Ni(II) and Cd(II) Simple and Competitive Adsorption on Activated Carbon Oxidized. Influence of the Oxidant Agents H₂O₂ and NaClO

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Abstract: Granular activated carbon, GAC, modified by oxidation with H₂O₂ and NaClO aqueous solutions and heat treatment at 900 °C. The N₂ adsorption isotherms at –196 °C and SEM and FTIR results were used to characterize the properties of the prepared ACs.

Textural parameters such as BET surface area and pore volumes were assessed by gas adsorption. The BET surface area values of solids are between 687 and 876 m²g⁻¹. Additionally immersion enthalpies of activated carbons in benzene, water, hydrochloric acid and sodium hydroxide solutions and Ni(II) and Cd(II) solutions of 500 mgL⁻¹ were determined, with values between 32 and 145 Jg⁻¹.

Ni(II) and Cd(II) adsorption isotherms were determined at pH 6 on activated carbons and competitive adsorption tests were realized between the two ions. The results show that for the tests carried out, the adsorption capacity decreases when the content of chemical groups on the surface also decreases.

Finally, the experimental results of the adsorption from solution were adjusted to the Langmuir and Freundlich models and a better fit with the first was found. With maximum adsorption capacities values for Ni(II) between 3.99 and 64.9 mgg⁻¹ for Cd(II) between 2.61 and 55.2 mgg⁻¹.

Values for competitive adsorption ions present in solution, Ni(II) and Cd(II), on the activated carbons, diminishes compared to those obtained in simple adsorption, this indicates the effect of the an ion competitive presence in adsorption another.

Keywords: Activated carbon, immersion calorimetry, surface chemistry, surface oxidation, simple and competitive adsorption.

INTRODUCTION

Contamination with toxic metals of water sources from different industries effluent has become in high-impact environmental problems [1-3]. The importance given to the treatment of this waste lies in the ability to accumulate metals in sediments and organisms tissues and consequently incorporated into food chains, which can cause health risks in humans [4]. Heavy metals are incorporated into the environment through natural sources such as volcanic eruptions and anthropogenic sources such as industrial wastewater discharges [5].

Adsorption, which is the technique employed in this work, is used in the contaminants removal from aqueous solution because of the versatility and development of diverse porous materials.

Between the porous solids is activated carbon, and its adsorption capacity depends not only on the porous texture or surface area, the chemical groups on the surface are another important factor in the adsorption process. Hence the interest in surface modification of activated carbon obtaining materials with specific applications [6]. Can be used several methods for surface chemistry modification, among which is the liquid phase oxidation of the surface, by using various oxidant agents, which produce diverse oxygen groups [7].

Chemical modification allows that adsorption occur by specific interactions. It is also important to consider factors specific to the solution in the moment adsorption; one of these is the pH, because its variation influences the chemical species in which presents the metallic ion and the charge oxygen groups which may have a basic or acid character [8].

A characterization technique of solid-gas or solid-liquid interaction is the immersion calorimetry, which allows calculating the heat quantity generated when the two phases are put in contact and which is characteristic of a specific adsorption system in determined temperature and pressure conditions [9].

In this work the surface chemistry of a granular activated carbon, GAC, was modified by oxidation with aqueous solutions of NaClO and H₂O₂ 13% to 34% respectively. Variation in the adsorption capacity of nickel and cadmium ions from aqueous solution on activated carbon were...
determined, by the realization of adsorption isotherms, simple and competitive, whose experimental data were fitted to the Langmuir and Freundlich models. For the energetic interactions between activated carbon and aqueous solutions of metallic ions immersion enthalpies of solid in these solutions were determined.

**METHODOLOGY**

**Adsorbent Materials**

An activated carbon, GAC, prepared from coconut shell by physical activation is subjected to oxidation with two aqueous solutions: sodium hypochlorite, NaClO, to 13% and hydrogen peroxide to 34%. For the oxidation with NaClO solution, 30 g GAC was mixed with 200 mL of the solution at 60 °C for 4 days to obtain a GAC-NaClO sample, which was washed until a constant pH.

