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Ni(II) and Cd(II) Simple and Competitive Adsorption on Activated Carbon Oxidized. Influence of the Oxidant Agents H_2O_2 and NaClO

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Abstract: In this study, granular activated carbon, GAC, was modified by oxidation with H_2O_2 and NaClO aqueous solutions and heat treatment at 900 °C. The N_2 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 were between 687 and 876 m^2g^{-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 in the tests carried out, the adsorption capacity decreased when the content of chemical groups on the surface also decreased.

Finally, the experimental results of adsorption from the solution were adjusted to the Langmuir and Freundlich models and the first model was found to be better. With maximum adsorption capacities, the values for Ni(II) were between 3.99 and 64.9 mgg^{-1} and for Cd(II) were between 2.61 and 55.2 mgg^{-1}

The values of the competitive adsorption ions present in the solution, Ni(II) and Cd(II), in the activated carbons, decreased compared to those obtained in the simple adsorption, indicating 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 of water sources with toxic metals discharged from different industries' effluent has become a high-impact environmental problem [1-3]. The importance given to the treatment of this waste lies in the ability to accumulate metals in sediments and organisms tissues, 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.

Among the porous solids, the most activated is carbon, and its adsorption capacity depends not only on the porous texture or surface area, but also on the chemical groups on the

surface. Hence the interest has been the surface modification of activated carbon for obtaining materials with specific applications [6]. Several methods can be used for surface chemistry modification, among which, liquid phase oxidation of the surface is the one that makes use of various oxidant agents, which produce diverse oxygen groups [7].

Chemical modification allows adsorption 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 the metallic ion is present and the charge oxygen groups, which may have a basic or acidic character [8].

A characterization technique of solid-gas or solid-liquid interaction is immersion calorimetry, which allows calculating the heat quantity generated when the two phases come in contact, 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 H_2O_2 with 13% and 34%, respectively. Variations in the adsorption capacity of nickel and cadmium ions in the aqueous solution on activated

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carbon were determined, by the realization of adsorption isotherms, which is simple and competitive, whose experimental data fitted the Langmuir and Freundlich models. For the energetic interactions between the 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 was subjected to oxidation with two aqueous solutions: sodium hypochlorite, NaClO up to 13% and hydrogen peroxide up to 34%. For 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 was obtained.

For oxidation of the activated carbon with the hydrogen peroxide solution, 30 g of the activated carbon GAC was mixed with 200 mL of H_2O_2 solution to 34% at room temperature for 18 hours to obtain the GAC-H_2O_2 sample. After this time, the solid was washed until a constant pH was obtained.

Once the activated carbons were washed, they were dried in an oven at 90° C for one night, and stored in the plastic bottles under nitrogen atmosphere. Furthermore, a sample heat, CA900, treated at 900 °C from GAC was obtained to perform thermal treatment 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 initial 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 N_2 physical adsorption at −196 °C and CO_2 at 0 °C in an automatic Autosorb 3B apparatus (Quantachrome). The apparent surface area and the micropore volume 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 3 kV accelerating voltage was used to characterize the morphology of ACs, which were dried overnight at approximately 105 °C under vacuum before the 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, Na_2CO_3, and $NaHCO_3$ 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 the 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 (pH_{PZC}) was evaluated by mass titration method, for which different quantities of the 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 the pH meter (Schott CG 840B) [13].

IR Spectroscopy

IR spectra were recorded 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 allowed us to observe the main bands of stretching vibration of carbon groups attached to oxygen and hydrogen, which provided information on the types of groups that were 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 the glass bulb were separately placed in the main heat reservoir and left until meeting the thermal stability conditions. 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. The recordings were then continued for an additional time period of 20 min after immersion, followed by electrical calibration of the calorimeter. The experiments were repeated 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 were prepared with analytical reagents (Merck), from $NiCl_2.6H_2O$ and $CdSO_4.8H_2O$, using double distilled water as the solvent, respectively. The concentration range used to study adsorption was 100 to 500 mgL^{-1}. The concentration readings of the various solutions were realized byan atomic absorption spectrophotometer Perkin Elmer, ANALYST 300.

