



ADSORPTION ISOTHERMS OF PHENOL AND ANILINE ON ACTIVATED CARBON

Loredana Elena VÎJAN^a and Mihaela NEAGU^b

^aDepartment of Physical Chemistry, Faculty of Science, University of Pitești, No 1, Târgu din Vale, Pitești, 110040, Roumania

^bDepartment of Environmental and Chemical Engineering, Faculty of Petroleum Refining and Petrochemistry, Petroleum-Gas University of Ploiești, No 39, București Blvd., Ploiești, 100680, Roumania

Received December 9, 2010

In this paper we have intended to study the influence of -OH and -NH₂ groups linked to the benzene nucleus on the adsorption on the surface of an activated carbon, as manifested in the parameter values of the Freundlich and Langmuir adsorption isotherms equations. The adsorption capacity of the two aromatic compounds on granular activated carbon was measured in static regime, at the same amount of activated carbon (2 g) and concentrations of 25 mg/L to 2 000 mg/L for the phenol solution and from 25 mg/L to 900 mg/L for the aniline solution. Experimental runs were made under ambient temperature and low basic pH. The relative position of the adsorption isotherms, obtained under identical conditions, showed that phenol is adsorbed better than aniline on the granular activated carbon with specific surface area of 1 376 m²/g.

INTRODUCTION

The water is the most precious natural resource, and because of its importance, it has become a predominant source of concern. It has captured more and more attention; the world became preoccupied with the maintenance and water purification. The industry is also very important in today's society and its impact on water is becoming more significant. The petroleum refineries and the industries of plastics and paint are harmful sources for the effluents, which have the potential to devastate the receiving waters. Therefore, it is necessary to install facilities for the treatment of the wastewater in places where these industries are located.

The adsorption of organic compounds from aqueous solutions by activated carbon is one of the most common methods used to treat polluted water. The adsorption capacity of carbon to aromatic compounds in aqueous solution depends on many factors, such as the physical nature of the adsorbent (the pore structure, the ash content, the functional groups), the nature of the adsorbate (the

molar mass, the size of molecules, the number and type of the functional groups, the polarity, pK_a) and the chemistry of solution (pH, ionic strength, concentration of adsorbent).¹

The removal of the substituted phenolic compounds by adsorption on activated carbon is subject to numerous studies in the literature. In most adsorption studies, the phenol is chosen as reference aromatic compound (marker), with which the adsorption behaviour of mono or bisubstituted species is compared.

Nevskaia² studied the adsorption behaviour of phenol, aniline and phenol-aniline mixtures in water on two types of carbons: mesoporous high surface area graphite and microporous activated carbon. The adsorption isotherms for each of the two organic compounds were experimentally determined. It was concluded that the adsorption of phenol and aniline on macroporous carbon is better reflected by Freundlich mathematical model and the adsorption on microporous carbon by extended Langmuir model. The different behaviour of the two types of carbons underscores the importance

* Corresponding author: loredana.vijan@upit.ro

of pore size and oxygen containing functional groups on the behaviour of the adsorbent surface. The different chemical nature of the two compounds influences their adsorption, as evidenced by the fact that from a mixture of phenol and aniline, aniline is preferentially adsorbed on macroporous carbon and with oxygen groups. In contrast, phenol is better adsorbed on microporous carbon.

Salame and Bandosz³ studied the role of surface chemistry in adsorption of phenol on activated carbons. They demonstrated that the phenol uptake is dependent on both the porosity and the chemical nature of surface of the carbons. It was found that the presence of carboxylic groups on the carbon surface has two effects, namely: the appearance of ester bonds between phenol -OH groups and surface -COOH ones and the weakening of the interaction between benzene ring and carbon surface, leading to an overall decrease of the phenol uptake.

The pH effect in the phenol adsorption on activated carbon has been studied by Rengaraj *et al.*⁴ They found that the highest retention of phenol on the activated carbon occurs in the pH range 4-9. Above pH 9 the retention capacity of phenol decreases due to the presence of hydroxyl ions which prevents the adsorption of phenol molecules. In contrast, at pH lower than 4, the retention of phenol on the polar surface of adsorbent is explained by the presence of hydrogen ions, which prevents ionization of phenol.

