Acid-activated Carbons from Peanut Shells: Synthesis, Characterization and Uptake of Organic Compounds from Aqueous Solutions

Luis C. Romero, Antonio Bonomo and Elio E. Gonzo* *Instituto de Investigaciones para la Industria Química (INIQUI-CONICET), Facultad de Ingeniería, Universidad Nacional de Salta (UNSa), Buenos Aires 177, A4402 FDC Salta, Argentina.*

ABSTRACT: Activated carbon with a high adsorption capacity for the removal of organic compounds from aqueous solutions was made from phosphoric acid-activated peanut shells. Adsorption isotherms for the uptake of phenol, iodine, Methylene Blue and tannic acid were obtained at 22°C. Freundlich, Langmuir and previously developed equation models all explained the experimental data satisfactorily. Further analysis using the Dubinin–Radushkevich equation showed that the maximum micropore volume accessible to the adsorbate decreased as the molecular size increased, suggesting a molecular sieve or gate effect. A comparison was made with the micropore volume as determined by nitrogen adsorption at −196°C. The results presented indicate that peanut shell residues provide a suitable option for the preparation of activated carbon with good surface properties and the ability to remove organic compounds from aqueous solutions.

INTRODUCTION

Activated carbons are high surface area porous materials with exceptional adsorptive properties. They are used in industry for purifying drinking water, domestic and industrial wastewaters, as well as environmental remediation. Activated carbon can be produced from a number of agricultural by-products. Normally, such precursors are exposed to several activation methods in an effort to achieve an activated carbon with the best qualities for a particular application (Toles *et al.* 1998; Sircar 2001; Norit Americas Inc. 2000).

Nut shelters, grain miller, oilseed crusher and raw sugar factories create huge amount of shells, hulls, cobs and fibre each year from renewable resources. The conversion of agricultural wastes to adsorbents such as activated carbon is a major economic and ecological issue. One such opportunity would be to convert peanut shell (an agricultural by-product) to high-value activated carbon. To design adsorption equipment, it is necessary to know the adsorption capacity of the activated carbon. Adsorption capacity is usually expressed by an isotherm derived from measured data.

The objective of the present work was to develop an acid-activated carbon from peanut shells using concentrated phosphoric acid. We then wished to characterize the activated carbon obtained, determining the specific surface area, total pore and micropore volume and pore-size distribution. Finally, the adsorptive capacity towards the uptake of organic compounds from aqueous solution was determined.

---

*Author to whom all correspondence should be addressed. E-mail: gonzo@unsa.edu.ar.

Four organic compounds, viz. phenol, iodine, Methylene Blue and tannic acid, were chosen for this study because of their range of molecular sizes and polarities, as well as their importance as environmental pollutants.

EXPERIMENTAL

Adsorbent synthesis

Peanut shells were obtained from Cooperativa Agropecuaria Limitada (COTAGRO), Córdoba, Argentina. The shells were ground and sieved to a 10–20 ASTM mesh (2.0–0.84 mm) particle size prior to activation.

It is well known that chemical activation using phosphoric acid at relatively moderate temperatures produces high surface area and high microporosity materials (Blanco Castro *et al.* 2000; Toles *et al.* 2000). For this reason, the peanut shells were mixed in a 0.9 acid/shell weight ratio with 40 wt% H_3PO_4 and allowed to soak for 1 h at room temperature. Then ca. 30 kg of the impregnated shells were treated in a rotary kiln heated by means of a natural gas burner at one end. The natural gas combustion was carried out using a 20% excess of air over the molar stoichiometric air/fuel ratio. The temperature was 160°C at the oven entrance and 500°C at the exit. A residence time of 1.5 h was employed. After such acid activation the sample was cooled to room temperature and then rinsed in hot deionized water until the pH of the wash water was ca. 7.0. The procedure was repeated until no residual phosphate was detected in the wash water with lead nitrate solution. After washing, the material obtained was dried at 110°C.

A 1 kg sample of the washed and dried material was ground in a ball mill and sieved, thereby allowing samples of mesh size between 30–50, 50–60, 60–80, 80–100 and > 100 to be obtained. These screened samples corresponded to particle sizes ranging in diameter from < 0.149 mm to 0.45 mm.

