

Research Article

Enthalpic Contribution of Ni(II) in the Interaction between Carbonaceous Material and Aqueous Solution

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Solid adsorbents were prepared from corn cob that was modified with a solution of HNO₃ 6 M at different contact times. The solids are characterized by physical N₂ adsorption at 77 K to know their surface area by applying the BET model and surface chemistry is determined using the Bohem method. Once we have prepared the adsorbents we determine the immersion enthalpy, ΔH_{im} , of the solids in Ni(II) aqueous solutions of different concentrations between 20 and 800 mg·L⁻¹, with values for ΔH_{im} between 10.0 and 35.3 J·g⁻¹. From the results obtained for the immersion enthalpy in function of the ion Ni(II) concentration we calculate the contribution to the immersion enthalpy that corresponds to the ion when it is treated with the system adsorbent-solution as a mixture in which the solid, the solvent, and the adsorbate are involved. The solution thermodynamics allows for establishing the enthalpic changes that bring the ion in function of the concentration and the intensity of the interaction of solid-metal ion that is favored by the presence of acid groups in the solid.

1. Introduction

The process of interaction between a solid and a liquid can be considered, in a simplified manner as a mixture of the two components of the system that produce changes in the thermodynamic properties with regard to the components before the interaction and the thermodynamic properties as enthalpy, entropy, and energy of Gibbs can be determined for mixing process [1].

The purpose of the thermodynamic properties determination of an interaction between various components is to know the intensity of the property and how it is affected in function of the mixture. So you can find works that are related to the determination of excess enthalpy for organic compounds [2], determinations of partial molar enthalpy in the components of different alloys [3], excess molar enthalpies for binary systems of solvent-solute [4], among others. The methodology for the calculation of the partial

thermodynamic properties, that is, the contribution of each component to the property thermodynamics total, can be extended to the solid-liquid interaction taking into account the particular characteristics of the solid and the interaction type that is being carried out. In this research the adsorption process of ion Ni(II) takes place on a carbonaceous material.

Myers and Monson [5] make an interesting discussion on the implementation of the solutions (mixtures) thermodynamics, to the adsorption process of a fluid component on a porous solid, and establish that by relatively simple way the formulation of mixtures thermodynamics can be extend to properties like the enthalpy differential for the adsorbent and the adsorbate.

1.1. Differential Enthalpy of the Mixture Components. The adsorbent-solution is a multicomponent system and for conditions of temperature T and pressure P specifically, the

variation of a property thermodynamics considered X (as the enthalpy for this case) can be expressed as

$$dX = \left(\frac{\partial X}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial X}{\partial P} \right)_{T,n_i} dP + \left(\frac{\partial X}{\partial n_1} \right)_{T,P,n_j} dn_1 + \left(\frac{\partial X}{\partial n_2} \right)_{T,P,n_j} dn_2 + \left(\frac{\partial X}{\partial n_3} \right)_{T,P,n_j} dn_3. \quad (1)$$

For the enthalpy system a similar expression is considered

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial H}{\partial P} \right)_{T,n_i} dP + \left(\frac{\partial H}{\partial n_1} \right)_{T,P,n_j} dn_1 + \left(\frac{\partial H}{\partial n_2} \right)_{T,P,n_j} dn_2 + \left(\frac{\partial H}{\partial n_3} \right)_{T,P,n_j} dn_3, \quad (2)$$

where

$$\left(\frac{\partial H}{\partial n_i} \right)_{T,P,n_j} = \overline{H}_i \quad (3)$$

corresponds to the partial molar enthalpy of component i to T , P , and n_j constant. The contribution of each one of the system components to the total enthalpy is established in this manner. Thus it is possible to determine experimentally a change in the enthalpy that manifests for the process that corresponds to the adsorbent-solution interaction and define the change in the enthalpy differential for each component of the mixture ΔH_{DIF_i} , as the difference between the partial molar enthalpy of component i , \overline{H}_i , and the molar enthalpy of component i pure, H_i^*

$$\Delta H_{\text{DIF}_i} = \overline{H}_i - H_i^*. \quad (4)$$

It is noted that we cannot determine absolute values of enthalpy, but we can determine the difference between the enthalpic content of component in the system and the pure component. The change in the differential enthalpy, ΔH_{DIF_i} , is also expressed as

$$\Delta H_{\text{DIF}_i} = \left(\frac{\partial \Delta H_{\text{exp}}}{\partial n_i} \right)_{T,P,n_j}. \quad (5)$$

