OBTAINING ADSORBENTS THROUGH THE CONTROLLED CARBONIZATION OF LIGNOCELLULOSIC RESIDUES

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Abstract

The influence of carbonization on the adsorptive capacity of lignocellulosic residues extracted through the evaporation of Kraft black liquor is studied in this paper. The main objective is to obtain specific adsorbents that remove Ni from aqueous acid solutions. The black liquor used comes from the processing of eucalyptus wood. The evaporation treatment takes place at 100ºC until the liquor is dried (percentage of solids 6-8%). Afterwards, the collected solid is carbonized in an N_2 atmosphere with variable treatment time and temperature in order to study their influence over the adsorptive capacity of the adsorbent. Such property is evaluated through the quantification of the Ni adsorbed from standard solutions containing 20ppm of Ni by the adsorbent. When quantifying the remaining Ni concentration in the solutions, it was found that the maximum adsorption achieved was of 99%. The characterization of the pure adsorbent indicated that the material possessed a surface area lower than 5 m^2/g and it also showed the presence of hydroxyl and carboxyl groups on the surface of the adsorbent. In addition, during the evaporation water is lost but the inorganic elements present in the liquor become part of the solid adsorbent collected. It s possible that the high adsorption of Ni is the result of the combined action of the surface organic groups and the residual inorganic elements. Finally, results indicate that the carbonization time bears little influence over the adsorptive capacity of the end material.

Key Words
Adsorption, Carbonization, Heat Treatment

Introduction

The widely used chemical process to transform Wood in pulp for the manufacture of role and other related products is the Kraft process (Baptista et al, 2006), (Gellerstedt et al, 2004). The principal target of this process is to achieve the separation of the cellulose fibers of the lignin and of any other compound with the purpose of producing the appropriate pulp. During this process there is generated a current of by-product known as black liquor that is characterized precisely by an intense black color, which changes his tone for dilution, to reddish coffee and shows tendency to form froth. This black liquor is a miscellany of organic and inorganic compounds, of solid dissolved and suspended. The solid ones in suspension are mainly cellulose fibres, whereas in solution more than 70% of the organic dissolved compounds are fragments of the soluble lignin (Rohella et al, 1996), carbohydrates and other compounds derived from the wood. Also in solution alkalis are without reacting, sodium sulphate and sodium bisulphate, chlorine, fillers like talc, kaolinite, titanium oxidize, aluminiun sulphate and metals like Cr, Hg, Pb, etc. (Rohella et al, 1996). The black liquor composition depends on the type of processed wood and the manufacturing process utilized.

Although the black liquor Kraft is utilized grasp as an energy source for modern kraft mill and the inorganic products recover, his use as source of chemical products keeps on being very poor. Lignin is the principal compound that is extracted from the black liquor and the volume of his applications turns out to be marginal opposite to that of the cellulose or the hemicellulose (Gosseling et al, 2004), components also of the wood as lignin. There are great studies that have been realized and keep on being realized in an attempt for extending the applications of lignin.

The relative amounts of monolignol units differ between plants, giving place to different types of lignin nevertheless all of them have in common several functional chemical groups, such ace hydroxil (phenolic or alcoholic), methoxyl, carbonyl and carboxyl, in various amounts (Boerjan et al, 2003), (Ralph et al, 2004), (Boeriu and Bravo, 2004), (Chakar et al, 2004).

Taking as a starting point this complexity of functional groups become oxygenated in lignin, many investigators have realized studies directed to the removal of heavy metals of liquid effluents that have included the use of different bioadsorbents such as: quitosan, vegetable crust, cork, fungi, seaweed, eucalyptus (Ibarra et al, 2005). In the particular case of the lignin, his specific activity as adsorbent it has been proved in diverse investigations, where it has been demonstrated that so much the lignin (Pérez et al, 2006a), as its derivatives are effective in the removal of: touches of poisonous metals, between them: Cr (Dupont and Guillon, 2003), Cu (Villaescusa et al, 2004), Ni (Basso et al,, 2002), (Pérez et al, 2006b), Cd (Demirbas, 2004), Hg (Koch and Roundhill, 2001); as well as also of pesticides (Rupp and Zuman, 1992), phenols, poly-aromatic hydrocarbons and cloric hydrocarbons (Dizhbite et al, 1999).

