Kinetic Study of Adsorption Processes of Some Azo Dyes on Activated Carbon

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Abstract

The adsorption of a number of azo dyes on activated carbon have been studied. Factors affecting adsorption such as time, concentration, pH and temperature variation have been investigated. The equilibrium constants are calculated from the ratio between the adsorbed and unbound concentration at different temperatures. The enthalpy of adsorption (ΔH) is estimated.

The kinetic of adsorption and desorption processes of the studied dyes have been conducted by using the integrated rate equation of the reversible first order reaction. The rate constants of both were determined at various temperatures. The activation energies and thermodynamic parameters of activation of the forward and backward are calculated.

The values of the (ΔH) revealed that, the adsorption process for all the studied dyes are exothermic and the forces control the adsorption are physical in nature. The values of activation energies indicated that, the process occurs in favor of the adsorption direction. The activation energies and other parameters of activation are in good agreement with the thermodynamically calculated ones.

Introduction

Azo dyes are very important compounds. They have wide applications and uses in many industrial fields. Their presence in waste water are not desirable because of their toxic nature to the life and environment. Therefore, the removal of such compounds from waste water is a vital task⁽¹⁾.

Activated carbons have long been used as adsorbents in industry due to their superior adsorption capacities. Their properties depend on the pore structure, which in turn depends on the preparation conditions as well as the chemical nature of the carbon surface^(2,3).

The term adsorption kinetic represents the rate of molecular uptake from the adsorbate solution to the adsorbent surface after overcoming all of the inter and intramolecular forces that trying to preclude the adsorption process^(4,5).

The kinetic data are valuable for determining the period required to reach equilibrium and assessing the adsorbent performance for effluent species adsorption. These data also help to understand the mechanism of adsorption which is essential for improving the efficiency of such processes. For these reasons, a great attention has been paid recently toward the development of such studies (6,7). However, there is still very limited literature concerning the adsorption / desorption kinetics of azo dyes on activated carbon. The main aim of this investigation is to study the adsorption and desorption kinetics and compensation effects for a number of azo dyes molecules which vary in both type and position of their functional groups.

Kinetic model

The rate equation of the reversible first order reaction⁽⁸⁾ is used to fit the adsorption kinetic data of the studied system. This equation is described as:

$$\ln (Xe - X) = \ln Xe - (k_1 + k_2) t \dots (1)$$

where Xe and X are the concentrations of the adsorbed dye at equilibrium and at definite time respectively, k_1 and k_2 are the rate constants of the forward and backward reactions respectively. A plot of $\ln(Xe - X)$ versus time gives a straight line of slope equal to $(k_1 + k_2)$.

Assuming (a) is the initial concentration of dye, the adsorption can be expressed by the following equation:

Since the value of the adsorption equilibrium constant (K) can be calculated from the ratio:

values of k_1 and k_2 can be obtained. The activation energies (E) for both the adsorption and desorption processes are calculated using Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT} \quad \dots (3)$$

Where k is the rate constant, A is a frequency factor, R is the universal gas constant (8.314 J.K⁻¹.mol⁻¹) and T is the absolute temperature. The value of E is calculated from

the slope of plotting lnk versus
$$\frac{1}{T}$$
, and A (sec⁻¹) is

determined from the intercept. The values of thermodynamic functions of activation (ΔH^* , ΔS^* and ΔG^*) are estimated from the following equations:

$$\Delta H^* = E - RT (KJ.mol^{-1}) \dots (4)$$

$$\Delta S^* = R \left[\ln A - \ln \left(\frac{K \cdot T}{h} \right) - 1 \right]$$

 $(J.K^{-1}.mol^{-1})$ (5)

where K` is Boltzman constant (1.38×10^{-23}) (J.K⁻¹) and h is Planck constant (6.6256×10^{-20}) J

Experimental

- 1. Materials
- a. Adsorbent: Activated carbon of commercial grade supplied by Merck Chemical Company is used as an adsorbent.
- b. **Adsorbate**: The studied dyes used as adsorbates were synthesized via dizonium salts in a similar way to the standard methods⁽⁹⁾. The chemical compositions and physio-chemical properties of these dyes are listed in Table (1).

Starting materials employed for the preparation of these dyes and other materials used in this study, such as resorcinol, o, m, and p-amino phenol, o, m, and p-nitro aniline, ethanol, NaNO₂, HCl and NaOH are of reagent grade and supplied by the BDH and Fluka Chemical Companies.

