusion model. One of these steps is adsorption at the outer surface of biosorbent, corresponding in both cases to the sharpest part of the curves and it is considered as a fast biosorption step. After this first step, a second stage can be noticed where biosorption rate decreases and equilibrium is reached; this decline in sorption rate can be attributed to the low concentrations of Pb ions in the solution. Thus, it can be established that biosorption of Pb ions onto NFC and CNC biosorbents is a process that is not controlled by pore or surface diffusion since an intermediate step was not noticed on kinetic curves for both materials. This behavior suggests that the binding of lead ions with the active sites of the adsorbent is preferably produced at the outer surface of the solid, and therefore intraparticular diffusion is not predominant. The equilibrium time for the two systems is practically the same, which may indicate that the surface adsorption mechanism may be similar; however, the NFC removal capacity at low concentrations of adsorbate is significantly higher compared to CNC.

Adsorption of metals from water involves physical and chemical adsorption processes. Physical adsorption preserves the individuality of the adsorbate and the adsorbent and contributes little to the metal adsorption. Chemical adsorption consists of transferring or sharing of electrons; therefore, the oxidation states of metals and their complexes may play important roles during the adsorption process (Kwon et al. 2015). To understand the adsorption process, various kinetic models such as the pseudo-first-order model, the pseudo-second-order model, and the Elovich equation were used to study the effect of contact time of lead adsorption and to determine kinetic constants from this models. The following equations can express these models:

Lagergren (1898) presented a first-order rate equation to describe the kinetic process. It is described as:

$$q_t = q_e[1 - \exp(-K_1t)]$$

where $q_e$ and $q_t$ (mg/g) are the adsorption capacities at equilibrium and time, $t$ (min), respectively. $K_1$ (min$^{-1}$) is the pseudo-first-order rate constant for the kinetic model.

Elavich equation has been usually reported for chemisorption of gases on solids. This equation can be expressed as follows:

$$q_t = 1/\beta \ln(1 + \alpha \beta t)$$

where $q_t$ represents the amount of gas adsorbed at time $t$, $\beta$ is the desorption constant, and $\alpha$ the initial adsorption rate (Ho & McKay 1998).

The pseudo-second-order kinetic model (Ho & McKay 2000) can be described on its nonlinear form as:

$$q_t = \frac{K_2q_e^2t}{1 + K_2q_e^2t}$$

where $q_t$ (mg/g) and $q_e$ (mg/g) are the amounts of metal ion adsorbed at time $t$ and at equilibrium, respectively, and $K_2$ is the rate constant g/(mg·min).
Biosorption kinetic data were fitted to these models by nonlinear regression analysis. It has been found that the pseudo-second-order model described better the adsorption data than the other models. The fitted plots of kinetic data to these models are shown in Figure 7(a) and 7(b) for NFC and CNC, respectively. Pseudo-second-order model (PSO)

![Figure 7](image-url)
showed the best fit according to their correlation coefficients, \( R = 0.9911 \) and \( R = 0.9939 \) for NFC and CNC, respectively. These model suggest that the adsorption is carried out on the adsorbent surface formed by chemical adsorption. Table 1 shows kinetic parameters for both adsorption systems. By comparing the pseudo-second-order constant \( (K_2) \) of NFC and CNC it can be established that adsorption of Pb(II) ions is significantly faster for CNC than for NFC, this fact was particularly visible at the first stages of the process.

**Effect of adsorbent dose**

The effect of the adsorbent dose on the removal of lead was studied for both biosorbents (NFC and CNC). For NFC it was found that the percentage of lead removed increased as the adsorbent dose also increased to 8 g/L, as shown in Figure 8. This behavior could be attributed to the rapid saturation of active sites due to its low availability (Balouch et al. 2015). Subsequently, the concentration decreased slightly and rose again until a maximum lead removal of 96% was reached. Increase in adsorption at higher doses reflects a more significant number of available adsorption sites. From this dosage, maximum removal did not show a significant increase. Therefore, the selected dose for this material was 8 g/L. For CNC biosorbent, it was found that the percentage of lead removed increased slightly as the adsorbent dose increased up to 8 g/L, as shown in Figure 8, indicating a lead removal of 22.8%. From this dosage, a decrease in the removal was observed due to aggregation of particles, leading to a reduction of the total surface of the adsorbent. Thus, this dosage was selected for NCC for subsequent experiments of lead removal.

