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# Removal of Selected Organic Compounds in Aqueous Solutions by Activated Carbon

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**Abstract:** The adsorption behaviour of Safranin-O (a cationic dye), phenol and nitrophenols i.e., m-nitrophenol, p-nitrophenol and o-nitrophenol was studied from aqueous solution on activated carbon under various experimental conditions. It was found that the Langmuir isotherm appears to fit the isotherm data better than the Freundlich isotherm. Dubinin-Raduskevitch (DR) isotherm was successfully used to model experimental data and modeling results showed that the uptake Safranin-O and phenols proceeded by physical adsorption. The adsorption capacity of activated carbon obtained from both Langmuir and D-R models for phenol and nitrophenols were found to be higher than for Safranin-O and following the order as: m-nitrophenol > p-nitrophenol > p-nitrophenol > phenol > Safranin-O. The kinetics of adsorption in view of three kinetic models, i.e., the first-order Lagergren model, the pseudo-second-order model and the intraparticle diffusion model was discussed. The pseudo-second-order kinetic model describes the adsorption both Safranin-O and phenols very well. The effect of temperature was also studied at the range between 293 and 323 K. Thermodynamic studies indicated that the adsorption both of Safranin-O and phenols onto activated carbon was an exothermic process. The negative values of free energy determined for these systems indicated that adsorption was spontaneous at the temperatures under investigation.

Key words: Activated carbon, phenol, nitrophenols, Safranin-O, adsorption

#### INTRODUCTION

Colored compounds are the most easily recognizable pollutants in the environment. Most industries use dyes and pigments to color their color products. Discharge of dye-bearing wastewater into natural streams and rivers from textile, paper, carpet and printing industries have a severe problem since dyes impart toxicity to aquatic life and are damaging the aesthetic nature of the environment. Generally, this discharge is directed to the nearest water sources such as rivers, lakes and seas. Textile dyeing process is an important source of contamination responsible for the continuous pollution of the environment. The volume of wastewater containing processed textile dyes is on steady increase. Over 7.0×10<sup>5</sup> tones and approximately 10000 different types of dyes and pigments are produced world wide annually (Pearce *et al.*, 2003; McMullan *et al.*, 2001). Many of the dyes used in industry are stable to light and oxidation, as well as resistant to aerobic digestion. The colored wastewater damages the aesthetic nature of water and reduces the light penetration through the water's surface and photosynthetic activity of aquatic organisms due to the presence of metals, chlorides, etc., in them (O'Neill *et al.*, 1999; Robinson *et al.*, 2001). Basic dyes known as the brightest class of soluble dyes are used by the textile industries such as acrylic, nylon, silk and wool dyeing. Their tinctorial value is

very high; less than 1 ppm of the dye produces obvious coloration. Basic dyes can also cause allergic dermatitis, skin irritation, cancer and mutations. Although biological treatment processes effectively remove BOD, COD and suspended solids they are largely ineffective in removing color from wastewater. Therefore it is necessary to remove the dye pollutions (Banat *et al.*, 1996; Robinson *et al.*, 2001).

Phenolic compounds are also considered to be the major and undesirable pollutions in wastewaters apart from basic dyes. Phenol derivatives are formed in the course of many industrial processes worldwide, for instance in the paper, petroleum and pesticide industries and are present in many manufactured goods, such as plastics, drugs, antioxidants and dyes. Hence, they frequently occur in the environment as a result of contamination from a variety of sources. Nitrophenols belong to major phenolic pollutants that have been analyzed in the environment. Nitrophenols, coming from pesticide degradation products, car exhaust and industrial waters are listed as priority pollutions by the US Environmental Protection Agency (Guo et al., 2004). They have great potential toxicities of carcinogenesis, teratogenesis and mutagenesis. Because of their detriment and vast scale distribution in the ecological environment, their separation and determination have been become one of the important studies of environmental analysis. Phenol is considered to have toxic effects on human health even when present in small concentrations. The ingestion of such contaminated water in the human body causes protein degeneration and tissue erosion of the central nervous system and also damages the kidney, liver and pancreas. Therefore removal, destruction or modification to less noxious structures of phenolic compounds is essential for purification of wastewaters as well as raw water (Caturla et al., 1988; Derylo-Marczewska and Marczewski, 2000).

