

**ADSORPTION OF ORGANIC COMPOUNDS ON PEANUT SHELLS
ACTIVATED CARBON. POTENTIAL THEORY CORRELATION FOR
ESTIMATING ADSORPTION CAPACITIES AND AFFINITY COEFFICIENTS**

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Abstract

Adsorption isotherms at 22°C of eight organic contaminants (acetone, pyridine, phenol, iodine, methylene blue, Congo red, reactive navy and tannic acid) onto an activated carbon obtained from peanut shells, have been studied. The experimental data were analyzed with the Potential Theory and the Dubinin – Astakhov equation and collapsed into one general characteristic curve. This analysis allows us to obtain the affinity coefficient for each organic compound using phenol as the reference substance. A useful correlation for the calculation of the affinity coefficient as a function of relative parachor is presented.

Keywords: Activated carbon; Adsorption, modeling; Adsorption capacity.

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1. INTRODUCTION

The adsorption capacity of a given activated carbon for the adsorption of single component in aqueous solution is extremely useful for characterizing the adsorbent surface, for remediation processes equipment design and to evaluate the ability of different models to correlate the data over a wide range of conditions.

The objective of this work is to present adsorption equilibria isotherms for a series of organic compounds in aqueous solution. The adsorptions were measured on an activated carbon prepared from peanut shells chemically activated with phosphoric acid at moderated temperatures.

Based on the Potential Theory of Adsorption of Polanyi and the Dubinin-Astakhov (DA) equation, an analysis is carried out with the major goal of obtaining a general correlation useful for predicting adsorption capacities of activated carbon for different organic compounds in aqueous solution as a function of adsorbate equilibrium concentration. Applying the DA equation and taken as reference one of the substance, allowed us to obtain the affinity coefficients of the organic compounds used in our study. A useful correlation for the affinity coefficient estimation as a function of the relative parachor, it is also presented.

2. THEORY

According to the Potential Theory of Adsorption introduced by Polanyi, and the Theory of Volume Filling of Micropores of Dubinin [1], there is a fixed volume of micropores $\omega^{\circ} (cm^3 / kg \text{ of carbon})$ that is filled to a capacity ω for any substance at a given value of the ratio between the adsorption potential (ε) and the affinity coefficient (β). The original form of Dubinin's potential theory for micropore adsorbents was the well known Dubinin-Radushkevich equation. However, when the different adsorbates fit a

variety of adsorption isotherms, a more general and flexible model, as the Dubinin-Astakhov [2] equation, is required:

$$\omega = \omega^{\circ} \cdot \exp \left[- \left(\frac{\varepsilon}{\beta \cdot E^{\circ}} \right)^n \right] \quad (1)$$

Where ω° is the total micropore volume accessible to the adsorbates molecules and E° is the reference substance adsorption energy. The empirical parameter n in eqn. (1), characterizes the surface heterogeneity of the carbon.

The adsorption potential ε for the adsorption of a solute from a binary solution is given by [3]:

$$\varepsilon = R.T. \ln \frac{1}{C_e \cdot \gamma} \quad (2)$$

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

The maximum adsorption capacity q° (in mass or molar units) is related to ω° by the normal liquid density ρ_L (g/cm³) or the normal liquid molar volume V_M (cm³/mol) of the adsorbate:

$$q^{\circ} (g / g_{carbon}) = \omega^{\circ} \cdot \rho_L \quad q^{\circ} (mol / g) = \frac{\omega^{\circ}}{V_M} \quad (3)$$

3. EXPERIMENTAL

3.1 Adsorbent

Recently Romero et al. [4], have shown that activated carbon obtained from peanut shells activated by phosphoric acid at moderate temperature present good surface properties and ability to remove organic compounds of different polarity and size, from aqueous solutions. Table 1 summarizes the characteristics of this activated carbon.

3.2 Organic compounds adsorption

Eight compounds were used in this study for the adsorption from aqueous solution by the carbon: acetone, pyridine, phenol, iodine, methylene blue, Congo red, reactive navy and tannic acid. These compounds have molecular weights ranging from 58 to 1701 g/mole and molecular diameters from 0.51 to 1.6 nm.

