



Adsorption of the Sudan dye (III) in methanol using activated carbon

Samer S. Abu-Alrub^a, Mohammad W. Amer^{b*} and Saad A. Alkahtani^a

^a Faculty of Pharmacy, Najran University, Najran 61441, Saudi Arabia

^b Scientific Research Centre, Royal Scientific Society, Amman 11941, Jordan

* Corresponding author e-mail: mohammad.amer@rss.jo , mohadamer@gmail.com

ABSTRACT

A simple method is used for the study of adsorption of Sudan (III) dye using activated carbon. Activated carbon was found to be effective for taking up the dye, with maximum capacity of 7.8 mg/g at 40 °C under the following experimental conditions: mass of carbon 0.2 g, volume of solution 50 mL, dye concentration range 10–50 mg/L and particle diameter 300-500 μm. The adsorption data of Sudan (III) were modeled using Langmuir, Freundlich and Temkin isotherms. The model parameters were found to be 0.507 (K_L), 7.8 mg/g (q_m), 0.8557 (R^2) for the Langmuir isotherm and 1.37 (n), and 0.8620 (R^2) for Freundlich isotherm and 2.22 (A), 4.51 (B) and 0.9402 (R^2) for Temkin isotherm. The activated carbon was proved to be an excellent absorbent for Sudan (III) as indicated by the distribution coefficient value (9.9 L/g) obtained under the conditions 10 mg/L dye, 0.2 g carbon mass, 3 days agitation, and pH 8.5.

Thermodynamic studies indicated that Sudan (III) adsorption onto activated carbon was an exothermic process at 293, 303 and 313 K. The values of free Gibbs energy (ΔG) were -4.8, -4.9 and -5.0 KJ/mol respectively. The enthalpy of adsorption was -2.4 KJ, indicating a physisorption process. The process occurred with positive entropy. Pseudo-second-order kinetic model was found to best represent the kinetic data considering closer values of experimental and calculated of q_e obtained for Sudan (III) dye.

Indexing terms/Keywords

Activated carbon; Sudan Dye; Adsorption; Isotherm models; Thermodynamics; Kinetics

Academic Discipline And Sub-Disciplines

Environmental Chemistry, Physical Chemistry, Materials and Adsorption Sciences

SUBJECT CLASSIFICATION

Chemistry

TYPE (METHOD/APPROACH)

Experimental study

Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Chemistry

Vol. 10, No. 10

editorjaconline@gmail.com

www.cirjac.com

1. INTRODUCTION

Sudan dye (III) is classified as synthetic azo-dye (Fig. 1). It has many industrial and scientific applications such as coloring of fuel and staining for microscopy [1, 2]. Sudan dye is used in plastics, oil and waxes [3] due to its low cost and availability [4]. The International Agency of Research on cancer (IARC) has classified Sudan dyes as class 3 carcinogens [5, 6] which has stimulated research into its determination. Analytical techniques have shown that Sudan dyes are present in measurable and dangerous concentrations in many foodstuffs. In some European countries, Sudan dyes have been found in food products such as chili powder, fish sauce, noodle soup, Worcester sauce and pizza [7].

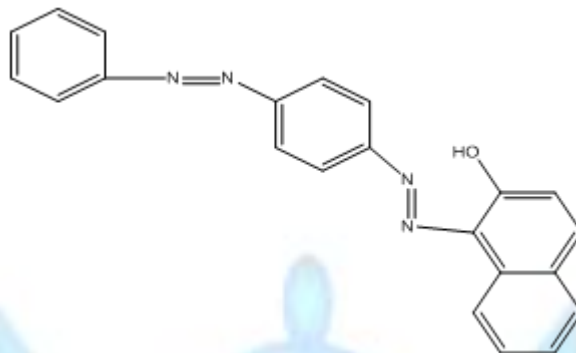


Fig. 1: Chemical structure of Sudan (III)

Analytical techniques have been used for the determination of Sudan dyes include: solid-phase spectrophotometry [8, 9, 10], HPLC-Fluorimetry [11], thin layer chromatography [12], capillary electrophoresis [13], HPLC coupled with photo-diode array [14], UV-visible spectrometry [15], chemiluminescence [16] and MS [17, 18, 19, 20, 21, 22].

The seriousness of the problem has aroused interest in techniques for removing Sudan dye from solution. Adsorption on activated carbon has long been used to a significant extent for the removal of dissolved organic and dyes from wastes and polluted waters [23]. Activated carbon is an effective adsorbent due to its extensive porosity and very large available surface area for adsorption [23]. It would therefore be useful to investigate the adsorption of Sudan dyes from solution on activated carbon.

In this work, the adsorption of Sudan dye (III) in methanol solution using activated carbon was studied as a model system to demonstrate the usefulness of activated carbon in the removal of this important carcinogen from solution. The effects of different experimental conditions were also investigated.

2. EXPERIMENTAL

2.1. Materials

All materials used in this work were analytical grade reagents and used as received without any further purification. The Sudan (III) dye was obtained from Lobal Chemie (India), and methanol from Sigma-Aldrich. Activated carbon was purchased from Nen Tech Ltd (UK) with particle diameter = 300 - 500 μ m.

2.2. Apparatus

Absorption spectra were obtained using a double beam UV-vis spectrophotometer (SP-300, Optima, Japan) and pH measurements were carried out with a Lovibond pH meter (Germany). A wise Bath shaker (Daihan Scientific, Korea) was used in this work.

2.3 Procedure

Adsorption of Sudan (III) dye

The adsorption properties of the dye were studied using the batch method. A known mass of activated carbon (300-500 μ m) particle diameter was contacted with 50 mL dye solution and the mixture was agitated for a known time. The final dye concentration in the solution and the amount adsorbed by the activated carbon could then be calculated by difference, the initial dye concentration in the solution being known. The effects of carbon mass, dye concentration, solution acidity, ionic strength, and temperature on Sudan (III) dye adsorption were all investigated as outlined below.