The various treatment methods for the removal of color and dye are coagulation using alum, lime, ferric sulfate, ferric chloride, chemical oxidation using chlorine and ozone, membrane separation processes, adsorption and so on. The removal of dyes from effluent in an economic fashion remains a major problem although a number of successful systems have been designed recently. Among the treatments options, adsorption has become one of the most effective and comparable low cost method for the decolourization of textile wastewater. Many types of adsorbents including natural materials, biosorbents and waste materials from industry and agriculture have been proposed by several workers. Some of the reported sorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alumite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell) industrial waste products, biosorbents (chitosan, peat) fly ash and others (starch, cyclodextrin) (Allen *et al.*, 1994; Annadurai and Krishnan, 1997; Annadurai *et al.*, 1999; Bagane and Guiza, 2000; Banks and Parinson, 1992; Chiou *et al.*, 2004; Chou *et al.*, 2001; Crini and Morcellet, 2002).

Removal of organic molecules including dyes and phenolic compounds from solutions is widely achieved by adsorption onto activated carbon in powder or granular form. Activated carbon which is currently the most widely used adsorbent for wastewater treatment is a structurally homogenous material of high surface area, has microporous structure and show radiation stability and as a consequence, showing a high efficiency for the adsorption of bigger size compounds such as dyes (Lin, 1993). It is therefore widely used in various industrial processes as adsorbent, catalyst or catalyst support. The adsorption capacity of activated carbon depends on various factors such as surface area, pore size distribution and surface functional groups of adsorbent; polarity, solubility and molecule size of adsorbate; solution pH and the presence of other ions in solution etc. (Crini, 2006; Shawabkeh and Abu-Nameh, 2007).

This study reports the results of the adsorption of Safranin-O, phenol and three nitrophenols i.e., *m*-nitrophenol, *p*-nitrophenol and *o*-nitrophenol from aqueous solutions on activated carbon. Chemical structures and characteristics of Safranin-O, phenol, *m*-nitrophenol, *p*-nitrophenol and *o*-nitrophenol are shown in Scheme 1, respectively (Vidic *et al.*, 1997). The main goal of this study is to compare of adsorption of Safranin-O, phenol and nitrophenols i.e., *m*-nitrophenol, *p*-nitrophenol

Organic compound	Molecular structure	pK, at 25°C	ophenol, m-nitrophenol, p-nitrophenol Aqueous solubility at 25°C (g $L^{-1}$ )
Safranin-O	H,C CH, H,N NH,	11	50
Phenol	ОН	9.89	93
o-nitrophenol	OH NO <sub>2</sub>	7.17	2.0
m-nitrophenol	OH	8.28	1.35
<i>p</i> -nitrophenol	NO <sub>2</sub>	7.15	1.69
	NO <sub>2</sub>		

and *o*-nitrophenol on activated carbon in terms of their molecular differences such as size, shape, polarity and solubility in water. The adsorption behaviour of Safranin-O and phenols were performed as a function of initial dye and phenol concentrations on activated carbon under kinetic and equilibrium conditions. The effect of temperature were also discussed the efficiency in Safranin-O and phenolic compounds removal from aqueous solutions.

## MATERIALS AND METHODS

Reagent grade phenol, *m*-nitrophenol, *p*-nitrophenol and o-nitrophenol (all from Merck) were of the highest purity available and used without further purification. Safranin-O was obtained from Fluka and its purity is higher than 99% were provided by Sigma Activated carbon was purchased from VWR PROLABO BDH. Chemical and physical characteristics of activated carbon were done by Turkish Scientific and Technical Research Center. The specific surface area, cross sectional area, bulk density and the porosity of the adsorbent were 1014.44 m² g $^{-1}$ , 16.2 Ų, 0.63 g cm $^{-3}$  and 0.4, respectively with the elemental analysis of the adsorbent quoted at C: 86.5%, H: 1.09% and N < 1% (w/w).

