



Evaluation of the Efficiency of Tea waste powder to Remove the Safranin O dye Compared to the Activated Carbon as adsorbent

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ABSTRACT

Tea waste and active carbon manufactured from dates' stone were used as adsorbents for removal Safranin O dye and the results were compared. Safranin O dye removal efficiency was studied by batch adsorption. The experimental results displayed that the removal efficiency of dye on the two adsorbent were greatest at high acidic solution of SO solution for tea adsorbent, while for Activated Carbon at high alkalinity for the same dye. This study shows the adsorption equilibrium isotherms were followed Freundlich and Langmuir isotherms, where safranin O dye adsorption obey Freundlich isotherm. The effect of temperature was studied and thermodynamic parameters were calculated.

Keywords: Safranin O dye, Activated Carbon, Tea waste, Adsorption equilibrium isotherm.

INTRODUCTION

Water pollution is the most serious problem due to development the technology of industries associated agricultural and domestic activities. Dyes and pigment have a large uses and found in all segment of environment. Dyes as known used for coloring and pigmentation in many kinds of industries like food, plastics, textile, paper rubber, etc. Safranin dye is considered as a toxic material and it has a tremendous impact on the human health¹. Different methods with varying degree

of success have been developed to control and management of water and waste water pollution. Some of them included chemical precipitation, coagulation, filtration, oxidation, ion exchange and adsorption². Among of these available methods used for water treatment, Adsorption considered the best technique associated with other methods because of easy operation, convenience, and simple in designation. Furthermore, this method can remove or reduce varying types of pollutants' and thus it widely applicable in water treatment and pollution control³. There are many locally materials



used as adsorbent materials. Tea leaves waste as waste from restaurants and cafes can be applied as a secondary product that helpful in our society, also its can be consider as a high efficient, available, easy and faster method of purification domestic and industrial water instead of filtration and flocculation⁴. Activated carbon (AC) has been found an important and widely used as an adsorbents industrial waste water⁵. Also the commercial activated carbon is expensive and in the present time, researchers efforts for focusing on cheaper, more economic and efficient adsorbents⁶. Active carbon had been prepared from different materials that considered as a plant waste like sawdust, pomegranate peel, peat, coal coconut shell, palm kernel shell, cotton stalk, spent tea leaves ... etc⁷. this research, we dealing with manufacturing of two adsorbents which are tea waste and activated carbon produced from dates stone. The two adsorbents are used for safranin-O removal in aqueous solution by batch adsorption. Several parameters was studied like contact time, pH value, initial concentration of dye and temperature.

MATERIALS AND METHODS

Preparing adsorbent materials

A-Tea leaves waste

After collecting the tea leaves from the kitchen and cafes waste, the brown tea wastes were washing with water repeatedly. Tea waste boiled in water for 3 h to eliminate the fully soluble colored ingredients, and then drying at room temperature for several days, grinding and sifting to the desired size and stored in plastic container for later use.

B-Manufacturing of activated carbon from dates' stones

The source of organic material was dates' stones and following steps were adopted in the preparation process:

- First the dates' stones were washed totally with water to extract the suspended materials and clingy sweet remnants that attached the dates' stones. Then the cleaned dates' stones and transferred to oven at 110 C° for drying and that made stones crushed and grinded easily.
- 50 g/ 25 ml aqueous solution of zinc chloride was added to 25 g of crashed dates' stones and completely mingling, then the mixture left

overnight for saturation.

- Carbonization of saturated dates' stones done according to Yahia A. Alhamed⁸ method by putting it in furnace at 500 C° for 1 hour.

C-Adsorbate preparation

The stock solution of safranin-o dye was 1000 mg/1 L in distilled water by weighing of 1 g of dye powder in chemical balance and dissolved in water them completed to 1 L. Series of diluted solutions were prepared to obtain the required concentrations under study. The UV-Visible spectrophotometer scan of safranin-o dye was determined, where λ_{max} equal to 518 nm. Fig. 1 illustrates the structural formula of safranin-O dye.