For the activated carbon oxidized with the hydrogen peroxide solution 30 g of activated carbon GAC was mixed with 200 mL of H₂O₂ solution to 34% at room temperature for 18 hours to obtain the GAC-H₂O₂ sample, after this time the solid was washed until a constant pH.

Once activated carbons were washed, dried in an oven at 90°C for one night, and stored in plastic bottles under nitrogen atmosphere. Furthermore a sample heat treated at 900°C from GAC was obtained, CA900, thermal treatment was performed in a horizontal furnace THERMOLYNE with a stainless steel tube and the activated carbon was placed in a quartz boat. The pyrolysis temperature was chosen based on the thermal stability of the surface groups present in the starting sample [10].

**Activated Carbon Physicochemical Characterization**

**Textural Characterization**

Textural parameters, such as the surface area and pore volume of the activated carbons, were evaluated by N₂ physical adsorption at −196 °C and CO₂ at 0 °C in an automatic Autosorb 3B apparatus (Quantachrome). The apparent surface area and the microporovolume were determined by the BET and Dubinin-Radushkevich models respectively [11].

Scanning electron microscopy (SEM) was used to identify the surface physical morphology. A JSM-6390LV (JEOL Ltd., Japan) instrument with a 3 kV accelerating voltage was used to characterize the morphology of ACs, which were dried overnight at approximately 105 °C under vacuum before SEM analysis.

**Oxygenated Surface Groups**

The acid and basic groups were evaluated by Boehm’s method. For this purpose 0.500 g of each activated carbon was taken, to which 50 mL each of 0.1 M NaOH, Na₂CO₃, and NaHCO₃ was added to determine the acidity of groups or 50 mL of 0.1 M HCl was added to determine the basicity. The mixtures were kept at a constant temperature of 25 °C with constant stirring for 48 h. Subsequently, a 10 mL aliquot of each of the solutions in contact with the activated carbon samples was titrated employing corresponding 0.1 M standard solutions of HCl or NaOH [12].

**pH at the Point of Zero Charge**

The pH at the point of zero charge (pHₚZC) was evaluated by the mass titration method, for which different quantities of activated carbon (between 0.600 and 0.010 g) were weighed out and placed in a 50 mL glass flask and mixed with 10 mL of a 0.1 M NaCl solution. The mixtures were kept at a temperature of 25 °C with constant stirring for 2 days. Then, the pH was measured in each solution using a pH meter (Schott CG 840B) [13].

**IR Spectroscopy**

IR spectra were taken using a Nicolet Impact 410 FT-IR with a diffuse reflectance cell. The sample was pulverized and made into a pellet with KBr. The infrared region allows us to observe the main bands of stretching vibration of carbon groups attached to oxygen and hydrogen, which provides information on the types of groups that are on the surface [14].

**Determination of Immersion Enthalpies**

Calorimetry experiments were performed using a Calvet type heat conduction calorimeter. The immersion liquids used for the calorimetric characterizations were water, benzene, Ni(II) and Cd(II) solutions of 500 mgL⁻¹. To determine the immersion enthalpies, an activated carbon sample of 0.100 g was placed in a glass bulb attached to the calorimetric cell. Then, 8 mL of the desired solvent was added to the cell. The cell and glass bulb were separately placed in the main heat reservoir and left until thermal stability conditions were reached. Once thermal equilibrium was achieved, the activated carbon sample was immersed in the solvent and the resulting temperature changes were recorded, until a stable baseline was obtained. Recordings were then continued for an additional time period of 20 min after immersion, followed by electrical calibration of the calorimeter. Experiments were repeated between three and four times for each solvent listed above [15].

**Simple and Competitive Adsorption of Ni(II) and Cd(II)**

Ni(II) and Cd(II) solutions are prepared with analytical reagents (Merck), from NiCl₂·6H₂O and CdSO₄·8H₂O respectively, using double distilled water as solvent. The concentration range used to study adsorption was 100 to 500 mgL⁻¹. The concentration readings of the various solutions were realized into an atomic absorption spectrophotometer Perkin Elmer, ANALYST 300.