Reagent grade phenol (Fluka), iodine (Fluka), methylene blue (Sigma), tannic acid (Aldrich), acetone (Aldrich), pyridine (Sigma), reactive navy (Cibacron Navy F-G) and Congo red (Aldrich) were used in preparing the aqueous solutions. The initial concentration was fixed for the adsorption of each adsorbate. The adsorption experiments were conducted using different dried carbon dose in 50 or 100 cm³ volume solution and placing into a 250 cm³-stoppered erlenmeyer. The sealed flask was shaken at 150 rpm for 3 days at 22°C, after which the sample was filtered. The adsorbate concentration in the residual as well as in the initial solution was analyzed by UV-VIS spectrophotometer (Beckman DU 520) at appropriated wavelengths (Table 4). Carbon samples with particle size smaller than 0.148 mm (> 100 mesh) were used in all experiments. The initial concentration of the solution were: 32.7 mM, 10.6 mM, 116.2 μM, 3.756 mM, 160 mM, 5 mM, 2.4 mM and 0.35 mM; for iodine, phenol, tannic acid, methylene blue, acetone, pyridine, reactive navy and Congo red, respectively. The Congo red adsorption isotherm was performed following the procedure indicated by Pelekani and Snoeyink [5]. In this case, two duplicate experimental points were determined. The adsorption of reactive navy was carried out according to the procedure of Yang and Al-Duri [6].

Under the concentration ranges studied, the equilibrium mixture pH were between 3.5 and 4.9, pH below the pK_a values of the components used. So they exist mostly as the undissociated forms.

The amount of solute adsorbed at equilibrium per unit weight of adsorbent q was determined as follows:

$$q = \frac{(C^{\circ} - C_e)V}{W} \quad (4)$$

Where C° and C_e are the initial and residual concentration at equilibrium, V the volume of solution used and W the weight of carbon.

4. RESULTS AND DISCUSSION

The Langmuir, Freundlich and a previous developed [7] models, were employed for modeling the adsorption isotherms. Non linear regression was used to find 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 experimental and estimated adsorption capacities, for each organic compound studied.

Experimental adsorption data and fit of isotherms model for methylene blue, pyridine, reactive navy, tannic acid, phenol, iodine and acetone as a function of the equilibrium concentration, are depicted in Figs.1 - 4. In these figures symbols represent experimental data, and the solid lines are the model fits.

Iodine, phenol, reactive navy and acetone, fit the Freundlich isotherm:

$$q(\text{mmol} / \text{g}) = a_F \cdot C_e^{b_F} \quad (5)$$

Values of parameters a_F , b_F , σ^2 and percent relative error Er%, for these compound is shown in Table 2.

Methylene blue and pyridine adsorption data fit the Langmuir equation:

$$q(\text{mmol} / \text{g}) = \frac{a_L \cdot C_e}{1 + b_L \cdot C_e} \quad (6)$$

Table 3 shows the values of parameters a_L , b_L , σ^2 and Er%.

As can be seen in Figure 2, the tannic acid adsorption isotherm follows a type II BET isotherm [8]. This behavior is characteristic of system where strong interaction between adsorbed species exists [9,10]. Using a previous developed adsorption isotherm [7], the following fitting equation was found:

$$q(\mu\text{mol} / \text{g}) = \frac{3.49583.Ce_{(\mu\text{M})}}{(1 - 0.0105065.Ce_{(\mu\text{M})})(1 + 0.10866.Ce_{(\mu\text{M})})} \quad (7)$$

With $\sigma^2 = 255.48$ and $\text{Er}\% = 4\%$.

The mean values obtained for the two point adsorption of Congo red were: $q = 0.236$ mmol/g and 0.402 mmol/g for equilibrium concentrations of $Ce = 14 \mu\text{M}$ and $101 \mu\text{M}$, respectively.

According to the Theory of Volume Filling of Micropores and equation (1), the characteristic curves for the different organic compounds used, were obtained. Figure 5 displays the general characteristic curve obtained by correlating all of the experimental adsorption equilibria with the potential theory model described by equation (1). The affinity coefficient β , were optimized geometrically in reference to phenol, which was given the reference β of 1. The resulting values of β , together with the values of V_M and others properties of the adsorbates, are listed in Table 4.

