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Study of the adsorption and electroadsorption process of Cu (II) ions within thermally and chemically modified activated carbon.

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Abstract

The aim of this work is to modify the porous texture and superficial groups of a commercial activated carbon through chemical and thermal treatment and subsequently study the kinetics of adsorption and electroadsorption of Cu (II) ion for these carbons.

Samples of three activated carbons were used. These were a commercial activated carbon, commercial activated carbon modified thermally (C-N₂-900) and finally commercial activated carbon modified chemically C-SO₂-H₂S-200). The activated carbons were characterized chemically and texturally and the electrical conductivity of them determined. Different kinetic models were applied. The kinetics of the adsorption and electroadsorption process of the Cu (II) ion fits a pseudo second order model and the most likely mechanism takes place in two stages. A first step through transfer of the metal mass through the boundary layer of the adsorbent and distribution of the Cu (II) on the external surface of the activated carbon and a second step that represents intraparticle diffusion and joining of the Cu (II) with the active centres of the activated carbon. Finally, the kinetics of the adsorption process are faster than the kinetics of the electroadsorption but the percentage of the Cu (II) ion retained is much higher in the electroadsorption process.

Keywords: Activated carbon; Adsorption; Electroadsorption; Kinetics models; Copper ions.

1. Introduction

The increased level of contamination of water due to the presence of heavy metals is a major problem for human health [1]. The environmental contamination has risen in parallel with the growth of industry and increasing world population [2]. Heavy metals are a contaminant that generate serious problems to all bodies of aqueous medium as they are not biodegradable, have high toxicity and are bioaccumulative [3-5]. Also they have a great tendency to form compounds, with mineral sources (carbonates, sulphates, etc.) and with organic substances through ion exchange, adsorption and chelation, therefore they accumulate in the environment, principally in the sediment of rivers, lakes and seas [2, 6].

Numerous recent data on the negative environmental impact of heavy metals have prompted a demand for the purification of industrial wastewater. Since heavy metals, especially, copper, zinc, cadmium, mercury, and lead until pesticide etc., are toxic [7-16] their concentration in wastewater should be reduced to environmentally acceptable levels before being discharged into the environment. In particular, copper is highly toxic because of its carcinogenic and mutagenic properties [17]. Principal sources of copper contaminates in industrial wastewater are electrolysis and metal cleaning, washing of brass units, boiler pipes, and cooking utensils, and fertilizer production. Therefore, the elimination of heavy metals from industrial wastewater is important to protect public health.

Some of the conventional techniques for removal of metals from industrial wastewater include adsorption, electrolysis, solvent extraction, chemical precipitation, membrane separation, ion exchange and other techniques [18-22]. It is known that solid phase adsorption is one of the most reliable. The adsorption process proved its advantage over other processes because of its cost effectiveness and the high quality of the treated effluents it produces.

The adsorption on activated carbon is an efficacious technique that allows the removal of copper traces in dissolution [11, 23]. To improve the capacity of adsorption of the activated charcoal, a controlled electric potential can be applied, a technique called electroadsorption.

Activated carbon found wide use as adsorbent due to its high adsorption capacity in process of adsorption/electroadsorption [24-29].

In this work, the adsorption/electroadsorption of the copper, in aqueous solution by activated carbons treated thermally and chemically with hydrogen sulfide (H_2S) and sulphur dioxide (SO_2), has been studied under a kinetic point of view. The influence of different adsorbent and the technique adsorption/electroadsorption on the process kinetic has been analyzed. Additionally, a kinetic modeling of the process has been performed and the experimental results have been fitted to three models, pseudo-first order, pseudo-second order, intra-particle diffusion [30-37].

The aim of this work is to take advantage of the H_2S and SO_2 emitted by different industries (natural gas, crude oil, and industrial streams...) [38, 39] to dope AC and then use it to increase the capability of adsorption and electroadsorption of copper.

2. Experimental

2.1 Adsorbent and adsorbate

An activated carbon (AC), particle size 1.5 mm, from Merck (E. Merck Darmstadt Germany) was used as the starting material. This commercial AC underwent two treatments with the purpose of obtaining two different electrode materials for studying and comparing their behaviour.

The first for heat treatment in N_2 to 900 °C (C- N_2 -900), as described by Valenzuela et al [40]. The aim of this treatment is only cleaning the pores of the commercial AC without modifying the starting material.

The second was obtained by treatment successively in SO_2 , and H_2S at 30 °C and transport with N_2 at 200 °C (C- SO_2 - H_2S -200). From the emissions of SO_2 and H_2S in the industry, the treatment with these gases of an activated carbon is carried out. About 18 g of carbon, placed in the experimental device at 30 °C, were floated with a stream first of SO_2 ($\phi = 50 \text{ cm}^3 \text{ min}^{-1}$) for 110 min and then of H_2S ($\phi = 50 \text{ cm}^3 \text{ min}^{-1}$) during 60 min. Afterwards, the H_2S flow was replaced by another of N_2 ($\phi = 100 \text{ cm}^3 \text{ min}^{-1}$) and the system was then heated at a rate of $5 \text{ }^\circ\text{Cmin}^{-1}$ from 30 up to 200 °C; the residence time at such a temperature was that needed to reach a constant weight, which took about 35 min [41]. This treatment allows obtaining an AC modified by sulphur.