The interactions of phenol and aniline with the surface of microporous activated carbon were studied by Laszlo⁵ in aqueous solutions in the pH range 3-11, in presence of molecular oxygen, proving that the adsorption is controlled by the pore diffusion mechanism and by the reactions involving oxygen captured by micropores. It seems that phenol and aniline are adsorbed most strongly in unbuffered conditions. The competitive adsorption between water and buffer ions was found. This thermal desorption study has argued that the physical adsorption of compounds occurs throughout the entire pH range and that the chemical adsorption require only conditions that favour electrostatic interactions. It was found that the thermal desorption only partially has removed the adsorbed compounds because changes in morphology and the chemical nature of the adsorbent surface were observed.

A comprehensive study of the comparative adsorption of phenol and aniline on activated carbon and clay is submitted in the PhD thesis of

Derakhshan (1999).⁶ For the adsorption on carbon activated with nitric acid favourable results were obtained. Due to its basic character, aniline is better adsorbed on the acidic surface of carbon. The adsorption isotherms were processed mathematically and they showed that the Langmuir model better reflected the adsorption of phenol and aniline than Freundlich model. The adsorption on the clays led to results difficult to interpret.

In this paper we intended to study of the influence of -OH and -NH₂ functional groups linked to the benzene nucleus to the adsorption phenomenon on the surface of a granular activated carbon. By the mathematical analysis of the adsorption isotherms of phenol and aniline on activated carbon, with Freundlich and Langmuir models, the experimental results were interpreted and the effect of the chemical nature of the adsorbent on the parameters of these two models was revealed.

RESULTS AND DISCUSSION

Characterization of the activated carbon

Granular activated carbon used in this study was commercially available, but its physico-chemical properties could not be obtained in detail. Therefore, the characterization of this granular activated carbon was necessary to correlate the structure of the adsorbent with the adsorption behaviour of two organic pollutants, phenol and aniline. So, the adsorbent used in this adsorption study to remove both organic pollutants in wastewater was characterized in terms of the most important physical properties, *i.e.* BET surface area = 1 376 m²/g, micropores area = 594 m²/g, average pore diameter = 2.96 nm and micropores volume = 0.27 cm³/g. In agreement to the classification International Union of Pure Applied Chemistry (IUPAC) of the pores in macropores (d>50 nm), mesopores (2<d<50 nm) and micropores (d<2 nm), based on diameter into the network, the activated carbon used in this study corresponds to the mesoporous carbon.

Fig. 1 shows the X-ray diffraction pattern of the granular activated carbon, obtained with a DRON UM1 diffractometer in Bragg-Brentano montage, in the following conditions: voltage = 36 kV, intensity = 30 mA, angular range 2θ = 20-80°, step = 0.05 and time of acquisition for a step = 1 second. The analysis of qualitative phase,

performed with PHAN program, showed the coexistence of the amorphous phase with the polycrystalline hexagonal phase of carbon. The reflections corresponding to the family of planes (002) at 20–27°, reflecting the Bragg theoretical

relative intensity of 100% and a broad peak at ~44° corresponding to the family of crystalline planes (101) were observed. Also, the value for the width at half maximum of the diffraction line 002, FWHM = 0.233, was determined.

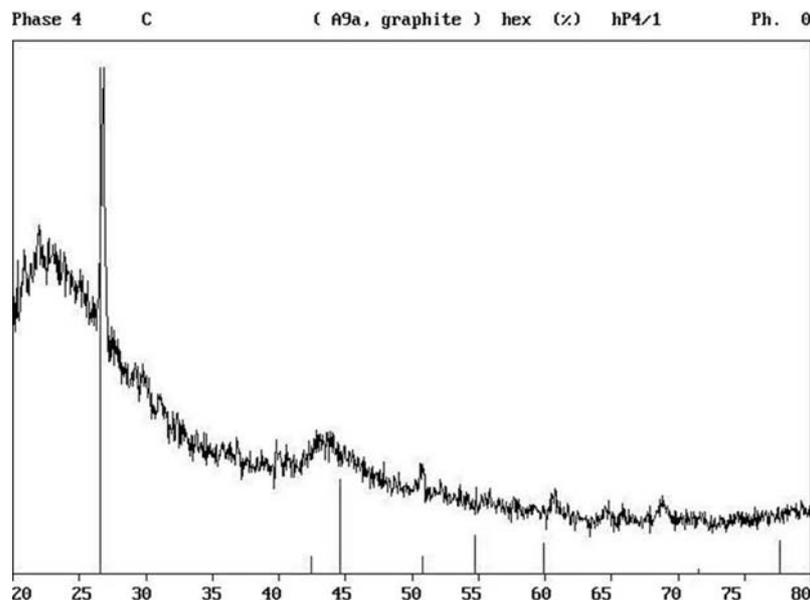


Fig. 1 – X-ray diffraction spectrum of the granular activated carbon.

