NICKEL EXTRACTION USING LIGNIN: SELECTION OF BEST CONDITIONS

Gladys Rincón, Narciso A. Pérez, Luisa A. Delgado, Clara I. Guerrero
Universidad Simón Bolívar, Grupo TECALL, Caracas-Venezuela. ZP 1080-A

Abstract

The Orinoco Belt is the largest known heavy and extra-heavy petroleum reserve worldwide. To turn this type of crude oil into useful products, it must be subjected to upgrading processes. One of these processes is delayed coking; which, in addition to light products, yields up to 30%w petroleum coke. The direct combustion of the coke produced is limited due to its high sulfur, nickel and vanadium content. The aim of the present work was to develop a low cost adsorbent for the separation of the abovementioned metals from petroleum products. Lignin was considered for this purpose, since it is a low cost waste product from the paper industry and has been used with satisfactory results for the removal of Ni from wastewaters. In order to evaluate the feasibility of using lignin as a large scale bioadsorbent for nickel, best adsorbing condition were determined. For this, lignin was soaked with nickel containing acid solutions varying parameters such as mg Ni solution/ g lignin, contact time, initial pH and temperature. In all cases, significant nickel adsorption was observed. Lignin saturation corresponded to 10mg Ni/g lignin, achieved after 2 hrs at a pH 4. The adsorption capacity was independent of the temperature, among an interval of 25 ºC to 90 ºC. The former results indicate that lignin could compete with active charcoal for Ni removal from acid solutions, and allowed to establish the bases for a future industrial scale design.

Introduction

The lignin is a phenolic polymer which is formed in the cellular wall of plants. It is the second abundant biopolymer in the nature after cellulose, it is responsible to give rigidity to the cellular wall and also it has an important paper in the transport of water, nutrients and metabolites (Rouchi, 2001). Different hypothesis (Lalvani et al, 1997) suggest that the functional groups presents in lignin which contain oxygen, i.e. metoxyls, aliphatic hydroxyls as much as phenolics, and carboxyl groups; serve like adsorption sites of metallic ions and other components. Derivative compounds of lignin, on the other hand, are sulfonate products (lignsulfonates) or desulfonates (alcaline lignins), obtained as by-products of the industry of paper manufacture. They have a big quantity of alcoholic and phenolic structures and functional groups that contain oxygen, like phenolic, carboxylic and sulphonic groups. In this way, the polianyonic character of these derivatives and their polymeric flexibility, allow them to act like adsorbents in different systems (Zhuang et al, 2003), (Bailey et al, 1999). (Basso et al, 2002), (Crist et al, 2004) demonstrated the effectiveness of lignin and derivatives in the process of removal of traces of nickel present in residual waters.

When the feed of Delayed Coking process has a high content of sulphur and heavy metals, the coke produced exceeds recommended limits of sulphur and metals, generating emissions nonwished during its use. Moreover, heavy metals are value in the market, for that its recovery represents an additional economic yield.

The group of Alternative Clean Technologies (TECALL) of the Simón Bolívar University (Venezuela) has patented a process for simultaneous demetalization and desulphurization of petroleum coke (De Chamorro and Romano, 2000). Despite of this process promotes an important removal of the metals present in the carbonaceous matrix. These metals are transfer to a stream of acid liquors named "LIM", of which they must be finally removed with the objective of reuse the LIM. To attain this objective, allows facilitating the scaling of the process and its latter commercial development.

This study looks for the treatment of Ni acid solutions with lignin to achieve the nickel extraction, which is the principal contaminating of this stream. The study has like propose to identify the operational variables that have more influence over the process results and their range of variability, to do later a technical feasibility study focus in the scaling of the process. The last objective of this project is the conjoint revalue of petroleum coke and lignin.

Materials and Methods

1. Materials

Alkaline lignin pulverized (Kraft-lignin) was utilized from black liquors of the industry of paper manufacture, precipitated with strong acids. In table 1, is shown the most important superficial characteristic of this lignin.

Table 1. Superficial Texture of the Lignin

Superficial characteristics	Lignin
BET area (m^2/g)	1.4
Total volume of pore (cc/g)	0.0018
Average diameter of pore (Å)	54

To the preparation of Ni-acid solutions was used a tritrisol Fixanal, in which Ni is in oxidation state equal to +2.

2. Treatment of Ni acid solutions with lignin

Acid solutions with known concentration of Ni (ASN) were put in contact with the 0.4 g of lignin for intervals from 5 minutes to 50 hours. Each experience was carried out with temperature and initial pH maintained constants in the next ranks: 25 to 90ºC and 2 to 5 of pH. Latter, the suspension was filtered and the remained liquid was analyzed using and Integra XL GBC inductively coupled plasma optical emission spectrometer (ICP-OES). The adsorbed quantity was accounting using the difference between the quantity fed and the remaining in the filtrated solution.