**Effect of pH on Pb removal**

The pH of the solution is one of the most critical parameters that control the adsorption process. The surface charge of an adsorbent can be modified by changing the pH of the solution. This parameter affects the solubility of the ions, the substitution of cations on the adsorbent surface, the ionization characteristics in adsorption, and the chemical speciation of the solution (Kwon et al. 2015). The effect of solution pH on the removal of Pb(II) ions with NFC and CNC, in a pH range from 3 to 8, is shown in Figure 9. It was found that the adsorption capacities of Pb(II) on NFC and CNC increased with increasing pH (pH > PZC), the concentration of protons decreases and the adsorbent surface charge becomes negative. Therefore, the electrostatic attraction increases between the metal ions and the adsorbent, which leads to a higher adsorption capacity rising the removal of lead to 96.3% at pH 5 on NFC. At pH 7 and 8 high adsorption lead is observed (95%); this may result due to the rapid formation of the precipitate of lead hydroxide, according to the equilibrium species diagram for lead where with a pH higher than 6 the absence of Pb(II) ions is observed and Pb(OH)\(_2\) concentration increases. With increasing pH the lead removal is unaffected, suggesting that the removal of lead is due to an adsorption process and precipitation of lead salt as Pb(OH)\(_2\), at alkaline pH, over pH 6 removal is due to a precipitation process. Besides, for biosorption behavior studies, pH values in the sorption system are often maintained at low levels, near pH 4.5–5, to avoid micro-precipitation phenomena. In CNC at pH 3, an increase occurs in the removal of lead up to 25% as a result of a high interaction between Pb(II) ions and the adsorbent, since a higher concentration of these ions is present at pH 3 based on the

![Table 1](http://iwaponline.com/ws/article-pdf/20/7/2715/788426/ws020072715.pdf)

<table>
<thead>
<tr>
<th>Model</th>
<th>NFC</th>
<th>CNC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagren</td>
<td>K(_{L}) (min(^{-1})) 0.28914</td>
<td>K(_{L}) (min(^{-1})) 0.1751</td>
</tr>
<tr>
<td>PSO</td>
<td>K(_{2}) (g/mg.min) 0.354</td>
<td>K(_{2}) (g/mg.min) 2.496</td>
</tr>
<tr>
<td>Elovich</td>
<td>(\alpha) (mg/min) 28,366</td>
<td>(\alpha) (mg/min) 0.0003</td>
</tr>
<tr>
<td>Qe (mg/g)</td>
<td>1.3168</td>
<td>Qe (mg/g) 0.303</td>
</tr>
<tr>
<td>R = 0.9892</td>
<td>R = 0.9911</td>
<td>R = 0.9951</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model</th>
<th>NFC</th>
<th>CNC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagren</td>
<td>K(_{L}) (min(^{-1})) 0.1751</td>
<td>K(_{L}) (min(^{-1})) 0.1751</td>
</tr>
<tr>
<td>PSO</td>
<td>K(_{2}) (g/mg.min) 0.303</td>
<td>K(_{2}) (g/mg.min) 2.496</td>
</tr>
<tr>
<td>Elovich</td>
<td>(\alpha) (mg/min) 0.0003</td>
<td>(\alpha) (mg/min) 0.303</td>
</tr>
<tr>
<td>qe (mg/g)</td>
<td>0.303</td>
<td>qe (mg/g) 0.303</td>
</tr>
<tr>
<td>R = 0.9951</td>
<td>R = 0.9939</td>
<td>R = 0.5824</td>
</tr>
</tbody>
</table>
equilibrium species diagram. It is important to note that the point of zero charge for this material is at pH 2.98.

A pH value of 6 was selected to carry out further removal experiments and to achieve effective lead adsorption. This value was selected to avoid precipitation of Pb insoluble salts at higher pH values, as well as to ensure good electrostatic interaction between biosorbents surface and lead ions in solution since the PZC values obtained for both materials are relatively low. Although CNC showed higher removal at pH 3, a pH value of 6 was selected for isotherm experiments because PZC for this biosorbent is very close to 3. A slight decrease in pH due to the
sorption process could change surface ionization, resulting in a reduction in the electrostatic interaction with the adsorbate, thus lowering lead adsorption capacity.

It is well known that beyond pH 6, lead uptake may occur due to precipitation of Pb(II) ions to its hydroxylated insoluble species (Cortés-Martínez et al. 2004; Kumari et al. 2015; Bagbi et al. 2016). This fact could lead to an adsorption-co-precipitation removal mechanism of lead from aqueous solutions producing a higher lead removal in batch systems. However, it could also represent operational difficulties in a high-scale continuous-mode application of the process, like occlusion of active sites and high volumes of toxic sludge production.