Adsorbent characterization

BET surface area and pore-size distribution

Such analysis was performed using a Quantachrome Autosorb-1 instrument and a Cahn RG electrobalance. Surface area measurements were obtained from the nitrogen adsorption isotherm measured at −196°C using the BET equation. Specific surface area determinations were carried out on two samples, one with a particle size corresponding to 50–60 mesh and the other of > 100 mesh, using both types of equipment. Almost identical specific surface areas were obtained for both samples. Micropore volumes were determined applying the Dubinin–Radushkevich (DR) equation (Wood 2001), with the total pore volume being calculated in this case from the total amount of nitrogen adsorbed at a relative pressure (P/P^0) of 0.95. The pore-size distribution was obtained using the procedure of Sun (2002).

Adsorption of organic compounds

The four compounds used for studies of adsorption by the activated carbon from aqueous solution, i.e. phenol, iodine, Methylene Blue and tannic acid, were selected because the adsorption capacities towards these adsorbates have been employed to rank activated carbons for different applications.

These compounds have molecular weights ranging from 94 to 1701 g/mol. Phenol and iodine have molecular diameters of 0.62 and 0.56 nm, respectively (Hsieh and Teng 2000) and serve as indicators for the adsorption of small molecules. Phenol is a small polar aromatic compound whose derivatives are frequently encountered in wastewaters. The iodine adsorption capacity of the carbon is useful for the characterization of the adsorbent (surface area) as well as the effect of non-polar molecules. The diameters of Methylene Blue and tannic acid molecules are 0.906 nm (Reid *et al.* 1987) and 1.6 nm (Hsieh and Teng 2000), respectively. The adsorption of these substances may be related to the adsorption capacity of the carbon to colour and larger molecules.

Reagent grade phenol (Fluka), iodine (Fluka), Methylene Blue (Sigma) and tannic acid (Aldrich) were used for preparing the corresponding aqueous solutions. Adsorption was conducted using adsorbate solutions of known initial concentration, employing different dosages of dried carbon in 50-cm³ or 100-cm³ volumes of solution contained in 250-cm³ stoppered Erlenmeyer flasks. The sealed flasks were shaken at 150 rpm for 3 d in a water bath maintained at 22°C, after which the sample was filtered. The adsorbate concentrations in the residual and initial solutions were both analyzed using a UV–vis spectrophotometer (Beckman DU 520) at appropriated wavelengths, i.e. 268, 474, 620 and 275 nm for phenol, iodine, Methylene Blue and tannic acid, respectively. The iodine stock solution for the adsorption capacity experiments had a concentration of 32.7 mmol/l and was prepared according to the Norit WIQC0024 technique (Norit Americas Inc. 1999). An initial concentration of 10.6 mmol/l was employed for phenol adsorption, 116.2 µmol/l for tannic acid adsorption and 3.756 mmol/l for Methylene Blue adsorption experiments. Carbon samples with particle sizes smaller than 0.149 mm were used as the adsorbent in all experiments.

The amount of solute adsorbed at equilibrium per unit weight of adsorbent (q) was determined from the equation:

$$q \ = \ \frac{(C_0 \ - \ C_e)V}{W} \tag{1}$$

where C_0 and C_e are the solute concentrations of the initial solution and residual solution at equilibrium, respectively, while V and W are the volume of solution and weight of carbon employed.

RESULTS AND DISCUSSION

Table 1 summarizes the surface characteristics of the activated carbon used in the present work. The mean pore width (L_m) was estimated from the total pore volume and specific surface area by assuming that the space in the micropores was similar to that between two parallel plates. The micropore volume was calculated from the nitrogen adsorption isotherm using the DR equation.