FTIR spectrum of this granular activated carbon demonstrates the complexity of surface chemistry, evidencing the presence of a series of functional groups, namely: -OH groups of alcohols, phenols and carboxylic acids and C=O groups of quinones, enols or conjugated ketones. Furthermore, the olefinic C=C and C=O groups were found. Although the basic functional groups obviously predominate, the surface of granular activated carbon contains also acidic functional groups. Overall, FTIR spectrum demonstrates the presence on the adsorbent surface of the alcoholic and phenolic groups, quinones and enols.

Adsorption results

To obtain the calibration curves (Fig. 2) for two organic pollutants, phenol and aniline, the solutions of concentration 100 mg/L from of each reagent were prepared. The stock solutions were diluted with the distilled water and these dilutions were analyzed with a Lambda 25 PerkinElmer spectrophotometer.

To test the activated carbon as adsorbent for the removal of the aromatic compounds from their aqueous solutions and to show the influence of the groups attached to the aromatic nucleus on the

adsorption process, we have carried out a series of the adsorption experiments in the static regime. We prepared the solutions with different initial concentrations (the initial concentration of solution is denoted C_i): from 25 mg/L to 2 000 mg/L for phenol, respectively at 25 mg/L to 900 mg/L for aniline. We introduced a volume of 100 mL of each solution (the initial volume of solution is denoted V_i) in a series of Berzelius glasses over a quantity of 2 g granular activated carbon.

The suspensions of carbon and the aqueous solutions of pollutant were subjected to magnetic stirring at constant temperature (25°C) and at constant rotational speed (200 rpm). The preliminary experiments showed that the adsorption equilibrium is reached after 2 hours. After stirring, the suspensions were filtered, the volume of filtrate (the final volume of solution is denoted V_f) was measured and the pH of these solutions was determined with a C-561 multimeter. The filtered samples were spectrometrically analyzed to determine the residual concentration of phenol or aniline in aqueous solution (the final concentration is denoted C_f). The adsorption results of phenol and aniline on the granular activated carbon are presented in Table 1.

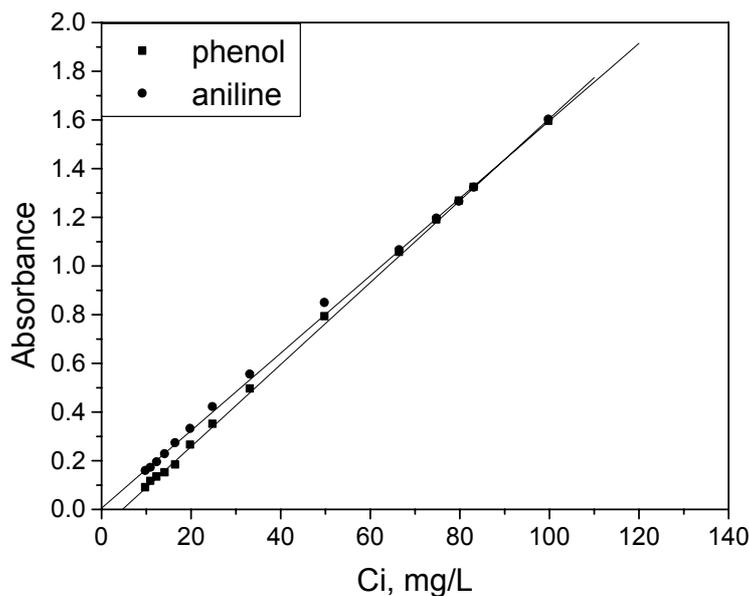


Fig. 2 – The calibration curves for phenol and aniline.