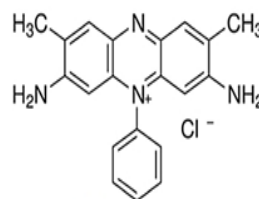


Fig. 1. The structural formula of safranin-Odye

Batch adsorption experiments

By batch adsorption, the effect of adsorption contact time, pH, adsorbate dosage, temperature, and adsorbent particle size on removal efficiency were studied. Experimental procedures were carried out for two adsorbent materials: leave tea waste and activated carbon prepared from dates' stones. In all practical experiments 0.15 g of tea waste and 0.05 g activated Carbon mixed with 50 ml of safranin-O dye (10 ppm) in shaking to evaluate the contact time, which equal to 10 min and 12 min for activated carbon and tea leaves respectively. The particle size of tow absorbents was 53 μ m and the natural dye pH equal to 5.

RESULTS AND DISCUSION

The effect of period time to achieved adsorption equilibrium was studied under following operating conditions: 10 ppm initial dye concentration, 0.15 g of tea waste and 0.05 g activated Carbon dosage, and pH= 5. The data obtained were illustrated in Fig. 2 as explained that adsorption efficiency was increased with proceeding of time, till the equilibrium state was 10 min for activated carbon and 12 min for tea leaves.

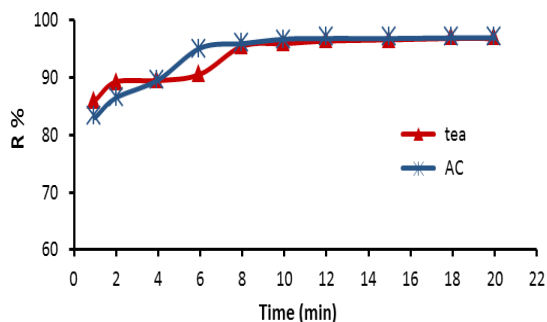


Fig. 2. Effect of contact time on removal safranin O dye percentage onto (tea waste and AC) surface at (25±3 C°) temperature

In contact time start, the removal process was fast due to available active sites in adsorbents, and these active site were saturated (the adsorbate molecules created monolayer on the surface of adsorbent) gradually so the removal percentage become constant at the equilibrium time⁹⁻¹¹. By changing of safranin-O concentration in the following 10, 20, 30, 40 and 50 ppm and the operating conditions were: room temperature, pH=5, and the adsorbent dosage was 0.15 g of tea and 0.05 g of activated carbon. Safranin-O concentration is represent an essential powerful factor effects on mass transfer of dye molecules between the solid and aqueous phases. Consequently, a higher dye concentration lead to improve the adsorption process¹². Fig. 3 illustrates the effect of safranin-O concentration for both of tea waste and activated carbon, where the removal and adsorption capacity of the safranin-O dye were different. When the concentration of dye is high the efficiency of removal decreased while adsorption capacity increased. This phenomena is depends on the abundance of the number of active sites on surface and the availability of dye molecules that occupied the active site. At low dye loading, occupation is incompletely in the active sites and then it's covered by dye molecules and the adsorption is at equilibrium¹³.

The data expression that as the dye concentration, the removal dye percentage reductions, because of saturation the active site that available on the surface of adsorbents. While at low dye concentrations, all the dye molecules existing in the adsorption medium may possibly interact with the active site, hence greater removal percentage was achieved¹⁴. The adsorbents doses of tea leaves and active carbon showed in

Fig. 4. as an effective factor for removal efficiency of safranin-O dye. At high doses of adsorbent, the removal efficiency increased. The enhancement in the removal efficiency can be explained to the increasing active sites of the adsorbent, and the surface area, where it is directly proportional with the adsorbent mass^{15,16}.