Each system component makes a contribution to the mixture enthalpy and therefore the change in the enthalpy differential can be determined, because this property is a suitable tool to describe mixture properties and the changes that occur when changing, for example the components quantities [6].

When we calculate the enthalpy differential for the components of a mixture, as a solution or an alloy [7], variations in the thermodynamic property are expressed by mol in the mixture; however in the case of a mixture as that described in this work which determines the change in the experimental enthalpy for the mixture of carbonaceous solids, water, and

ion Ni(II), the contribution cannot be calculated by mol but per gram of each system component.

In this work we determined the immersion enthalpy, ΔH_{im} , of the carbonaceous adsorbent materials in aqueous Ni(II) solutions of different concentrations and calculate the relationship of mass of Ni(II) with respect to the system mass, $X_{\text{Ni(II)}}$, and the enthalpy change by μg of ion Ni(II), ΔH_{exp} , from which we calculate the change in the differential enthalpy of Ni(II) in the mixture, $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$. Established are correlations between, $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$, the total acid groups content, and the carboxylic groups content on the solids surface with the purpose of observing the difference in behavior of dilute and concentrated solutions of Ni(II).

2. Experimental and Methods

2.1. Preparation and Characterization of the Carbonaceous Solids. The carbonaceous solid adsorbents are prepared from corn cob that is dried in an oven at 100°C and 5 hours later is crushed to a particle size of 4-5 mm and it chars in a horizontal oven for 1 hour in a nitrogen atmosphere to 450°C , to increase the material porosity.

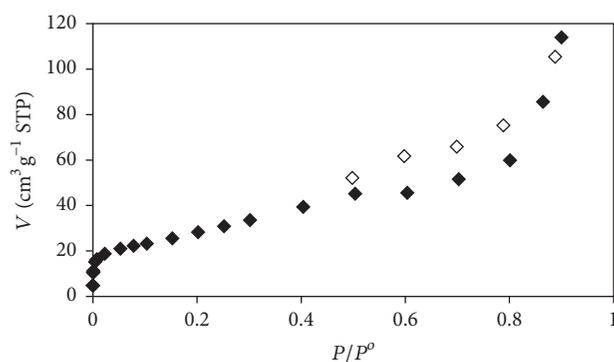
The carbonized solid is subjected to oxidation with a HNO_3 solution 6 M at 60°C and at different contact times of 3, 6, and 9 hours with the purpose that the surface increases the oxygenated groups content. Once the time established elapses the solids are washed with distilled water until a pH around 6.5. The solids are called CC by corn cob for solid without treatment acid and CCox followed by the contact time with the HNO_3 solution.

The solids were characterized by means of the N_2 adsorption at 77 K for the surface area and for determining the oxygenated groups content the method proposed by Boehm [8] is followed, to put 100 mg of solid in contact with 50 mL of NaOH , Na_2CO_3 , and NaHCO_3 solutions with concentration 0.1 M and 50 mL of HCl solution 0.1 M; mixtures are kept at a temperature of 25°C , with constant agitation, for five days. Finally 10 mL aliquots of solutions are titled in contact with the solid.

2.2. Determination of the Immersion Enthalpy. It uses a heat conduction microcalorimeter to determine the immersion enthalpy of the carbonaceous solids in aqueous Ni(II) solutions, which are prepared from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of the trademark Merck with concentrations between 20 and 800 mgL^{-1} . 10 g of the solution at 25°C and a solid sample of 100 mg are added to the calorimetric cell (weight with accuracy of 0.1 mg) that is placed inside the cell in a glass ampoule and starts the potential registration output from the thermal sensor for a period of approximately 15 minutes taking potential readings every 20 seconds; it is necessary to perform the breaking of the glass ampoule, record the thermal effect generated, and continue with the potential readings for approximately 15 more minutes; finally the system is calibrated electrically [9].