TABLE 1. Surface Properties of Activated Carbon Employed

S_g (BET) (m²/g)	S_g (iodine) (m²/g)	V_T (P/P⁰ = 0.95) (cm³/g)	V_{micro} (cm³/g)	V_{meso} (cm³/g)	L_m (nm)	Bimodal PSD peaks maximum (nm)
1735	1693	1.12	0.91	0.21	1.3	0.8–1.6

As can be seen from Table 1, 81.25% of the total pore volume related to micropores, the total pore volume corresponding to the amount of nitrogen adsorbed in both micropores and mesopores. Hence, subtraction of the micropore volume (V_{micro}) from the total amount adsorbed (V_T) provided the mesopore volume (V_{meso}).

Analysis of the pore-size distribution (PSD) showed the existence of a bimodal distribution in the micropore range. Thus, the pore volume distribution exhibited two distinct peaks at ca. 0.8 nm and 1.6 nm pore width, with a broad shoulder beginning at ca. 2 nm with a maximum at 2.6 nm. Finally, a peak also occurred at 14 nm. It is of note that the pore volume corresponding to the mean pore width calculated from the total pore volume and the specific surface area was almost zero.

The Langmuir, Freundlich and a previous developed model were employed for modelling the adsorption isotherms, with non-linear regression analysis being used to determine the isotherm constants. In this analysis, the experimental adsorption data were fitted to the isotherm adsorption model by minimizing σ^2, the sum of the square of the difference between the experimental and estimated adsorption capacities, for each organic compound studied:

$$\sigma^2 \; = \; \min\left[\sum_{j=1}^{N_{ij}} \left(q_{ij}^{exp} - q_{ij}^{cal}\right)^2\right] \tag{2}$$

where N_{ij} is the number of experimental data points for compound i, q_{ij}^{exp} is the amount adsorbed as measured experimentally and q_{ij}^{cal} is the correlated amount adsorbed as calculated from the particular adsorption isotherm model employed.

Figure 1 shows the equilibrium adsorption isotherm of phenol. The experimental data gave a good fit to the Freundlich adsorption equation:

$$q \; = \; 0.974 C_e^{0.413} \tag{3}$$

with $\sigma^2 = 0.007123$ and an average relative error (E%) of 1.6% when q was expressed as mmol/g and C_e as mmol/l.
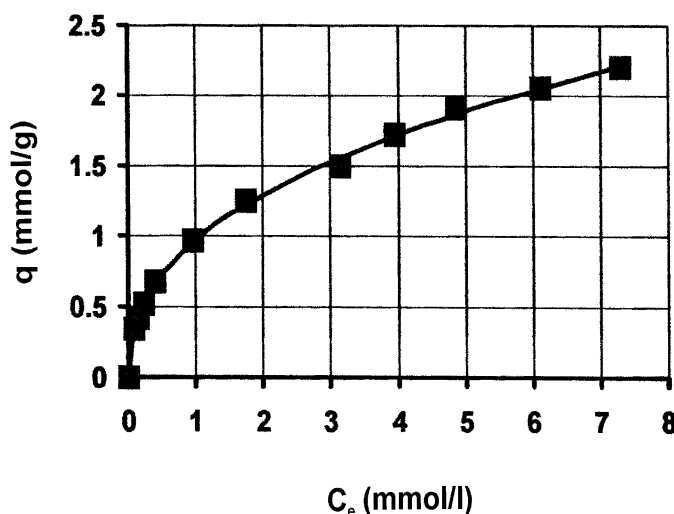

Figure 1. Adsorption isotherm of phenol: (■) experimental data and (—) Freundlich equation fit.
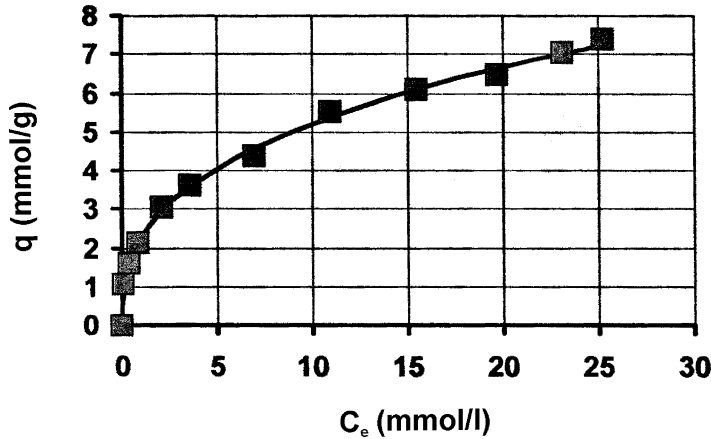
Figure 2. Adsorption isotherm of iodine: (■) experimental data and (—) Freundlich equation fit.

