Kinetic and isotherms of biosorption of Hg(II) using citric acid treated residual materials

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Resumen
En este trabajo se estudió la adsorción de Hg(II) a partir de biomasa residuales de bagazo de palma y cáscaras de ñame tratadas químicamente con ácido cítrico. La determinación del metal en solución fue llevada a cabo mediante la formación del complejo \( \text{Hg(CNS)}_4^{2-} \) que fue medido a través de absorción en la región ultravioleta (281nm). Se encontró que los grupos hidroxilo y carboxilo presentes en los biomateriales modificados químicamente son los que tienen una mayor contribución al proceso de remoción, determinándose una máxima capacidad de adsorción de 385,80 y 356,86mg/g para las cáscaras de ñame y el bagazo de palma tratadas con ácido cítrico, respectivamente. Para este sistema se encontró que el modelo cinético de Elovich y el modelo isotermal de Freundlich son los que mejor describen el comportamiento de adsorción de Hg(II) en ambos biomateriales.

Palabras clave: Ácido cítrico, bioadsorción, mercurio, residuos lignocelulósicos.

Abstract
In this paper was studied the adsorption of Hg(II) by using lignocellulosic residual biomass from bagasse palm and yam peels, which were chemically treated with citric acid. The concentrations of Hg(II) ions in the supernatant were analyzed by the formation of the \( \text{Hg(CNS)}_4^{2-} \) complex, which was measured through the absorption in the ultraviolet region (281nm). It was determined that the hydroxyl and carboxyl groups present in the chemically modified biomaterials have a huge contribution in the adsorption process. We estimated a maximum capacity of adsorption about 385,80 and 356,86mg/g for citric acid treated yam peels and bagasse palm, respectively. It was also determined that the Elovich kinetic model and the Freundlich isotherm model were the best to describe the adsorption process of Hg(II) onto both biomaterials.

Keywords: Bioadsorption, citric acid, mercury, lignocellulosic residues.
1. Introduction

Industrial effluents are considered as one of the major environmental issues that mankind is facing nowadays. They are considering as one of the main causes of pollution in surface water sources due to the presence of toxic substances, such as the heavy metals. Among them, nickel, chromium, cadmium and mercury are some of the most dangerous materials released by different industries, such as oil refineries, textile, metal, paper and chemical manufactory (Deniz, 2013; Inglezaki et al., 2002). In general, type and concentration of heavy metals present in industrial effluents depend on the production process and the raw material that is being used. It is important to note, that the mercury that is used for the industrial production of chlorine, caustic soda, polyvinylchloride and polyurethane foam production is one of the most toxic substances for the human being, since it can cause ataxia, shaking and kidney, sensorineural and cognitive damage (Asasian et al., 2012).

In order to fulfill current regulations, industries are required to submit their effluents to different treatments that could reduce their pollution load. Some of them include chemical precipitation and coagulation, ionic exchange, electrochemical techniques, the use of zeolites and membranes, and ultrafiltration processes. However, these treatments can’t achieve suitable performances at low concentration levels of heavy metals. Such case scenario leads to the generation of undesired by-products in the form of slurries that require additional treatment, increasing thus operational costs (Venkata et al., 2011; Ronda et al., 2014; Li et al., 2015).

In addition, agricultural exploitation generates large quantities of by-products and/or wastes. Disposition of this material represents a major environmental issue that causes soil and water contamination, since only a small percentage of these residues are used as natural fertilizers, fuels or additives in animal feedstock. The importance of studying residual biomass for the removal of metallic ions from water solutions continues becoming then evident (Ramos, 2010). More attention is being drawn towards bioadsorption systems for the removal of mercury from industrial effluents due to their high efficiency and simplicity (Asasian et al., 2014).

Adsorption on activated carbon stands out among conventional treatments. It involves the transfer of certain components from a fluid phase to a solid one, and a final physical or chemical attachment to the absorbent. Although this treatment has been widely used in water purification and heavy metal removal from industrial effluents, its high costs represents a drawback that makes it necessary to find new technologies with similar or lower efficiencies at a better cost. Use of residual biomass represents one of these alternatives (Kaghazchi et al., 2010).

Bioadsorption then arises as a technique that involves the use of biomass or natural substrates like agricultural residues, microorganisms and casein for the adsorption of metals. This method has been studied in the last decades as a promising alternative for removal of heavy metals from water sources. High yields of ionic metal removal have been achieved with this technique at low costs (Rao et al., 2011). There are different types of biomass that could be used as adsorbent materials, such as natural biomass, residual biomass and energy crops. These biomaterials possess specific structures and ionic metal adsorption capacities that make them suitable materials for such purpose, such as phosphates from nucleic acids; amine, amide and carboxylic groups from proteins; and hydroxyl, carbonyl and sulphate groups present in polysaccharides. However, it is possible that during the adsorption process, some of the metals are not able to access to the chemical groups presents in the biomass due to steric effects, reducing in this way the adsorption capacity of these biomaterials (Volesky, 2001).

