ADSORPTION OF PHENOL AND ITS DERIVATIVES FROM AQUEOUS SOLUTIONS ON ACTIVATED CARBON

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Abstract

Adsorption isotherms of some phenolics from aqueous solutions onto activated carbon were studied in the concentration range (5 to 200) mg/L at 25 °C. The equilibrium data for the adsorption of phenol, (ortho and para cresol, aminophenol, chlorophenol and nitrophenol) on activated carbon is tested with various adsorption isotherm models: Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich and Generalized equation. The results revealed that the adsorption isotherm models fitted the data in the order: Langmuir > Generalized > Tempkin > Freundlich > Dubinin–Radushkevich isotherms.

Uptake of ortho and para substituted phenols increases in the order: phenol < cresol < aminophenol < chlorophenol < nitrophenol, which correlates well with the respective increase in hydrophobicity and decrease in water solubility and pKa value. The maximum adsorption capacity is calculated for each adsorbate. The adsorption of cresol and aminophenol isomers on activated carbon decreases in the following order: p-isomers > o-isomers > m-isomers.

Key words: Adsorption, isotherms, phenols, Activated carbon.

امتزاز الفينول و مشتقاته من المحاليل المائية على الفحم المنشط

خلاصة البحث:

تمت دراسة أيسوثيرمات الامتزاز للفينول و مشتقاته (أورثو و بارا – كريسول ، أمينوفينول، كلوروفينول و نيتروفينول) على الفحم المنشط من المحاليل المائية في مدى التراكيز بين (5 – 200 ملجم/لتر). تم تطبيق عدد من معادلات (ايسوثيرمات) الامتزاز (لانجمير ، فريندلش ، تمبكن ، دوبنين - رادوسكوفتش و الايسوثيرم العام) على نتائج الامتزاز.

أوضحت النتائج أن امتزاز هذه الفينولات على سطح الفحم المنشط يتبع أيسوثيرمات الامتزاز حسب الترتيب : لانجمير > الايسوثيرم العام > تمبكن > فريندلش > دوبنين- رادوسكوفتش . كذلك تمت دراسة أثر المجاميع المعوضة في المواقع أورثو و بارا على الفينول على عملية الامتزاز، بينت النتائج أن الامتزاز يزداد كلما كانت المجموعة المعوضة ساحبة للإلكترونات حسب الترتيب التالي :

نيتروفينول > كلوروفينول > أمينوفينول > كريسول > فينول .

تمت دراسة أثر الموقع المعوض على امتزاز ايسومرات الكريسول و الأمينوفينول و أوضحت النتائج أن الامتزاز يزداد حسب الترتيب التالي للايسومرات :

بارا- > أورثو- > ميتا-

1. Introduction

The adsorption of phenol and substituted phenols from an aqueous solution on activated carbons has been intensively investigated. However, this subject remains highly controversial (Radovic et al., 2000).

Adsorption is one of the most efficient methods for removing color, odor, and organic pollutants from process and waste effluents. Adsorption from solution is a competitive process with equilibrium determined by many factors resulting from adsorbent, adsorbate and solvent properties. The porous structure of a solid, its energetic heterogeneity (depending also on a solute) and surface chemical properties (functional groups) are the main factors influencing adsorption equilibria.

Activated carbons (ACs) are the most widely used adsorbents as an alternative of physiochemical and biological methods for treating wastewaters of industries producing drugs, cosmetics, papers, rubbers, plastics, paints, printing inks, art and craft, leather and food, due to their excellent adsorption capability (Zhang et al., 2006). Because of their large surface area, pore volume, a microporous structure and a high degree of surface reactivity, they are widely used as adsorbents in waste-water treatment processes and for environmental control (Goyal et al., 2001; Gauden et al., 2006; Tseng et al., 2006).

The surface of ACs contains many active chemical groups, part of which are dissociable ones. The role of various oxygen functional groups in the mechanism of organics adsorption was discussed widely in order to relate the adsorption uptake with the changes of chemical character of carbon surface (Anna and Adam, 2002).

It is well known that phenolic compounds and dyes are common pollutants in municipal water and industrial effluents (Jiang et al., 2003). They are the basic structural units of a wide variety of synthetic organic pollutants including many pesticides (Lu and Sorial, 2004). Chlorinated phenols impart disagreeable taste to water and are toxic to aquatic life. O-cresol has been identified as a hazardous compound for many aquatic organisms by the Environmental Protection Agencies (Singh and Yenkie, 2001). In 1982, the European Community issued another pollutant list including many chlorophenols and established their maximum allowable concentration in drinking water (0.5 μg/L) (Noguera et al., 2001).

