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Use of biopolymers for the removal of heavy metals produced by the oil industry—A feasibility study

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Abstract The possibility of using lignin from the paper industry's black liquor to absorb nickel (Ni) and vanadium (V), was studied. The work comprised two stages: first, the identification of lignin's main functional groups and the surface characterization of the solid; second, an experimental study of lignin's behavior towards the Ni and V cations. Results revealed the presence of aromatic groups as well as substituted methoxy groups on the lignin's surface. This explains lignin's adsorptive capacity exhibited in the experimental evaluations. The removal of Ni and V ions was higher than expected solely through the physical adsorption mechanism. This higher capacity is associated with a proposed complex formation on the surface of the lignin. For Ni(II), lignin showed a higher adsorption compared to commercial adsorbents. In the case of V, the behavior is reversed, in order to elucidate this result, further research is recommended.

Keywords Adsorption · Lignin · Nickel · Vanadium · Revaluation

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1 Introduction

Venezuela is an important petroleum coke producer on a worldwide scale. Coke is generally classified as a fossil fuel; however, Venezuelan petroleum cokes exhibit a high sulfur and heavy metal (mainly Nickel and Vanadium) concentration. This limits the commercial acceptability of this material (Lee et al., 1997) due to OSHA restrictions on the remainders generated in its combustion (Roper, 1992). The quality and price of fossil fuel is related to its heavy metal content, this is a major determinant of its commercial value.

During the past few years, Venezuela's Universidad Simón Bolívar Alternative Clean Technologies Group (TECall) has been working on the development of a process for simultaneous removal of sulfur and heavy metals from coke (De Chamorro and Romano, 2000). The process, based on the extraction by microwaves, has led to an important degree of metals removal; however, it represents only a partial solution since the metals remain trapped in an acid liquor stream identified as "LIM", from which they must be separated to recycle the liquor.

Efforts to remove the heavy metals from the liquid streams have included the use of different bioadsorbents such as turba, chitosan, vegetable cortex, cork, fungi, algae, and lignin among others (Bailey et al., 1999). A 1997 study pursued by the American Marine Engineering Corporation (Crist et al., 2004), selected lignin as one of the most promising adsorbents that should be further evaluated.

Lignin is a phenolic biopolymer formed on the secondary walls of plant cells. After cellulose, it is the second most abundant natural biopolymer. It is responsible for cell wall rigidity and plays an important role in water, nutrient and metabolite transport (Rouchi and Washington, 2001). Different hypotheses suggest that lignin's oxygen-bearing functional groups, such as methoxy groups, aliphatic as well as phenolic hydroxylic groups, and carboxylic groups serve as active sites for the adsorption of metallic ions and other components. Lignin derivatives obtained as sub-products of the paper pulp industry, such as lignosulfonates (sulfonated products) or alkaline lignin, also contain oxygen-bearing functional groups including phenols and carboxylics as well as sulfonylic groups. Thus, the polyanionic characters of these derivatives together with their polymeric flexibility allow their successful use as adsorbents in various systems (Zhuang et al., 2003).

Adsorption may proceed through two mechanisms: physisorption or chemisorption. The former is a physical, exothermic phenomenon, where weak Van der Waals-type interactions induce the adsorption, and no bond formation takes place. In the second adsorption mechanism, the chemical nature of the adsorbent plays an important role. Changes in the electronic distribution and molecular bonds take place. Frequently, the functional groups of the adsorbent coordinate the adsorbate ions forming chelates (Morrison and Boyd, 1976). Most adsorption processes comprise a combination of both mechanisms. Therefore, in order to study the behaviour of an adsorbent, two parameters must be considered: available surface area for physisorption and the presence of active functional groups capable of bonding the adsorbate ions (Cussler, 1997).

Different studies have shown that lignin derivatives are efficient adsorbents for the removal of toxic metal traces such as chromium (Lalvami et al., 2000; Dupont and Guillon, 2003), copper (Sciban and Klasnja, 2004; Wieber et al., 1988), lead (Crist et al., 2004; Lalvani et al., 1997a; Srivastava et al., 1994), zinc (Wieber et al., 1988; Lalvani et al., 1997b), nickel (Basso et al., 2002a), cadmium (Basso et al., 2002b), and mercury (Zhuang et al., 2003; Ray et al., 2002), as well as for pesticides (Rupp and Zuman, 1992), surfactants and dyes (Perineau and Gaset, 1981), phenols, polycyclic aromatic hydrocarbons and chlorinated hydrocarbons (Dizhbite et al., 1999; O'Neil et al., 1987).

