

## ADSORPTION ISOTHERM FOR THE HAZARD REMOVAL DYES.

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**ABSTRACT:** *The adsorbent mixed sulfated titania active carbon over silica STAC/SiO<sub>2</sub> was synthesized by sol- gel method and was tested for its efficiency in removing Eosin and Saffranin dyes . The parameters studies include contact time, initial dye concentration, magnetic stirring and temperature. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity ( $Q_m$ ) obtained from the Langmuir isotherm plots with the temperature variation study showed that the Eosin and Saffranin adsorption was endothermic and spontaneous with increased randomness at the solid solution interface. 100% removal of saffranin dye was observed at 40 C. Thermodynamic parameters such as  $\Delta H^\circ$  ,  $\Delta S^\circ$  ,  $\Delta G^\circ$  were evaluated . The positive  $\Delta H^\circ$  value suggest that the adsorption of Eosin and Saffranin dyes on STAC/SiO<sub>2</sub> involves physisorption mechanism. The adsorbent was found to be both effective and economically viable.*

**Keywords :** STAC/SiO<sub>2</sub> adsorbent , Sol- Gel method , Eosin and Saffranin dyes

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## INTRODUCTION

The main advantage of using a sol- gel technique is the achievement of good control of surface properties such as composition , thickness and topography **J.Zita et al., 2010 & C.C Wang et al., 1999& J.Zhu et al ., 2007& Y.U.Ahu et al., 2003& O.Kesmez et al ., 2009 & L.Chen et al., 2009& J.X.Liu et al., 2003 & H.E.Chao et al ., 2003.** This method allows preparation of materials with exceptional purity, homogeneity and composition **I. Mai et al., 2009 & M.Sabramanian et al., 2008.** Titania can act as photocatalyst in the reactions such as hydrogenation of olefins due to strong oxidizing power of its holes, its redox selectivity, high photostability, and easy preparation **Felora Heshmatpour et al., 2011.** Photochemical reactions catalyzed by semiconductors have been extensively studied for water decomposition, degradation of toxic organic pollutants, organic synthesis, dye sensitized solar cells, and energy conversion. Color is one of the characteristic of an effluent. This can be easily detected and traced back to its source **Gholam Reza et al., 2010&**

**Gaanappriya et al., 2012.** Industry is a huge source of water pollution; it produce pollutants that are extremely harmful to people and the environment. Most of dyes are stable to biological degradation .Waste waters from dyeing industries are released in to nearby land or rivers without any treatment. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes . Colored water and solutions containing toxic heavy metals from many industries like dye, textile, paper plastic, plating and mining facilities produce polluted water **A.Jafar Ahmed et al.,2011&Sekaran G., et al ., 1995&Arivoil et al., 2007.**

## MATERIALS AND METHODS

### Materials

Titanium (IV) n-butoxide (98% ), tetraethylorthosilicate TEOS ( purity 99% ) were purchased from Merck company . Absolute ethanol ( purity 95% ) , Hydrochloric acid ( 32% ) , sulfuric acid (98%) and Tetra hydro furan THF (purity 99%) were purchased from Elnaser company. Active carbon prepared from nuclei balah. Eosin and saffranin dye were applied.

### Synthetic Method

#### Preparation of Adsorbent and Adsorbate Solution

##### a. Preparation of Adsorbent

1. The  $\text{SiO}_2$  sol was obtained by hydrolyzing 31.1900 g of tetraethylorthosilicate in a mixture of 21.2600 g of THF, 6.7400 g of  $\text{H}_2\text{O}$  and 0.7500 g of 2M HCl under a magnetic stirring at 65 to 70 °C for 3h **Guangshan Zhu et al., 2007.**
2. Sulfated titania sol was prepared by placing 10.000 g of ethanol and 10.000 g of titanium butoxide (98%) into a flask under magnetic stirring at room temperature , followed by adding a mixture of 6.500 g of ethanol ,1.500 g of distilled water and 5.000g of  $\text{H}_2\text{SO}_4$  (18M).
3. The  $\text{SiO}_2$  sol and sulfated titania ST sol mixed with 0.2 g of active carbon at a proper molar ratio, under stirring magnetically for 12 to 24 h. Finally, the cross linking agent  $\text{Si}(\text{OC}_2\text{H}_5)_4$  was added to the system to form a transparent binary gel . The gel was dried at room temperature for 2days, ground into fine powder and then heated at 50 °C for about 5h, followed by heating to 550 °C and calcining at 550 °C for 3h. The calcined product was stored in a desiccator for later use.