Table 1

The adsorption data for phenol and aniline

C_i , mg/L	phenol				aniline			
	V_f , L	pH after filtration	A	C_f , mg/L	V_f , L	pH after filtration	A	C_f , mg/L
2000	0.097	7.56	2.2929	140.78				
1600	0.097	7.58	1.3171	82.87				
1200	0.097	7.63	0.8044	52.45				
1000	0.097	7.66	0.5665	38.33				
900	0.097	7.72	0.5098	34.96	0.097	7.75	1.22121	76.42
800	0.097	7.78	0.3269	24.10	0.097	7.74	0.76023	47.44
700	0.097	7.81	0.2999	22.50	0.097	7.73	0.60521	37.70
600	0.097	7.92	0.2562	19.91	0.097	7.72	0.40528	25.13
500	0.097	8.02	0.1879	15.86	0.097	7.71	0.33233	20.55
400	0.097	8.06	0.1246	12.1	0.097	7.69	0.25425	15.64
300	0.097	8.16	0.0718	8.96	0.097	7.67	0.16236	9.86
200	0.097	8.22	0.0089	5.23	0.097	7.67	0.10534	6.28
150	0.097	8.28	0.0046	4.98	0.097	7.66	0.07826	4.58
100	0.097	8.29	0.0024	4.85	0.097	7.66	0.07235	4.21
50	0.097	8.37	0.0007	4.74	0.097	7.64	0.03146	1.64
25	0.097	8.41	0.0001	4.71	0.097	7.62	0.02289	1.1

During the process of adsorption, a dynamic equilibrium for the distribution of the solute (the adsorbed substance) between the fluid phase and the solid surface is established. In the case of adsorption in the liquid phase, this equilibrium can be expressed by the adsorption isotherm, which describes the relationship between the content of compound retained by the adsorbent and the adsorbent concentration from the liquid phase at equilibrium. The amount of compound retained in the adsorbent pores is closely related to the physical and chemical properties of the adsorbent but also depends on the mechanism of adsorption process, namely the physical or chemical adsorption.⁷⁻⁸

The systematization of the large number of experimental data led to a total of six main types of the adsorption isotherms.⁹ The Langmuir isotherm stand out, being characteristic of adsorption on nonporous or microporous adsorbents. These isotherms have the following features: they are obtained both at the critical temperature of the sorbent and above this temperature, they are describing both chemical and physical adsorption, the saturation value of the adsorbed amount corresponds with the formation a monolayer.⁹ Other type of isotherm frequently encountered in the adsorption process of the organic pollutants on granular activated carbon is the Freundlich

isotherm. The Langmuir model assumes that the sorbent surface is completely uniform while the Freundlich model considers that this surface is nonuniform.

The mathematical form⁹⁻¹⁰ of the Langmuir model is shown in equation (1):

$$q_e = \frac{k_L C_f}{1 + b C_f} \quad (1)$$

where q_e is the adsorption capacity (the mass of adsorbed pollutant per unit mass of carbon), C_f the final concentration of the solution (at equilibrium), k_L the characteristic coefficient of adsorbate-adsorbent pair, b the adsorption parameter. The adsorption parameter "b" represents the net enthalpy of adsorption and it is described by the ratio of rate constants of the adsorption and desorption processes.¹¹⁻¹²

The Langmuir equation can be rearranged as:

$$\frac{1}{q_e} = \frac{b}{k_L} + \frac{1}{k_L C_f} \quad (2)$$

and, by a linear plot $\frac{1}{q_e} = f\left(\frac{1}{C_f}\right)$, the values of two constant, k_L and b , can be obtained.

The essential characteristics of Langmuir isotherm can be expressed by an equilibrium parameter, which is a dimensionless constant defined as:

$$R_L = \frac{1}{1 + k_L \cdot C_i} \quad (3)$$

that indicates the nature of adsorption, such: the unfavorable adsorption $R_L > 1$, the linear adsorption $R_L = 1$, the favorable adsorption $0 < R_L < 1$ and the irreversible adsorption $R_L = 0$.¹³

The Freundlich isotherm is based on the mathematical expression of the equation:

$$q_e = k_F \cdot C_f^n \quad (4)$$

where q_e is the adsorption capacity, C_f the equilibrium concentration of the solution (after adsorption), k_F the characteristic coefficient of adsorbate-adsorbent pair, a measure of the adsorption capacity of the adsorbent, given by the influence of the different energies associated with

the heat of adsorption, n is an exponent. The constant „n” represents a measure for surface sites energetic nonuniformity and the parameter $\frac{1}{n}$ quantifies the intensity of adsorption, in some studies being called “the intensity parameter”.^{11-12,14}

