

## STUDY OF THE BEHAVIOR OF METAL ADSORPTION IN ACID SOLUTIONS ON LIGNIN USING A COMPARISON OF DIFFERENT ADSORPTION ISOTHERMS

N. PÉREZ, M. SÁNCHEZ, G. RINCÓN and L. DELGADO

*Dpto. Procesos y Sistemas, Univ. Simón Bolívar, 1080 Caracas, Venezuela.  
naperez@usb.ve*

**Abstract**— The adsorption process of Nickel and Vanadium dissolved in acid liquor on lignin is studied in this work. Different adsorption isotherm models are used to adjust liquid-solid systems: Langmuir, Freundlich and Redlich-Peterson. It was obtained that the metal adsorption using lignin proceeds by similar chemical mechanisms. Possibly the Nickel is adsorbed in heterogeneous monolayers, contrary to Vanadium which is adsorbed in homogeneous ones. Results of the parameters obtained for every adsorption model and adsorption system are reported too.

**Keywords**— adsorption, heavy metals, lignin, isotherms.

### I. INTRODUCTION

The heavy metals removal from liquids is a growing necessity due to two fundamental reasons: the necessity to diminish the effluent contamination for avoids possible damage to ecosystem and to the health of human being, and due to the high cost of these metals; presenting its removal as an economical feasible way to recover it for its future reutilization (Bailey *et al.*, 1999).

Many technologies have been developed with the last propose (Bailey *et al.*, 1999), however the most of them require process or separation agents that are expensive.

One of the ways has been the adsorption of these metals with activated carbon, which has many advantages, for example, to be a proved technology. However the high cost of the activated carbon and its limited regenerative capacity has difficult the establishment of this technology for these proposes.

Venezuela has one of the bigger heavy crude oil reserves of the world. These reserves are characterized by the high content of impurities like sulfur (S), nickel (Ni) and vanadium (V). Because of the problems in the industrial use of the crude and its derivatives, is necessary to find alternatives to diminish these impurities. With this propose the group of Tecnologías Alternativas limpias (Clean Alternative Technologies, TECall) of the Simon Bolivar University has developed a process that consists in the metal extraction from carbonaceous materials using a treatment with acid solution and stimulated by microwave (Chamorro and Kraüter, 2000).

During the treatment, the removed metals are dissolved in the acid solution, becoming this acid liquor

the main effluent of the microwave process LIM (*liquor of microwave irradiation*). However, to achieve that this process to be industrially feasible, the LIM has to be recovered to reuse it. In this sense, TECall, propose the use of an industrial byproduct (“lignin”) that is coming from black liquors of the pulp industry like metals adsorbent, fundamentally because its low cost and its observed adsorptive capacity (Acemioğlu, 2004).

In this work the results obtained when two heavy metals, like Ni and V, are put in contact with lignin are presented. The experience is performed at laboratory scale with controlled conditions of initial pH, temperature, contact time, and adsorbent and adsorbate concentrations. The goal is to evaluate the adsorptive capacity of lignin to adsorb the metals and to predict the possible adsorption mechanism in which is developed the adsorption by means of an analysis of three different adsorption isotherms.

### II. THEORY

The adsorption of a substance is its accumulation in certain surface. The result is the formation of a liquid or gaseous film on the surface of a solid body.

Into a material, all the chemical connections (ionic, covalent or metallic) of constituent atoms are satisfied. However, by definition, the surface represents a discontinuity of those connections. For these incomplete connections, it is strongly favorable to react with anything that is available, and for that reason it takes place in a spontaneous form. The exact nature of the connection depends on the specimens particularity implied, but the adsorbed material generally is classified like physisorbed or chemisorbed.

The simplest form of adsorption is the physisorption, due to weak attractive forces, generally Van der Waals forces. Because these forces are omnipresent, any clean surface exposed to the atmosphere accumulates a layer of physisorbed material.

The chemisorption happens when is formed a chemical connection, in this case defined as an electron interchange. The interchange degree and its symmetry depend on the involved materials.

In physisorption the adsorbed species (physisorbed) conserves its chemical nature, whereas a chemisorbed species undergoes a more or less intensive transformation, to give a different species. On the other hand, in a physisorption process the adsorbate can be adsorbed forming successive layers, whereas a chemisorption

process is restricted to a monolayer, since the solid surface is completely covered with the adsorbed substance. The chemical transformation of the chemisorbed specie requires a certain activation energy that is not necessary in the physisorption, reason why the last one usually happens to smaller temperatures.

