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Removal of Congo Red Dye from Aqueous Solutions by Activated Carbon Prepared from Olive Stones

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Abstract: ***In this study the prepared activated carbon made from olive stones (AC) was used as an alternative, available, low cost, and friendly material in removal of a congo red dye (CR) from wastewater. Obtained results indicate nice fitting to Langmuir and Freundlich isotherms and represented an efficient removal of CR by AC in a short time at normal conditions, also the reaction process clearly follows a pseudo-second order model.***

Keywords: Wastewater; congo red; Langmuir and Freundlich isotherms

1. Introduction

Water is one of the most fundamental components of human life and a significant source for conserving and sustaining the ecosystem and the environment[1]. Dyes manufacturing industries are significant industries which are widely used in leather, paper printing and cosmetics. Nowadays, the production of dyes is nearly about 800,000 tons per year worldwide. Consequently, 10-15% of synthetic dyes are wasted into the environment through the operation of dyes industries[2].

Synthetic dyes are major source of pollution worldwide [3].There is an enormous number of dyes used in Textile industry. Congo Red dye (CR)was discovered in 1883 by Paul Bottinger and used in Textile industry. CR dye is classifies as a part of azo class[4]. Nowadays a huge number of dyes such as CR are widely used for the dyeing of cellulosic textiles[5].

There is no Doubt that the Textile industry lead to several problems of human health and environmental hazard. In other words, Dyes could continue to exist for long time because of high thermal and photo stability to resist biodegradation. In addition, one of the most implications of the environment associated with dyes is their absorption and reflex ion of sunlight infiltrate the water. However, Dyes can affect a human health by inhalation of dye particles which lead to respiratory problems[3].There are several methods for the removal of dyes such as adsorption, coagulation flocculation, ultra-filtration, nano-filtration, adsorption onto activated carbon etc[6].In this paper the removal of Congo Red dye (CR) by activated carbon made from olive seeds was investigated

2. Materials and Methods

2.1. Chemicals and reagents

Congo red and Orthophosphoric acid 85% were purchased from BDH Chemical LTD England.

2.2. Preparation of Activated carbon

Olive cake sample was collected from olive oil refinery in Alkhoms city during the year of 2018. Activated carbon was prepared by washing olive stone material with tap water first followed by washing and then boiling the sample for a few minutes in distilled water .The sample was dried in an oven for 24 h at 110 C^o. Olive stones were separated using 500 Micronsieve. Chemical activation was carried out by impregnation with orthophosphoric acid 60% w with impregnation ratio 1.6for 48h in a shaker. The acidized sample was then put in a closed crucibleand carbonized in a furnace at 600 C^o for two hours. The carbonized sample was left to cool and then washed with water to remove the acid. After drying in an oven for 24h at 110$C^o$the sample was then crushed and sieved (using 75Micron sieve).

2.3. Adsorption experiments

Batch adsorption experiments were performed at room temperature (22C^o-26C^o). The experiments were carried out by adding known amounts of AC to CRsolution 100mg/L in 50ml stopper conical flasks, these flasks were placed on a shaker (Johanna Ottogmbh, ks50a,the absorbance of CR was measured at 497 nm by UV-Vis Spectrophotometer with 1cm Plastic cuvette cell, (JENWAY, MODEL- UV-6305).6171BR00525 Germany).The shaker speed was fixed at 150 rpm to maintain the equilibrium condition.

3. Results and discussion

3.1. Effect of contact time

Contact time is an essential factor to obtain the equilibrium time of adsorption process. This experiment carried out at different periods (3, 6, 15, 20, 30, 45, 75 min) and each sample was filtered from AC by gravity filtration method. Then the removal percent (R %) was obtained using equation (1).

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

Where;
R is the percent of CR removal, C_o is the initial concentration of CR, C_e is the concentration of CR at equilibrium.

The results demonstrated that the removal percent (R %) of CR increases with the increase in contact time (t).

Experiments show fast absorption capacity for CR at the beginning (less than 5 minutes), and then gradual adsorption (started from 5 up to 45 minutes). However, the equilibrium was reached after 45 minutes as illustrated in the next figure.