The lignin and other lignocellulosic materials have been studied as precursors of activated coal. The most of the works made on pyrolisis of lignocellulosics materials they emphasize the composition of volatile products, nevertheless the information on the characteristics of the solid is little (Sharma et al, 2004). A recent rewied realized by Suhas, (Suhas et al,, 2007) comments on the most excellent studies on this topic and concludes that it is possible to obtain activated carbons from lignin with such a high quality as the commercial carbons, nevertheless it establishes that adaptation of the available knowledge on other carbonaceous materials towards the lignin still needs from investigation and concludes that it is necessary to deepen the studies of the pyrolisis of lignin during carbonization phases and activation.

On the other hand, the majority of the studies on lignina and similar products use it in pure form, which presupposes a chemical treatment for the lignin extraction from black liquor. The study that here appears tries to explore the route of the global revaluation of the black liquor Kraft using a simply thermal process developed in two stages. In the first one of them a process of simple evaporation is executed, to atmospheric pressure and a maximum temperature of 110ºC that allows to obtain a solid gross residue which should contain the miscellany of organic and inorganic compounds originally dissolved in the black liquor. Later, in the second phase, the preparation of a char is studied by means of carbonization of the solid residue, to atmospheric pressure and in a status of temperatures of 350ºC to 550ºC. The obtained char is characterized by means of elementary analysis, superficial area, diameter and volume of pores, ^{1}HRMN and FTIR. Later the potential adsorbent is evaluated from the char prepared to extract Ni from watery solutions.

Materials and Methods

1. Raw Material

There was used a sample of Black Liquor (BL), given by MOCARPEL company of the group Smurfit Cartón of Venezuela. This liquor contains 7% of soluble lignin. Also there was used a commercial sample of alkaline lignin Kraft (INDULIN AT), which contains 3% of ashes, 97 % lignin, 5 % moisture and pH = 6,5 provided by WESTVACO company.

2. Obtainment of Lignocellulosic Residual

To obtain the lignocellulosic material black liquor was submitted to evaporation. Three methodologies were evaluated: a) use of light from below, b) use of light from the top and c) evaporation in plate of warming. In the cases a and b ones worked with a light bulb of 150 watts and voltage was regulated up to a maximum of 120 volts. In all cases the following procedure was applied: 100ml of BL were warmed between 90 ºC and 110 ºC, the times of dried were 2, 4,5 and 192 hours respectively (just c got agitation). From now on the solid residue obtained by this route will be named Lev. This **Lev** was characterized by means of elemental analysis (%C, %H, %S), ^{1}HNMR and FTIR. Additionally, an analysis of UV-visible spectroscopy was made to determine the content of lignin of the **Lev**. For this test the method of purification of lignin was used developed by Sun (Sun et al., 1999).

3. Carbonization of Lignocellulosic Residue

The **Lev** once obtained was carbonized, in a tubular electrical oven, which operates in inert ambient (N_2), at atmospheric pressure and to variable conditions of temperature and time. There were processed samples of 0.5g of **Lev**.

Two series of essays were designed: First one there was evaluated the effect of the temperature of carbonization, supporting the time of constant carbonization in 20 minutes, changing the temperature between 350 ºC and 550 ºC. In the second series there was evaluated the effect of the time of carbonization, supporting the constant temperature in 500 ºC, changing the times between 10 and 60 minutes. All the experiences were realized by triplicate.

From now on material lignocelulósico carbonized will be named **LC**. The **LC** characterized by means of elementary analysis (%C, %H, %S), FTIR, and analysis of superficial specific area, volume and diameter of pores for BET method.

4. Essays of Adsorption

It is claimed that **LC** acts like sorber in the treatment of nickel contaminated effluents. To evaluate lignocellulosic material as potential sorbent the following procedure was applied: a standard solution of 1000 ppm from $NiCl_2.6H_2O$ (Ni^{2+}) standardized titrisols was prepared for nickel. Later dilutions of 20 ppm were carried out, fitting the pH to 4. An aliquot of 100 mL of this solution (20 ppm Ni) was added to 250 mg of **LC** sample to evaluate. The samples were left in agitation by 2 h, filtered and the remaining Ni solution is analyzed using inductively coupled plasma - atomic emission spectroscopy (ICP-AES). This procedure was realized by triplicate.

5. Equipments

For elemental analysis there was used a Macanal 10 equipment, Herrmann Moritz, which uses a high combustion gravimetric method for the determination of C and H, and volumetry for S. The ^{1}HNMR analysis was made on Broker Aspect model 3000 (500 MHz) with a spectrometer Jeol model Eclipse 400 MHz, using deuterium oxide as solvent (100 mg /mL). For FTIR it was used a NICOLET 760 ESP and Eomnic V 3.0 on KBr pills. The analyses of superficial area and diameter of pores carried out with an ASAP 2000 Micromeritics instrument. The nickel content on water solutions was realized with an Integra XL GBC inductively coupled plasma atomic emission spectrometer (ICP-AES). The UV was realized with a HP 8452A Diode Array spectrophotometer.

