Adsorption of Phenols onto Chemically-Activated Carbons Developed from Wild Cherry Stones

M. N. Alaya[1,♠], A. M. Youssef[2], M. Karman[1] and H. E. Abd El-Aal[1]

[1]Department of Chemistry, Faculty of Science, University of Aleppo, Syria.
[2]Department of Chemistry, Faculty of Science, University of Mansoura, Mansoura, Egypt.
♠e-mail: *mnalaya@myway.com*

Abstract

Phosphoric acid-activated carbon WP's and zinc chloride-activated carbons WZ's were developed from wild cherry stones. The textural properties of the activated carbons were determined from nitrogen adsorption data at 77 K and the chemistry of the carbon surface, i.e. the surface carbon-oxygen groups (type and amount) was determined from the base and acid neutralization capacities (Boehm method). The adsorption of phenol, p-nitrophenol, p-chlorophenol, dinitrophenol and dichlorophenol was followed at 298 K. The activated carbons obtained were characterized by high surface area and large pore volumes as well as by high surface concentration of C-O groups. The investigated carbons exhibited high adsorption capacities towards phenols with these capacities increased with the increase of molecular weight and the decrease of the solubility of phenol in water. However, no general relationship could be observed between the adsorption capacities of carbons and any of their textural parameters or their surface chemistry. This may be attributed to the many factors controlling phenol adsorption and the different types and mechanisms of adsorption involved.

Keywords :

1. Introduction

Adsorption from solution is a competitive process with equilibrium determined by many factors resulting from adsorbent, adsorbate and solvent properties [1-5]. The porous structure of a solid, its energetic heterogeneity (depending also on a solute) and surface chemical properties are the main factors influencing adsorption equilibria. The surface of the activated carbon contains many active chemical groups, part of which is dissociable ones. The role of various carbon-oxygen (C-O) groups in the mechanism of organics adsorption was discussed widely in order to relate the adsorption uptake with the changes of the chemistry of carbon surface [6-8].

The adsorption of organic molecules from water onto activated carbon has gained increasing interest during the past decade. Activated carbons are widely used for separation and purification processes involving aqueous solution systems. A series of studies has been conducted in our laboratory to prepare and characterize activated carbons obtained from several fruit stones and nutshells [9-12]. Recently, phosphoric acid-activated carbons have been prepared from peanut shells and were characterized as adsorbents with extended surface area and high adsorption capacity for organic molecules [13, 14].

Phenols and substituted phenols are a major class of organic pollutants that contaminate the ecosystem and accumulate in food chain [15, 16]. Treatment of drinking water for the removal of organic impurities, in general, and phenolic compound, in particular has attracted special attention in environmental science and technology. Several methods are used for municipal water purification, mainly filtration processes with the application of various high area-adsorbents, e.g. granular activated carbons [17, 18].

Adsorption of aromatic compounds from solution particularly phenols, has been studied extensively [19, 20]. Leng and Pinto [21] have found that the uptake of phenol is a combined effect of physisorption and surface polymerization. They found out that phenol uptake increases as a result of the removal of carboxylic functional groups from the carbon surface. The presence of surface functional groups prevents activated carbons from adsorbing phenol when the adsorption takes place under oxic conditions [22]. This is a result of the reaction in the ability of activated carbon to promote adsorption via oxidative coupling.

The purpose of this work was to study the effect of the differences found in the textural characteristics and surface chemistry of a large number of chemically-activated carbons, on their capacities towards phenols adsorption. The carbons were prepared in our laboratory from washna stones (wild cherry stones) using (20-85 wt%) phosphoric acid as activating agent and by carbonization at 500 °C, or by using (20-65

wt%) zinc chloride as activating agent and by carbonization at 600°C.

2. Experimental

2.1. Materials

Preparation of zinc chloride-activated carbons WZ's was performed according to the procedure described elsewhere [23]. The designations given to these carbons are based on: W stands for washna stones, Z stands for ZnCl₂, the Arabic number following the letter Z refers the amount of Z in wt% used in activation and the second Arabic number refers to the carbonization temperature (°C). Thus, for example, the designation WZ65-600 refers to the carbon obtained by the carbonization of washna stones impregnated with 65 wt% zinc chloride prior to carbonization at 600°C. Phosphoric acid-activated carbons WP's were prepared according to a procedure described elsewhere [24]. In designating these carbons, the letter P stands for H_3PO_4, the Arabic number following this letter indicates the wt% of P whereas the second Arabic number indicates the carbonization temperature. Thus, the designation WP50-500 stands for the carbon prepared by carbonization at 500°C of washna stones impregnated with 50 wt% phosphoric acid.