The concentrations of Sudan (III) remaining in solution were determined spectrophotometrically, 510nm, the wavelength at the maximum absorption of the dye (λ_{max}). Linear calibration curve was obtained using a series of standard samples in the concentration range of 1.0-8.0 mg L⁻¹. A linear calibration graph was obtained with correlation coefficient squared (R^2) = 0.9887. The adsorption was expressed in terms of the distribution coefficient K_d defined as the equilibrium adsorption capacity divided by the equilibrium concentration.



2.3.1 Effect of contact time

The effect of contact time between the dye and the activated carbon was investigated. Different dye solutions were agitated for different time periods (1-8 days). All other variables were kept constant as follows: mass of carbon = 0.2g, temperature = 25 °C, volume of solution = 50 ml, initial concentration 35 mg/L, pH = 8.5 and carbon particle diameter = 300 - 500µm.

2.3.2 Effect of adsorbent mass on dye removal

Different masses of activated carbon (0.10-0.35 g) were mixed with 50-mL of 35 mg/L dye solution. The mixtures were agitated for 3 days. The following variables were maintained constant: pH = 8.5, temperature = 25 °C, volume of solution = 50 mL, and carbon particle diameter = 300-500 µm.

2.3.3 Adsorption isotherm determination

The adsorption isotherm of Sudan (III) on activated carbon was recorded at different temperatures. A fixed amount of activated carbon was added to set of dye solutions (10-50 mg/L). The mixtures were agitated for a time which earlier experiments (section 2.3.1) had shown was sufficient to reach equilibrium. The following variables were maintained constant: agitation time = 3 days, mass of carbon = 0.2 g, temperature = 25 °C, volume of solution = 50 mL, pH = 8.5 and particle diameter = 300 - 500µm.

2.3.4 Effect of ionic strength

Solutions of Sudan (III) of variable ionic strengths (0.5-3.0 mol/L NaCl) were prepared and agitated with activated carbon for 3 days. The remaining dye concentration in each solution was determined. The following variables were maintained: mass of carbon = 0.2 g, temperature = 25 °C, volume of solution = 50 mL, initial concentration 35 mg/L, pH=8.5 and particle diameter = 300 – 500µm.

2.3.5 Effect of solution pH

Different solutions of Sudan (III) dye were prepared at different pH values (1, 3, 10, and 12) were measured using the pH meter which was adjusted using three standards of buffer solution (pH 4, 7, 10). The mixtures were carefully agitated for 3 days. The following variables were maintained constant at: mass of carbon = 0.2 g, temperature = 25 °C, volume of solution = 50 mL, contact time = 3 days, initial concentration 35 mg/L, and particle diameter = 300–500 µm.

2.3.6 Effect of temperature

Adsorption isotherm of Sudan (III) dye was recorded at different temperatures (20, 30, and 40 °C). The following variables were maintained: agitation time = 3 days, mass of carbon = 0.2 g, initial concentration= 35 mg/L, temperature = 25 °C, volume of solution = 50 mL, pH=8.5 and particle diameter = 300 - 500µm.

3. RESULTS AND DISCUSSION

Adsorption properties of the activated carbon

3.1 The effect of contact time

Adsorption of dye by 0.2g of activated carbon was determined over 1-8 days (section 2.3.1). The results of these experiments are shown in Fig. 2.

As the contact time increased, the adsorption of Sudan (III) increased to become nearly constant for times ≥ 3 days. The adsorption of dye by the activated carbon had almost reached equilibrium after 3 days; the increases in K_d after this time corresponded to only small changes in the amount of dye adsorbed.

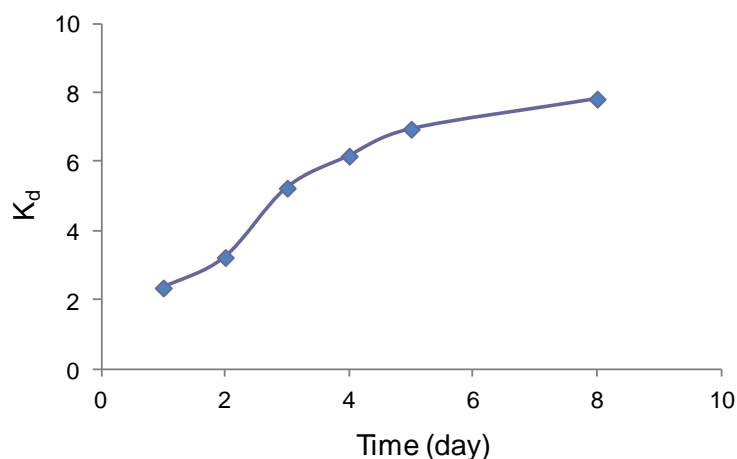


Fig. 2: Dye uptake by the activated carbon as a function of contact time

3.2. Effect of carbon mass on dye uptake

The effect of varying mass of activated carbon (0.10-0.35) on dye uptake is illustrated in Fig. 3.

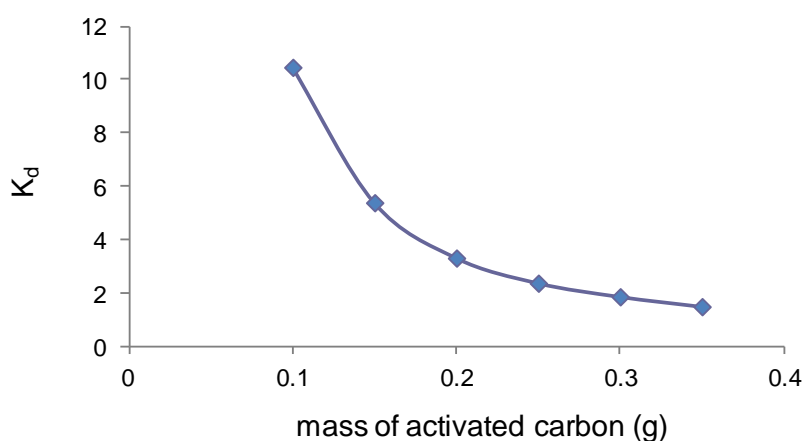


Fig. 3: Dye uptake as a function of carbon weight

The distribution value decreased markedly with increasing carbon mass from 0.1 to 0.2 g and changed more slowly to higher masses. Accordingly, the optimum mass of activated carbon was maintained at 0.2 g.

