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## **COLOUR REMOVAL FROM AQUEOUS SOLUTION OF TAR- CHROMIUM GREEN 3G DYE USING NATURAL DIATOMITE**

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**Abstract.** Removal of Tar-Chromium Green 3G dye from aqueous solution at different dye concentrations, different temperatures and adsorbent doses has been studied. It was seen that the maximum of 88% adsorption has been achieved from the wastewater using 3.0 g material at 30°C temperature for shaking time of 60 min. The adsorption isotherms are described by means of the Langmuir and Freundlich isotherms at different temperatures of 25, 30 and 35°C, and the results were discussed. The equilibrium data satisfied both the Langmuir and Freundlich models. Moreover, thermodynamic parameters such as  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were also studied. It was found that the values of standard free energy ( $\Delta G$ ) and the values of standard enthalpy ( $\Delta H$ ) were negative and entropy ( $\Delta S$ ) was found to be positive. Thermodynamic studies showed that the reaction for uptake by diatomite is exothermic in nature. The results of this study showed that diatomite could be employed as effective and low-cost materials for the removal of the dye from aqueous solution.

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*keywords:* chromium dyes, adsorption, diatomite, Langmuir and Freundlich model, thermodynamics

### **1. Introduction**

Dyes and pigments from several industrial branches can be emitted into water systems. The presence of dyes in water is highly visible and affects water transparency (Wang and Huiting, 2005). Coloured wastewater is a consequence of batch processes both in the dye manufacturing industries and in the dye-consuming industries. Two percent of dyes that are produced are discharged directly in aqueous effluent, and 10% are subsequently lost during the textile coloration process (Easton, 1995). An indication of the scale of the problem is given by the observation that the annual market for dyes is more than  $7 \cdot 10^5$  Mg per year (Robinson et al., 2001). The main reason for dye loss is the incomplete exhaustion of dyes on to the fibre. The amount of dye lost is dependent upon dyestuff type, the application route and the depth of shade required (Pearce et al., 2003). Untreated disposal of the coloured water into the receiving water body not only causes damage to aquatic life, but also to human beings by mutagenic and/or carcinogenic effect. It can cause severe damage to the

reproductive system, liver, brain and dysfunction of kidneys. and cause damage to the aesthetic nature of the environment (Baskaralingam et al., 2006). Therefore, the undesirable dye pollutions are required to be removed from wastewaters before being discharged to the environment.

During the past three decades, several physical, chemical and biological decolorization methods such as aerobic and anaerobic microbial degradation, coagulation and chemical oxidation, membrane separation process, electrochemical, dilution, filtration, flotation, softening and reverse osmosis have been proposed (Singh et al., 2003). However, all of these methods suffered with one or another limitation, and none of these were successful in removing color from the wastewater completely (Dogan et al., 2009).

Amongst the numerous techniques of dye removal, the adsorption process is one of the effective techniques that have been widely used to remove certain classes of pollutants from wastewaters, especially those that are not easily biodegradable. A desired adsorbent should have sufficient adsorption capacity, high thermal and chemical stability, low cost and low environmental impact. The successful implementation of solid-liquid phase dye adsorption requires stable and effective adsorbents from wastewater (Chiou et al., 2004).

For this purpose, recently, some researchers have focused on the use of low cost sorbents. Some low cost materials used as sorbent for dye sorption from wastewaters were as follows, bentonite (Koyuncu, 2009; Tahir and Nasseem, 2007), natural and modified diatomite (Yuan et al., 2010; Al-Ghouti et al., 2009; Er et al., 2009; Koyuncu and Kul, 2011), silica (Qiu et al., 2011; Blitz et al., 2007) fly ash (Eren and Acar, 2006), chitosan (Uzun, 2006), and others (Malkoç and Nuhoglu, 2006; Parap et al., 2006; Marungueng and Pavasant, 2007).

Diatomite may be thought as other inexpensive materials which can be used as sorbents. Diatomite ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) is a soft, light colour sedimentary rock formed from accumulation of siliceous crusts of diatoms, which are aquatic organism from algae, and have fossil characteristics. It has a unique combination of physical and chemical properties, which make it applicable as a substrate for adsorption of organic pollutants as filtration medium in a number of industrial uses. Its high permeability and high porosity make it a cheap alternative to activated carbon. The feasibility of using diatomite for removal of color from textile wastewaters was attempted by Erdem et al. (2005) and Hameed (2008).