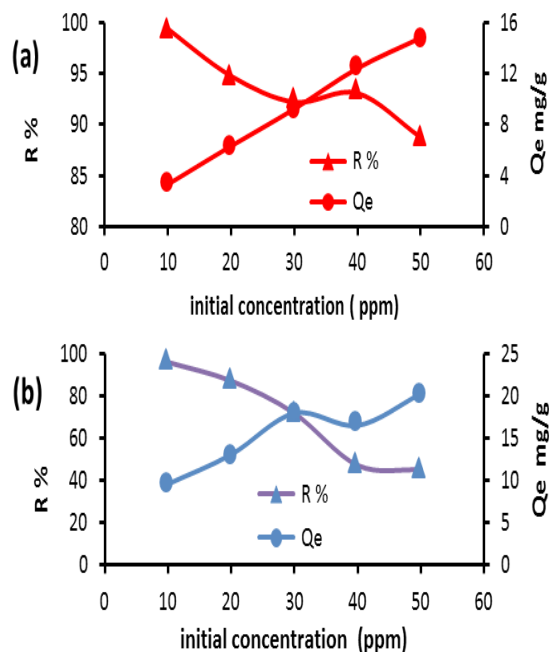


Fig. 3. Effect of safranin-O dye concentration on removal efficiency and adsorption capacity (a- tea waste and b- AC) surface at (25±3 C°) temperature

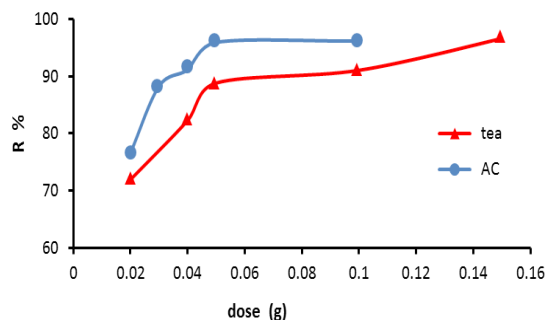


Fig. 4. Effect of tea waste and active carbon doses on removal efficiency of safranin-O solution

The powder particle size of tea leaves and activated carbon effect on efficiency removal was studied by differing the particle adsorbents size in the range (53, 75 and 125 μm), and the working conditions were: room temperature, pH=5 and the adsorbent dosage were 0.05 g charcoal and 0.15 g of tea. In Fig.5 illustrates a plot of removal dye

percentage vs. particle size of adsorbent. When size of (tea leaves and activated carbon) particle is fine, the removal percentage obviously increased. The result show that the particle size of adsorbent was 125 μm the removal percentage was 79.03%, while at a size of 53 μm the removal percentage reached to 93.7% for tea waste adsorbent. In case of the activated carbon, the removal percentage increased from 80.9% to 95.4% when particle size reduced from 125 to 53 μm for AC adsorbent. The increasing in the removal dye percentage to parallel reduce in adsorbent particle size, as the smaller in particle size, the surface area is greater⁹.

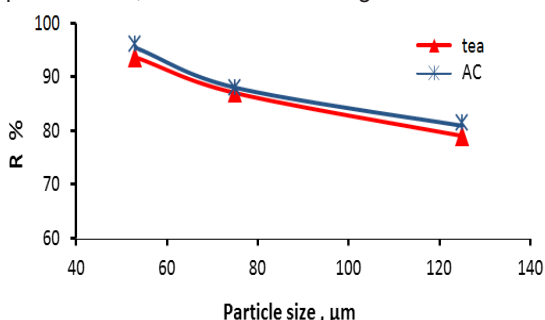


Fig. 5. particle size change of adsorbent on removal safranin O dye percentage onto (a- tea waste and b- AC) surface at (25 \pm 3 C $^\circ$) temperature

The change in the pH value of adsorbate solution alter average charge of adsorbent surface and effect on the ability of adsorption also pH value changes the adsorbate charge and this another factor influence the adsorption process. In Fig. 6 showed alteration of pH value on safranin O dye that adsorbed by tea leaves and active carbon.