3.3. Effect of dye concentration (adsorption isotherm)

Effect of dye adsorption was studied at different initial concentrations of Sudan (III) (10-50 mg/L) while keeping the other variables constant (see section 2.3.3). The distribution values were calculated at each concentration and are presented in Fig. 4.

The extent of Sudan (III) adsorption was studied over a wide concentration range (10-50 mg/L). The K_d value is decreased significantly as concentration increased, from 9.98 to 2.47 when the initial dye concentration increased from 10 to 50 mg/L. The value of K_d would be expected to be even larger than 9.98 at lower initial dye concentration because the remaining dye concentration (C_e) will be very small [24].

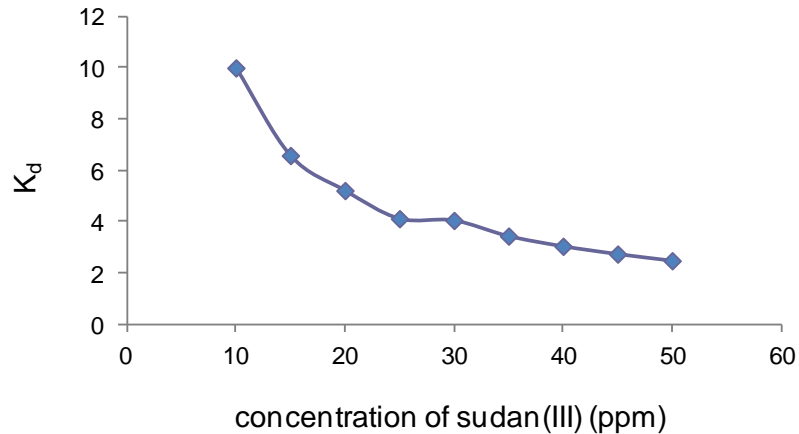


Fig. 4: Effect of concentration of dye on K_d

3.4. Effect of ionic strength on dye adsorption

The adsorption of Sudan (III) by activated carbon at different ionic strength values is presented in Fig. 5.

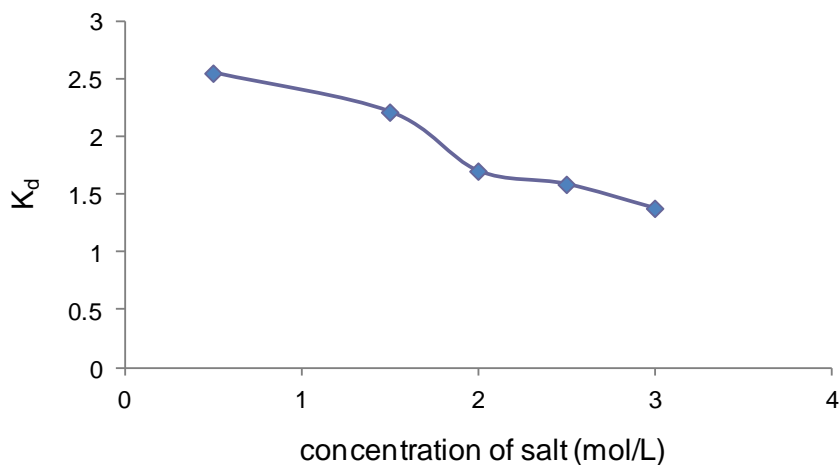


Fig. 5: Effect of solution ionic strength on Sudan (III) uptake

The adsorption of activated carbon decreased when more than 0.5M salt was introduced to the mixture. A number of kinds of intermolecular forces have been suggested to explain the aggregation between dye molecules in solutions. Various intermolecular forces (including van der Waals forces, ion-dipole forces, and dipole-dipole forces) which occur between dye molecules in solution can cause aggregation of the dye molecules. These attractive forces increase when salt is added to the dye solution and the increased aggregation inhibits adsorption at the carbon surface [24].

3.5. pH-dependence of dye sorption by activated carbon

The effect on dye uptake of varying pH values (1-12) is given in Fig. 6.

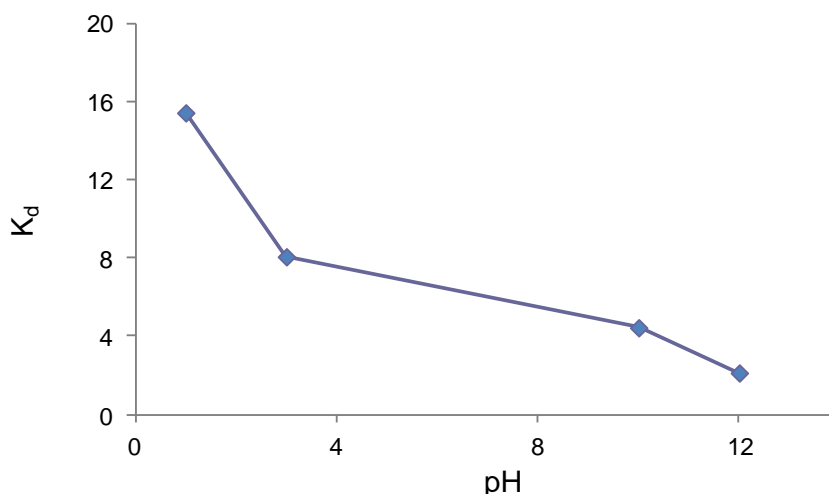


Fig. 6: Effect of solution pH on dye distribution value

The adsorption of Sudan (III) by activated carbon depended on the pH. The change in Sudan (III) uptake with solution pH can be explained by the following mechanisms:

- 1) At pH < 3, electrostatic interactions between the protonated surface of the activated carbon and negatively charged dye molecules, promoting adsorption.
- 2) Hydrophobic interactions between the activated carbon and the hydrophobic part of dye molecule. The large reduction in adsorption in a basic medium can be attributed to the electrostatic repulsion between the negatively charged activated carbon (due to adsorption of OH⁻ ions on the surface) and the deprotonated dye molecule [24].