The amount of accumulated material depends on the dynamic balance reached between the adsorption rate of the material on the surface and the desorption rate, that normally depends on temperature. While adsorption rate is greater and the desorption one is smaller, the available surface fraction that will be covered by adsorbed material at equilibrium will be greater.

The analysis and design of an adsorption process requires the adsorption equilibrium, which is the most important piece of information in the understanding of the adsorption process (Vasanth and Sivanesan, 2006).

Isotherms help to determine the adsorptive capacity of material and further help to evaluate the mechanism of performance of the adsorption system. Further it allows evaluate how an adsorption system can be improved (Vasanth and Sivanesan, 2006).

So far, most of the adsorption theories have been developed for gas–solid systems because the gaseous state is better to understand than the liquid. The solid–liquid adsorption process is influenced by parameters such as pH, solubility of solute in the solvent, solution temperature and also the initial solute concentration (Vasanth and Sivanesan, 2006).

Some models of adsorption isotherms have been used to predict the waste removal from residual water with certain adsorbents. Frequently the Langmuir, Freundlich and Redlich-Peterson isotherms are used for this propose (Bailey *et al.*, 1999).

### A. Langmuir Isotherm

Langmuir in 1916 proposed a theory to describe the adsorption of gas molecules over metal surfaces. This model depends on the assumption that intermolecular forces decrease rapidly with distance, and consequently predicts the existence of a monolayer of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes places at specific homogeneous sites within the adsorbent. It is then assumed that once a molecule occupies a site, no further adsorption can take place at the site. Moreover, the Langmuir equation is based on the assumption of an adsorbent of homogeneous structure where all adsorption sites are identical and energetically equivalent (Langmuir, 1916).

Theoretically, the adsorbent has a finite capacity for the adsorbate. Then the saturation value is reached when no further sorption can take place. The adsorption capacity can be represented by the following equation:

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (1)$$

where  $C_e$  (mmol/L) is the aqueous phase adsorbate concentration at equilibrium,  $q_e$  (mmol/g) is quantity of

solute adsorbed at equilibrium,  $q_m$  is equal to  $q_e$  for the complete monolayer and  $K_L$  (L/mmol) is the Langmuir isotherm constant (Vasanth and Sivanesan, 2006).

The essential characteristic of the Langmuir isotherm can be represented by a separation factor (dimensionless) called equilibrium parameter ( $R_L$ ) (Acemioğlu, 2004), and has the following form:

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (2)$$

where  $b$  is the Langmuir constant (L/mmol) y  $C_0$  is the initial concentration of the adsorbate (mmol/L). The value  $R_L$  indicates the isotherm type. A value between 0 and 1 indicate a favorable adsorption process (Acemioğlu, 2004).

### B. Freundlich Isotherm

The Freundlich model is an empirical equation employed to describe heterogeneous systems, it is characterized by a heterogeneity factor  $1/n$ . When  $n = 1/n$ , the Freundlich equation reduces to Langmuir model. The empirical equation can be described by:

$$q_e = K_F \cdot C_e^{1/n} \quad (3)$$

where  $C_e$  (mmol/L) is the liquid-phase adsorbate concentration at equilibrium,  $q_e$  (mmol/g) the quantity of solute adsorbed at equilibrium,  $K_F$  (L/(mmol<sup>1-1/n</sup>·g)) is the Freundlich constant, and  $1/n$  is the heterogeneity factor. This isotherm is another form of the Langmuir, an approach for adsorption on an “amorphous” surface. The amount of adsorbed material is the sum of adsorption on all sites. The Freundlich isotherm is derived by assuming an exponential diminution in the distribution function inserted into Langmuir equation. It describes reversible adsorption and is not restricted to the formation of a monolayer (Freundlich, and Heller, 1939).

### C. Redlich-Peterson Isotherm

Redlich and Peterson (1959) incorporated three parameters into an empirical isotherm. The Redlich-Peterson isotherm model combines elements from both the Langmuir and Freundlich equations, and the mechanism of adsorption is a hybrid unique and does not follow ideal monolayer adsorption. The Redlich-Peterson equation is widely used as a compromise between Langmuir and Freundlich systems. For further applications of the isotherm for use in kinetic or mass transport models, it is important to have the most accurate correlating equation (Redlich and Peterson, 1959).