##### b. Preparation of Adsorbate Solution

Stock dye solution (0.1 mg/l) was prepared by dissolving desired quantity of commercially available dye in distilled water. By proper dilution of the stock solution , other concentration for experimentation was obtained

### Adsorption Dynamic Experiments

#### Batch Equilibrium Metho

Experiments were carried out in a batch process at room temperature . Known weight of STAC/ $\text{SiO}_2$  was added to 10ml of the dye solution with an intial concentration 0.001 mg/l. The contents were shaken using magnetic stirring rotating with different speeding from 2 to 7 rpm. The solution was then filtered at preset intervals of time and residual dye concentration was determined by biochemical analyzer. Experiments

were also conducted in order to evaluate the effect of different variables such as initial dye concentration, contact time and temperature.

## RESULTS AND DISCUSSION

### Effect of initial dye concentration

The experimental results for the adsorption of acidic and basic dye at various concentration (0.1, 0.01 and 0.001 mg/l) are shown in figure. The respective data are represented in table -1 and figure 1 , revealing that, percent of adsorption decreased with increasing in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dye concentration. It means that the adsorption is highly dependent on the initial dye concentration. It is because of the reason that, at lower concentration .the ratio of the initial number of dye molecules to the available surface area is low. However, at high concentration, the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent on initial concentration **ISI,Activated Carbon,IS877:-Feb1992 &Jafar Ahmed,et al., 2010**. The percent removal of basic (saffranin) dye is much higher than the percent removal of acidic (eosin) dye.

Table-1: equilibrium parameters for the adsorption of dyes onto STAC/SiO<sub>2</sub>

Dye conc., mg/L	C <sub>e</sub> mg/L		Q <sub>e</sub> (mg/g)		Dye Removal%	
	Eosin dye	Saffranin dye	Eosin dye	Saffranin dye	Eosin dye	Saffranin dye
0.1	7.8	5.7	5.4	4.0	69.5	70.5
0.01	7.5	5.5	6.1	4.9	95.0	90.4
0.001	4.5	3.4	4.3	3.4	96.2	100.0

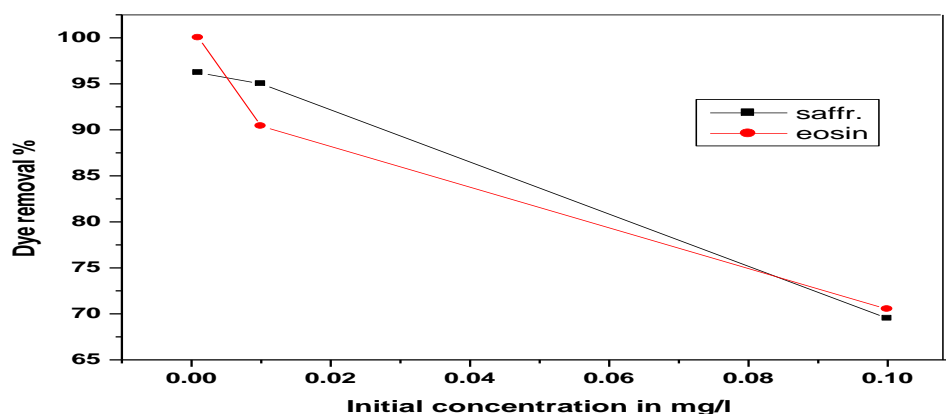


Figure-1:Effect of initial concentration on the adsorption of eosin and saffranin dye by STAC/SiO<sub>2</sub> ; contact time = 24h, temp=22 °C.