3. Operational variables and ranks for the design criteria

3.1 Adsorbate concentration

Only the maximum quantity of adsorbate was established, this was obtained from the maximum quantity of metal that one hopes that contains the LIM after the process of demetalization of the coke, proposed for (De Chamorro and Romano, 2000). This quantity is equivalent to 40ppm.

3.2 Residence time

The maximum value was established over the base of the time used in the conventional adsorption process: 50 hours. The minimum is equal to the minimum used commonly in vessels: 5 minutes. (Turton et al, 1998)

3.3 Concentration of adsorbent

The rank of study was established from a previous experiences of adsorbent solubility made in the laboratory (Pérez et al, 2006). From these is established that the rank is from 0.5 to 4g of lignin/ L of solution.

3.4 Initial pH

The pH is limited for the minimum acidity that prevent the lignin to solubilize and, the maximum that can be employed without the hydrogen ions start to compete with metals by the active centers of the lignin. The rank of pH was established between 2 and 6.

3.5 Adsorption temperature

The rank of temperatures was established from 25 to 90ºC, due to for a higher temperature is needed to control de evaporated flows of the system in study.

Results and Discussion

Estimation of design criteria

Adsorbate concentration

To evaluate the adsorbent potential, were put in contact 200ml solutions with different concentration of Ni with an initial pH of 4, during 2 hours, with 0.4g of lignin.

This study was started with nickel concentration equal to 5ppm and it was becoming higher progressively to achieve 40ppm. The concentration was increased upper the maximum established from the LIM with the objective to obtain the 4 zones that must compound an isotherm, to guarantee that the values result from the adjustment of models are valid (Vasanth et al, 2006). From the figure 1, it can be observed that the saturation for these conditions of the nickel-lignin system is around 20ppm.

The value of saturation indicates that lignin is a competitive adsorbent comparing with activated carbon for Ni (Pérez et al, 2006), and corroborates the fact proposed for (Basso et al, 2002), that indicate the ionic affinity between the adsorbent and the adsorbate, is more important for adsorption of liquids than the structural characteristics of the adsorbent.
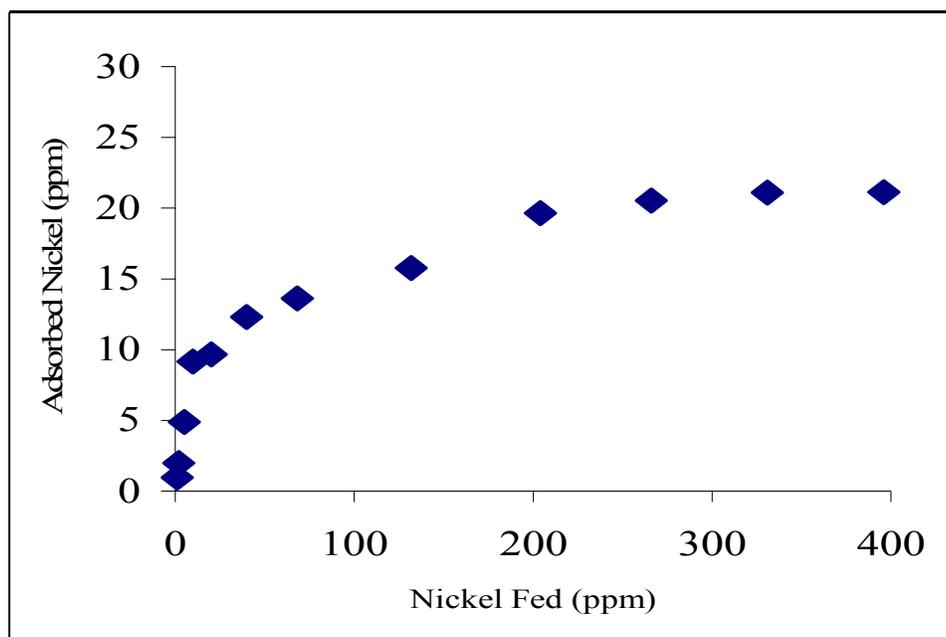

Figure 1. Adsorption Potential of Lignin.

To continue this work, it will utilize the acronym "ASN20" to refer to the solutions with 20ppm of Nickel.

