ADSORPTION OF PHENOLICS FROM AQUEOUS SOLUTION ON ACTIVATED CARBON: EFFECT OF MOLECULAR STRUCTURE

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Abstract

Adsorption isotherms of some phenolics from aqueous solutions onto activated carbon were studied in the concentration range (0.030 to 2.083) mmol.dm^{-3} at 25 °C. The pH of the solutions ranged from 6.5 to 6.8 . The adsorption data were correlated well with the Langmuir adsorption isotherm in the range of concentrations studied. The effect of the introduction of NH_2 , CH_3 , Cl , and NO_2 groups to phenol molecule, the effect of substituted position in cresols and aminophenols, and the effect of the number of substituted NO_2 groups in nitrophenols on adsorption were investigated. Electrostatic interaction and hydrogen bonding between the carbon surface and the solute molecules is postulated to explain the adsorption data.

Introduction

Adsorption of phenols on carbons is an important subject especially because of ecological aspects.[1] 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 and surface chemical properties (functional groups) are the main factors influencing adsorption equilibrium.[2]

It is well known that phenolic compounds and dyes are common pollutants in municipal water and industrial effluents.[3] Chlorinated phenols impart disagreeable taste to water and are toxic to aquatic life.[4] O-cresol has been identified as a hazardous compound for many aquatic organisms by the Environmental Protection Agencies.[5] 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^{-1}) .[6]

Due to the toxicity of phenols, their removal from water is an important issue. Different water treatment technologies are used to remove phenolic pollutants, for example, biological degradation, chemical oxidation or adsorption.[7,8] Activated carbon is the only adsorbent used to any significant extent in water and wastewater treatment. The surface of activated carbon contains many active chemical groups, parts 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.[2]

It was well known that the structure of the adsorbate molecule has a significant effect on its adsorption. Singh[9] reported that aniline and phenol appear to adsorb on carbon from aqueous solution without the phenolic and amino groups being involved in the adsorption process, thus ruling out the possibility of adsorption through the formation of hydrogen bonds with the oxygen groups on the carbon surface.

In the present work we have studied the adsorption isotherms, the effect of substituents, the effect of substituted position and the effect of the number of substituted NO_2 groups on the adsorption of phenolics on activated carbon from aqueous solution.

Experimental Section

Materials

Powdered activated carbon (Powder, extra pure, minimum methylene blue adsorption (0.15 % solution) ≥ 12 ml / 0.1g) was supplied by BDH, Poole (England). The carbon had been soaked in distilled water for 24 h to remove fines and soluble ash and dried to constant weight at (100 to 110)°C. Drying for 24 h was usually sufficient to maintain constant weight[10], after which the carbon was sieved to 325 mesh and stored in a calcium chloride desiccator until use. Phenol (≥99%), p-nitrophenol (≥98%), 2,4-dinitrophenol (≥98%), and 2,4,6-trinitrophenol (≥98%) were supplied by Hannover chemicals. p-aminophenol (≥99%), o-aminophenol (≥99%), m-aminophenol (≥98%), o-chlorophenol (≥98%) and o-nitrophenol (≥99%) were obtained from BDH. 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. 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 .

Analysis

The concentration of solutes was determined with a single beam, Pye-Unicam-8700 UV/Visible spectrophotometer 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.

Experimental 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 shaking a fixed mass of carbon with (50 ml) of pollutant solution of known concentration in a (100 ml) glass-stoppered flask at 298.15 K using a (Dunboff Metabolic Shaking Incubator , GCA/Precision Scientific, Chicago, U.S.A.). Various solute concentrations were used and the system was allowed sufficient time to reach equilibrium. The adsorbed amounts were calculated from :

$$Q_e = V_{sol}(C_o - C_e)/m \text{ ....(1)}$$

where Q_e is the adsorbed amount per gram of carbon (mmol.g^{-1}), C_e is the initial solute concentration (mmol.dm^{-3}), C_e is equilibrium concentration in (mmol.dm^{-3}), *m* is the mass of carbon per dm^{-3} of solution (g.dm^{-3}) and Vsol is the total volume of solution.

Results and Discussion

Adsorption Isotherms

Adsorption isotherms of all solutes on activated carbon from aqueous solutions in the concentration range (0.030 to 2.083) mmol.dm^{-3} are presented in Figures (1-4) i.e., the relation between the mass of phenolic compound adsorbed per unit mass of activated carbon (Q_e) and their equilibrium concentration (C_e).

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.

Adsorption isotherms data were analyzed in terms of the Langmuir equation, which is represented as:

$$Q_e = K_L C_e /(1 + aC_e) \text{ .... (2)}$$

where K_L and *a* are the Langmuir experimental constants. Rearranging equation 2, we get:

$$C_e / Q_e = 1/K_L + (a/K_L)C_e \text{ .... (3)}$$

A plot of (C_e / Q_e) versus C_e give K_L and *a* from the slope and the intercept. The parameters of Langmuir equation obtained for all systems were listed in Table 1 together with the standard deviation (σ) which was calculated by using the relation:

$$\sigma = \left[\frac{\sum (Q_e^{exp} - Q_e^{calc})^2}{P - N} \right]^{0.5} \text{ ....(4)}$$

where *P* and *N* are the number of data points and parameters respectively. It is evident that the adsorption data correlate well with the Langmuir adsorption isotherm in the range of concentrations studied. In Figures (1-4) the solid and the dashed lines represent the experimental data and the calculated data (eq 2) respectively.