Indeed, phenol has been used as a model compound, in many instances (Smisek and Cerny, 1970), to simulate a range of toxic chemicals. Global phenol production reached 1.8 million tons in 2001 (Kujawski et al., 2004). However, phenol is toxic to aquatic life and humans even at low concentrations (5 – 25 mg/L) (Han et al., 2006).

Due to the toxicity of phenols, their removal from water is an important issue, especially because of ecological aspects (Tseng et al., 2006). Different water treatment technologies are used to remove phenolic pollutants, for example, biological degradation, chemical oxidation, or adsorption (Wagner and Schulz, 2001).

The specific mechanisms by which the adsorption of many compounds, especially organic compounds, take place on activated carbons are still ambiguous. This is because liquid-phase adsorption is a very complicated process (Moreno-Castilla, 2004). In liquid-phase adsorption, the adsorption capacity of ACs for aromatic compounds depends on a number of factors (Haghseresht et al., 2002):

- The physical nature of the adsorbent—pore structure, ash content, and functional groups.
- The nature of the adsorbate, its pKa, functional groups present, polarity, molecular weight, and size.
- The solution conditions such as pH, ionic strength, and the adsorbate concentration.

There are also many important factors such as the type of precursor of ACs, aqueous solubility of phenolic compound and oxygen availability in solution. The aim of this study is to investigate the nature of interaction between the activated carbon surface and the adsorptive molecules, and the effect of the chemical nature of these molecules on the adsorption process. The investigations were conducted using single solute systems.

2. Materials and Methods

2.1 Activated Carbon

Commercial activated carbon was used in the batch experiments (Powder, extra pure, minimum methylene blue adsorption (0.15 % solution) ≥ 12 ml / 0.1g). The carbon had been soaked in distilled water for 24 hrs to remove fines and soluble ash and dried to constant weight at 110 °C. Drying for 24 h was usually sufficient to maintain constant weight (Mc Kay et al., 1984), after which the carbon was sieved to 325 mesh and stored in a calcium chloride desiccator until use.

2.2 Adsorbates

Phenol (≥99%), p-nitrophenol (≥98%), p-aminophenol (≥99%), o-aminophenol (≥99%), m-aminophenol (≥98%), o-chlorophenol (≥98%), p-chlorophenol (≥98%) and o-nitrophenol (≥99%) were supplied by Sigma–Aldrich, Inc. Cresol isomers were supplied by Merck chemical company with declared purity of ≥ 99%. All chemicals used were of analytical grade, and they were used without further purification (Table 1). The adsorption isotherms were all determined using distilled water and all the chemicals used were readily soluble in water. The pH of the solutions ranged from 6.5 to 6.8 .

2.3 Analytical procedure

Both initial and final equilibrium concentrations of solutes was determined with a single beam UV/Visible spectrophotometer (Pye-Unicam-8700, Philips, England) using a (1.0 cm) light-path cell. In accordance with the Beer-Lambert law, the absorbance was found to vary linearly with concentration in the range of concentrations used. Each equilibrium concentration value was an average of three measurements.

2.4 Isotherms procedure

Stock solutions of the adsorbates were prepared with distilled water in the desired initial concentration and subsequent concentrations were made by dilution. Adsorption isotherms were obtained by adding a fixed mass of carbon with 50 ml of pollutant solution of known concentration in a 100 ml glass-stoppered flask. The flasks were then placed in a shaking water bath (Scott-Science, LSB-015S, UK) at a constant temperature of 298.15 K for 24 hrs to ensure that equilibrium conditions were obtained.

Table 1

Some physico-chemical properties of phenols [Dabrowski et al., 2005] :

Adsorbate	*Molecular Weight*	*Boiling Point °C*	*Aqueous Solubility at 25°C* (gl^{-1})	pK_a *at 25°C*
Phenol	*94.11*	182	93.0	9.89
o-cresol	108.14	191	25.0	10.20
p-cresol	108.14	202	26.0	10.01
m-cresol	108.14	202	23.0	10.17
o-aminophenol	109.13	-	Slightly soluble	8.05
p-aminophenol	109.13	284	28.0	8.72
m-aminophenol	109.13	164 at 11 mmHg	2.6	9.28^{*}
o-chlorophenol	128.56	204	28.0	8.52
p-chlorophenol	128.56	220	27.0	9.37
o-nitrophenol	139.11	215	2.0	7.17
p-nitrophenol	139.11	279	1.69	7.15

2.5 Adsorption Isotherms

Adsorption isotherms are expressed in terms of a relationship between the concentration of adsorbate in the liquid and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose (Hameed and Ahmad, 2009).

Various adsorption isotherm models such as Langmuir, Freundlich, Langmuir-Freundlich, Tempkin, and Dubinin–Radushkevich, which are available in the literature, are described in the following sections bringing out the differences among them and the significance of the characteristic parameters of each isotherm model.

