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Removal of Erythrosine Dyes from Aquatic Environment Using *Ziziphus nummularia* Kernel

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Abstract: In this paper, the feasibility of using a low-cost agricultural waste, *Ziziphus nummularia* kernel, for the removal of erythrosine toxin color from wastewater that causes inflicts irreparable damage on environmental cycle and human health was investigated. Erythrosine is known as severely pollutant to the aquatic environment. *Ziziphus nummularia* kernel had no significant application; it was suggested that the *Ziziphus nummularia* kernel to be used as a natural adsorbent of erythrosine dyes. From the experimental data, the low cost natural adsorption material responded very efficient for the removal of dye. It this work, the effect of pH, contact time, dye concentration, temperature and the amount of adsorbent for the rate of bleaching of the dye were investigated. Application of adsorption models, Langmuir and Freundlich adsorption isotherms were evaluated. The adsorption process was in good agreement with Langmuir adsorption isotherm. Result of bleaching erythrosine dyes with concentration of 20 mg L^{-1} on *Ziziphus nummularia* kernel sorbent with concentration of 0.1 g L^{-1} showed 93.7% of dye efficiently removed. The adsorbent capacity 101 mmol of dye g^{-1} of adsorbent was achieved.

Key words: *Ziziphus nummularia* kernel ・ Erythrosine ・ Removal of dyes ・ Adsorption

INTRODUCTION

Discharge of colored wastewater from textile, paper, plastics, cosmetics and food industries in the waterways are the first detectable contaminants and in appearance create adverse conditions. Since most of the dyes are stable against light and heat and remain biologically indecomposable, it is difficult to remove them from the water. In some cases, decolorization of the industrial wastewater proved to be a major environmental issue [1]. Furthermore, color-causing substances include one or more benzene rings which due to their toxicity and irresolvability may cause irreparable damage to the environment if these substances are introduced into the environment without treating. Therefore, it is required to adopt appropriate methods for treatment of such wastewater before its discharge to the environment [2]. Different methods for bleaching of textile wastewater are discussed in literature, among these applied chemical treatment, the liquid phase adsorption is an effective method for the removal of the suspended solids, odors, oils and organic materials from the aqueous solutions [3, 4]. About 10,000 different commercial dyes and pigments exist. Industrial manufacturers and consumers of these dyes and pigments generate wastewater which contains organic and colored compounds and about 10 to 15% of these dyes may enter the environment during the dying process [5]. Roughly, annual global production rate of effluents from textile industry is estimated to be 7×10^5 tons [5]. Adsorption is a technique which can be easily implemented and gives high performance. Although activated carbon (AC) is an adsorbent with wide applications and high efficiency. AC has some disadvantages such as high cost and lack of recovery. These restrictions have caused a great deal of research in the field of using inexpensive and readily available adsorbent such as natural adsorbent materials [6-9]. The aim of present work is to evaluate and define the performance of *Ziziphus nummularia* kernel for the removal of erythrosine dyes from the industrial

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wastewater. For this purpose, the influence of various parameters such as initial dye concentration, contact time, amount of adsorbent dosage, temperature and pH on the adsorption has been taken into account. Finally, the adsorption isotherm of erythrosine on *Ziziphus nummularia* kernel based on existing scientific theoretical models was investigated.

MATERIAL AND METHOD

Experimental: Erythrosine with chemical formula of $C_{20}H_8I_4O_5$ (200–425 mesh) was purchased from the Merck (Darmstadt, Germany) without further purification. The chemical structure of the dye is illustrated in Figure 1. All of the chemical reagents were of analytical grade. The Velp Scientica/ARE heating magnetic stirrer was used for mixing the samples. Unico model 2100/UV/VIS spectrophotometer for determining the amount of dye adsorption was used. Also, pH & mv meter-Bench Top-Behine sat-2002 for the measurements of pH was used. Moreover, Panasonic mill and single test sieve was used for grinding aggregated samples. Other chemical reagents involved were purchased from Merck.