3.6. Effect of temperature on dye adsorption

The adsorption isotherms were determined for the dye at different temperatures (20 °C, 30 °C, 40 °C) in the concentration range 10 – 50 mg/L. Adsorption results are presented in Fig. 7.

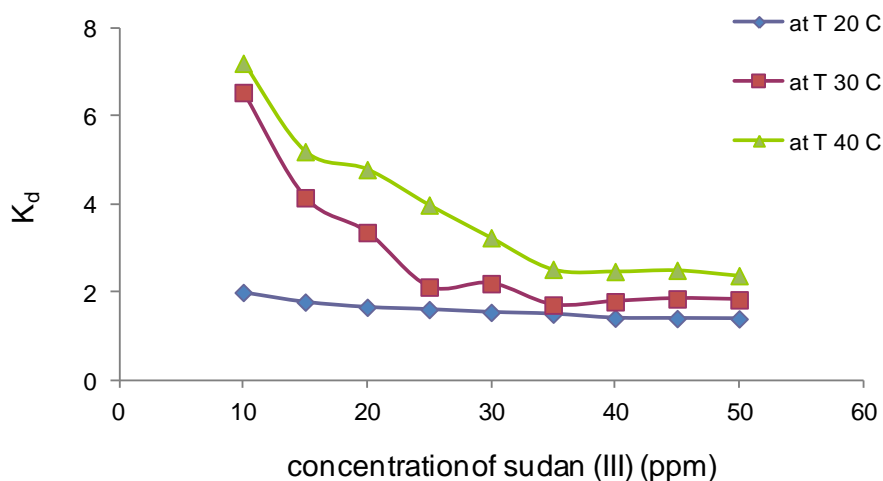


Fig. 7: Adsorption isotherms of dye on activated carbon at different temperatures

K_d of the dye increased with increasing temperature; indicating this is not physical adsorption. There must be chemical interaction between the activated carbon and the dye. But the temperature had a larger effect on K_d at lower concentration but a smaller effect at higher concentration. The high adsorption at higher temperature could be due to either increased penetration of dye inside micropores at higher temperatures or the creation of new active sites.

3.6.1. Analysis of adsorption isotherms by the Langmuir, Freundlich and Temkin models

The adsorption data were modeled using the Langmuir, Freundlich and Temkin isotherms. The Langmuir model (all adsorption sites assumed similar) was used to estimate the maximum adsorption capacity corresponding to the saturation of the activated carbon surface using the linearized form of Langmuir isotherms:

$$K_d = q_e/C_e = q_m K_L - K_L q_e \quad \dots \dots \dots (1)$$



Where K_d is the distribution coefficient, q_e is the amount adsorbed per gram of adsorbent at equilibrium, C_e are the concentration of adsorbate in the solution at equilibrium, q_m is the maximum adsorption capacity corresponding to complete saturation of the activated carbon surface, K_L is the Langmuir equilibrium constant. Therefore, a plot of (q_e / C_e) against (q_e) should be a straight line with slope = $- K_L$ and an intercept = $q_m K_L$ for Langmuir model.