The sorbates used were phenol (P), 4-nitrophenol (PNP), 4-chlorophenol (PCP), 2,4-dinitrophenol (DNP) and 2,4-di-chlorophenol (DCP). All phenols were purchased from Merck as analytical reagent grade products. The aqueous phase was prepared by dissolving the phenol in deionized water without pH adjustment.

2.2. Techniques

The adsorption of nitrogen at 77 K was carried out using Gemini 2375 V3.03 adsorption instrument. Prior to adsorption the carbon sample was out gassed at 200°C overnight at a reduced pressure of 10^{-4} Torr. Using Mattson 500-FTIR spectrometer, using the KBr disc technique, identified the functional groups on the surface of some selected carbons. Base neutralization capacities (BNC) were determined according to Boehm titration's [25]. The quantity is expressed in meq/g. These were carried out by neutralization of 0.1 M $NaHCO_3, Na_2CO_3$, NaOH and NaOEt by the carbon sample. Thus 0.25 g of carbon was mixed with 50 ml of the respective solution in 100 ml Quick Fit polyethylene bottles. The suspensions were flushed with nitrogen. Mechanical shaking was continued for 48 h. The residual concentration of each solution was determined by titrating the supernatant against 0.1 M HCl. The total acid neutralization capacities were determined by neutralization of 0.1 M HCl by the carbon sample and the residual concentration of HCl was determined by titrating the supernatant against 0.01 M

Table 1. Characteristics of the phenols investigated

Phenol	MW (g/mol)	Solubility (g/l at 298 K)	pK_a	λ_{max} (nm)	$\in$	A_m (nm²)
P	94.1	93	9.89	210.5	5870	0.437
PCP	128.6	27	9.37	225.7	8740	0.482
PNP	139.1	17	8.42	317.0	6586	0.519
DCP	163.0	15	7.80	285.0	7257	0.539
DNP	184.1	0.64	5.40	353.5	12620	0.597

NaOH.

The adsorption of phenols from their aqueous solutions was carried out using closed glass containers in which 0.1 g of the carbon and 100 ml of unbuffered solution were introduced. The suspensions were mechanically shaken in a bath at 298 ± 0.1 K. The amounts of the phenol adsorbed were determined by measuring the initial and equilibrium concentrations before and after the process in Jasco UV-Visible spectrophotometer at the respective λ_{max}. The characteristics of phenols listed in Table 1, previously reported [7, 26, 27], were considered both for λ_{max} and molar extinction coefficient $\in$ and the molecular area A_m of the adsorbate molecule.

3. Results and Discussion

3.1. Textural properties

The adsorption of nitrogen on the activated carbons investigated proved to be rapid with the equilibrium attained within 20-30 min, indicating thus that the pore structures are all accessible to nitrogen and that the adsorption of nitrogen is not controlled by activated diffusion. The isotherms (not illustrated) were of Type I according to Sing classification [28], except of WP65 and WP85 samples which exhibit isotherms between VI and I types with a clear hysteresis loop. The specific surface areas were calculated using the conven-

Table 2. Textural properties of the carbons investigated

Carbon	S_{BET} (m²/g)	V_T (ml/g)	r_m (nm)
WZ20-600	576	0.244	0.85
WZ35-600	971	0.428	0.88
WZ50-600	1451	0.721	0.99
WZ65-600	1746	1.041	1.20
WP20-500	706	0.304	0.86
WP35-500	1110	0.515	0.93
WP50-500	1790	1.048	1.17
WP65-500	1360	0.937	1.38
WP85-500	1310	1.050	1.60

tional BET equation [29], adopting the value of 0.162 nm^2 for the molecular area of nitrogen [30]. Table 2 gives some textural parameters of the investigated carbons including the surface area S_{BET} (m^2/g), the total pore volume V_T (ml/g) and the mean pore radius r_m (nm). The latter was obtained using the relationship [31]:

$$r_m \text{ (nm)} = 2V_T \times 10^3/S_{BET}$$

It is evident from Table 2 that: (i) S_{BET} and V_T of zinc chloride-activated carbons increased with the increase of the amount of $ZnCl_2$ used in activation. For phosphoric acid-activated carbons, S_{BET} increased with wt% of H_3PO_4. The maximum V_T of WP's was calculated for WP50-500 (1.048 ml/g), approximately the same value (1.050 ml/g) was calculated for WP85-500. (ii) Generally, r_m increased with the increase of the amount of the activating agent. For carbons activated with ≤ 50 wt% $ZnCl_2$, their r_m values lie in the microporous range, i.e <1.0 nm, the increase of the amount of this activating agent to 65 wt% was associated with a shift of r_m to 1.16 nm, i.e. to the lower margin of the mesoporous range. For phosphoric acid-activated carbons r_m values lie in the microporous range for carbons activated with ≤ 35 wt% H_3PO_4 whereas r_m of carbons activated with >35 wt% are located in the mesoporous range.

