Thermodynamic and Kinetic Study of 6-methoxy benzthiazole azo- ß-naphthole Dye Adsorption by Activated Carbon

Emad A. S. Al-Hyali[1], Noor .h.m.saeed[1] , Ibrahim A.AL-Jarjari[2]

[1] *Chemistry Dept., College of Education, University of Mosul, IRAQ*

[2] *Chemistry Dept., College of Education, University of Dohok, IRAQ*

(Received: 8 / 6 / 2011 ---- Accepted: 6 / 2 / 2012)

Abstract

A commercial activated carbon was used for the adsorption of azo dye from aqueous solution employing batch method. This dye was synthesized in our laboratory from the reaction of 6-methoxy-2-amino-benzothiazole and ß-naphthole 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 dye adsorbed onto activated carbon is 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, Benzothiazoles

Introduction

Benzothiazoles is a bicylic ring system with multiple applications. Its use started in the 1950s when a number of 2-amino Benzothiazole (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 [(1)]. The benzothiazole 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 [(1)] as intermediates for agro-chemical drugs and dyes. They were showed antitumor 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. One of the most popular Uses of this substance (2-ABT) is as a starting material for the preparation of Various azo dyes and shiff bases when attached to substituted aromatic compound and benzaldehyde respectively . The synthesized compounds were Found to be stable and beneficial for different applications. 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 [(2)].

During the dying process, it was estimated that, (10-25) % of dye are lost in the effluent [(3-4)]. Since some dyes and their biodegration produests are toxic and carcinogenic, their disposal into wastewater without advanced treatment causes environmental problems and damages the ecosystem [(5)]. Therefore, their removal became a vital task.

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)].

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 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)].

The dye considered in this study. It was derived from the reaction of 6-Methoxy-2-amino benzothiazole with ß-naphthole via diazonium ion.

In this study, the capacity of commercial type of activated carbon (CAC) to remove the dye, derived from 2-ABT and ß-naphthole, 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

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:

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

Where q_e and q_t are the amounts of adsorbed dye on the commercial activated carbon 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:

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

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**.**

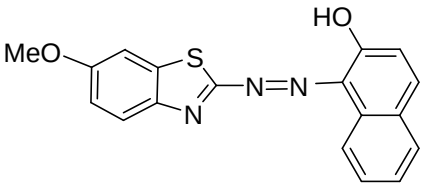
Experimental

Materials and methods

Dye characterization

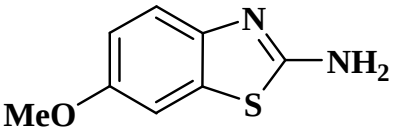
The dye used in this study is derived from 2-amino-6-methoxy benzothiazole which was allowed to react with ß-naphthole via diazonium ion. Name and structure of the synthesized dye is shown in Table (1).

Table (1): Name and structure of the studied dye

Name and Abbrerition	Structure
6-methoxy bnzothiozol azo –ß- naphthol (6MBT- ßN)	

Synthesis of 2-amino-6 -methoxyBenzothiazole (2A6MBT) [21]

into a solution of (0.1 mole) of 4-methoxy aniline and (0.4 mole) of potassium thiocynate, (0.1 mole) of bromine dissolved in 100 mL of glacial acetic acid was added dropwise while keeping the temperature below (10°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 recrystallized from Ethanol solvent. The physical properties of the synthesized compounds are given in Table (2):