Table(1): Names, structures, melting points and

 λ_{max} of the studied dyes

_{max} of the studied dyes							
Dye name	Dye structure	m.p. °C	$\begin{array}{c} \lambda_{max} \\ Nm \end{array}$				
o-hydroxy phenyl azo resorcinol (o-HAR)	OH HO N=N-OH	191	435				
m-hydroxy phenyl azo resorcinol (m-HAR)	HO HO OH	210	427				
p-hydroxy phenyl azo resorcinol (p-HAR)	HO—N=N—OH	224	379				
o-nitro phenyl azo resorcinol (o-NAR)	NO ₂ HO N=N-OH	188	450				
m-nitro phenyl azo resorcinol (m-NAR)	O ₂ N HO OH	181	418				
p-nitro phenyl azo resorcinol (p-NAR)	O_2N $N=N$ OH	197	448				
o-methyl phenyl azo resorcinol (o-MAR)	CH ₃ HO N=N-OH	193	434				
Phenyl azo resorcinol (PAR)	HO N=N-OH	155	431				

2. Preparation of stock solution of the tested dyes

Exact weights of the prepared dyes were dissolved in 100 ml volumetric flask using mixed water-ethanol solvent of 50% (V:V). Ethanol was used for clarification of complete solubility. Fresh samples were used for the study.

3. Calibration curves

A range of concentrations of each of the tested dyes were prepared for the construction of a calibration curve at its maximum wavelength (λ_{max}). The absorbance values of the solutions were measured at this λ_{max} corresponding to the various solute concentrations depending on the Beer's law (A = ϵ bc). Calibration curves were obtained and used in all of the pH values studied. The concentration of free (unbound) dye in the supernatant was determined from the calibration curve, and the amount of dye bound on the unit volume of absorbent was estimated by difference.

4. Effect of contact time

A series of experiments were carried out to find the optimum time to reach equilibrium for each dye. The experiments were conducted at 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 minutes, at a constant temperature, dye concentration of 3×10^{-4} M and 40 mg of activated carbon/50 ml of solution. The samples were sealed and agitated in a thermostatic shaker at constant rate of 120 rpm. The samples were filtered through 0.45 μ m membrane filter to remove the carbon particles. The residual dyes concentration was determined with UV-Visible Cecil CE-1021 Spectrophotometer at the maximum wavelength corresponding to the various dyes.

5. Effect of concentration

The effect of concentration is conducted at equilibrium conditions within the range of 3×10^{-4} to 1×10^{-3} M. Four samples of different concentrations of the tested dyes are prepared. 40 mg of the carbon is added to each of them, shacked for 70 min, filtered and the amount of adsorbed dye is estimated using the calibration curves.

The removal efficiency is expressed in terms of adsorption percentage and calculated as follow:

% Adsorption =
$$\frac{X}{a} \times 100 \dots (6)$$

where X is the concentration of the adsorbed dye which represents the difference between the initial concentration (a) and the dye concentration in the solution after treatment (a - X).

6. Effect of pH

The study is first conducted at the natural pH dye solution. The effect of initial pH for each dye is then investigated by adjusting the pH solution at 4, 7 and 9, respectively prior to adsorption experiment. Other conditions were kept as same as the equilibrium measurement.

7. Estimation of the enthalpy of adsorption

Value of enthalpy of adsorption helps to determine the nature and the kind of forces those control the process of attachment with the solid surface.

The adsorption equilibrium constants are calculated at various temperatures from the ratio between the adsorbed and free dye concentrations.

The value of ΔH is calculated from the slope of the straight line ($\Delta H/R$) that resulted from plotting lnK versus (1/T) when applying the Van 't Hoff's equation which can be expressed as:

$$\ln K = \ln Ko - \frac{\Delta H}{RT} \quad (7)$$

where R is the gas constant (8.314 J.mol⁻¹.K⁻¹), T is the absolute temperature and lnK_0 is the intercept.

8. Kinetic study

Kinetic of the studied dyes on activated carbon is carried out as follow:

1.4 mg of the carbon is added into a 10 ml solution of the tested dye of initial concentration $(3 \times 10^{-4} \text{ M})$. Different samples are shacked for 10, 20, 30, 40, 50 and 60 minutes. The samples are then filtered rapidly and the dye content of the filtrates are determined spectrophoto-metrically. The amount of the dye adsorbed is estimated by difference.