Among the above-mentioned pollutants, heavy metals are particularly toxic since they are non-biodegradable and tend to accumulate in living organisms causing various diseases and biochemical disorders (Bailey et al., 1999). For instance, nickel (II) has been reported as toxic to fish and plants and as a potent carcinogen in concentrations higher than 1 ppm (Sharma et al., 1991). Vanadium (V) has been reported as a carcinogenic agent in rats in concentrations higher than 0.5 ppm (Roper, 1992).

Traditional methods to remove heavy metal traces from residual water streams include chemical precipitation, membrane filtration, ionic exchange, and active charcoal adsorption (Bailey et al., 1999). Regarding adsorption methods, high investment and active charcoal regeneration costs impose the need to search for new low-cost adsorbents (Sciban and Klasnja, 2004).

This paper presents results of the preliminary evaluation of the use of lignin, obtained from the black liquor produced by the pulp and paper industry, to extract and remove heavy metals contained in acid liquor solutions obtained from a petroleum coke demetalization process. The final goal is to simultaneously revalue the by-products of the black liquor as well as the coke.

2 Experimental

2.1 Adsorbents used

Two adsorbents were used: an acid-precipitated basic lignin from the pulp and paper industry's black liquor, and a commercially activated carbon (CAC) produced by CALGON Corporation located in Pittsburgh, USA, with the commercial denomination "PWA" (CAS# 7440-40-0). The latter material was selected as a reference because of its recognized use as an adsorbent, its well-known fundamental properties and structure, its adsorption capacity to the metal ions, and its carbon origin is similar to lignin's (Jankowska et al., 1991). Also, other works as Basso et al. (2002a), utilized CAC as a reference for the heavy metals adsorption process evaluation.

2.2 Lignin molecular characterization

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and infrared spectroscopy (IR) were used to identify the main functional groups present in lignin.

Table 1 Controlled operational conditions

Operational condition	Mechanism of control
Adsorption time	Measurement of time with digital chronometers.
Adsorbent/Adsorbate ratio	Measurement of fed mass of lignin and volume of acid liquor fed.
pH	Measured continuously by means of a digital pHmeter, and adjusted to the desired value adding H_2SO_4 (0,1. M) or NaOH (0.1 M) to the mix.
Temperature	Measured continuously. Although not controlled, there were no changes during the experiments.

^{1}H NMR spectra were obtained with a 400 MHz Joel Eclipse spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent. IR spectra were acquired using an infrared Nicolet 760 with Fourier Transformed (FT-IR) and an Eomic v.3.0 analyzer. Acidic functional groups were identified using a previously published method (Boehm, 2002) developed to study the acidic active sites on the CAC surface. Surface characterization included the determination of surface area, pore volume and diameter, using an ASAP Micromeritcs 2000 surface analyzer.

2.3 Evaluation of the adsorptive behaviour

To evaluate lignin's adsorptive capacity, LIM solutions of known Ni and V concentration were prepared and put in contact with the lignin adsorbent at a concentration of 1 g adsorbent/L of solution for two hours at 25°C. pH was fixed at 4 and 5, values which favours the adsorption (Pérez et al., 2006). The suspension was then vacuum-filtered and washed two times with distilled water. The Ni and V concentrations of the resulting solutions were measured using an Integra XL GBC inductively coupled plasma optical emission spectrometer (IPC-OES). The difference between the initial and the final metal concentrations corresponds to the adsorbed amount. An identical procedure was used to evaluate adsorption behaviour of the CAC.

3 Results and discussion

3.1 Selection of experimental conditions

Different works (Dermibas, 2004; Parajuli et al., 2005) have demonstrated the dependence of lignin's adsorption capacity on operational conditions such as pH, temperature, etc. In order to establish the experimental operational conditions, some experiments were performed fixing parameters such as pH, adsorbent/adsorbate ratio, temperature and adsorption time. The variables and their means of control are shown in Table 1.

During this selection, it was checked that the structural characteristics of lignin were not altered in the range of operational conditions selected. They were maintained constant. Pérez et al. (2006) showed that the adsorption is strongly dependent on the solid surface charge, while the surface charge is mainly dependent on the solution pH at the zero point of charge (pHzpc), where the total charge from the cations and anions at the surface is equal to zero. The value for this parameter was equal to 2, reason why the selected pH was above to pHzpc, and therefore the solution in these conditions is able to adsorb cations.