TABLE I: Physiochemical characterization of the carbonized oxidized solids.

| Solid | Surface area ($\text{m}^2 \text{g}^{-1}$) | Carboxylic groups (mmolg^{-1}) | Phenolic groups (mmolg^{-1}) | Lactonic groups (mmolg^{-1}) | Total acidity (mmolg^{-1}) | Total basicity (mmolg^{-1}) |
|-------|--|--|--|--|--|---|
| CC | 130 | 0.13 | 0.23 | 0.10 | 0.46 | 0.28 |
| CCox3 | 122 | 0.26 | 0.16 | 0.15 | 0.57 | 0.12 |
| CCox6 | 115 | 0.38 | 0.17 | 0.20 | 0.75 | 0.10 |
| CCox9 | 110 | 0.46 | 0.42 | 0.38 | 1.26 | 0.07 |

FIGURE 1: N_2 adsorption isotherm for solid carbonaceous CC.

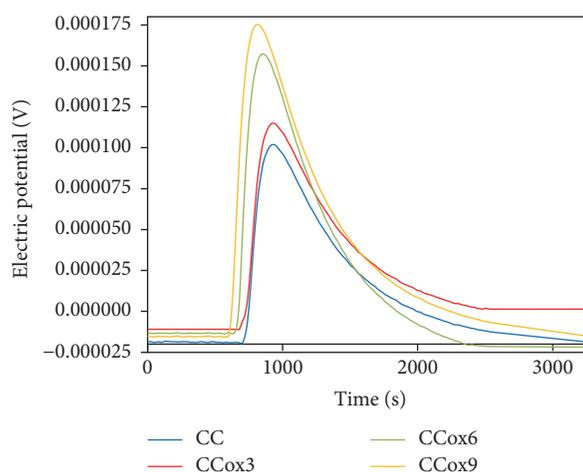
3. Results and Discussion

Once the carbonaceous solids that from the corn cob were prepared, these are characterized by N_2 adsorption with the aim of knowing the surface area values and pores total volume using the BET model. Figure 1 shows the N_2 adsorption isotherm for solid CC which is carbonized in an inert atmosphere.

For the carbonized CC a type IV isotherm is observed with hysteresis cycle that presents a plateau at relatively high pressures; in the adsorption branch a slope is observed high near the saturation and the desorption occurs at intermediate pressures. This characteristics type corresponds to a hysteresis cycle type H3 that is associated with capillaries in the slit form open with parallel walls and capillaries with wide bodies and short and narrow neck [10]. Solids that are subjected to oxidation with the HNO_3 solution presented similar isotherms and the apparent surface area for these was determined by the BET model.

Table 1 presents the results obtained for the solids characterization in regard to their surface area values and the oxygenated groups content that are generated by the oxidation process that occurs in the carbonized solids.

According to the results the carbonized solids show surface area of similar values around $110 \text{ m}^2 \text{g}^{-1}$ that is slightly modified by the oxidation treatment because oxygen groups are generated in the surface that limit the incipient porosity produced by the carbonization process. It is observed that the greatest contact time between the solid and the nitric acid solution presents the solid with a higher content in groups of acid character, with a value of 1.26 mmolg^{-1} and the smallest value for the total basicity. The results in regard to the surface groups content are comparable to a work in which activated carbons are prepared by chemical activation with KOH [11].

FIGURE 2: Immersion calorimetric curves of the carbonaceous solids in an aqueous ion $\text{Ni}(\text{II})$ solution of 100 mgL^{-1} .

The immersion enthalpy of the carbonaceous solids with mentioned characteristics in aqueous $\text{Ni}(\text{II})$ solutions is determined in a wide concentration range in order to observe the behavior with regard to the enthalpy change for immersion in dilute and concentrated solutions. Figure 2 presents the calorimetric curves that are obtained for the solids to an ion $\text{Ni}(\text{II})$ concentration of 100 mgL^{-1} .