**Adsorption isotherms**

In equilibrium, a particular relationship prevails between solute concentration in solution, and the amount of solute adsorbed per unit mass of adsorbent. The equilibrium concentrations vary as a function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is referred to as adsorption isotherm (Febrianto et al. 2009).

Figures 10 and 12 show the effect of varying initial concentration of Pb(II) ions from 50 to 1,750 mg/L on the adsorption equilibrium under the following conditions: pH 6, 180 min, 8 g/L adsorbent dose and temperatures of 25, 30, and 40 °C for both NFC and CNC materials, respectively. According to Balasubramanian et al. (2009), the adsorption capacity and percentage of removal are equally important in adsorption experiments because both factors usually take part in deciding the adsorption performance of a given adsorbent. Under these conditions, a maximum adsorption capacity (Q_{max}) of 87.10 mg Pb/g NFC was obtained at 40 °C, at 25 °C and 30 °C Q_{max} were 84.64 mg/g and 80.02 mg/g, respectively (Figure 10). Giles et al. (1974) conducted a classification of five different types of isotherms with its subtypes based on slopes and curvatures presented. The systems under study were evaluated according to this classification. These systems have features typical of type H; this is a particular case of type curves L. Where Pb(II) ions are present at low concentrations in solution, a high affinity for the adsorbent can be assumed, and the solute can be totally adsorbed or, at least, no measurable amount remains in the solution. The initial part of the isotherms is therefore vertical. Species adsorbed on H type systems are often large units, i.e. ionic micelles or polymeric molecules (Giles et al. 1960). This behavior reflects a high affinity at low concentrations, which decreases with an increasing solute concentration in equilibrium as is the case of these systems, which have a favorable biosorption of lead by NFC. According to Doumer et al. (2016), they
suggest that complex formation on the surface of the material is due to the presence of carbonyl and carboxyl groups, wherein the ion exchange can be the primary removal mechanism; this is consistent as was previously discussed in FTIR.

The data obtained in the adsorption isotherms were fitted to isotherm models to explain and predict the experimental behavior, and study the nature of adsorption. The Langmuir, Freundlich and Langmuir–Freundlich models were used to fit experimental data. These modes can be expressed as follows:

The Langmuir isotherm model is representative of monolayer adsorption. The equation is expressed as:

$$ q_e = \frac{Q b C_e}{1 + b C_e} $$  \hspace{1cm} (6)

where $q_e$ (mg/g) is the equilibrium sorption capacity and $Q$ (mg/g) is the maximum sorption amount to form complete monolayer coverage on the surface of nanocellulose at high equilibrium solute concentration $C_e$ (mg/L). Also, $b$ is the Langmuir constant related to the affinity of binding sites (Langmuir 1918).

The Freundlich model describes the sorption on an energetically heterogeneous surface. This model can be expressed as:

$$ q_e = K_F C_e^n $$  \hspace{1cm} (7)

where $K_F$ and $n$ (dimensionless) are the Freundlich parameters. $K_F$ is the adsorption coefficient characterizing the strength of the adsorption. The higher the value of $K_F$ is, the higher the adsorbent loading that can be achieved. The exponent $n$ is indicative of the heterogeneity (Freundlich 1907).

The Langmuir–Freundlich equation is used primarily to describe heterogeneous surfaces:

$$ q_e = \frac{K_{LF} C_e^{n_{LF}}}{1 + (\alpha_{LF} C_e)^{n_{LF}}} $$  \hspace{1cm} (8)

where $q_e$ is the concentration of solute per unit weight of biomass and $C_e$ is the concentration of solute in the solution. $K_{LF}$, $\alpha_{LF}$, $n_{LF}$ are empirical constants.

The results obtained in the lead adsorption isotherms using NFC as adsorbent were fitted by nonlinear regression analysis to these models. Langmuir–Freundlich equations showed a good fit to experimental data (Figure 11) according to their correlation coefficients, $R = 0.8823$, $R = 0.9577$, and $R = 0.9735$ at 25, 30 and 40 °C, respectively. The Langmuir–Freundlich model suggests that at low ion concentrations in equilibrium, heterogeneous adsorption occurs due to different adsorption sites because the functional groups that influence adsorption have different energies. Just as shown by the results obtained in FTIR where there are different functional groups involved in the removal of lead. NFC-Pb system at high concentrations followed a Langmuir-like behavior, meaning that once a molecule occupies a site, no subsequent adsorption occur and predicts a monolayer adsorption capacity (Pérez et al. 2001). The Langmuir, Freundlich and Langmuir–Freundlich parameters for the adsorption of Pb(II) onto NFC at the studied temperatures are listed in Table 2.