To determine the isotherms, 50 mL of every known concentration solution was taken and 500 mg of each activated carbon was added 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 a concentration equal to that of simple systems. Moreover, the concentrations of competitive metal, e.g. 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} were increased, covering all possible options to obtain 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 was adjusted to a value of 6, and the mixtures were allowed to stand for 100 hours until equilibrium was reached, followed by stirring to keep 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

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, respectively, and in Table **1,** the results obtained for the textural characterization are presented based on 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_o) estimated by the DR model, the volume Total (V_t) calculated at the saturation pressure and the narrow micropores (V_n) evaluated by applying the DR model to the CO_2 adsorption experimental data.

Table 1. **Textural parameters of the activated carbons determined from the N_2 and CO_2 adsorption isotherm at -196 °C and 0 °C.**

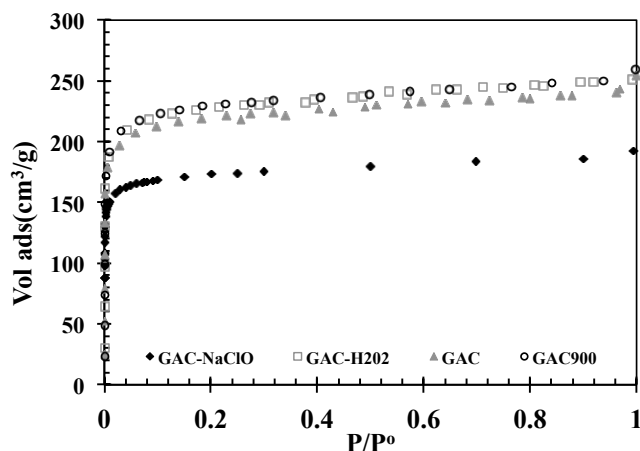| Sample	N_2			CO_2
	Área $_{BET}$ (m^{2}g^{-1})	V_0 (cm^{3}g^{-1})	Vt (cm^{3}g^{-1})	Vn (cm^{3}g^{-1})
GAC	842	0.34	0.38	0.35
GAC900	876	0.35	0.40	0.28
GAC-NaClO	687	0.27	0.30	0.21
GAC-H$_2$O$_2$	873	0.35	0.39	0.36

Fig. (1). N_2 adsorption isotherms at -196 °C of the GAC-NaClO, GAC-H$_2$O$_2$, GAC, GAC900 samples.

As observed in Fig. (**1**), the activated carbons exhibited adsorption isotherms of Type I, in which a larger amount

adsorbed with relatively low pressures were observed, showing characteristic behavior of microporous materials, being consistent with the pore volumes values obtained by the DR model. Furthermore, the total micropores volume (V_o) 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].
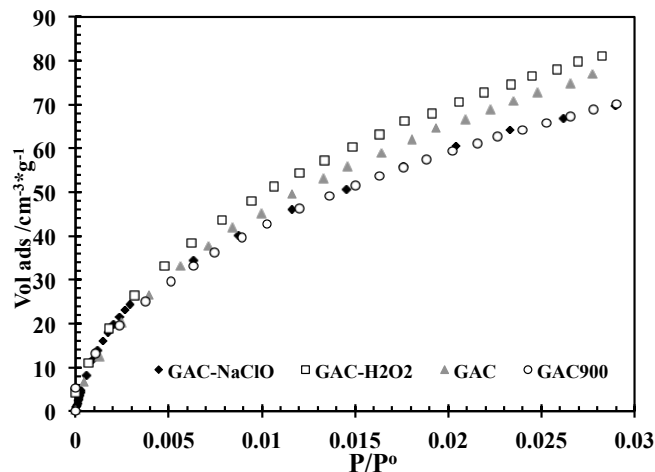

Fig. (2). CO_2 adsorption isotherms at 0 °C of the GAC-NaClO, GAC-H$_2$O$_2$, GAC, GAC900 samples.

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

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

Surface Morphology of Activated Carbons

As the activated carbon was subjected to heat treatment under nitrogen, with GAC900, an increase in the 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 GAC sample presented a variety of surface groups, with greater amount of phenolic groups and higher total acidity with respect to the total basicity, showing the

Table 2.   Density of surface groups determined by Boehm titration and pH in the point of zero charge.