The peak in the potential curve in function of time is proportional to the heat quantity that is generated in the solid-liquid contact. It is observed that the solid that presents the highest peak when immersed in the ion solution is the one that was submitted for oxidation for 9 hours and that has the highest acid groups content that have the ability to interact with the $\text{Ni}(\text{II})$, showing that the effect in the surface modification increases the immersion enthalpy of the solid in the solution [12]. The effect that occurs in the immersion increases the potential of the thermal sensor indicating that the process is of exothermic character and involving the interactions that occur between the three mixture components to be studied.

From curves like the ones shown in Figure 2 calculate the immersion enthalpy of solids in solutions that are tested in conditions of low and high dilution with the purpose of comparing the enthalpy change of the immersion process. Figure 3 presents the relation between the immersion enthalpy and the mass of ion $\text{Ni}(\text{II})$ present in the mixture along with water and the carbonaceous solid.

To appreciate the $\text{Ni}(\text{II})$ contribution to the total immersion enthalpy the solid adsorbent quantities and water must

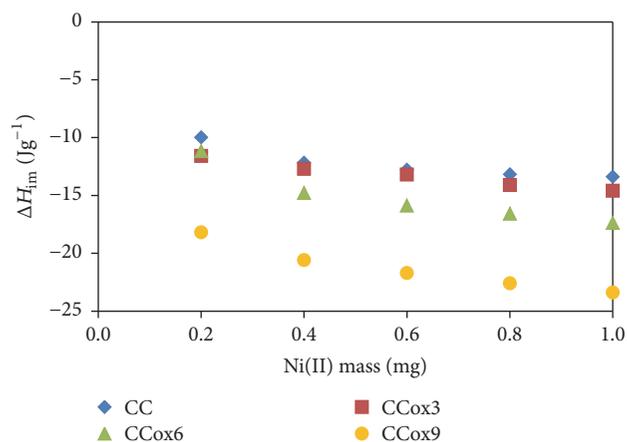


FIGURE 3: Immersion enthalpy of the carbonized solids in aqueous Ni(II) solutions in function of the ion mass.

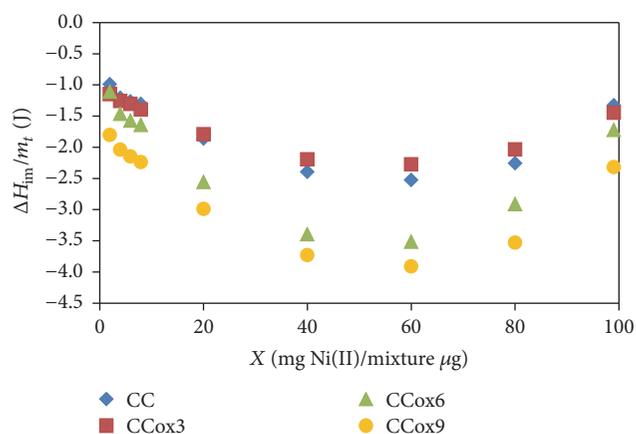


FIGURE 4: Immersion enthalpy per mixture mass as a function of the Ni(II) mass fraction.

be kept constant that acts as a solvent of smaller amount of ions that have a positive electrical charge [13]. Figure 3 shows the negative values of enthalpy change and exothermic character, which are greater for the two solids that were in contact with the HNO_3 solution for 6 and 9 hours. The highest values of enthalpy indicate greater solid-liquid interaction, in that the solid to be oxidized during 3 hours shows a similar behavior to the carbonized one that had not been subjected to oxidation.

The ion Ni(II) contribution to the immersion enthalpy, ΔH_{im} , is calculated assuming that the system is a mixture of three components for which a mass relationship is established instead of a molar relationship (which would allow knowing the partial molar properties) since it does not know the moles of solid but if it is a mass, this defines the variable mass fraction, $X_{\text{Ni(II)}}$, as the Ni(II) mass in the solution on the total mixture mass. In the same way we can calculate the solid and the solvent contribution to the enthalpy total change; however the ion contribution is of greater interest since that is the adsorbate [14]. Figure 4 shows the relation of $\Delta H_{\text{im}}/\text{mixture mass}$ in function of the Ni(II) mass fraction for the range of concentrations which are studied.

