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Thermodynamic and Kinetic Study of Benzothiozoles Derived Dyes Adsorption by Activated Carbon

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Abstract

A commercial activated carbon was used for the adsorption of two azo dyes from aqueous solution employing batch method. These dyes were synthesized in our laboratory from the reaction of 6-substituted 2-amino-benzothiozoles and resorcinol via diazonium ions. The effect of pH, temperature, and contact time on dye removal was investigated. The apparent thermodynamic parameters were estimated and the obtained results concluded that, the dyes adsorbed onto activated carbon are driven by entropy effect, exothermic and spontaneous processes. The kinetic of adsorption was conducted by using the pseudo-first and pseudo-second order kinetic models. The results of the kinetic analysis showed that, the second order equation was more appropriate and better fit the experimental data.

Key words: Adsorption kinetic, Thermodynamic of adsorption, Benzothiozoles

الخلاصة

تضمن البحث استخدام نوع من الكاربون المنشط التجاري لامتزاز اثنين من أصباغ الازو من محاليلها المائية بطريقة الوجبة الواحدة. هاتان الصبغتان حضرتا في مختبراتنا من تفاعل مشتقات أل 2، -امينو بنزوثايوزول مع الريزورسينول باتجاه تكوين ايون الدايزونيوم.

وقد اشتمل هذا البحث على اختبار تأثير بعض المتغيرات على إزالة الأصباغ من محاليلها المائية مثل الدالة الحامضية لوسط الامتزاز ودرجة الحرارة وزمن التماس مع الصبغة. وقد تم حساب الدوال الثرموداينمكية الظاهرية للنظام المدروس. أشارت النتائج التي تم الحصول عليها ان امتزاز هذه الصبغة على الكاربون المنشط يسير بتأثير الانتروبي وان عملية الامتزاز هي عملية تلقائية وباعثة للحرارة.

ودرست حركية الامتزاز من خلال تطبيق نموذجي معادلتي المرتبة الأولى الكاذبة والثانية الكاذبة. أظهرت نتائج الدراسة الحركية ان معادلة المرتبة الثانية هي أكثر ملائمة للنظام المدروس وتنطبق بصورة أفضل على البيانات العملية.

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Introduction

Azo dyes are compounds with one or several azo (N=N) bridges linking substituted aromatic molecules making them more stable and exhibiting high resistance to biodegradation. These dyes are usually of synthetic origin and now days there are more than 10.000 dyes produced worldwide annually and available commercially (1).

During the dying process, it was estimated that, (10-25)% of dyes are lost in the effluent (2-3). Since some dyes are toxic and carcinogenic, their disposal into wastewater without advanced treatment causes environmental problems and damages the ecosystem (4). Therefore, their removal became a vital task. Two dyes are considered in this study. They were derived from the reaction of 6-substituted 2-amino benzothiozole with resorcinol via dizonium ion. Benzothiozole is a bicylic ring system with multiple applications. Its use started in the 1950s when a number of 2-amino benzothiozoles (2-ABT) were intensively studied as central muscle relaxants. Since then medicinal chemists have not taken active interest in this chemical family. Biologist's attention was drawn to this series when the pharmacological profile of Riluzole was discovered (5). The benzothiozole derivatives have then been studied extensively and found to have diverse chemical reactivity and broad spectrum of biological activity.

The 2-ABT derivatives were found (5) as intermediates for agro-chemical drugs and dyes. They were showed ant tumor activity and studied as antimicrobial and antifungal agents. Many other applications of 2-ABT derivatives are found in the literature which beyond the scope of this research.

Various methods such as sedimentation, equalization, neutralization, flotation, chemical precipitation, coagulation and flocculation, reverse osmosis, electrochemical coagulation, adsorptions,…,etc. have been investigated for the removal of dyes from aqueous solutions(6-9).

Adsorption seems to be the most potential technique for future use in industrial wastewater treatment because of its superior simplicity of design, initial cost ease of operation and insensitivity to toxic substance (10). Many research groups have investigated the feasibility of using various low cost substances such as chitin (6), natural clay (11), rice husk (12), plant leaf (13), jackfruit peel (14), …etc. as adsorbents for the removal of dyes from wastewater.