Sample	Carboxílic Molec.nm^{-2}	Lactonic Molec.nm^{-2}	Phenolics Molec.nm^{-2}	Total Acidity Molec.nm^{-2}	Total Basicity Molec.nm^{-2}	pHpcc
GAC	0.052	0.029	0.061	0.141	0.065	5.4
GAC900	-	0.008	0.024	0.032	0.191	8.9
GAC-NaClO	0.035	0.056	0.350	0.442	0.106	6.4
GAC-H$_2$O$_2$	0.106	0.024	0.074	0.204	0.073	6.2

pH value at point of zero charge, pH_{PZC}, less than 7.These groups by heat treatment at 900 °C dramatically decreased and the oxidation treatment favored 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 promoted the formation of acidic groups, mainly favoring the formation of phenolic groups [17].The increase in these acidic groups was close to 70% compared to the original sample. An increase in the basic character of the surface was also observed, being 25% due to the treatment to which the sample was subjected. The change in the surface chemistry was also evidenced in the value of pH_{PZC} which was 6.5.

Fig. (**3**) shows the infrared spectra obtained for the starting active carbon GAC and the solids obtained once activated carbon oxidized with sodium hypochlorite and hydrogen peroxide solutions.
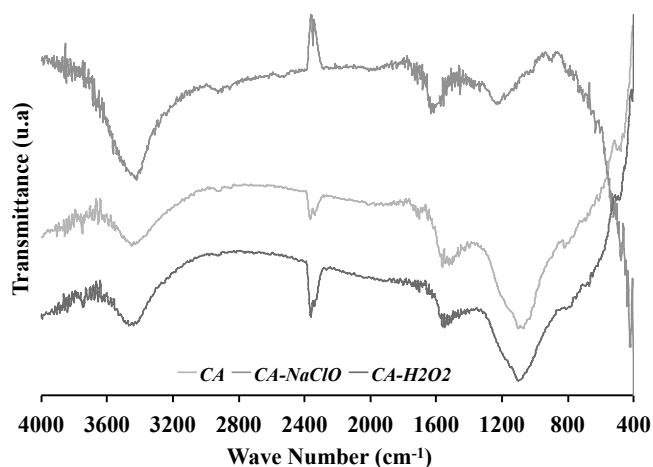
Fig. (3). FTIR spectra for different samples modified by oxidation treatment.

Mainly it was observed that after the oxidation process, there was an increase in the intensities of the peaks that are characteristic of oxygen functional groups. In the spectra, there are three bands of interest: one located between 3200-3600 cm^{-1} related to O-H stretching vibration of alcohols, carboxylic acids and chemisorbed water, another at 1500 and 1700 cm^{-1} associated with stretching vibration of C=O in ketones, esters and/or carboxyl groups. While, the peaks between 1000 and 1200 cm^{-1} are associated with groups C-O as phenol, ester, ether bonds and carboxylic acids. In the case of CA-NaClO, the activated carbon peak about 3400 cm^{-1} increased its intensity with respect to the original sample

showing an increase in the number of groups such as carboxylic acids [10].

Fig. (**3**) shows the most important changes that occurred after the treatment of the GAC sample with the GAC-NaClO and GAC-H$_2$O$_2$ samples. The FTIR of the GAC900 sample was not shown because this spectra did 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 altered 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 the solid in an apolar liquid is proportional 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. Consequently, a relation can be established between the immersion enthalpy and the surface chemical groups.

Figs. (**4**, **5**) show the thermograms obtained by immersion of the activated carbon GAC and the activated carbons oxidized in benzene and water.
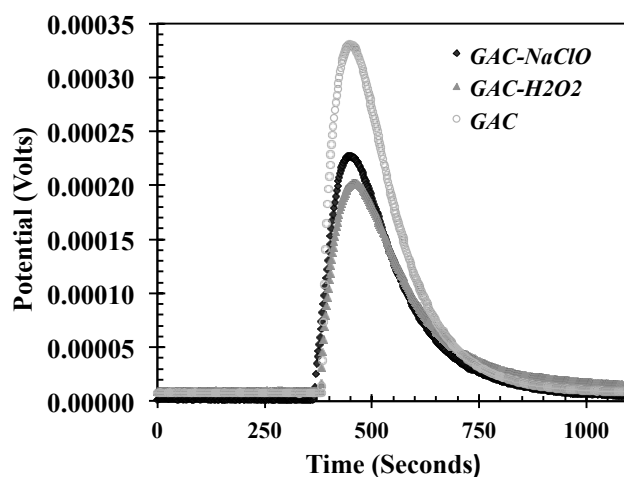
Fig. (4). Immersing thermograms of activated carbon GAC and activated carbons oxidized in benzene.