**Mechanism of lead adsorption by NFC**

Metal cations in aqueous solution can be found mainly as hexa-hydrated ions; thus, the inner-sphere (IS) or the outer-sphere (OS) metal complex formation mechanisms may be the way these metal cations adsorb onto the surface of NFC. Consequently, water molecules surrounding hydrated Pb(II) ions are replaced by carboxylate ions present on the surface of NFC, when IS mechanism takes place; as a consequence, a semi-covalent bond between the carboxylate and the lead ions occur. Contrarily, when OS complex formation occurs, water molecules that hydrate the Pb ions remain when the reaction to form the complex with the corresponding functional group happens. Accordingly, the interaction is driven by electrostatic interactions between the carboxylate groups and the hydrated cation (Maatar & Boufi 2015):

$$ S_1 OH + M^{2+} + H_2 O \rightarrow S_1 OM OH + 2H^+ $$  \hspace{1cm} (9)

$$ S_1 OH + S_2 OH + M^{2+} \rightarrow (S_1 O)(S_2 O)M + 2H^+ $$  \hspace{1cm} (10)

where $S_1$ is the active site on the adsorbent surface, and $M^{2+}$ is the divalent metal ion. The possible mechanism of
complexation of lead with the carboxyl groups can be summarized as follows:

\[
S_1\text{COO}^- + M^{2+} + H_2O \rightarrow (S_1\text{COO})(S_1\text{COO})M \quad (11)
\]

Another major group found from FTIR study conducted to cellulose nanofibers is the amino group which, as already discussed, is an important factor influencing the mechanism of lead removal. Therefore, the following mechanism can be proposed for the NFC:

\[
M^{2+} + RNH_2 \rightarrow M(RNH_2)^{2+} \quad (12)
\]

Also, the complexes formed can react with free hydrogen ions in solution:

\[
RNH_2 + H^+ \rightarrow RNH_3^+ \quad (13)
\]
Since the equilibrium constant for protonation of this group ranges from 6.3 to 7.2, at pH 6 some part of the amino groups present on the NFC is protonated, resulting on competition between these two mechanisms during the adsorption process. At high concentrations of M$^{2+}$, some [M(RNH$_2$)$_2$]$^{2+}$ complexes can become [M(R$_2$NH)$_2$]$^{2+}$, while at low concentrations, M$^{2+}$ can interact and join two binding sites on the surface (Hokkanen et al. 2014).

Lead adsorption isotherm data onto CNC at different temperatures are shown in Figure 12. Maximum adsorption capacities (Q$_{\text{max}}$) of 17.9, 28.20 and 30.36 mg Pb/g of CNC were obtained at 25, 30 and 40 $^\circ$C, respectively. Based on the classification of Giles, three isotherms belong to the type group L. According to the behavior they exhibit, these are isotherms characterized by an initial high slope that decreases with increasing ion concentration in equilibrium, resulting in increased difficulty molecules find an available bonding site (Giles et al. 1960; Álvarez-Puebla et al. 2004). These isotherms are the result of a high affinity for Pb CNC at low concentrations. Isotherm at 25 $^\circ$C has a slope according to the classification of Giles that belongs to L3 type. The initial surge in the isotherm indicates that Pb is adsorbed at low concentrations, as the most active sites of the adsorbent are available for adsorption. After that, it is followed by the formation of a plateau that can be attributed to monolayer formation where it is difficult to find a vacant site available to fill the available binding sites on the adsorbent, leading to a second growth on the slope. Theoretically, this could indicate the emergence of a new mechanism of removal as precipitation or nucleation (Álvarez-Puebla et al. 2004). The increased adsorption may be due to a negative temperature coefficient for the solubility of the solute. The Langmuir, Freundlich and Langmuir–Freundlich parameters for the adsorption of Pb(II) onto CNC at the studied temperatures are listed in Table 2. The Freundlich isotherm model fits well isotherm data for all temperatures tested (Figure 13), according to their correlation coefficients (Table 2); this suggests that the adsorption of lead in CNC can take place on several layers having a heterogeneous nature (Pérez et al. 2001). The Freundlich constant ‘$n$’ is the measure of the deviation from linearity of the adsorption. If a value for ‘$n$’ is below to unity, that implies that a chemical mechanism governs the adsorption process, but if the value of $n$ is above the unity, adsorption is a favorable physical process (Yarkandi 2014). The values of $n$ at equilibrium are between 1.38 and 2.03, indicating favorable adsorption at studied temperatures and therefore this would seem to suggest that a physical mechanism takes place. That was already stated on the discussion of kinetic experiments, where the adsorption mechanism predicted was physical and chemical adsorption. The Langmuir–Freundlich model also shows a good
fit to experimental data, indicating heterogeneity of the system.