The equation for this model is:

$$q_e = \frac{K_R \cdot C_e}{1 + a_R \cdot C_e^\beta} \quad (4)$$

where  $q_e$  (mmol/g) is the solid-phase sorbate concentration at equilibrium,  $C_e$  (mmol/L) is the concentration of adsorbate in equilibrium with liquid phase,  $K_R$  (L/g) and  $a_R$  (L/mmol<sup>1-1/β</sup>) are the Redlich-Peterson isotherm constants, and  $\beta$  is the exponent, which lies between 1

and 0. The application of this equation has been discussed widely, and its limiting behavior is summarized here:

- When  $\beta=1$  the equation is reduced to the Langmuir model:

$$q_e = \frac{K_R \cdot C_e}{1 + a_R \cdot C_e} \quad (5)$$

- When  $\beta=0$  the equation is reduced to Henry's law:

$$q_e = \frac{K_R \cdot C_e}{1 + a_R} \quad (6)$$

The linear form of these equations is obtained applying logarithms properties to both sides of the equations. The Table 1 shows the linear form of Langmuir, Freundlich and Redlich-Peterson isotherm.

An evaluation of the isotherms can be done just plotting the known data and determining the rest using the slop and the intersection point of the line. For example for the Langmuir case, has to be plotted the known data as  $C_e/q_e$  against  $C_e$ , and with the slop is determined the  $1/q_m$  value, and with the intersection point is obtained  $1/K_L \cdot q_m$ . Similarly,  $\ln(q_e)$  is plotted against  $\ln(C_e)$  for the Freundlich isotherm, and with the slop and the intersection point can be determined  $1/n$  and  $\ln(K_F)$  respectively. The Redlich-Peterson case is a little more complicated, because there are three unknown parameters. The form to find these parameters is based in the maximization of  $R^2$  from the linear fit to the data. In this way the  $K_R$  values are modified until obtain the best fit of the data.

Table 1. Linear form of the isotherms

<i>Langmuir</i>	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L \cdot q_m}$	(7)
<i>Freundlich</i>	$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$	(8)
<i>Redlich-Peterson</i>	$\ln\left(K_F \frac{C_e}{q_e} - 1\right) = \ln(a_R) + \beta \cdot \ln(C_e)$	(9)

#### Lignin like adsorbent

The adsorption of metals onto these materials (biosorbents) can be attributed to the proteins, carbohydrates, and phenolic compounds that have carboxylic groups, hydroxyl, sulphate, phosphate and amine that can coordinate with metallic ions. The process of adsorption of metals consists in different mechanisms that quantitative and qualitatively differs according to the metallic specie in solution and to the origin and processed of the adsorbent (Villaescusa *et al.*, 2004).

The lignin is an amorphous biopolymer, formed from fenolic groups, and containing hydroxyl groups, metoxyl, ether and carboxylic groups into its polymeric net (Parajuli *et al.*, 2005), which are responsible of the high adsorptive capacity of the lignin (Bailey *et al.*, 1999).

In spite of the amount of studies made during the last five decades, the lignin structure has not been

totally elucidated, specially the one coming from hardwood (Capanema *et al.*, 2005). The chemical structure, molecular weight, molecular weight distribution and the cross linking grade depend on factors such as: the age and type of the plant (hard wood, soft wood, grasses, etc.) and the part of the plant (tail, leaf, bark, etc.) from which the lignin is isolated (Singh *et al.*, 2005). Due to its high level of complexity and the absence of a universal character, has been very difficult to achieve a consensus around its structure.

Even been in capacity to approach a low molecular weight, the lignin is insoluble in water. Further more lignin has a strong resistance to chemical reaction, and a molecular weight that vary from 2000 to 15000 g/mol, which reveal a potential use like adsorbents of heavy metals for its removal of waste waters (Dermibas, 2004).

It is important to emphasize that the physisorption depends principally on the superficial area; and the chemisorption involves others aspects such as: the electronic distribution, the pore size, the active groups and the connection form of the adsorbed molecules (Barrow, 1964), whereas the chemisorption involves a huge variety of chemical reactions that are not able to be understand with a couple of simple processes. The coexistence of both processes at the same time, can explain that a substance with a no large superficial area is able to adsorb an ionic material competitively and with relative simplicity. For this reason, the lignin can be studied as adsorbent.