Identification of a potential dye sorbent must be in good agreement with its dye binding capacity, regeneration properties, requirement and limitations with respect to environmental conditions. Activated carbon remains the most effective and widely used adsorbent for the removal of dyes from aqueous solutions(15).

The term adsorption kinetic represents the rate of molecular uptake from the adsorbate solution to the adsorbent surface after overcoming all of the internal intramolecular forces that trying to preclude the adsorption process. Kinetic data are valuable for determining the period required to reach equilibrium and assessing the adsorbent performance for effluent species adsorption (16,17). These data also help to understand the mechanism of adsorption which is essential for improving the efficiency of such process. For this reason, a great attention has been paid recently toward the development of such studies (13,14,16,17) .

In this study, the capacity of commercial type of activated carbon (CAC) to remove the two dyes, derived from 2-ABT and resorcinol, is estimated.

By employing batch method, the effects of pH, temperature and contact time on the dye recovery were investigated. Equilibrium and kinetic analysis were conducted.

Kinetic models

A study of the adsorption kinetics is desirable because it provides information regarding the controlling mechanism of adsorption such as mass transfer and chemical reactions which are important for determining the efficiency of the process. First and second order kinetic models were used to investigate the adsorption mechanism and the potential rate controlling steps.

The first order rate expression of Lagergreen is generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where q_e and q_t are the amounts of adsorbed dye on the CAC (mg/gm) at equilibrium and at time t respectively, and k_1 (min^{-1}) is the rate constant of the first order adsorption. After integration and applying boundary conditions t=0 to t=t and q=0 to $q=q_e$, the integrated form of eq(1) becomes:

$$\ln(q_e - q_t) = \ln q_e - kt \quad \ldots\ldots\ldots (2)$$

A plot of ln (q_e-q_t) versus time should give a linear relationship if the kinetic model is applicable and the real value of equilibrium adsorption capacity (q_e) can be obtained by extrapolating the experimental data to t = 0.

The second order model may also describe the kinetics of adsorption. It shows how the rate depends on the adsorption capacity on solid but not on the concentration of the adsorbate (19,20), and the adsorption mechanism being the rate controlling step, which may involve valency forces through sharing or exchange of electrons between dye and adsorbent.

The second order kinetic model expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad \ldots\ldots\ldots (3)$$

Where k_2 (g mg^{-1} min^{-1}) is the rate constant of the second order adsorption. The integrated linear form of eq(3) is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots\ldots\ldots (4)$$

If second order kinetics is applicable, the plot of t/q_t against t should give linear relationship and the calculated value of equilibrium capacity (q_e calc.) must well fit the experimental data.

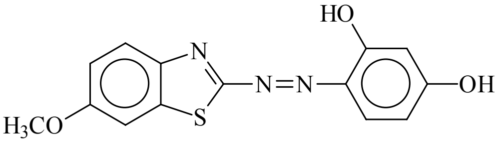
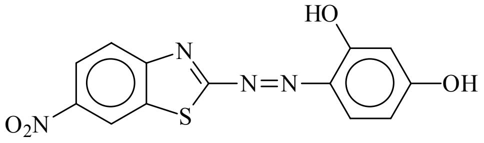
Experimental

Materials and methods

Dyes characterization

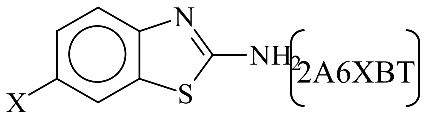
The two dyes used in this study are derived from 2-amino-6-methoxy (or nitro) benzothiozoles which were allowed to react with the resorcinol via dizonium ion. The names and structures of the synthesized dyes are shown in Table (1).