To determine isotherms were taken 50 mL of every known concentration solution and is added 500 mg of each activated carbon in a 100 mL airtight container. In the case of competitive adsorption, five solutions of each metal (200, 400, 600, 800 and 1000 mgL⁻¹) were prepared and mixed in a relation 1: 1, in order to achieve mixing with concentration equal to those of simple systems and which increasing concentrations of competitive metal, eg mix 1: solution of Ni(II) 500 mgL⁻¹ and Cd(II) 100 mgL⁻¹; mix 2: solution of
Ni(II) 500 mgL$^{-1}$ and Cd(II) 200 mgL$^{-1}$, covering all possible options to get 25 concentration relations in competitive systems and demonstrate the effect of the concentration of ion on the initial competitive adsorption capacity of the solid in simple systems. The initial pH of solution is adjusted to a value of 6, the mixtures were allowed to stand for 100 hours until equilibrium was reached, stirring and keeping the temperature constant at 25 °C. After this equilibrium time the solution was filtered to remove the solid and concentration of the ions was determined by atomic absorption.

RESULTS AND DISCUSSION

Texture and Chemical Characterization

$\text{N}_2$ and CO$_2$ adsorption isotherms at -196 °C and 0 °C respectively, are shown in Figs. (1, 2) for the original activated carbon GAC and modified activated carbons and in Table 1 the results obtained for the textural characterization are presented from $\text{N}_2$ and CO$_2$ adsorption experimental data, the parameters presented are: surface area (BET area) calculated by the BET model, the micropore volume ($V_T$) estimated by the DR model, the volume Total ($V_t$) calculated at the saturation pressure and the narrow micropores volume ($V_n$) which is evaluated by applying the DR model to the CO$_2$ adsorption experimental data.

Table 1. Textural parameters of the activated carbons determined from the $\text{N}_2$ and CO$_2$ adsorption isotherm at -196 °C and 0 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{Area}_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_t$ (cm$^3$/g)</th>
<th>$V_n$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>842</td>
<td>0.34</td>
<td>0.38</td>
<td>0.35</td>
</tr>
<tr>
<td>GAC900</td>
<td>876</td>
<td>0.35</td>
<td>0.40</td>
<td>0.28</td>
</tr>
<tr>
<td>GAC-NaClO</td>
<td>687</td>
<td>0.27</td>
<td>0.30</td>
<td>0.21</td>
</tr>
<tr>
<td>GAC-H$_2$O$_2$</td>
<td>873</td>
<td>0.35</td>
<td>0.39</td>
<td>0.36</td>
</tr>
</tbody>
</table>

As observed in Fig. (1) the activated carbons exhibit adsorption isotherms Type I, in which a larger amount adsorbed relative pressures low is observed, characteristic behavior of microporous materials, this is consistent with the pore volumes values obtained by application DR model. Furthermore the total micropores volume ($V_n$) and the narrow micropores volume ($V_n$) in the absence of kinetic and diffusional restrictions can be similar showing dimensionally uniform porous structures as in the case of the GAC sample, a difference in contrast between these two values indicates a range in the micropores size [16].

![Fig. (2). CO$_2$ adsorption isotherms at 0 °C of the GAC-NaClO, GAC-H$_2$O$_2$, GAC, GAC900 samples.](image)

When analyzing the results obtained observe that the sample subjected to the oxidation treatment with sodium hypochlorite, CA-NaClO, exhibit a decrease in the surface area of 18.4%, the total and narrow microporous volume with respect to the original activated carbon this behavior is due to the oxidation treatment promotes the formation of surface oxygen groups that are located at the edges of the openings of the pores which limits the accessibility of the nitrogen molecule to the porous structures [17].

According to the chemical characterization of the activated carbons, the groups developed are acid type, specifically carboxylic acid carboxyl. So, in a process for modifying the surface solid a number of processes are present such as: the formation of surface group, opening new porous structures together with the widening and deepening of existing structures. The equilibrium between these processes ultimately determines the effect on the surface area of the solids [18].

Surface Morphology of Activated Carbons

As to activated carbon was subjected to heat treatment under nitrogen, GAC900, an increase in surface area was observed with respect to the GAC sample, this result confirms the presence of oxygen groups on the surface, as evidenced by titration Boehm (see Table 2), since this type of treatment promotes selective decomposition of surface oxygen functional groups in CO and CO$_2$ in accordance with the thermal stability of each group.