The heat generated by contacting the solid with the solvent is proportional to the area under the peak which is

evident in the graph of potential a function of time; therefore, higher energetic effect in the case of immersion of the activated carbon GAC benzene was observed, with a lower number of functional groups. While, when the activated carbons were immersed in water, the heat produced was higher for oxidized activated carbons.
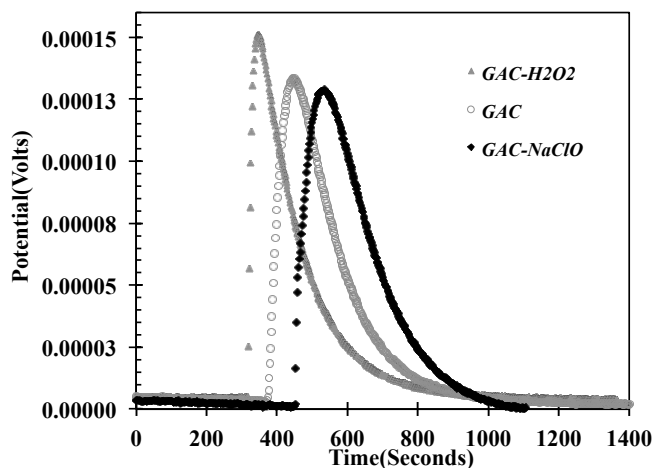

Fig. (5). Immersion thermograms of activated carbon GAC and activated carbons oxidized in water.

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 was observed that the values in the immersion enthalpies changed with the surface chemistry modifications obtained by the oxidation of the original activated carbon. The immersion enthalpy of the activated carbons in liquids showed that the 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 the values of -32.3 Jg^{-1} and -34.4 Jg^{-1} respectively. This 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 two oxidized samples, it was observed that the behavior of the immersion enthalpy in the liquid was different from that as described above, since for the GAC-

NaClO, lower immersion enthalpy was observed in hydrochloric acid -45.1 Jg^{-1} and higher was obtained for immersion in benzene -125 Jg^{-1} and water -64.1 Jg^{-1}. Regarding immersion in Ni(II) and Cd(II) solutions, the values were -61.7 and -54.8 Jg^{-1} respectively, in contrast with the activated carbon oxidized with H$_2$O$_2$ solution, in which, the interaction with the solution of Cd(II) was higher.

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

Fig. (**6**) shows the relation between the 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 increased with the content of total acid groups. Similar behavior was found in other studies examining the modification in the functional groups of activated carbons [20].
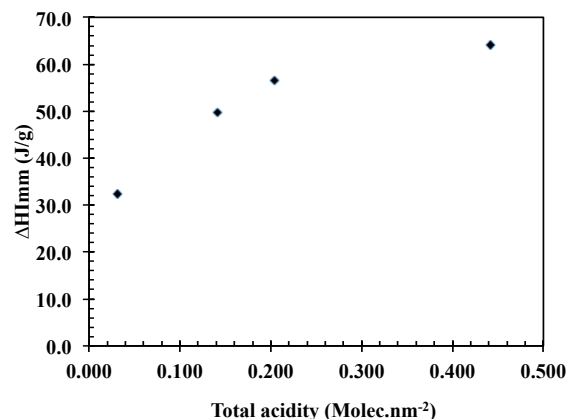

Fig. (6). Relation between the immersion enthalpy of activated carbons in water and density of acid groups.