Table (1): Names and structure of the studied dyes

Name	Structure
6-Methoxy benzothizole azo resorcinol (MBAR)	
6-Nitro benzothizole azo resorcinol (NBAR)	

Synthesis of 2-amino-6- substituted - Benzothiozoles (2A6SBT) (21)

into a solution of (0.1 mole) of 4-substituted aniline and (0.4 mole) of potassium thiocyanate, (0.1 mole) of bromine dissolved in 100 mL of glacial acetic acid was added dropwise while keeping the temperature below (10^{o}C). After the addition of all bromine solution, the mixture was stirred for (10) hours, then filtered off and the precipitate dissolved in warm distilled water. The resulted solution neutralized with 50% NaOH. The precipitate was filtered off and recrystilized by using a suitable solvent. The physical properties of the synthesized compounds are given in Table (2):



Where : X= NO_2 2-Amino-6-nitro benzothiozole (2A6NBT)
X= OCH_3 2-Amino-6-methoxy benzothiozole (2A6MBT)

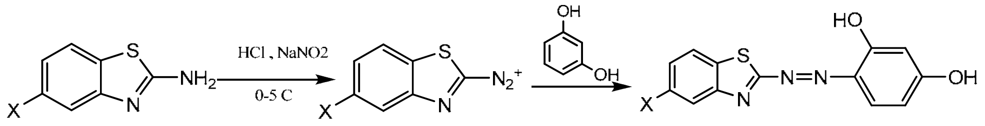
Table (2): the physical properties and IR spectroscopy data for the prepared compounds

Comp	**MP/ °C**	**solvent of recovery**	**IR (cm^{-1})**		
			1-NH_2	**C=N**	**C-S**
2A6NBT	247-248 247*	EtOH	3460	1615	775
2A6MBT	163-164 165*	Benzene	3500	1620	780

* Published M.P °C

Synthesis of MBAR and NBAR dyes

The synthesized compounds mentioned in Table (2) (2A6NBT and 2A6MBT) were readily converted to the azo dyes NBAR and MBAR respectively, by the reaction with resorcinol using concentrated hydrochloric acid and sodium nitrite via diazonium ion while keeping the temperature in the range between (0-5 °C) (using standard method(22)) as in the following equation:



Characteristics of the synthesized dyes are listed in Table (3).

Table (3): characterization of the synthesized dyes:

Parameter	NBAR	MBAR
Color	Dark brown	Dark orange
pH in 50% Ethanol- Water	2.9	6.5
λ_{max} nm	355	446
M.P/ °C	142-145	94-95

Adsorbent

A commercial activated carbon (CAC) supplied by Merck is used as adsorbent in this study. Its surface area is 900BET, N_2, m^2/g.

Equilibrium study:

The adsorption experiments were carried out as a batch method, were samples of 0.05 g of activated carbon were equilibrated with 100mL of solution containing certain amounts of the studied dyes. The initial pH of the dye solution was adjusted by using diluted solution of NaOH or HCl and measured with JENWAY pH meter 3310.

The various temperatures of the dye solutions (25,35,45,55, and 65 °C) were controlled by a thermostatic bath. The time of equilibrium was estimated to be (80-90 minutes). The concentration of dye in supernatant is determined spectrophotometrically with UV-VIS spectrophotometer of CECIL CE-1021 type at the λ_{max} indicated in Table (3).

The amount of adsorbed dye is evaluated by the following equation:

× V (mg of dye/ g of adsorbent)............(5) $q_e = \frac{C_o - C_e}{M}$

Where C_o and C_e are the initial and equilibrium concentrations (mg/L) respectively and M is the mass of adsorbent (g), V is the volume of solution (L).

Kinetic study

Kinetic of the studied dyes on activated carbon is performed as follow: 0.05 g of the carbon is added into 100mL solution of the tested dye of certain initial concentration. Different samples are shacked (in 50% water-EtOH) for 10,20,30,40,50,60 and 70 minutes. The amounts of the adsorbed dye (q_t is calculated at time 10-70 minutes and the value of q_e is determined at 90 minutes) are determined spectro-photometrically and estimated by eq.(5).