The aim of the present study is to investigate the effect of initial dye concentration, temperature, and adsorbent dosage on the adsorption of Tar-Chromium Green 3G, the adsorption isotherm and thermodynamics were studied in detail.

## **2. Materials and methods**

### **2.1. Materials**

Diatomite (230 mesh in size) with surface area of  $49.040 \text{ m}^2/\text{g}$  from Çaldıran (Van/Turkey) was used as an adsorbent and the chemical composition of the adsorbent

was obtained with a XRD instrument. According to XRD it contained 76.50% SiO<sub>2</sub>, 7.25% Al<sub>2</sub>O<sub>3</sub>, 3.85% Fe<sub>2</sub>O<sub>3</sub>, 0.50% TiO<sub>3</sub>, 0.45% Na<sub>2</sub>O, 0.85% K<sub>2</sub>O and 0.43% loss on ignition

The dye was provided by Van Textile Fabrics (Van/Turkey). The molecular structure and formula of Tar-Chromium Green 3G was not provided for commercial reasons. It represents a basic dye.

## 2.2. Adsorption studies

The adsorption experiment was carried out at natural pH of solutions. Each of 50 cm<sup>3</sup> 5mg/dm<sup>3</sup> of dyes solutions was put in five 100 cm<sup>3</sup> erlenmeyer flasks and diatomite adsorbent was added to each of other five erlenmeyers in different adsorbent doses (0.5-5g). Samples of 50 cm<sup>3</sup> of each dyes solutions were shaken with a shaker (New Bounswick Scientific G.24). Working conditions were: 30°C, 195 rpm for 300 min. The 30°C, 195 rpm shaking rate was kept as constant and the time variable was 15, 30, 60, 180 and 300 min. The samples were filtrated and analyzed by a UV- vis spectrophotometer (Cintra 202 Duple Beam) set at a wavelength of 480 nm, providing maximum absorbance. The effect of temperature and time variable on adsorption at recorded experimental conditions were also studied. At the end of the each experiment, supernatants were analyzed by UV- vis spectrophotometer (Cintra 202 Duple Beam) set at a wave-length of 480 nm.

The amount of dye adsorbed by diatomite  $q_e$  (mg/g), was calculated by the following mass balance relationship

$$q_e = \frac{(C_o - C_e)V}{W}, \quad (1)$$

where  $q_e$  is the amount of dye adsorbed (mg/g).  $C_o$  and  $C_e$  are the initial and equilibrium solution concentrations of dye respectively.  $V$  is the volume of the solution, and  $W$  is the weight of the adsorbent used.

## 3. Results and discussion

### 3.1. Effect of initial dye concentration

The adsorption of Tar-Chromium Green 3G dyes on natural diatomite as a function of concentration was studied at 30°C by varying concentrations from 5 to 75 mg/dm<sup>3</sup>, while keeping all other parameters constant. The adsorption result for the dye is shown in Fig. 1. The results show that the colour removal of Tar-Chromium Green 3G was decreased when the initial dye concentration was increased. At low concentrations, adsorption sites took more the available dye more quickly. However, at higher concentrations, dye has to migrate to the adsorbent surface by intraparticle diffusion. The percentage of dye removal increased from 5 mg/dm<sup>3</sup> to 45 mg/dm<sup>3</sup> when the initial concentration of dye was from 5 to 75 mg/dm<sup>3</sup> for 3g of adsorbent at equilibrium contact time of 60 min. It indicates that the initial concentration provided

a powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases. Similar observation has been reported by Dogan et al. (2009), and a similar trend was reported for the Cr(VI) removal using Bael Fruit (Anandkumar and Mandal, 2009), a basic dyes, onto live activated sludge (Basıbuyuk and Foster, 2003).

Figure 2 shows that the removal efficiency was increasing sharply in 60 minutes time. The removal of dye is decreasing over next 60 minutes treatment time. The decrease can be explained by a reaching maximum specific holding capacity of diatomite for a system being in the state of adsorption equilibrium between solution and the surface area. Similar adsorption behaviour was reported in the kinetic experiments with trivalent chromium by Gürü et al. (2008) using Tar-Chromium Red-B (Koyuncu and Kul, 2011).