2.3. The chemistry of the surface

The chemistry of the surface of a carbon is equally important to its textural properties in determining its adsorption capacity particularly in adsorption from solution. The chemistry of the carbon surface is attributed to the existence of C-O functional groups of acidic or basic nature. The chemistry of the carbon surface is determined from its base and acid neutralization capacities expressed in meq/g. The various surface functional groups available on the carbon can be detected using selective neutralization by equilibration with series of bases of increasing strength $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$ (NaOEt). $NaHCO_3$ neutralizes carboxylic groups whereas those neutralized by Na_2CO_3 but not by

$NaHCO_3$ were believed to be lactones. The weakly acidic groups neutralizes by NaOH but not by Na_2CO_3 were postulated as phenols. The reaction with NaOEt was not considered as a true neutralization reaction since it did not involve exchange by H$^+$ or Na$^+$ ions. The groups reacting with NaOEt but not with NaOH were suggested as carbonyl [32]. The functional groups on the surface of investigated carbons are listed in Table 3 expressed as meq/g. The pH of the point of zero charge pH_{PZC} of the carbons are also listed in Table 3.

It is evident from Table 3 that: (i) Phosphoric acid-activated carbons are rich with carboxylic and carbonyl groups compared with zinc chloride-activated ones. (ii) Zinc chloride-activated carbons are rich with phenolic and lactonic groups compared with phosphoric acid-activated carbons. (iii) Points of zero charge pH_{PZC} of WP activated carbons exist at relatively lower pH compared with pH_{PZC} of WZ activated carbons. The above-mentioned differences refer to the role of the activating agent in determining the chemistry of the surface of the activated carbon. The mechanism of activation with phosphoric acid is probably different than the mechanism of zinc chloride activation. The former dominates before carbonization when phosphoric acid activates the degradation of cellulosic structure of the cellulosic precursor [33] whereas the mechanism of the latter dominates during carbonization as a result of the removal of the hydrogen contained in the precursor as HCl instead of being removed as methane or lower hydrocarbons [34].

FTIR was also used to determine the surface functional groups for some selected carbons. Even though the carbonized materials, are rather complex, FTIR still can give some information about the probable functional groups on the surface. Representative FTIR spectral patterns are shown in Figs. 1 and 2. As a matter of fact the spectra of all the carbons investigated are more or less similar. Differences are only observed in the intensity of the peaks characterizing the same functional groups. Some broad bands and shoulders are shown which makes the assignment rather difficult. However, well-developed bands are common in the spectra of the