1.1 Adsorption kinetics

Adsorption kinetics describes the rate in which the adsorbate is caught. Its residence time within the solid-solution interphase depends on this velocity, allowing the prediction of the metal removal rate. Ionic metals removal from water solutions by bioadsorption generally depends on the chemical mechanisms that involve interaction of ionic metals
with active groups in the bioadsorbent. Therefore, bioadsorption kinetics indicates the evolution of each stage that is involved along its development, and it specifies the one that exerts controls over the whole process (chemical reaction, diffusion and/or mass transfer) (Pinzón-Bedoya & Vera-Villamizar, 2009).

In this sense, a number of kinetic models have been proposed to describe the mechanism in which biosorption takes place. These models are summarized in Table 1.

Once the adsorption process has taken place, it results in a concentration of remaining metals that is in equilibrium with the material that has been adsorbed onto the bioadsorbent. The metal-solid distribution can then be represented by a relation between the amount of solute per mass of adsorbent ($q_e$) and the metal concentration in the solution at equilibrium ($C_e$). Adsorption isotherms provide this relationship for two equilibrium phases. Table 2 describes the main isotherms models that are reported in the literature.

### Table 1. Kinetic models for adsorption (Tejada et al., 2012).

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Equation</th>
<th>Parameters</th>
<th>Description</th>
</tr>
</thead>
</table>
| Pseudo-first order  | $q_t = q_e \left(1 - e^{-k_1 t}\right)$ | $q_e$, equilibrium adsorption capacity (mg/g)  
$q_0$, pseudo-first order constant (min$^{-1}$)  
$t$, time (min) | It is based on the assumption that there is an adsorption site for each metal ion. |
| Pseudo-second order | $q_t = \frac{t}{\left(\frac{1}{k_2 \cdot q_e}\right) + \left(\frac{t}{q_e}\right)}$ | $k_2$, pseudo-second order constant (g/mg.min) | It is based on the assumption that the adsorbate is adsorbed onto two active sites in the biomass. |
| Elovich equation    | $q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$ | $\alpha$, Elovich constant (mg/g min)  
$\beta$, Elovich exponent (g/mg) | It is based on the assumption that the active sites of the adsorbent are heterogeneous, and therefore they exhibit different activation energies, based on a second order reaction mechanism. |
| Intraparticle diffusion | $q_t = k_3 \sqrt{t}$ | $k_3$, diffusion constant (mg/g min$^{1/2}$) | It is based on the solute transfer through the internal porous structure and its actual diffusion in the solid, which causes the adsorbent to acquire an homogeneous structure. |
The use of citric acid chemically treated residual biomass from yam peel and palm bagasse for the removal of mercury is proposed in the current study.

2. Materials and methods

2.1 Preparation of the adsorbent

Bagasse of African palm was obtained as residual material from an oil palm extraction plant that is located in the department of Bolivar (Colombia). Yam peels were obtained from a food company in the city of Cartagena. Both biomasses were washed with distilled water four times in order to remove impurities. They were then dried for 23 hours in an oven at 90°C, grinded using an electronic mill and finally filtered for a particle size of 1.0 nm. Both materials were later submitted to chemical treatment with 0.6 M citric acid with a 40 g biomass/200 mL acid proportion under constant agitation at 200 rpm and 60°C for two hours. Once contact time had passed, the adsorbent were filtered and washed with distilled water in order to remove residual citric acid. Then, they were dried at 55°C for 24 hours (Pitsari et al., 2013).

This modification is based on a carboxylation mechanism, which intends to add carboxyl groups to the treated fiber. First step is the formation of an anhydride between two adjacent carboxyl groups. This results in the removal of a water molecule during heating of citric acid and biomass. The anhydride then reacts with a hydroxyl group of the biomass cellulose and produces an ester, thus increasing the chances of bonding the metal ion represented by mercury Hg(II) (Pitsari, et al. 2013).

2.2 Adsorption tests

A solution of mercury was prepared by dissolving 0.507 g of mercury chloride HgCl2 in 1.0 L of deionized water, producing a standard solution of 375 mg Hg(II) ions/L. It was then diluted until achieving the target concentrations. Adsorption kinetic of the process was carried out at a Hg(II) concentration of 100 ppm at room temperature (30°C) for a period of 300 minutes. pH of the solution was fixed at 6.0. Such value has been reported as the most suitable for adsorption of mercury ions (Pitsari et al., 2013). The studied kinetic was adjusted according to pseudo-first and pseudo-second order models, Elovich equation and intraparticle diffusion. Freundlich and Langmuir isotherms were also applied in this study. The fitting of the experimental data and models were determined using the sum of squared errors from the Solver tool by Excel.