Optimum fitting for the equilibrium adsorption of iodine could also be obtained via the Freundlich adsorption isotherm (Figure 2):

$$q \;=\; 2.2643 C_e^{0.3604} \tag{4}$$

with $\sigma^2 = 0.15385$ and $E\% = 2.5\%$ when q was again expressed as mmol/g and C_e as mmol/l.

Iodine adsorption provides a universal test for the adsorptive properties of an activated carbon and may be defined as mg iodine adsorbed per g carbon at a residual concentration of 20 mmol/l. As a rule of thumb, 1 mg iodine adsorbed under such conditions corresponds to an internal surface area of 1 m^2 as measured by the BET method (Norit Americas Inc. 1999). In our case, the value of q was 6.665 mmol/g when C_e was equal to 20 mmol/l (Figure 2). This corresponds to 1693 mg/g so that $S_g = 1693$ m^2/g, i.e. very close to that obtained applying the BET equation to the nitrogen adsorption isotherm. This result confirms the above rule.

The experimental data for the adsorption of Methylene Blue are depicted in Figure 3. In this case, the best fit was found with the Langmuir equation:

$$q \;=\; \frac{30.027 C_e}{1 \,+\, 25.82 C_e} \tag{5}$$

with $\sigma^2 = 2.056 \times 10^{-4}$ and $E\% = 0.5\%$ when q was again expressed as mmol/g and C_e as mmol/l. As seen from the figure, the saturation capacity of the carbon was reached at a very low equilibrium concentration of Methylene Blue, i.e. $C_e \approx 0.16$ mmol/l (50 ppm). This is one of the reasons for employing Methylene Blue solutions as a standard analysis for ranking activated carbons.

Finally, Figure 4 shows the adsorption of tannic acid as a function of the equilibrium concentration of the adsorbate. In this case, the isotherm was of type II in the BET classification (Gregg and Sing 1982), i.e. sigmoidal in shape. This behaviour is a characteristic of strong interaction between the adsorbed molecules (Guerasimov *et al.* 1977) and is also found in the adsorption of metallic ions at relatively high pH values (Shawabkeh *et al.* 2002). Such behaviour is not
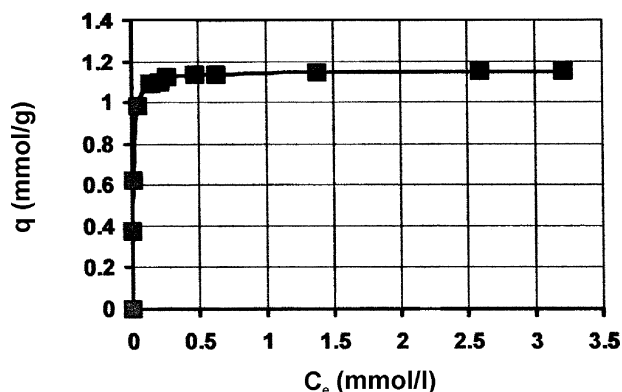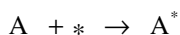
Figure 3. Adsorption isotherm of Methylene Blue: (■) experimental data and (—) Langmuir equation fit.

unexpected when account is taken of the polarity and size of tannic acid molecules. If the following adsorption process is considered:

$$A + * \rightarrow A^*$$

it is possible to write the model isotherm (Gonzo and Gonzo 2003) as:

$$q = \frac{q^{\circ}KC_A}{(1 - KC_A)(1 + kKC_A)} \tag{6}$$

where q° is the saturation capacity of the carbon and K is the adsorption equilibrium constant. The quantity k is a parameter in the equation for the activity coefficient of the adsorbed species, $\gamma_{(A^*)}$, as defined by Kiseliev (1967):