For the purpose of studying the effect of molecular structure on adsorption, three groups of compounds were considered:

1st group:

The adsorption of phenol, o-aminophenol, o-cresol, o-chlorophenol, and o-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. As can be seen from Figure 1, the adsorption decreases in the order:

o-nitrophenol > o-chlorophenol > o-aminophenol > o-cresol > phenol.

It is generally accepted that the capacity of activated carbon adsorption is higher when the adsorbate has a higher molar mass or smaller solubility in water.[11,12] 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. It was suggested that a mixed mechanism between the π-π dispersion interaction and the bonding of water molecules to the surface groups.[13] On the other hand, the results published by Franz et al.[14] and Moreno-Castilla[15] showed that solute molecules (phenols) creates hydrogen bonds with the surface oxides and the adsorption of water on active sites can be neglected. Thus it can be seen that the process of hydrogen bonding and the competition between a solute and solvent is important and cannot be neglected.

It is concluded that the mechanism of adsorption of organics from dilute aqueous solutions in carbon micropores is micropore filling, combined with adsorption on the active sites. The localization of the π-electrons of the basal planes by surface functionalities has small influence on the adsorption mechanism. Thus, the π-π interactions during the micropore filling are screened by the electrostatic interactions of the solute molecules with the surface groups.[13] At neutral pH the rate of adsorption on carbon surface is determined by the interactions of the basic centers of the adsorbed compound with positively charged surface-active sites. Generally, the more negative the benzene ring the larger the adsorption. Judging from the electrophilic nature of the studied phenols, the present results are somewhat in agreement with this effect.

2nd group :

The adsorption of cresol and aminophenol isomers was investigated to study the effect of substituted position on the adsorption. Figures (2 and 3) show that the adsorption decreases in the order of : p-isomer > o-isomer > m-isomer. The order of decrease is in accordance with the increase of solubility of these isomers.

The same order was observed for the adsorption of anisidine isomers[16]. With regard to adsorption capacity, the present ordering is somewhat opposite to many of those observed using another adsorbents. For example, it was found that there is no noticeable difference between the adsorption of cresol isomers on granular activated carbon[16], but their adsorption on activated carbon fibers[17] decreases in the order of : o-isomer > m-isomer > p-isomer. Furthermore, a sequence of p-isomer > m-isomer > o-isomer has also been reported for their adsorption on either fly ash or Al(III) and Fe(III)-impregnated fly ash.[18]

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 between activated carbon and other adsorbents.

3rd group :

The adsorption of p-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol was investigated to study the effect of the number of substituted nitro-groups on the adsorption of nitrophenols. Figure 4 shows that the adsorption decreases in the order:

2, 4-dinitrophenol > p-nitrophenol > 2, 4, 6-trinitrophenol

Within the NO_2 and Cl substituted phenols it was observed that as the number of NO_2 or Cl groups on a compound increased, both the polarity and adsorbability of the compound increased.[19] This increase of adsorbability with increased polarity of the molecule could be attributed to electronic interaction that occurs at the sorbent surface as a result of resonance. An increase of adsorbability with increasing polarity has also been observed for some organics on activated carbon.[20]

The molecules interacting with surface oxides are adsorbed perpendicular to the carbon surface.[21] The above order of the adsorption of nitrophenols may be attributed to the observation that substitution of four positions in the aromatic ring decreases the stability of the ring.[22] Hence, the adsorption of 2,4,6-trinitrophenol is decreased by the steric hindrance of the three nitro groups.

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/dm^3 at 25 °C. The equilibrium data for the adsorption of individual compounds studied were found to correlate well with the Langmuir equation for adsorption isotherms in the range of concentration studied.

The localization of the π-electrons of the basal planes by surface functionalities has small influence on the adsorption mechanism. Electrostatic interactions, together with the hydrogen bonds, are the driving forces for the adsorption of phenols onto carbon. The more electron withdrawing substituent in the aromatic ring the more adsorption capacity of the phenolic compound.

The adsorption of cresol and aminophenol isomers on activated carbon decrease in the following order : p-isomer > o-isomer > m-isomer. The introduction of NO_2 groups to the phenol molecule generally has a favorable effect on adsorption, but in the case of 2,4,6-trinitrophenol the solute molecule is destabilized by the steric hindrance of the three nitro groups.

Table (1)
Parameters of the Langmuir equation (eq. 2) and standard deviation σ (eq. 4).