Table 1: Time versesthe value of removalpercent

t (min)	Removal %
3	60.31
6	63.9
15	64.96
30	65.81
45	66.44
75	66.44

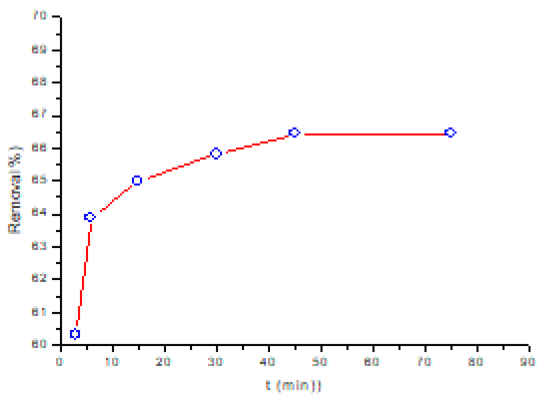

Figure 1: Effect of contact time on Congo red uptake

3.2. Adsorption isotherms

The data were fitted in two types of adsorption isothermmodels in order to find out some important parameters about the adsorption of Congo red on the prepared activated carbon made of olive seeds.

Table 2: Values needed for Isotherm models

Activated carbon dosage /g	Ce = equilibrium concentration mg/l	Abs.	(Co - Ce)	$qe = \frac{Co - Ce}{V}$	Ce/qe	$\log q_e$	$\log C_e$
0.05	40.02	1.26	5.998	119.962	0.334	2.079	1.602
0.08	15.57	0.49	8.443	105.532	0.148	2.024	1.192
0.1	5.54	0.174	9.446	94.457	0.0587	1.975	0.744
0.14	1.42	0.044	9.858	70.417	0.020	1.848	0.151
0.16	0.97	0.03	9.903	61.893	0.016	1.792	-0.013
0.18	0.65	0.02	9.935	55.193	0.012	1.742	-0.184
0.2	0.34	0.01	9.966	49.832	0.007	1.698	-0.473

a) The linearized Langmuir isotherm equation is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{KQ_{max}} + \frac{C_e}{Q_{max}} \text{.......... (2)}$$

Where: qe (mg/g) is the maximum amount of an entity adsorbed at equilibrium, Q_{max}(mg/g)is the maximum amount of material per unit mass of adsorbent to form a complete monolayer on the surface, k (mg/g) signifies the entity's monolayer capacity of the adsorbent, C_e (mg/L) is the concentration of an entity at equilibrium. If the adsorption system follows a Langmuir adsorption model, then a plot of C_e/q_e versus C_e would produce a straight line from which Q_{max} and k could be evaluated from the slope of the line and the intercept respectively

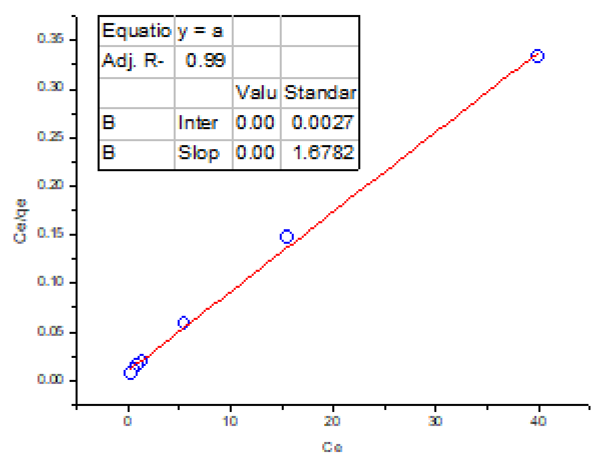

Figure 2: Langmiur isotherm for Congo red adsorption on activated carbon

b) The linearised Freundlich isotherm equation is represented as follows:

$$\text{Log}q_e = \log k + \frac{1}{n}\log c_e \text{.......... (3)}$$

If the adsorption system follows a Freundlich adsorption model, then a plot of $\text{Log}q_e$ versus $\log c_e$ would produce a straight line from which n and k could be evaluated from the slope of the line and the intercept respectively.