2A6MBT

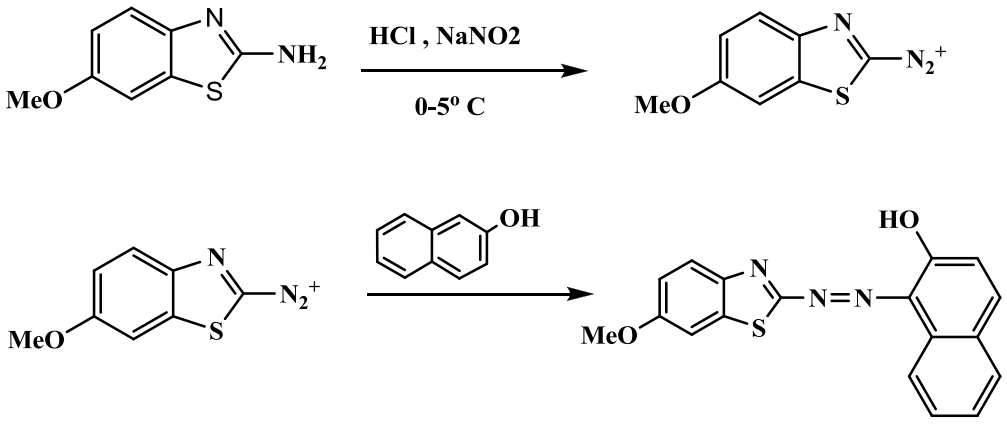
Table (2): the physical properties and IR spectroscopy data for the prepared Compounds

Comp	MP/ °C	solvent of recrystallization	IR (cm^{-1})		
			NH_2	C=N	C-S
2A6MBT	163-164 165*	Benzene	3500	1620	780

* Published M.P °C

Synthesis of 6-Methoxy benzthiazole azo- ß-naphthole (6MBT- ßN) dye

The synthesized compound mentioned in Table (2) was readily converted to the azo dye 6MBT- ßN, by the reaction with ß-naphthole 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:



6MBT- ßN

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

Table (3): characterization of the synthesized dye

Parameter	6MBT- ßN
Color	Reddish brown
pH in 50% Ethanol- Water	4.3
λ_{max} nm	509.5
M.P/ °C	229-231

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 Samples of 0.05 g of activated carbon were equilibrated with 100mL of solution containing certain amounts of the studied dye. 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 (298,308,318,328, and 338°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:

$$q_e = \frac{C_o - C_e}{M} \times V \quad \text{(mg of dye/ g of adsorbent)} \ldots\ldots\ldots\ldots (5)$$

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 dye 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 dye from its aqueous solutions were achieved by batch method. A range of concentrations of the tested dye were used for the construction of calibration curve at the maximum wavelength (λ_{max}) depending on the Beer lambert law. The calibration curve was 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 experiments were carried out in order to optimize equilibrium time . The results obtained at three different pHs are shown in Figure (1) for the dye 6MBT- ßN.

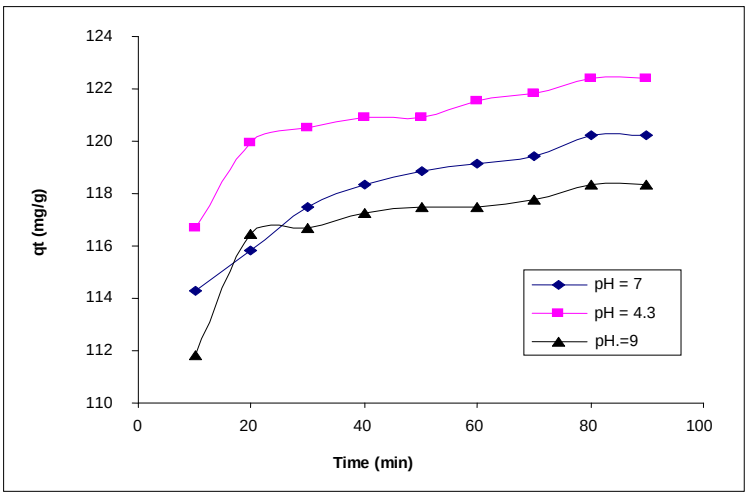


Figure (1): Effect of contact time of the removal of 6MBT- ßN dye of various pHs.

Figure 1 shows that the extent of uptake level of the dye 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 the studied dye 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 dye could be understood by investigating the initial pH of the aqueous medium of the dye. 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 dye on CAC was examined in the acid (natural pH of the dye solution pH=4.3) and basic (pH=9.0) medium in addition the neutral pH of the dye solution (pH = 7.0). The experiments were carried out at the dye initial concentration of (67) mg/L for **6MBT- ßN** dye. 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) decreased with increasing pH and showed similar adsorption pattern.