**Adsorption Isotherm**

The experimental data were analyzed according to the linear form of Langmuir and Freundlich isotherm **Jia Y.F ., et al., 2002** & **Namasivayam,C., et al ., 1996**: The langmuir isotherm is :

$$C_e / Q_e = 1/Q_m b + C_e / Q_m \quad (1)$$

Where  $C_e$  is the equilibrium concentration (mg/L) ,  $Q_e$  is the amount adsorbed (mg/g) and  $Q_m$  and  $b$  are langmuir constants related to adsorption efficiency and energy of adsorption respectively. The linear plots of  $C_e / Q_e$  versus  $C_e$  suggest the applicability of the langmuir isotherms (Figure 2). The values of  $Q_m$  and  $b$  were determined from slope and intercept of the plots and are represented in table -2 for acidic and basic dye. From table -2, it is clear that the value of adsorption efficiency  $Q_m$  and adsorption energy  $b$  of the adsorption was varied in descending order as :

**Eosin dye > Saffranin dye**

Table -2: Langmuir and Freundlich Constant and Statistical Parameters

Adsorbate	Freundlich Constants				Langmuir Constants		
	$K_F$	$n$	$R^2$	$S_L$	$Q_m$	$b$	$R^2$
(1)-Eosin dye	1.253	1.215	0.9145	0.9876	13.561	9.3556	<b>0.8414</b>
(2)-Saffranin dye	<b>1.560</b>	<b>1.562</b>	<b>0.8905</b>	<b>0.9846</b>	<b>6.408</b>	<b>2.9680</b>	<b>0.8936</b>

The Freundlich equation was employed for the adsorption of dyes on the adsorbents. The Freundlich isotherm was represented by:

$$\text{Log } Q_e = \text{log } K_F + 1/n \text{ log } C_e \quad (2)$$

Where  $Q_e$  is the amount of dye adsorbed (mg/g) ,  $C_e$  is the equilibrium concentration of dye in solution (mg/L) and  $K_F$  and  $n$  are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption respectively. Linear plots of  $\text{Log } Q_e$  versus  $\text{log } C_e$  show that the adsorption of dyes obeys the freundlich isotherm (Figure 2). The values of  $K_F$  and  $n$  are given in tables -2 for acidic and basic dye respectively, which indicating that the adsorption capacity was varied in descending order:

**Saffranin dye > Eosin dye**

The intensity of adsorption is an indicative of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption **Langmuir,et al., 1918** & **Freundlich,H, 1906**. The values of  $n$  are greater than one ,indicating that the adsorption is much favorable **Krishna,D.G.;et al., 2002**. To confirm the favourability of the adsorption process ,the separation factor ( $S_L$ ) was calculated and the values were found to be between 0 and 1 and confirm that the adsorption process is favourable.

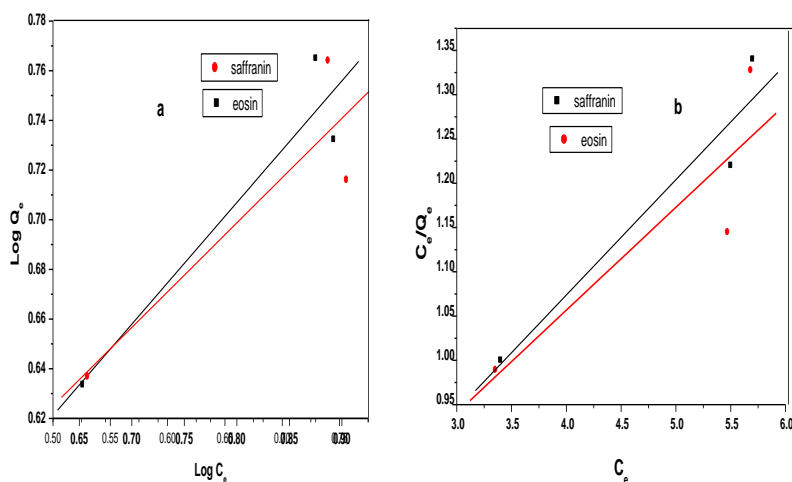


Figure-2: Freundlich isotherm(a) and (b) Langmuir isotherm for eosin dye and saffranin dye.