Regarding the hydrophobic character of the surface, which was evaluated by analyzing the relationship between the immersion enthalpy in benzene and immersion enthalpy in water, it was found that this decreased with the oxidation process and gradually increased with heat treatment and was

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

Muestra	$-\Delta H_{imC_6H_6}$ (Jg^{-1})	$-\Delta H_{im\,H_2O}$ (Jg^{-1})	H.F*	$-\Delta H_{imHCl}$ (Jg^{-1})	$-\Delta H_{imNaOH}$ (Jg^{-1})	$-\Delta H_{im\,500ppm\,Ni(II)}$ (Jg^{-1})	$-\Delta H_{im\,500ppm\,Cd(II)}$ (Jg^{-1})
CA	106	49.7	2.13	51.4	57.3	49.9	34.4
CA 900	145	32.4	4.48	58.2	35.2	32.3	34.4
CA-NaClO	125	64.1	1.95	45.1	94.9	61.7	54.8
CA-H₂O₂	117	56.4	2.07	36.0	69.7	45.6	57.7

*H.F. hydrophobic Factor $\frac{\Delta H_{imc_{6}H_{6}}}{\Delta H_{imH_{2}O}}$

The standard deviations of results are between 0.1 - 1.5 Jg^{-1}.

higher in the solid treated at 900 °C. It was also considered that the hydrophobic character of the activated carbons decreased with the increase in the functional groups present in the solid surface, modifying the wetting characteristics. The activated carbon became more compatible to the water [10], which maximized the adsorption properties of ions in the solution 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 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 the activated carbon GAC-NaClO.

The experimental results for Ni(II) and Cd(II) adsorption suited to the Langmuir and Freundlich models and it was observed that the results of Langmuir model were the best. 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, for each activated carbon; however, in the case of Ni(II), greater adsorption capacity was observed on the activated carbon GAC-H$_2$O$_2$, presenting higher carboxylic content in the groups mainly interacting with the nickel ions .

For the case of Cd(II) ions, it was observed that the optimal experimental data were obtained by the Langmuir model, with the maximum adsorption capacity obtained for the activated carbon GAC-NaClO, presenting a higher phenolic content.

The significance 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 the aqueous solutions must primarily establish specific interactions between the functional groups and ions.
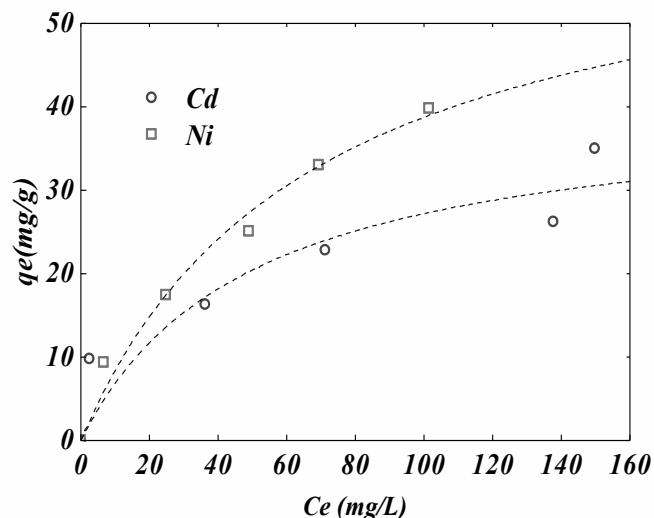

Fig. (7). Simple adsorption isotherms of Cd (II) and Ni (II) on the activated carbon CA-NaClO.

Competitive Adsorption

Ni (II) and Cd (II) are simple adsorption isotherms in solution depending on the temperature, the solution pH and surface chemistry, however; when it comes to multicomponent systems, the adsorption isotherms from one of the adsorbates are dependent on the concentration and the 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. This determines the effect of the Cd(II) concentration in the

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

Ni(II)						
Sample	**Langmuir Model**			**Freundlich Model**		
	Q$_m$	**K$_L$**	**R^2**	**K$_F$**	**N**	**R^2**
GAC	29.7	0.0120	0.993	0.111	1.15	0.815
GAC900	3.99	0.0063	0.992	0.116	15.1	0.850
GAC-NaClO	32.7	0.0114	0.998	0.098	0.85	0.857
GAC-H$_2$O$_2$	64.9	0.0148	0.992	0.159	0.36	0.942
Cd(II)						
Sample	**Langmuir Model**			**FREUNDLICH model**		
	Qm	**K$_L$**	**R^2**	**K$_F$**	**N**	**R^2**
GAC	23.3	0.0105	0.991	0.117	1.71	0.819
GAC900	2.61	0.0165	0.983	0.092	14.9	0.553
GAC-NaClO	55.2	0.0015	0.993	0.165	1.12	0.988
GAC-H$_2$O$_2$	40.6	0.0203	0.937	1.350	5.80	0.846