2.5.1. Langmuir isotherm

Langmuir isotherm is applicable for monomolecular layer adsorption. It is described as a homogenous one assuming that all the adsorption sites have equal adsorbate affinity, and the adsorption at one site does not affect the adsorption at an adjacent site (Langmuir, 1918). The Langmuir equation may be written as:

$$\theta = \frac{Q_e}{Q_m} = \frac{bC_e}{1 + bC_e} \qquad (1)$$

where, b is adsorption equilibrium constant (Lmg^{-1}) that is related to the apparent energy of adsorption and Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent ($\mathrm{mg\ g}^{-1}$) and Q_e is the amount adsorbed on unit mass of the adsorbent ($\mathrm{mg\ g}^{-1}$) when the equilibrium concentration is C_e ($\mathrm{mg\ L}^{-1}$). The linear form of equation (1) is:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{1}{Q_m} C_e \qquad (2)$$

This equation shows that a plot of (C_e/Q_e) versus C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption e equilibrium. The slope and the intercept of this line then give the values of constants Q_m and b, respectively.

Further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor (Gupta and Babu, 2009), given by the equation:

$$R_L = \frac{1}{1 + bC_o} \qquad (3)$$

where b is the Langmuir constant and C_o is the highest initial concentration. The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

2.5.2. Freundlich isotherm

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution is not constant at different concentrations. For adsorption from solution the Freundlich isotherm is expressed by Eq. (4):

$$Q_e = K_F C_e^n \qquad (4)$$

where, K_F ($\mathrm{mg}^{1-1/n}\ \mathrm{L}^{1/n}\ \mathrm{g}^{-1}$) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The Freundlich coefficients can be determined from the plot of $\log Q_e$ versus $\log C_e$ on the basis of the linear form of equation as given by Eq. (5):

$$\log Q_e = \log K_F + n \log C_e \qquad (5)$$

2.5.3. Langmuir–Freundlich isotherm

This isotherm (also known as the generalized isotherm) is a combination of Langmuir and Freundlich isotherms (Kargi and Ozmihci, 2004). It depends on the value of cooperative binding constant (N_b). The generalized isotherm can be written as:

$$Q_e = Q_m \frac{C^{N_b}}{K_G + C^{N_b}} \qquad (6)$$

where K_G is the saturation constant (mg L^{-1}); N_b is the cooperative binding constant; and Q_m is the maximum adsorption capacity of the adsorbent (mg g^{-1}) (obtained from the Langmuir isotherm model). The linear form of Eq. (6) is:

$$\log\left(\frac{Q_m}{Q_e} - 1\right) = \log K_G - N_b \log C_e \qquad (7)$$

The isotherm constants K_G and N_b are obtained from the slope and intercept of the plot of $log\ [(Q_m/Q_e) - 1]$ versus $log\ C_e$.

2.5.4. Tempkin isotherm

The derivation of the Tempkin isotherm assumes that the heat of adsorption of all the molecules in the adsorption layer decreases linearly with the coverage of molecules due to the adsorbate–adsorbate repulsions and the adsorption of adsorbate is uniformly distributed (Kavitha Namasivayam, 2007). In addition, it also assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich isotherm. The Tempkin isotherm has generally been applied in the following form :

$$Q_e = \frac{RT}{b_T} \ln(A_T C_e) \qquad (8)$$

Eq. (8) can be linearized as given by Eq. (9)

$$Q_e = B_T \ln A_T + B_T \ln C_e \qquad (9)$$

where, $B_T = (RT)/b_T$, T is the absolute temperature in K and R is the universal gas constant ($8.314\ Jmol^{-1}\ K^{-1}$). The constant b_T is the Tempkin constant related to the heat of adsorption ($Jmol^{-1}$). A_T is Tempkin isotherm constant (Lg^{-1}), it is known as equilibrium binding constant corresponding to the maximum binding energy (Akkaya and Ozer, 2005). The slope and the intercept from the plot of q_e versus $ln\ C_e$ determines the isotherm constants A_T and b_T.