The maximum removal of dye 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 **6MBT- ßN** dye adsorbed at equilibrium is increased from 118.324 to 120.216 and to 22.378 mg/g with decreasing the pH from 9 to 7. The kinetic and equilibrium studies, due to this variation in pH, were carried out at different pH conditions.

Thermodynamic Stady

In order to evaluate the efficiency of the removal process of dye 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:

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

$$K_d = q_e / C_e \quad \ldots\ldots\ldots (7)$$

$$\Delta G^o = -RT \ln K_d \quad \ldots\ldots\ldots (8)$$

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 and ΔS^o values are obtained from the slope and intercept of the plot of lnK_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).

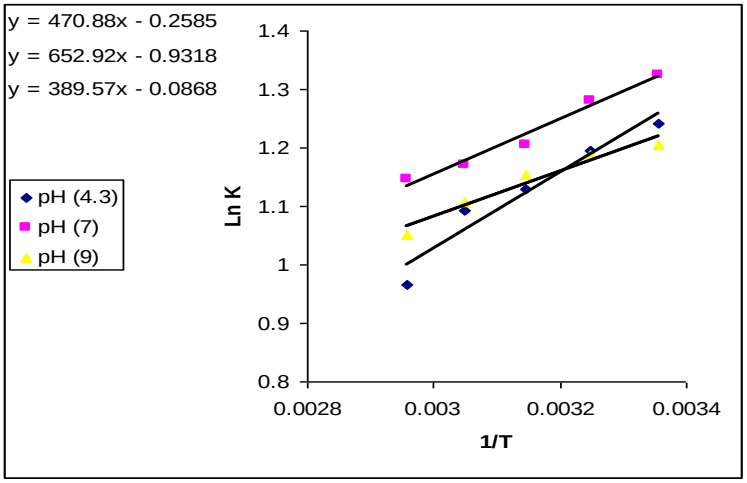


Figure (3): The application of eq (6) to calculate the thermodynamic parameters of: 6MBT-ßN **dye**

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

Dye	pH	-ΔG°/ (kJ.mol^{-1}) at					-ΔH/ kJ mol^{-1}	-ΔS°/ J. mol^{-1}.K^{-1}	R^2
		298/K	308/K	318/K	328/K	338/K			
6MBT-ßN	4.3	7.549	7.551.	7.334	7.349	7.413	8.912	4.17	0.9654
	7.0	7.080	7.052	6.879	6.858	6.255	12.495	17.14	0.9532
	9.0	6.798	7.000	7.022	6.953	6.792	7.416	1.14	0.9582

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

The negative values of ΔS^o of 6MBT-ßN dye at all pHs suggests favorable adsorption and represent an indication to the order increase of the studical system due to adsorption [24].

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
6MBT-ßN	4.3	0.034	6.123	122.380	0.9343
	7.0	0.033	7.923	120.216	0.9897
	9.0	0.035	5.445	118.324	0.8603

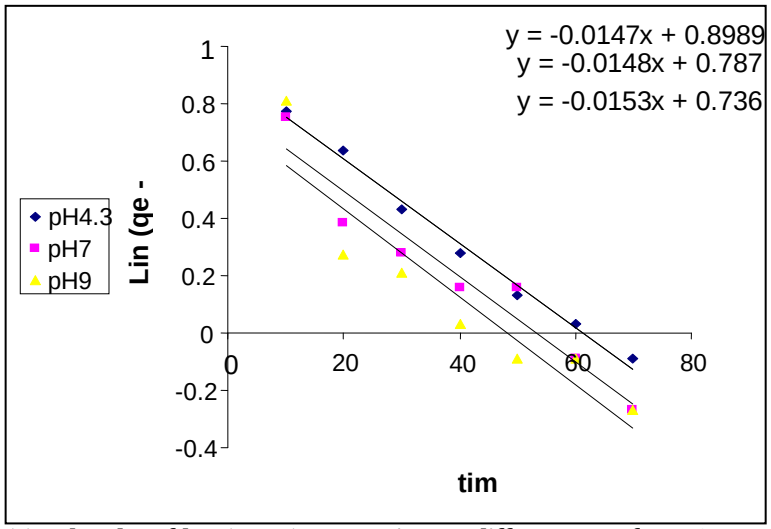


Figure (4): The plot of log (qe-qt) versus time at different pHs for: 6MBT-ßN **dye**