Residence time

Solutions of ASN20 were prepared and put in contact to lignin for a concentration of 1g of lignin/L of solution, for an initial pH of 4. In figure 2, is represented the behavior of the contact time versus the adsorption capacity of the lignin.

It can be observed that in the first hour of contact, is adsorbed around 50% of the metal presents in the liquor. The quantity that is adsorbed is increased until around 97% for a time equal to 10 hours. The figure 2 also indicates, that after of the maximum value is achieved, the adsorption capacity doesn't show significant changes, it allows to infer that the velocity of desorption for the metal is negligible.

A minimum quadratic fitting was made to the experimental data, obtaining a relation between adsorbed nickel and residence time, as it is shown in equation 1.

$$Ni_{Ads.} = -12{,}81 \cdot t^2 + 80{,}66 \cdot t - 49{,}60 \qquad (1)$$

Where:

$Ni_{Ads.}$ = Adsorbed Ni (%).

t= Residence time (h)

The derivative of equation 1 gives a value equal to 3.15hours like maximum residence time. This value was established like design time.

Adsorbent concentration

With the objective of study the behavior of adsorbent concentration, solutions of ASM20 were put in contact for a time equal to 3.15h and an initial pH of 4, with different concentration of lignin. In figure 3, is presented the percentage of adsorbed nickel in lignin. It can be observed that the adsorbed Ni quantity is increased with an increase of lignin concentration, to achieve a maximum. This behavior is similar to the most of adsorbents, because the changes that can be produced in solution pH when more lignin is added, don't affect the ionic specie of Ni (Ni^{+2}).
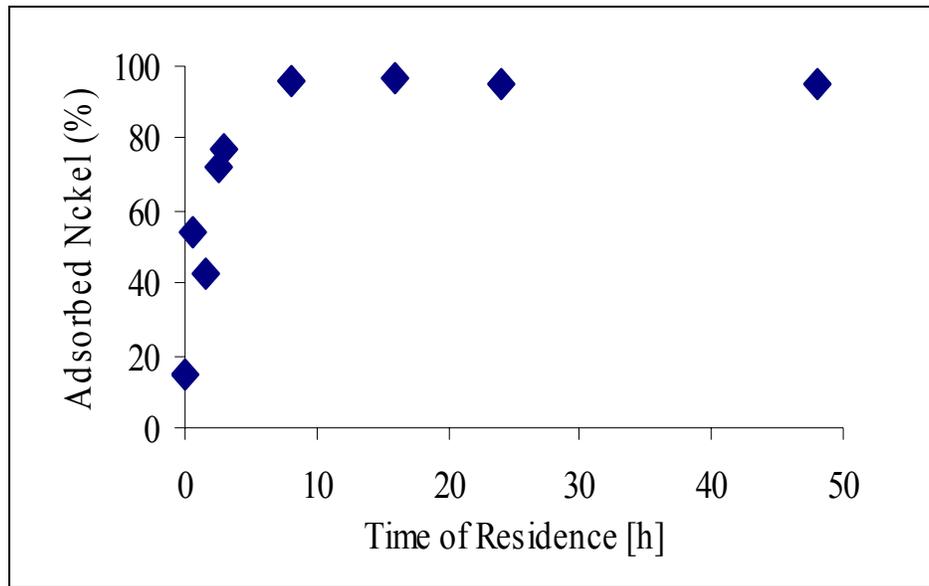

Figure 2. Residence Time Versus Lignin Adsorption Capacity.

Due to the employed criterion for the selection of adsorbent concentration was that the quantity of adsorbent had to be sufficient to adsorb all the metal fed, observing figure 3, can be established this value when concentration was equal to 1g of lignin/L of solution. Upon this value, the lignin added represents an excess.
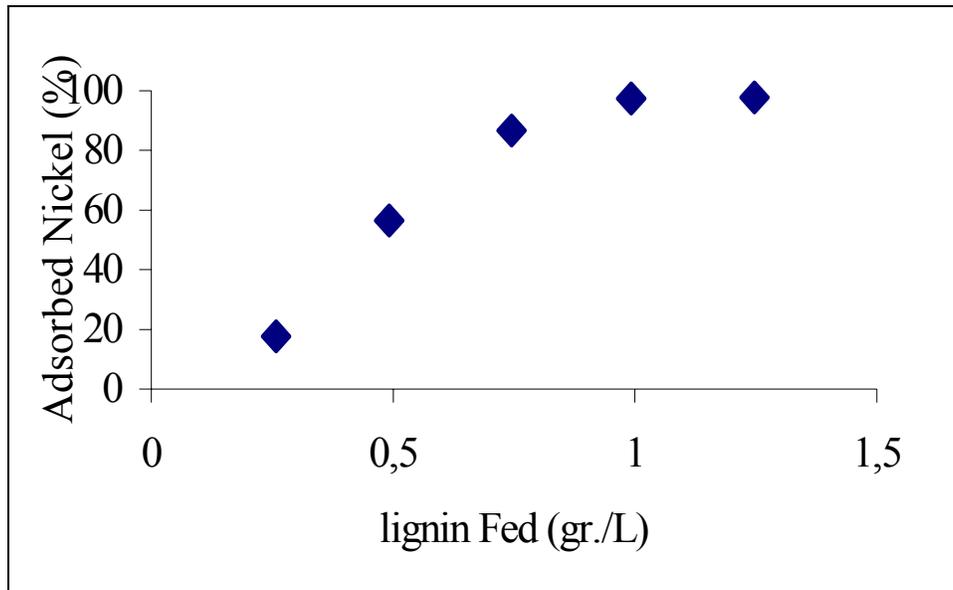
Figure 3. Percentage of **N**ickel Adsorbed for Lignin.