The original sample GAC presents a variety of surface groups, with greater amount of phenolic groups and higher total acidity with respect to the total basicity, which present a value at the pH at point of zero charge, pH$_{\text{PZC}}$, less than 7,
these groups by heat treatment at 900 °C dramatically decreases and the oxidation treatment favor the oxygen groups formation on activated carbon surface as evidenced by the increase in the total acidity and basicity parameters.

Activated carbon oxidation with sodium hypochlorite solution promotes formation of acidic groups, mainly favoring the formation of phenolic groups [17] the increase of these acid groups is close to 70% compared to the original sample. Also is observed an increase in the basic character of the surface, which is 25% due to the treatment to which the sample is subjected. The change in surface chemistry is also evidenced in the value of pH_{pzc} which is 6.5.

Fig. (3) shows the infrared spectra obtained for the starting active carbon GAC and the solids obtained once activated carbon oxidizes with sodium hypochlorite and hydrogen peroxide solutions.

The Fig. (3) shows the most important changes that occur after treatment the GAC sample versus the GAC-NaClO and GAC-H_{2}O_{2} samples. The FTIR of the GAC900 sample is not shown because this spectra does not change significantly against the GAC prepared.

The most representative changes were observed between 2100-2400 cm⁻¹ and 1200-1600 cm⁻¹, due to the chemicals used in this research alter the chemical surface treatment of the activated carbons prepared.

**Calorimetric Characterization**

The immersion enthalpy of a porous solid in a liquid can be related to the pore structure and parameters associated with the surface chemistry of the solid.

The immersion enthalpy of a porous solid in a liquid can be related to the surface area accessible to the molecule of the liquid. Surface chemistry of the solid is evaluated when the immersion liquid has specific interactions, thus the enthalpy of immersion in water is indicative of the hydrophobic or hydrophilic nature of the solid surface as a consequence can be established relations between the immersion enthalpy and the surface chemical groups.

Figs. (4, 5) show the thermograms obtained for immersion the activated carbon GAC and activated carbons oxidized in benzene and water.

![Fig. (4). Immersing thermograms of activated carbon GAC and activated carbons oxidized in benzene.](image)

The heat generated by contacting the solid with the solvent is proportional to the area under the peak which occurs in the graph of potential a function of time therefore higher energetic effect in the case of immersion the activated carbon.
carbon GAC benzene is observed, which has a lower number of functional groups, while when activated carbons immerse in water heats produce are higher for oxidized activated carbons.

![Immersion thermograms of activated carbon GAC and activated carbons oxidized in water.](image)

Fig. (5). Immersion thermograms of activated carbon GAC and activated carbons oxidized in water.

The results obtained when determining the immersion enthalpies of activated carbons in benzene, water, hydrochloric acid and sodium hydroxide solutions and Ni(II) and Cd(II) solutions of 500 mgL⁻¹, all of exothermic nature, are presented in Table 3.

According to the results of immersion enthalpies shown in Table 3 it is observed that the values in the immersion enthalpies change with the surface chemistry modifications that are obtained in the oxidation of the original activated carbon. The immersion enthalpy of activated carbons in liquids show that activated carbon GAC900 has the highest value for immersion in benzene of -145.0 Jg⁻¹, HCl of -58.2 Jg⁻¹ and the lowest value for the immersion in water -32.4 Jg⁻¹, sodium hydroxide -35.2 Jg⁻¹ and in the Ni(II) and Cd(II) solutions with values of -32.3 Jg⁻¹ and -34.4 Jg⁻¹ respectively; which indicates that this solid is the one with the higher hydrophobic character, and this influences the adsorption of ions Ni(II) and Cd(II).