Results and Discussion

1. Obtainment of Lignocellulosic Residual-Yield

The extraction of lignocellulosic material from Kraft black liquor was evaluated by liquid evaporation. Three experimental methods were studied; the results are presented in Table 1. It is observed that any of three used methods the same yield is reached, nevertheless the employment of the lamp with low light allows to realize the essay in a very favourable minimal time of 2 hours for the rest of the study. Also it is important that with any of three used methods the obtained residue has the appearance of the solid soft one, highly hygroscopic and soluble in water. This agrees with the proper characteristics of the fundamental units that shape lignin, showed by (Ralph et al, 2004). This has sections with high polarity and with her possibility of absorbing water. There was selected the evaporated residual by lamp with low light to continue the study, and an analysis of UV-visible spectroscopy was made to him, determining a final content of 39.24% of lignin. This evaporated remainder happens to be called **Lev**.

Table 1. Comparative Table for Evaporation Methods.

Methodology	**Yield (g)**
A	8.2285
B	8.2325
C	8.2260

2. Characterization of the Lignocellulosic Residual

For evaporated material characterization there were realized the following analysis.

2.1. Elementary Analysis and Yield

The results of the immediate analysis and the elementary analysis realized to the solid residue extracted from black liquor by evaporation, **Lev**, are given in Table 2. The most beetling of this set of values is such a low carbon percentage that makes suppose that the lignocellulosic material contains a high place of heteroatoms. Also this low quantity of carbon with regard to the showed one by chemical precipitations of black liquors can owe to the presence of other chemical compounds used in the process Kraft (for example NaOH) that by means of the chemical precipitation are supported in the liquor and nevertheless, by means of this procedure remains caught in the **Lev**. Also it is observed that the percentage of ashes is high as it would be expected due to the evaporation process and the reported for the others investigations.

Table 2. Immediate and Elementary Analysis of **Lev**.

Analyses	**Percentage of weight (%)**
Immediate	
Moisture	10.30 ± 0.01
Ash	20.09 ± 0.08
Volatile matter	0.80 ± 0.02
Elemental	
C	10.65 ± 0.05
H	4.09 ± 0.03
S	0.46 ± 0.01

2.2. FTIR Analysis

Table 3 presented a compilation of signals observed in infrared spectra obtained from **Lev** samples and commercial Indulin AT sample. The information is brought paired at intervals where the signs appears in the spectras showed in Figures 1 and 2. In the Indulin AT spectra a peak appears over 2938 cm^{-1}, attributed to strechings of methyl-aliphatic groups. On **Lev** this band is screened by hydroxilic groups. Also, in the same **Lev** spectra a signal or band over 2178 cm^{-1} attributable to triple linkage and to strechings of sulphydric groups (-SH), which corroborates the presence of the sulfur brought by the elementary analysis (Table 2). In a general way it is possible to affirm that both spectras are similar in several aspects, which means that **Lev** must have a chemical structure similar to that of Indulin AT lignin, being provided also with inorganic compounds that might be acting in the extraction of the nickel.

Table 3. Typical Signals for Infrared Spectra

INTERVAL (cm^{-1})	Signals
3200 – 3600	Wide band corresponding to the stretchings (strechings) of the group hidroxilo (-OH)
1650 – 1780	Peaks attributed to stretchings or lengthening of double linkage (C=C) in aromatic rings or ésthers / ether linkage C-O type.
1413 – 1463	(Methyls) observe intense peaks corresponding flexions and distortions on aliphatics in aromatics.
1260	Strechings C=O and vibrations of aromatic rings of the type guayacil
1127	Distortions C-H of aromatic, vibrations of rings of the type siringil.
1033	Distortions C-H in aromatic (Guayacil more than Syringil), vibrations C - O corresponding to primary alcohols and carbonils C=O not brought together.
927-620	Vibrations on aromatic C-H out of the plane