Initial pH

Solutions of ASM20 were put in contact with lignin for a concentration equal to 1g of lignin /L of solution, for a time equal to 3.15h and for different initial pH.

In figure 4, is presented the behavior of initial pH over adsorptive capacity of lignin. It can be observed that for pH below 2.5 the percentage of adsorbed Ni is negligible. This is due to the fact that the H^+ protons in solution form something like a barrier over the surface of lignin, obstructing the adsorption of the metallic specie, Ni^{+2}. When pH was increased, it was observed an important increase in the adsorption of the metal (pH of 3.5-5). But for a pH higher to 5, the adsorbed quantity decreased appreciatively. This diminution is a product of the higher solubility of lignin in the ASN, when the media is lightly acid. This avoids that the lignin can be separated from the aqueous solution using filtration. It was established that initial pH must be equal to 5.

Adsorption temperature

Solutions of ASN20 were put in contact, at initial pH equal to 5, with lignin at concentration equal to 1g of lignin /L of solution, during 3.15h for different temperatures.
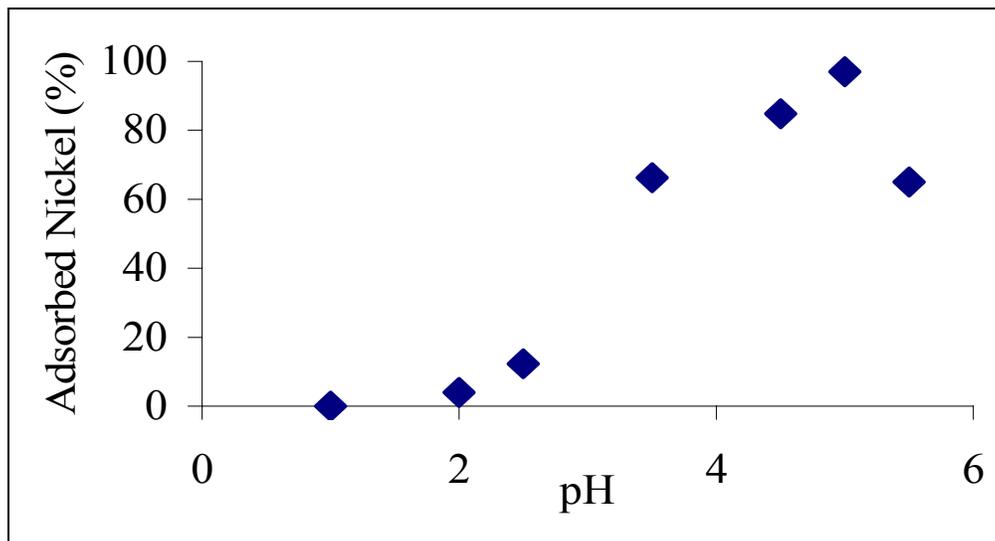

Figure 4. Influence of Initial pH over Nickel-Lignin System.