In the case of the two oxidized samples, it is observed that the behavior of the immersion enthalpy in the liquid is different from that as described above since for the GAC-NaClO the lower immersion enthalpy is observed in hydrochloric acid -45.1 Jg⁻¹ and higher are obtained for immersion in benzene -125 Jg⁻¹ and water -64.1 Jg⁻¹. Regarding to immersion in Ni(II) and Cd(II) solutions values are -61.7 and -54.8 Jg⁻¹ respectively; contrasting with the activated carbon oxidized with H₂O₂ solution in which the interaction with the solution of Cd(II) is higher.

The immersion enthalpies values in water of the activated carbons are indicative of the surface chemical change as result of the treatments to which was subjected activated carbon CAG [19], that are the development or decomposition of surface groups. A greater quantity of surface oxygen groups as in the case of GAC-NaClO produces increased immersion enthalpy due to the interactions established between the water molecule and oxygen surface groups that develop in the activated carbon.

Fig. (6) shows the relation between immersion enthalpies of activated carbons in water and the density of total acid surface groups in this graph it is evident that the immersion enthalpy in water increases as the content of total acid groups so does such behavior is found in other studies in which the modification of the functional groups on activated carbon [20] is studied.

![Relation between the immersion enthalpy of activated carbons in water and density of acid groups.](image)

Fig. (6). Relation between the immersion enthalpy of activated carbons in water and density of acid groups.

Regarding the hydrophobic character of the surface to be evaluated by the relation between the immersion enthalpy in benzene and immersion enthalpy in water, it was found that this decreases with the oxidation process and gradually increases with heat treatment and was higher in the solid treated at 900 °C, is considered that the hydrophobic character of the activated carbons decreases with the

### Table 3. Immersion enthalpies of activated carbons in different liquids.

<table>
<thead>
<tr>
<th>Muestra</th>
<th>-ΔH_{im} H₂</th>
<th>-ΔH_{im} H₂O</th>
<th>H.F*</th>
<th>-ΔH_{im} HCl</th>
<th>-ΔH_{im} NaOH</th>
<th>-ΔH_{im} 580ppm Ni(II)</th>
<th>-ΔH_{im} 580ppm Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA</td>
<td>106</td>
<td>49.7</td>
<td>2.13</td>
<td>51.4</td>
<td>57.3</td>
<td>49.9</td>
<td>34.4</td>
</tr>
<tr>
<td>CA 900</td>
<td>145</td>
<td>32.4</td>
<td>4.48</td>
<td>58.2</td>
<td>35.2</td>
<td>32.3</td>
<td>34.4</td>
</tr>
<tr>
<td>CA-NaClO</td>
<td>125</td>
<td>64.1</td>
<td>1.95</td>
<td>45.1</td>
<td>94.9</td>
<td>61.7</td>
<td>54.8</td>
</tr>
<tr>
<td>CA-H₂O₂</td>
<td>117</td>
<td>56.4</td>
<td>2.07</td>
<td>36.0</td>
<td>69.7</td>
<td>45.6</td>
<td>57.7</td>
</tr>
</tbody>
</table>

*H.F. hydrophobic Factor \( \frac{ΔH_{imm,H₂O}}{ΔH_{imm,H₂}} \)

The standard deviations of results are between 0.1 - 1.5 Jg⁻¹.
Ni(II) and Cd(II) Simple and Competitive Adsorption

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Increases of functional groups present in the solid surface which modify the wetting characteristics and activated carbon becomes more compatible to the water [10], which maximizes the adsorption properties of ions in solution that is established by specific interactions.

Ni(II) and Cd(II) Adsorption Capacity Determination from Aqueous Solution

Ni (II) and Cd (II) adsorption experiments were performed at pH 6 as according to the species diagram of metals, at this pH the species are in cationic form [21]. The ions adsorption is mainly attributed to the interaction with the functional groups.

Ni(II) and Cd(II) Adsorption Simple

Fig. (7) shows the adsorption isotherms obtained for the two ions separately on activated carbon GAC-NaClO.

The experimental results for the Ni(II) and Cd(II) adsorption are fitted to the Langmuir and Freundlich models and is observed that the Langmuir model fit best said results; in Table 4 the values obtained for the models parameters and the correlation coefficients for each of these are shown.

Langmuir model can obtain the maximum adsorption capacity, Qm, of each activated carbon; for the case of Ni(II) greater adsorption capacity is observed on the activated carbon GAC-H2O2, which presents a higher carboxylic groups content that are interacting with the nickel ions mainly.