- 2. The method in point one is repeated at different temperatures (10, 15, 25, 35 and 45 °C).
- 3. The method in point (1) is repeated at zero °C for all the studied dyes and the samples are filtered at times of 2, 4, 6, 8 and 10 minutes.

Results and discussion

All the adsorption experiments of the studied dyes from aqueous solutions were carried out in a batch system. these experiments were performed by employing single solutions of the dye of interest.

Effect of contact time

A series of experiments were carried out in order to find the optimum time required to reach equilibrium. The results obtained are shown in Figure (1). The uptake level of the dye increases as the time increase from zero to 100 minutes. These results indicate that, the adsorption process proceeds in two stages; an initial rapid increase between zero and 10 minutes being very sharp, followed by a slower stage in which the uptake rate gradually decreases with time indicating that adsorption was rapid and approached maximum at about 60-70 minutes for all the studied dyes. The time (70 min) is used for the following steps in this study.

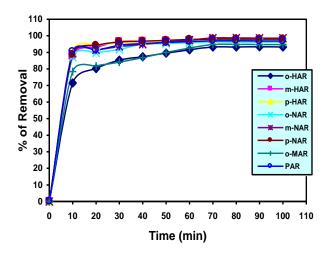


Figure (1): %of Removal of dye as a function of time at 3×10^{14} M

Effect of concentration

The results of varying concent-ration of dye when keeping other parameters constant are listed in Table (2).

Table (2): The effect of dye concent-ration on the % removal efficiency (at 10 °C)

i ciiio i di ciiii	emovar efficiency (at 10°C)						
Compound	3×10^{-4}	5×10^{-4}	7×10^{-4}	1×10^{-3}			
	M	M	M	M			
o-HAR	93.3	88.5	81.71	73.19			
m-HAR	97.0	95.8	90.8	66.0			
p-HAR	97.5	96.2	95.3	93.0			
o-NAR	96.2	94.5	92.8	90.4			
m-NAR	98.6	97.7	95.4	93.5			
p-NAR	98.0	97.4	96.2	94.8			
o-MAR	94.7	92.5	88.7	65.4			
PAR	96.9	91.2	89.4	56.0			

The results of Table (2) show that:

- 1. The removal efficiency of these dyes by activated carbon is highly dependent on their concentrations in the solutions when other factors affecting the adsorption are kept constant. They also indicate that the adsorption process is efficient at low concentration. This may be explained as follow: the increase of concentration increases the dye molecules in the solution, and since the number of active sites available for adsorption for a certain amount of adsorbent is constant, the competition among the molecules to reach the solid surface will increase causing poisoning of these sites and preclude the adsorption process as a result⁽¹⁰⁾.
- 2. The hydrogen bonds present in the system and other attraction forces in addition to the resonance and inductive effect have great influence on the adsorption efficiency. This can be clarified by doing the following comparison: the adsorption ratios of the hydroxyl substituted dyes increase in the order: p-HAR > m-HAR > o-HAR. While the removed efficiency of the nitro substituted dyes increase in the order: m-NAR > p-NAR > o-NAR. This behavior can be explained in terms of the inductive and resonance effects of the electron releasing (OH) and withdrawing (NO₂) groups which have opposite effect. On the other hand, the formation of inter and intra molecular hydrogen bonds by the OH groups hinder the adsorption process and reduces their removal efficiency when compared with the analog nitro compounds.
- 3. The steric effect could be pronounced when looking at the increasing order of the ortho substituted dyes: PAR > o-NAR > o-MAR > o-HAR exception (when the molecular sizes of the substituents are considered only) is noticed for the o-HAR dye which could be attributed to the formation of intramolecular hydrogen bonds.

Effect of pH

The effect of varying pH of dye solution prior to the adsorption when keeping other factor constant is investigated at the natural pH of the dye solution as well as other three values (4,7 and 9). This study is aimed to find the most suitable form of the dye molecule (acidic, neutral or basic) for adsorption. The results obtained are given in Table (3).