Batch Removal Experiments: The adsorption of dye by *Ziziphus nummularia* kernel was studied in batch at room temperature. The batch mode adsorption was selected due to its simplicity. A 0.5 g adsorbent was suspended in 50 mL solution of the 50 mg L^{-1} of Erythrosine at pH 7.0. This sample was stirred for 30 min at 300 rpm. After a time period of agitation, the suspensions were centrifuged at 2500 rpm for 5 min. The supernatants were then collected and analyzed for dye concentration at wavelength of 527 nm by UV-Vis spectrophotometer. The effects of experimental parameters on adsorption capacity of the adsorbent in batch experiments were investigated. Particle size in all experiments was in the range of $35 < d \le 60 \mu m$.

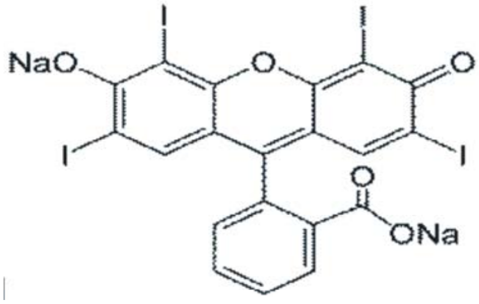

Fig 1: Chemical structure of the erythrosine

In order to calculate the efficiency of dye removal from the solution, equation (1) was used. Besides, equation (2) was applied to calculate the adsorption capacity or the amount of dye adsorbed per unit weight of the adsorbent. Here C_o and C_e are initial concentration and dye concentration in terms of milligrams per liter, at time *t* which is known as equilibrium, *V* is the volume of the solution in terms of liter and *m* is the mass of the sorbent in terms of gram [10].

$$R(\%) = \frac{C_0 - C_e}{C_o} \times 100 \tag{1}$$

$$q_e = \frac{(C_o - C_e)v}{m} \tag{2}$$

RESULTS AND DISCUSSION

Effect of pH: Changes in pH of the solution created an environment for the surface charge of the adsorbent, degree of adsorb ionization and ionization of the adsorbent active groups. Therefore, changes in pH can play an important role in the removal of the dye [11].

Effect of pH on erythrosin dye removal process is shown in Figure 2. As it can be obsrved, the desired percentage removal was obtained in a wide range of pH. Consequently, pH 7 was selected for further studies.

Effect Of Contact Time: Effect of contact time was investigated from 5 to 90 min with initial concentration of dye 20 mg L^{-1}. Figure 3 shows the effect of contact time in adsorption process of *Ziziphus nummularia* kernel. The results showed that a dramatic increase in dye adsorption (i.e., over 80%) occurred within 30 min. No significant change was observed in equilibrium concentration after 30 min. In other words, after 30 minutes, the dye and the adsorbent reached to equilibrium. Based on obtained results, a contact time of 30 min was selected in the subsequent studies.