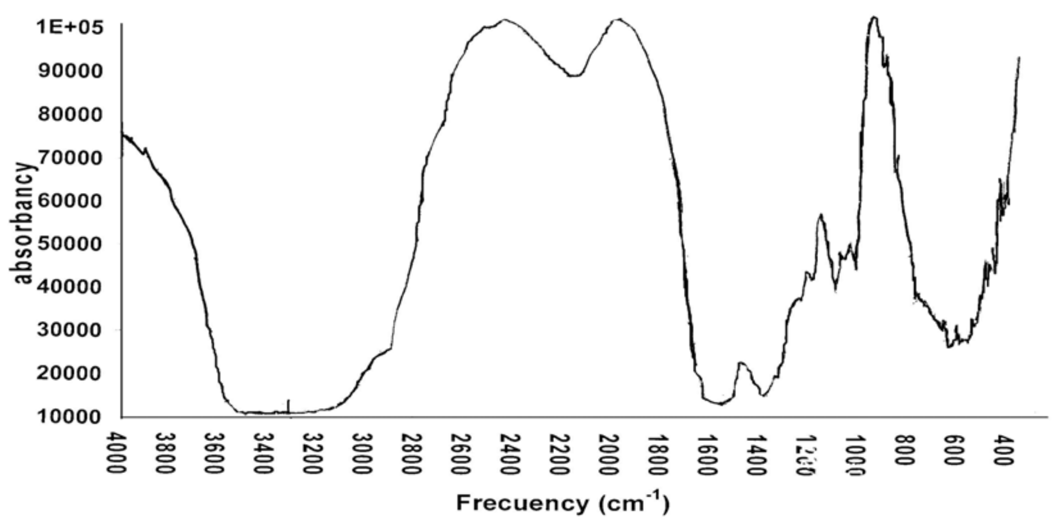

Figure 1. Lev FT-IR Spectra.

2.3. ^{1}HNMR Analysis

With the purpose of identifying the principal functional present groups in **Lev**, there was realized a nuclear magnetic resonance of protons (^{1}HNMR). The signals were grouped in typical sectors of chemical displacement (δ), associated with certain functional groups (Table 4), bearing in mind the effect of different types groups coexistence in the molecule and the affectation they can exercise on the obtained record of the equipment. Although the resolution of peaks (Figure 3) shows the presence of certain functional groups belonging to aliphatic chains, metoxi groups and aromatics type guayacil and siringil, it is necessary to deepen more this type of studies that lead to the characterization of lignocellulosic material. The intense peak about 1.8284 ppm corresponds with the signal of the solvent, whereas the singlet signal that appears on 8.39 ppm assumes to the aromatic ones or displaced vinyls to high fields, it is a weak signl to be a carbonaceous compound, but one must take in account that this sample is composed by organic material and inorganic (as it appreciates in the Table 2). Nevertheless, the presence of these is enough to indicate that they are responsible for the chemical adsorption of nickel (Mohammed et al, 2004), (Ray et al, 2002), (Sun et al, 2005). For what is needed to realize the isotherms of adsorption and them to fit to some of the models of prophecy of the adsorptive process as Langmuir or BET for, according to the best approach to justify the existence of some of the mechanisms (Pérez et al, 2006b). It is important to point out that it is not possible to obtain a quantitative value of these groups because the C and H_2 quantity is not known by entire accuracy and that shape the **Lev** molecular structure, which is an indispensable requisite for quantification of the same ones. Although the size of peaks allows to know qualitatively group proportion inside molecule.

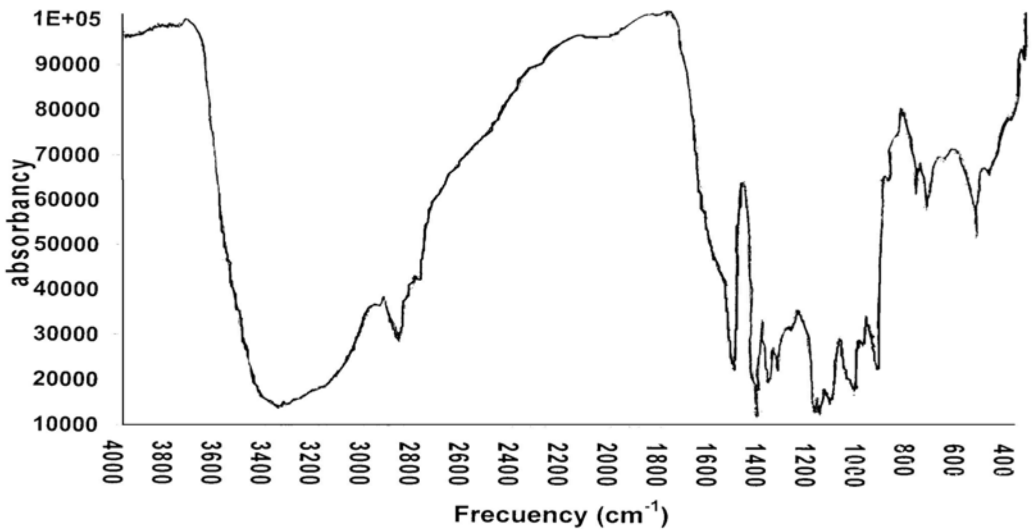

Figure 2. Indulin AT FT-IR Spectra.