2.5.5. Dubinin–Radushkevich (D–R) isotherm

D–R isotherm equation is applied to estimate the mean free energy of adsorption (*E*). If the value of *E* is between 1 and 16 kJ mol^{-1}, then physical adsorption prevails, and if the value is more than 16 kJ mol^{-1}, then chemisorption prevails. The non-linear form of *D–R* equation is given by Eq. (10):

$$Q_e = Q_m \exp(-B\varepsilon^2) \qquad (10)$$

The linear form of this isotherm equation is given by eq. (11):

$$\ln Q_e = \ln Q_m - B\varepsilon^2 \qquad (11)$$

where B ($mol^2\ kJ^{-2}$) is a constant which relates to the adsorption energy; Q_m ($mg\ g^{-1}$) is the maximum adsorption capacity. The (D-R) isotherm constants, B & Q_m are estimated from the slope and the intercept of the plot between $\ln Q_e$ and ε^2. The ε parameter is the Polyani potential which can be correlated to C_e by the following equation (Haghbeen et al., 2009):

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

where R is the gas constant in kJ mol^{-1} and T is the absolute temperature in Kelvin. The advantage of the D–R method is that the constant B obtained from eq. (11) can be used for calculating the mean free energy (E) of sorption per mole of the solute after it is adsorbed onto the surface by the following equation:

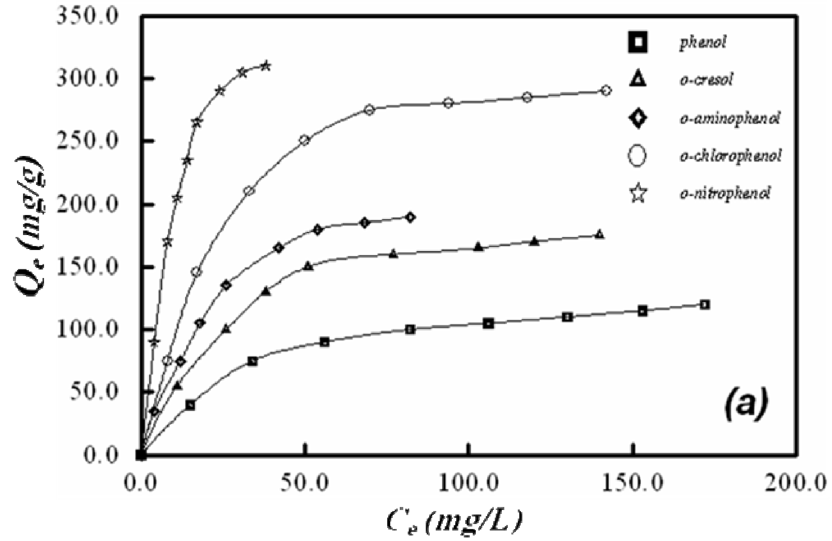
$$E = \frac{1}{\sqrt{(-2B)}} \qquad (13)$$

The value of (E) in the range of $8–16\ kJmol^{-1}$ indicates physical adsorption, while its value in the range of $20–40\ kJ\ mol^{-1}$ is indicative of chemisorptions (Karima et al., 2009).

3. Results and discussion

3.1 Adsorption isotherms:

The adsorption isotherms for all solutes on activated carbon from aqueous solutions in the concentration range (5 – 200) mg L^{-1} are shown in Fig. 1, where the abscissa is the equilibrium solute concentration in water (C_e , mg L^{-1}) and the ordinate is the equilibrium concentration adsorbed on the activated carbon (Q_e , mg g^{-1}).



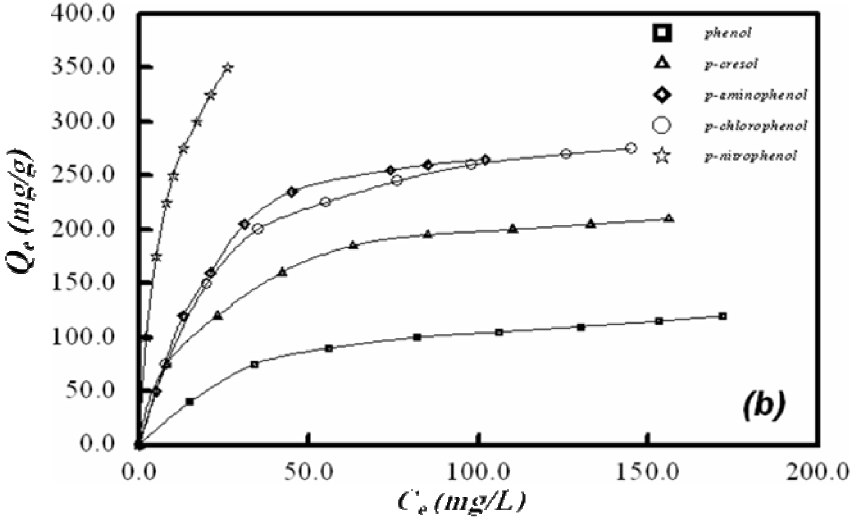


Figure 1. Adsorption isotherms of substituted phenols onto activated carbon from aqueous solution at 25 °C, (a) o- substituted phenols, (b) p- substituted phenols.