Hg(II) concentration in the supernatant was analysed by UV-Vis spectroscopy. Measures were taken based on the formation of Hg(CNS)42-complex, whose presence is observed at a wavelength

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$q_e = k_F C_e^{1/n}$</td>
<td>$k_F$, adsorption capacity indicator (mg/g)$^{1-1/n}$; $n$, adsorption intensity.</td>
<td>Multilayer adsorption in heterogeneous surfaces with interaction between the adsorbed molecules.</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_e = q_{max} \frac{b C_e}{1 + b C_e}$</td>
<td>$q_{max}$, maximum adsorption capacity (mg/g); $b$, affinity of the union sites (g/mg).</td>
<td>Monolayer adsorption without interaction between the adsorbed molecules.</td>
</tr>
</tbody>
</table>

Table 2. Adsorption isotherms models (Gautama, 2014).
of 281 nm in the UV region. This complex is formed by the addition of 4.0 mL to a 5% w/w solution of NH4 (SCN) in 1.0 mL of a metal containing solution and then diluting it up to 10 mL. In the same way, characterization of modified biomasses was carried out before and after the mercury adsorption process in order to determine the possible chemical groups that are responsible for the metal ion bond (Vieira & Beppu, 2006).

3. Results and discussion

Figure 1 shows the results for the adsorption kinetics of Hg(II). An increasing adsorption capacity can be observed in both biomasses after their modification with citric acid. A maximum percentage of 93% mercury removal was achieved after 200 minutes of contact time.

In the case of yam peels, adsorption capacity increased by 20% once it was treated with citric acid. On the other hand, palm bagasse exhibited a 10% increase. This is attributed to the presence of carboxyl groups within the chemical structure of citric acid, which is shown in Figure 2. These groups contribute to the creation of additional adsorption sites for metal ions, along with hydroxyl groups that are commonly found in lignocellulosic biomass.

An adjustment of the experimental data is shown in Figures 3 (a), (b) and 4 (a), (b). It can be observed that Elovich kinetic model is the one that describes more accurately the adsorption process, since the calculated \( q_t \) value for that equation is the one that is closest to the experimental data, as it is shown in Table 3. Thus, adsorption of Hg(II) ions onto the studied biomasses is assumed to be controlled by a second order reaction, with an heterogeneous adsorbent surface and different activation energies. In this model, \( \alpha \) and \( \beta \) are related to chemisorption energy and covered surface, respectively.

Figures 5 (a), (b) and 6 (a), (b) show the adsorption isotherms curve fittings obtained for the adsorption of Hg(II) ions onto the studied biomasses. In addition, Table 4 summarizes these results. From this analysis, it was established a high correlation of the experimental data with the Freundlich isotherm model, especially for biomass without chemical modification. According to this, it is possible that the evaluated biomasses behave as heterogeneous surfaces, which can facilitate the formation of multilayer during the adsorption of the metal ion (Alves & Gil, 2009.)

The adjustment to the Freundlich isotherm model is in agreement with the results obtained from the kinetic study, where it was pointed out that a second order kinetics is the controlling mechanism for the adsorption of Hg(II) ions onto the studied biomasses.
Table 3. Kinetic Parameters for the adsorption of Hg(II).

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameters</th>
<th>Yam peels</th>
<th>Modified yam peels</th>
<th>Palm bagasse</th>
<th>Modified palm bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>$q_e$ (mg/g)</td>
<td>15,72</td>
<td>18,51</td>
<td>15,90</td>
<td>18,05</td>
</tr>
<tr>
<td></td>
<td>$k$ (min$^{-1}$)</td>
<td>0,045</td>
<td>0,304</td>
<td>0,077</td>
<td>0,277</td>
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<tr>
<td></td>
<td>$q_i$ (mg/g)</td>
<td>54,23</td>
<td>2,10</td>
<td>31,93</td>
<td>2,43</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>$k_1$ (g/mg.min)</td>
<td>$5 \times 10^4$</td>
<td>184,73</td>
<td>$5 \times 10^4$</td>
<td>$5 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>14,33</td>
<td>18,43</td>
<td>15,11</td>
<td>17,95</td>
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<tr>
<td></td>
<td>$q_i$ (mg/g)</td>
<td>141,65</td>
<td>2,80</td>
<td>66,88</td>
<td>3,58</td>
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<tr>
<td>Elovich</td>
<td>$\beta$ (g/mg)</td>
<td>0,397</td>
<td>1,86</td>
<td>0,551</td>
<td>1,93</td>
</tr>
<tr>
<td></td>
<td>$\alpha$ (mg/g.min)</td>
<td>5,81</td>
<td>$3,7 \times 10^{12}$</td>
<td>58,25</td>
<td>$5,2 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>$q_i$ (mg/g)</td>
<td>19,32</td>
<td>0,355</td>
<td>3,32</td>
<td>0,514</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>$k_3$ (mg/g.min$^{1/2}$)</td>
<td>1,01</td>
<td>1,39</td>
<td>1,04</td>
<td>1,35</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>155,74</td>
<td>432,23</td>
<td>261,89</td>
<td>401,77</td>
</tr>
</tbody>
</table>

Figure 3. Kinetic model adjustment for the adsorption of Hg(II) onto (a) unmodified yam peels, and (b) yam peels modified with citric acid.