### Effect of contact time

The experimental data for the adsorption of eosin and saffranin dye are shown in figure-4 and represented on table -3. The data show that the percent removal of dye increase with increasing contact time from 30-180 min to reach 99.60% for acidic dye and 94.5% for basic dye, this means that the contact time is more effect for removal of eosin than saffranin dye. Figure-3 show that , the curve is single , smooth and continuous , leading to saturation , suggesting the possibility of monolayer coverage of the dyes on the adsorbent surface.

### Effect of magnetic stirring

The experimental data for the adsorption of eosin and saffranin dye with increasing the speed of stirring from 2 to 7 rpm are shown in figure-5 and represented on table -4. The figure show that the percent removal of dye increase with increasing the speed to reach 96.4 % for acidic dye and 100 % for basic dye . It means that the adsorbent show most effect removal for basic dye than the acidic on changing the speed of stirring.

### Effect of temperature

The adsorption capacity of the adsorbent increased with increasing temperature of the system from 10-40 °C from 87.7% to 100% for acidic dye and from 23.6% to 98.4% for basic dye . Also this means that the adsorption is must dependent on the changing of temperature and the adsorbent used is much available adsorbent for acidic than basic dye. Thermodynamic parameters such as change in free energy ( $\Delta G^\circ$  , k J mol<sup>-1</sup>) , enthalpy ( $\Delta H^\circ$  , k J mol<sup>-1</sup>) and entropy ( $\Delta S^\circ$  , J k<sup>-1</sup>mol<sup>-1</sup>) were determined using the following equations.

$$K_0 = C_{\text{solid}}/C_{\text{liquid}} \quad (3)$$

$$\Delta G^\circ = -RT \ln K_0 \quad (4)$$

$$\log K_0 = \Delta S^\circ / 2.303 RT - \Delta H^\circ / 2.303 RT \quad (5)$$

Where  $K_0$  is the equilibrium constant,  $C_{\text{solid}}$  is the solid phase concentration at equilibrium (mg/L),  $C_{\text{liquid}}$  is the liquid phase concentration at equilibrium (mg/L),  $T$  is the temperature in Kelvin and  $R$  is the gas constant. The  $\Delta H^\circ$  and  $\Delta S^\circ$  values obtained from the slope and intercept of van t Hoff plots have represented in table -5. The values  $\Delta H^\circ$  is with range of 1 to 93 k J mole<sup>-1</sup> indicates that physisorption. The positive values of  $\Delta H^\circ$  show the endothermic nature of adsorption and it governs the possibility of physical adsorption **Balasubramanian,N., et AL 2003 & Karunakaran,K., et al 2010**. Because in the case of physical adsorption ,while increasing the temperature of the system ,the extent of dye adsorption increases ,this rules out the possibility of chemisorption .The low  $\Delta H^\circ$  value depicts dye is physisorbed onto adsorbent. The negative values of  $\Delta G^\circ$  shows the adsorption is highly favorable and spontaneous. The positive values of  $\Delta S^\circ$  Show the increased disorder and randomness at the solid solution interface of dye with adsorbents, while the adsorption there are some structural changes in the dye and the adsorbent occur.The adsorbed water molecules ,which have displaced by the adsorbate species , gain more translation entropy than is lost by the adsorbate molecules,thus allowing the prevalence of randomness in the system.