For the case of Cd(II) ions is observed that the best fit of the experimental data presented to the Langmuir model, the maximum adsorption capacity is obtained for the activated carbon GAC-NaClO which presents a higher phenolic groups content.

The importance of oxygenated groups on the activated carbon surface in the metallic ions adsorption from aqueous solution has been studied by several authors [10, 22], it is generally considered that the adsorption of ions dissolved in aqueous solutions must primarily established specific interactions between functional groups and ions.

Table 4. Langmuir and Freundlich models parameters obtained from the Ni(II) and Cd(II) adsorption on activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni(II) Langmuir Model</th>
<th>Freundlich Model</th>
<th>Cd(II) Langmuir Model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Qm</td>
<td>K_L</td>
<td>R²</td>
<td>K_F</td>
</tr>
<tr>
<td>GAC</td>
<td>29.7</td>
<td>0.0120</td>
<td>0.993</td>
<td>0.111</td>
</tr>
<tr>
<td>GAC900</td>
<td>3.99</td>
<td>0.0063</td>
<td>0.992</td>
<td>0.116</td>
</tr>
<tr>
<td>GAC-NaClO</td>
<td>32.7</td>
<td>0.0114</td>
<td>0.998</td>
<td>0.098</td>
</tr>
<tr>
<td>GAC-H2O2</td>
<td>64.9</td>
<td>0.0148</td>
<td>0.992</td>
<td>0.159</td>
</tr>
</tbody>
</table>

Competitive Adsorption

Ni (II) and Cd (II) simple adsorption isotherms in solution depend on the temperature, the solution pH and surface chemistry, however when it comes to multicomponent systems, the adsorption isotherms from one of the adsorbates is dependent on the concentration and nature of other adsorbates present in the solution. This is because the adsorbate competes with other solutes for the same interaction sites where adsorption occurs. Because this are evaluate the effect of the Cd(II) concentration in the presence of Ni(II) and viceversa are assessed as an approximation for the solution of such problems of
contamination, because industrial waste water generally present mixtures of ions.

As simple adsorption isotherms, data for Ni(II) and Cd(II) competitive adsorption were fitted to the Langmuir and Freundlich models, the parameters obtained for each isotherm in which the concentration one of the ions is kept constant (the concentration in mg L\(^{-1}\) is written next to the ion) are shown in Table 5.

For multicomponent adsorption systems, according to the results obtained for the correlation coefficients in the adjustments, it was found that the model that best adjust the experimental data was the Langmuir. Maximum adsorption capacity values higher for the Cd(II) adsorption when the Ni(II) concentrations remain constant are obtained in the activated carbon GAC-\(\text{NaClO}\) and for Ni(II) adsorption when the Cd(II) concentrations remain constant for activated carbon GAC-\(\text{H}_2\text{O}_2\); also is observed that the adsorbed quantities of each ion are less than when this carried out separately for each ion.