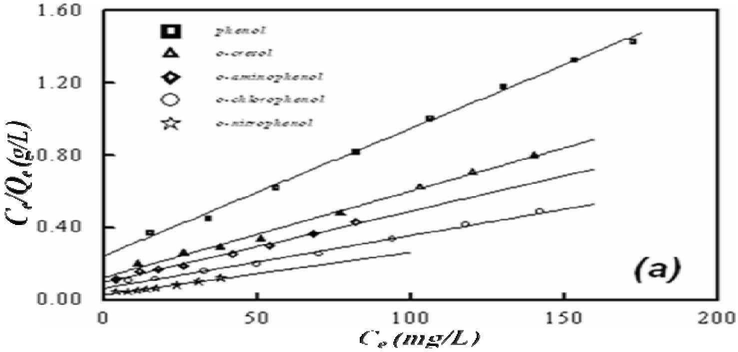
The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Hameed and Ahmad, 2009). Adsorption isotherms are important to describe how adsorbates will interact with activated carbon surface and are critical in optimizing the use of activated carbon as adsorbent. In this regard, the correlation of adsorption data using either a theoretical or empirical equation is essential to practical adsorption operation.

Any adsorption isotherm is characterized by certain constants that express the surface properties and the affinity of the adsorbent towards the adsorbate. The most popular classification of adsorption isotherms of solutes from aqueous solutions has been proposed by (Giles et al., 1974 a, b). Four characteristic classes are identified, based on the configuration of the initial part of the isotherm (i.e., class S, L, H, C). The Langmuir class (L) is the widespread in the case of adsorption of phenolic compounds from water, and it is characterized by an initial region, which is concave to the concentration axis. According to the above classification, adsorption isotherms of phenolic compounds on activated carbon displayed an (L) curve pattern (see Fig. 1). Type (L) suggests that the aromatic ring adsorbs parallel to the surface and no strong competition exists between the adsorbate and the solvent to occupy the adsorption sites ((Dabrowski et al., 2005).

In this study, five adsorption isotherms were applied to fit the equilibrium data of the adsorption of phenolics on activated carbon:

3.1.1. Langmuir isotherm:

The classical equation of Langmuir (Eq.1) is used to fit the experimental equilibrium adsorption data. The linear plot of specific adsorption (C_e/Q_e) against the equilibrium concentration (C_e) shows that the adsorption of phenolics on activated carbon obeys the Langmuir model (Fig. 2). The Langmuir constants (Q_m & b) were determined from the slope and the intercept of the plot and are presented in Table 2. The high values of coefficient of determination (*$0.982 < R^2 < 0.999$)* obtained indicate a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of phenolic compounds onto activated carbon surface. The essential feature of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L (Eq. 3). R_L values are found in the range of ($0.222 < R_L < 0.674$) which confirms the favourable adsorption process for phenolics removal using activated carbon.



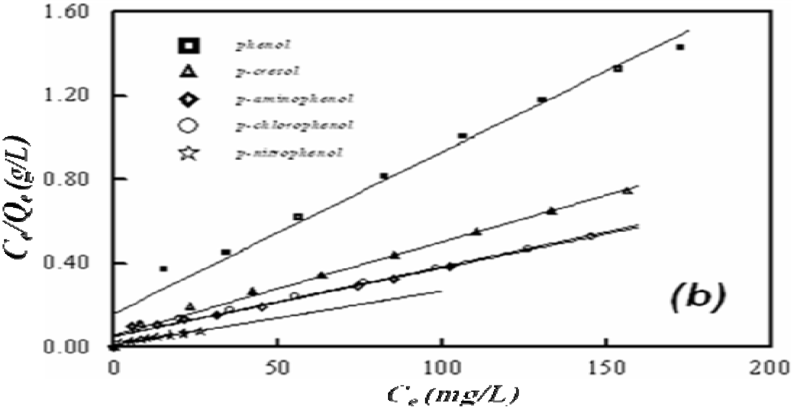


Figure 2. Langmuir isotherms of the adsorption of substituted phenols onto activated carbon, (a) o- substituted phenols, (b) p- substituted phenols.

3.1.2. Freundlich isotherm:

The Freundlich constants (K_F & n) are obtained by plotting the graph between ($logQ_e$) and ($logC_e$). The values of (K_F & n) are reported in Table 2. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of adsorbate adsorbed onto activated carbon for a unit equilibrium concentration. The slope (1/n) ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Values of ($1/n$) below 1 indicates a normal Langmuir isotherm, while ($1/n$) above 1 indicative of cooperative adsorption (Tan et al., 2009). It is found that coefficients of determination obtained from Freundlich isotherm model ($0.899 < R^2 < 0.982$) are lower than that for Langmuir isotherm model as given in Table 2.

Table 2. Isotherm constants and regression data for various adsorption isotherms for adsorption of substituted phenols on activated carbon from aqueous solutions.