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

Sample	Isotherm	Langmuir Model			Freundlich Model		
		Q_m	K_L	R^2	K_F	N	R^2
GAC-NaClO	**Ni(II) Constant Isotherm**						
	Ni 100/ Cd	52.24	0.0598	0.987	0.171	1.494	0.913
	Ni 200/ Cd	47.03	0.0519	0.956	0.168	1.847	0.925
	Ni 300/ Cd	47.18	0.5839	0.946	0.768	4.252	0.902
	Ni 400/ Cd	27.81	1.9096	0.976	0.478	2.074	0.894
	Ni 500/ Cd	36.72	0.9836	0.954	1.098	4.276	0.915
	Cd(II) Constant Isotherm						
	Cd 100/ Ni	29.13	5.0670	0.957	1.091	2.009	0.820
	Cd 200/ Ni	25.12	1.0292	0.961	1.175	3.623	0.823
	Cd 300/ Ni	25.64	0.7396	0.971	1.268	4.737	0.825
	Cd 400/ Ni	14.12	1.1239	0.943	1.229	4.389	0.832
	Cd 500/ Ni	21.44	0.2847	0.953	1.112	5.281	0.910
GAC-H$_2$O$_2$	**Ni(II) Constant Isotherm**						
	Ni 100/ Cd	28.9	0.0467	0.974	0.720	0.93	0.720
	Ni 200/ Cd	23.5	0.2050	0.935	0.751	1.08	0.751
	Ni 300/ Cd	21.9	0.1982	0.944	0.712	1.30	0.712
	Ni 400/ Cd	19.9	0.1593	0.958	0.709	1.20	0.709
	Ni 500/ Cd	20.2	0.0591	0.988	0.702	0.78	0.702
	Cd(II) Constant Isotherm						
	Cd 100/ Ni	55.1	0.0024	0.984	0.982	1.13	0.982
	Cd 200/ Ni	56.1	0.0017	0.989	0.975	1.48	0.975
	Cd 300/ Ni	66.7	0.0011	0.975	0.970	2.64	0.970
	Cd 400/ Ni	59.3	0.0011	0.955	0.951	3.42	0.951
	Cd 500/ Ni	55.3	0.0009	0.962	0.970	2.58	0.970

presence of Ni(II) and vice-versa   as an approximation for the solution of such problems of contamination, because industrial waste water generally has mixtures of ions.

As simple adsorption isotherms, data for Ni(II) and Cd(II) competitive adsorption were used in the Langmuir and Feundlich models. The parameters obtained for each isotherm in which the concentration of one of the ions was 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 treated the experimental data was the Langmuir. The maximum adsorption capacity values, higher for Cd(II) adsorption when   Ni(II) concentrations remained constant, were observed in the activated carbon GAC-NaClO and for Ni(II) adsorption. These were observed when the Cd(II) concentrations remained constant for activated carbon GAC-H$_2$O$_2$.Moreover, it was also observed that the adsorbed quantities of each ion were less than when adsorption was carried out separately for each ion.

CONCLUSION

When an activated carbon was modified by surface oxidation with H$_2$O$_2$ and NaClO aqueous solutions, a variation in the surface area and acidic groups content was observed with values varying between 0.032 and 0.442 molecules.nm^2.

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

Activated carbons obtained were used to study   single and competitive Ni(II) and Cd(II) adsorption from the aqueous solution. The experimental results were suitable for Freundlich and Langmuir models. The second model was proved to be the best for the adsorption data with maximum values of adsorption capacities of Ni(II) between 3.99 and 64.9 mgg^{-1} and of Cd(II) between 2.61 and 55.2 mgg^{-1}.

Experimental data for Ni(II) and Cd(II) competitive adsorption isotherms from the aqueous solution on the activated carbons reduced compared to those obtained by simple adsorption of the ions. This indicates the effectiveness of the presence of a competitive ion in adsorption because the two ions compete for the same sites of interaction with the solid surface.

Ni(II) adsorption was observed to be higher in the activated carbon GAC-H$_2$O$_2$ which presented a higher content of carboxylic acids on the surface, whereas; the Cd(II) adsorption was higher in the activated carbon GAC-NaClO with 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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