Table (3): Effect of pH of dye solution on the % removal efficiency

Dye	pH = 4	Natura	pH = 7	pH = 9
		1 (pH)		
o-HAR	98.6	93.3	93.0	77.3
		(5.95)		
m-HAR	98.9	97.0	94.6	80.8
		(6.63)		
p-HAR	99.5	97.5	95.4	88.5
		(6.68)		
o-NAR	99.3	96.2	93.0	82.7
		(4.19)		
m-NAR	99.6	98.0	96.0	91.3
		(6.76)		
p-NAR	98.6	98.6	95.6	89.5
		(4.0)		
o-MAR	99.7	94.7	94.2	83.4
		(7.2)		
PAR	99.3	96.9	96.5	86.8
		(5.43)		

The results in Table (3) show that, for all tested dyes, the maximum removal efficiency is achieved in acidic solutions. The adsorption efficiency decrease when we move to the neutral and basic media. The reduction in the adsorption ratios are varied according to the nature, position and type of interactions that, the substituents may undertake.

The highest reduction in the adsorption ratio is noticed in the basic medium. This may due to the formation of a negative charge on the phenoxide ion which will be more likely to be attracted to the solvent or other molecules in the solution than the solid surface and reduces the adsorption efficiency in the end⁽¹¹⁻¹³⁾.

Effect of temperature

The results of the investigation of the effect of varying temperature (when keeping other factors constant) on the adsorption process of the tested dyes in the range (10-45 °C) are given in Table (4).

Table (4): Effect of temperature on the adsorption efficiency at concentration 3×10^{-4} M and natural pH

3 × 10 W and natural pil						
Compound	% of adsorption at temperature (°C)					
Compound	10	15	25	35	45	
o-HAR	93.3	92.6	92.0	91.3	90.6	
m-HAR	97.0	96.8	96.0	95.3	94.6	
p-HAR	97.5	96.6	95.5	94.4	92.9	
o-NAR	96.2	95.7	94.4	93.3	91.7	
m-NAR	98.6	98.0	96.9	95.8	94.6	
p-NAR	98.0	97.4	96.1	95.0	93.8	
o-MAR	94.7	92.0	87.1	82.2	80.0	
PAR	96.9	95.8	94.0	93.0	91.7	

The study indicated that the adsorption efficiency decreases with increasing temperature no mater what type of substitutents on the aromatic ring present^(13,14). This observation is quite common, and suggest that the adsorption is exothermic and physical in nature in which the increase in temperature increases the desorption process.

Calculation of enthalpy of adsorption

The estimation of the heat of adsorption is conducted depending on the adsorption isotherm knowledge and variation of temperature.

The values of K at different temperatures are determined at the thermodynamic equilibrium from the ratio between the adsorbed and free dye concentrations. The straight lines obtained from plotting lnK versus (1/T) (shown in Figure 2) of Van 't Hoff's equation are used to calculate the ΔH values. The values of K and ΔH obtained are listed in Table (5).

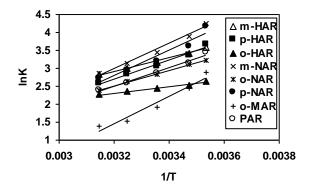


Figure (2): Relations between ln K versus 1/T used to calculate ΔH

Table (5): Calculated values of adsorption equilibrium constants and enthalpy of

adsorption

adsorption							
Dye	Temp.	K	- ΔH (KJ.mol ⁻¹)				
	283	13.925					
	288	12.513					
o-HAR	298	11.500	7.425				
	308	10.530					
	318	9.638					
	283	36.037					
	288	30.250					
m-HAR	298	24.000	15.807				
	308	20.276					
	318	16.857					
	283	39.000					
	288	28.705					
p-HAR	298	21.222	22.241				
	308	16.858					
	318	13.084					
	283	25.315					
	288	22.255					
o-NAR	298	16.857	17.647				
	308	13.925					
	318	11.048					
	283	70.428	29.090				
m-NAR	288	49.000	25.050				
	298	31.258					
	308	22.809					
	318	17.518					
	283	70.000					
	288	37.461					
p-NAR	298	24.641	28.857				
	308	19.000					
	318	15.129					
o-MAR	283	17.867					
	288	11.500					
	298	6.752	31.953				
	308	4.618					
	318	4.000					
PAR	283	31.258					
	288	22.809					
	298	17.518	21.436				
	308	13.285					
	318	11.048					

Looking at the results of Table (5), the values of ΔH show that, the adsorption of the tested dyes is exothermic process. These values are also indication of the physical nature (40 KJ.mol⁻¹>) of the forces that control the adsorption of such dyes on activated carbon. The values of ΔH are in line with the Gibbs free energy, ΔS and adsorption ratios (see Table 6).