3.2 Lignin surface characterization

Table 2 presents the results of surface area as well as pore size and diameter obtained for lignin. These results show that, according to IUPAC classification, conventional lignin is a mesoporous material with a small surface area (Gregg and Sing, 1982). In this case, the surface area of lignin is 1000 times smaller than CAC's surface area and the pore distribution is not significant. According to Martin (1980) surface area is not the main factor to consider while evaluating the adsorptive potential of a material. Instead, the type and availability of functional groups present in the material are more relevant characteristics.

Table 2 Surface texture of lignin and CAC

Superficial characteristic	Lignin	CAC
BET area (m^2/g)	1.37	1111
Total pore volume (cc/g)	0.0018	0.27
Average diameter of pore (Å)	54	21

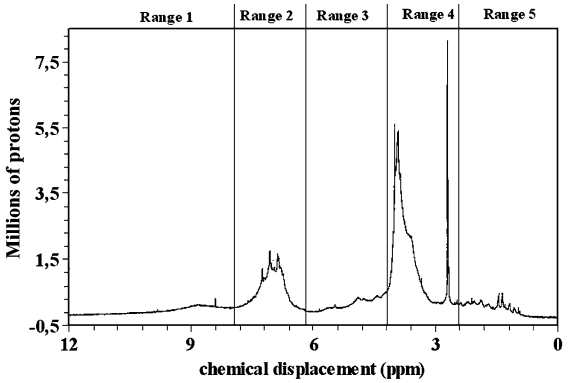

Fig. 1 ^{1}H NMR spectrum of lignin

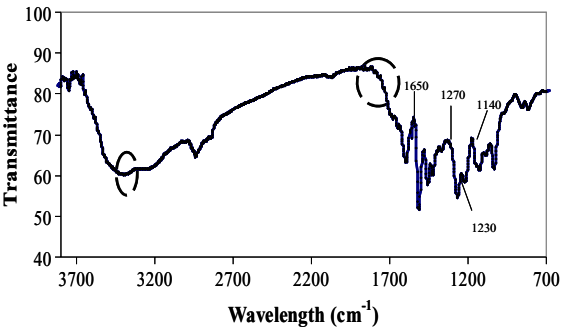

Fig. 2 IR spectrum of lignin

Indeed, lignin's small surface area reported in Table 2 indicates that if lignin exhibits adsorptive capacity, it would not be as a result of the presence of pores that could retain the adsorbate molecules, but rather from the presence of superficial functional groups capable of binding the adsorbate through complex formation. These factors would point to a prevailing chemical adsorption rather than a physical adsorption mechanism.

Figure 1 shows the ^{1}H NMR spectrum obtained for lignin. Signals were classified into five regions corresponding to the chemical shift (δ) intervals that are characteristic for certain functional groups, according to patterns developed from different models and standards (Sarkanen and Ludwing, 1971; Silverstein et al., 1992), as follows:

Range 1: 12–8 ppm; strongly unshielded protons from carboxylic acids (COO−H) and aldehydes (CO−H).

Range 2: 8.03–6.28 ppm; aromatic (7.52–6.65 ppm) and vinylic as well as phenolic protons (6.7–6.4 ppm).

Range 3: 6.28–4.12 ppm; protons attached to saturated α, β and γ carbons of the bonds between guayacyl (3-methoxy-4-hydroxyphenyl) groups.

Range 4: 4.12–2.5 ppm; methoxy group protons, mainly between 3.85 and 3.71 ppm.

Range 5: <2.5 ppm. 2.50–2.19 ppm: aromatic etoxy groups; 2.19–1.58 ppm: aliphatic etoxy groups; <1.58 ppm strongly shielded aliphatic chain protons.

The spectrum reveals that the most intense signals correspond to regions 4 and 2. This indicates that lignin is highly aromatic with abundant phenolic and methoxy groups bonded to the biopolymer. There are no other significant signals in the spectrum, besides the one from the solvent signal (DMSO-d_6; 2.5 ppm) and some small signals below 1.2 ppm corresponding to small aliphatic end chains that are strongly shielded by the polymer's structure.

