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Effect of pH and bed height in the adsorption of Nickel on the lignin presents in packed beds

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ABSTRACT

Nowadays, it is proving the feasibility to remove metals contained in heavy petroleum cokes way acid digestion with microwaves; nevertheless so that the process will be feasible industrially, it is necessary remove the metals of produced acid. In the search of a material be able to achieve this, it is found the lignin, which has showed an important capacity to do it. On particular this work is based on the evaluating of the effect that have the Nickel (+2) removal contained in acid liquors, over pH of the system and the height of the packed column with lignin. The main purpose was identifying how these parameters could affect to take the process to a big scale. Experiments consisted in pass an acid solution with 20ppm of Ni and pH of 3.5 (equivalent to the product of acid digestion of the coke); through a column of 1.08cm of internal diameter, with heights of beds from 2 until 15cm, during periods of time between 5min and 1 hour. The nickel concentration in the effluent was determined using inductive coupled plasma. The results showed that the lignin used is an effective adsorbent to Nickel, with an adsorption of 97% of fed metal. It was also found, that the bed height has a directly proportional influence over the quantity adsorbed, while pH has no changes independently of the bed height used; although, exits a pH variation depending of the capacity of the bed. If bed is not saturated, the pH has low values; while when bed is saturated, pH achieves values near to 7. This variation could be related to the adsorption of hydrogen ions over the lignin, these ions could compete with Ni ions for the same active sites, indicating when the column attains the saturation.

Keywords: Nickel, adsorption, lignin, packed bed.

INTRODUCTION

The removal of heavy metals, dyes and toxic materials of effluents, is a requirement at industrial level to satisfy the demanding environmental norms. This carries an increase in the processing costs and therefore an increase of the price of obtained products, diminishing the competitiveness of the companies. For this reason it is necessary to study and evaluate new low cost processes that allow the removal of the wished substances to the minimum value.

In this sense studies with satisfactory results in the toxic heavy metal removal from waters contaminated have been made, the removal is achieved by means of: chemical precipitation, ionic interchange, inverse osmosis and extraction with reliable (Taty-Costodes et. al., 2005). In addition, at the moment a great amount of studies focused in the use of biomass like adsorbent exist, since this adsorbent can accumulate high quantities of discharges heavy metals, has a low cost, it is available in enormous amounts as by-product or remainder of other processes and is efficient (Upendra and Manas,2006a).

Lignin is one of the forms as the biomass can be found and is after the cellulose, the main component of the wood. From the structural point of view, it can be considered polymeric substance that has hydroxyl and metoxi groups as well as it exhibits an abundant amount of functional groups that contains oxygen conforming phenolyc, carboxylic and sulphonic groups, and enolic structures. These groups allow to give to the Lignin a polyanionic character, and its polymeric flexibility is what it allows to surround and to neutralize manifold loaded metallic ions, forming complex macro-molecules "lignin-metal" by means of coordinated ionic and covalent connections (Rincón and Bustamante, 2004). Nevertheless the greater difficulty of its characterization is that the lignin definition is a generic name of a type of hydrocarbons, and therefore exist many types of lignins with variable properties and compositions according to their origin and the treatment which has been put under it (Sarkanen and Ludwing, 1971).

Many uses for the lignin have been proposed, and some have and increasing in importance industrial character. It serves like agglutinating, filling, dispersing and lately it has been developed like adsorbent of polluting agents.

For this last use, most of the studies made with bio-adsorbents (and in particular of lignin) have been in batch or by loads form, and the works where it is used the adsorption in packed beds for the metal removals are very few (Asok, et. al., 2006).This disable the handling of great amounts of effluents and therefore the possibility of making this separation process on greater scale, because it is not having the certainty of the possible functionality of the process on industrial scale (Upendra and Manas, 2006b).

Nevertheless, the few works reported on the use of biomass as adsorbent in packed beds, are agreed in the feasibility of the use of this type of material, taking in consideration like variables of the process the following ones: height of the bed, pH of operation, rate of flow of the adsorbate as well as the concentration of the solution.

In this sense, Zulfadhly et. al. 2001a, demonstrated to the ability of a macro fungus denominated Pycnoporus Sanguineus to adsorb Lead (II), Copper (II), and Cadmium (II), as well as Runping, et. al. 2005, investigated the capacity to adsorb Lead (II) and Copper (II) using chaff like adsorbent. Upendra and Manas, 2006c analyzed the removal of Cadmium (II) by rinds of rice dealt with Sodium Carbonate. This study has allowed the construction of the curves of rupture required to predict the parameters characteristic and the behavior of the column, for the design of an adsorption column.