### III. MATERIALS AND METHODS

#### A. Adsorbent used

Acid precipitated basic lignin from the pulp and paper industry's black liquor was used. In Table 2, it is shown the most important superficial characteristic of this lignin.

#### B. Evaluation of the adsorptive behavior

To evaluate of lignin's adsorbing potential, LIM solutions of known Ni and V concentrations were put in contact with the lignin adsorbent at concentration of 1 g/L of solution during two hours at 25°C, and a 5 pH value, this value was kept constant adding H<sub>2</sub>SO<sub>4</sub> (0,5 mol/L). Next, the suspension was vacuum filtered and washed with distillate water, and the Ni and V concentrations of the resulting solutions were measured using an Integra XL GBC optical ICP spectrometer (inductively coupled plasma.) The difference between the initial and the final metal quantities corresponds to the adsorbed amount.

Table 2. Superficial texture of the lignin

Superficial characteristics	lignin
BET area (m <sup>2</sup> /g)	1.37
Total volume of pore (cc/g)	0.0018
Average diameter of pore (Å)	54

**IV. RESULTS AND DISCUSSION**

Results of adsorption of the studied metals on the lignin are shown in Fig. 1. This figure represents the amount of metal adsorbed per amount of lignin (adsorbent agent) ( $q_e$ ). It is observed that the Ni adsorption performance is better than the V one for all the initial concentrations evaluated. In Fig. 1, the four regions identified for an isotherm by Vasanth and Sivasenan (2006) can be clearly differentiated, which are necessary as a guarantee of the reliability of the parameters obtained using the isotherm analysis.

For the case of Ni, the final concentration at equilibrium per amount of absorbent is over 0.009 mmol/g whereas the concentration of V is around 0.008 mmol/g. These results were compared with the results obtained by González (2005), who obtained the adsorption curve of Ni and V over activated carbon CAC. The final concentrations at equilibrium obtained by González (2005) for the Ni and V, were 0.004 and 0.014 mmol/g respectively. These quantities are similar to those obtained in this work, reason why it is possible to say that the lignin is a competitive adsorbent, although it has a superficial area 1000 times smaller.

Carrillo (1999) mentioned that the superficial area is not a satisfactory indicator of the adsorptive capacity for an adsorption in liquid phase, in this case the relevant factor is the distribution and size of the pores. When the pore size and the adsorbed molecule size are similar the attraction is higher (Martin, 1980). In this sense, the lignin has the advantage of an average pore size equivalent to the mesopores, this size is appropriated for adsorbents.

In order to predict the adsorption mechanism of Ni and V on the lignin, the Langmuir model was initially used due to its simplicity; in spite of it would suppose in this case, the homogeneity of the lignin surface used. Figure 2 shows the Langmuir isotherms for the studied systems. Each one of these isotherms was fitted using a linear regression obtained standard deviation values ( $R^2$ ) higher than 0.99 in both cases (Table 3). It indicates that contrary to the expected results, a convenient fitted of this model for the studied case is reached. The existence of an adsorption process by homogeneous monolayers would seem improbably due to the knowledge of the

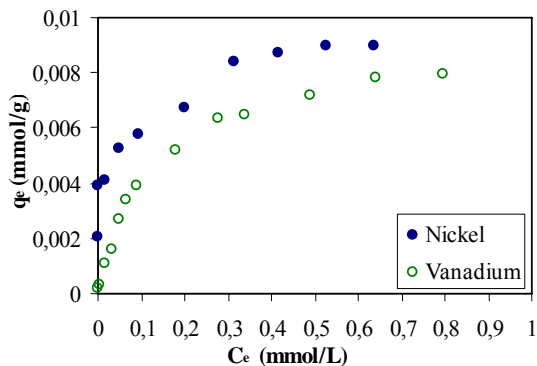


Figure 1. Adsorption of metals on the lignin

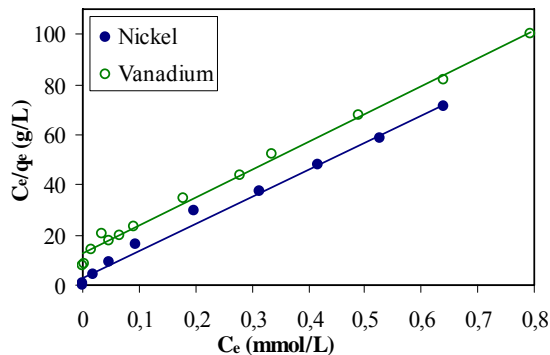


Figure 2. Isotherm of Langmuir

Table 3. Parameters of the fit by Langmuir isotherm

	Nickel	Vanadium
$C_e/q_e$ (g/L)	$107.77 \cdot C_e + 3.1135$	$111.79 \cdot C_e + 12.293$
$R^2$	0.9905	0.9930
Parameters		
$K_L$ (L/mmol)	34.314	9.0945
$q_m$ (mmol/g)	0.00928	0.00895