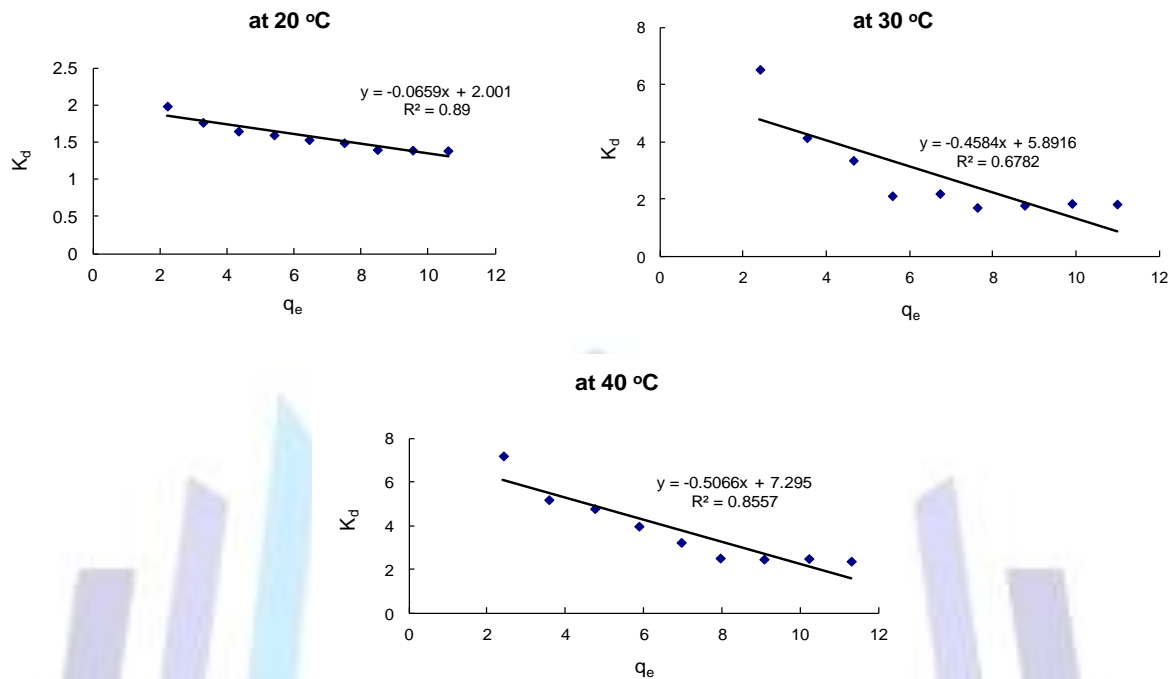


Fig. 8: Langmuir modeling of adsorption data at different temperatures

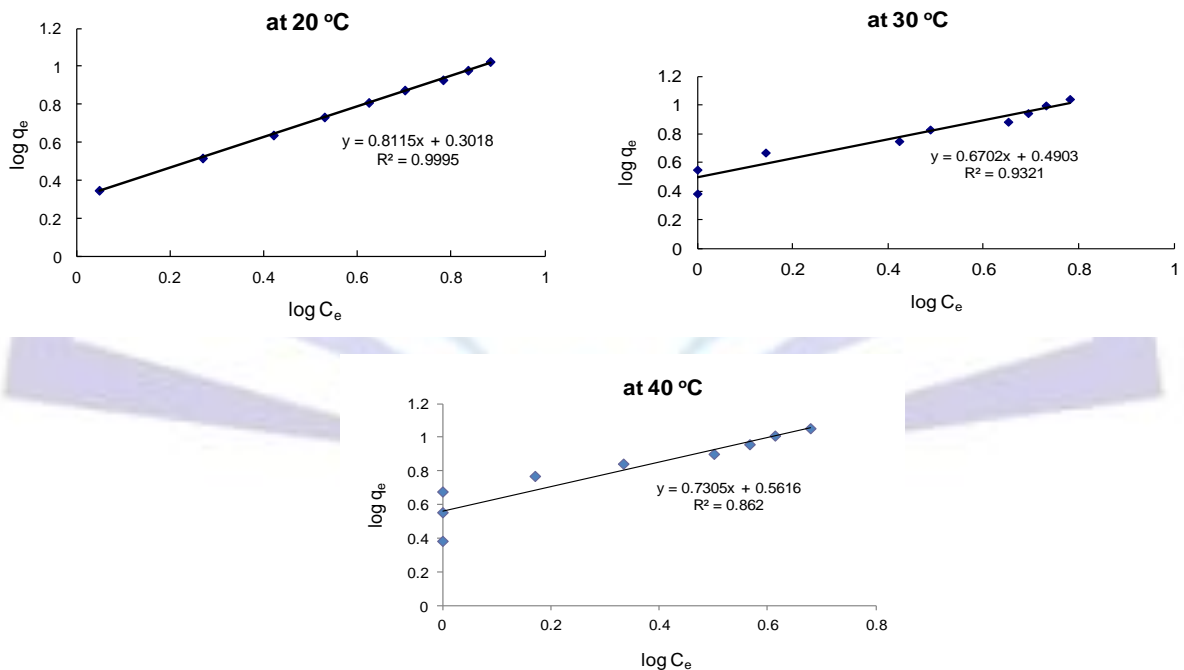


Fig. 9: Freundlich modeling of adsorption data at different temperatures

The Freundlich model (adsorption sites varying in their interaction with the sorbate) is an empirical equation used to estimate the adsorption capacity of the activated carbon for the dye the linearized form of the Freundlich isotherm:

$$\log q_e = \log K_F + 1/n \log C_e \dots\dots\dots (2)$$

A plot of $\log q_e$ versus $\log C_e$ gives a straight line with a slope of $1/n$ and intercept of $\log K_F$. Where K_F and n are the Freundlich constants. The value of n indicates the affinity of the dye towards the activated carbon [25].

The Temkin model gives useful information about adsorbate-adsorbate interactions. This model causes decrease in heat adsorption of the molecules in the layer and bonding energies and appears uniform distribution in the adsorption process [26]. This isotherm can be expressed with the following formula:

$$q_e = B \ln A + B \ln C_e \quad \dots\dots\dots (3)$$

In equation (3) q_e is the amount adsorbed per gram of adsorbent at equilibrium, A denotes Temkin constant used to examine adsorbate-adsorbate interaction and B is the constant related with adsorption heat. A and B can be determined from plot of q_e vs. $\ln C_e$. The models are presented in Figs. (8, 9 and 10).