The effects of important parameters such as initial concentrations of Safranin-O and phenols and temperature on the adsorptive removal of Safranin-O and phenols were studied by batch experiments. In each kinetic experiment, a known quantity of adsorbent contacted with an adsorbate solution in a

250 mL flask at desired temperature was shaken in a thermostat rotary shaker at constant agitation speed (250 rpm) for a given time intervals. At various time intervals the flasks were successfully removed, the liquid was separated from the solid by centrifugation and the remaining concentration of dye and phenols in solution were measured spectrophotometrically on a UV-1700 Shimadzu at a wavelengths of 520 nm for SO and 270, 317, 274, 279 nm for phenol, *p*-nitrophenol, *m*-nitrophenol and *o*-nitrophenol, respectively. Equilibrium adsorption isotherms for Safranin-O and phenols were undertaken at 25±1°C. The adsorption behaviors of the Safranin-O and phenols on the activated carbon were studied at four temperatures (298, 303, 313 and 323 K). The adsorption equilibrium isotherm experiments were repeated in duplicate and the average values are reported.

The concentration retained in the adsorbent phase (q<sub>e</sub>, mg g<sup>-1</sup>) was calculated by using the following equation;

$$q_{s} = \frac{\left(C_{0} - C_{t}\right)V}{W_{s}} \tag{1}$$

where,  $C_0$  is the initial dye concentration and  $C_t$  is concentration of the dye and phenols (mg  $L^{-1}$ ) at any time (t). V is the volume of solution (L) and  $W_s$  is the mass of activated carbon (g).

#### RESULTS AND DISCUSSION

It is seen that in all the concentrations studied of Safranin-O and Phenol while the concentration of Safranin-O decreased with time up to 150 min the concentration of Phenol decreased with time up to 100 min and then the curves become flattened (Fig. 1a, b). It is also seen that the equilibrium time is independent of solution concentration. The same behaviours were also seen for p-nitrophenol, m-nitrophenol and o-nitrophenol. Based on these findings, the shaking time was used in all further experiments. The amount adsorbed,  $q_e$  (mg  $g^{-1}$ ) is plotted against the equilibrium concentration,  $C_s$  (mg  $L^{-1}$ ) to obtain the adsorption isotherms. Adsorption isotherm data of Safranin-O and phenols are shown in Fig. 2a and b. The shape of the isotherms indicates L behavior according to Giles and

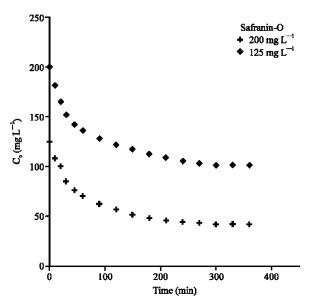


Fig. 1a: Variations in the initial concentrations of Safranin-O with time

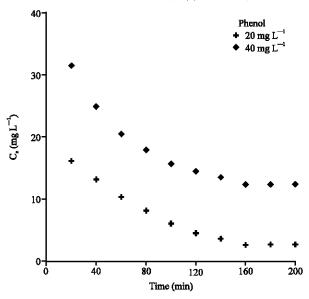


Fig. 1b: Variations in the initial concentrations of phenol with time

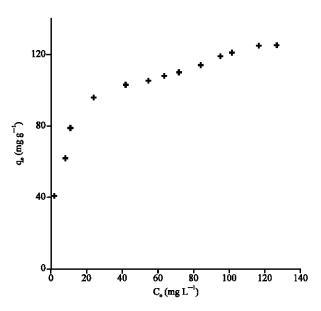


Fig. 2a: The adsorption isotherms of Safranin-O onto activated carbon at 298 K

Smith classification (Giles et al., 1974). Type L suggests that the aromatic rings adsorbs parallel to the surface and no strong competition exists between the adsorbate and the solvent to occupy the adsorption sites.

The correlation of the experimental adsorption data with a number of adsorption models was undertaken to gain an understanding of the adsorption behavior and the heterogeneity of the adsorbent surface. The linearized forms of Langmuir (1918), Freundlich (1906) and Temkin (1941) isotherm equations can be represented Eq. 2-4 as follows:

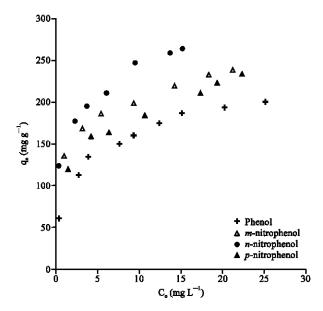


Fig. 2b: The adsorption isotherms of Phenol and Nitrophenols onto activated carbon at 298 K

$$\frac{C_{e}}{q_{e}} = \frac{C_{e}}{q_{max}} + \frac{1}{bq_{max}}$$
 (2)