These results allow us to predict that lignin could adsorb Ni and V because the methoxy and phenolic groups act as chelating agents. The IR spectrum, reproduced in Fig. 2, further complements the chemical characterization.

This spectrum reveals the following (applying the characterization of Boeriu et al. (2004)):

- A broad OH stretching absorption band between 3500 and 3400 cm^{-1} that reveals the presence of alcoholic and/or phenolic −OH groups;
- A sharp peak at 1659 cm^{-1} which corresponds to the C=C stretching of the aromatic skeleton;
- Peaks at 1270, 1230 and 1140 cm^{-1}, those correspond to the aromatic group-bonds and the symmetric and asymmetric stretching of the ether C−O bonds;
- No strong signals around 1700 cm^{-1} are present, which reveals that lignin does not contain significant amounts of carboxylic groups.

IR results confirm the presence of functional groups capable of adsorbing the target heavy metals. Furthermore, oxygen-containing acid groups were characterized applying the method developed by Boehm (2002). This method is based on the relative strength of the different acid groups and their consequent susceptibility to being neutralized by bases of different strength. Since this lignin dissolves in basic media, the resulting dark coloring of the lignin solutions masks the color of any acid/base indicator. Therefore, a pH

Table 3 Neutralization capacity of the bases used for lignin titration

	Acid-base neutralization capacity (meq/100 g)		
Sample	$NaHCO_3$	Na_2CO_3	NaOH
Lignin	0	4.145	6.769

Table 4 Amount of oxygen-containing acid groups

	Amounts of functional groups (mmol/g)			
Sample	Carboxylic acids	Lactones	Phenols	Total
Lignin	0	0.04145	0.02624	0.06769

electrode was used to determine the final titration points. Table 3 summarizes the results of the titration experiments.

Table 4 shows the concentration of acidic functional groups calculated from the titration results. For instance, lignin did not neutralize any $NaHCO_3$. Therefore, zero concentration of carboxylic acid groups was inferred. Results of Table 4 reveal that around 60% of lignin's oxygenated acidic groups are lactone type (cyclic esters), while the remaining 40% are phenolic. Both groups may act as chelating agents of heavy metals. Values shown in Table 4 allow one to estimate the concentration of these groups in the surface, which is equal to 0.06769 mmol/g of lignin. Due to this, if every group is capable of adsorbing only one metallic ion (Morrison and Boyd, 1976), this concentration must be the maximum concentration of ions that can be adsorbed in this way.

3.3 Ni and V extraction from acid solutions

Figure 3 reproduces the Ni and V adsorption isotherms obtained for both lignin and CAC. Least square fits were used to determine the mathematical equation that best suits the experimental behaviour.

Adsorption isotherms reproduced in Fig. 3 show that Ni is more efficiently adsorbed by lignin than by CAC; whereas for V, the behaviour is opposite. This could indicate that both metals interact with lignin through different adsorption mechanisms. It is known that CAC interacts with the adsorbate mainly through physical phenomena that require pore sizes similar to the metal ion radius. Indeed, the predominant micropore radio of the CAC used herein is closer to the V than the Ni ion

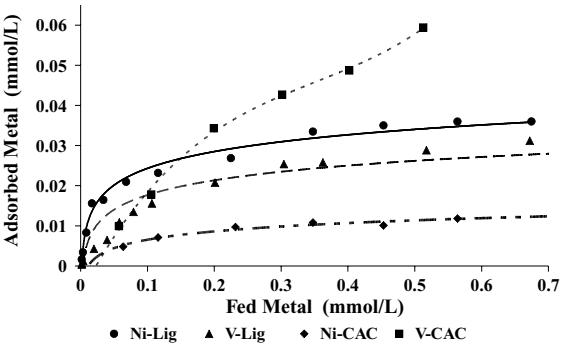

Fig. 3 Adsorption isotherms for V and Ni over lignin and CAC

radio (Skoog and West, 1977); thus, V adsorption is favoured.

As mentioned previously, for lignin the predominant adsorption mechanism is deducedly of a chemical nature. Therefore, the difference in the ionic radius is not expected to be the determining factor. Both elements (V and Ni) are transition metals; thus, both may form organometallic complexes with lignin. Consequently, the presence of free orbitals available for complex formation with the chelating agent (lignin), is crucial. Figure 3 shows that both ions interact similarly with the adsorbent, but in the case of Ni, this interaction seems to be more efficient. This is because the adsorbed quantity is always greater throughout the study.