On the other hand, the Group of Clean Alternative Technologies (Grupo de TEcnologías ALternativas Limpias, TECall) of the Simón Bolívar University has developing studies from demetalation and simultaneous desulphuration of the Venezuelan petroleum coke with the purpose of improving its quality when is diminishing the high concentrations of sulfur and heavy metals (Nickel and Vanadium). They have achieved to obtain a petroleum coke cleaner than can be commercialized to greater cost, also that the environmental impact generated by its use an adsorbent be smaller. Although in this process is generated an acid liquor that contains the heavy metals retired from the coke, and that needs to be regenerated to reuse it in the process.

In the look for a regenerated process, Perez et. al., 2006 studied by means of a process by lots, the Nickel adsorption from acid solutions using like adsorbent commercial lignin originated of the Kraft process of paper pulp production. In this study, they consider pH, time of contact, adsorbent amount and the initial concentration of the metal, as variables that can influence the process. The results show that when it is working with standardized acid solutions of the metals, it obtain that the Nickel presents great affinity by the Lignin, being the maximum percentage of Nickel adsorption of 97% of the present in the acid solution, when the pH of the initial solution is 4 and the initial concentration of Nickel is 20ppm.

As a continuation of this precedent work, in this work is pretending to show that the lignin can be an adsorbent of nickel when is operating on scale a bank of continuous form, as well as to observe the effect that pH of operation and the height of bed can have on the adsorptive capacity of the lignin present in packed beds. This knowledge will allow having a greater certainty of how the process will behave when the size of the plant is superior, moment in which the fluid-dynamic, mass and heat transfer effects become to phenomena with greater importance than the kinetic and the thermodynamic of the reaction considered from the studies by lots at laboratory level.

EXPERIMENTAL PROCEDURE

For the experiment, synthetic acid solutions with nickel ions prepared in the laboratory similar to the employees at level of laboratory with 20 ppm of initial Nickel and pH fit with H_2SO_4 in 3.8, were used. This allowed having a point of comparison with respect to the results of efficiency of adsorption between the previous works made by lots and the process to be made of continuous form.

For the adsorption, was designed and constructed to a continuous system on bank scale that uses columns of glass walls for the adsorption, with amounts of lignin weighted and packed in columns of 10, 15 and 20 cm og height and 1.08 cm of internal diameter. They were fed by the bottom with an acid solution that was stored in a container of 2 liters of capacity and that was impelled by means of a peristaltic pump with a flow of 1 L/hr. The solution that leaves the tower by the top was sent to a storage tank, which has connected a pHmeter in line. In order to avoid the drag of the lignin, in the adsorption tower were added layers of cotton in the ends.

For the determination of the amounts adsorbed by the lignin, an analyzer of Inductive Coupled Plasma (ICP) for the identification of the nickel concentrations in the exit solutions of the adsorption tower was used. The adsorbed amounts were determined as the difference between the fed quantities of metals and the exit quantities. Figure 1 is a representation of the raised process.

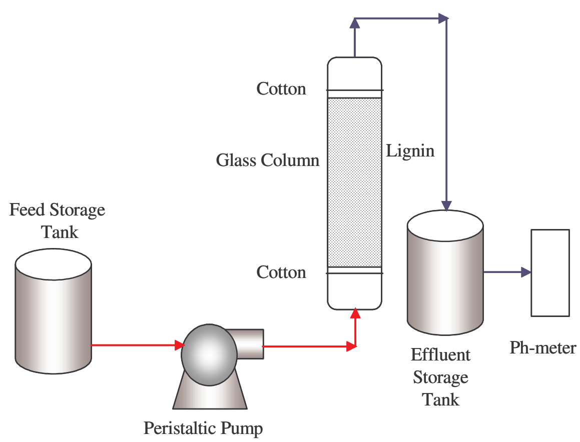

Figure 1: Experimental scheme

As far as the made experiences, these were divided in three, based on the looked for objectives: Initially different heights of the lignin was proven maintaining constant the rest of the variables, taking samples every 10 minutes until reaching one hour, with the purpose of identifying the rupture curves for each one of the height columns. In table 1 are showed, the conditions of this first experience.

Table 1: Experimental conditions for obtaining process of the rupture curve

Initial pH	Concentration ppm	Height cm	Time min
3.8	20	10-15-20	60

Secondly, it was desired to study the pH profile of the solution as it went through the bed and how this could be affected by the height of the bed. To achieve this, was developed an experiment using changes in the height, with a work time of 20 minutes. In table 2 the conditions used in this part are showed.