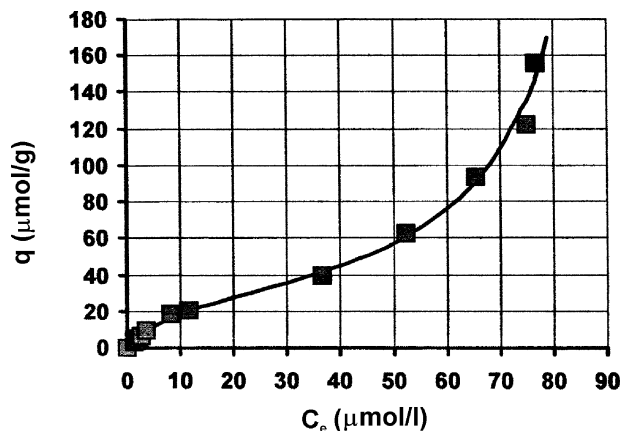$$\gamma_{(A^*)} = \exp(-kq/q^{\circ}) \tag{7}$$

Figure 4. Equilibrium adsorption of tannic acid: (■) experimental data and (—) equation (8) fit.

When equation (6) was fitted to the experimental data, the following isotherm was obtained:

$$q = \frac{3.49583C_e}{(1 - 0.010506C_e)(1 + 0.10866C_e)} \qquad (8)$$

where:

$$q^o = 332.7 \text{ μmol/g}; \quad K = 0.0105065 \text{ (1/μmol)}; \quad k = 10.3; \quad \gamma_{(A*)} = \exp(-0.031q) \quad (9)$$

with $\sigma^2 = 255.479$ and an average relative error (E%) of 4%.

To determine the effects of micropore volume on the adsorption of the organic compounds studied from aqueous solution, the adsorption data were interpreted using the DR equation (Holland *et al.* 2001):

$$q = q_m^o \exp(-B\varepsilon^2) \qquad (10)$$

where q_m^o is the maximum amount of adsorbate that can be adsorbed in the adsorbent micropores and B is a constant related to the average free energy of adsorption (E_{ad}) for a particular adsorbent–adsorbate system. Hsieh and Teng (2000) have provided the relationship between E_{ad} and B:

$$E_{ad} = (2B)^{-\frac{1}{2}} \qquad (11)$$

The adsorption potential (ε) for adsorption from a liquid solution is given by Barton (1993) as:

$$\varepsilon = RT \ln\left(\frac{1}{C_e\gamma}\right) \qquad (12)$$

where C_e is the equilibrium concentration (g/g) and γ the appropriate activity coefficient.

According to Dubinin's Theory of Volume Filling of Micropores (Wood 2001), the maximum micropore volume (ω^o) accessible to the adsorbate can be obtained by multiplying q_m^o by the liquid molar volume (V_M) of the adsorbate:

$$\omega^o = q_m^o V_M \qquad (13)$$

In turn, the DR equation (10) can be linearized as:

$$\ln q = \ln q_m^o - B\varepsilon^2 \qquad (14)$$

allowing linear plots to be obtained from an application of equation (14).

Such plots are shown in Figures 5 and 6 for the adsorption of phenol and iodine from the aqueous phase and in Figure 7 for the adsorption of gaseous nitrogen. These allowed the values of q^o and E_{ad} to be determined for each organic compound. The maximum micropore volume accessible to each adsorbate was obtained using equation (13) and the corresponding results are listed in Table 2. The maximum micropore volumes (ω^o) found from the liquid-phase adsorption of the organic compounds were smaller than those determined via nitrogen adsorption measurements. Table 2 also lists the ratio $R = \omega_i^o/\omega_{N_2}^o$. This ratio decreased as the molecular size of the adsorbate increased, indicating that the micropores were not totally utilized by the adsorbate molecule and thereby suggesting that a molecular sieving action occurred.
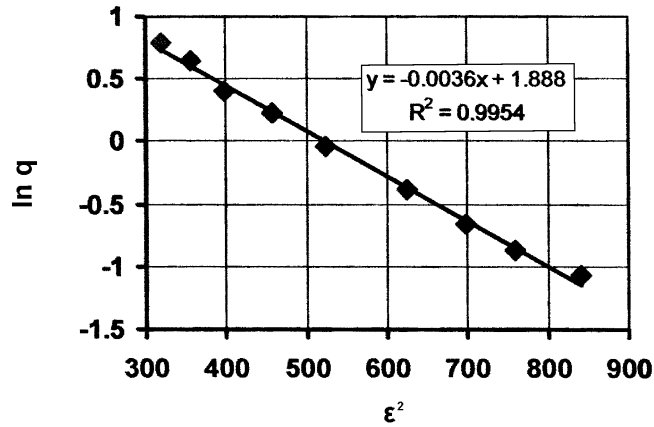
Figure 5. Dubinin–Radushkevich linearized equation plot for the liquid-phase equilibrium adsorption of phenol: q (mmol/g), ε (kJ/mol).