Table (6): Comparison between the enthalpy and

adsorption efficiency at 10 °C

Dye	%	- ΔH
Dye	adsorption	(KJ.mol ⁻¹)
p-HAR	97.5	22.241
m-HAR	97.0	15.807
o-HAR	93.3	7.425
PAR	96.9	21.436
o-NAR	96.2	17.647
o-MAR	94.7	31.953
o-HAR	93.3	7.425
m-NAR	98.6	29.090
p-NAR	98.0	28.857
o-NAR	96.2	17.647

The comparison in Table (6) shows that the increase in the adsorption ratio is accompanied by increase in the negative value of the heat of adsorption. Exception are noticed in the o-MAR dye when compared with the other ortho substituted ones. The low value of adsorption efficiency of this dye is not consistent with the great negative value of ΔH . This may indicate that there is another factor beyond the seen affecting the adsorption and causes such deviation.

Kinetic study

The adsorption kinetic of the studied dyes on activated carbon is carried out as a batch experiments. A single solution of concentration 3×10^{-4} M is used. The investigation is performed at temperature range of (15-45 °C). The rate of uptake (adsorption) was estimated spectrophotometrically at the λ_{max} of each dye.

Preliminary experiments showed that the uptake level is very fast with initial increase being very sharp within the first ten minutes, indicating high affinity between carbon and dyes. The adsorption process is then became slower, and the uptake rate gradually decreased with time possibly due to intra-particle diffusion. Finally, saturation is reached beyond which no further adsorption can take place⁽⁷⁾. The results suggest that equilibrium could be reached in about 60-70 minutes. This observation is consistent with other Accordingly, the investigation was extended to include two parts. The first part, is devoted to study the adsorption kinetic in the first ten minutes. The pseudo first order equation is applied for this purpose. The study is performed at initial concentration of 3×10^{-4} M and temperature 0 °C. The reason of undertaking this part of study is to reduce the rate of adsorption, so it could be followed kinetically. The obtained results are listed in Table (7). These results show that the adsorption data of most of the tested dyes are fitted well to the pseudo first order equation. These are indicated by the linear relationships and the values of correlation coefficients.

Table (7): Kinetic results of the first ten minutes adsorption of the studied dyes at 0 °C

	Dye	K	.k (min ⁻¹)	t _{0.5} (min)	R*
ĺ	o-HAR	128.993	0.065	10.59	0.9811
	m-HAR	43.811	0.146	4.73	0.9928
	p-HAR	47.348	0.215	3.21	0.9933
	o-NAR	17.337	0.274	2.53	0.9956
	m-NAR	94.29	0.424	1.63	0.9961
	p-NAR	84.507	0.282	2.45	0.9947
	o-MAR	20.383	0.166	4.16	0.9983
	PAR	19.545	0.712	0.97	0.9326
		201 1			

^{*} r = correlation coefficient

The second part of this investigation is concerned with studying the rate of adsorption and desorption of the dyes of interest on activated carbon during the next 10-60 minutes. The work is conducted by using definite amount of carbon, initial concentrations of 3×10^{-4} M and different temperatures. The reversible first order equation (eq. 1) is applied to fit the experimental data. The values of the equilibrium constant (K), rate of adsorption (k_1) and desorption (k_2) are determined as illustrated earlier. Their values are listed in Table (8).

Table (8): Values of adsorption equilibrium constant and rate of adsorption and desorption at different

temperatures

•				
Dye	Temp. K	K	$K_1 \times 10^{-2}$	$k_{-1} \times 10^{-3}$
	• • • •	12 -12	(min ⁻¹)	(min ⁻¹)
	288	12.513	2.407	1.924
o-HAR	298	11.500	2.272	1.976
0 111 111	308	10.530	2.082	1.977
	318	9.638	2.183	2.265
	288	30.250	3.010	0.995
m-HAR	298	24.000	2.841	1.184
III-IIAK	308	20.276	3.030	1.495
	318	16.857	3.681	2.184
	288	28.705	3.788	1.319
a IIAD	298	21.222	4.278	2.016
p-HAR	308	16.858	3.861	2.290
	318	13.084	6.884	5.261
	288	22.255	1.311	0.589
MAD	298	16.857	1.425	0.845
o-NAR	308	13.925	1.773	1.273
	318	11.048	3.961	3.585
	288	49.000	1.127	0.230
37.5	298	31.258	1.492	0.477
m-NAR	308	22.809	2.079	0.911
	318	17.518	3.235	1.847
	288	37.461	2.591	0.691
	298	24.641	2.028	0.823
p-NAR	308	19.000	3.325	1.750
	318	15.129	3.658	2.418
	288	11.500	1.242	1.080
	298	6.752	1.559	2.309
o-MAR	308	4.618	2.869	6.212
	318	4.000	3.424	8.560
	288	22.809	1.897	0.831
	298	17.518	2.005	1.145
PAR	308	13.285	2.883	2.170
	318	11.048	5.126	4.640
	310	11.070	3.120	7.070