Taking the logarithm of Freundlich equation, the following equation is obtained:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_f \quad (5)$$

which allows for the determination of two constants, k_F and n , on the basis of linear plot $\ln q_e = f(\ln C_f)$. The regression line has the slope

equal to $\frac{1}{n}$ and the intercept equal to $\ln k_F$. The

values of n ranges from 2-10 indicating good adsorption capacity, 1-2 indicating moderate adsorption capacity and less than one indicates poor adsorption capacity.¹⁵⁻¹⁶

On the basis of the experimental data obtained with the activated carbon for phenol and aniline, the quantities of the adsorbed pollutant were calculated. Thus, we have calculated the adsorption capacity, q_e (mg/g) with the relation below:

$$q_e = \frac{(C_i - C_f) \cdot V}{m} \quad (6)$$

where: C_i , C_f are the initial concentration of solute and final concentration of solute, respectively; V is the volume of solution and m is the mass of adsorbent used in the experiment. In Table 2 the calculated values of the adsorption capacities for 2 g of carbon and the final concentrations (at equilibrium) of the pollutants in their aqueous solutions are presented.

For determining the values of parameters from Freundlich and Langmuir models, the adsorption experimental data for two compounds, on 2 g activated carbon and different concentrations of polluting agent were processed with the equations (2) and (5). Thus, the linear plots, $\ln q_e = f(\ln C_f)$ and $\frac{1}{q_e} = f\left(\frac{1}{C_f}\right)$, for two systems are given in Figs. 3 and 4.

Table 2

The adsorption capacities for phenol and aniline

phenol		aniline	
C_f , mg/L	q_e , mg/g	C_f , mg/L	q_e , mg/g
140.78	93.17	76.42	41.29
82.87	75.98	47.44	37.70
52.45	57.45	37.70	33.17
38.33	48.14	25.13	28.78
34.96	43.3	20.55	24
29.42	38.57	15.64	19.24
22.50	33.91	9.86	14.52
19.91	29.03	6.28	9.695
15.86	24.23	4.58	7.28
12.1	19.41	4.21	4.79
8.96	14.57	1.64	2.42
5.23	9.75	1.1	1.195
4.98	7.26		
4.85	4.76		
4.74	2.27		
4.71	1.02		

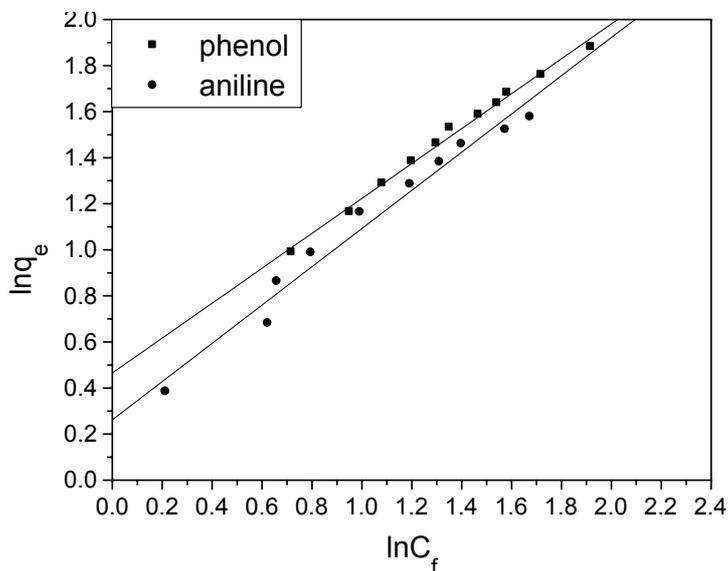


Fig. 3 – Freundlich isotherms obtained using linear regression methods.