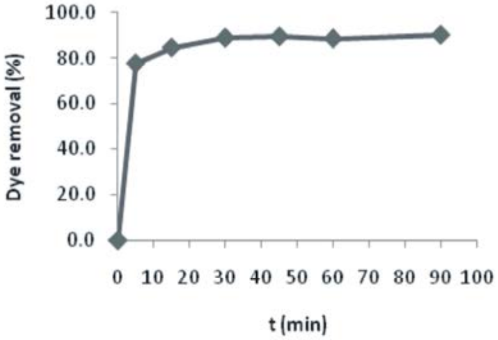

Fig 2: Effect of contact time on the adsorption process

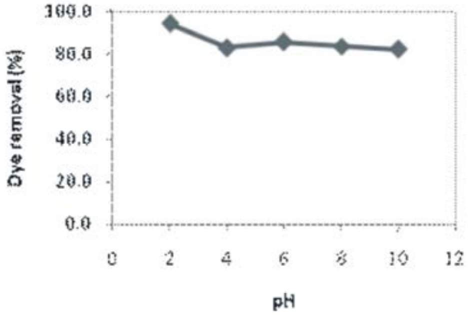

Fig 3: Effect of pH on adsorption process

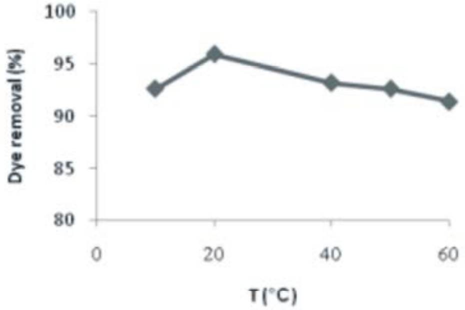

Fig 4: Effect of temperature on adsorption process

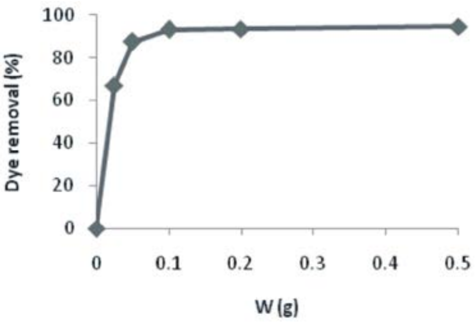

Fig 5: Effect of adsorbent dose on the adsorption process

Effect Of Temperature: Change of wrythrosine dye removal percentage in the solution has investigated at different temperatures versus processing time, for which the result is presented in Figure 4. As the illustrated data are shown, the best percentage of the removal has been achieved at 20°C (about ambient temperature). A decrease in the adsorption rate may occur while temperature is increasing; that may show the nature of adsorption is more favorable at lower temperatures.

Effect Of Adsorbent Dose: Figure 5 shows the effect of the adsorbent dose on the removal of erythrosine dyes at 20 ppm concentration of the dye as pollutant and for 30min. The percentage of the dye adsorption increases as the adsorbent dose increases and vice versa. Adsorption rate tends to increase with the increase in the adsorbent dose due to the higher number of the available adsorption sites. In this context, the optimal dose of the sorbent is 0.1 g.

Adsorption Isotherm: Adsorption isotherms are adsorption properties and equilibrium data that describe how the pollutants react with the sorbent materials. Moreover, adsorption isotherms play a key role in optimizing the use of adsorbents. Effective communication for the equilibrium curve and optimal design of the adsorption system for removal of the dye are of great importance. Many isotherm models are already suggested for the analysis of experimental data and description of the equilibrium in adsorption such as Langmuir, Freundlich and Temkin [11-15].

These models have been designed to express a view on the adsorption mechanism, surface properties and adsorbents tendency and describe the experimental data of the adsorption. Therefore, establishing a proper relationship between the equilibrium diagrams is very important for the optimization of the conditions and design of the adsorption systems.

Freundlich Isotherm: Freundlich adsorption model is expressed by the following equation:

$$\ln q_e = 1/n \ln C_e + \ln K_F \tag{3}$$

Here, q_e is the amount adsorbed per unit mass of the adsorbent at equilibrium condition in terms of mg g^{-1}, C_e is equilibrium concentration of the pollutants in terms of mg L^{-1}, K_F is adsorption capacity at unit concentration and 1/n is intensity of adsorption. The 1/n signifies the type of isotherm that if $1/n = 0$, then it is irreversible; $0< 1/n <1$ is desirable; and $1/n > 1$ is undesirable [16]. The obtained data are plotted according to equation 3. Figure 6 is shown the data fitted with respect to Freundlich isotherm; having R^2 of 0.98.

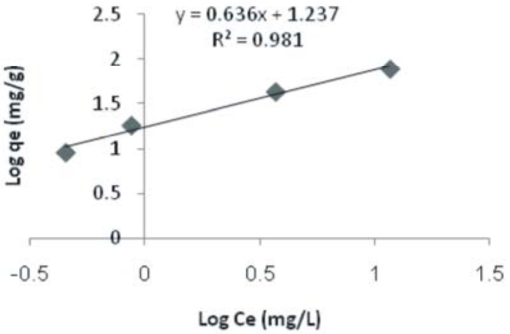

Fig 6: Frendlich model

Langmuir Isotherm: Let us consider the next model as kown as Langmuir which is expressed by the following relation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{4}$$

where q_e and C_e are defined as before, $q_0$is the amount of the sorbent required for single-layer capacity per unit mass of the adsorbent in terms of mg g^{-1} and the constant *b* is in terms of mg L^{-1}, which is related to the binding energy. The basic characteristic of the Langmuir isotherm is a non-dimensional constant, called equilibrium parameter (R_l), which can be defined through the following equation.

$$R_l = \frac{1}{(1 + bC_o)} \tag{5}$$

In the above equation, C_o is the initial concentration of dye in terms of ppm. R_L indicates the type of isotherm that if R_L =0, it is irreversible; $0<R_l<1$ is desirable; R_L=1 is linear; and finally R_l> 1 is undesirable [17]. Figure 7 is illustrated according to adsorption data based on Langmuir isotherm. The date fitted with respect to discussed isotherm having, R^2 value of 0.99.