Table 3. Surface carbon-oxygen groups and pH_{PZC} of the carbons investigated

| Carbon	Carboxyl (mg/g)	Lactonic (mg/g)	Phenolic (mg/g)	Carbonyl (mg/g)	Total acidic (mg/g)	Total basic (mg/g)	pH_{PZC}
WZ20-600	0.1190	0.2295	0.1560	0.1752	0.6797	0.0875	4.1
WZ35-600	0.0680	0.3545	0.1830	0.1575	0.7630	0.1500	5.9
WZ50-600	0.0935	0.2345	0.1260	0.1425	0.5965	0.1500	5.5
WZ65-600	0.0935	0.2400	0.1205	0.1703	0.6243	0.1375	5.9
WP20-500	0.1763	0.0590	0.1000	0.2067	0.5420	0.0125	2.2
WP35-500	0.1955	0.1210	0.0602	0.2865	0.6632	0.0250	2.2
WP50-500	0.2210	0.2850	0.0995	0.2963	0.8978	0.0375	3.0
WP65-500	0.1955	0.1967	0.0885	0.2510	0.7287	0.0375	3.5
WP85-500	0.1700	0.1712	0.1380	0.2560	0.7352	0.0750	5.1
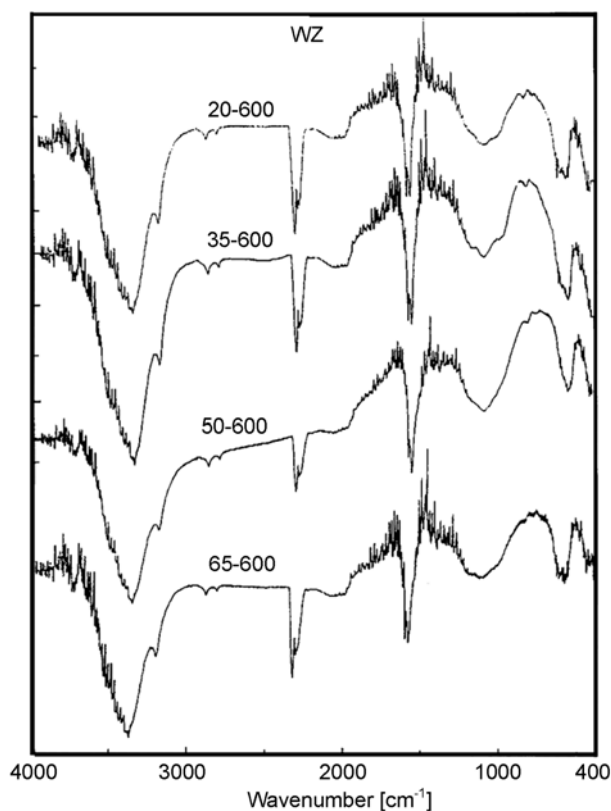
Fig. 1. FTIR spectra of WZ20-600, WZ35-600, WZ50-600 and WZ65-600 carbons.
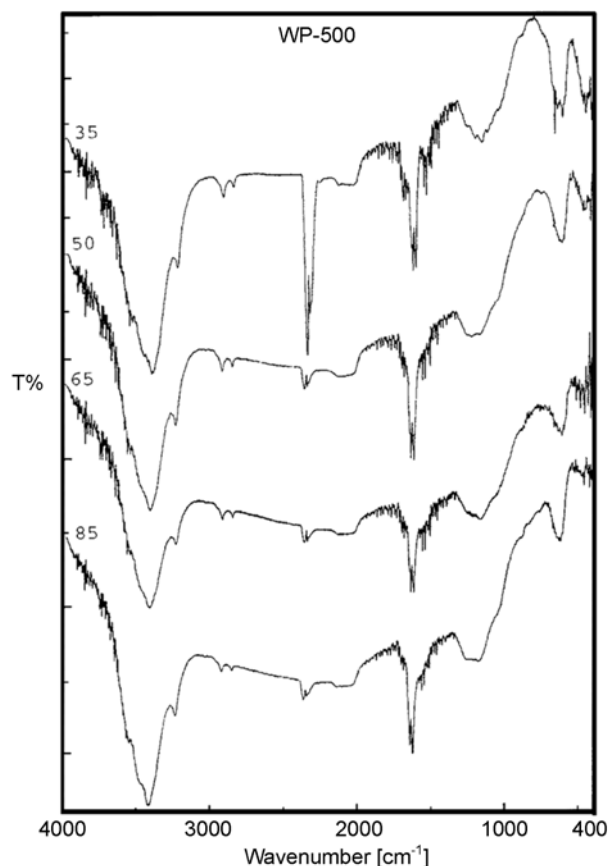

Fig. 2. FTIR spectra of WP35-500, WP50-500, WP65-500 and WP85-500 carbons.

investigated carbons. These are: the intense and broad bands covering the range 3166-3600 cm^{-1} in which stretching vibration of –OH groups and probably with adsorbed water molecules is expected [35], -OH phenol or carboxylic functionalities absorb at 3477 cm^{-1} [36] and OH-ether hydrogen bonds at 3235 cm^{-1} [37]. The weak bands at 2920 and 2855 cm^{-1} are ascribed to antisymmetric [38, 39] and symmetric vibrations of –CH$_3$, respectively. The intense band at 2380 and 2347 cm^{-1} are connected with COO (CO$_2$) and or P-H stretching vibration [35]. The weak band at 1769 cm^{-1} is connected with stretching C=O vibration arising from groups such as lactones, quinines [37] and carboxylic acids [40]. The sharp band at 1644 cm^{-1} suggests the presence of C=O stretching vibration in acid conjugated with rings [41, 42] whereas the sharp band at 1627 cm^{-1} may be due to the asymmetric and symmetric stretching COO$^-$ vibration or to the skeletal C=C aromatic vibration [37, 42]. The bands located in the range 1000-1300 cm^{-1} may be assigned to stretching vibration of C–O bands in carboxy, phenol and ether groups [35, 36, 43].

3.3. Adsorption of phenols

The first stage in adsorption from solution is the deter-

mination of the rate of adsorption and the time required to reach equilibrium. Preliminary experiments have been carried out in this concern using WZ50-600 and WP50-500. The results obtained indicated that the order in which the equilibrium was attained is about the same for WZ's and WP's carbons: P $\geq$ PNP $\geq$ PCP > DCP > DNP. This order is expected when the molecular dimensions of these phenols are considered. Although the time required to reach equilibrium was 50 h, more than 90% of adsorption was observed after 24 h equilibration.