A dissolution of copper (II) Panreac, 25 ppm, prepared with water Ultrapure Milli-Q™ was used as adsorbate.

2.2 Characterization of the adsorbent

2.2.1 Characterization of the prepared samples.

The chemical characterization was carried out using three tests: elemental analysis, immediate analysis, and surface functional groups analysis.

The chemical composition of the samples is given in Tables 1 and 2. Ultimate analysis data (C, H, N) (Table 1) were obtained in a Perkin-Elmer, model 240 C, elemental analyser. The S content for C-S and for C-C was determined using Leco equipment. For the sample C-SO₂-H₂S-200, which contains a higher amount of sulphur, the Eschka method (standard analysis, UNE 32008) was followed. Oxygen content was estimated by difference.

Immediate analysis data (moisture, volatile matter and ash) (Table 2) were gained by the thermogravimetric method described previously [41]. Briefly, this consists of effecting a fast (heating rate = 80° C min⁻¹) heat treatment of the material in N₂, from 30 to 950° C and in the subsequent combustion of the pyrolyzed residue. The fixed carbon content was calculated also by difference.

The surface functional groups and structures of the AC samples were analysed by FT-IR spectroscopy. Spectra were recorded in a Perkin Elmer® 1720 spectrometer between 4000 and 400 cm⁻¹, with 50 scans being taken at 2 cm⁻¹ resolution.

2.2.2 Textural characterization

The texture of an activated carbon plays an important role in determining its properties. The treatments applied to the commercial AC might have modified its textural characteristics, necessitating assessment of some textural aspects of the prepared samples. In this study, the textural characterization of the AC samples was accomplished by nitrogen adsorption and mercury porosimetry.

Specific surface area and micropore and mesopore distribution were studied by nitrogen adsorption. Nitrogen adsorption isotherms were analysed by means of

nitrogen adsorption at -196 °C using a semiautomatic adsorption apparatus Autosorb-1 (Quantachrome®).

Mercury porosimetry experiments were carried out in a mercury porosimeter Autoscan-60 (Quantachrome®). The computational program of the porosimeter used the values of surface tension and contact angle of 0.480 N·m⁻¹ and 140°, respectively. The mesopore (V_{me}) and macropore (V_{ma}) volumes were obtained from the mercury intrusion curves, which face the cumulative pore volume (V_{cu}) and pore radius (r), as follows:

$$V_{ma} = V_{cu}(r = 250 \text{ \AA}) \quad (1)$$

$$V_{me} = V_{cu}(r < 20 \text{ \AA}) - V_{ma} \quad (2)$$

2.3 Electrical conductivity

Based on a standard procedure previously reported [42], the DC electrical conductivity (σ) was measured at room temperature by the technique of impedance spectroscopy over the frequency range from 20 to 10⁶ Hz at a voltage of 1 V. The masses of ACs used, after oven-drying at 110 °C overnight, were around 0.09 g. Each accurately weighed sample was then poured into a hollow thick-walled PVC cylinder with an inner diameter of 0.8 cm, and compressed in air between two close-fitting brass plungers forming the electrodes, the lower one being fixed and the upper one movable. The compression pressures ranged from 99.5 to 756.0 kPa, which were achieved by applying different loads between 5 and 38 N on the upper piston. This was developed by a universal testing machine (Shimadzu(R)) with a precision of 1 μ m in the compression plate movement.

2.4 Preparation of the electrodes and electroadsorption

The electrodes to study were prepared from various raw materials. These raw materials were Carbon Black (Vulcan 3, V3), Polyvinylidene fluoride (PVDF) supply by Sigma-Aldrich Química S.L. and activated carbons (ACs). The activated carbons

were obtained from AC through treatment with N₂ at 900 °C (C-N₂-900) and SO₂, H₂S at 200 °C (C-SO₂-H₂S-200).

AC (Merck), C-N₂-900 and C-SO₂-H₂S-200 were used as materials in preparation of electrode.

The ACs powders were previously dried at 110 °C for 24 hours. The disc-shaped electrodes were prepared from powders of the modified ACs mixing them with PVDF and V3 in an agate mortar. The addition of carbon black to the AC powders improves its electrical properties [43].

Each accurately weighed sample (approximately 0.1 g) was poured into a hollow thick-walled titanium cylinder with an inner diameter of 8 mm, and compressed in air between two close-fitting titanium disks, the lower one fixed and the upper one movable, using a titanium piston. A compression pressure of 100 bars was applied for 3 minutes using a uniaxial hydraulic press (CARVER® 3912). After this process, disc-shaped electrodes of the two mixtures prepared were obtained.

Electrodesorption process has been carried out in a cuvette with 80 ml of solution of copper (II) 25 ppm, and in the presence of an activated carbon electrode and other graphite, using a voltage of 0.3V.

2.5 Analytical method

The Cu (II) concentration was measured with the aid of a Perkin Elmer flame atomic absorption spectrometer, Model Thermo Corporation, using an air-acetylene flame. Hollow cathode lamps of Cu ($\lambda = 324.8$ nm) from the same manufacturer were used as radiation sources.