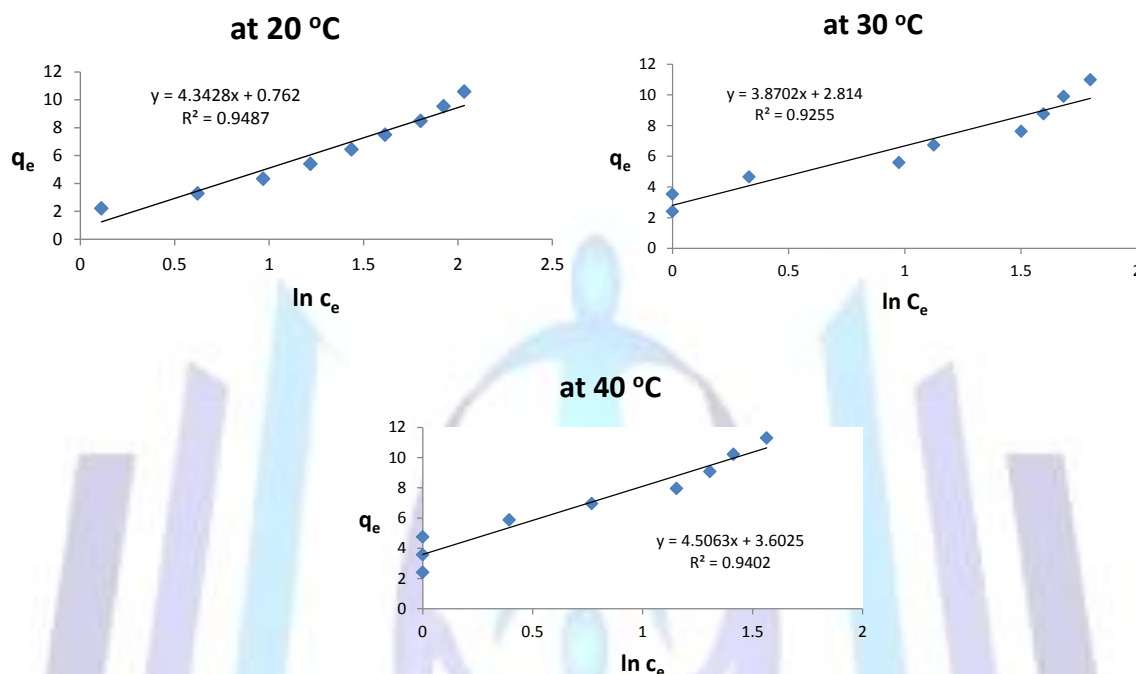


Fig. 10: Temkin modeling of adsorption data at different temperatures

The R^2 values indicated that the Freundlich model was a better fit for Sudan (III) adsorption on activated carbon than the Langmuir and Temkin model. For Langmuir model and at all temperatures, R^2 values were in the range 0.6782 – 0.8900 and for the Temkin model, R^2 values were in the range 0.9255 – 0.9487 while for the other model better R^2 values were larger, in the range: 0.8620-0.9995.

The parameters; q_m , K_L , n , K_F , A and B of adsorption isotherms were calculated from the intercepts and the slopes of the corresponding linear plots for dye adsorption onto the activated carbon at different temperatures. Values of these parameters with the corresponding least-squares fits (R^2) are given in Table 1 at optimum experimental conditions.

Table (1): Langmuir, Freundlich and Temkin parameters

Langmuir			Freundlich				Temkin			
T(°C)	R^2	K_L	T(°C)	R^2	K_F	n	T(°C)	R^2	A	B
20	0.8900	0.066	20	0.9995	0.302	1.23	20	0.9487	1.19	4.34
30	0.6782	0.458	30	0.9321	0.490	1.49	30	0.9255	2.07	3.87
40	0.8557	0.507	40	0.8620	0.562	1.37	40	0.9402	2.22	4.51

Consequently, it can be conclude that the type of sorption on the adsorbent is heterogeneous. There is a variation in the interaction between dye molecules and activated carbon for different adsorbing sites. This is as expected for activated carbon [25]. The n values for adsorption of Sudan (III) were all more than unity, which reflects the favorable adsorption of the dye over the studied temperatures (20-40 °C). The well-known large variation in the interaction energy sorbate molecules and activated carbon adsorbing sites, would also tend to make the values of n more than unity [25].

3.6.2. Thermodynamic parameters of adsorption

Thermodynamic parameters were determined using the distribution coefficient, K_d (q_e/C_e) which depends on temperature. The change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated with the adsorption of Sudan (III) were calculated using equations (4) and (5):



$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \dots\dots\dots(4)$$

where R is the universal gas constant (8.314 J/mol Kelvin), T is temperature (Kelvin) and K_d is the equilibrium constant.

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \dots\dots\dots(5)$$

According to the above equations, ΔH° and ΔS° functions can be calculated from the slope and intercept of the plot of $\ln K_d$ versus $1/T$; respectively. This is represented in Table 2 and in Fig. 11.

Table (2): Thermodynamic functions for the adsorption of Sudan (III) onto activated carbon

ΔH° (kJ/mol)	ΔS° (J/mol.K)	ΔG (kJ/mol)	
		303 K	313 K
-2.4	8.5	-4.9	-5

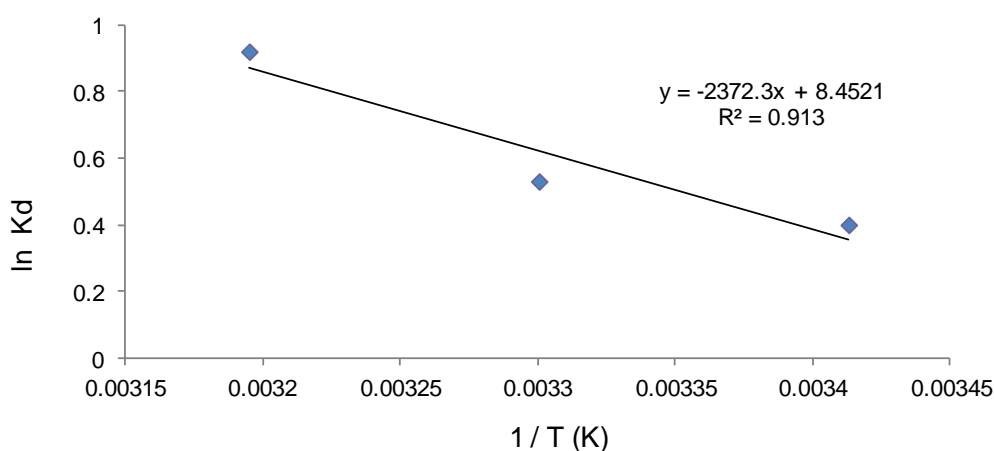


Fig. 11: Thermodynamics function

The adsorption process was exothermic for Sudan (III) as ΔH° was negative, which means that the dehydration energy is lower than the adsorption energy. The positive values of entropy for dye adsorption may be due to some structural changes in the adsorbate and adsorbent during the adsorption process from aqueous solution onto the adsorbent. In addition, positive value of ΔS° indicates the increasing randomness at the solid-liquid interface during the adsorption of dye on the adsorbent. The free Gibbs energy change calculated for adsorption of dye decreases as the temperatures increase, indicates that the interaction are thermodynamically favorable. We can conclude the adsorption of dye is spontaneous.

3.7. Adsorption kinetic models

In adsorption studies, kinetic models are applied to experimental data in order to obtain information about the mechanism and the rate of adsorption. By this way mass transfer, diffusion control, and chemical reaction mechanisms can be understood better. With this aim, pseudo-first- and pseudo-second-order reaction kinetics is commonly used [26].