After the determination of the equilibrium time, the complete isotherms of phenols were determined at 298 K, Figs. (3-7). Experimental data are plotted as the amount adsorbed × (mmol/g) versus the equilibrium concentration in mM. The isotherms are of L Type according to Giles classification, but with less developed plateau. The Langmuir adsorption model described the adsorption equilibria. The linear form is expressed as

$$\frac{C}{x} = \frac{1}{B x_m} + \frac{C}{x_m}$$

Where B (the Langmuir constant) is a direct measure of the intensity of the adsorption process and x$_m$ is the monolayer
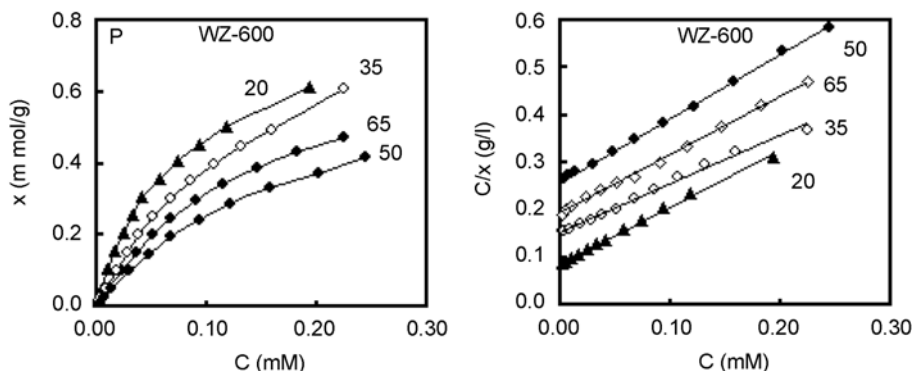
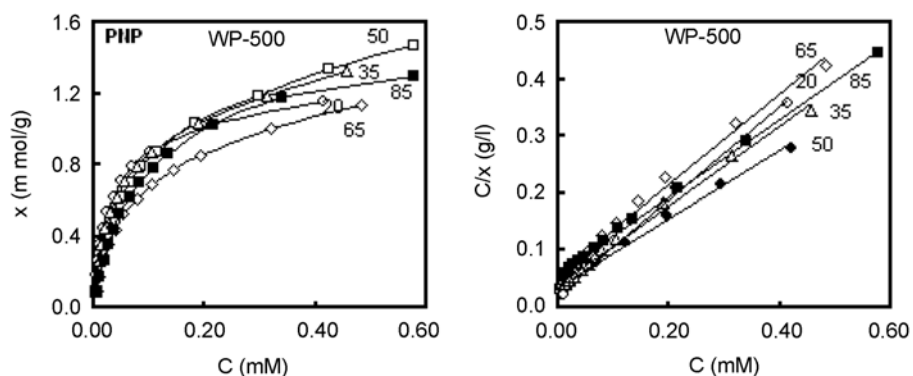**Fig. 3.** Representative phenol adsorption isotherms at 298 K.

Fig. 4. Representative p-nitrophenol adsorption isotherms at 298 K.
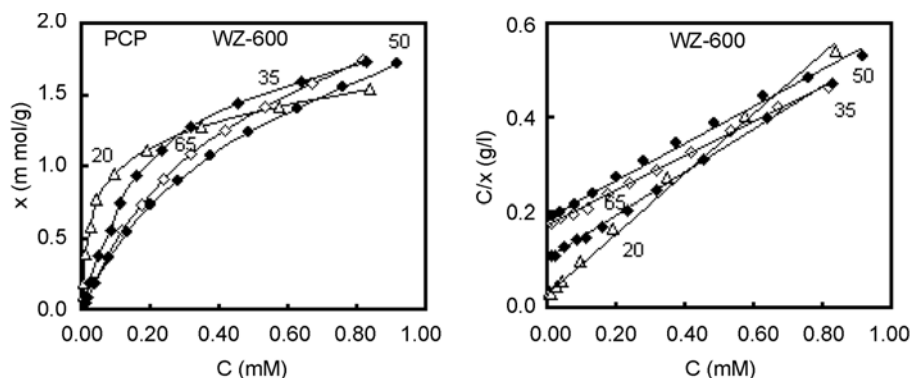

Fig. 5. Representative p-chlorophenol adsorption isotherms at 298 K.

capacity (mmol/g). The linear Langmuir plots are shown in Figs. (3-7). Evidently, the experimental data fit very well the Langmuir model as indicated by the high values of correlation coefficient R^2, being > 0.99. The values of x_m as determined by all phenol-carbon systems investigated are listed in Table 4, expressed in mg/g. Even though, no general trend could be detected between the adsorption capacity x_m and any of the textural parameters or between x_m and any of the chemical characteristics of the surface, the following obser-