The non-linear regression analysis of all experimental data, using equation (1) as fitting model, gives:

$$\omega = 6574.5 \cdot \exp \left[-0.4 \left(\frac{\varepsilon}{\beta} \right)^{0.76} \right] \quad (8)$$

With ε in (kJ/mol) and ω in (cm^3/kg). Correlation from equation (8) is also plotted in Fig. 5 (line). It shows a reasonable agreement with the experimental data for all the

organic compounds. The average relative error in the values of ω , predicted by equation (8), was 4.7%. This low value of the overall error indicates that equation (8) satisfactorily represents the whole system of adsorption equilibria. Therefore, the Potential Theory and the DA equation are quite accurate to correlated experimental data of organic compounds adsorption on peanut shells activated carbon over a broad range of experimental conditions. On this unique correlation fall the data for weakly as well as strongly adsorbed compounds, data for polar and non polar substances and adsorbates with molecular diameters ranging from 0.51 nm to 1.6 nm.

The aim of much previous work has been to find a relation between the affinity coefficient and some characteristic parameter of the adsorbate-adsorbent system. It is well known that β depends on the size of the carbon slit pore [11,12]. However, as we work with a single type of carbon, an analysis can be done to correlate affinity coefficients with characteristic parameters of the adsorbates like as molar polarizability, molar volume or the Parachor (P_{ar}) [1]. The Parachor is given by:

$$P_{ar} = V_M \cdot \gamma_s^{0.25} \quad (9)$$

Where γ_s is the surface tension. A comparison of parachor values is equivalent to a comparison of the molecular size and attractions of the substance involved. In adsorption from binary liquid solutions, both solvent and solute are present in the adsorbent pores. Barton [3] has postulated that the micropore volume characteristic of each adsorbate should depend on the relative parachor values of solute and solvent:

$$X = \frac{P_{ar} - P_{arW}}{P_{arW}} \quad (10)$$

Being P_{arW} the water parachor. X can be considered as the number of excess water parachor possessed by the adsorbate. Figure 6, shows a plot of β versus X , for our system that included adsorbates with a wide range of molecular sizes (Table 4).

A good fit of the data is found with the relation:

$$\beta = 1.8439[\exp(-0.017.X) - \exp(-0.282.X)] \quad (11)$$

Equation (11) is the classical relation found when two opposite effects are taking part. One of them is shown by the first part of the plot in figure 6 (corresponding to small molecules), where a fairly linear increase in β with increasing X values is observed. That is, as the ratio (R) between molecular diameter of the targeted adsorbate to mean pore width increases, increases the value of β (or E) because contact points between the adsorbate and the adsorbent surface increase [13]. Demonstrating that when the adsorbate access to the inner and narrow micropore where the pore wall provide overlapping potential, increases the free energy of adsorption [14,15]. The opposite effect is well justified for microporous materials where geometrical constraints are of importance [16]. The restricted accessibility of wide pore due to gate effects (entrances being blocked by constrictions or larger pores placed behind smaller pores)[12] or molecular sieving [15] i.e. the exclusion of large organic molecules from adsorbent pores, decreases the free energy of adsorption, and therefore β . Li et al. [15] as well as Ismadji and Bhatia [17], have concluded that the pore volume of micropore with width corresponding to an optimum value of the ratio R , controlled the adsorption capacity of an activated carbon. This is observed in Figure 6, where the maximum is found at $X = 10.6$, approximately.

Since polarizability of many substances are not available, and considering that such constant varies directly as its molar volume in the liquid state [1], a plot of β as a function of relative molar volume of the adsorbate (V_M / V_{Mref}) was performed. A similar trend than with parachor was found. However, the best agreement with experimental affinity coefficients was found with equation (11) with $\sigma^2 = 0.1001$ and a relative percent error of 11.9%.

5. CONCLUSIONS

Adsorption equilibria isotherms for a series of organic compounds on peanut shells activated carbon were measured over a broad range of concentrations at 22°C. The Potential Theory and the Dubinin-Astakhov equation correlated well with all the data. A single general characteristic curve was obtained that can be used to predict the adsorption equilibria of these organic substances over a wide range of conditions. According to the Potential Theory, the general correlation obtained, Eq. (8), can be applied over very broad range of temperatures and concentrations without resorting to extensive extrapolation of data. This experimental data should also prove to be useful for evaluating the correlative ability of different adsorption isotherm models.

A correlation was found to predict β values as a function of the relative parachor X of a given adsorbate, which cover a wide range of molecular size of the organic solutes.