Table 2: Experimental conditions for the pH profile determination

Initial pH	Concentration ppm	Height cm	Time Min
3.5	20	2-4-6-8	20

Finally, to identify a relation between the saturation of adsorbent and the pH of the solution, a similar experience to the number 2 was made, but allowing with a bigger time of operation and a lower initial pH of adsorption. In table 3 are showed the conditions for this experience.

Table 3: pH and bed saturation relation

Initial pH	Concentration ppm	Height cm	Time Min
3	20	5	60

RESULTS AND DISCUSION

Obtaining rupture curves:

The Nickel adsorption is showed in figure 2, through the obtained rupture curves for different heights of bed. These curves represents the C/Co relation against the time, where C is the concentration of solute in the effluent in the liquid phase (mg/l) and Co is the initial concentration of solute in the liquid phase (mg/l). It can be appreciated the typical form of the rupture columns because the adsorption is a finite process.

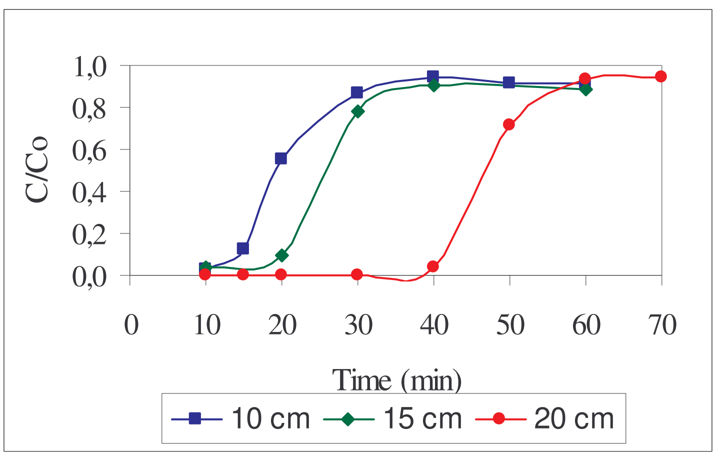

Figure 2: Rupture curves

The increase of the adsorption of the metal and the time of rupture (C/Co = 0.1) is related to the height of the bed due to that the increase of the amount of adsorbent employee allows to have greater active points for the adsorption of Nickel (Zulfadhly, et. al. 2001b). Also it is observed that the maxima adsorption is of 97% when it is on the rupture point; this is agreed with the percentage of adsorption found when working in a process by lots (González, 2005).

In the same form, in table 4 is showed the specific values for the time of rupture as well as the amount of required lignin to adsorb the amounts treated until the moment of the rupture. Being important to emphasize that the lignin becomes a more and more efficient adsorbent as the bed become greater, which can be related to the greater time of residence of the solution within the bed while the height is increasing, diminishing any difusional effect present in the used assembly. Nevertheless was not possible to use greater columns due to the requirement of greater pressures within the tower, this became risky the experiences with glass columns.

Table 4: Treated volume of effluent and lignin mass required to obtain the rupture curve

Height cm	Rupture Time min	Treated Volume L	Lignin Mass g	Lignin Mass per milliliter g/ml
10	14	0.2216	3.82	17.24
15	20	0.3166	5.29	16.70
20	41	0.6491	8.00	12.32

Profile of pH in the tower:

The experimental results obtained in this section, along with their possible ranks for an accepted error of 5% between them, are showed in figure 3. When is studying the relation between the height of the bed and the variation of pH within the tower, could be observed that the profile stayed constant in the time independently of the used height, which is typical of non-soluble systems. If the lignin would be very soluble in the solutions fed, an increase in the present amount in the tower would increase the amount of lignin available to be solubilize and therefore would be possible to observe changes in pH of the tower because the lignin is a substance able to interchange protons.

On the other hand, was observed that pH of the tower is superior to the fed one, which indicates that when the lignin make contact with the solution, diminishes the proton availability in the solution which could be being adsorbed by lignin. Also, it is observed that do not exist great variations of pH as the height is increased, which allows to infer that who really defines the behavior of pH in the column is pH of the initial solution and not the height of the bed as is showed in figure 3.

