Comparative assessment of Al₂O₃-modified biomasses from agricultural residues for nickel and cadmium removal

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Abstract

The biodiversity of aqueous environments has been affected due to the disposal of wastewater highly contaminated with heavy metal ions, causing much damage to ecosystems. These pollutants are very toxic and bioaccumulate in living organisms. This work attempts to evaluate the adsorption of nickel and cadmium ions using three biomasses from agricultural residues (corn cob – CC, orange peel – OP, and oil palm bagasse – PB) modified with alumina nanoparticles. The biomasses were characterized via compositional analysis and a point of zero charges to quantify the presence of lignin, cellulose, hemicellulose, and the feasible pH, taking advantage of the biomass charge. After modification with Al₂O₃ nanoparticles. The resulting adsorbents were characterized via FT-IR analysis to identify the functional groups that most contributed to the adsorption performance. Furthermore, the influence of Al₂O₃ nanoparticles was analysed on the adsorption capacities of the evaluated biomasses using batch systems at a temperature of 25°C and pH 6. All biomasses displayed a high content of cellulose, estimating a weight percentage of about 19.9%, 14.3%, and 13.1% for PB, OP, and CC samples, respectively. The FT-IR spectrum confirmed hydroxyl and carboxyl functional groups, which contribute to enhancing the adsorption capacities of the modified biomasses. Functional adsorption capacity was observed for all biomasses after modification with Al₂O₃ nanoparticles, achieving at pH 6.0 a cadmium removal from 92% (CC-Al₂O₃ and PB-Al₂O₃) up to 95.8±0.3% (OP-Al₂O₃). In nickel ions, it was estimated a broader adsorption capacity at pH 6.0 of about 86±0.4% after using the CC-Al₂O₃ sample, 88±0.1% for the PB-Al₂O₃ adsorbent, and 98±0.2% for the OP-Al₂O₃ sample, confirming the suitability of these Al₂O₃-modified biomasses for the removal of heavy metal ions.

Key words: adsorption, agricultural residues, alumina nanoparticles, cellulose, heavy metal ions

INTRODUCTION

There is an increasing concern about the contamination of water sources by heavy metal ions coming from different anthropogenic activities [KAVAND et al. 2020]. These progressively dangerous pollutants are absorbed by marine animals that are part of the food chain generating a high risk to consumer health [FONSECA-CORREA et al. 2019]. Additionally, they affect the environmental conditions of aquatic life in the receiving environments, such as lakes and rivers [ES-SAHBANY et al. 2019]. Heavy metals like nickel (Ni) and cadmium (Cd) are characterized by high toxicity, the hardness of degradability, and facile accumulation via the food chain [DENG et al. 2020]. Despite this, nickel occurs naturally, higher concentrations above 5–10 μg·dm⁻³ in drinking water can produce serious health problems [MADDODI et al. 2020]. Illnesses include nervous disorders, neurological problems, bone degeneration, and deficiency of the gastrointestinal system, kidneys, and liver [OLIVERO-VERBEL et al. 2007].

Health problems in humans derived from metal exposure and the deterioration in surface water quality have been the motivation to search for alternatives to remove or reduce the content of these pollutants before discharging...
them into the environment [ES-SAHBANY et al. 2019]. The treatment of residual waters in Colombia must comply with environmental regulations; however, only 10% of total wastewater receive proper treatment, despite there being capacity for up to 20% [Twenergy 2014]. There is no strict control in managing wastewater, and wastewaters contaminated with heavy metals end up in surface water above the maximum permissible limit. Various separation technologies are used to reduce the concentration of heavy metal ions in industrial effluents, for example, coagulation, reduction, differential precipitation, ion exchange, electrochemical treatment, separation by a membrane, solvent extraction, and flotation, among others. These methods require a high operating cost, which makes it unattractive for the industry [ISLAM et al. 2019].

Among the wastewater treatment technologies, the adsorption technique offers a more attractive alternative in terms of efficiency, economy, and advantages, since no toxic waste is generated [XU et al. 2016]. The adsorbents coming from residual biomasses allow the completion of the cycle of exploitation of derived-crops, and the cost associated with their acquisition is low [BHATNAGAR et al. 2015]. Besides, its composition as lignocellulosic material has a high affinity for interaction with heavy metals ions. Its presence can be determined by qualitative analysis as infrared spectroscopy, or quantitative as the potentiometric titration of Böehm [TOMAR et al. 2014].

Although these biomaterials used in the remediation of polluted waters have a particularly good performance during the adsorption process, proposing improvement of this quality generates expectation. According to recent studies, components such as nanomaterials or chemical agents are capable of forming bonds with some heavy metals [HERRERA-BARROS et al. 2019; LI et al. 2020]. Nanomaterials composed of alumina (Al₂O₃) and titanium dioxide (TiO₂) can absorb nickel and cadmium ions, as confirmed in the literature [FEITOZA et al. 2014].