**Mechanism adsorption of lead by CNC**

For the CNC-Pb system, a possible reaction mechanism is proposed using the 1:1 and 1:2 OS complex formation model for the binding sites present on CNC surface (phenolic and carboxyl groups), which can be described by the following equations (Guo *et al.* 2008):

\[
S_1\text{OH} + M^{2+} \rightarrow S_1\text{O-M}^+ + H^+ \quad (14)
\]

\[
2S_1\text{OH} + M^{2+} \rightarrow (S_1\text{OM})_2 + 2H^+ \quad (15)
\]

According to the equilibrium phase diagram in aqueous solution for lead (not shown), Pb(II) ions exists mostly as free ions at low pH values; thus, the concentration of such ions decreased when the pH value of solution increased. At these conditions, the carboxylic groups on the surface of CNC played an important role in the Pb adsorption behavior by producing monodentate complexes $S_1\text{O-M}^+$. Moreover, biosorption of Pb ions started on phenolic groups at the same pH conditions. Hence, both monodentate complexes $S_1\text{O-M}^+$ and bidentate complexes $(S_1\text{O})(S_2\text{O})\text{M}$ were present when biosorption of lead occurred on the above-mentioned surface functional groups. This fact can be attributed to the decrease in free Pb ions concentration, so the $S_1\text{O-M}^+$ complexes transformed to $(S_1\text{O})(S_2\text{O})\text{M}$ complexes (Guo *et al.* 2008).

According to the results observed in the characterization by FTIR, the -SO$_3$ groups present in the surface of NCC participate in the removal of the lead ions, since there is a noticeable decrease in the FITR bands corresponding to these groups after contact with lead; thus, the following reaction mechanism is proposed:

\[
S_1 - SO_3^- + S_2 - SO_3^- + M^{2+} + H_2O \\
\rightarrow (S_1\text{SO}_3)(S_2\text{O}_3)\text{M} + H_2O \quad (16)
\]

where $S_1$ and $S_2$ represent active sites on the biosorbent surface, linked to the functional group -SO$_3$; the reaction is...
carried out by binding a hexahydrate Pb(II) ion occupying two -SO₃ adjacent sites, forming OS complexes.

Based on the above, it can be established that both Pb(II) ion adsorption processes in NFC and CNC are different. It can also be established that the hydrolysis of cellulose nanofibers obtained from water hyacinth decreases the adsorption capacity of Pb(II) ions. Moreover, it can also be concluded that both biosorbents are effective for the removal of lead from aqueous solutions, but changes in their performance should be considered when these materials treat lead polluted real waters.

**Thermodynamic parameters**

The analysis of thermodynamic parameters makes it possible to estimate the feasibility of the adsorption process and the effect of temperature. In the case of this work the following parameters were estimated: the change in Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and atrophy ($\Delta S^\circ$). The effect of temperature on the adsorption capacity is defined as the energy of adsorption (Mondal 2010). Gibbs free energy change can show whether a process is spontaneous or not. Negative values of $\Delta G^\circ$ involve a spontaneous process, while positive values mean that it is necessary to provide energy to the system because the system is not able to evolve by itself. It is calculated from the equation (Pérez et al. 2001):

$$\Delta G = \Delta H^\circ - T \times \Delta S^\circ$$  \hspace{1cm} (17)

Enthalpy change provides information about the process exothermic or endothermic character. It can also estimate the activation energy and allows to differentiate whether it is a process that occurs via physical adsorption (low values) or chemical (higher values) (Pérez et al. 2001).

The entropy of adsorption allows predicting the magnitude of the changes on the surface of the adsorbent. If changes are profound in enthalpy, reversibility is affected by obtaining a negative value of the entropy of adsorption. Otherwise, it indicates a high possibility of reversibility (Pérez et al. 2001).