Results and Discussion

All the adsorption experiments of the considered dyes from their aqueous solutions were achieved by batch method and by employing single solutions of the dye of interest. A range of concentrations of the tested dyes were used for the construction of calibration curves at the maximum wavelength (λ_{max}) of each dye depending on the Beers law. The calibration curves were used for the estimation of the unbound dye concentration in the supernatant, while the amount of the adsorbed dye was determined by difference.

Effect of contact time

A series of experiments were carried out in order to optimize the time required to reach equilibrium. The results obtained at three different pHs are shown in Figure (1 and 2) for the dyes NBAR and MBAR respectively.

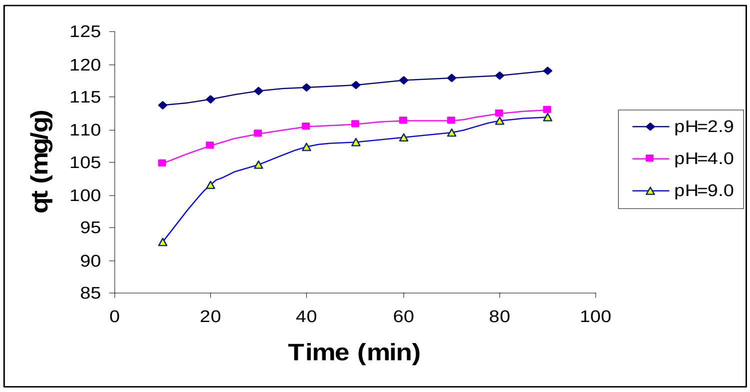


Figure (1): Effect of contact time of the removal of NBAR dye of various pHs.

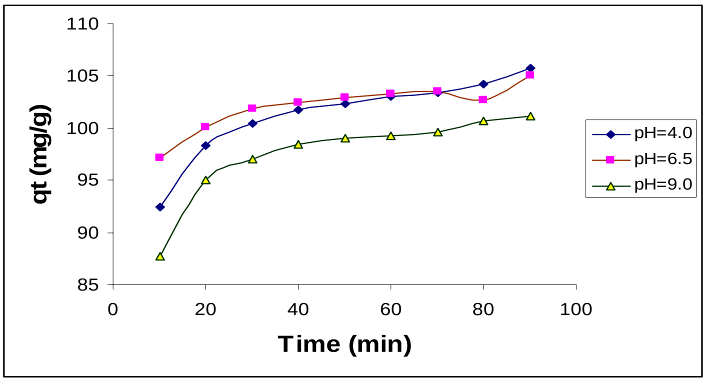


Figure (2): Effect of contact time of the removal of MBAR dye at different pHs.

The results of Figures 1 and 2 show that the extent of uptake level of the dyes increases as contact time increase. The removal of dye by adsorption process proceeded in two stage; an initial rapid increase in the first ten minutes of contact time being very sharp, and become slower and the uptake rate gradually decreases with the increase of contact time. The adsorption approached maximum and reached equilibrium within about 90 minutes for both of the dyes considered and at all the pHs indicated. At this time (90 minutes), the thermodynamic factors were calculated. The kinetic study is performed within the range of (10-70) minutes where the adsorption process is slow enough and the amount of adsorbed dye could be followed and estimated.

Effect of pH

The role of surface chemistry of CAC considered on the adsorbent capacity of the studied dyes could be understood by investigating the initial pH of the aqueous medium of the dyes. This may affect the uptake level of adsorbate in an adsorption process since the nature of both adsorbate and adsorbent could vary by changing the pH.

In this study, the effect of pH on adsorption of the studied dyes on CAC was examined in the acid (pH=4) and basic (pH=9) medium in addition to the natural pH of the dye solution (pH of MBAR = 6.5 and NBAR = 2.9). The experiments were carried out at the dye initial concentrations of 60 and 67 mg/L for the MBAR and NBAR dyes respectively. 0.05 g of the adsorbent is added into 100 mL of the dye solution at 25^o C. The results obtained showed that, the adsorption capacity (q_e) of both dyes decreased with increasing pH and showed similar adsorption pattern.