$$\ln q_{_{e}} = \ln K_{_{F}} + \left(\frac{1}{n}\right) \ln C_{_{e}} \tag{3}$$

$$\mathbf{q}_{e} = \mathbf{k}_{1} \ln \mathbf{k}_{2} + \mathbf{k}_{1} \ln \mathbf{C}_{e} \tag{4}$$

where,  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mg  $g^{-1}$ ;  $C_e$  the final concentration at equilibrium in mg  $L^{-1}$ ;  $q_{max}$  the maximum adsorption at monolayer coverage in mg  $g^{-1}$ ; b the adsorption equilibrium constant related to the energy of adsorption in L mg $^{-1}$ ;  $K_F$  a Freundlich constant representing the adsorption capacity in (mg  $g^{-1}$ ) (L mg $^{-1}$ )  $^{1/n}$ ; n a constant depicting the adsorption intensity;  $k_1$  the Temkin isotherm energy constant in L mg $^{-1}$  and  $k_2$  the Temkin isotherm constant. The main difference between these three isotherm models is in the variation of heat of adsorption with the surface coverage. Langmuir model assumes uniformity, Freundlich model assumes logarithmic decrease and Temkin model assumes linear decrease in heat of adsorption its surface coverage.

The experimental isotherm data were fitted to these equations by applying linear regression analysis. One way to assess the goodness of fit of experimental isotherm data to these equations is to check the regression coefficients obtained during the regression analysis. As shown in Table 1, adsorption data for all compounds obeyed mostly Langmuir isotherm. The efficiency of adsorption process can be predicted by the dimensionless equilibrium parameter  $R_{\rm L}$ , which is defined by the following equation:

$$R_{L} = \frac{1}{1 + bC_{0}} \tag{5}$$

Table 1: Parameters of Langmuir, Freundlich and Tempkin adsorption isotherm equations at 298 K

	Langmuir	Freundlich parameters			Tempkin parameters					
	$\mathbf{q}_{ ext{max}}$	b						k <sub>1</sub>		
Parameters	$(mg g^{-1})$	$(L mg^{-1})$	$R_L$	$\mathbb{R}^2$	$K_{F}$	1/n	$\mathbb{R}^2$	$(L mg^{-1})$	$k_2$	$\mathbb{R}^2$
Safranin-O	131.58	0.1045	0.0714	0.9936	37.69	0.2567	0.9642	20.45	3.525	0.9830
Phenol	204.08	0.4900	0.0752	0.9922	83.11	0.2802	0.9705	32.71	14.17	0.9678
p-nitrophenol	250.00	0.3738	0.0963	0.9937	110.19	0.2297	0.9712	39.08	13.09	0.9462
o-nitrophenol	256.41	0.5820	0.0750	0.9917	135.94	0.1826	0.9835	33.64	50.40	0.9635
m-nitrophenol	294.11	0.6938	0.0866	0.9953	151.98	0.2101	0.9794	39.79	49.70	0.9341

where, b is the Langmuir constant (L mg $^{-1}$ ),  $C_0$  the initial concentration of SO and phenols in mg L $^{-1}$ . Isotherm is considered to be unfavourable when  $R_L > 1$ , linear when  $R_L = 1$ , favorable when  $0 < R_L < 1$  or irreversible when  $R_L = 0$ . The  $R_L$  values calculated for the adsorption of SO and phenols studied are given in Table 1 for the highest initial concentrations. Since all the  $R_L$  values are between 0 and 1, the adsorption processes in all cases are favourable.

It is known that the Langmuir and Freundlich isotherm constants do not give any idea about the adsorption mechanism. In order to understand the adsorption type, equilibrium data was tested with D-R isotherm. D-R equation can be written as:

$$\ln q = \ln q_{max} - K' \epsilon^2 \tag{6}$$

where,  $\varepsilon$ , RT 1n (1+1/ $C_e$ ), K' is the constant related to the adsorption energy, R the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the temperature in Kelvin. The quantities of q,  $q_{max}$  and  $C_e$  have the same meaning as above. Straight lines are obtained upon plotting lnq versus  $\varepsilon^2$  indicating that adsorption of both Safranin-O and phenols on activated carbon also obey the D-R isothermal equation in the entire concentration range studied. Values of  $q_{max}$  and K' calculated from the intercepts and slopes of the plots were given in Table 2. From the value of K' it is possible to calculate the mean free energy of adsorption ( $E_a$ ), defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution using the following Eq.:

$$E_a = (-2K')^{-0.5} \tag{7}$$

It is known that magnitude of  $E_a$  is useful for estimating the type of adsorption and if this value is between 8 and 16 kJ mol<sup>-1</sup> the adsorption type can be explained by ion exchange. But the value of  $E_a$  found in this study is within the energy range of physical adsorption ( $E_a < 8$ ). The calculated values of  $E_a$  are between 2 and 4 kJ mol<sup>-1</sup> for Safranin-O and phenols (Table 2). This indicates that adsorption of Safranin-O and phenols onto activated carbon are physical in nature.