Another phenomenon that could be present is the restricted accessibility of wide pores due to gate effects (i.e. entrances blocked by constrictions or larger pores placed behind smaller pores) as pointed out by Stoeckli *et al.* (2001). It is interesting to note that the magnitude of R for iodine was greater than the corresponding value for phenol, even though phenol has a smaller molecular weight. This was due to the molecular diameter (d) of phenol being larger than that of iodine. It is clear that an optimum value of the pore width existed in the micropore range. This allowed the adsorption capacity of the carbon towards each adsorbate to be maximized, depending on the molecular diameter of the latter.
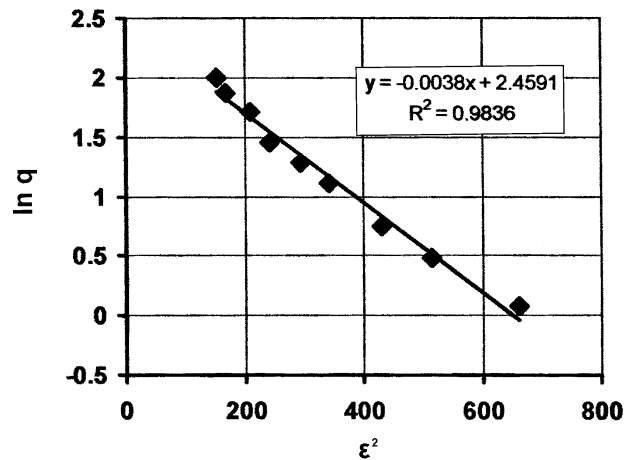

Figure 6. Dubinin–Radushkevich linearized equation plot for the liquid-phase equilibrium adsorption of iodine: q (mmol/g), ε (kJ/mol).
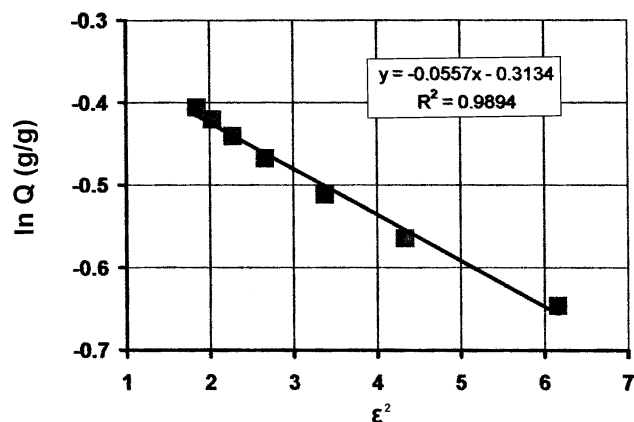
Figure 7. Dubinin–Radushkevich linearized equation plot for the gas-phase equilibrium adsorption of nitrogen: Q (g/g), ε (kJ/mol).