Figure 4. Kinetic model adjustment for the adsorption of Hg(II) onto (a) unmodified palm bagasse peels, and (b) palm bagasse modified with citric acid.
Different authors have studied the use of residual biomass for the removal of mercury from aqueous solutions. Some of these studies include the use of tree ferns with an adsorption capacity of 26,5 mg/g at 25°C (Ho & Wang, 2008); eucaliptus bark with an adsorption activity of 33,11 mg/g at pH 9 (Lohani et al., 2008); papaya wood achieved a removal capacity of 70,8 mg/g at pH 6,5 (Basha et al., 2009); ceiba sawdust, bean pods, and chickpea
crop wastes exhibited adsorption activities of 25.88; 23.66; and 22.88 mg/g, respectively (Madhava et al., 2009). In the same way, modification of these materials has been studied, and high efficiencies are achieved with biomasses such as pistachio nuts and liquorice residues that are impregnated with zinc chloride. A maximum removal capacity of 147.1 mg/g was observed when using these materials (Neda et al., 2012). When comparing the previous results with the ones that are presented in this study, it is evident that citric acid modification is highly effective, since the achieved adsorption activities are greater than those reported in the literature. Other modifications are recommended to be studied, along with their application in industrial wastewaters.

Regarding FTIR results for the analyses that were performed to the modified biomass samples before and after the adsorption process, the possible functional groups within the biomass structure that intervene in the metal ion adsorption could be as follows: in the FTIR of the modified palm bagasse that is shown in Figure 7, a peak can be observed at 3336 cm⁻¹, corresponding to vibration of hydroxyl groups (-OH). Peaks from 3000 to 2800 cm⁻¹ are related to vibration of C–H groups; 2360 cm⁻¹ vibration indicates the presence of carboxyl acids due to stretching of the OH group. The peak at 1732 cm⁻¹ is characteristic of C=O carbonyl group, vibration around 1450 and 1540 cm⁻¹ could be attributed to aliphatic and aromatic groups, and to deformation of methyl, methylene and methoxy groups. Wavelengths between 1050 and 1450 cm⁻¹ could be assigned to vibration of carboxylic acids and alcohols. Figure 8 shows FTIR analysis of citric acid treated palm bagasse after the adsorption of Hg(II) ions. From this figure, it was evidenced the displacement of peaks ranging from 3396 cm⁻¹ up to 1018 cm⁻¹. This suggests the attachment of the Hg(II) ions to the functional chemical groups hydroxyl and carboxyl presented in the modified biomass.

**Figure 7.** FTIR analysis of the citric acid modified palm bagasse.

**Figure 8.** FTIR analysis of the citric acid modified palm bagasse after adsorption of Hg (II) ions.
FTIR analysis of the modified yam peels that is shown in Figure 9, evidences a peak between 3668 and 3400 cm$^{-1}$, which is characteristic of the O-H group in carboxyl acids. A peak in 2920 cm$^{-1}$ is also shown, and can be attributed to stretching of C–H groups in alkanes, while the one at 2300 cm$^{-1}$ is related to carboxyl acids, as a result of O-H stretching. Lastly, frequency between 1050 and 1450 cm$^{-1}$ can be assigned to vibration of carboxyl acids and alcohols. FTIR analysis once the adsorption process had taken place is shown in Figure 10. There, a significant change in transmittance can be observed between the wavenumbers of 3200 cm$^{-1}$ and 1032 cm$^{-1}$. This suggests the intervention of hydroxyl and carboxyl acid groups in the adsorption of Hg(II) onto the studied material.

4. Conclusions

The potential use of agroindustrial residues like palm bagasse and yam peels as mercury adsorbants is established. These materials are recommended to be used for the removal of other contaminants. It was observed that modification with citric acid improved the adsorption capacity of both yam peels and palm bagasse by 20 and 10%, respectively. This is attributed to the presence of hydroxyl and carboxyl groups within the chemical structure of citric acid. These groups promote the availability of active sites for the adsorption of ions.

According to Elovich’s kinetic model, it is concluded that the controlling mechanism for the adsorption of Hg(II) onto the studied materials corresponds to a second-order reaction with an heterogeneous adsorbent surface and different activation energies. This was corroborated with the analysis of the isothermal models, from which it was found a best curve fitting to the experimental data using the Freundlich isothermal model.

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6. References


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