The linear relationships obtained from the plot of $\ln (Xe - X)$ versus time (at 25 $^{\circ}C$) is shown in Figure (3). The same trends were obtained at other temperatures.

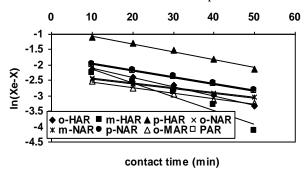


Figure (3): Values of ln(Xe – X) versus time (min) at 25 °C

The Arrhenius equation (eq. 3) is used to calculate the values of activation energies for the forward (Table 9) and backward (Table 10) processes for all the studied dyes. The straight lines obtained from plotting lnk_1 and lnk_2 versus (1/T) are shown in Figures (4) and (5), respectively.

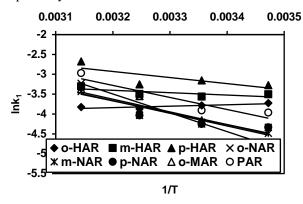


Figure (4): Relation between lnk_1 versus (1/T) for the tested dyes

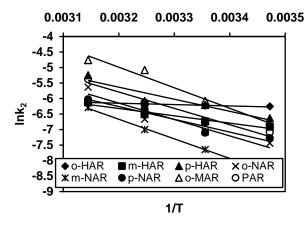


Figure (5): Relation between lnk_2 versus (1/T) for the tested dyes

The results in Tables (9) and (10) show that the values of activation energies of the desorption of all dyes on activated carbon are higher than those of adsorption process, which indicate that the process occurs in favor of adsorption direction. This result is supported by the values of K and adsorption efficiencies. The negative values of ΔS^* refer to the increase in order in the intermediate state according to the absolute rate theory (i.e. activated complex theory)⁽¹⁶⁾. The overall results show that there is a good consistency between the values of the thermo-dynamic parameters of activation and activation energies with the thermody-namically determined ones.

Table (9): Values of thermodynamic functions of activation of adsorption process

		E_1	ΔH_1^*	$-\Delta S_1^*$	ΔG_1^*		
Dye		KJ.	KJ.	J.mol ⁻¹ .	KJ.		
		mol ⁻¹	mol ⁻¹	K^{-1}	mol ⁻¹		
o-HAl	R	3.908	1.389	238.813	73.749		
m-HA	R	4.955	2.436	231.746	72.655		
p-HA	R	12.624	10.105	203.269	71.696		
o-NA	R	26.528	24.009	164.577	73.876		
m-NA	R	26.502	23.983	164.970	73.969		
p-NAl	R	11.045	8.526	212.415	72.887		
o-MA	R	27.807	25.287	159.578	73.639		
PAR		25.188	22.669	165.978	72.961		

Table (10): Values of thermodynamic parameters of activation of desorption process

	E_2	ΔH_2*	$-\Delta S_2*$	ΔG_2^*
Dye	KJ.	KJ.	J.mol ⁻¹ .	KJ.
	mol ⁻¹	mol ⁻¹	K^{-1}	mol ⁻¹
o-HAR	11.074	8.555	235.119	79.796
m- HAR	19.602	17.083	209.156	80.457
p-HAR	32.356	29.837	162.605	79.106
o-NAR	43.282	40.763	131.940	80.741
m- NAR	52.479	49.960	106.815	82.325
p-NAR	34.218	31.699	153.516	78.214
o- MAR	55.019	52.500	84.758	78.182
PAR	43.876	41.357	127.043	79.815