The results showed that, the maximum removal of dyes with CAC was observed at the lower pH values when the negative charge on the carbon surface is highly reduced due to the excess of protons present in solutions. The amount of MBAR dye adsorbed at equilibrium is increased from 101.137 to 105.07 and to 105.754 mg/g with decreasing the pH from 9 to 6 (natural pH of dye in 50% EtOH-H_2O solvent) and to 4 respectively, while the amount of NBAR dye is increased from 111.92 to 113.04 and then to 118.96 mg/g with the decrease of pH from 9 to 4 and to 2.9 (natural pH of dye in 50% EtOH-H_2O solvent) respectively. The kinetic and equilibrium studies, due to this variation in pH, were carried out at different pH conditions.

Equilibrium study

In order to evaluate the efficiency of the removal process of dyes by CAC, thermodynamic parameters including ΔG° ($kJ.mol^{-1}$), ΔH° ($kJ.mol^{-1}$) and ΔS° ($J.mol^{-1}.K^{-1}$) were calculated by applying the following of equation:

$$\ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad \text{………} \ (6)$$

$$K_d = q_e \ / \ C_e \quad \text{……….}(7)$$

$$\Delta G^o = -RT \ln K_d \quad \text{……….} \ (8)$$

Where K_d is the adsorption distribution coefficient, C_e is the concentration (mg/L) of remained dye in the solution at equilibrium, R is the universal gas constant (8.314 J mol^{-1}. K^{-1}) and T is the absolute temperature which lies in the range (298-338C°) in this study. The ΔG° value indicates the degree of spontaneity of adsorption process and the higher negative value reflects more energetically favorable adsorption. The ΔH^o and ΔS^o values are obtained from the slope and intercept of the plot of $\ln K_d$ versus 1/T as shown in Figure (3). The values of correlation coefficients (R^2) at different pHs and the thermodynamics parameters are given in Table (4).

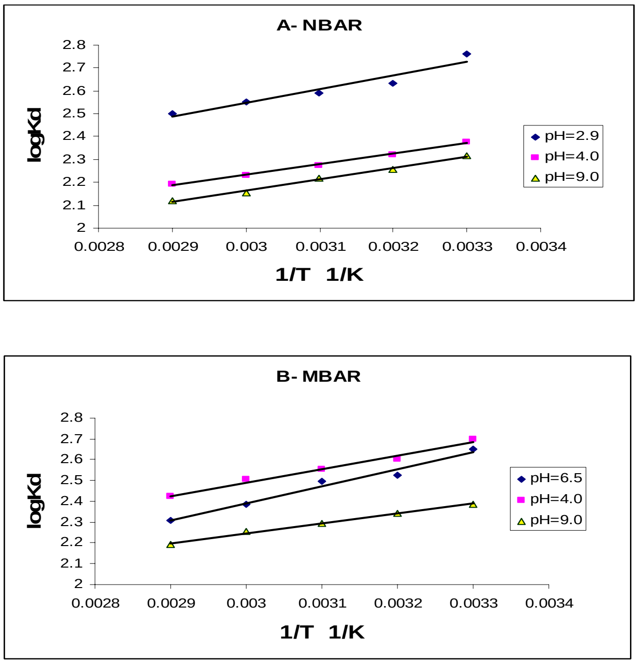


Figure (3): The application of eq (6) to calculate the thermodynamic parameters of: A- NBAR dye B- MBAR dye

Table (4): Thermodynamic parameters of the studied dyes on CAC

Dye	pH	-ΔG°/ (kJ.mol^{-1}) at					-ΔH°/ kJ mol^{-1}	ΔS°/ J. mol^{-1}.K^{-1}	R^2
		298/K	303/K	318/K	328/K	338/K			
NBAR	2.9	6.841	6.749	6.854	6.957	7.028	5.021	6.115	0.9332
	4.0	5.892	5.953	6.010	6.086	6.157	3.857	6.990	0.9950
	9.0	5.738	5.778	5.879	5.852	5.981	4.090	5.723	0.9919
MBAR	4.0	6.683	6.665	6.750	6.831	6.807	5.387	4.549	0.9844
	6.5	6.551	6.463	6.597	6.509	6.493	6.692	-0.195	0.9776
	9.0	5.914	6.003	6.066	6.146	6.158	4.007	6.642	0.9946

According to the results listed in Table (4), the negative value of ΔG^o indicates that, the adsorption process of both dyes occurred spontaneously. The negative values of ΔH° confirm the exothermic nature of adsorption.