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Table 1
Surface Properties of the Activated Carbon

| S_g (BET) (m^2/g) | S_g (Iodine) (m^2/g) | V_T (P/P ^o =.95) (cm^3/g) | V_{micro} (cm^3/g) | V_{meso} (cm^3/g) | Mean pore width (nm) | Bimodal PSD Peaks maxm. (nm) |
|----------------------------|-------------------------------|---|-----------------------------|----------------------------|----------------------------|------------------------------------|
| <i>1735</i> | <i>1693</i> | <i>1.12</i> | <i>0.91</i> | <i>0.21</i> | <i>1.3</i> | <i>0.8 - 1.6</i> |

Table 2: Parameters of Freundlich isotherms

| Compounds | a_F | b_F | σ^2 | Er% |
|---------------|-------|-------|------------|-----|
| Iodine | 2.264 | 0.360 | 0.1538 | 2.2 |
| Phenol | 0.974 | 0.413 | 0.00712 | 1.6 |
| Acetone | 0.195 | 0.357 | 0.00073 | 2.3 |
| Reactive navy | 0.341 | 0.269 | 5e-5 | 1.6 |

Table 3: Parameters of Langmuir isotherms

| Compounds | a_L | b_L | σ^2 | Er% |
|----------------|--------|-------|------------|-----|
| Methylene blue | 30.027 | 25.82 | 0.00021 | 0.5 |
| Pyridine | 1.726 | 1.867 | 0.00156 | 4.6 |

Table 4: Molar volume, Affinity coefficients, relative Parachor and UV-V wavelength

| Compounds | PM (g/mol) | V_M (cm³/mol) | β | X (c) | Wavelength (nm) |
|-----------------------|-----------------------|--|---------------------------|--------------|----------------------------|
| Acetone | 58.08 | 74 (a) | 0.58 | 2.1 | 265 |
| Pyridine | 79.1 | 80.9 (a) | 0.85 | 2.8 | 256 |
| Tannic Acid | 1701 | 1370 (b) | 0.88 | 44.8 | 275 |
| Phenol | 94 | 89 (b) | 1 | 3.24 | 268 |
| Iodine | 254 | 68 (b) | 1.06 | 2.43 | 474 |
| Reactive navy | 924.5* | 840 (c) | 1.16 | 25.3 | 597.2 |
| Congo red | 650.7* | 422.9 (d) | 1.29 | 16.6 | 497 |
| Methylene blue | 319.5 | 234.5 (c) | 1.53 | 10.0 | 620 |

* Does not include associated sodium ions.

(a) Ref. [3]; (b) Ref. [11]; (c) Ref. [18]; (d) Ref. [5].

Caption to figures:

Fig. 1. (No needs caption).

Fig. 2. Experimental adsorption isotherm for Tannic Acid. Line, the best fit to Eq. (7).

Fig. 3. Experimental adsorption isotherms for Phenol and Iodine. Line, fit to Freundlich model.

Fig. 4. Experimental adsorption isotherm for Acetone. Line, fit to Freundlich equation.

Fig. 5. Dubinin–Astakhov general characteristic curve. Symbols represent experimental data, and the line represents the best fit to Eq. (8).

Fig. 6. Correlation between Affinity Coefficient β and relative Parachor X. The solid line represents the best fit to Eq. (11).