Temkin Isotherm: Temkin model is another adsorption isotherm model constructed to describe the adsorption phenomenon. The corresponding equation can be expressed as follows:

$$q_e = (RT / b)\, ln\, A + (RT / b)\, ln\, C_e \tag{6}$$

$$RT / b = B \tag{7}$$

$$q_e = B_T ln A_T + B_T ln C_e \tag{8}$$

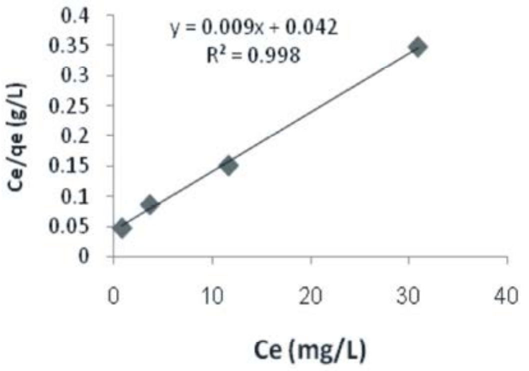

Fig 7: Langmuir model

Table 1: Coefficients of erythrosine dye adsorption isotherm

	Langmuir model	
b (L.mg^{-1})	Q_0 (mg.gr^{-1})	R^2
0.2329	101	0.998
	Frendlich model	
N	K_f (mg.g^{-1})	R^2
1.5723	3.4452	0.9816
	Temkin model	
B (J.mol^{-1})	A (L.gr^{-1})	R^2
43.519	1.6418	0.9935

Table 2: Calculation for kinetic parameters first and second order reactions

First-order Reaction model		
R^2	K_1 (min^{-1})	q_e (mg/g)
0.4887	0.0006	68.08
Second-order Reaction model		
R^2	K_2 (mg/gmin)	q_e (mg/g)
0.9999	0.05192	35.714
Richie Kinetic model		
R^2	q_e (mg/g)	K_r (min^{-1})
0.9783	36.364	1.175
Elovich model		
R^2	a (mg.g^{-1}.min^{-1})	b (g.mg^{-1})
0.9025	31.381	0.5786

In the above equation, A is in terms of L.g^{-1} and B is in terms of J.mol^{-1}. They are both Temkin's constants which are determined by plotting $q_e$versus LnC_e.

Table 1 summarized data for the adsorption processes in desired agreement with Langmuir adsorption isotherm [17]. Figure 8 shows date fitted with respect to Temkin adsorption model having R^2 value of 0.99.

Kinetic Studies: The term 'kinetic' shows the motion or the change. In the present study, kinetics refers to the rate of a reactionas the change in the concentration of the

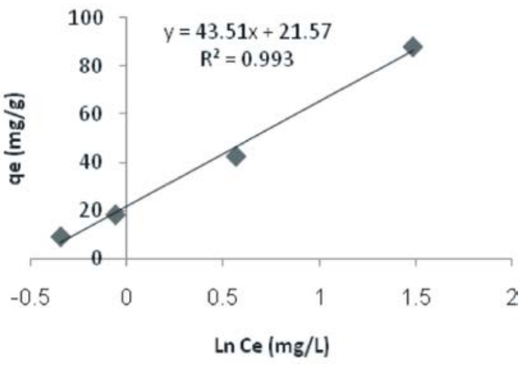

Fig 8: Temkin model

reactant or product over time. Kinetic tests are usually performed at several concentrations of adsorbent. By conducting kinetic experiments under different conditions, the contributory factors in the adsorption rate and adsorption rate-limiting step can be identified. For the analysis of the adsorption kinetics, the first and second kinetics models can be used.

First Order Kinetic Model: To express the adsorption rate of the dissolved substances from the aqueous solution, the following equation is employed:

$$dq\ /dt\ = K_1(q_e - q_t) \tag{9}$$

By integrating both sides of the above equation for the boundary conditions at t = 0 to t = t and q = 0 to q = q_e, the following linear form will be obtained:

$$ln\ (q_e - q_t)\ =\ ln\ q_e - K_1 t \tag{10}$$

This equation has been applied to describe the adsorption kinetics of different systems. Figure 9 depicts the kinetics data for first-order reaction; the kinetic data does not show any promising results as data are scattered.