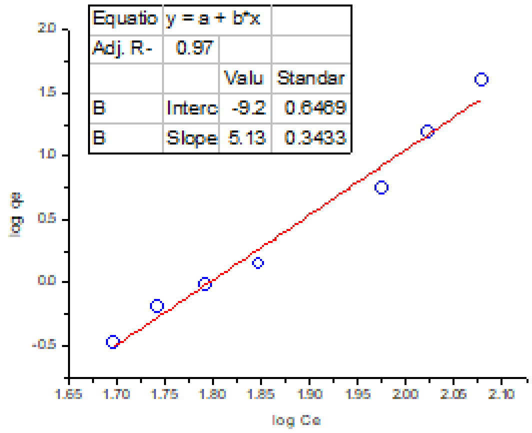

Figure 3: Freundlich isotherm for Congo red adsorption on activated carbon

The estimated value of "K" required for evaluation of the monolayer adsorption capacity of adsorbent is summarized in table (3)

Table 3: Parameters of Langmuir and Freundlich isotherms

Langmuir isotherm model			Freundlich isotherm model		
Q_{max} (mg/g)	K (mg/L)	R^2	K	1/n	R^2
125	0.89	0.99	$6.3X10^{-10}$	5.13	0.97

3.3. Adsorption Kinetics

Kinetics of the adsorption process was studied by fitting the data into pseudo-second order model

$$\frac{t}{qt} = \left(\frac{1}{kq_e^2}\right) + \left(\frac{1}{q_e}\right)t \text{.......... (4)}$$

Where q_e (mg/g) and q_t(mg/g) are the amounts of CR dye adsorbed at the equilibrium and at *t*(min) respectively, and (K, mg/g. min) is Kinetic rate constant. Plotting t/qt against *t*(as in figure 4) results a straight line where the values of K and q_e are obtained respectively from the intercept and slope of that line. Table 4 shows the kinetic parameter (K, q_e) of the pseudo-second order model.

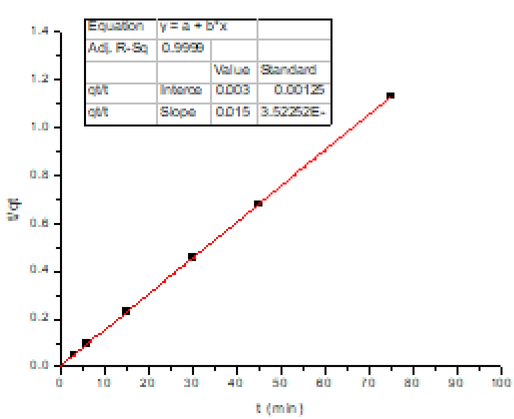

Figure 4: Pseudo-second order kinetic model

Table 4: Parameters of pseudo-second order model

qe(mg / g)	k (mg/g. min)	R^2(correlation coefficient)
66.66	0.075	0.99999

3.4. Comparison with other studies

The activated carbon from olive stones prepared in this study showed good maximum uptake capacity $Q_{max}$for the removal CR dye. The Value of Q_{max} achieved in this study is comparably higher than the values of Q_{max} obtained from other studies using various sorbents. Table (5) shows the maximum uptake capacity Q_{max} for different sorbents.

Table 5: Comparison of the maximum uptake capacity Qmax of various adsorbents for the removal of CR dye

Adsorbent	Q_{max}(mg/g)	Reference
Cashew nut shell	5.18	7
Cattail root	38.79	8
coir pith activated carbon	6.70	9
Bael shell carbon	98.04	10
Olive stone activated carbon	125	This study

4. Conclusion

In this study, we investigated the removal of CR from aqueous media by activated carbon made from olive stones. Parameters such as contact time and adsorbent dosage were evaluated. The equilibrium was reached after 45 min with percent removal of CR equal to 66.44%. The maximum monolayer adsorption capacity obtained from Langmuir isotherm model was equal to 125 mg/g. The experimental data of equilibrium were well fitted to the Langmuir and Freundlich isotherm models. The adsorption of CR on the activated carbon made from olive stones follows a pseudo-second order kinetic model.

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