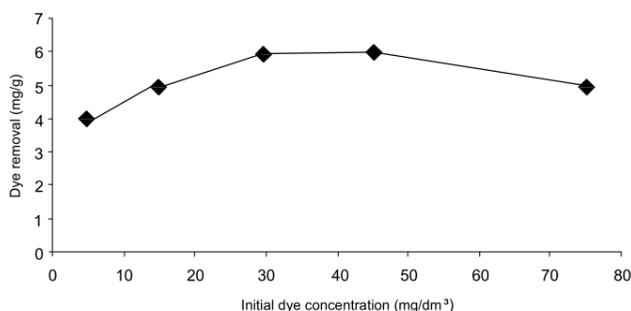


Fig.1. Effect of initial dye concentration on diatomite

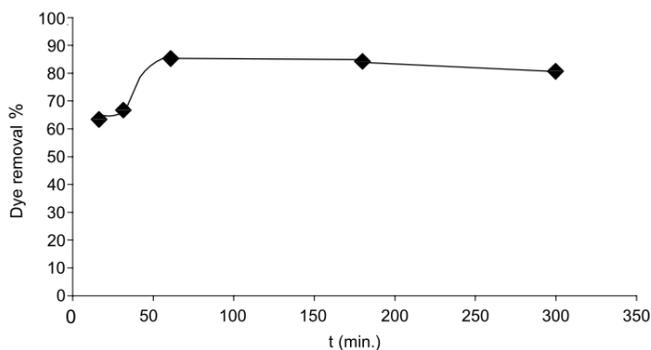


Fig. 2. Removal of Tar-Chromium Green 3G on diatomite for different times, 3 g diatomite, 30°C, 195 rpm

### 3.2. Effect of adsorbent mass

Figure 2 shows the removal of Tar-Chromium Green 3G by diatomite at different adsorbent doses (0.5-5g) for the 50 cm<sup>3</sup> of 5 mg/dm<sup>3</sup> of the dye solution. It is evident from the figure that as the mass of the adsorbent dose increases, the percentage of dye removal also increases. This is due to increase in the surface area with a high dosage

of the adsorbent (Gürü et al., 2008). However, it has no impact when more than about 3g diatomite is used. It can be a result of the removal efficiency of dye which decreased with decreasing surface area of adsorbent and increasing particle size and decreasing the external surface area of diatomite.

### 3.3. Effect of temperature

The rates of adsorption were investigated in the temperature range of 25, 30 and 35°C for the initial dye concentration of 5 mg/dm<sup>3</sup> at the natural pH. The effect of temperature on the adsorption is shown in Fig. 3. It is observed that at higher temperatures adsorption is lower, and the process was physical adsorption. A decrease of adsorption may be explained by physical adsorption which decreases with increasing temperature, and the adsorption process is exothermic. A similar observation has been reported by other investigators for Cr(VI) removal (Anandkumar and Mandal, 2009) and trivalent chromium (Gürü et al., 2008) in kinetic experiments with Maxilon Yellow and Maxilon Red (Dogan et al., 2009).

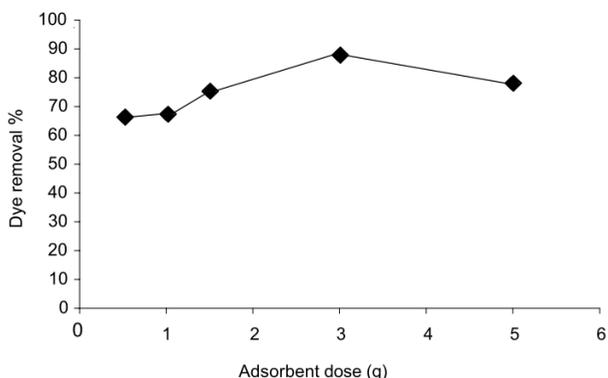


Fig. 3. Effect of adsorbent dosage on the removal of Tar-Chromium Green 3G by diatomite