The differences in adsorbing behavior of lignin and CAC towards Ni and V suggest that the affinities between the metals and the surfaces of the adsorbents are different. To study these affinities, Langmuir adsorption isotherms were constructed in order to further examine these interactions (Fig. 4). Large slope values indicate poor adsorption; small slope values correspond to high adsorbent-adsorbate affinity. As Fig. 4 shows, the Ni and V isotherms for both adsorbents present different slopes. This difference can be used to compare the affinity and with it, the adsorptive capacity of lignin over the metals studied.

Table 5 shows the equations of the straights settled by the Langmuir model along the standard deviation obtained. For instance, for the Ni-lignin pair, the slope has a value of 109.7 L/g, while for the Ni-CAC pair, the value is 298.12 L/g. This indicates that Ni has a higher affinity for lignin than for CAC. On the other hand, the slope values of 111.75 L/g and 31.324 L/g for V-lignin and V-CAC, respectively, reveal a higher affinity of V towards the CAC surface than towards the lignin surface.

Table 5 Linearized Langmuir model parameters for the systems studied

System	Equation	R^2
Ni-CAC	$y = 298.12x + 29.335$	0.9827
Ni-Lig	$y = 109.7x + 2.248$	0.9904
V-CAC	$y = 31.324x + 16.542$	0.9257
V-Lig	$y = 111.75x + 12.311$	0.9934

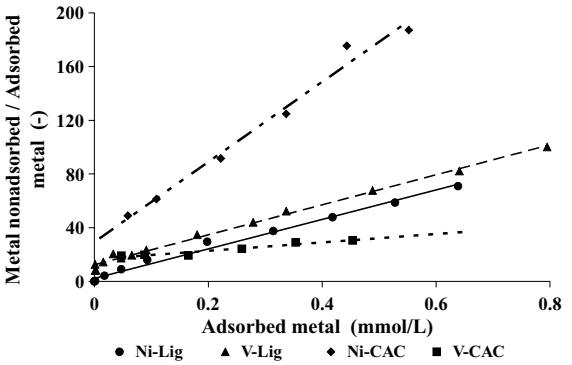

Fig. 4 Langmuir isotherms for the systems studied

When comparing the Ni and V behavior towards lignin, the similarity of the Langmuir isotherm slopes indicates that the metals exhibit similar affinity for the adsorbent.

From Figs. 3 and 4, the maximum amount of adsorbed Ni and V per grams or unit mass of adsorbent can be estimated dividing the adsorbed Ni and V amounts by the lignin concentrations used. This value is 0.09 mmol/g for Ni and 0.078 mmol/g for V. Both values are larger than the total molar concentration of acid groups present on lignin's surface (0.06769 mmol/g). This reveals that lignin retains more metal ions than expected solely from a single adsorption mechanism. This could be the reason for the higher adsorption values obtained. These mechanisms could operate in one of two ways: precipitation over the surface, due to the dragging of adsorbed ions; or because the chelates formed over the first superficial layers become the new active sites, thus increasing the number of active adsorption sites.

Using X-ray photoelectron spectroscopy (XPS), Swiatkowski et al. (1996) demonstrated that, whenever the adsorption values surpass the available acid functional groups, solid precipitation on the surface takes place along with the chelate formation. Consequently, it could be considered that this is the case in the lignin-heavy metal system.

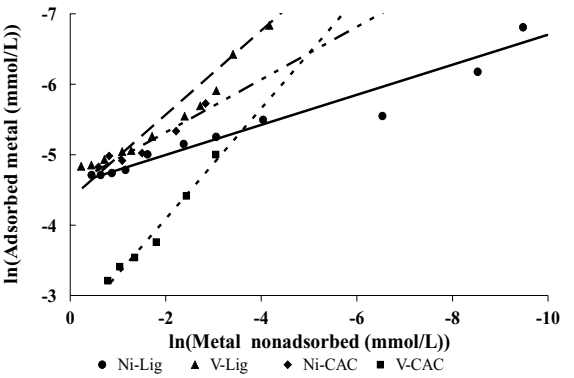

Fig. 5 Freundlich isotherms for the systems studied

The Langmuir model assumes the formation of an adsorbed solute monolayer, with no side interactions between adsorbed ions. It also assumes that the sorbent surface is homogeneous and contains only one type of binding sites. Since lignin is supposed to be rather heterogeneous, and solid precipitation along with chemisorption is proposed for lignin, the experimental data were adjusted to the Freundlich model (Barrow, 1964; Levine, 1996) which considers the formation of a multilayered structure and allows mixed adsorption mechanisms. In the Freundlich model, the slope value is related to the interactions that occur between adsorbed ions. Large slope values indicate no interaction; low slope values correspond to significant interactions between adsorbed species.