The study of adsorption kinetics of Safranin-O, phenol, m-nitrophenol, p-nitrophenol and o-nitrophenol describe the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. In case of m-, p- and o-nitrophenols trends of their kinetics curves are similar to those of phenol and therefore, similar reasoning can be given. Adsorption rate constants for the Safranin-O and phenol were calculated by using pseudo-first-order, second-order and intraparticle diffusion kinetic models and which were used to describe the mechanism of the adsorption. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients ( $R^2$ ). A relatively high  $R^2$  values indicate that the model successfully described the kinetics of the Safranin-O and Phenol adsorption.

A pseudo-first-order equation can be expressed in a linear form as:

$$ln(q_e - q) = ln(q_e) - k_1 t \tag{8}$$

Table 2: Parameters of D-R adsorption isotherm at 298 K

D-R parameters	Safranin-O	Phenol	p-nitrophenol	o-nitrophenol	m-nitrophenol
$\mathbf{q}_{\max}$	267.26	198.87	244.47	252.00	285.1700
$E_a$ (kJ mol <sup>-1</sup> )	2.678	3.5400	2.8910	3.5430	4.8920
$\mathbb{R}^2$	0.9754	0.9685	0.9658	0.9621	0.9701

Table 3: Comparison of the pseudo-first and second-order kinetic models of Safranin-O and phenol adsorption for the different initial concentrations on activated carbon at 298 K

	Initial	First order kine	tic model	Second order kinetic model				
	concentrations	k <sub>1</sub> (min <sup>-1</sup> ) R <sup>2</sup>		$q_{e \text{ (exp)}} \text{ (mg g}^{-1}\text{)}$	q <sub>e</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> (g/mg min)	$\mathbb{R}^2$	
Safranin-O	125 mg L <sup>-1</sup>	0.0145	0.9921	113.40	119.05	1.9×10 <sup>-4</sup>	0.9997	
	$200 \ { m mg \ L^{-1}}$	0.0124	0.9813	129.89	138.89	$1.6 \times 10^{-4}$	0.9987	
Phenol	$20  \mathrm{mg}  \mathrm{L}^{-1}$	0.0216	0.9784	203.45	232.56	2.5×10 <sup>-5</sup>	0.9866	
	$40{\rm mg}{ m L}^{-1}$	0.0275	0.9820	189.46	192.31	1.29×10 <sup>-4</sup>	0.9885	

where,  $q_e$  and q are the amount of Safranin-O and phenol adsorbed (mg  $g^{-1}$ ) on the adsorbents at the equilibrium and at time t, respectively and  $k_i$  is the rate constant of adsorption (min<sup>-1</sup>) (Lagergren, 1898). Values of  $k_i$  were calculated from the plots of  $\ln (q_e$ -q) versus t for different concentrations of Safranin-O and Phenol, respectively and shown in Table 3.

The pseudo-second-order adsorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where,  $k_2$  is the rate constant of pseudo-second-order adsorption (g mg min). Integrating and applying the initial conditions, we have a linear form as:

$$\left(\frac{t}{q_{t}}\right) = \frac{1}{k_{2}q_{e}^{2}} + \frac{1}{q_{e}}(t) \tag{10}$$

where,  $q_e$  is the amount of dye adsorbed at equilibrium (mg  $g^{-1}$ ). Values of  $k_2$  and  $q_e$  were calculated from intercept and the slope of the linear plots of  $t/q_t$  versus t (Ho and McKay, 1999).

It may be observed from Table 3 that the adsorption of Safranin-O and Phenol on activated carbon fits pseudo-second order kinetics better than the first order. The same observation can be said phenol adsorption. It can be seen from the better fit of  $q_e$  values by using pseudo-second order kinetics when experimental  $q_e$  values are compared.