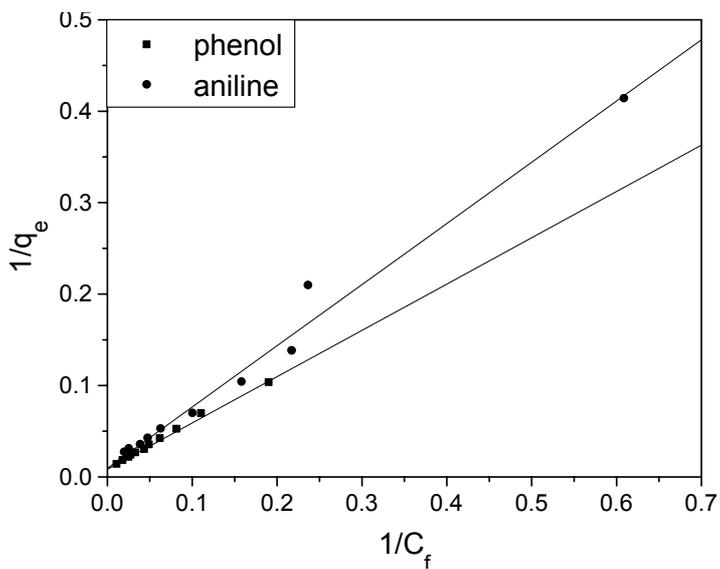


Fig. 4 – Langmuir isotherms obtained using linear regression methods.

In Table 3, the results of linear regression of Freundlich and Langmuir equations are presented: the equation parameters and the quality parameters of the linear regression.

The analysis of the linear regression for the equilibrium data of phenol and aniline shows that the adsorption isotherms are the Langmuir type because in this case were obtained best values for the regression coefficient, R and the average standard deviation, SD compared with the Freundlich representations. This result confirms that indeed the adsorption of phenol and aniline takes place on a uniform carbon surface.

Analyzing the parameter values k_F for the two pairs adsorbate-adsorbent, a higher value of this parameter was obtained for phenol, which shows a higher adsorption capacity of the activated carbon than for aniline. In respect of the intensity parameter, n, it has similar values for the two compounds, these values giving an indication of favourability of adsorption.^{15,16}

Analyzing the parameter values k_L for the two pairs adsorbate-adsorbent, a higher value of this parameter was obtained for phenol compared with

aniline while the parameter b has similar values for the two compounds. The calculated values of R_L parameter for phenol and aniline are in the range 0-1 and this result indicates a favourable adsorption of these pollutants onto the surface of activated carbon tested.

In addition, the determination of adsorption parameters was done by nonlinear regression.

The curve fitting was performed using TableCurve 2D v5.01 software, imposing a 90% confidence level. This method is more rigorous than linear regression because it uses the original form of the isotherm equation. The adsorption parameters, the correlation coefficient (R^2) and the standard error of estimate (SE) obtained from fitting the Langmuir and Freundlich models onto the equilibrium data (Fig. 5) are reported in Table 4.

As it can be seen, according to the regression criteria, the Langmuir isotherm is the most suitable model characterizing the adsorption of phenol and aniline on activated carbon surface. It indicates the monolayer arrangement of pollutant (phenol, aniline) onto the surface of adsorbent (activated carbon).

Table 3

The result of the linear regression for the equilibrium data

	Freundlich				Langmuir			
	$k_F, \frac{\text{mg}}{\text{g}} \left(\frac{\text{L}}{\text{mg}}\right)^{\frac{1}{n}}$	n	SD	R	$k_L, \text{L/g}$	b, L/mg	SD	R
phenol	2.92±0.18	1.32±0.04	0.0231	0.9966	1.97±0.04	0.016±0.0003	0.0017	0.9981
aniline	1.83±0.23	1.21±0.07	0.0677	0.9868	1.50±0.06	0.015±0.0003	0.0159	0.9918