The results of Table (5) and Figure (4) show that, although the correlation coefficients obtained are week and 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
2A6MBT	4.3	0.0186	121.951	122.380	1
	7.0	0.0129	120.482	120.216	1
	9.0	0.0190	119.047	118.324	1

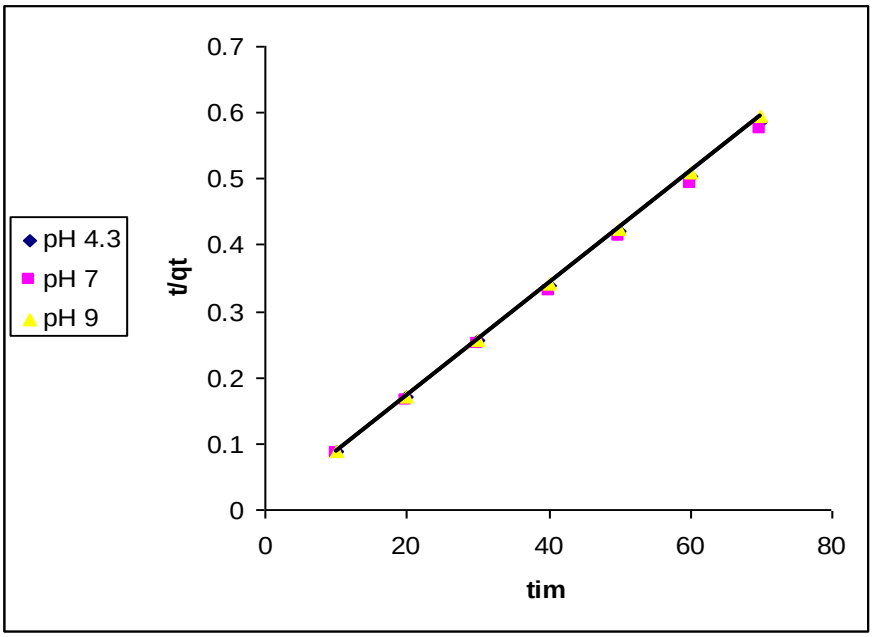


Figure (5): The plot of t/qt versus time at different pHs for 6MBT-ßN dye

The results listed in Table (6) indicate that, the application of 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, the adsorption of the studied system is a second order model [16,26].

Conclusion

In this study. The removal of 6MBT-ßN dye from its 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 the dye.

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 negative values of ΔS° gave an indication to the increase in the order of the considered system.

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

.

References

[1]. Arpana R.; Siddiqi, N.; Khan, S. A., Benzothiazole s: A new profile by biological activities, Indian Journal of Pharmaceutical Sciences, Jan, 2007, 10.

[2]. Gong, R.; Li M.; Yang, C.; Sun, Y.; Chen, J., Removal of cationic dyes from aqueous solution by adsorption on peanut hull**,** J. Hazard. Mater. B, 2005, 121, 247.

[3]. Young, L.; Jain, Y.U., Lingninase-Gatalyzed Decolorization, Water Res. 1997, 31, 1187.

[4]. Danis, U.; Gurases, S.; Canpolat, N., Removal of some azo dyes from wastewater using PAC as adsorbent, 1st International Workshop on Environmental Quality and Environmental Engineering in the Middle East Region, Konya, Turkey,1993.

[5]. Wang, S.; Boyjo, Y. M.; Choueib, A., A comparative study of dye removal using fly ash treatment by different methods, Water Res., 2002, 36, 2824.