In this work, we modified palm bagasse, corn cob, and orange peel biomasses with alumina nanoparticles which are conventionally obtained by the Sol-Gel method. The primary purpose of this modification is to enhance the specific surface area and pore structure of the biomass allowing for a more efficient adsorption of heavy metal ions.

MATERIALS AND METHODS

ADSORBENT PREPARATION

Biomass preparation. The corn cobs, orange peels, and oil palm bagasse all come from local farms in the Department of Bolivar (Colombia). These biomasses were cut into small pieces, washed thoroughly, and dried in an oven at 70°C for 24 h [LIANG et al. 2010]. Then, they were crushed and sieved to a particle size of 0.35 mm, which is within the range stated in the literature [LASHEEN et al. 2012]. These, size-reduced particles were washed with ethyl alcohol to remove impurities [HERRERA-BARROS et al. 2018a]. The pretreated biomasses were characterized via compositional analysis, and the point of zero charge was estimated.

Preparation of alumina nanoparticles. The synthesis of Al₂O₃ nanoparticles was carried out using the Sol-Gel method, which required the preparation of 0.5 M solution of aluminium nitrate [Al(NO₃)₃] and 0.5 M solution of citric acid [C₆H₈O₇]. Both solutions were mixed under continuous stirring at 60°C until the overall colour became yellow. Then, the stirring temperature was increased by 10°C until a gel formed. This gel was sent to a muffle at 200°C for two hours and 750°C during the next two hours to improve its crystal structure [LI et al. 2006; HERRERA-BARROS et al. 2018b].

Incorporation of alumina nanoparticles into the biomass. Modifying biomasses with alumina nanoparticles (Al₂O₃) is performed as follows: a suspension of 0.5 g of the biomasses was dispersed in 20 cm³ of the organic solvent Dimethylsulfoxide (DMSO) using a shaker for 24 h at 120 rpm. Afterward, 3 cm³ of Tetra-ethyl-ortho-silicate (TEOS) chemical reagent was added and kept under mechanical stirring at 120 rpm in a shaker for 48 h at room temperature. During this procedure, the (TEOS) molecules are expected to hydrolyse and condense on the surface of the biomasses, forming Polysiloxane (Si-O) bond bridges [HERRERA, RINALDI 2008], which also serves to fix the nanoparticles into the biomaterials matrix. Then, 0.2 g of the synthesized alumina nanoparticles (Al₂O₃) were added under continuous stirring at 120 rpm for 12 h. Once the functionalization process was completed, ethanol washing was conducted followed by vacuum filtration and drying at room temperature. Figure 1 shows the schematic process for the modification of the biomasses with the alumina nanoparticles (Al₂O₃).

CHARACTERIZATION TECHNIQUES

Composition analysis. The composition of lignocellulosic biomass in terms of inorganic and organic components were determined by analytical methods following the methodology proposed by TEJADA-TOVAR et al. [2020]. Table 1 lists the compounds considered in each characterization method.

![Fig. 1. Schematic representation of biomass modification with alumina nanoparticles; source: own elaboration](image-url)
Table 1. Analytic techniques applied for biomass characterization

<table>
<thead>
<tr>
<th>Organic/inorganic</th>
<th>Method</th>
<th>Elements</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>AOAC 949.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>AOAC 949.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>AOAC 984.13 Kjeldahl</td>
<td>calcium</td>
<td>atomic absorption spectroscopy (AAS)</td>
</tr>
<tr>
<td>Pectin</td>
<td>acid digestion - thermogravimetric analysis</td>
<td>potassium</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>photocalorimetric</td>
<td>iron</td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>acid digestion - thermogravimetric analysis</td>
<td>copper</td>
<td></td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>acid digestion - thermogravimetric analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ashes</td>
<td>thermogravimetric analysis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: own elaboration.

Point of zero charge (pHz). The procedure to determine the point of zero charge for the biomasses is described as follows: 50 cm³ of distilled water was pH-adjusted to different values of 3, 4, 5 and 6 using 1 M solutions of NaOH and HCl. Then, 0.5 g of biomass was added to and continually stirred at 30°C for 48 h. The final pH was measured using a pH-meter for all the cases of pH variation. These values of initial and final pH were used to build a plot, from which the point of zero charge could be estimated.

Characterization of biomasses modified with alumina nanoparticles. Fourier-transform infrared spectroscopy (FTIR) was used to identify functional groups on the prepared materials. A Thermo Nicolet 6700 FTIR spectrometer recorded The FTIR spectra of biomass after modification with Al₂O₃ nanoparticles in a resolution region ranged from 600 to 4000 cm⁻¹. Moreover, a JEOL JSM-6490LV scanning electron microscope (SEM) coupled to an Energy-dispersive X-ray spectroscopy (EDS) was used to determine the morphology of the biosorbent and Al₂O₃ nanoparticles.