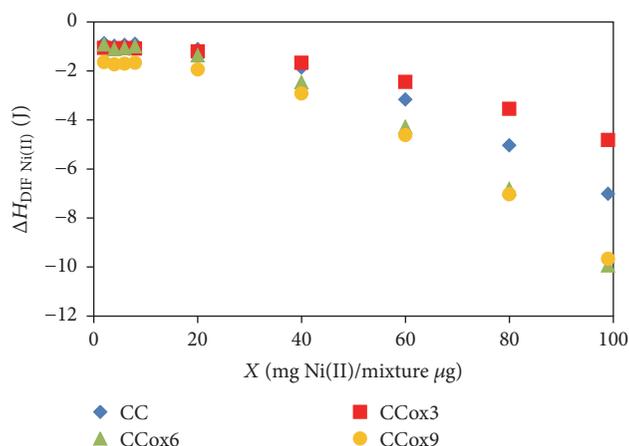


FIGURE 5: Ion Ni(II) differential enthalpy change in function of their mass fraction in the mixture.

Figure 4 shows curves for the four solids with peaks toward the mass fraction, $X_{\text{Ni(II)}}$, around 60 and indicates different behaviors for the low and the high ion concentrations that indicate different interactions in the ion adsorption process on the solid that generates a enthalpy total change for the mixture.

From Figure 4 calculate the change in the Ni(II) differential enthalpy, $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$, which corresponds to the partial derivative of the immersion enthalpy with regard to the mass fraction, $(\partial \Delta H_{\text{im}} / \partial X_{\text{Ni(II)}})$, and represents the difference between the ion Ni(II) enthalpy when it is in the mix and the pure ion enthalpy. In this way it is stated that it is not possible to calculate the ion Ni(II) absolute enthalpy in the mixture but the difference between the two states. Figure 5 presents the results obtained for $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$, in function of $X_{\text{Ni(II)}}$.

Figure 5 is an interesting result because it shows that when increasing the ion Ni(II) quantity in the mixture its contribution to the total enthalpy becomes greater. For the dilute concentrations in the three solids CC, CCox3, and CCox6, the values are similar and note that overlap for the carbonized CCox9 shows a greater change of enthalpy. For mass fractions of the ion greater than 20 (mg Ni(II)/ μg mixed) it is noted that the Ni(II) differential enthalpy increases with a greater contribution to the CC carbonized without treatment with respect to the one that was oxidized during three hours, while for solids with greater oxidation time this enthalpic contribution is similar. In this way by the calculation of the change in the ion differential enthalpy, $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$, it is useful to see the difference in the interactions and the influence of the superficial oxygen groups in the solid adsorbent.

It is known that the interaction between metal ions that are in aqueous solution and a solid adsorbent has different influences, including the oxygen groups content of the solid surface [15]. For this reason once it is estimated the $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$ relates to the content of carboxylic groups on the solid surface and with the total acidity that this presents. Figure 6 shows the result of such relationships in a diluted Ni(II) solution with a mass ratio X of 2, to an intermediate concentration solution of ion, with an X 40, and a ion concentrated solution.