Table 4. Typical Signals for ^{1}H NMR.

Interval (δ)	Signals
Between 12 and 8 ppm	In this sector there usually registers displacements corresponding to strongly unscreened COO-H ó CO-H protons for carboxylic acids or aldehyds that can be a part of the terminal groups of the bio-polymer.
Between 8 and 6 ppm	Signs corresponding to protons that shape aromatic rings and also small contributions of protons can be vinylics displaced to higher fields.
Between 6 and 4 ppm	The protons belonging to carbons are α, β, γ saturated for different β-O-4, β-5, β - β linkages between the guayacil groups (Figure 4).
Between 4 and 2.5 ppm	Signs attributed to metoxi groups.
Less than 2.5 ppm	Below 2.5 ppm there are signals for protons belonging to acetoxyls aliphatics groups. Whereas below 1.5 ppm there are observed signals attributed to protons of aliphatics variations strongly screened (methyls and methylenes).

3. Lignocellulosic Residual Carbonization. Char formation

With the purpose of improving the potential biosorbent of the lignocellulosic residue, **Lev**, one submitted to a process of soft carbonization, in inert ambience (N_2). It was hoped that this treatment should to eliminate residues pollutants from evaporation process, inner gases and smalls aliphatic groups that they could hinder in the adsorption process where the metal is removed from watery solutions.

3.1. Elemental Analysis

The carbonization treatment gave place to the formation of a char, defining the term "char" as the solid residue remained after pyrolysis. In this case the resultant char was a solid miscellany of chemical organic and inorganic compounds. The results brought in the Table 5 point out that mass yields for carbonization are similar in both studied temperatures. Sharma in experimental similar conditions observes a decrease of the yields as it increases the temperature: approximately 67% on 350ºC and 54% on 550ºC (Sharma et al, 2004). In our case, it seemed that in this status of temperatures, this factor does not influence important on carbonization yields for **Lev**. It is possible that lignocellulosic derivatives from **Lev** are constituted by structures so condensed that to 550ºC is still not a sufficiently high temperature like to provoke modifications in the same one. For the elementary composition, there is observed an increase of the content of carbon that should seem parallel to a decrease of the content of hydrogen. This increase of %C must mean an increase in the aromatic character of **LC** since these values of C and H explain themselves the loss of functional groups of low molecular weight during carbonization. It is worth while mentioning here, that continuing N_2 flow supported inside the reactor, during the essay in addition to guaranteeing an inert ambience was serving also to push gases that were forming, towards the system of gas recovery. This means that the yield of brought char is clearly the result of primary reactions of carbonization, since the secondary reactions of condensation and coke production that could happen in the organic volatile phase it is not possible under the experimental used conditions.

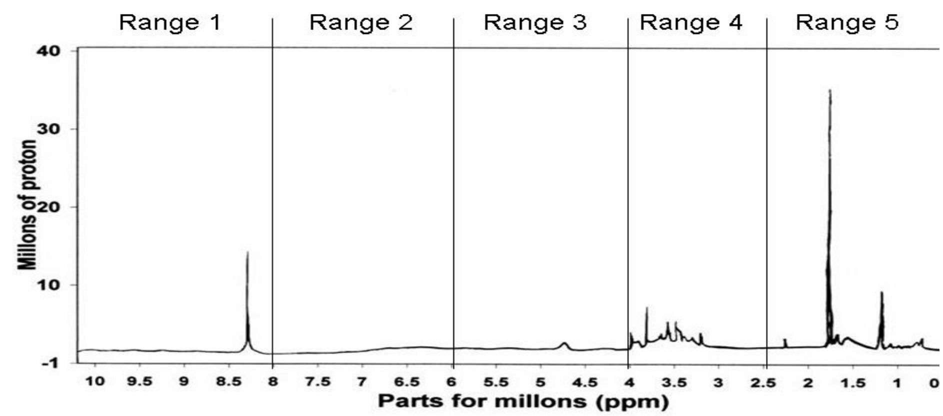

Figure 3. **Lev** NMR ^{1}H Spectra

Table 5. Elementary Analysis of **Lev** and **LC** Carbonized to Different Temperatures and a 20 min Fixed Time.