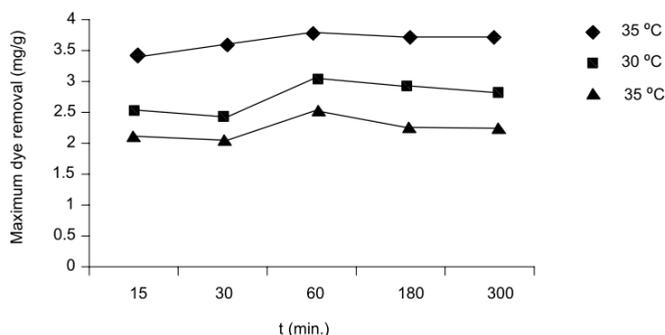


Fig. 4. Effect of temperature on the removal of Tar-Chromium Green 3G by diatomite (conditions:  $C_0$  5 mg/cm<sup>3</sup>, natural pH, adsorbent 3.0 g,  $t = 15 - 300$  min)

### 3.4. Isotherm study

The isotherm analysis of adsorption process were carried out using the Langmuir and Freundlich models at different temperatures.

The Langmuir and Freundlich isotherm parameters were determined for their linear forms. In the case of the Freundlich isotherm:

$$q_e = kC_e^{1/n} \quad \text{Freundlich isotherm,} \quad (2)$$

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \quad \text{Freundlich isotherm (linear form),} \quad (3)$$

where  $q_e$  is the amount of dye adsorbed at equilibrium time (mg/g),  $C_e$  is the equilibrium concentration of the dye in solution (mg/dm<sup>3</sup>),  $k$  and  $n$  are isotherm constants which indicate the capacity and intensity of the adsorption, respectively.

Figure 4 presents the plots of  $\ln q_e$  against  $\ln C_e$  for the adsorption of dye onto diatomite in the range from 25, 30 to 35°C at natural pH, respectively. Figure 4 shows that the plots for diatomite provide the Freundlich isotherm correlation coefficients 0.980, 0.976 and, 0.973 respectively. On the other hand, the values of  $n$  between 2 and 10 show good adsorption (Gürü et al., 2008; Erdem et al., 2005). The values of  $k$  and  $n$  were calculated from the intercept and slope of the plot of  $\ln q_e$  versus  $\ln C_e$ , respectively. Therefore, the adsorption of Tar-Chromium Green 3G onto diatomite fits well with the Freundlich models. These constants are given in Table 1. The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration. The Freundlich equation is suitable for a highly heterogenous surface and adsorption isotherm lacking a plateau, indicating a multi-layer adsorption.

The Langmuir model is as follows:

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad \text{Langmuir isotherm,} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad \text{Langmuir isotherm (linear form),} \quad (5)$$

where  $Q_o$  and  $b$  are Langmuir constants, which indicate the adsorption capacity (mg/g) and energy of adsorption, respectively.

Figure 5 shows the plots obtained for diatomite with the Langmuir isotherm correlation coefficients at 25, 30 and 35°C, 0.998, 0.961 and, 0.935 respectively. The values of  $Q_o$  and  $b$  are found from the slope and intercept of the plot of  $C_e/q_e$  versus  $C_e$ , respectively. The constants  $Q_o$ ,  $b$  determined at different temperatures are given in Table 1.

Table 1. Isotherm parameters of textile dye adsorption onto natural diatomite

Temperature	Langmuir constants			Freundlich constants		
	$q_m$ (mg/g)	$b$ (l/g)	$R^2$	$K_f$ (mg/g)	$n$	$R^2$
25°C	26.04	0.08	0.998	1.73	5.88	0.980
30°C	16.66	0.40	0.932	1.40	3.84	0.976
35°C	10.10	0.55	0.917	0.78	3.70	0.973

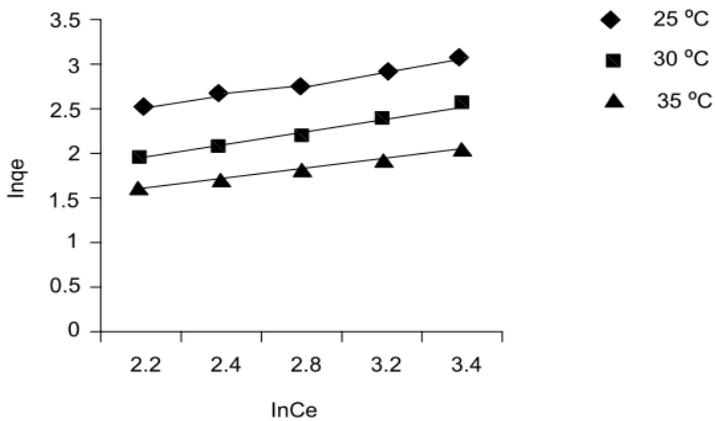


Fig. 5. Freundlich isotherms of the dyes adsorption onto diatomite at different temperatures