Adsorbate	*Langmuir*				*Freundlich*		
	Q_m	b	R^2	R_L	K	n	R^2
Phenol	142	0.030	0.997	0.554	67.350	2.419	0.926
o-cresol	209	0.039	0.995	0.531	23.340	2.319	0.901
p-cresol	235	0.053	0.999	0.290	39.619	2.871	0.955
m-cresol	158	0.018	0.982	0.674	-	-	-
o-aminophenol	255	0.040	0.993	0.451	18.153	1.757	0.962
p-aminophenol	331	0.044	0.992	0.307	27.659	1.896	0.913
m-aminophenol	218	0.023	0.994	0.500	-	-	-
o-chlorophenol	343	0.015	0.994	0.500	36.822	2.221	0.899
p-chlorophenol	321	0.043	0.999	0.268	37.531	2.355	0.922
o-nitrophenol	423	0.083	0.983	0.222	51.811	1.870	0.915
p-nitrophenol	443	0.132	0.997	0.299	77.446	2.072	0.982

3.1.3. Langmuir–Freundlich isotherm:

This isotherm fuses both Langmuir and Freundlich isotherm together. The linear form of this isotherm is given by equation (7). The isotherm constants K_G and N_b are obtained from the slope and intercept of the plot of $log(Q_m/Q_e - 1)$ versus $logC_e$ as shown in Fig. 3. Coefficients of determination obtained from Langmuir-Freundlich isotherm model ($0.978 < R^2 < 0.997$) are less than that obtained from Langmuir isotherm model but they are greater than that obtained from other isotherm models as given in Table 3. This shows that the equilibrium exeperimental data for adsorption of phenolics on activated carbon can be represented by the Generalized isotherm model.

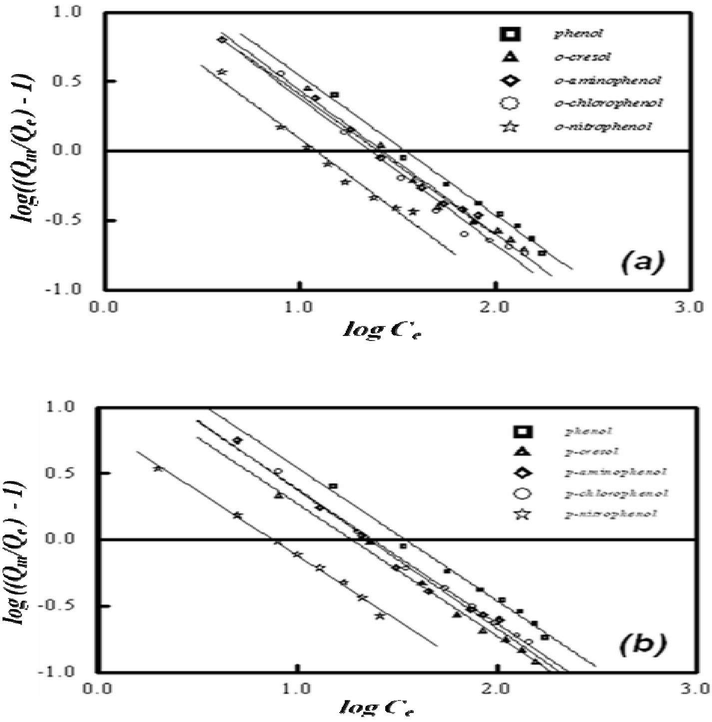


Figure 3. Langmuir–Freundlich isotherms of the adsorption of substituted phenols onto activated carbon, (a) o- substituted phenols, (b) p- substituted phenols.

3.1.4. Tempkin isotherm

A plot of Q_e versus lnC_e at a constant temperature is used to calculate the Tempkin isotherm constants, A_T and b_T . This isotherm contains a factor that explicitly takes into account the adsorbate – adsorbent interactions. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate – adsorbent interactions. The constants A_T and b_T obtained from Tempkin isotherm model are listed in Table 3. The obtained coefficients of determination R^2 for this isotherm model are high ($0.952 < R^2 < 0.996$) which confirms the better fit of equilibrium data as compared with Frendlich isotherm model, but it is not as good as Langmuir and Generalized isotherm models.

Table 3. Isotherm constants and regression data for various adsorption isotherms for adsorption of substituted phenols on activated carbon from aqueous solutions.