Analysis	**Lev**	**LC 350ºC**	**LC 550ºC**
%C	10.50± 0.05	27. ± 0.7	31. ± 0.7
%H	4.9 ± 0.3	4.6 ± 0.3	4.7 ± 0.3
%S	0.6 ± 0.1	--	0.6 ± 0.3
Yields		53	55

3.2. Superficial Area Volume and Diameter of Pores

Table 6 show values of superficial area for **LC** bigger than 5 m^2/g; usually associated to lignin; nevertheless keep on being very low values compared with the brought ones for any activated commercial coal. It was hoped that combination of temperature and inorganic present residues in the sample, should give place to a similar process to a “chemical activation”, with which the superficial area should increase in an important way. Seemingly, in this case, appears a major influence for organics of the **Lev** that the inorganic one. According to Table 2, **Lev** one has a lower volatile matters, meaning that inflating and the bubble detachment with later hardening forming a porous char with superficial valuable area observed during the carbonization of other carbonaceous materials it did not happen with **Lev**. Also, it is observed that increasing temperature provoked rather a decrease of the superficial area as well as a decrease of the diameter and volume of pores. It is possible in this case the carbonization has provoked broken walls from macro and mesopores with the consequent decrease on superficial specific area, diameter of pores used as well as the volume of pores micropores which mean that, probably really minor size pores have formed, although in few proportion. Another thing that could have happened was that **Lev** was behaving as a completely heterogeneous miscellany that, on having carbonized it, could eliminate some chemical substances that in spite of being in the **Lev** did not belong to the carbonaceous counterfoil and therefore they do not affect the volatilizarse to the carbonaceous remaining material. Nevertheless this information must be taken carefully due to the limitations of the used equipment for the estimation of variable these when these have so low values compared with other carbonaceous materials.

3.3. FTIR Analysis

Figures 4 and 6 correspond to infrared analysis of **LC** samples, carbonized to three different temperatures: 350ºC, 500ºC and 550ºC. The Figures point out that carbonization process has been really light for all functional groups that had been identified previously in the **Lev** sample. In all **LC** spectras appear screened the methyl, methylene, aliphatic and hydroxyl groups between 2800 and 3400 cm $^{-1}$. It appreciates the same signal or band over 2178 - 2495 cm $^{-1}$ attributable to triple linkage and to strechings of sulphydrils groups (-SH). The presence of these last ones is interesting since we suppose that those are they that can promote the adsorbent character of the prepared **LC**, and that are used in addition for the specific adsorption to Ni.

Table 6. Change of the Superficial Area, Volume and Diameter of Pores According to the Temperature, In the Carbonized Lignocellulosic Residue.

Temperature (°C)	Superficial area (m^2)	Pore diameter (°A)	Pore volume (cm^3/g)
350	18.5	185	0.085283
500	17.0	82	0.034858
550	8.8	48	0.010458