Figure 1

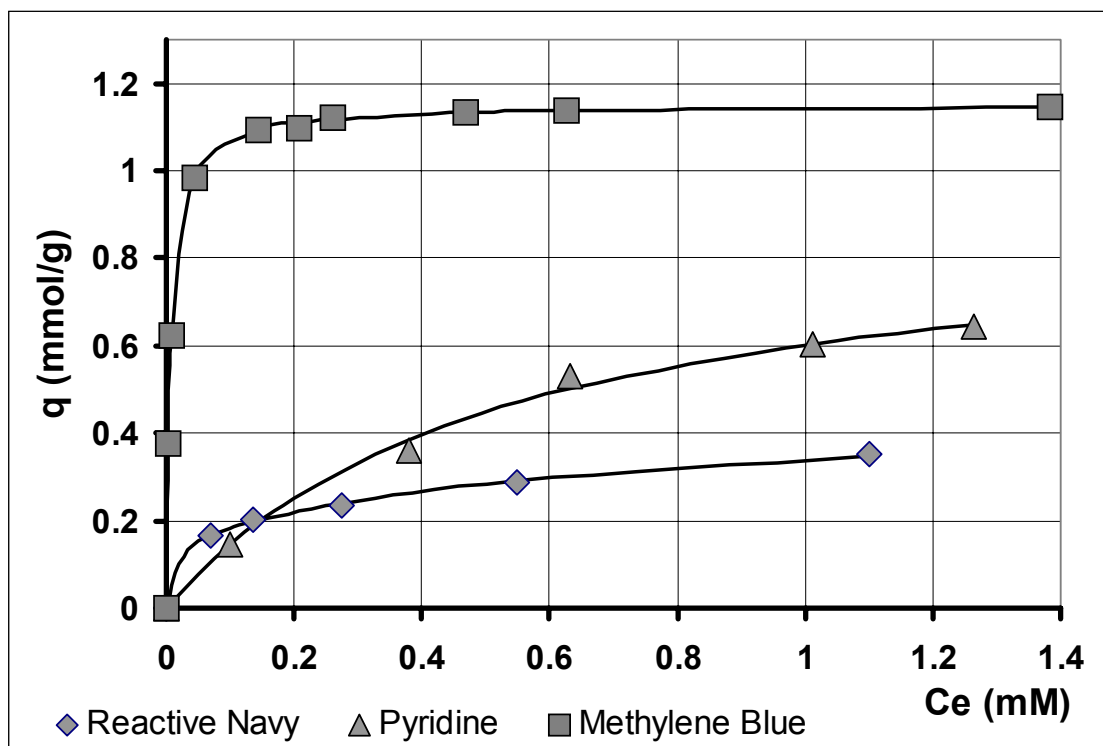


Figure 2

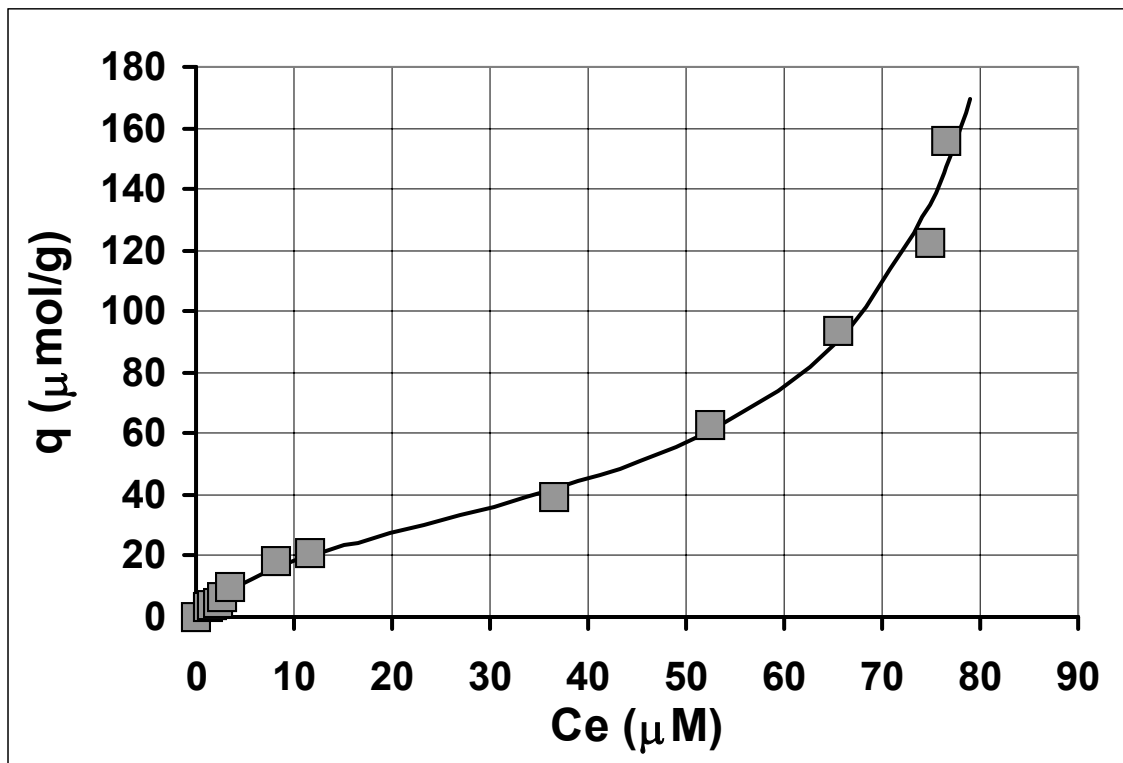