RESULTS AND DISCUSSION

CHARACTERIZATION TECHNIQUES

Table 2 shows organic and inorganic components in the evaluated biomasses. The palm bagasse showed the highest cellulose and lignin content with 19.90±0.35% and 17.11±0.27%, representing around 37% of the biomass weight. In the corn cobs and orange peels, the lowest amount of cellulose and lignin was measured, achieving only 20% of the total composition of these biomasses among these biopolymers. Additionally, the orange peel displayed a pectin content of 18.15±0.04%, which is twice as much as the amount detected in the corn cob and four times higher than that in the palm bagasse samples. We compared the results with those found in the literature for the same biomaterials. RIVAS-CANTU et al. [2013] showing that orange peel has high cellulose, pectin, and hemicellulose content with all values reading above 35, 20, and 5%, respectively. For this type of oil palm waste, the reported composition found in literature ranged between 27 and 35% of cellulose, 15 and 19% of hemicellulose, 48 and 55% of lignin, and 1 and 4% of ashes [DUNGANI et al. 2018]. Regarding the corn cobs, the chemical composition typically ranged in 42.8% of hemicellulose, 35.1% of cellulose, and 4.8% of lignin [YANNI et al. 2010].

Table 2. Compositional analysis of biomasses

<table>
<thead>
<tr>
<th>Organic/inorganic</th>
<th>Composition (OP)</th>
<th>Composition (CC)</th>
<th>Composition (PB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% wt.</td>
<td>mg-1</td>
<td>mg-1</td>
<td>mg-1</td>
</tr>
<tr>
<td>Carbon</td>
<td>44.4±0.12</td>
<td>39.89±0.41</td>
<td>38.27±0.45</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.21±0.02</td>
<td>3.28±0.09</td>
<td>4.71±0.05</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.81±0.02</td>
<td>0.46±0.04</td>
<td>2.03±0.11</td>
</tr>
<tr>
<td>Pectin</td>
<td>18.15±0.04</td>
<td>7.98±0.33</td>
<td>4.88±0.17</td>
</tr>
<tr>
<td>Lignin</td>
<td>7.14±0.03</td>
<td>6.51±0.18</td>
<td>17.11±0.27</td>
</tr>
<tr>
<td>Cellulose</td>
<td>14.28±0.07</td>
<td>13.08±0.25</td>
<td>19.90±0.35</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>7.02±0.05</td>
<td>6.47±0.07</td>
<td>7.00±0.12</td>
</tr>
<tr>
<td>Ashes</td>
<td>2.08±0.02</td>
<td>1.20±0.08</td>
<td>4.23±0.14</td>
</tr>
<tr>
<td>Calcium</td>
<td>5.26±0.09</td>
<td>0.06±0.002</td>
<td>1.21±0.04</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.22±0.14</td>
<td>0.24±0.02</td>
<td>0.35±0.03</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.44±0.008</td>
<td>0.03±0.005</td>
<td>2.73±0.08</td>
</tr>
<tr>
<td>Iron</td>
<td>0.23±0.0009</td>
<td>0.0002±0.00003</td>
<td>0.0002±0.00002</td>
</tr>
<tr>
<td>Copper</td>
<td>0.01±0.003</td>
<td>0.002±0.0001</td>
<td>0.04±0.005</td>
</tr>
</tbody>
</table>

Source: own study.

Point of zero charge (pHz). The point of zero charge provides information about the solution’s pH that will promote the predominance of the negative charges in the adsorbent surface. Solution pH value lower than the pHZ requires that the biomass surface be positively charged, affecting the adsorption of cations due to electrostatic repulsion by equal charges [MARTIN LARA 2008]. Intersecting the curve for initial pH versus final pH with the line y = x (Fig 2) leads to the estimation of pHZ value. The pHZ of palm bagasse was 4.5, while for corn cobs and orange peel, it was 4.8 and 4.1, respectively. These values revealed that the biomasses have an acidic surface, i.e., the concentration of acidic sites is higher than the basic sites. In this sense, the selected pH value for adsorption experiments will be adequate to reach high removal yields.
Fig. 2. Point of zero charge of biomasses; source: own study
because of the biomasses’ acid charge. As the corn cobs achieved the highest value of point of zero charge, it may require a higher solution pH to have the same adsorption performance than the orange peels and the palm bagasse. A comparison of these results with those found in previous works (Tab. 3) validates the measurement accuracy. The accuracy of pHzs for palm bagasse and orange peels ranged around 7–8 % compared to the estimations of [ROMERO-CANO et al. 2016; SATHORN et al. 2008].