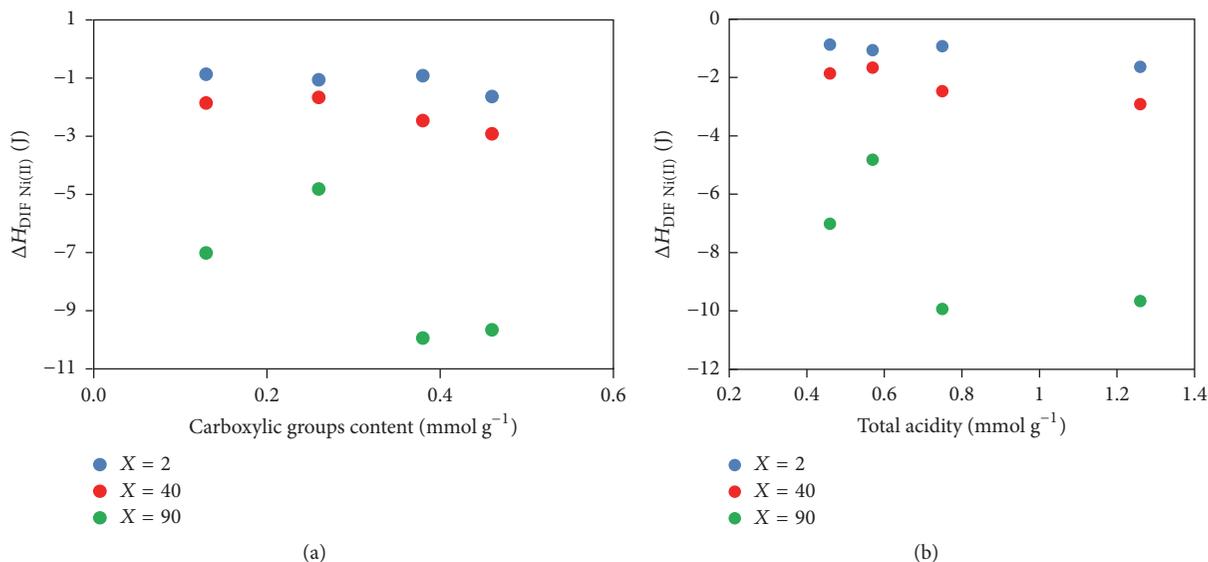


FIGURE 6: Ion Ni(II) differential enthalpy change, $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$, in function of the oxygen content groups on the carbonized surface. (a) Carboxylic groups content, (b) total acidity.

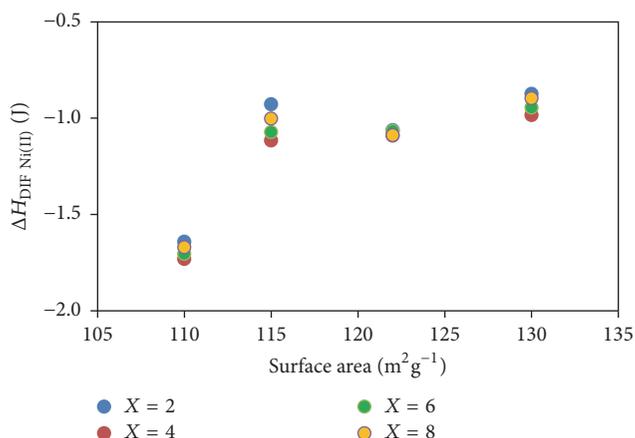


FIGURE 7: Ion Ni(II) differential enthalpy change in function of the carbonized surface area.

Relations show a similar behavior for the solutions with mass fractions of 2 and 40 for the change in the differential enthalpy ion are between -0.87 and -1.73 J but when the ion concentration increases the change in the enthalpy becomes larger and is marked by two trends: for the carbonized less oxidized solids the difference of enthalpy decreases and for solids with greater oxidation values the enthalpy differential is nearby; the above indicates that the solid interactions with ion in the mixture are intensified with the presence of oxygen groups, as shown by different works that determine the metal ions adsorption capacity in aqueous solution on solid adsorbents [15–17]. It is noted that $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$ is sensitive to the ion quantity present in the mixture and to the solid surface chemistry.

As the other characteristic of the solids that generates an energetic contribution in the mixture the surface area in Figure 7 shows the relation between the $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$ and the carbonized surface area.

The results show that the higher values for $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$ are to the carbonized CCox9 that presented the lowest value of surface area ($110 \text{ m}^2 \text{ g}^{-1}$) and the highest oxygen groups content confirming the fact that the oxygen groups in the carbonized solids interact with the ion to a greater extent than the single attraction of the surface. For the carbonized CCox3 differential enthalpy values are obtained similar between -1.06 and -1.09 J for different quantities of the ion in the mix, which can indicate effects compensation on the solid-ion interaction.