TABLE 2. Characteristic Parameters from the Dubinin–Radushkevich Equation

Adsorbate	MW (g/mol)	d (nm)	V_m (cm^3/mol)	q^o (mmol/g)	E_{ad} (kJ/mol)	ω^o (cm^3/g)	$R = \omega_i^o/\omega_{N_2}^o$ (%)
Nitrogen	28	0.315[b]	34.7[c]	26.1	3.0	0.91	100
Phenol	94	0.62[d]	89[d]	6.61	11.8	0.59	65
Iodine	254	0.56[d]	68[d]	11.69	11.5	0.80	88
Methylene Blue	319.5	0.91[a]	234.5[a]	1.74	22.4	0.41	45
Tannic acid	1701	1.6[d]	1370[d]	0.333	9.13	0.22	24

[a]Reid *et al.* (1987). [b]Lide (1998). [c]Gregg and Sing (1982). [d]Hsieh and Teng (2000).

CONCLUSIONS

The results presented indicate that peanut shells residues provide a suitable option for the preparation of activated carbon via phosphoric acid activation, at least in terms of the adsorption capacity towards the organic compounds examined. The activated carbon obtained had good surface properties coupled with an ability to remove organic compounds of different polarity and size from aqueous solution.

A new model equation was used to predict the adsorption capacity of the activated carbon studied towards the liquid-phase adsorption of tannic acid. This model fitted a type II BET adsorption isotherm well, being characteristic of a system where strong interactions occur between adsorbed molecules.

Analysis of the experimental data via the DR equation showed that the carbon micropore volume accessible to the different organic substances studied decreased as the size of the molecule increased, suggesting that a molecular sieving action and/or gate effects occurred in the systems studied. Models obtained using the DR isotherm may be applied over a broad range of

temperatures without having to resort to extensive extrapolation of the data, since this equation takes the effect of temperature into account.

REFERENCES

Barton, S.S. (1993) *J. Colloid Interface Sci*. **158,** 64.

Blanco Castro, J., Bonelli, P.R., Cerrella, E.G. and Cukierman, A.L. (2000) *Ind. Eng. Chem., Res.* **39,** 4166.

Gonzo, E.E. and Gonzo, L.F. (2003) *Abstr. XIII Congr. Argentino de Fisicoquímica y Química Inorgánica*, Bahía Blanca, Argentina, Vol. 1, B56, p. 109.

Gregg, S.J. and Sing, K.S.W. (1982) *Adsorption, Surface Area and Porosity*, Academic Press Inc., London.

Guerasimov,Y., Dreving, V., Eriomin, E., Kiseliov, A., Levedev, V., Panchenkov, G. and Shliguin, A. (1977) *Curso de Química Física*, Vol. 1, Mir, Moscow.

Holland, Ch.E., Al-Muhtaseb, S.A. and Ritter, J.A. (2001) *Ind. Eng. Chem., Res*. **40,** 338.

Hsieh, C.T. and Teng, H. (2000) *Carbon* **38,** 863.

Kiseliev, A.V. (1967) *Problemas de la Química de Superficie y Teoría Molecular de la Adsorción*, Mir, Moscow.

Lide, D.R. (Ed) (1998) *CRC Handbook of Chemistry and Physics*, 78th Edn, CRC Press, Tokyo.

Norit Americas Inc. (1999) *Norit Testing Methods*, Technique WIQC0024.

Norit Americas Inc. (2000) *Activated Carbon*, Technical Information.

Reid, R.C., Prausnitz, J.M. and Poling, B.E. (1987) *The Properties of Gases and Liquids*, McGraw-Hill, Singapore.

Shawabkeh, R.A., Rockstraw, D.A. and Bhada, R.K. (2002) *Carbon* **40,** 781.

Sircar, S. (2001) *Adsorp. Sci. Technol*. **19,** 347.

Stoeckli, F., Lopez-Ramon, M.V., Hugi-Cleary, D. and Guillot, A. (2001) *Carbon* **39,** 1103.

Sun, J. (2002) *Carbon* **40,** 1051.

Toles, C.A., Marshall, W.E. and Johns, M.M. (1998) *Energeia* **9,** 1.

Toles, C.A., Marshall, W.E., Johns, M.M., Wartelle, L.H. and McAloon, A. (2000) *Bioresource Technol*. **71,** 87.

Wood, G.O. (2001) *Carbon* **39,** 343.