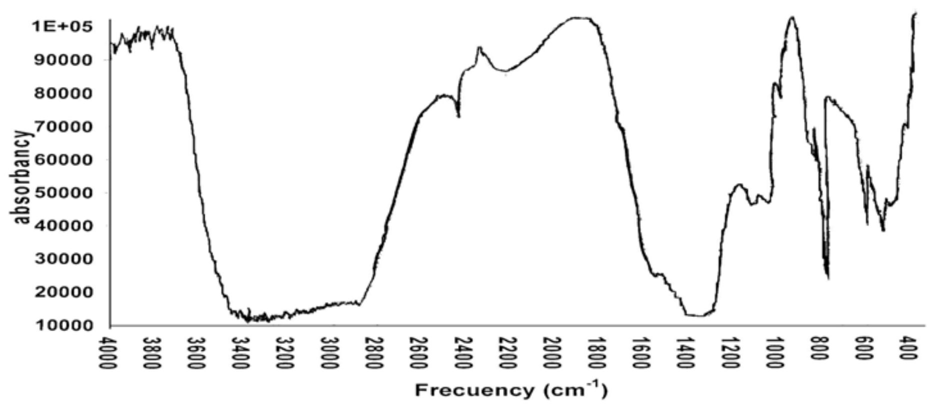

Figure 4. FTIR Spectra from **LC** at 350°C

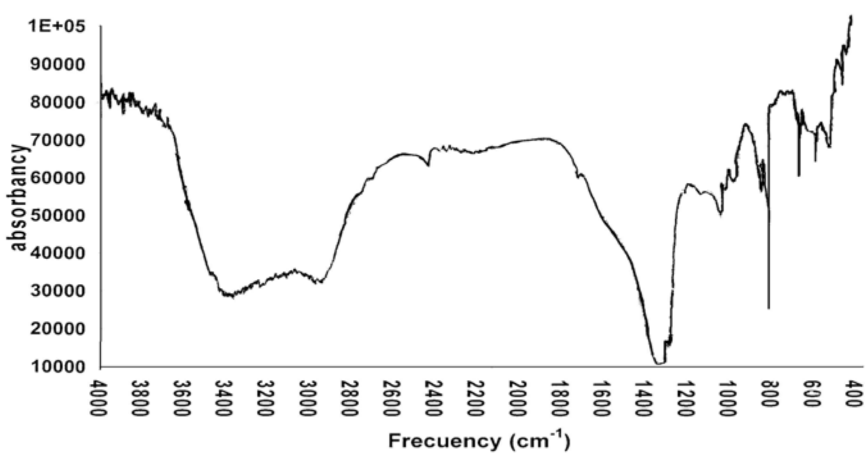

Figure 5. FTIR Spectra from **LC** at 500°C

3.4. Capacity of the lignocellulosic carbonized residue (LC) to extract nickel from watery solution

The capacity of the carbonized residue, **LC**, was evaluated by extracting nickel from watery standard solutions (see Table 7). There were analyzed the samples obtained to different carbonization temperatures fixed to 20 minutes time, showed that any of three studied cases was always exceptionally high and with the same value, which means that carbonization temperature seemed not to have any influence on this property of the solid one. In Figure 7 are given the values obtained on having analyzed samples of carbonized **Lev** supporting the fixed temperature in 500ºC but changing the time of carbonization. In this study a light decrease is observed in the aptitude to extract nickel in carbonized samples during a period bigger than 30 minutes. Nevertheless, at 60 minutes of carbonization the extraction still keep on in a very high value. In accordance with these results it is believed that the positive effect of the carbonization begins to decline after a certain time been due possibly to changes in the chemical structure of the lignocellulosic residue that could be promoted to this temperature.

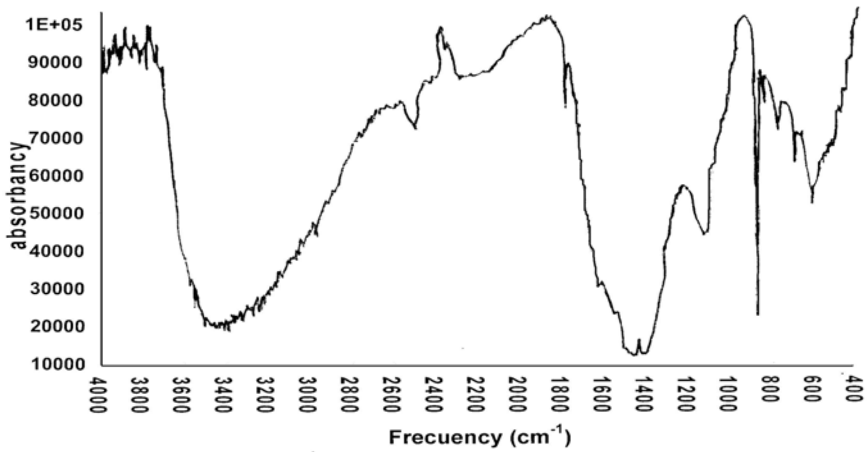

Figure 6. FTIR Spectra from **LC** at 550°C

Table 7. Results of Superficial Area and Diameter of Pores According to the Temperature