Figure 5 shows the application of the Freundlich model to the experimental data, while Table 6 shows the equations of the straight settled for the Freundlich model along the standard deviation. It can be observed that the data adjust reasonably well to the Freundlich model. An analysis of the slopes of the straight lines obtained shows that the larger slopes for CAC-metal systems indicate a weaker interaction between adsorbed ions; that is, less tendency towards the formation of multilayers. For lignin, the interactions between adsorbed ions seem to be more important for Ni than for

Table 6 Linearized Freundlich model parameters for the systems studied

System	Equation	R^2
Ni-CAC	$y = 0.3745x - 4.5689$	0.9257
Ni-Lig	$y = 0.214x - 4.5701$	0.9560
V-CAC	$y = 0.7839x - 2.5222$	0.9786
V-Lig	$y = 0.5976x - 4.3731$	0.9739

Table 7 Parameters of Langmuir and Freundlich models

	Langmuir		Freundlich	
System	Qm (mol/L)	Kl (−)	Kf (−)	*n* (−)
Ni-CAC	0.0034	10,163	0.0104	2.6702
Ni-Lig	0.0091	48,799	0.0104	4.6729
V-CAC	0.0319	1,894	0.0803	1.2757
V-Lig	0.0089	9,077	0.0126	1.6750

V, suggesting that the latter may form multilayers on the lignin surface.

The difference in the adsorptive capacity of both adsorbents can be checked from the slopes obtained from Tables 5 and 6. Observing that, the slopes of the straight lines of the V adjustment, are steeper to the CAC that to lignin, it can be said that CAC is a better adsorbent. In the Ni case, the larger values for the slopes with lignin show a pronounced affinity to the metal and a bigger adsorptive capacity.

From results of Tables 5 and 6, can be obtained, as is showed by Barrow (1964), the equilibrium constant of Langmuir, "K1", the equilibrium constant of Freundlich, "Kf", besides the parameter of equilibrium concentration of the monolayer of Lagmuir, "Qm", and the heterogeneity factor "n", of Freundlich. These are shown in Table 7.

Again, in Table 7 can be verified, that the biggest value of K1 is for Ni-Lig system. That indicates this system has the bigger capacity of adsorption for every adsorbent studied. This is opposite to happen with the V-CAC system, which have a bigger adsorptive capacity than is expected from the K1 analysis, because it allow an equilibrium concentration of V over the monolayer, at least 30 times superior that the rest of the systems.

On the other hand, analysing the results of the heterogeneity (n), looks like that the lignin adsorbs every metal on a way more heterogeneous than the CAC, and that the adsorption more homogeneous is for the system V-CAC, reason why could be favouring a formation of multilayers for the rest of systems.

However, experimental data for CAC as well as for lignin fits the Langmuir model better. This appears to contradict expected results considering that lignin surface should be heterogeneous, and the amount of adsorbed ions is larger than the amount of oxygenated acid groups (active sites). The phenomenon affecting the process is mainly precipitation over the surface and not the formation of multilayers. Nevertheless, this finding does not fall within the objectives of this work. Further works investigating the adsorption mechanism of the Ni-, V-lignin systems will be carried out, these will consider the use of models of three parameters, as Unilan or Redlich Peterson to describe the systems.

4 Conclusions

- Lignin from the pulp and paper industry's black liquor proved to be a suitable adsorbent for Ni and V ions. Lignin competes favourably with CAC for Ni adsorption, but not for V adsorption.
- The small surface area of lignin and the presence of oxygenated acid groups on its surface points to a predominantly chemical adsorption mechanism through chelate formation.
- Precipitation of metal ions along with chemisorption may occur since the amount of ions adsorbed is larger than the amount of active sites present.
- Although the proposed metal ion precipitation suggests the formation of multilayers on lignin, experimental data fits the Langmuir model better than the Freundlich model. Therefore, adsorption mechanism studies should be further pursued.

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