vations could be predicted: (i) The amounts of phenol adsorption follow the order: DVP > DNP > PCP > PNP > P, i.e. disubstituted phenols are more adsorbed than monosubstituted phenol and the latter are more adsorbed than phenol. (ii) The molecular volume is not a controlling factor in determining the adsorption of phenol by activated carbons investigated. (iii) Less soluble phenols are more adsorbed than highly soluble ones. (iv) The entire pore structures of the carbons investigated are accessible to the phenols studied
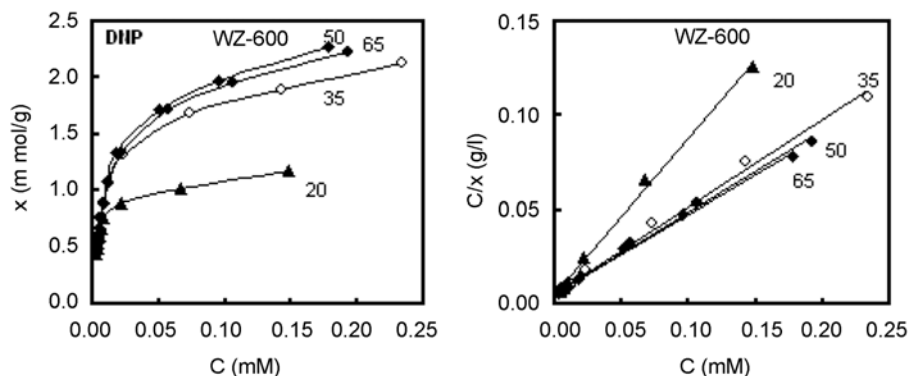
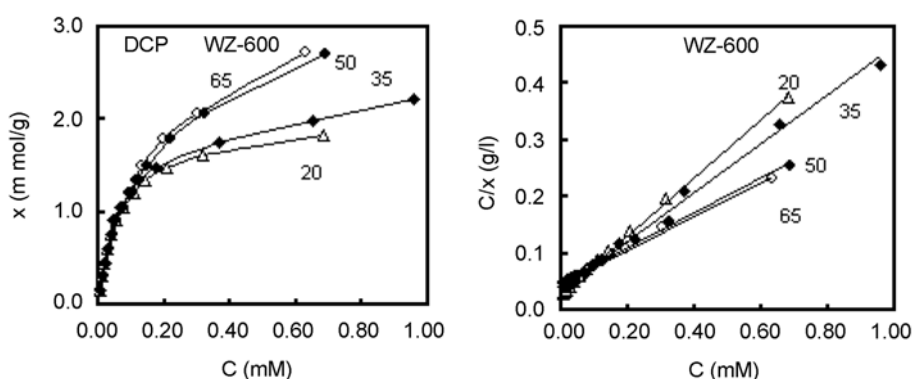**Fig. 6.** Representative dinitrophenol adsorption isotherms at 298 K.

Fig. 7. Representative dichlorophenol adsorption isotherms at 298 K.

Table 4. Monolayer capacities x_m (mg/g) as determined for the carbons investigated from the adsorption of P, PCP, PNP, DCP and DNP at 298 K

Carbon	X_m (mg/g)				
	P	PNP	PCP	DNP	DCP
WZ20-600	78	167	204	220	320
WZ35-600	93	183	283	401	381
WZ50-600	70	192	330	430	527
WZ65-600	66	173	315	392	504
WP20-500	70	169	220	310	310
WP35-500	55	199	288	372	435
WP50-500	51	219	331	400	525
WP65-500	44	176	290	323	391
WP85-500	48	205	308	376	503

in this work. Apart from these observations, no evidences have been obtain to suggest the dependence of phenol adsorption on the texture or chemistry of the carbons investigated to agree with previously reported foundations [44-48]. This may ascribe to the many differences that may exist between the different adsorption systems and also to the different types and mechanisms of adsorption involved. The

texture of the carbon includes the surface area, pore volume distribution, pore geometry and shape. As to the chemistry of the carbon surface, one can mention the type of C–O groups, their concentration, their distribution on the surface and possibly other factors. To summarize: adsorption of phenols on activated carbons is complicated subject and is still open for further investigations.

It remains now to point out that x_m values listed in Table 4 are relatively high referring thus to the high potentialities of the carbons investigated in removing phenols and possibly other organics from potable and waste waters. The high values of x_m indicated that large fraction of the total surface area is occupied by adsorbed phenols. This may be better understood if x_m values are converted to apparent surface areas using the A_m values reported in Table 1. Table 5 summarizes the surface areas of the carbons investigated as determined from the respective x_m values reported in Table 4. Generally, large surface areas are calculated from phenol adsorption. The surface areas measured by the adsorption of phenol amounts to 5.6-37.4% S_{BET}. For monosubstituted phenols PNP and PCP, % S_{PNP}/S_{BET} and S_{PCP}/S_{BET} are considerably higher, being 24.7-65.2 for the former and 36.1-80.1 for the latter. Surprisingly for some carbons higher surface areas were measured by disubstituted phenols DNP and DCP

Table 5. Surface areas of the carbons investigated as calculated from the adsorption of P, PCP, PNP, DCP and DNP at 298 K

Carbon	Surface area (m²/g)				
	P	PNP	PCP	DNP	DCP
WZ20-600	78	167	233	427	636
WZ35-600	93	183	235	776	758
WZ50-600	70	192	276	832	1048
WZ65-600	66	198	262	759	1003
WP20-500	70	169	220	600	617
WP35-500	55	199	288	720	867
WP50-500	51	219	331	774	1046
WP65-500	44	176	290	625	778
WP85-500	48	205	308	727	1002

compared with their respective S_{BET} measured from nitrogen adsorption.