Second Order Kinetic Model: Another equation for kinetic analysis of adsorption is quadratic equation, which is expressed as follows:

$$dq\ /dt\ =\ K_2(q_e - q)^2 \tag{11}$$

K_2:Quadratic equation rate constant of absorbent (g mol^{-1} min^{-1})

By integrating the above equation for the boundary conditions as t = 0 to t = t and q = 0 to q = q_i, the following equation can be obtained.

$$t\ /q_t = 1/K_1 q_e^2 + t/q_e \tag{12}$$

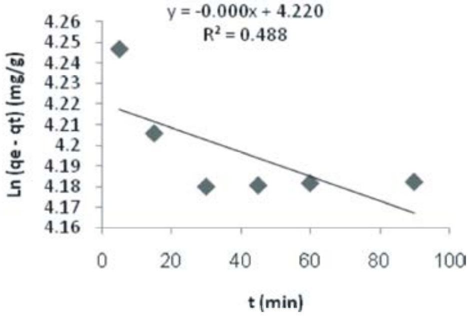

Fig 9: Kinetics data for first-order reaction

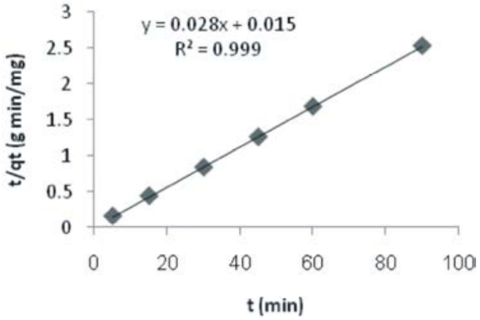

Fig 10: Kinetics data for the second-order reaction

By plotting t/q_t versus *t*, a straight line is obtained, for which the slope and the intercept are $1/q_e$ and $1/K_2 q_e^2$, respectively. Consequently,the equilibrium adsorption capacity, q_e and the adsorption rate constant can be determined [18]. The kinetics data for the second-order reaction is more satisfactory as data are shown in Figure 10, well fitted with R^2 value of 0.999.

Elovich Model: Elovich model is explained by the following equation:

$$q_t = 1/b\ ln\ (\ a\ b\ )\ +\ 1/b\ ln\ t \tag{13}$$

where a is initial adsorption rate in terms of $mg.g^{-1}.min^{-1}$, b is pay constant in terms ofg.mg^{-1} and q_t is the amount of the dye adsorbed at time t in terms of $mg.g^{-1}$. By plotting q_t versus ln (t) values of *a* and *b* are defined. Figure 11 illustrates Elovich model which is shown adsorption data are fairly fitted.

Richie Kinetic Model: Richie Kinetic Model is expressed by the following equation:

$$1/q_t = 1/K_r q_e t\ +\ 1/q_e \tag{14}$$

In the above equation, K_r is the rate constant in terms of $min^{-1}$where as q_e and q_t are defined as before. By plotting $1/q_t$ versus 1/t values of q_e and K_r are obtained. Figure 12 depicts Richie kinetic model which is shown adsorption data are fitted well with theoretical projected model.

The SEM images of the *Ziziphus nummularia* kernel adsorbent before and after adsorption are shown in Figs. 13 and 14. As the image is clearly observed in Fig. 13 no deposition of dye is shown on the surface; while the dye is seriously deposited on active cite of the *Ziziphus nummularia* kernel adsorbent (see SEM image of Figure 14).