2.6 Kinetic experiments

In order to study the adsorption/electrodesorption kinetics, fixed amounts of adsorbent and volumes of adsorptive solution (80 mL) of a given initial concentration 25 ppm were kept in contact at constant temperature for a given period of time previously set. With the aim of checking the evolution of the adsorption process with time, the concentration of solute was analyzed as described in the previous section. The

equilibrium time, t_e , may be defined as the minimum period of time that is necessary to keep the value of concentration unvaried (i.e., to reach the equilibrium concentration or C_e) [44].

The adsorbed amount q_t ($\text{mg}\cdot\text{g}^{-1}$) at given time, t , was determined using a well-known mass balance Eq. (3):

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (3)$$

Where q_t is the mass (mg) of solute that is adsorbed onto 0.1 g of the adsorbent once a time, t , is elapsed; C_0 represents the concentration of Cu (II) ($\text{mg}\cdot\text{L}^{-1}$) initially present in solution; C_t is the concentration of such Cu(II) ($\text{mg}\cdot\text{L}^{-1}$) a time, t ; V represents the volume of solution (L) placed in each adsorption cell; and W is the mass of AC (g) kept in contact with the solution.

The removal efficiency (X%) was determined according to the following Eq. (4):

$$X\% = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (4)$$

In general, the retention of metal ions from aqueous solutions by adsorption/electroadsorption depends on chemical mechanisms involving the interactions of the metal ions with the specific active groups associated with activated carbon [45]. Therefore, the adsorption/electroadsorption kinetics indicates the evolution of each of the stages through which it is carried out and which one is which controls the process (chemical reaction, diffusion and/or mass transfer). To verify the above, the data have been considered using the models described below, in order to determine the best fit of the experimental data to each one of them.

2.6.1 Pseudo first order model

The pseudo-first order equation – also known as Lagergren equation – is based on the assumption that the metal ion is assigned a site of adsorption of the adsorbent material, which in terms of speed of reaction is expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

where k_1 is the adsorption rate constant (1/s), q_t denotes the mg of solute that is retained per mass unit of the adsorbent at a given time, t (mg/g), and q_e is the value of q (mg/g) reached once the equilibration time, t_e , is elapsed. Eq. (5) may be integrated as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

Consequently, if the kinetic data fit to the pseudo-first order model a plot of $\log(q_e - q_t)$ versus t should give rise to a straight line. The slope and the intercept of this line can be easily used to determine the values of k_1 and q_e , respectively.

2.6.2 Pseudo second order model

Blanchard et al. [46] proposed the so-called pseudo-second-order model in the 1980. Approximately, 15 years later Ho and MacKay [47] published a modified equation that has been widely applied in the last years [48-58]. In this model is assumed that the adsorbate is adsorbed in two active sites of the activated carbon. The mathematical expression of this model is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

where k_2 is the adsorption rate constant of pseudo-second order model (g/mg min). The integrated form of Eq. (7) is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Analogously to the pseudo-first order model, from the slope and the intercept, respectively, of the t/q versus t plots the values of q_e and k_2 can be calculated for the pseudo-second order kinetic model.

2.6.3 Intraparticle diffusion model

The hypothesis of the mechanism of intraparticle diffusion inside the pores of the adsorbent particle is based on solute transport through the internal structure of the pores of adsorbent and the diffusion itself in the solid, which leads to the adsorbent having a homogeneous porous structure. Weber and Morris (1963) concluded that in a process controlled by adsorption in pores, the initial speed is directly proportional to the concentration of the solute. Intraparticle diffusion is characterized by the dependency between the specific adsorption and the square root of the time, being the slope the speed of the intraparticle diffusion.

Based on the above, the equation that defines the intraparticle diffusion is given by:

$$q_t = k_{id}t_e^{\frac{1}{2}} + C \quad (9)$$

where k_{id} is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$) and C (mg/g) is a parameter related to the thickness of the boundary layer. In general, noticeable boundary layer effects are expectable if the value of C is high. In other words, if the q_t versus $t^{1/2}$ plot provides a straight line passing through the origin (i.e., with a value of $C = 0$), then it may be assumed that the adsorption process is mostly controlled by intraparticle diffusion. On the contrary, if the q_t versus $t^{1/2}$ plot exhibits more than one single linear plot, then it may be concluded that the adsorption process consists of two or more individual steps.

This equation has been used by different researchers [59-62] in order to determine whether intraparticle diffusion is the rate-limiting stage of the dynamics of adsorption/electroadsorption of metal ions.

3. Results and Discussion

In this section, the results obtained experimentally as well as those calculated from them are described and discussed.

3.1 Characterization of the prepared samples

Chemical and textural analyses were performed in order to obtain detailed information of the starting material and the prepared samples.

3.1.1 Chemical analyses

The data of the elemental analysis of the samples are presented in Table 1.

Table 1

Data of the elemental analysis.

Samples	% C	% O	% N	% H	% S
AC	83.58	14.26	1.13	0.88	0.15
C-N ₂ -900	87.74	10.42	1.16	0.50	0.18
C-SO ₂ -H ₂ S-200	76.50	11.49	1.28	0.54	10.19
a dry base					

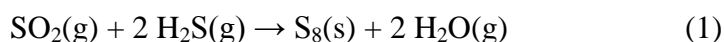
AC hydrogen content (0.88%) has a value that can be regarded as normal for carbons between 0.5% and a 2.0%, depending on the starting material and method of preparation [63, 64]. In terms of the content of nitrogen (1.10%), this is superior to the average value determined for the activated carbons prepared from woods above, where this value is of the order of a 0.9% [65]. This significant difference between both values is the result of processes of pyrolysis and activation that tend to produce an enrichment in nitrogen (around 0.9% in vegetable carbons and 1.5% in activated carbons). Also it is considered that most of the nitrogen in activated carbons tends to be part of inorganic salts.