As in the mixture that is considered the solid and the solvent quantities have remained constant, by application of the Gibbs-Duhem equation:

$$\begin{aligned} (X_{\text{sólido-solvente}}) \left(\frac{\partial \Delta H_{\text{DIF}_{\text{sólido-solvente}}}}{\partial X_{\text{Ni(II)}}} \right) \\ + (X_{\text{Ni(II)}}) \left(\frac{\partial \Delta H_{\text{DIF}_{\text{Ni(II)}}}}{\partial X_{\text{Ni(II)}}} \right) = 0. \end{aligned} \quad (6)$$

This expression indicates that the variations of the partial quantities, in this case the change in the enthalpy differential, with regard to the system composition are not independent of a temperature and constant pressure [13]. Using (6) we can calculate the differential enthalpy change for solid and solvent in the mixture and this in function of ion Ni(II) mass fraction presents a behavior contrary to the ion Ni(II) differential enthalpy change, $\Delta H_{\text{DIF}_{\text{Ni(II)}}}$, as what happens with the partial molar properties in the development of the mixture thermodynamics. Figure 8 presents the results obtained for these relations to the CC carbonized without acid treatment CC.

Presenting the two trends in the enthalpy differential change, most of the values show exothermic character, and note that the change in the ion differential enthalpy increases when that of the set solid-solvent decreases. Also shown

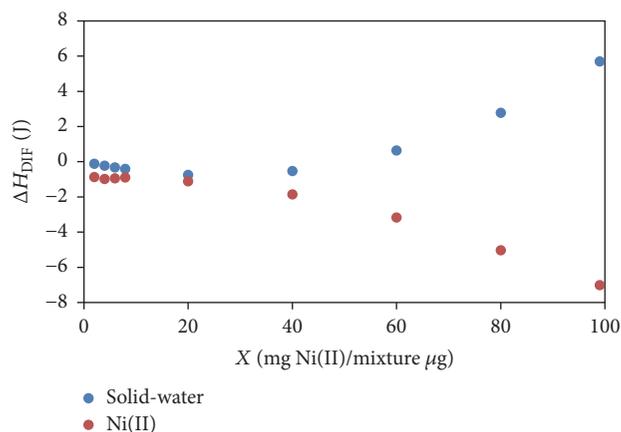


FIGURE 8: Change in the differential enthalpy (solid-solvent) and Ni(II) in function of the mass fraction of Ni(II) to the carbonized CC.

for low mass fractions changes in enthalpy are small and from a mass fraction of 40 the behaviors are larger and opposite.

4. Conclusions

Prepare four carbonized solids from corn cob with different oxygen groups contents in the surface. The surface area values of the solids are between 110 and 130 m²g⁻¹ and the total acidity is between 0.46 and 1.26 mmolg⁻¹.

From the determination of the immersion enthalpy of the carbonized solids in aqueous solutions of different Ni(II) concentration and assuming the relations of the mixtures thermodynamics, calculate the contribution of ion to the enthalpy total.

The change in the Ni(II) differential enthalpy, $\Delta H_{DIF_{Ni(II)}}$, in the carbonized is between -0.87 and -7.03 J which indicates an increase in the enthalpy change with the ion Ni(II) quantity.

$\Delta H_{DIF_{Ni(II)}}$ is related with the carboxylic groups content and with the total acidity on the surface of the solid. It is noted for a mass fraction of Ni(II) in the mixture of 90 that in the carbonized less oxidized solids the enthalpy difference decreases and for solids with greater oxidation values the enthalpy differential is nearby, which indicates that the interactions of solid with ion in the mixture are intensified with the presence of oxygen groups.

The enthalpic contribution is calculated for the whole solid-solvent in the CC carbonized without treatment acid, with values between -0.12 and 2.78 J with an opposite behavior to that of the ion Ni(II) enthalpic contribution in the mixture, complying with the Gibbs-Duhem equation.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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