Adsorbate	***Langmuir–Freundlich***			***Tempkin***			***(D–R)***		
	K_G	N_b	R^2	A_T	b_T	R^2	Q_m	B	R^2
Phenol	35.059	1.003	0.989	0.285	79.832	0.984	107	39.965	0.937
o-cresol	29.702	1.035	0.978	0.350	52.754	0.959	158	23.818	0.910
p-cresol	18.504	0.997	0.992	0.635	52.388	0.981	186	11.152	0.836
m-cresol	-	-	-	-	-	-	-	-	-
o-aminophenol	26.218	1.013	0.992	0.407	44.409	0981	150	5.023	0.802
p-aminophenol	26.254	1.044	0.986	0.145	33.418	0.982	223	7.684	0.882
m-aminophenol	-	-	-	-	-	-	-	-	-
o-chlorophenol	27.211	1.053	0.978	0.401	32.216	0.962	262	15.532	0.916
p-chlorophenol	24.940	1.015	0.997	0.430	35.875	0.986	241	14.310	0.905
o-nitrophenol	13.676	1.049	0.978	0.677	24.468	0.978	282	3.95	0.931
p-nitrophenol	7.175	0.977	0.995	1.290	25.297	0.996	286	1.106	0.854

3.1.5. Dubinin–Radushkevich (D–R) isotherm:

The adsorption equilibrium data of phenolics on activated carbon was then examined with the (*D-R*) isotherm equation. The constants Q_m and B obtained for this isotherm model together with R^2 values are shown in Table 3. Values of coefficient of determination ($0.802 < R^2 < 0.937$) indicate that the (*D-R*) isotherm model does not fit well with the equilibrium expiremental data as compared with the other models considered. The maximum adsorption capacity, Q_m , obtained using this isotherm model is less than the values obtained from Langmuir isotherm model. The values of the constant B for phenolics are related to the sorption energy E (Eq. 13). The mean adsorption energy is the free energy change when one mole of the adsorbate is transfered to the surface of the solid from infinity in the solution (Tahir and Rauf, 2006). Values of E are found to be between (103.77 & $672.37\ Jmol^{-1}$) corresponding to physical adsorption (Benhammou et al., 2005).

3.2 Effect of substituent:

The adsorption of phenol, ortho and para (aminophenol, cresol, chlorophenol, and nitrophenol) was studied to compare the effect of the introduction of NH_2, CH_3, Cl, and NO_2 groups to phenol on the adsorption. There are clear differences in the adsorption behavior of these phenolics and this is shown in Fig. 1. The adsorption decreases in the order:

nitrophenol > chlorophenol > aminophenol > cresol > phenol.

This can be explained by differences in molecular size, solubility, dissociation equilibrium and benzene ring reactivity (Streat et al., 1995).

There are many factors influencing the adsorption of phenols on activated carbon, those due to the physical and chemical properties of the substrate in question (molecular dimensions, solubility, acidity and benzene ring reactivity) (Daifullah and Girgis, 1998). The forces of attraction between activated carbon and a molecule are greater the closer the size of the molecule to the pore size in the carbon (Benefield et al., 1982). The solubility parameter of the phenolics appears to play a major role in determining the amounts adsorbed. A decrease in both solubility and *pKa* of the solute is always associated with an increase in adsorption capacity (Dvorak et al., 1993).

The interaction of the aromatic ring with the surface of the activated carbon is considered to be the major influence in this process, interacting through the π-electron system of the ring. Mattson et al. (1969) suggested that the adsorption of phenols on carbon occurs by a donor-acceptor complex mechanism involving carbonyl oxygen groups on the carbon surface acting as an electron donor and the aromatic ring of phenols as an acceptor. On the other hand, the results published by Franz et al. (2000), and Moreno-Castilla (2004), showed that solute molecules (phenols) create hydrogen bonds with the surface oxides.

Phenolic compounds are adsorbed strongly by activated carbon and many interact with carbon surface in several ways, depending on the adsorption conditions (Pimenta and Kilduff, 2006). Physical adsorption process dominates at short equilibrium times, low temperature, low pH, and low concentrations of molecular oxygen. The physical adsorption (physisorption) of phenolic compounds to activated carbon surface is thought to arise from dispersion forces acting between π-electrons in the molecule and π-electrons in the graphitic basal planes on the surface (Coughlin and Ezra, 1968).

Electron density of the aromatic ring is strongly influenced by the nature of the substituent present in it. In the present study it is observed that substituted phenols which have electron withdrawing groups are more strongly adsorbed and those having electron donating groups are lesser adsorbed. A nitro-group in substituted phenols lowers the electron density in the π-system of the ring in comparison to phenol itself. Chlorophenols are also adsorbed more than phenol because of the electron-withdrawing inductive effect of chlorine. If the electron donating group (e.g. hydroxyl group) is present, as in the case of cresol, it increases the overall electron density in the aromatic ring and thus the uptake of adsorbate is less.

It is concluded that the adsorption capacity of phenolic compounds grows with the increase in hydrophobicity of their substituents, and the decrease in water solubility (Deryło-Marczewska and Marczewski, 2002). The mechanism of phenol adsorption is determined not only by ‘‘π– π dispersion interaction’’ and ‘‘donor–acceptor complex formation’’ but also by so called ‘‘solvent effect’’. This usually neglected effect, together with the above-mentioned effects, occurs simultaneously during adsorption and modifies strongly adsorption properties of phenols toward activated carbons.