Adsorbate	K_L	a	σ
	L g^{-1}	L mmol^{-1}	mmol g^{-1}
Phenol(P)	4.115	2.733	0.030
p-aminoP	14.492	4.768	0.044
o-aminoP	10.101	4.323	0.061
m-aminoP	5.076	2.543	0.043
o-chloroP	15.385	5.769	0.085
p-nitroP	58.823	18.529	0.089
o-nitroP	34.482	11.310	0.050
p-cresol	12.346	5.667	0.042
o-cresol	8.065	4.177	0.087
m-cresol	2.778	1.908	0.043
2,4-dintroP	111.111	38.444	0.036
2,4,6-trinitroP	19.230	10.940	0.045

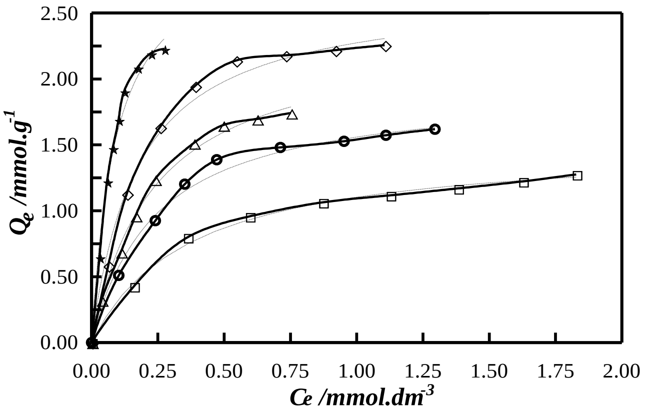

Fig.(1) : Adsorption isotherms of o-substituted phenols onto activated carbon from aqueous solution at 25 ^{o}C. (□), phenol; (○), o-cresol; (△) o-aminophenol;(◇),o-chlorophenol; (★)o-nitrophenol.

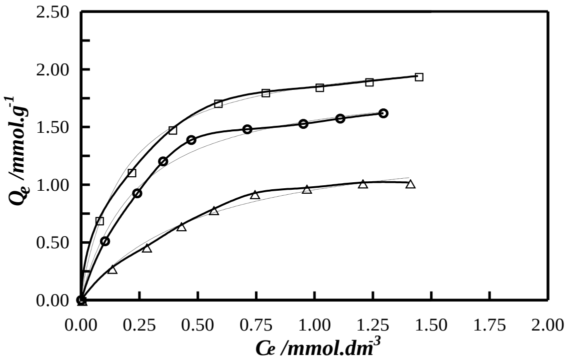

Fig. (2) : Effect of substituted position on the adsorption of cresol isomers onto activated carbon from aqueous solution at 25 °C. (□), p-cresol;○),o-cresol;(△)m-cresol.

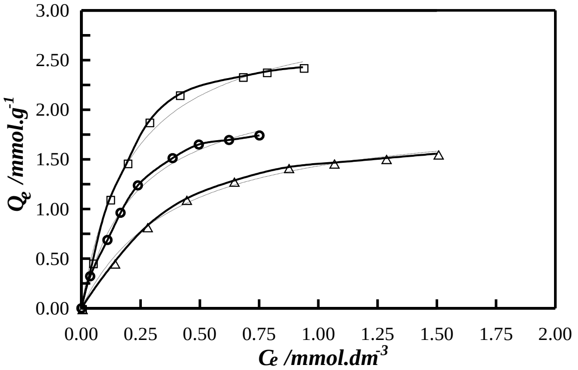

Fig. (3) : Effect of substituted position on the adsorption of aminophenol isomers onto activated carbon from aqueous solution at 25 °C.(□), p-aminophenol;○),o-aminophenol; (△)m-aminophenol.

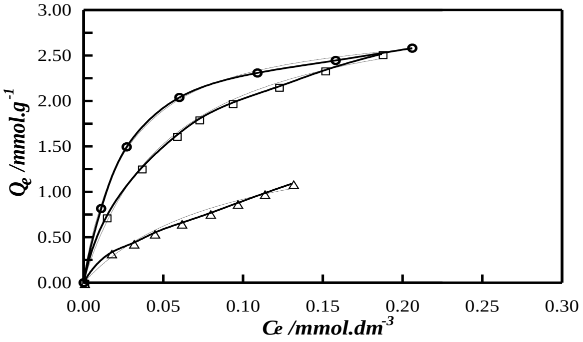

Fig. (4) : Effect of the number of substituent on the adsorption of nitrophenols onto activated carbon from aqueous solution at 25 °C.(□),p-nitrophenol;(○), 2,4-dinitrophenol;(△)2,4,6-trinitrophenol.

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الخلاصة

تم دراسة ايزوثيرمات الأمتزاز لبعض الفين ولأت من محاليلها المائية بتراكيز 0.030–2.083 مللي مول /لتر وبحامضية 6.5–6.8 على سطح الكاربون المنشط عند درجة حرارة 298.15 كلفن. اوضحت النتائج ان الأمتزاز على سطح الكاربون يتبع معادلة لانكماير وبمدى التراكيز المدروسة. كما تم دراسة تاثير المجاميع المعوضة NH_2 و CH_3 وCl و NO_2 في الفينول وتاثير موقع هذه المعوضات كما في المعوض NO_2 في مركبات النايترفينول. تم مناقشة النتائج على اساس التاثيرات المتبادلة من القوى الالكتروستاتيكية والاواصر الهيدروجينية بين سطح الكاربون والمذابات من الفينولات.