[6]. McKay, G.; Blair, H. S.; Gardner J. K., Adsorption of dyes on chitin: Equilibrium study, J. Appl. Polym. Sci., 1982, 27, 3043.

[7]. Barton, S.S., The adsorption of methylene blue on active carbon, Carbon, 1987, 25, 343.

[8]. Karthikeyan, J., A study on color removal from textile dye wastes by chemical treatment, Ph.D thesis, IIT Kanpur, India.

[9]. Karthikeyan, J., Removal of color from industrial effluents, pollution management in industries, Environmental publications, Karad, India, 1997.

[10]. Eren, Z.; Acar, F. N., Adsorption of reactive blacks from an aqueous solution : Equilibrium and kinetic studies, Desalination, 2006, 194, 1.

[11]. EL-Geundi, M.S., Homogenous surface diffusion model for the adsorption of basic dyestuffs onto natural clay in batch adsorbers, Adsor. Sci. Technol.1991, 8217.

[12]. Malik, P.K., Use of activated carbon prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36, Dyes and Pigments, 2003 56, 239.

[13]. Ponnusami, V.; Aravindhan, R.; Karthik N.; Ramadoss, R. G.; Srivastva, S.N., Adsorption of methylene blue onto gulmharplant leaf powder, Equilibrium Kinetic and Thermodynamic Analysis, J., Environ. Protec. Sci., 2009, 3, 1.

[14]. Hameed, B.H., Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent J. Hazard. Mater., 2009, 162, 344.

[15].Yasin, Y.; Hussein, M. Z.; Ahmed, F. H., Adsorption of methylene blue onto treated activated carbon, The Malaysian Journal of Analytical Science, 2007, 11, 400.

[16]. Suten, D.; Bilba, D., Equilibrium and kinetic study of reactive dye Brilliant Red HE-3B Adsorption by activated charcoal, Acta Chim. Solv., 2005, 52, 73.

[17]. Hameed, B.H., Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, J. Hazard. Mater., 2009, 161, 753.

[18]. Ahmad, A.A.; Hameed, B.H.; Aziz, N., Adsorption of direct dye on palm as: Kinetic and equilibrium modeling, J. Hazard. Mater., 2007, 141, 70.

[19]. Ho, Y.S., Review of second order models for adsorption system, J. Hazard. Mater. B, 2006, 136, 681.

[20]. Eren, Z.; and Acar, F.N., Equilibrium and kinetic mechanism for reactive black 5 sorption onto high lime soma flay ash, J. Hazard. Mater., 2007, 143, 230.

[21]. Wisch, S. C., Derivatives of 2-amino-6-methoxybenzothiazole, J. Am. Chem. Soc., 1949, 71, 3417.

[22]. Vogel, A text book of practical organic chemistry, 3rd ed., Longmans, Green and Co. Ltd, London1964, 622.

[23].Ncibi, M.C.; Mahjoub, B.; Seffen, M., Adsorptive removal of textile reactive dye using posidonia oceanica (L.) Fibrous biomas, Int. J. Environ. Sci. Tech., 2007, 4, 433.

[24].Smith, J. M., and Van Ness, H.C., Introduction to chemical engineering thermodynamics, 4th ed., Mc-Graw Hill, Singapore.
[25].Aksu, Z.; Donmez, G., A comparative study on the bisorption characteristics of some yeasts for removal blue reactive dye, Chemosphere, 2003, 50, 1075.
[26].Admn, A., Adsorptive removal of reactive azo dyes using industrial residue, M.Sc. Thesis, Addis Ababa Univ., 2008.

الملخص

تضمن البحث استخدام نوع من الكاربون المنشط التجاري لامتزاز احدى أصباغ الازو من محاليلها المائية بطريقة الوجبة الواحدة. حضرت هذه الصبغة في مختبراتنا من تفاعل مشتقات أل ،2–امينو بنزوثايوزول مع البيتانفثول 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. إشارت 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.