In figure 5, it is shown the effect of the temperature over the adsorptive capacity of lignin. It can be observed for the studied rank, that the process of adsorption of Ni is not significantly affected for the temperature. From 60ºC, it is observed a lightly diminution of the adsorptive capacity of lignin. It can be justified due to the little changes that occur in the pH, product of an increase in the temperature.
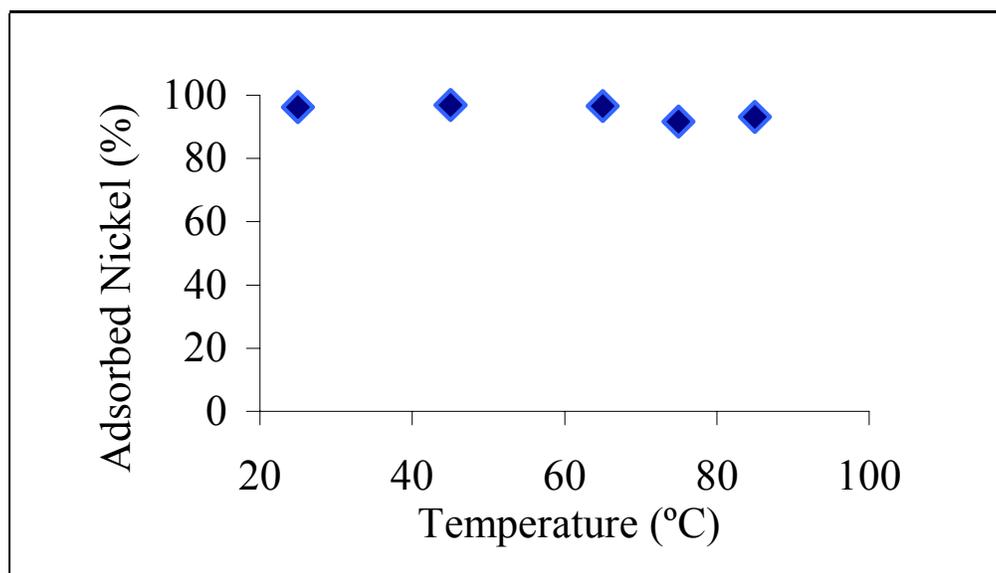

Figure 5. Influence of Temperature over the Nickel-Lignin System.

From this behavior, it can be inferred also, that the velocity corresponding to the arrival of the absorbate to the active center isn't a limiting stage, because otherwise the change of the temperature had produced a change in the capacity to adsorb when being increased the movement of particles within the solution. It is proposed to operate with a temperature equal to 25ºC. This last figure also indicates the dependency of the process to the kinetic and the independency to the thermodynamics, because for all operation conditions employed the equilibrium is not achieved. This is very important to a future design, due to it represents the possibility to modify operation conditions to increase the yield of the process without a lost of selectivity of the lignin as adsorbent.

Conclusions

From this work, it can be concluded that operational variables which have greater influence over the adsorption process for the nickel-lignin system are: concentration of adsorbate, residence time, concentration of adsorbent and initial pH.

The adsorption capacity of lignin corresponded to 10mg Ni/g lignin.

A residence time equal to 3.15h, was established like design time and the initial pH equal to 5.

The adsorption capacity was independent of the temperature, among an interval of 25 ºC to 90 ºC.

From these results is possible to continue with the design of an adsorption plant to extract nickel from LIM using lignin.

Acknowledgments

References

Bailey, S.; Olin T.; Bricka, R.; Dean, A. 1999. A rewiew of potencially low-cost sorbents for heavy metals. *Water Research* 33:2469-2479.

Basso, M.; Cerrella, E.; Cukierman, A. 2002. Lignocellulosic Material as Potentials Biosorbents of trace Toxics Metals from Wastewater. *Industrial Engineering Chemistry* 41:3580-3585.

Crist, R.; Martin, J.; Crist, R.D. 2004. Use of a Novel Formulation of Kraft Lignin for Toxic Metal Removal from Process Waters. *Separation Science and Technology* 39(7):1535-1545.

De Chamorro, M. and Romano, M. 2000. Simultaneous demetallization and desulphuration of carbonaceous materials via microwaves. *U.S. Patent n° 6.038.777*.

Lalvani, S.; Wiltowski, T.; Murphy, D.; Lalvani, L. 1997. Metal removal from process water by lignin. *Environmental Technology* 18:1163-1168.

Pérez, N., Rincón, G., Delgado, L., González, N. 2006. Use of biopolymers for the removal of heavy metals produced by the oil industry -A feasibility study. *Adsorption* 12:279-286.

Rouchi, A. and Washington, C. 2001. Only facts will end lignin war. *Science and Technology* 79(14):52-56.

Turton, R. and Bailey R. 1998. *Analysis, Synthesis and Design of Chemical Processes*. Prentice Hall International Series, New York, USA.

Vasanth Kumar, K. and S. Sivanesan. 2006. Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon. *Journal of Hazardous Materials* 134: 237-244.

Zhuang, J.; Walsh, T.; Lam, T. 2003. A new technology for the treatment of mercury contaminated water and soils. *Environmental Technology* 24 (7):897-902.