The sulphur content of the AC is within the values found for other activated carbons derived from lignocellulosic raw materials.

Regarding the sample C-N₂-900, prepared from the AC, some significant changes in its elemental composition occur with respect to the starting material. Thus, it can be seen that carbon content increases significantly, and nitrogen and sulfur contents increase slightly, while the hydrogen and oxygen experience a substantial decrease (H goes from 0.9 to 0.5 and O from 14.3 to 10.4). These variations in the values listed in Table 1 are the result of the removal of volatile materials as a result of heat treatment to which it was subjected in N₂ atmosphere.

Finally, sample C-SO₂-H₂S-200, has a sulphur content higher than the rest of the samples, as expected, and less oxygen content than the starting AC sample. This behavior can be easily justified if it is considered that the adsorbed and/or

chemoadsorbed SO₂ (and to a lesser extent the groups with links C-S-O) react with H₂S (g) according to the reaction (1):



This justifies the high sulphur content. In addition, the isothermal treatment at 200 ° C not only facilitates the fusion of sulphur in carbon, but also produces partial volatilization of the sulphur formed (carryover in nitrogen flow).

In Table 2, data for the immediate analysis are displayed.

Table 2
Immediate analysis.

Samples	Humidity	Volatile mat. ^a	Ashes	C _{Fix} ^a
	%	%	%	%
AC	10.87	7.20	1.60	80.33
C-N ₂ -900	5.35	3.87	1.61	89.17
C-SO ₂ -H ₂ S-200	3.86	12.77	1.41	81.96

^a dry base

The humidity content of the different samples varies between 3.86 and 10.87%. The high humidity value of the sample AC (10.87%) is in accordance with the high adsorptive capacity of the activated carbons. These materials can retain significant amounts of water, depending on the temperature and/or the vapour pressure of water in the surroundings. This would explain the lower humidity content than for the sample prepared in an inert atmosphere and at temperature of 900° C.

In the sample C-SO₂-H₂S-200, the H₂S that acts as a reducer, decreases the groups or molecules with atoms of oxygen, so it will retain less water. At temperature of 200 ° C the reductive nature of the H₂S is greater, so there would be less oxygen atoms left able to fix water molecules.

In Table 2, it is evident that the volatile material content of the sample C-N₂-900 is significantly lower than the AC. This could be due to the sample C-N₂-900 being prepared from the AC in an inert N₂ atmosphere and at temperature of 900 ° C, which leads to the loss of volatile materials at this temperature.

On the other hand, for C-SO₂-H₂S-200, the volatile material and carbon fixed contents are consistent with a large presence of sulphur, which proves the effectiveness of the method when introducing sulphur into the carbon. Finally, it is apparent that the contents of ashes are very similar, in all the samples.

In light of the data provided by FT-IR spectrum, between 4000 and 450 cm⁻¹ (Fig. 1) are a number of absorption bands. These bands are very similar for all samples except for those corresponding to the sample treated with sulfur compounds which have bands assigned to groups C=S y S=O.

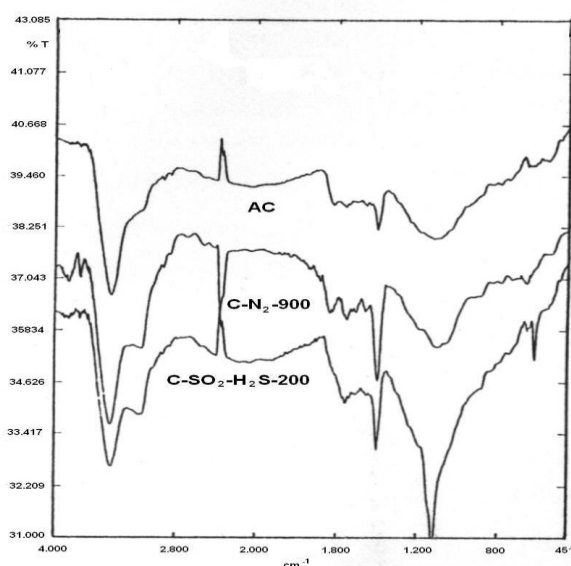


Fig. 1. FT-IR spectrum of the samples.

The most significant bands are included in Fig. 1 and are explained as shown below. A band and a shoulder situated above 3000 cm⁻¹ is usually attributed to vibration ν (O-H) in hydroxyl groups involved in link by hydrogen bridges (H₂O...H...OH₂)⁺ type between water molecules and superficial acidic groups protons [66].

Between 1700 and 1400 cm⁻¹ are a series of bands or peaks that have been associated with groups C=O highly conjugated in a quinone configuration [67-70], with skeletal vibrations in aromatic rings whose intensity is increased with the presence of phenolic or ether groups, with structures C-O type [71].