The negative value of ΔS^o of MBAR dye at pH= 6.5 (the natural pH) suggests favorable adsorption (24). The positive values of entropy characterize the increased disorder of the system, due to loss of the water which surrounding the dye molecules at the sorption on activated carbon. This could suggest that, the driving force of the adsorption process is by entropy effect. This observation was demonstrated by other experimental results (16).

Kinetic Study

In this study, the pseudo first and pseudo second order kinetic models (eqs (2) and (4) respectively) are used to test the experimental data of adsorption in order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction.

The application of the pseudo first order equation on the data obtained at the three different pHs indicated below gave the results listed in Table (5) and shown in Figure (4).

Table (5): First order kinetic rate constant, calculated and experimental q_e values and R^2 obtained at various pHs values.

Dye	pH	K/min^{-1}	q_e calc/ mg/ g	q_e exp/ mg/ g	R^2
NBAR	2.9	0.0257	6.984	118.960	0.9926
	4.0	0.0271	9.162	113.040	0.9555
	9.0	0.0333	21.498	111.920	0.9630
MBAR	4.0	0.0270	13.807	105.754	0.9457
	6.5	0.0260	8.435	105.070	0.9460
	9.0	0.0343	13.387	101.137	0.9169

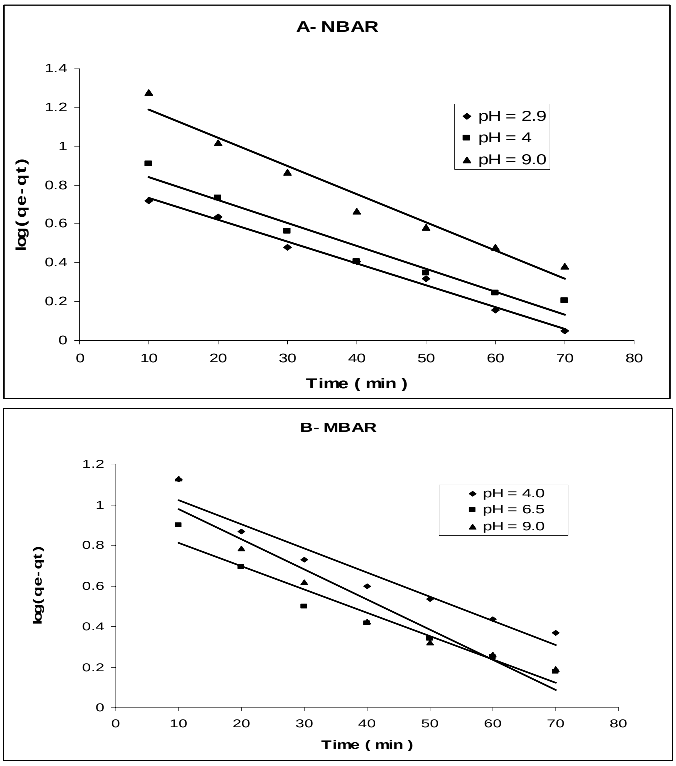


Figure (4): The plot of log (qe-qt) versus time at different pHs for: A- NBAR dye B- MBAR dye

The results of Table (5) and Figure (4) show that, although the correlation coefficients obtained could be acceptable to some extent, the theoretical (q_e cal) values were lower than the experimentally determined ones. In addition, the applicability of first order reaction is just fit over certain period of time and not to the whole range of contact time. This time limited applications of the Lagergreen model was mentioned in the scientific literature (10,23,25) . Therefore these studied systems could not be considered as a first order reaction.

When the pseudo second order kinetic model is applied (eq.(4), the plot of t/q_t versus time gave linear relationships, from which the calculated value q_e and k_2 are determined from the slope and intercept in each case. The results obtained are given in Table (6) and shown in Figure (5).