Van ‘t Hoff equation allows obtaining $\Delta H^\circ$ and $\Delta S^\circ$ values graphically. This equation arises from the equation of the Gibbs free energy as follows:

$$\Delta G^\circ = -R \times T \times \ln K_c$$  \hspace{1cm} (18)

Combining and rearranging Equations (17) and (18), the following equation can be obtained:

$$- R \times cT \times \ln K_c = \Delta H^\circ - T \times \Delta S$$  \hspace{1cm} (19)

$$K_c = \frac{C_c}{C_{ad}}$$  \hspace{1cm} (20)

where $K_c$ is the equilibrium constant $C_{ad}$ and $C_c$ (mg/L) are the equilibrium concentrations of solute in the sorbent and the solution, respectively, and $R$ is the universal gas constant (J/mol K), and $T$ is the temperature in Kelvin (Pérez et al. 2001; Yarkandi 2014). The equilibrium constants ($K_c$) were calculated at different temperatures for Pb(II) ions adsorbed by NFC and CNC from isotherm data. The thermodynamic parameters were calculated using these values and Van ‘t Hoff equation:

$$\ln K_c = \frac{-\Delta H^\circ}{R \times T} + \frac{\Delta S^\circ}{R}$$  \hspace{1cm} (21)

A plot of $\ln K_c$ vs. $1/T$ for Pb(II) adsorption on both biosorbents should be linear and the intercept equivalent to $\Delta S^\circ /R$, while the slope would be numerically equal to $\Delta H^\circ / R$.

Enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were obtained from the slope and intercept of the curve of $\ln K_c$ vs. $T$. According to the results obtained (Table 3), the free energy of adsorption ($\Delta G^\circ$) was negative in all conditions with the two adsorbents (NFC and CNC); this reflects the spontaneous nature of the process in both systems. Enthalpy of adsorption positive values means that the adsorption process was

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta H^\circ$ (J/mol)</th>
<th>$\Delta S^\circ$ (J/mol K)</th>
<th>$\Delta G^\circ$ (J/mol)</th>
<th>$T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFC</td>
<td>884.741912</td>
<td>2,749.0106</td>
<td>-3,235,288.35</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-3,265,527.46</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-3,293,017.57</td>
<td>40</td>
</tr>
<tr>
<td>CNC</td>
<td>495.591828</td>
<td>3,184.52213</td>
<td>-250,858.128</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-254,361.103</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-257,545.625</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 3 | Thermodynamic parameters for adsorption of lead onto NFC and CNC
endothermic. The positive value of $\Delta H^\circ$ might be explained by assuming that when metal ions were brought into contact to the surface, their solvating water molecules were eliminated. This dehydration process requires energy and, presumably, it exceeded the exothermicity of the metal ions attaching to the surface (Maatar & Boufi 2015). The enthalpy associated with both mechanisms and processes is below 40 kJ/mol, suggesting coexisting physical and chemical adsorption (Acemioglu 2004). The $\Delta S^\circ$ was also positive, indicating increased randomness at the solid/solution interface during the adsorption process, even though the metal ions were immobilized on the adsorbate. Also, they reflect the affinity of NFC and CNC to Pb$^{2+}$ ions.

**CONCLUSIONS**

Water hyacinth is a good source from which to obtain cellulose nanofibers and nanocrystals. High adsorption capacities indicated that NFC and CNC have potential as biosorbents for removal of lead from water. FTIR spectra and SEM of NFC and CNC indicated a chemical and physical difference on their structures, as well as different sorption mechanisms for Pb. The pseudo-second-order model describes the adsorption kinetics data for both materials. The Langmuir–Freundlich model best describes the relationship of equilibrium adsorption Pb(II) for NFC under the three temperatures studied, while Freundlich models describe the process using CNC, which implies heterogeneity in both processes. Lead adsorption onto deprotonated carboxylic and hydroxyl sites by ion exchange with coordination was the dominant mechanism that could reasonably explain the observed adsorption behavior. According to the thermodynamic parameters, the removal process led by NFC and CNC is a spontaneous and endothermic process that can be reversible.

**ACKNOWLEDGEMENTS**

The authors acknowledge the financial support provided by Coordinación de la Investigación Científica-UMSNH, Grant CIC-UMSNH-2019.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


First received 22 April 2020; accepted in revised form 14 July 2020. Available online 31 July 2020