heterogeneity of the adsorbent. In addition, parameters of the Langmuir model are also presented in Table 3.

The existence of a multilayer process was corroborated fixing the experimental data conveniently in order to obtain the Freundlich isotherms, which were fitted using a linear regression as is shown in Fig. 3. Table 4 shows the parameters obtained for the studied systems using the Freundlich isotherms.

The standard deviation values resulted lower than those obtained using the Langmuir model. It suggests that the adsorption in the studied systems do not seem to carry through multilayers, therefore the quantity of adsorbent could be a limiting in the process, and when it is saturated, results impossible to adsorb more metal. On the other hand, it can be observed that the regressions obtained from Langmuir model are better than those from Freundlich model, this fact reflects that the adsorption process is fundamentally chemical, because the Freundlich model represents principally the case of physical adsorption whereas the Langmuir model represents the case of chemical adsorption.

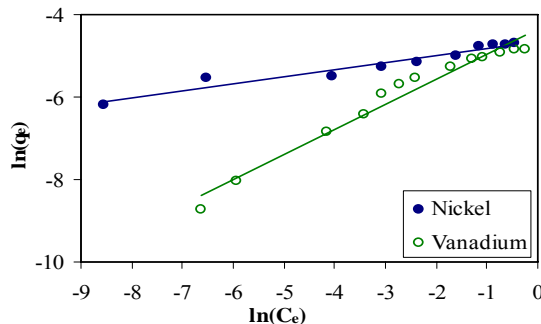


Figure 3. Isotherm of Freundlich

Table 4. Parameters of the fit by Freundlich isotherm

	Nickel	Vanadium
$\ln(q_e)$	$0.171 \cdot \ln(C_e) - 4.6563$	$0.6089 \cdot \ln(C_e) - 4.3541$
$R^2$	0.9476	0.9683
Parameters		
$K_F$ (L/mmol <sup>1-1/n</sup> g)	0.0095	0.0126
$1/n$	0.171	0.6089

As it was initially assumed that the adsorption process would not carry through homogeneous monolayers, and the fitting by Freundlich model was poor for the studied systems, the Redlich-Peterson model (Fig. 4), which represents the adsorption model as monolayers that can be homogeneous, was used to adjust the process.

When the experimental data were fitted using this model the best standard deviation values were obtained for the Ni compared with the other models previously used (around 0.998), but not for the V (around 0.984). It is inferred that as Freundlich model predict, the adsorption mechanisms of both metals seem to be different, being the physisorption more important for the V than for the Ni.

It could be explained because the V ions are bigger than the Ni ones and they has higher possibility to be grabbed in the mesopore of the lignin used, making possible a high physical adsorption for this case.

Table 5 shows the parameters obtained for the Redlich-Peterson model. A difference between these parameters for Ni and V is observed. This is an additional evidence that corroborates the nonequality between both mechanisms.

### V. CONCLUSIONS

Some conclusions can be obtained through the realization and analysis of the isotherms for Ni and V on the lignin:

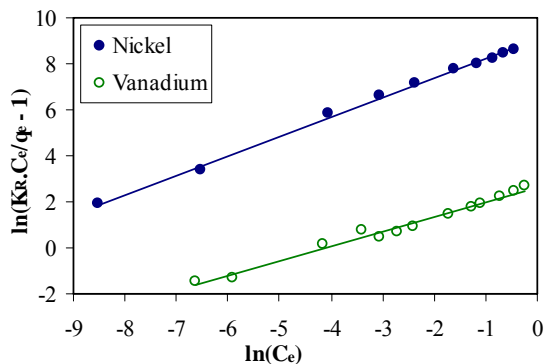


Figure 4. Isotherm of Redlich-Peterson

Table 5. Parameters of the fit by Redlich-Peterson isotherm

	Nickel	Vanadium
$\ln(K_R \cdot C_e / q_e - 1)$	$0,8428 \cdot \ln(C_e) + 9,0604$	$0,6391 \cdot \ln(C_e) + 2,6380$
$R^2$	0,9977	0,9840
Parameters		
$K_R$ (L/g)	80	0,152
$a_R$ (L/mmol <sup>1-1/β</sup> )	8607,6	13,985
$B$	0,8428	0,6391

The lignin is an adsorbent agent for Ni and V, being best for the first one.