3.7.1. Pseudo-first-order model

The linearized form of the pseudo-first order equation of Lagergren is generally expressed as follows:

$$\log [q_e - q_t] = \log [q_e] - [k_1/2.303]t \dots\dots\dots(6)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g). k_1 is the rate constant of pseudo first-order adsorption. The plot of $\log (q_e - q_t)$ versus t should give a linear relationship; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

Based on Table 3 and Fig. 12, the correlation coefficient R^2 were found to be low and the values of calculated adsorption capacities (q_e , calculated) were far much lower than experimental ones (q_e , experimental), suggesting that the adsorption process did not fit the pseudo-first order model.



Table (3): Kinetic parameters

Initial dye Concentration (mg/L)	q_e ; experimental (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1	q_e ; calculated (mg/g)	R^2	k_2	q_e ; calculated (mg/g)	R^2
35	8.16	9.21×10^{-3}	0.90	0.6921	1.43×10^{-4}	8.58	1.00

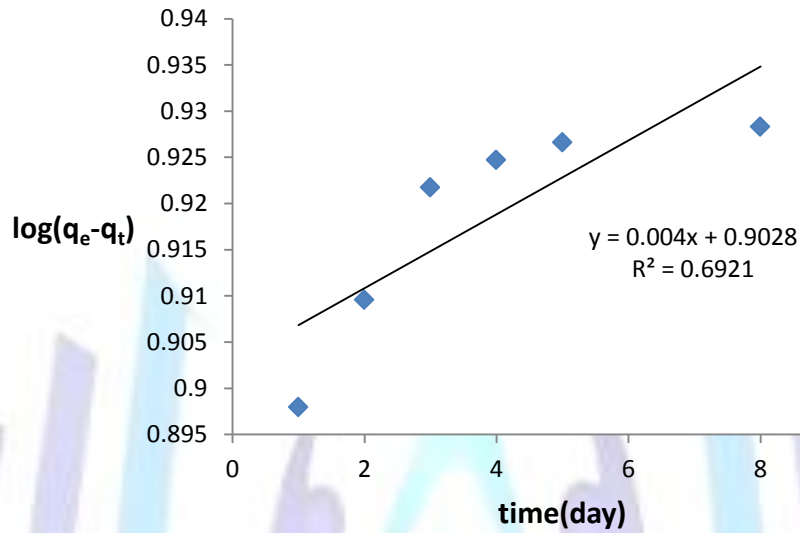


Fig. 12: Pseudo-first-order kinetic plots for adsorption of Sudan III by activated carbon

3.7.2. Pseudo-second-order model

The pseudo second order kinetic model is represented by the following linear equation:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \dots\dots\dots(7)$$

Where q_e , q_t , and t , have the same meaning as explained above. k_2 is the rate constants of pseudo second order sorption [g/mg.min]. If pseudo-second order kinetics is applicable, the plot of t/q_t against t should give a linear relationship; q_e and k_2 can be determined from the slope and intercept of the plot (Table 3, Fig. 13). The regression coefficient R^2 is found to be 1, and the calculated maximum adsorption capacity values of q_e -calculated which are quite close to the experimental values q_e -experimental for adsorption of Sudan III dye onto activated carbon indicate that the pseudo second order model fits with the kinetic data very well.

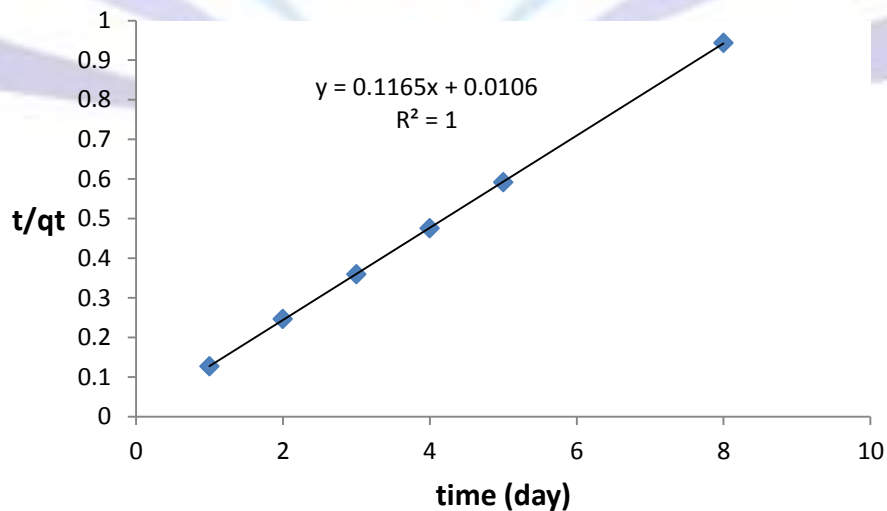


Fig. 13: Pseudo-second-order kinetic plots for adsorption of Sudan III by activated carbon



4. CONCLUSION

Activated carbon was found to be an effective adsorbent for Sudan (III) from solution. The maximum adsorption value of Sudan (III) was 7.8 mg/g. Adsorption of Sudan (III) decreased as mass of carbon increased and decreases with temperature. The process of Sudan (III) adsorption was found to be spontaneous at 20, 30, and 40°C. Adsorption of Sudan (III) on activated carbon was more favorable at acidic conditions. K_d value was 15.42 at pH 1. The adsorption of Sudan (III) increased as the NaCl content was decreased. Adsorption isotherms of the Sudan (III) on activated carbon were better fitted to the Freundlich equation than the Langmuir and Temkin equations. Accordingly, active sites with a range of interaction energies were available for adsorption of Sudan (III) on activated carbon. The kinetic results provided the best correlation of the experimental data of Sudan III dye onto activated carbon by pseudo second order equation.

ACKNOWLEDGMENTS

We thank the University of Najran for financial support.