3.2 Effect of substituted position:

The adsorption of cresol and aminophenol isomers was investigated to study the effect of substituted position on the adsorption. Fig. 4 shows that the adsorption decreases in the order of : p-isomer > o-isomer > m-isomer. The order of decreasing adsorption capacity is in accordance with the increase of solubility of these isomers (Nevskaia et al., 1999).

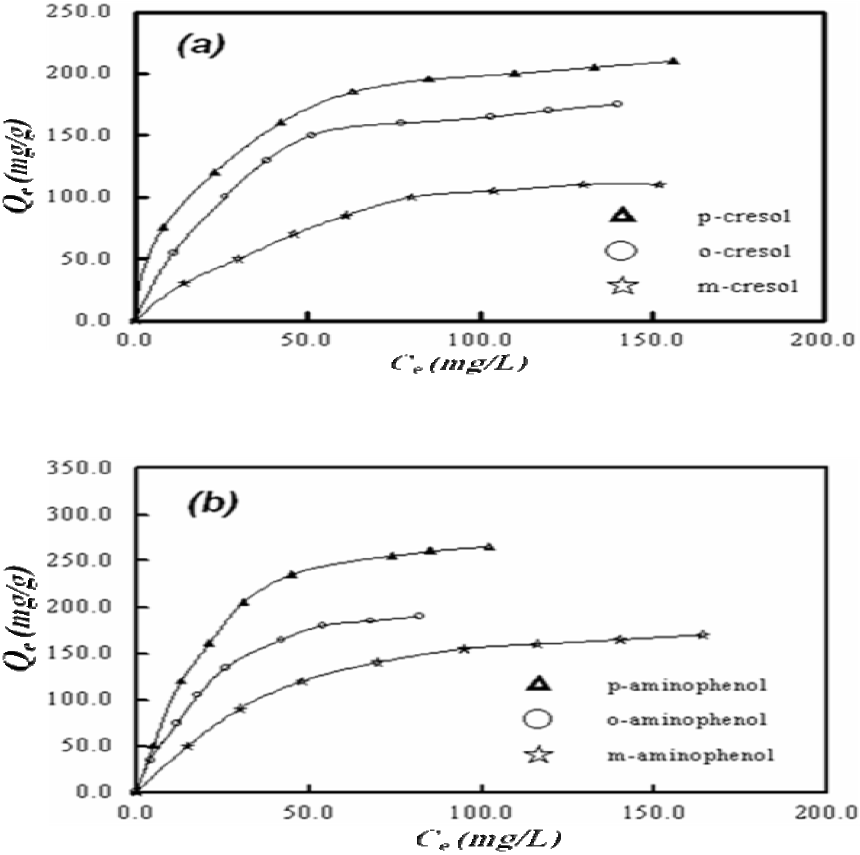


Figure 4. Effect of substituted position on the adsorption of: (a) cresol isomers, (b) aminophenol isomers, onto activated carbon from aqueous solution at 25 °C.

It was found that there is no noticeable difference between the adsorption of cresol isomers on granular activated carbon, but their adsorption on activated carbon fibers decreases in the order of : o-isomer > m-isomer > p-isomer (Juang et al 1996). Furthermore, a sequence of p-isomer > m-isomer > o-isomer has also been reported for the adsorption of cresol isomers on either fly ash or Al(III) and Fe(III)-impregnated fly ash (Singh and Rawat, 1994), and also the same order is observed in the adsorption of chlorophenol isomers on Hypersol-Macronet polymers (Streat and Sweetland, 1997).

It appears therefore that isomers do not follow any particular pattern in their adsorption. Such discrepancies are probably due to the differences in pore structure and pore size in activated carbon and other adsorbents.

4. Conclusions

Equilibrium studies for the adsorption of phenolic compounds from aqueous solutions onto activated carbon have been carried out in the concentration range (5 to 200) mg/l at 25 °C. The equilibrium adsorption data are tested with various isotherm models such as Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich, and Generalized isotherm models. The equilibrium data are best fitted with Langmuir isotherm model which confirms the monolayer adsorption of phenolics onto activated carbon.

The adsorption properties of phenolic compounds on activated carbon are affected by many factors such as acidity (pK_a), solubility, possible interactions (intramolecular or intermolecular hydrogen bonding) and steric effects (molecular size). The adsorption capacity of these phenolics grows with the increase in hydrophobicity of their substituents, and the decrease in water solubility. The adsorption of cresol and aminophenol isomers on activated carbon decrease in the following order: p-isomer > o-isomer > m-isomer.

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