Table-3: Effect of contact time on the adsorption of Eosin and Saffranin dyes onto STAC/SiO<sub>2</sub>

Time of contact, min	6.29	$Q_e$ (mg/g)	36.Dye	Removal %
	Eosin	Saffranin	Eosin	Saffranin
30	7.10	3.20	94.67	58.18
60	7.15	3.38	95.33	69.94
120	7.23	4.85	96.40	88.18
150	7.46	5.11	99.47	92.91
180	7.47	5.20	99.60	94.54

Table-4: Effect of speed of stirring on the adsorption of Eosin and Saffranin dyes onto STAC/SiO<sub>2</sub>

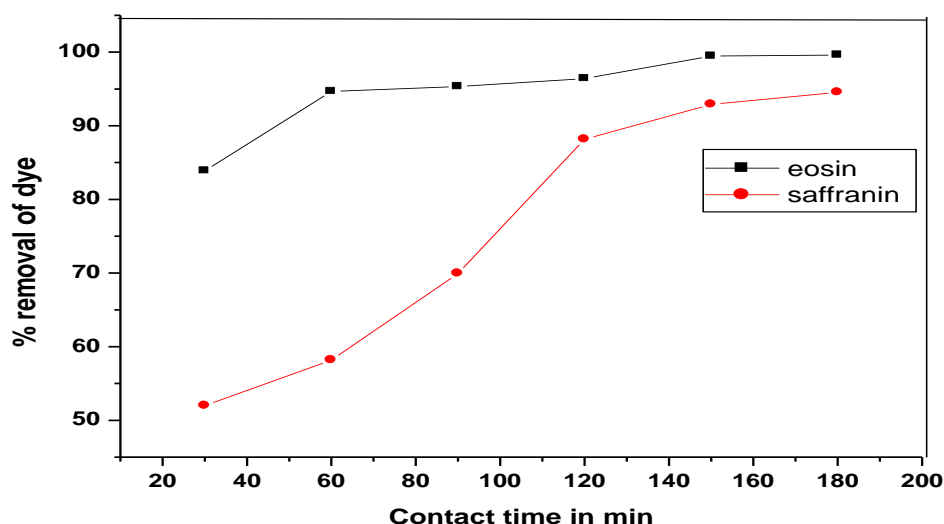
Speed of stirring, rpm	2.70	$Q_e$ (mg/g)	36.Dye	Removal %
	Eosin	Saffranin	Eosin	Saffranin
3	6.29	4.67	85.33	85.00
4	6.60	4.82	88.00	87.64
5	7.17	5.15	95.60	93.64
6	7.22	5.38	96.27	97.82
7	7.23	5.50	96.40	100.00

Table-5: Effect of temperature on the adsorption of Eosin and Safranin dyes onto STAC/SiO<sub>2</sub>

Adsorbate.	$Q_e$ (mg/g)				Dye Removal%			
	10° C	20° C	30° C	40° C	10° C	20° C	30° C	40° C
(1)-Eosin dye	5.90	7.10	7.25	7.30	78.67	94.67	96.67	<b>97.33</b>
(2)-Safranin dye	<b>1.30</b>	<b>3.10</b>	<b>5.14</b>	<b>5.41</b>	<b>23.60</b>	<b>56.36</b>	<b>93.45</b>	<b>98.36</b>

Table-6: equilibrium constant and thermodynamic parameters for the adsorption of dyes onto STAC/SiO<sub>2</sub>

Adsorbent	$\Delta H^\circ$	$\Delta S^\circ$	$K_o$				$\Delta G^\circ$			
			10° C	20° C	30° C	40° C	10° C	20° C	30° C	40° C
(1)-Eosin dye	19.76	66.35	7.15	16.85	249	1499	-4.62	-6.87	-13.87	-18.99
(2)-Safranin dye	29.94	40.01	0.309	1.29	14.27	60.11	-2.72	-0.62	-6.68	-10.68

Figure-3: Contact time effect on the adsorption of eosin and safranin dye by STAC/SiO<sub>2</sub>; Initial conc., = 0.01 mg/L, temp=23 °C.