The C-SO₂-H₂S-200 spectrum shows differences from other samples that clearly highlight the changes occurring on the surface chemistry of carbon when the material is subjected to successive treatment in SO₂ y H₂S. For this sample, the radiation adsorption of the groups C=S and S=O in the region of the spectrum between 1350 y 900 cm⁻¹ is apparent. It could be considered that, due to an unknown reaction mechanism, some of these groups or other ones with a similar composition formed on the surface of carbon vibrate with similar wave numbers.

In view of the results provided by FT-IR, it can be deduced that the treatment of the carbon influences the superficial chemical composition of the samples. Nevertheless, from the results obtained during the preparation of the samples and the data from the elemental and immediate analysis, it is probable that a fraction of the superficial sulphur is not detected by FT-IR.

3.1.2 Textural characterisation

The parameters of the porous texture (Table 3) have been determined from the adsorption isotherms of N₂ (Fig. 2) and the mercury porosimetry.

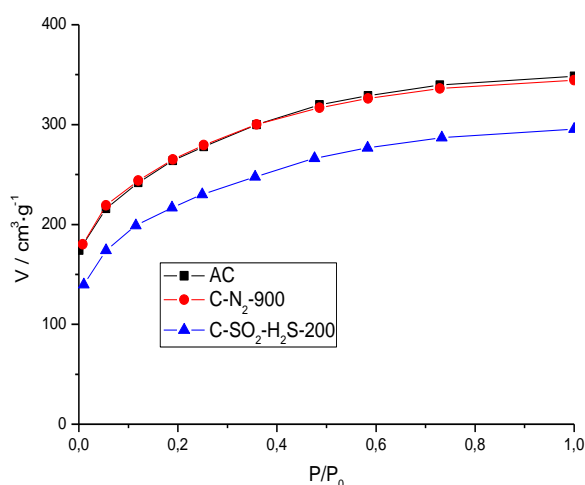


Fig. 2. Adsorption isotherms of N₂ at -196 °C.

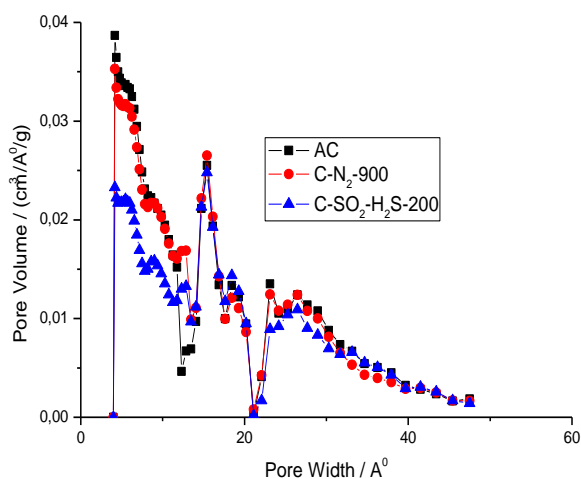
In the Fig. 2 it is observed that, all the isotherms present an bend opened, characteristic of the microporous materials and with a slightly mesopore tendency. Therefore, the samples study object are fundamentally carbons with micro-mesopore structure.

Table 3

Textural parameters.

Samples	S_{BET} ($m^2 \cdot g^{-1}$)	V_{mi} ($cm^3 \cdot g^{-1}$)	V_{me} ($cm^3 \cdot g^{-1}$)	V_{me-p} ($cm^3 \cdot g^{-1}$)	V_{ma-p} ($cm^3 \cdot g^{-1}$)
AC	921	0.367	0.163	0.100	0.260
C-N ₂ -900	922	0.367	0.159	0.050	0.280
C-SO ₂ -H ₂ S-200	764	0.302	0.158	0.090	0.240

From the data obtained for the prepared samples (Table 3), it can be deduced that the development of the porosity in the regions of micro and mesopores is higher for the samples AC and C-N₂-900 against the sample C-SO₂-H₂S-200. It is also seen that the samples AC and C-N₂-900 show a nearly identical porous development. This fact seems to indicate that the thermal treatment performed in an inert atmosphere on the initial activated carbon AC to prepare the sample C-N₂-900 does not affect, in a significant way, the increase in the porosity. This could be due to the fact that AC is a commercial carbon that already underwent treatment in a nitrogen atmosphere during its preparation and the only possible variation may be due to the temperature in which it was prepared.

**Fig. 3.** Pore size distribution curves of the samples.

As can be seen in Table 3, the contribution of the micropores and narrow mesopores not only influence the porous texture, but also the participation of the V_{me-p} mesopores and V_{ma-p} wide macropores. These values show that the sample AC ($V_{me-p} = 0.100$

$\text{cm}^3 \cdot \text{g}^{-1}$) thermally treated C-N₂-900 ($V_{\text{me-p}} = 0.050 \text{ cm}^3 \cdot \text{g}^{-1}$) undergoes a decrease in the $V_{\text{me-p}}$ with respect to AC and that this decrease is probably due to the transformation of the mesopores into macropores as a result of the treatment. Equally the C-SO₂-H₂S-200 sample undergoes a loss of mesopores and macropores probably as a result of the sulphur deposited in pores (see Table 1).

3.1.3 Conductivity

The electrical conductivity is defined as the ability of a body to allow the passage of electric current through it. Therefore, it is seen in Fig. 4 that as the pressure on carbonaceous samples increases, the number of contacts between the particles increases and as a result the conductivity increases in all samples.