Figure 3

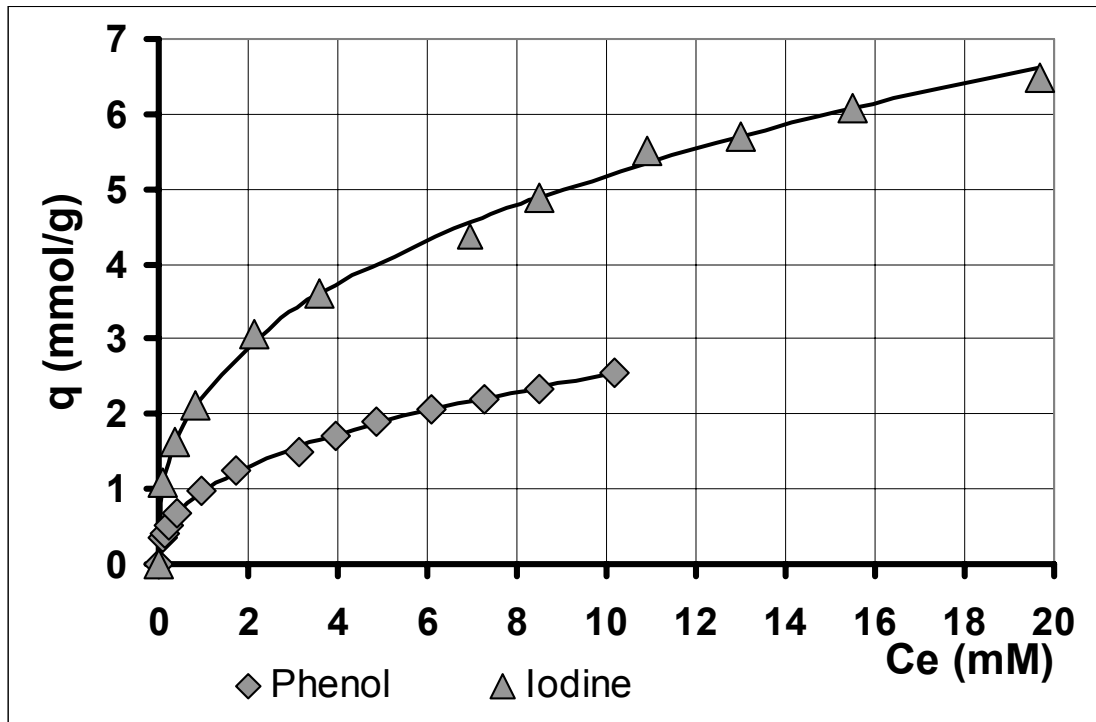


Figure 4