REFERENCES

- [1] Riin. R., Ivo. L., Sergei. Y., and Koit. H. A review of analytical techniques for determination of sudan I-IV dyes in food matrixes. *J Chromatogr A*, 1217, 2747-2757 (2010).
- [2] Common decision on emergency measures regarding chilli products, curcuma and palm oil, OJ, (2005/402/EC) L135/34 (2005).
- [3] Orawon. C., Wanida. W., Weena. S., Kate. G., Yifang. Z., and Zhiwei. Z. Analysis of sudan I, sudan II, sudan III, and sudan IV in food by HPLC with electrochemical detection: Comparison of glassy carbon electrode with carbon nanotube-ionic liquid gel modified electrode. *Food Chem*, 109, 876-882 (2008).
- [4] Monica. A., Mohammed. Z., Alberto. E., and Angel. R. Determination of sudan dyes in food samples using supercritical fluid extraction-capillary liquid chromatography. *J Supercrit Fluid*, 55, 977-982 (2011).
- [5] IARC Monographs on the Evaluation of the Carcinogenic Risk Chemical to Man, vol, 8, IARC, Lyon, p. 125 (1975).
- [6] Commission Decision 2003/460/EC, European Union (2003).
- [7] Pardo. O., Yusa. V., Leon. N., and Pastor. A. Development of a method analysis of seven banned azo-dyes in chilli and hot chilli food samples by pressurized liquid extraction and liquid chromatography with electrospray ionization-tandem mass spectrometry. *Talanta*, 78, 178-186 (2009).
- [8] Valencia, M., Uroz, F., Tafersiti, Y., and Capitan-vallvey, L. F. A flow-through sensor for the determination of the dyes sunset yellow and its subsidiary sudan I in foods. *Quimica Analitica*, 3(19), 129-134 (2000).
- [9] Chen, Q., Mou, S., Hou, X., Ni, Z., and Riviello, J. Determination of eight synthetic food colorants on drinks by high-performance ion chromatography. *J Chromatogr A*, 827, 73 (1998).
- [10] Daood, H., and Biacs, M. Simultaneous determination of Sudan dyes and carotenoids in red paper and tomato products by HPLC. *J Chromatogr Sci*, 43, 461-465 (2005).
- [11] Pielesz. A., Baranowska. I., Rybak. A., and Wlochowicz. A. Detection and determination of aromatic amines as products of reductive splitting from selected azo dyes. *Ecotox Environ safe*. 53(1), 42 (2002).
- [12] Marshall. P. Thin layer chromatography of sudan dyes. *J Chromatogr A*, 136(2), 353-357 (1977).
- [13] Mejia. E., Ding. Y., Mora. M., and Garcia. C. Determination of banned sudan dyes in chilli powder by capillary electrophoresis. *Food Chem*, 102(4), 1027-1033 (2007).
- [14] Cornet. V., Govaret. Y., Moens. G., Van Loco. J. and Degroodt. J. Development of a fast analytical method for determination of sudan dyes in chilli and curry-containing foodstuffs by high performance liquid chromatography-photodiode array detection. *J Agr Food Chem*, 54(3), 639-644 (2006).
- [15] Zhang. P., Zhang. J., Gong. W., Gopalan. A., and Lee. K. Rapid separation of sudan dyes by reverse-phase high performance liquid chromatography through statistically designed experiments. *J Chromatogr A*, 1098(1-2), 183-187 (2005).
- [16] Zhang. Y., Zhang. Z., and Sun. Y. Development and optimization of an analytical method for the determination of sudan dyes in hot chilli pepper by high-performance liquid chromatography with on-line electrogenerated BrO₂-luminol chemiluminescence detection. *J Chromatogr A*, 1129(1), 34-40 (2006).
- [17] Calbiani. F., Careri. M., Elviri. L., Mangia. A., and Zagononi. I. Accurate mass measurements for the confirmation of sudan azo-dyes in hot chilli products by capillary liquid chromatography-electrospray tandem quadrupole orthogonal-acceleration time of flight mass spectrometry. *J Chromatogr A*, 1058(1-2), 127-135 (2004).
- [18] Ma. M., Luo. X., Chen. B., Su. S., and Yao. S. Simultaneous determination of water-soluble and fat-soluble synthetic colorants in foodstuff by high performance liquid chromatography-diode array detection-electro spray mass spectrometry. *J Chromatogr A*, 1103(1), 170-176 (2006).



- [19] Mazzetti. M., Fascioli. R., Mazzoncini. I., Spinelli. G., Morelli. I., and Bertoli. A. Determination of 1-phenylazo-2-naphthol (sudan I) in chilli powder and in chilli-containing food products by GPS clean up and HPLC with LC/MS confirmation. *Food Addit Contam*, 21(10), 935-941 (2004).
- [20] Rovellini. P. Determination of sudan azo dyes: HPLC-APCI-ion trap-MS/MS method. *Rivista Italiana delle Sostanze Grasse*, 82(6), 299-303 (2005).
- [21] Tateo. F., and Bononi. M. Fast determination of Sudan I by HPLC/APCI-MS in hot chilli, spices, and oven-baked foods. *J Agr Food Chem*, 52(4), 655-658 (2004).
- [22] Vanloon, G. and Duffy, S., *Environmental analytical chemistry: A Global perspective*. Oxford University Press (2000).
- [23] Weber W. J. Jr. *Physico-chemical Processes for Water Quality Control*, Wiley-Interscience, New York (1972).
- [24] Issa, A. and Al-Degs, S. Simple spectrophotometric determination of reactive dyes after preconcentration using activated carbon. *Jordan J Chem*, 89-101 (2009).
- [25] Fuqiang, L., Jinlong, C., Aimin, L., Zhenghao, F., Junjie, G. and Quanxing, Z. Equilibrium adsorption of single component and binary mixtures of aromatic compounds onto a polyfunctional Hypercrosslinked polymeric Adsorbent. *Adsorp Sci Tech.*, 22, 13-24 (2004).
- [26] İsmail Özbay, Utkan Özdemir, Bilge Özbay & Sevil Veli. Kinetic, thermodynamic, and equilibrium studies for adsorption of azo reactive dye onto a novel waste adsorbent: charcoal ash. *Desalination and Water Treatment*. 51, 6091-6100 (2013).