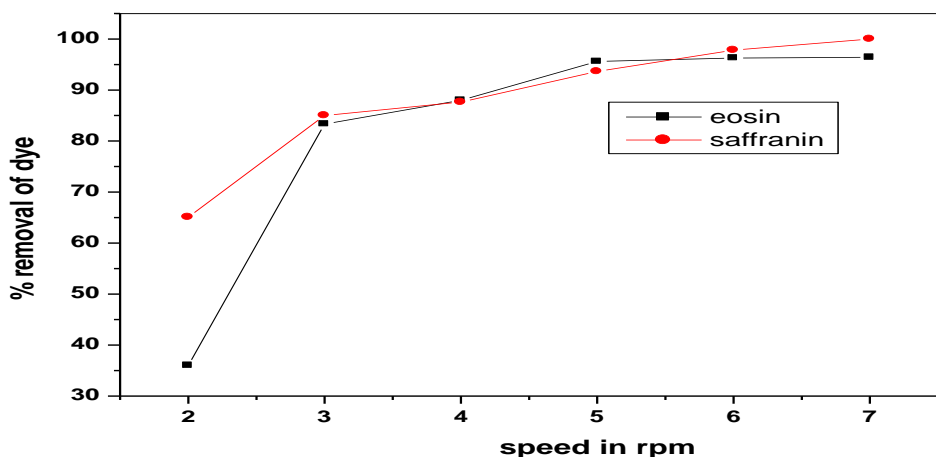


Figure-4:Effect of speed of stirring on the adsorption of eosin and saffranin dye by STAC/SiO<sub>2</sub> ; contact time = 30 min, temp=22 °C.

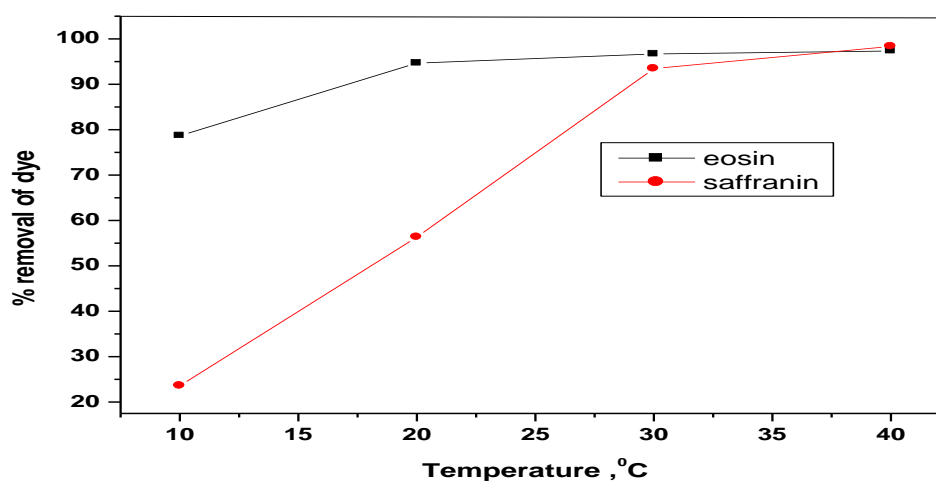


Figure-5:Effect of temperature on the adsorption of eosin and saffranin dye by STAC/SiO<sub>2</sub> ; contact time = 30 min, initial conc., = 0.01 mg/L.

## CONCLUSION

The Langmuir and Freundlich adsorption isotherms were applied for the experimental data and isotherm parameters were reported. The amount of the Eosin and Saffranin dyes adsorbed increased with increasing contact time, speed of stirring and temperature. However, by increasing contact time the amount of Eosin adsorbed is higher than the amount of Saffranin also by increasing the speed of stirring and temperature, the STAC/SiO<sub>2</sub> is more effective for the removal of Saffranin dye than Eosin dye. The dimensionless separation factor showed that the STAC/SiO<sub>2</sub> can be used for the effective removal of acidic and basic dyes from aqueous solutions. The



values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  show that the STAC/SiO<sub>2</sub> has considerable potential as adsorbent for the removal of Eosin and Saffranin dyes.

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