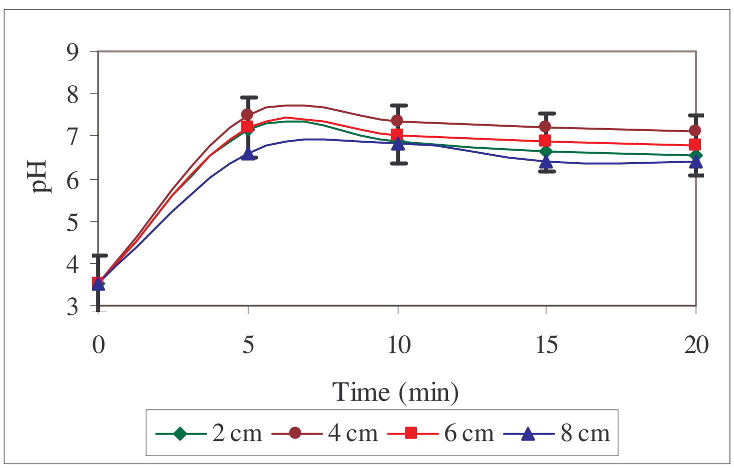

Figure 3: pH and be height relationship

Relationship saturation of adsorbent and pH of the last solution:

At last, was studied the relation of pH and the rupture curve for a bed of 5 cm and pH of 3. In this case, there is an agreement between the change of pH and the rupture point. When is working to low pH, the bed has the capacity to adsorb; while when pH reaches values near 7 the bed is saturated. Is for this, that the variation of pH on the exit could be related to the hydrogen ion adsorption on the lignin. These ions would compete with ions of Ni by the same active centers. The pH could be then, an indicative of when the column is saturated as is showed in figure 4. The importance of this finding is that in this form it is possible to be known in line, if the lignin is saturated, without to do a determination of metals, facilitating the process control, and also indicates that the lignin behaves as a resin of ionic interchange.

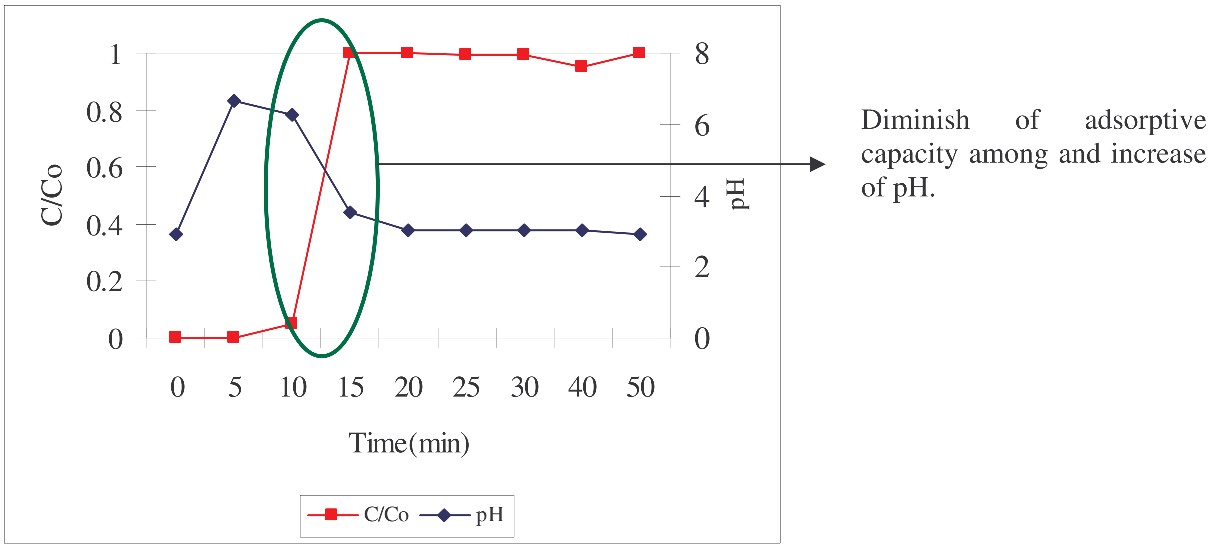

Figure 4: pH and rupture curve relationship

CONCLUSIONS

When this work is finished, is possible to indicate the following conclusions:

- The lignin is a efficient bio-adsorbent for the Nickel adsorption in flows of acid liquor product of the demetalation of coke via microwaves in systems of packed beds
- Was observed an analogy with respect to the Nickel removal of 97 %, between the continuous process and the process by lots.
- The pH maintains the same profile independently of the bed used in the studied rank. The pH and the height of the bed influences in the adsorptive process of studied metals.
- An increase of the efficiency of the lignin while the height of the bed is increased could be an indicative of difusional effects within the bed, which must be studied in future.
- The saturation of the bed could be predicted using a measuring instrument of pH in the exit of the column.
- Settled a plant to absorb of nickel and vanadium on scale bank.
- The obtained data of this work allowed the design of the pilot plant.
- The study demonstrates the feasibility of the bio-polymer use in the adsorption of nickel and vanadium of originating industrial waste water currents.

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