The adsorption process obtained for both metals is fundamentally chemical.

The adsorption of Ni could be to carry through the formation of monolayers of heterogeneous shapes on the lignin.

The adsorption of V could be to carry through the formation of homogeneous monolayers with high possibility to be adsorbed for physical process.

It is recommendable to account the adsorption energies present in the process for each metal in order to corroborate if a physical or chemical mechanism is being developed.

### VI. ACKNOWLEDGMENTS

This work was supported by Simon Bolivar University's DID through project DI-CAI-008-05, by FONACIT through project No. 2005000432, and by the Alfa lignoCarb Program (Alfa0412FAFI).

### REFERENCES

- Acemioğlu B., "Removal of Fe(II) ions from aqueous solution by Calabrian pine bark wastes", *Bioresource Technology*, **93**, 99 – 102 (2004).
- Bailey S., T. Olin, R. Bricka and D. Adrian, "A review of potentially low-cost sorbents for heavy metals", *Water Research*, **33**, 2469 – 2479 (1999).
- Barrow G., "Fisicoquímica", Editorial Reverté, 1964, 686 – 705.
- Capanema E., M. Balakshin and J. Kadla, "Quantitative Characterization of a Hardwood Milled Wood Lignin by Nuclear Magnetic Resonance Spectroscopy", *Journal of Agricultural and Food Chemistry*, **53**, 9639 – 9649 (2005).
- Carrillo M., "Estudio de la eficiencia del carbón activado en la remoción de MTBE en muestras de aguas contaminadas", Trabajo de grado de Licenciatura en Química. Universidad Simón Bolívar. (1999)
- Chamorro M. and M. Kraüter, "Simultaneous demetalization and desulphuration of carbonaceous materials via microwaves", U. S. Patent n° 6.068.737, May (2000).
- Demirbas A., "Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignification", *Journal of Hazardous Materials*, **109**, 221 – 226 (2004).
- Freundlich, H., and W. Heller, "On Adsorption in Solution", *J. Amer. Chem. Soc.*, **61**, 2228 (1939).
- González N., "Estudio de la adsorción de níquel y vanadio por ligninas", Trabajo de grado de Licenciatura en Química. Universidad Simón Bolívar. (2005)
- Langmuir I., "The constitution and Fundamental Properties of Solids and Liquids", *J. Am. Chem. Soc.*, **38**, 2221 - 2295 (1916).
- Martin R., "Activated Carbon Product Selection for Water and Wastewater Treatment", *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 435 – 441 (1980).
- Parajuli D., K. Inoue, K. Ohto, T. Oshima, A. Murota, M. Funaoka and K. Makino, "Adsorption of heavy

- metals on crosslinked lignocatechol: a modified lignin gel”, *Reactive and Functional Polymers*, **62**, 129 – 139 (2005).
- Redlich O. and D. L. Peterson, “A Useful Adsorption Isotherm”, *J. Phys. Chem.*, **63**, 1024 (1959).
- Singh R, S. Singh, K. Trimukhe, K. Pandare, K. Bastawade, D. Gokhale and A. Varma, “Lignin–Carbohydrate complexes from sugarcane bagasse: Preparation, purification, and characterization”, *Carbohydrate Polymers*, **62**, 57 – 66 (2005).
- Vasanth K. and S. Sivanesan, “Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon”, *Journal of Hazardous Materials*, In Press, Corrected Proof, Available online 25 January 2006.
- Villaescusa I., N. Fiol, M. Martínez, N. Miralles, J. Poch and J. Serarols, “Removal of copper and nickel ions from aqueous solutions by grape stalks wastes”, *Water Research*, **38**, 992 – 1002 (2004).

**Received: May 24, 2006.**

**Accepted for publication: August 11, 2006.**

**Recommended by Editor R. Gómez.**