References

- 1. E.A. Clarke and R. Anliker, (1980), "Organic dyes and pigments. In: The Handbook of Environmental Chemistry", Vol. 3, Part A, Anthropogenic Compounds, Hutzinger, O.[Ed] ,Spriner-Verlag, Heidelberg, 181-215.
- 2. S.P. Nandi, P.L. Walker and Jr., (1971), "Adsorption of dyes from aqueous solution by coals, chars and active carbon", Fuel, 50, 4, 345-366.
- 3. N. Paul, (1980), "Carbon Adsorption Handbook", Second Printing.
- Knaebel Kent, (2003), "Adsorbent Selection", Adsorption Research, Inc., Dublin, Ohio, 43016, 1-23.
- 5. P. Somasundaran, S. Shrotri and L. Huang, (1998), "Thermo dynamics of adsorption of surfactants at solid-liquid interface", Pure and Appl. Chem., 70, 3, 621-626.
- 6. B. Armağan, M. Turan, M.S. Celik, (2004), "Equilibrium studies on the adsorption of reactive azo dyes into zeolite", Desalination, 170, 33-39.
- 7. A.A. Abia and J.C. Igwe, (2005), "Sorption kinetics and intraparticulate diffusivities of Cd, Pd and Zn ions on maize cob", African Journal of Biotechnology, 4, 6, 509-512.
- 8. F. Daniels and R.A. Alberty, (1966), Physical Chemistry, 3rd ed., John Wiley and Sons, Inc., 338.
- 9. I. Vogel, (1964), "A Textbook of Practical Organic Chemistry", 3rd ed., Longmans, Green and Co. Ltd., London, 662-623.

- M.M. Aslam, I. Hussan, M. Malik and Asif Matin, (2003), "Removal of copper from industrial effluent by adsorption with economical viable material", Institute of environmental sciences and engineering (IESE), National University of Science and Technology (NUST), Tamiz. Ud. Din Read Raqalpindi Cantt, Pakistan, E-mail: masud92pak@hotmail.com, 1-8.
- 11. R.T.G. Al-Abady, (2005), "Thermodynamic and kinetic study of adsorption of some azo dyes on activated carbons and other developed adsorbents", M.Sc. Thesis, Mosul University, Iraq, 98-123.
- 12. M.C. Keith Davis, (1973), "Adsorption of phenols from non-polar solvents onto silica gel", J. Chem. Soc. Faraday Trans, 1, 69, 1117-1126.
- E.A. Al-Hyali, O.M. Ramadhan and S.A. Al-Dobone, (2005), "Effect of substituents type on adsorption of aromatic carboxylic acid and their relation to concentrations, temperature and pH", Raf. Jour. Sci., 16, 3, 68-78.
- T. Farere et al., (1998), "Adsorption of anionic dyes on the biopolymer chitin", J. Braz. Chem. Soc., 9, 5, 435-440.
- 15. I.A. Al-Jarjari, (2005), "Study the factors affecting adsorption of some azo dyes and their complexes", M.Sc. Thesis, Mosul University, Iraq.
- H.E. Avery, (1977), "Basic Reaction Kinetics and Mechanism", The Macmillan Press LTD, London, 64-67.

دراسة حركية امتزاز بعض اصباغ الازو على الفحم المنشط

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الخلاصة

لمعدل سرعة التفاعل للتفاعلات العكسية من المرتبة الأولى. وحسبت قيم طاقة التنشيط والدوال الثرموداينميكية للتنشيط لكلا العمليتين من خلال حساب قيم ثوابت السرعة عند درجات حرارية مختلفة.

أظهرت قيم انثالبي الامتزاز إن عملية الامتزاز لجميع الأصباغ المدروسة هي باعثة للحرارة وان القوى المسؤولة عن الامتزاز هي ذات طبيعة فيزيائية، فيما أظهرت قيم طاقة التنشيط إن عملية الامتزاز تحدث بالأفضلية بالاتجاه الأمامي. وبصورة عامة تتفق قيم الدوال الثرموداينميكية للتنشيط مع قيم انثالبي الامتزاز.

تضمن هذا البحث دراسة العوامل المؤثرة على امتزاز عدد من أصباغ الازو على الفحم المنشط مثل زمن التماس والتركيز والدالة الحامضية لوسط الامتزاز فضلا عن التغير في درجة الحرارة. حسبت قيم ثابت توازن الامتزاز عند درجات حرارية مختلفة من النسبة بين كمية المادة الممتزة والمتبقية في المحلول عند التوازن والتي استخدمت لاحقا لحساب انثالبي الامتزاز.

اشتمل البحث أيضا على دراسة حركية عمليتي الامتزاز والابتزاز للصباغ المدروسة على الفحم المنشط من خلال تطبيق المعادلة المتكاملة