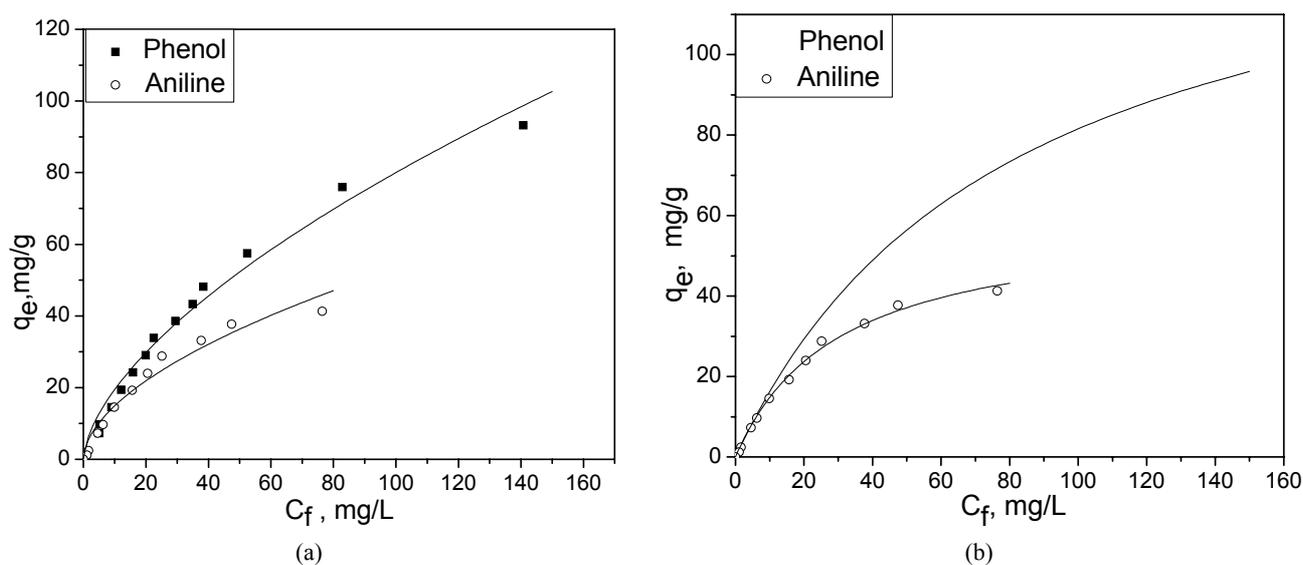


Fig. 5 – Freundlich (a) and Langmuir (b) isotherms obtained using nonlinear regression methods.

Table 4

The result of the nonlinear regression for the equilibrium data

	Freundlich				Langmuir			
	$k_F, \frac{\text{mg}}{\text{g}} \left(\frac{\text{L}}{\text{mg}}\right)^{\frac{1}{n}}$	n	R ²	SE	$k_L, \text{L/g}$	b, L/mg	R ²	SE
phenol	4.74±0.54	1.63±0.07	0.9841	3.52	1.83±0.03	0.012±0.0004	0.9991	0.84
aniline	4.18±0.74	1.81±0.16	0.9663	2.82	1.97±0.09	0.033±0.0026	0.9962	0.94

EXPERIMENTAL

Granular activated carbon was obtained from Ecopur System SRL, Roumania. Phenol and aniline were obtained from Merck Roumania SRL. Phenol was used without further purification while aniline was purified by distillation. The stock solutions of 2 000 mg/L and 1 000 mg/L phenol and 1 000 mg/L aniline were prepared in doubly distilled water. The working solutions were prepared by diluting the stock solutions with doubly distilled water just before use.

In order to investigate the chemical and physical properties of the granular activated carbon, a Micromeritics ASAP 2010, a DRON-UM1 diffractometer modernized, a Hitachi S-4500 Field Emission Scanning Electron Microscope and Nicolet Magna 750 FTIR spectrophotometer were used. The pH measurements were made with a C-561 multimeter, equipped with a SP10B epoxy pH electrode, a SK10B conductivity cell and a ST10N temperature sensor. Absorbance was measured on a Lambda 25 UV-Vis spectrophotometer from Perkin-Elmer, USA.

The structures of the organic compounds, benzene, phenol and aniline, were built within the HyperChem Release 7.5 program and optimized by the semiempirical AM1 method (parameters: SCF control of 0.01, RHF spin pairing, Polak - Ribiere optimizer, RMS gradient 0.01 kcal/mol.Å).

CONCLUSIONS

Were determined the adsorption capacity of the two aromatic compounds on granular activated carbon, in static regime, at same amount of activated carbon (2 g) and concentrations from 25 mg/L to 2000 mg/L of the phenol solutions and from 25 mg/L to 900 mg/L for the aniline solutions. Experimental determinations were made under conditions of ambient temperature and low basic pH. The retained concentrations of phenol and aniline were determined by spectrophotometric analysis with a Lambda25 PerkinElmer UV-VIS spectrophotometer. The relative position of the adsorption isotherms for two organic polluting agents showed that phenol is adsorbed better than aniline, on granular activated carbon with specific surface area of 1376 m²/g.

The adsorption data in static regime (the static adsorption capacities, the final concentrations of solutions after adsorption) were processed using the equations of Freundlich and Langmuir

adsorption isotherms, resulting in characteristic parameters of adsorption phenol/ aniline on activated carbon and the parameters for assessing the quality of the regression. The analysis of the regression results of the equilibrium adsorption data of the two aromatic compounds shows that the adsorption isotherms are of Langmuir type. Although linear regression was frequently used to determine the most fitted isotherm, nonlinear method offered a better way to predict the equilibrium isotherm parameters.