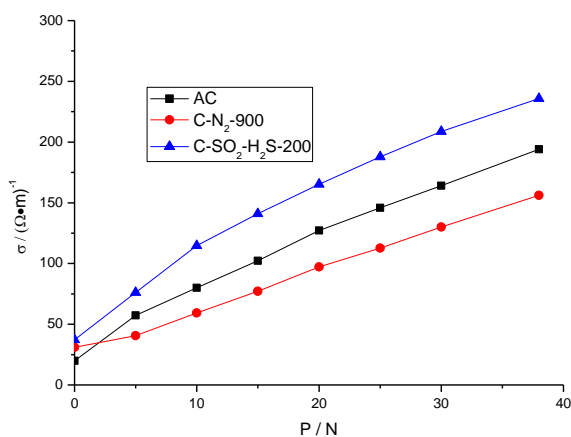


Fig. 4. Electrical conductivity of the samples against the pressure.

The conductivity increases in the following order $\text{C-SO}_2\text{-H}_2\text{S-200} > \text{AC} > \text{C-N}_2\text{-900}$. The C-SO₂-H₂S-200 sample has a higher conductivity value than the others, probably due to the presence of functional groups C=O, C=S, S=O etc. (Fig. 1). The SO₂ (g) behaves as an oxidant against the carbon, causing partial gasification of the material by attack of the reducing superficial groups and even the carbon atoms. This would result in the retention of sulphur chemically attached to the carbon atoms, as well as to the adsorption and chemisorption of SO₂ on the carbon surface. Subsequent treatment with H₂S (g) may result in the drag of SO₂ (g) adsorbed as the reaction of part of this with the H₂S (g).

This global process, ultimately leads to the presence of superficial groups on the surface of the carbon (Fig. 1) that result in the increase in electrical conductivity in the C-SO₂-H₂S-200 sample.

The value of conductivity of the other samples AC > C-N₂-900, could on one hand be due to the presence of graphitized ordered structures and on the other to the presence of surface groups in its structure. In Table 3, it is shown that the textural effect doesn't exert a significant influence as evidenced by similar values for the samples AC and C-N₂-900 although the conductivities of them are different.

Therefore, everything seems to indicate that when AC undergoes a new thermal treatment in nitrogen atmosphere (C-N₂-900), two things can happen: on one hand, volatile components of the material can be transported from the position they occupy in the carbonous matrix to the pores or the outer surface; on the other hand, volatile species (including radical species) can be produced by rupture of carbon structural units (loss of superficial groups) and as a result loss of electrical conductivity with respect to the AC sample.

In the commercial AC sample, it is likely that at the temperature at which it is prepared, during the release of volatile material, rearrangement of the parallel layers of carbon atoms could take place, a process known as of graphitization, with the result of a more orderly structure. This effect would explain the high value of the conductivity of the AC sample with respect to the C-N₂-900 sample.

All the above would be consistent with literature by other authors [72], indicating that the electrical conductivity is mainly determined by the intensity of the graphitization, the porous structure and the existence of a heterogeneous surface of elements such as oxygen, nitrogen, sulphur, etc.

3.2 Kinetic study

Equilibrium times of the adsorption and electroadsorption kinetics of CuSO₄ on different activated carbons are presented in Table 4. The electroadsorption was determined using a voltage of 0.3V [68].

Table 4

Equilibrium times and percentage of retention of Cu (II) ions in the kinetic process of adsorption and electroadsorption.

Samples	t_e (adsorption)	X	t_e (electroadsorption)	X
	min	%	min	%
AC	1440	48.8	2880	85.9
C-N ₂ -900	1440	56.3	2880	87.3
C-SO ₂ -H ₂ S-200	1440	27.7	2880	73.8

It is deduced from the table that the electroadsorption process presents equilibrium times higher than the adsorption process. This behaviour could be related, in the process of adsorption, to the presence of superficial groups. In the process of electroadsorption, it could be related to superficial groups and the ionic mobility of copper ions caused by electrical voltage. This last effect gives rise to the increase in the number of contacts between the active sites on the surface of the activated carbon and copper ions. The percentage of retention of copper ions in the adsorption process is 48.8% for AC and 56.3% for C-N₂-900 and is directly related to the porous structure and the presence of superficial groups. In the C-SO₂-H₂S-200 sample, the low value (27.7%) is related to the quantity of sulphur deposited that clogs the pores (Table 1). However, the percentage of retention in the samples that underwent electroadsorption is significantly higher than in the adsorption process (AC, 85.9%, C-N₂-900, 87.3% and C-SO₂-H₂S-200, 73.8%) that would justify the effect of electrical voltage and ultimately the goodness of the method.

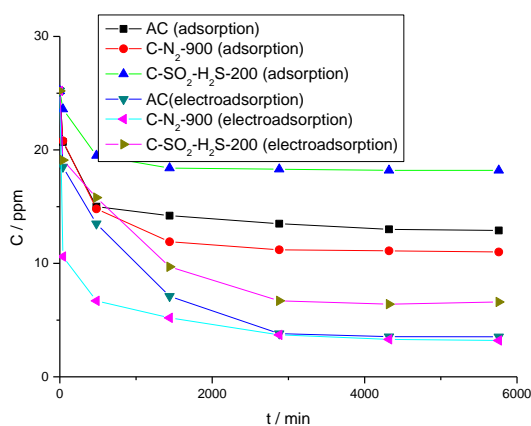


Fig. 5. Adsorption and electroadsorption kinetics of the prepared samples

3.2.1 Kinetic modelling of the process

Kinetic models of adsorption and electroadsorption are important in retaining ion copper from wastewater. In this study were tested different kinetic models described in paragraph 2.6. The velocity constants of each kinetic equation for the different samples were calculated as described in paragraphs 2.6.1 to 2.6.3. The statistical parameters such as the regression coefficient between experimental values and the ones predicted by the kinetic model were calculated to find the best fit.