Even though, the discrepancies reported in literature concerning the factors determining the adsorption of phenols onto activated carbons and the mechanisms of their adsorption, one can assume that adsorption of phenols proceeds via different mechanism. These are: (i) physical adsorption due to dispersive interaction between the aromatic part of the phenol molecule and the carbon's basal planes [49]. (ii) The interaction between surface carboxylic groups with phenols via ester formation, causing chemisorptions on the carbon surface [50]. (iii) Strong donor-acceptor complexes between phenol molecule and CO group [51]. To summarize, phenol adsorption onto activated carbons could take place on carbon-oxygen-free surface as well as via interaction with the surface carbon-oxygen groups. This may explain the high adsorption of phenols on activated carbons and the high surface areas occupied by adsorbed phenol molecules.

4. Conclusions

Adsorption of phenols from aqueous solution on chemically-activated carbon depends on many factors that make the prediction of a general relationship between phenol adsorption capacity and any of the textural parameters or any of the characteristics of surface chemistry of these carbons rather difficult. However, these carbons exhibited high phenol adsorption capacities.

The adsorption increased with the increase of molecular weight of the phenol and with the decrease of its solubility in water.

Adsorbed phenols occupy a large fraction of the total surface area, which means that phenols are adsorbed on carbon-oxygen-free surface via dispersive forces between the aromatic part of the phenol and carbon's basal planes. Chemisorption of phenols takes place via ester formation with the surface carboxylic groups and via donor-acceptor

complex formation with surface carbonyl groups.

References

[1] Cookson, J. J. "*Carbon Adsorption Handbook*", ed. Cheremisioff, P. N., Ellerbusch, F., Ann Arbor Science, Ann Arbor, 1978, 241.

[2] Mattson, J. S.; Malbin, H. B. M. D.; Weber, W. J. Jr. Crittenden, J. C. *J. Colloid Interface Sci.* **1969**, *31*, 116.

[3] Perrich, J. R. "*Activated Carbon Adsorption for Wastewater Treatment*", CRC Press, Boca Raton 1981.

[4] Youssef, A. M.; El-Nabarawy, Th., Samara, S. E. *Colloids and Surfaces A* **2004**, *235*, 153.

[5] Youssef, A. M.; Mostafa, M. R. *Indian J. Technol.* **1992**, 413.

[6] Youssef, A. M.; El-Nabarawy, Th.; El-Shafey, E. I. *Carbon Science* **2006**, *7*, 1.

[7] Daifullah, C. J.; Girgis, B. S. *Water Res.* **1998**, *32*, 1169.

[8] Ramakrishna, K. R.; Viravagharan, T. *Water Sci. Technol.* **1997**, *36*, 189.

[9] Youssef, A. M.; Alaya, M. N.; Nawar, N. *Adsorp. Sci. Technol.* **1994**, *11*, 225.

[10] Alaya, M. N.; Hourieh, M. A.; Youssef, A. M.; El-Sejarieh, F. *Adsorp. Sci. Technol.* **2000**, *18*, 27.

[11] Alaya, M. N.; Youssef, A. M.; Karman, M.; Abdel Al-Aal, H. E. *Carbon Science* **2006**, *7*, 9.

[12] Youssef, A. M.; El-Nabarawy, Th.; Mostafa, M. R. *Adsorp. Sci. Technol.* **1997**, *14*, 59.

[13] Abdel-Rahman, A. A. H., Ph.D. Thesis, Mansoura Univ., Egypt **2001**.

[14] Youssef, A. M.; El-Khouly, A. I.; Ahmad, A. I.; El-Shafey, E. I. *Adsorp. Sci. Technol.* **1995**, *12*, 211.

[15] Radovic, L. R.; Moriro-Castilla, C.; Rivera-Utrilla, J. *Chem. Phys. Carbon* **2001**, *27*, 227.

[16] Terzyk, A. P. *Adsorp. Sci. Technol.* **2003**, *21*, 539.

[17] Terzyk, A. P. *J. Colloid Interface Sci.* **2004**, *275*, 9.

[18] Neveskaia, D. M.; Castijos-Lopez, E.; Guerro-Ruiz, A.; Munoz, V. *Carbon* **2004**, *42*, 653.