By comparing the values of k_F parameter for the two adsorbate-adsorbent pairs, it is observed that in the case of phenol, the higher value of this parameter indicates a higher adsorption capacity of activated carbon than for aniline. Analyzing the values of k_L parameter for the two adsorbate-adsorbent pairs, it is observed that phenol has a higher value of this parameter than aniline, while the b parameter has close values for the two compounds. So, phenol was adsorbed more strongly than aniline. This result is in agreement with the structure of the organic compounds and the chemistry of the adsorbent surface. Because both -OH and -NH₂ groups are the activating groups, the electron density increases in aromatic nucleus and decreases in groups attached on the aromatic nucleus, leading to a partial negative charge at the aromatic nucleus. In addition, aniline is basic in nature, being attracted to acidic surfaces while phenol is acidic in nature, being attracted to basic surfaces. These observations are reinforced by the results of computational study with AM1 method, which led to the minimum and maximum values of the electrostatic potential, namely: $V_{\min}=-17.01$ kcal/mol and $V_{\max}=39.42$ kcal/mol for aniline, respectively $V_{\min}=-36.67$ kcal/mol and $V_{\max}=160.83$ kcal/mol for phenol.

In conclusion, the adsorption of phenol and aniline on granular activated carbon with the basic groups on the surface, imply the electron donor-acceptor complexes and also the dispersion forces between π -electrons in the organic compounds and π -electrons in granular activated carbon. The basic groups on the surface of carbon act as the electron

donors and the aromatic rings of the phenol and aniline as the electron acceptor. Moreover, it can be concluded that the dispersion forces related to the π - π interactions control the adsorption of phenol and aniline on granular activated carbon.

Acknowledgements: Authors thank PhD Carmen Topală and PhD student Sorin Moga for the FTIR spectrum and X-ray diffraction spectrum of the adsorbent used in this adsorption study.

REFERENCES

1. F. Haghseresht, S. Nouri, J.J. Finnerty and G.Q. Lu, *J. Phys. Chem. B*, **2002**, *106*, 10935-10943.
2. D. M. Nevskaja, E. Castillejos-Lopez, A. Guerrero-Ruiz and V. Munoz, *Carbon*, **2004**, *42*, 653-665.
3. I.I. Salame and T.J. Bandosz, *J. Colloid Interface Sci.*, **2003**, *264*, 307-312.
4. S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabind and V. Murugesan, *J. Hazard. Mater.*, **2002**, *89*, 185-196.
5. K. Laszlo, E. Tombacz and C. Novak, *Colloid. Surface. A - Physicochem. Eng. Aspects*, **2007**, *306*, 95-101.
6. N. Derakhshan, PhD thesis, "Comparison of Activated Carbons and Clays for the Removal of Organic Contaminants from Water", The University of Queensland, Australia, **1999**, <http://www.cheque.uq.edu.au/ugrad/theses/1999/pdf/navaderakhshan.pdf>
7. C. Moreno-Castilla, *Carbon*, **2004**, *42*, 83-94.
8. R.T. Yang, "Adsorbents: fundamentals and applications". New Jersey, John Wiley & Sons, Inc., Hoboken, 2003.
9. L.E. Vîjan and V. Stanciu, "Cataliză și materiale cu proprietăți catalitice", Editura Universității din Pitești, Pitești, 2008, p. 103-119.
10. T. Wigmans, *Carbon*, **1989**, *27*, 13-22.
11. J.Jr. Weber Walter and F.A. DiGiano, "Process Dynamics in Environmental Systems", New York: Environmental Science and Technology: A Wiley Interscience Series of Texts and Monographs, 1996.
12. C.T. Chiou, "Partition and Adsorption of Organic Contaminants in Environmental Systems", Hoboken, New Jersey: Wiley-Interscience, 2002.
13. Y. Bulut and H. Aydın, *Desalination*, **2006**, *194*, 259-267.
14. Q. Lu and O. Wai, *Int. J. Numer. Meth. Fluids*, **1998**, *26*, 771-789.
15. E.N. El Qada, S.J. Allen and G.M. Walker, *Chem. Eng. J.*, **2008**, *135*, 174-184.
16. B. Subramanyam and A. Das, *Int. J. Environ. Sci. Tech.*, **2009**, *6*, 633-640.