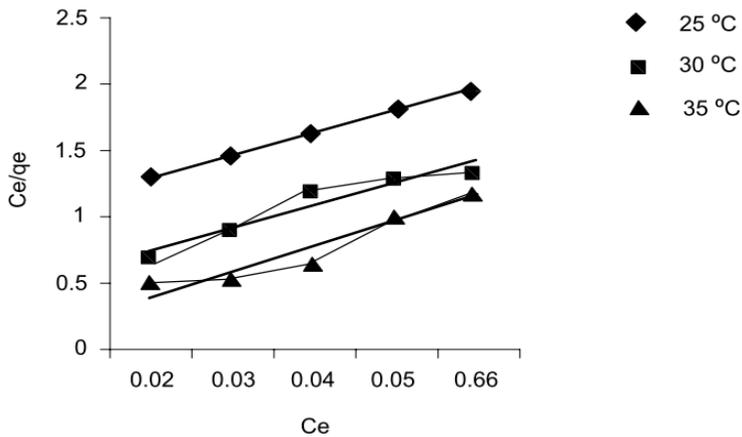


Fig. 6. Langmuir isotherms of the dyes adsorption onto diatomite at different temperatures

### 3.5. Thermodynamic study

Various thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  of dyes adsorption on diatomite were determined by using the following equations (Gürü et al., 2008; Ertaş et al., 2010; Nasseem and Tahir, 2001):

$$\Delta G = -RT \ln K_c, \quad (6)$$

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}, \quad (7)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}, \quad (8)$$

$$K_c = \frac{C}{C_e}, \quad (9)$$

where  $R$  is the gas constant,  $K_c$  is the equilibrium constant,  $T$  is the absolute temperature (in Kelvin).  $C$  and  $C_e$  are the equilibrium constants (concentrations) of dye on adsorbent and in solution, respectively.

The values of  $\Delta H$  and  $\Delta S$  were calculated from the slopes and intercepts of the plot of  $\ln K_c$  versus  $1/T$  which are linear. Their plots are shown in Fig. 6 and the thermodynamic parameters are given in Table 2. It is clear from the table that the negative values of  $\Delta G$  confirm that the dyes adsorption onto diatomite is a spontaneous process. The negative values of  $\Delta H$  shows an exothermic process. On the other hand, the positive values of  $\Delta S$  indicate the randomness at the solid/liquid interface during the adsorption of dye onto diatomite. Similar thermodynamic results have been recorded for adsorption of trivalent chromium onto natural diatomite (Gürü et al., 2008; Ertas et al., 2010).

Table 2. The thermodynamic parameters for the adsorption of Tar-Chromium Green 3G onto diatomite at different temperatures

Temperature (K)	$K_c$	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/molK)
298	1.772	-1.417	-1.314	0.345
303	2.444	-2.251	-2.308	0.188
308	2.690	-2.532	-2.446	0.282

#### 4. Conclusion

Diatomite, a low cost adsorbent is locally available in Turkey. Diatomite is approximately 500-fold cheaper than commercial activated carbon, CAC. Crystal structure of diatomite contains some ion-exchangeable cations such as  $Mg^{+2}$ ,  $Ca^{+2}$  and  $Na^+$ . These cations can be exchanged with organic and inorganic cations. The surface charge of diatomaceous earth may arise from chemical reactions. It has a unique combination of physical and chemical properties (high permeability). The high porosity makes it a cheap alternative to activated carbon (Erdem et al., 2005). Therefore, it is suitable material for removal of dyes,

The adsorption isotherms of Tar-Chromium Green 3G on diatomite can be described well by the Langmuir and Freundlich isotherm models. A comparison of the Langmuir and Freundlich models on the overall adsorption showed that the

Tar-Chromium Green 3G and and diatomite was better described by the Freundlich model rather than by Langmuir model. The maximum dye removal was 88% under all experimental conditions studied.

The thermodynamic parameters calculated from the temperature dependent adsorption isotherms indicate that the adsorption process is spontaneous and exothermic.

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