### Table 5. Langmuir and Freundlich models parameters obtained from the Ni(II) and Cd(II) competitive adsorption on activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isotherm</th>
<th>Langmuir Model</th>
<th>Freundlich Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Q_m)</td>
<td>(K_L)</td>
</tr>
<tr>
<td>GAC-(\text{NaClO})</td>
<td>Ni(II) Constant Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni 100/ Cd</td>
<td>52.24</td>
<td>0.0598</td>
<td>0.987</td>
</tr>
<tr>
<td>Ni 200/ Cd</td>
<td>47.03</td>
<td>0.0519</td>
<td>0.956</td>
</tr>
<tr>
<td>Ni 300/ Cd</td>
<td>47.18</td>
<td>0.5839</td>
<td>0.946</td>
</tr>
<tr>
<td>Ni 400/ Cd</td>
<td>27.81</td>
<td>1.9096</td>
<td>0.976</td>
</tr>
<tr>
<td>Ni 500/ Cd</td>
<td>36.72</td>
<td>0.9836</td>
<td>0.954</td>
</tr>
<tr>
<td>GAC-(\text{H}_2\text{O}_2)</td>
<td>Cd(II) Constant Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd 100/ Ni</td>
<td>29.13</td>
<td>5.0670</td>
<td>0.957</td>
</tr>
<tr>
<td>Cd 200/ Ni</td>
<td>25.12</td>
<td>1.0292</td>
<td>0.961</td>
</tr>
<tr>
<td>Cd 300/ Ni</td>
<td>25.64</td>
<td>0.7396</td>
<td>0.971</td>
</tr>
<tr>
<td>Cd 400/ Ni</td>
<td>14.12</td>
<td>1.1239</td>
<td>0.943</td>
</tr>
<tr>
<td>Cd 500/ Ni</td>
<td>21.44</td>
<td>0.2847</td>
<td>0.953</td>
</tr>
<tr>
<td>GAC-(\text{NaClO})</td>
<td>Ni(II) Constant Isotherm</td>
<td></td>
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</tr>
<tr>
<td>Ni 100/ Cd</td>
<td>28.9</td>
<td>0.0467</td>
<td>0.974</td>
</tr>
<tr>
<td>Ni 200/ Cd</td>
<td>23.5</td>
<td>0.2050</td>
<td>0.935</td>
</tr>
<tr>
<td>Ni 300/ Cd</td>
<td>21.9</td>
<td>0.1982</td>
<td>0.944</td>
</tr>
<tr>
<td>Ni 400/ Cd</td>
<td>19.9</td>
<td>0.1593</td>
<td>0.958</td>
</tr>
<tr>
<td>Ni 500/ Cd</td>
<td>20.2</td>
<td>0.0591</td>
<td>0.988</td>
</tr>
<tr>
<td>GAC-(\text{H}_2\text{O}_2)</td>
<td>Cd(II) Constant Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd 100/ Ni</td>
<td>55.1</td>
<td>0.0024</td>
<td>0.984</td>
</tr>
<tr>
<td>Cd 200/ Ni</td>
<td>56.1</td>
<td>0.0017</td>
<td>0.989</td>
</tr>
<tr>
<td>Cd 300/ Ni</td>
<td>66.7</td>
<td>0.0011</td>
<td>0.975</td>
</tr>
<tr>
<td>Cd 400/ Ni</td>
<td>59.3</td>
<td>0.0011</td>
<td>0.955</td>
</tr>
<tr>
<td>Cd 500/ Ni</td>
<td>55.3</td>
<td>0.0009</td>
<td>0.962</td>
</tr>
</tbody>
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### CONCLUSION

An activated carbon is modified by surface oxidation with \(\text{H}_2\text{O}_2\) and \(\text{NaClO}\) aqueous solutions, a variation in the surface area and acid groups content is observed with values that for these last varies between 0.032 and 0.442 molecules.mm\(^{-2}\).

Immersion enthalpies of activated carbons are determined as characterization parameter in different liquids: benzene, water and HCl, \(\text{NaOH}\), Ni(II) and Cd(II) solutions; the results show that the immersion enthalpies in benzene are greater than the immersion enthalpies in water indicating the hydrophobic character of the solids.

Activated carbons obtained are used in the study of the single and competitive Ni(II) and Cd(II) adsorption from aqueous solution. The experimental results are fitted to the Freundlich and Langmuir models, the second model best fits the adsorption data with values for maximum adsorption capacities of Ni(II) between 3.99 and 64.9 mgg\(^{-1}\) and for Cd(II) between 2.61 and 55.2 mgg\(^{-1}\).
Ni(II) and Cd(II) Simple and Competitive Adsorption

Experimental data for Ni(II) and Cd(II) competitive adsorption isotherms from aqueous solution on the activated carbons diminish compared to those obtained by simple adsorption of the ions, this indicates the effect presence of a competitive ion in the adsorption on the other, it can be because the two ions are competing for the same sites of interaction with the solid surface.

Ni(II) adsorption is higher in the activated carbon GAC-H$_2$O$_2$ which presents a higher content of carboxylic acids on the surface, whereas the Cd(II) adsorption is higher in the activated carbon GAC-NaClO which has a higher content of phenol groups on the surface.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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