In adsorption studies, it is necessary to determine the rate-limiting step. Therefore, the results obtained from the experiments were used to study the rate-limiting step in the adsorption process. The rate constant for intraparticle diffusion  $(k_{id})$  is calculated by the following equation:

$$q = k_{id} t^{0.5} (11)$$

where, q is the amount dye adsorbed (mg  $g^{-1}$ ) at time (t) and  $k_{id}$  (mg  $g^{-1}$  min<sup>0.5</sup>) is the rate constant for intraparticle diffusion. Values of  $k_{id}$  were calculated from the slope of the linear plots of q versus t<sup>0.5</sup> (Namasivayam and Yamuna, 1995). The  $k_{id}$  values were obtained from the slope of the linear portions of the curves and were found to be as 10.517 and 12.33 mg  $g^{-1}$  min<sup>0.5</sup> for the initial concentrations of 125 and 200 mg  $L^{-1}$ , for Safranin-O and 10.824 and 21.409 mg  $g^{-1}$  min<sup>0.5</sup> for the initial concentrations of 20 and 40 mg  $L^{-1}$  for Phenol, respectively. It is seen from Fig. 3a and b, that all the plots have the same general features (the initial curved portion and a linear portion). The initial curved portion is attributed to the boundary layer diffusion, while the linear portion is responsible for the intraparticle

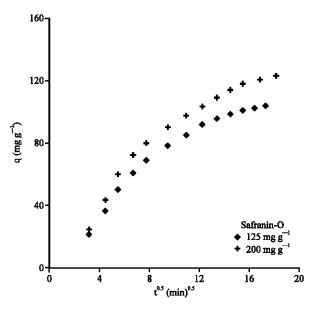


Fig. 3a: Plots of amount of Safranin-O adsorbed vs t<sup>0.5</sup> for intraparticle diffusion of SO

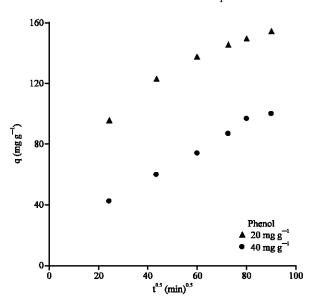


Fig. 3b: Plots of amount of phenol adsorbed vs  $t^{0.5}$  for intraparticle diffusion of phenol

diffusion. The linear portions of the curves do not pass the origin in Fig. 3a and b. This indicates that mechanism of Safranin-O and Phenol removal on Activated Carbon is complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step. Similar trends were also observed for nitrophenols.

The adsorption of Safranin-O and phenols on activated carbon were studied at temperatures of 293, 303, 313 and 323 K. The free energy of adsorption ( $\Delta G$ ) was calculated from the following equation;

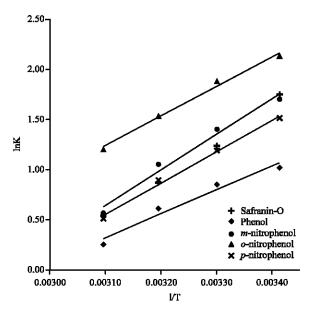


Fig. 4: Plot of lnK vs. 1/T for estimation of the thermodynamic parameters for the adsorption of Safranin-O, Phenol and Nitrophenols onto activated carbon

$$\Delta G = -RT \ln K \tag{12}$$

where, K is the equilibrium constant and T is the solution temperature (K); R is the gas constant (8.314 J mol<sup>-1</sup> K). The apparent enthalpy of adsorption, ( $\Delta$ H) and entropy of adsorption, ( $\Delta$ S), were calculated from adsorption data at different temperatures using the Van't Hoff equation (Shawabkeh and Tutunji, 2003):