Table (6): the second order kinetic rate constants, q_e calc and q_e exp and R^2 values at different pHs

Dye	pH	k_2 g.mg^{-1}.min^{-1}	q_e calc mg/ g	$q_e$exp mg/g	R^2
NBAR	2.9	0.0141	119.040	118.960	0.9999
	4.0	0.0111	112.360	113.040	0.9998
	9.0	0.0040	112.360	111.920	0.9999
MBAR	4.0	0.0052	105.263	105.754	0.9998
	6.5	0.0119	104.263	105.070	0.9999
	9.0	0.0067	102.040	101.137	0.9997

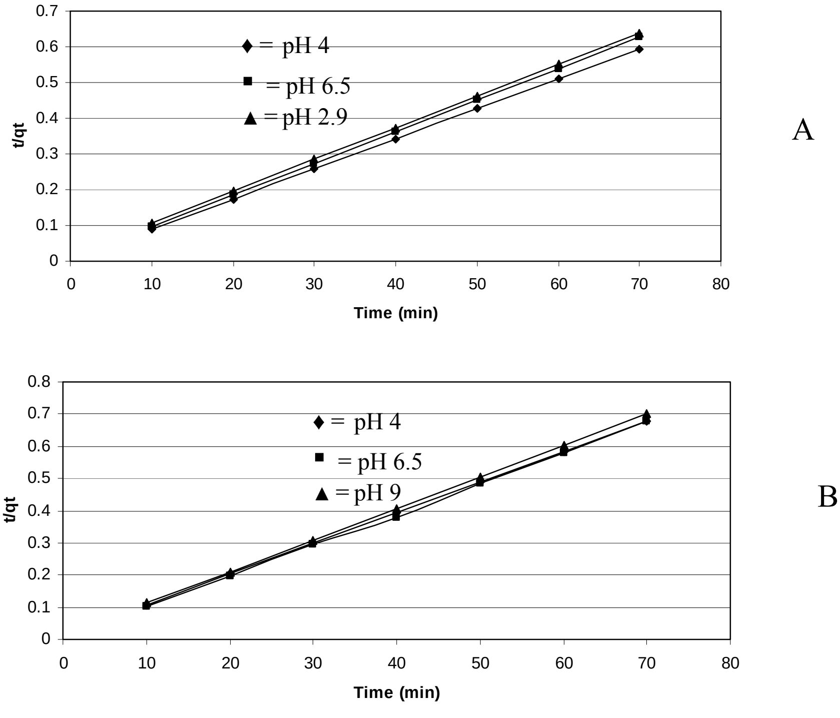


Figure (5): The plot of t/qt versus time at different pHs for:
A. NBAR dye B. MBAR dye

The results listed in Table (6) indicate that, the second order model shows satisfactory fit with the experimental data of the studied systems with high correlation coefficients. The calculated q_e values also agreed very well with the experimental q_e values. These results suggest that each of the adsorption experiments is a second order model (16,26).

Conclusion

Two dyes, derived from substituted benzothiozoles and resorcinol, are synthesized in this study. The removal of these dyes from their aqueous solutions by adsorption on CAC is conducted. The effect of contact time at different pH solution is determined. The results showed sharp increase in the uptake level in the first 10 minutes. The rate of adsorption is then decreased and reached equilibrium within 90 minutes for both dyes.

Comparison of adsorption capacities is carried out at different pHs. It was found that, the removal capacity of the dyes is higher in the acidic medium.

The thermodynamic parameters of the adsorption system are estimated in the range of 298-338 K and at different pHs. The obtained results showed that, the adsorption could occur spontaneously and is exothermic in nature. The values of $\Delta S°$ gave an indication to the increase in the disorder of the considered system and suggested that, the adsorption process could be driven by entropy change.

The results of the application of two kinetic models explained that, the pseudo second order is better fit the experimental data of the adsorption system. This conclusion is deduced by the values of R^2 of the straight lines obtained as well as the consistency between the calculated and experimental values of q_e.

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