[19] Radovic, L. R.; Silva, L. E.; Ume, J. I.; Menedez, J. A.; Leon Y Leon, C. A.; Scaroni, W. A. *Carbon* **1997**, *35*, 1339.

[20] Bertoncini, C.; Odetti, H.; Bottani, E. J. *Langmuir* **2000**, *16*, 7457.

[21] Leng, C. E.; Pinto, N. G. *Carbon* **1997**, *35*, 1375.

[22] Tessmr, C. H.; Vidic, R. D.; Uranowski, I. J. *Environ. Sci. Technol.* **1997**, *31*, 1872.

[23] Youssef, A. M. *Carbon* **1974**, *12*, 433.

[24] Alaya, M. N.; Hourieh, M. A.; El-Sejarieh, F. Youssef, A. M. *Adsorp. Sci. Technol.* **2001**, *19*, 321.

[25] Boehm, H. P. "*Chemical Identification of Surface Groups*" in *Advances in Catalysis*, Vol.16, Accademic Press, New York **1966**, p.174.

[26] Caturla, F.; Martin-Martinez, J. M.; Molina-Sabio, M.;

Rodriguez-Reinoso, F.; Torregrosa, R. *J. Colloid Interface Sci.* **1988**, *124*, 528.

[27] Dabrowski, A.; Podkoscielny, P.; Hubicki, Z.; Barczak, M. *Chemosphere* **2005**, *85*, 1049.

[28] Sing, K. S. W.; Everett, D. A.; Haul, R. A. W.; Moscou, L.; Pirotti, R. A.; Rouguerol, J.; Siemieniwska, T. *Pure Appl. Chem.* **1985**, *57*, 603.

[29] Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

[30] Harkins, W. A.; Jura, G. *J. Am. Chem. Soc.* **1943**, *65*, 430.

[31] Youssef, A. M.; Radwan, N. R. E.; Abdel-Gawad, I.; Singer, G. A. A. *Colloids and Surfaces* **2005**, *252*, 143.

[32] Bansal, R. C.; Donett, J. B.; Stoeckli, H. F., "*Active Carbon*", Marcel-Dekker, New York, **1988**.

[33] Khalil, L. B.; Girgis, B. S.; Tawfik, T. A. M. *Adsorp. Sci. Technol.* **2000**, *18*, 373.

[34] Youssef, A. M.; Ghazy, T. M.; El-Nabarawy, Th. *Carbon* **1982**, *20*, 113.

[35] Grajek, H. *Adsorp. Sci. Technol.* **2001**, *19*, 303.

[36] Zawadzki, J. *Carbon* **1980**, *18*, 281.

[37] Gomez-Serrano, V.; Acedo-Ramos, M.; Lopez-Peinado, A. J.; Valenzula-Calaharro, C. *Fuel* **1994**, *73*, 387.

[38] Sanakar, M.; Sekaran, J.; Sadullo, S.; Ramasami, T. *J. Chem. Technol. Biotechnol.* **1999**, *74*, 337.

[39] Guo, J.; Lua, A. C. *J. Chem. Technol. Biotechnol.* **2000**, *75*, 971.

[40] George, W. O.; McIntyre, P. S., "*Infrared Spectroscopy*", John Wiley and Sons, Chichester **1987**, p. 347.

[41] William, D. H.; Fleming, I., "*Spectroscopic Methods in Organic Chemistry*", McGraw-Hill Book Company, UK **1973**.

[42] Van der Mass, J. H., "*Basic Infrared Spectroscopy*", Hyden & Sons Ltd, London **1969**.

[43] Fanning, P. E.; Vannice, M. A. *Carbon* **1993**, *31*, 721.

[44] Magne, P.; Walker, P. L. Jr. *Carbon* **1986**, *24*, 101.

[45] Vidic, R. D.; Suidan, M. T. *Environ. Sci. Technol.* **1991**, *25*, 1612.

[46] Mahajan, O. P.; Morino-Castilla, C.; Walker, P. L. Jr. *Sep. Sci. Technol.* **1980**, *15*, 1733.

[47] Morino-Castilla, C.; Rivera-Utrilla, J. *Carbon* **1995**, *33*, 845.

[48] Tessemer, C. H.; Vidic, R. D.; Uranowski, L. J. *Environ. Sci. Technol.* **1997**, *31*, 1872.

[49] Salame, I. I.; Bandosz, T. G. . *J. Colloid Interface Sci.* **2003**, *264*, 307.

[50] Salame, I. I.; Bandosz, T. G. *J. Phys. Chem. B* **1999**, *103*, 3877.

[51] Bahatia, S. K.; Kalam, A.; Joglekar, H. S.; Joshi, J. B. *Chem. Eng. Commun.* **1990**, *98*, 139.