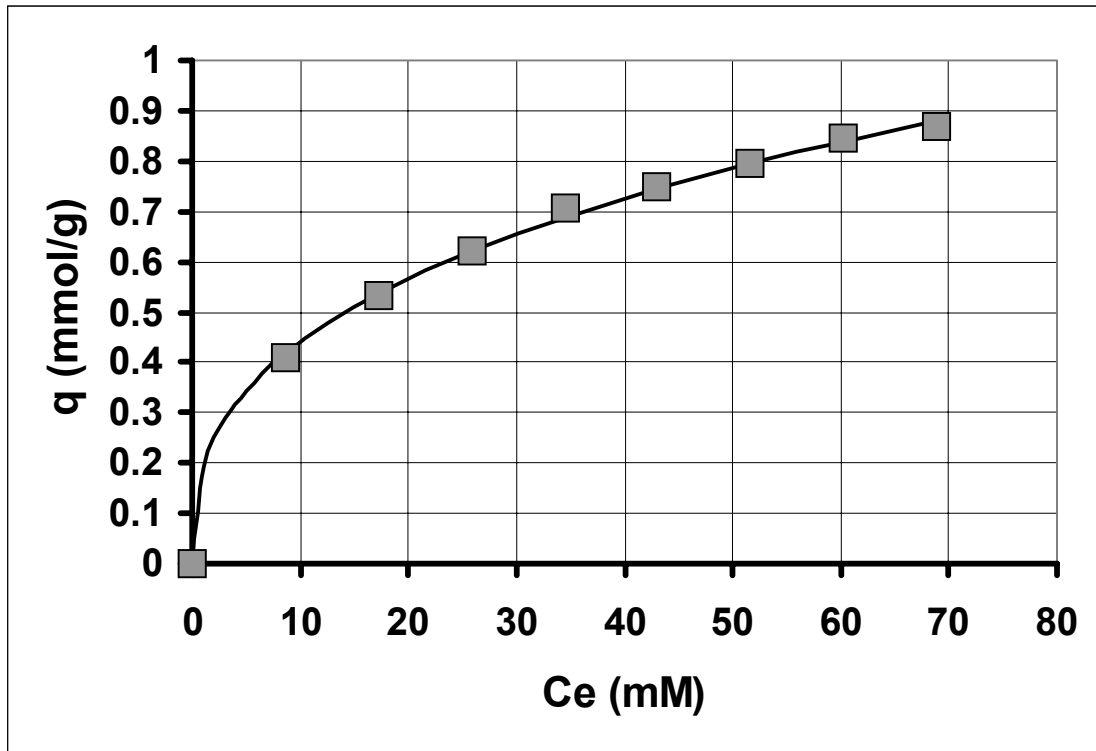


Figure 5

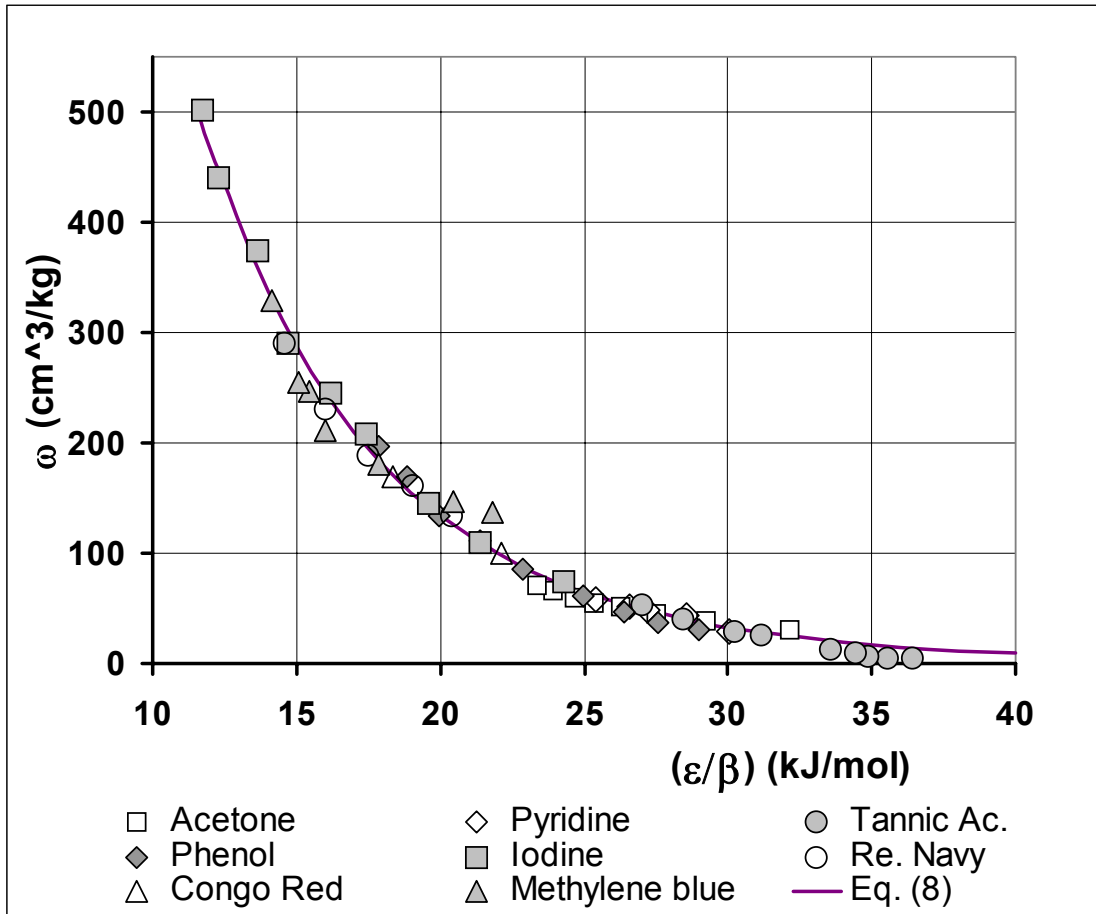


Figure 6