3.2.1.1 Pseudo first order kinetics

The pseudo first order equation (Eq. 5) is represented, for the adsorption and electroadsorption processes in Fig. 6.

The values of the velocity constant k_1 and the correlation coefficient R^2 are presented in Table 5.

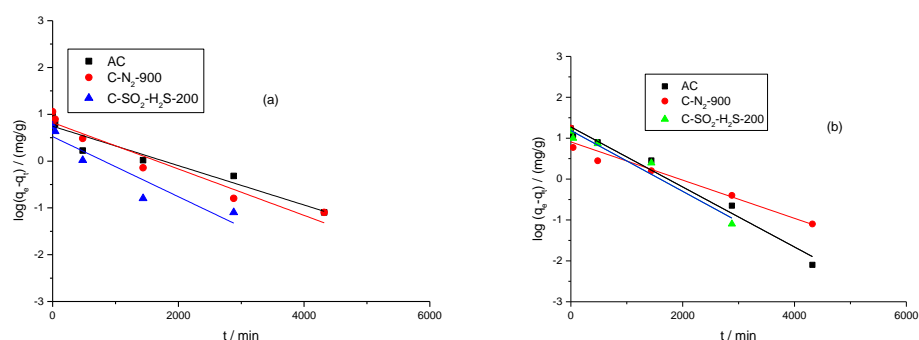


Fig. 6. Graphical representation of the pseudo first order model: (a) adsorption, (b) electroadsorption.

Table 5

Kinetic parameters of adsorption (A) and electroadsorption (B).

Samples	(A) Adsorption								
	Pseudo –first order			Pseudo –second order			Diffusion		
	q_e	k_1	R^2	q_e	k_2	R^2	C	k_{id}	R^2
AC	5.6	$9.7 \cdot 10^{-4}$	0.912	10.0	$7.7 \cdot 10^{-4}$	0.999	4.9	$7.6 \cdot 10^{-2}$	0.661

C-N ₂ -900	6.6	$1.1 \cdot 10^{-3}$	0.930	11.6	$6.4 \cdot 10^{-4}$	0.999	4.9	$1.0 \cdot 10^{-1}$	0.702	2.4	$5.2 \cdot 10^{-2}$
C-SO ₂ -H ₂ S-200	3.3	$1.5 \cdot 10^{-3}$	0.942	5.7	$1.5 \cdot 10^{-4}$	0.999	0.571				
(B) Electroadsorption											
Samples	Pseudo –first order			Pseudo –second order			Diffusion				
	q _e	k ₁	R ²	q _e	k ₂	R ²	C	k _{id}	R ²		
AC	18.8	$1.7 \cdot 10^{-3}$	0.976	18.3	$1.9 \cdot 10^{-4}$	0.996	5.7	$1.8 \cdot 10^{-1}$	0.869	12.3	$8.0 \cdot 10^{-2}$
C-N ₂ -900	8.1	$1.1 \cdot 10^{-3}$	0.934	17.8	$6.3 \cdot 10^{-4}$	0.999	0.846			4.8	$1.6 \cdot 10^{-1}$
C-SO ₂ -H ₂ S-200	15.4	$1.7 \cdot 10^{-3}$	0.951	15.8	$2.1 \cdot 10^{-4}$	0.994	0.870				

From the results in Table 5 and Fig. 6, it may be concluded that the pseudo first-order model does not fit the data of adsorption and electroadsorption kinetics of the Cu (II) in the prepared samples and thus the process is not entirely a first order reaction. Similarly, other research [69] has found that this model is not optimal to fit the data of adsorption kinetics on activated carbons.

3.2.1.2 Pseudo second order model

Additionally, the pseudo second order kinetic model was applied to assess fit with the experimental data. The graphs were produced with the kinetic equation of pseudo second order from the experimental data for the different samples. The resulting graphs are shown in Fig. 7. Adsorption rate, velocity constant k_2 and the regression coefficient R^2 values are shown in Table 5.

Q_e and k_2 values decrease in the process of adsorption and are very similar for AC and C-N₂-900 samples that is in perfect accordance with its pores distribution and the presence of superficial groups. The C-SO₂-H₂S-200 sample has lower q_e and k_2 values than the other samples. All this could be due to the presence of sulphur in its pores that would hamper the process of adsorption.

q_e values in the process of electroadsorption are very similar between 18.3 and 15.8 although the k_2 values lower than those determined in the process of adsorption for the same samples.

The pseudo second order kinetic model describes well the adsorption and the electroadsorption of the Cu (II) ions according to the regression coefficients; these are usually above 0.990 and are higher than the pseudo first order model ones. This can be explained by the adsorption mechanism, which involves valency forces through the shared use or exchange of electrons between the Cu (II) ions and the adsorbent.