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{13}$$

Values of  $\Delta H$  and  $\Delta S$  were computed from the slopes and intercepts of linear variations of ln K with the reciprocal of temperature (Fig. 4). As seen in Table 4  $\Delta G^{\circ}$  values were negative in the studied temperature range of 293-323 K for both Safranin-O and phenols indicating that the adsorption process led to a decrease in Gibbs free energy. Negative  $\Delta G^{\circ}$  indicates the feasibility and spontaneity of the adsorption process. The negative values of  $\Delta H^{\circ}$  indicate that the process is exothermic. Physical adsorption and chemisorption can be classified, to a certain extent, by the magnitude of the enthalpy change. It is accepted that bonding strengths of <84 kJ mol<sup>-1</sup> are those of physical adsorption type bonds. Chemisorption bond strengths can range from 84 to 420 kJ mol<sup>-1</sup>. Based on this the adsorption of Safranin-O, phenol and nitrophenols on activated carbon appears to be a physical adsorption process. The enthalpy of adsorption of organic molecules from aqueous solution on activated carbon is usually within the range 8-65 kJ mol<sup>-1</sup>. The negative values of  $\Delta S^{\circ}$  suggest that the decreased randomness at the solid-solution interface during the adsorption of the Safranin-O and phenols in aqueous solution on the activated carbon. The less negative values of  $\Delta S^{\circ}$  found for phenols reveal that a more ordered arrangement of phenol molecules is shaped on the adsorbent surface.

On the basis of the data, it is concluded that active carbon can be used to remove Safranin-O and phenols from aqueous solutions. The experimental adsorption data showed good correlation with

Table 4: Thermodynamic parameters for Safranin-O, phenol, p-nitrophenol, m-nitrophenol and φ-nitrophenol adsorption on activated carbon under different temperatures

	activated carbon their afficient temperatures											
	Safranin-O Phenol						p-nitro	ophenol				
T (K)	K	∆G (kJ/mol)	∆H (kJ/mol)	∆S (J/molK)	K	∆G (kJ/mol)	∆H (kJ/mol)	∆S (J/molK)	K	∆G (kJ/mol)	∆H (kJ/mol)	∆S (J/molK)
293	5.75	-4.263	-31.31	-92.64	2.77	-2.485	-19.95	-59.20	4.52	-3.678	-25.91	-75.74
303	3.45	-3.124			2.33	-2.141			3.28	-2.998		
303	3.45	-3.124			1.84	-1.587			2.43	-2.316		
313	2.39	-2.264			1.28	-0.671			1.66	-1.369		

	m-nitro	phenol			⊘-nitroph	<i>⊙</i> -nitrophenol					
T		ΔG	$\Delta \mathbf{H}$	ΔS		ΔG	∆н	ΔS			
(K)	K	(kJ/mol)	(kJ/mol)	(J/molK)	K	(kJ/mol)	(kJ/mol)	(J/molK)			
293	5.47	-4.141	-29.54	-86.27	8.41	-5.188	-24.65	-66.13			
303	4.05	-3.527			6.55	-4.736					
313	2.86	-2.732			4.62	-3.982					
323	1.75	-1.504			3.32	-3.222					

the Langmuir isotherm model. Regardless of temperature, the capacity of the activated carbon used to adsorb these compounds presented following order:

m-nitrophenol > o-nitrophenol > p-nitrophenol > Phenol > Safranin-O.

The lowest adsorption affinity of Safranin-O onto activated carbon comparing with nitrophenols including Phenol can be explained by molecular size of Safranin-O. Phenols, having the smaller molecular size, are quickly adsorbed onto activated carbon surface when comparing with Safranin-O. This was also confirmed by the equilibrium time. Solubility which is the main physicochemical features of phenols playing an important role in adsorption mechanisms. The solubility of phenol was higher than all studied nitrophenols, thus, phenol could be dissociated easily in the water. The higher adsorption affinity of m-nitrophenol onto activated carbon among the studied all nitrophenols can also be explained lower solubility in water. The difference between phenol and nitrophenols come from having -NO<sub>2</sub> group of nitrophenols since -NO<sub>2</sub> group acts as a strong electron-withdrawing group. As a conclusion the presence of nitro group on reduction of the electron density of the aromatic ring and the interaction of phenols and carbon is enhanced which leads to an increase in adsorption capacity. It can be concluded that this is also possibly the major mechanism for the adsorption of nitrophenols onto activated carbon. Thermodynamical parameters were also evaluated for the basic dye Safranin-O and phenols and revealed that the adsorption is exothermic in nature. Although activated carbons are relatively expensive and difficult to regenerate, adsorption over activated carbon is one of the most effective methods employed in the treatment of wastewaters containing both different classes of dyes and low-molecular weight organic compounds such as phenols. Our experimental results also showed that the activated carbon with a large surface area (1014.44 m<sup>2</sup> g<sup>-1</sup>) could potentially be used in the removal of safranin-O, phenol and nitrophenols in aqueous solutions and industrial wastewater managements.

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