% Adsorption Ni	Temperature (ºC)
99.18	350
99.20	500
99.21	550

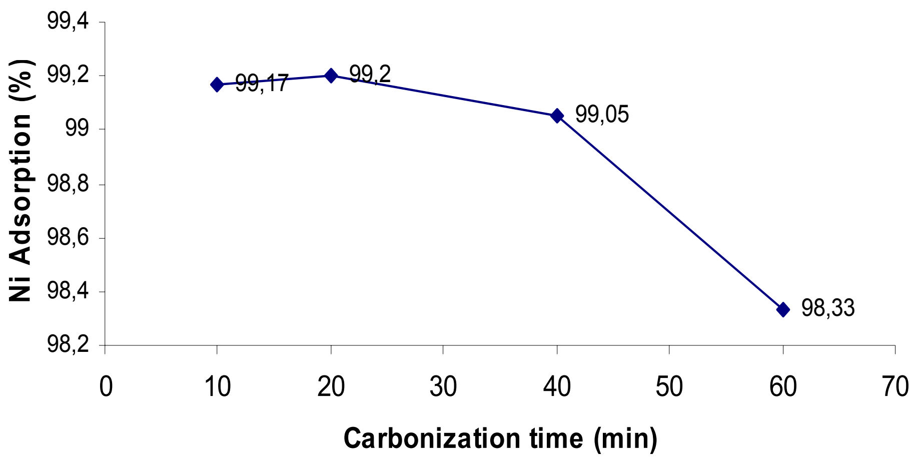

Figure 7. Nickel Adsorption vs. Carbonization Time. T=500 ºC

The nickel extraction from watery solution could happen due to an adsorption process between the oxygenated present groups in lignin structure, made clear by the analysis of FTIR (see Figure 4-6), and neither the Ni^{+2} cation. It is necessary to point out that as a consequence of the evaporation process of Kraft black liquor, good part of inorganic salts presents in the black liquor, particularly sodium, they should stay in the counterfoil of the lignocellulosic residue formed, on the surface or deposited on inner counterfoil itself, and perhaps some metallic atoms come up to being a part of the polimeric structure of the residue. These support the idea for both contributions to the adsorption process.

There is known the existence of two kinds of sorption, the chemical one, in which stable linkage forms with the oxygenated groups of the adsorbent and other one of physical type, in which the superficial area plays a preponderant roll. For lignin, some investigators (Khezami et al, 2005), (Parajuli et al, 2005), (Pérez et al, 2006a), (Pérez et al, 2006b), has suggested a mechanism of quimisorption, with formation of chelates, to explain metal extraction with lignocellulosic materials, according to this proposal it would be possible to achieve the separation of nickel from watery solution by means of his inclusion in the structure of the polimeric residue. The oxygens, electron donors, present in superficial groups hydroxil would operate as a ligand in the complex process with the catión of Ni^{2+} present in the watery way, which would take part as electron catcher, as appears in the example of the Figure 8. The result of the above mentioned process, leads to the formation of stable coordination complexes in the surface of the solid phase, where they retain the metallic catión. The metallic ions that initially were in solution, interacting with water ligands molecules, pass to the adsorbent where his number of coordination should be satisfied with water molecules going well together or with the amorphous latticework of the bio-adsorbent, this way the latticework could be considered to be one tying anionic that interacts with the orbital ones "d" of the positive ions. It is accepted that nickel (II) tends to form octahedric complexes with the water. This ion possesses 8 electrons in the five orbital ones "d" degenerate. When this electronic degeneration is unfolded by the octahedric field of the ligands, 6 electrons locate in t_{2g} (minor energy) and 2 electrons in e_g (major energy) (Huheey, 1978). (Butler and Nahod, 1998) they indicates that, if an ion possesses "d" electrons located in his orbital anticonjunctive (eg), it is foreseen that the replacement of going well together will be easier because the linkage of the metal in solution (acuo-complexes) is weaker.

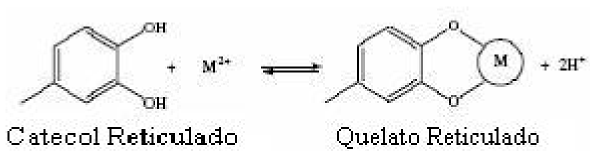

Figure 8. Example of Metal Adsorption in Lignin

Conclusions

The made study allows to conclude that it is possible to directly process the black liquor of Kraft to obtain adsorbent an appropriate one for the Ni removal of watery solutions. The preparation involves an eminently thermal process realized in two stages: First of them it consists of a simple process of evaporation, executed to atmospheric pressure and a temperature of 110 ºC. The second stage consists of a process of carbonization of the remainder coming from the evaporation, to a temperature of 500 ºC and during a time of up to 60 minutes. The carbonized remainder was proven for the removal of Ni in watery solutions, reaching values of extraction of 99%. Additionally, results indicate that nickel removal occurs by an adsorption process supported more on the nature of the chemical structure than on his morphology. Since the material possesses physical properties unable to sustain a physical adsorption, nevertheless the analyses of FTIR and ^{1}HNMR demonstrate existence of capable nickel adsorber groups, which do not turn out to be affected by realized carbonization.

Acknowledgments

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