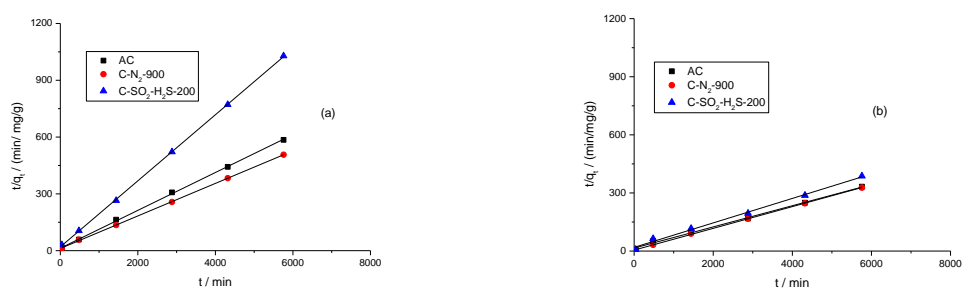


Fig. 7. Graphical representation of the pseudo second order model: (a) adsorption, (b) electroadsorption.

3.2.1.3 Intraparticle diffusion

Adsorption and electroadsorption kinetics tend to be controlled by different mechanisms. The intraparticle diffusion kinetic model permits study of the copper ions' diffusion mechanism in the prepared samples. The adsorption and electroadsorption kinetics with activated carbons are due to mechanisms of external diffusion, by transport of the adsorbate from the outer layer to the adsorbent surface, and intraparticle, from the adsorbent surface to the internal binding sites. For this reason, both types of models are used to evaluate the predominant mechanism [75]. According to Weber and Morris (1963) [76], if the intraparticle diffusion is the limiting stage of the speed of the process, the graphical representation of the amount of copper ions retained against the square root of the time of contact, should give a straight line, which will pass through the origin of coordinates. This would indicate that the intraparticle diffusion would be the only limiting mechanism of the speed of the process in removing ion copper from the dissolution. The first linear part corresponds to the adsorption period (Fig. 8a) between 0 and 30 min, and represents the external mass transfer or heavy metal diffusion through the limit layer of the adsorbent, with a rapid distribution of Cu (II) on the external surface of the activated carbon. Because of the spontaneity of the adsorption process, this first part of the

process can be considered fairly common to what has happened with other adsorbents [77]. The second linear portion corresponds to the adsorption period between 30 and 90 minutes, and represents the intraparticle diffusion and union of the Cu (II) with the internal active sites of the activated carbons.

Fig. 8b shows multilinearity in the electroadsorption process with two well-differentiated regions for all the activated carbons tested. The first linear part corresponds to the electroadsorption period (Fig. 7b) between 0 and 45 min, and represents the diffusion of the ions copper through the limiting layer of the adsorbent. The second linear portion corresponds to the electroadsorption period between 45 and 90 minutes, and represents the intraparticle diffusion and union of the Cu (II) with the internal active sites of the activated carbons.

The kinetic parameters corresponding to the intraparticle diffusion are presented in Table 5. Lower regression coefficients (R^2) are observed than for the pseudo second order kinetic model.

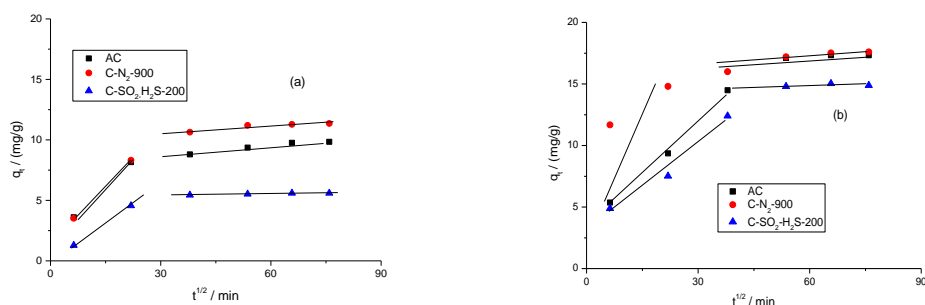


Fig. 8. Graphical representation of the intraparticle diffusion model: (a) adsorption, (b) electroadsorption.

4. Conclusions

Both the AC and the samples prepared by thermal or chemical treatment have a very similar porous development, suggesting that the porosity does not exercise a determining influence on the behaviour of the samples in the Cu (II) ion retention process.

The equilibrium time in the adsorption process (1440 min) is lower than the equilibrium time in the electroadsorption process (2880 min). The kinetics of these processes would be a pseudo second order one and with a kinetic mechanism that takes place in two stages. A first stage with the diffusion of copper ions through the limiting layer of the adsorbent and a second one corresponding to the intraparticle diffusion and union of the Cu(II) with the active sites of the carbons.

Given the results, two well-differentiated behaviours can be observed. On one hand, the presence of superficial groups seems to be the determinant of the adsorption process, and on the other, in the electroadsorption process the electric current joins to the effect of superficial groups that can be the cause of the presence of polarized groups that facilitate the process of retention of copper ions. This polarization of the superficial groups would be more pronounced in the C-SO₂-H₂S-200 sample.

Finally, the electroadsorption process enables a much higher percentage of efficiency than the adsorption process to be obtained.

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