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Previous works</th>
<th>This work</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm bagasse</td>
<td>4.20</td>
<td>4.5</td>
<td>PANUMATI et al. [2008]</td>
</tr>
<tr>
<td>Corn cob</td>
<td>4.08</td>
<td>4.8</td>
<td>SEPULVEDA et al. [2015]</td>
</tr>
<tr>
<td>Orange peels</td>
<td>4.50</td>
<td>4.1</td>
<td>ROMERO-CANO et al. [2016]</td>
</tr>
</tbody>
</table>

Table 3. Comparison of point of zero charge for palm bagasse, corn cob and orange peels biomasses

Characterization of biomasses modified with alumina nanoparticles. Figure 3 depicts the Fourier-transform infrared spectroscopy (FTIR) spectra of biomasses chemically modified with alumina nanoparticles. Similar trends appear for all the spectrum with sharp absorptive peaks around 650–670 cm⁻¹, 1000–1100 cm⁻¹, 1500–1550 cm⁻¹, and 3700–3800 cm⁻¹. Such peaks correspond to the bonds between alumina nanoparticles and functional groups characteristic of the lignocellulosic materials like carboxyl and hydroxyl. The following functional groups are present by stretching vibrations in the adsorbents associated with the incorporation of nanoparticles into the biopolymer matrix: O-Al-O (650–700 cm⁻¹), Al-O-M; M=Al or Si (950–1200 cm⁻¹), Al-C=O (1500–1700 cm⁻¹), Al-COOH (2600–3800) [CARMONA TELLEZ 2008].

Fig. 3. Fourier-transform infrared spectroscopy spectra: a) Al₂O₃-modified orange peels, b) Al₂O₃-modified corn cob, c) Al₂O₃-modified palm bagasse; source: own study

Figure 4 shows the appearance of biomasses modified with alumina nanoparticles, observing an amorphous morphology characteristic of the lignocellulosic materials. The EDS (Fig. 4d) confirmed the incorporation of Al₂O₃ nanoparticles, from which the highest weight percentage of aluminium (Al) was estimated at 7.5% and 7.0% for the OP-Al₂O₃ and CC-Al₂O₃ samples. In comparison, the PB-Al₂O₃ adsorbent displayed the lowest aluminium content of 2.3%.

Fig. 4. Scanning electron microscope images and Energy-dispersive X-ray spectroscopy (EDS) weight percentage for biomasses chemically modified with Al₂O₃ nanoparticles: a) orange peels (OP-Al₂O₃), b) palm bagasse (PB-Al₂O₃), c) corn cobs (CC-Al₂O₃), d) weight percentage according to EDS measurements; source: own study
ADSORPTION RESULTS

Results showed the promising adsorption performance of the evaluated adsorbents for nickel and cadmium ions removal. As depicted in Figure 5, all biomasses displayed adsorption capacity for nickel and cadmium ions, determining an average uptake of 76% for nickel and 85% for cadmium at pH 6.0. After modification with the Al₂O₃ nanoparticles, it was observed that an adsorption increase of 7% for cadmium uptake using corn cobs (92.3±0.4%) and palm bagasse (92.7±0.3%), while for the nickel adsorption this increase was around 10–12% (86±0.4% for corn cobs and 88±0.1% for palm bagasse). In orange peels functionalized with the Al₂O₃ nanoparticles, an adsorption increase of 10% was observed for cadmium removal (95.8±0.3%) and 22% for nickel uptake (98±0.2%). For palm bagasse and the corn cobs biomasses before and after modification with nanoparticles, the adsorption yield follows the order Cd(II) >Ni(II). The fact they were adsorbing more efficiently one metal more than others may be attributed to the several characteristics of heavy metal ions such as atomic number, valence, and degree of ionization [Kocaöba 2008]. This adsorption specificity of biomasses towards cadmium and nickel ions was also reported by Merrikh-Pour and Jalali [2013] using natural zeolite in the competitive study.

CONCLUSIONS

This work was focused on comparing the performance of three different adsorbents prepared from oil palm bagasse, corn cob, and orange peel biomasses were modified with alumina nanoparticles. The metal-oxide nanomaterials were incorporated into the biomasses through a polysiloxane matrix. The characterization of these biomasses allowed us to estimate the content of cellulose, lignin, and pectin, and determine the point of zero charges. These points of zero charges ranged between pH 4 to 5, which were lower than the selected initial solution pH of 6. The adsorption experiments conducted in batch mode revealed the potential of these biomasses for nickel and cadmium uptake. The orange peel modified with alumina nanoparticles allowed the highest adsorption capacity (>95%) for both metal cations. Comparing these results with available experimental data for the same biomasses, a possible enhancement in adsorption performance can be identified due to the incorporation of alumina nanoparticles.

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REFERENCES