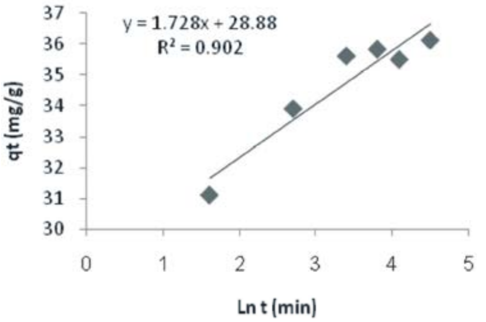

Fig 11: Elovich model diagram

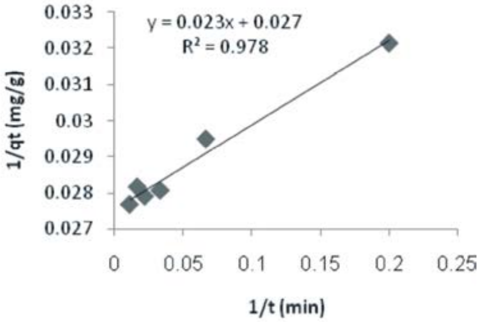

Fig 12: Diagram of Richie Kinetic Model

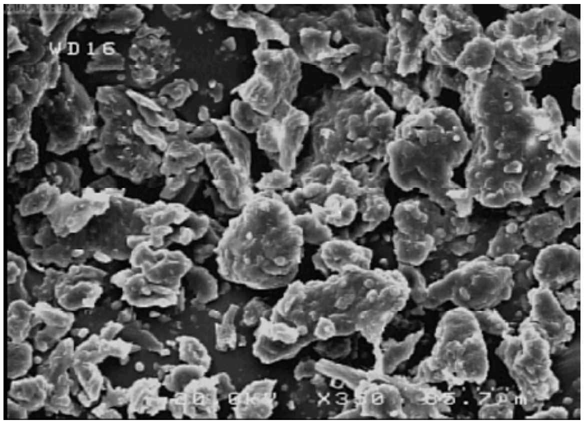

Fig 13: SEM image of the *Ziziphus nummularia* kernel adsorbent before adsorption

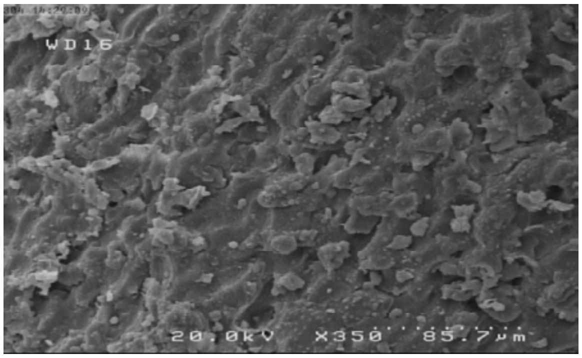

Fig 14: SEM image of the *Ziziphus nummularia* kernel adsorbent after adsorption

CONCLUSIONS

The results of the present study showed that *Ziziphus nummularia* kernel is an effective adsorbent for the removal of erythrosine dyes from wastewater. Therefore, application of natural adsorbents can be a viable alternative to industrial adsorbents because they are often non-expensive and easily available. Langmuir and Freundlichisotherm equations were used to describe the equilibrium data. It was observed that the adsorption process is in good agreement with Langmuir adsorption isotherm and seems to follow the assumptions and conditions of this isotherm. Result of bleaching erythrosine dyes with concentration of 20 mg L^{-1} on *Ziziphus nummularia* kernel sorbent with concentration of 0.1 g L^{-1} shows an efficiency about 93.7% dye removal. The adsorbent capacity was 101 mmol per gram.

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Persian Abstract

چکیده

در این مقاله امکان استفاده از هسته میوه رملک به عنوان یک نمونه از ضایعات کشاورزی ارزان قیمت جهت حذف رنگ سمی اریتروزین از پساب که موجب بروز بیماری ها و صدمات جبران ناپذیری به چرخه محیط زیست و انسانها می شود مورد بررسی قرار گرفته است. با توجه به غیرقابل استفاده بودن هسته رملک می توان بیان نمود که استفاده از هسته رملک به عنوان یک جاذب طبیعی رنگ اریتروزین روشی کارآمد و مقرون به صرفه می باشد. مطالعه حاضر یک پژوهش کاربردی است که در مقیاس آزمایشگاهی انجام شده است در این تحقیق تاثیر فاکتورهای موثر pH، زمان تماس، غلظت رنگزا، دما و مقدار جاذب در میزان رنگبری رنگزای فوق مورد بررسی قرار گرفته و نتایج حاصل توسط ایزوترم های جذب لانگمویر و فرندلیچ ارزیابی شده است. ظرفیت جاذب مورد مطالعه ۱۰۱ میلی مول به ازای هر گرم جاذب به دست آمده است.