Figure 6 shown, in case of tea waste, we note that the removal efficiency of safranin O dye increases when the pH of solution decreases. This phenomenon is caused by the presence of an increase of H⁺ ions changes the dye net charge, which increases the attraction with the negative charge of the surface. While when active carbon is used for adsorption of safranin dye, there is a slightly increase in the removal efficiency of dye with increased pH solution. At high pH, the OH⁻ ions on the surface of the adsorbent increases, where attraction forces between positively dye cation and negatively charged sites will increase¹⁷.

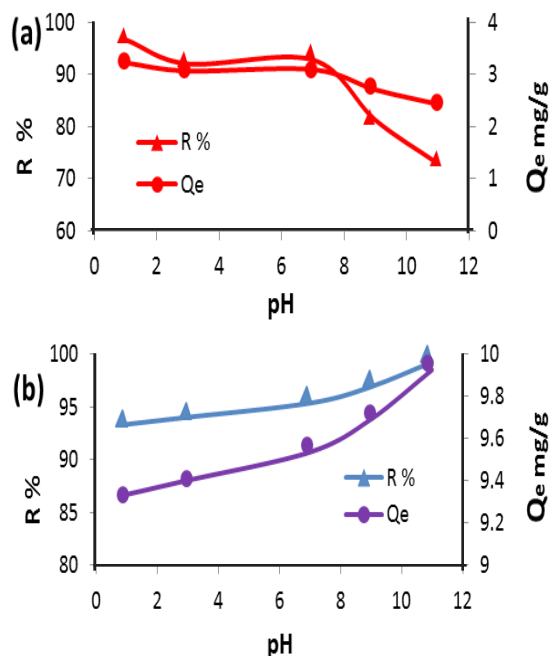


Fig. 6. pH alteration of dye solution on removal efficiency and adsorption capacity of safranin O dye onto (a- tea waste and b- AC) surface at (25 \pm 3 C $^\circ$) temperature

To identify the adsorption process nature, the thermodynamic parameters: Gibbs' free energy changes (ΔG°), entropy changes (ΔS°) and enthalpy change (ΔH°) calculated according to the following equations:

$$\Delta G = - RT \ln K_d \quad (1)$$

$$\ln K_d = - \frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (2)$$

Where: K_d is the equilibrium partition constant, R is the universal constant of gases (8.314 J/mol. K) and T is the absolute temperature in Kelvin.

The values of ΔS° and ΔH° calculated from the intercept and the slope of $\ln K_d$ versus $1/T$ in equation (2), this shown in Table (1). See Figure (7).

The parameters of thermodynamic at different temperatures are existing in the Table 1. The adsorption safranin-O dye on the both of adsorbents (synthesis active carbon and tea leaves waste) were spontaneous, this concluded From the negative value of ΔG° , generally this results is favorable^{18,19}. Furthermore, the adsorption was more spontaneous when rise temperature from

288K to 333K, the ΔG_o change from -26.01 to -20.08 KJ/mol for tea, and the ΔG_o change for charcoal from -17.381 to -35.196 KJ/mol. The nature of adsorption safranin-O dye on the charcoal was endothermic due to positive value of ΔH_o , while The adsorption on the tea was exothermic due to negative value of ΔH_o . Additionally, the positive sign of the ΔS_o value 392.595 (J/mol.K) for adsorption safranin-O dye on the active carbon indicating that the entropy raised at solid-liquid interface during adsorption safranin-O dye on the charcoal²⁰. Interface when used the tea as adsorbent, that the S_o value -131.519 (J/mol. K) which have negative sign. Adsorption isotherms is play an important role in explaining the interaction form between adsorbed species from solution and adsorbent, Certain adsorption models are accessible, but there are two significant isotherm are Freundlich isotherm, and Langmuir isotherm. Fig.(8) shows adsorption isotherms for safranin O dye on the both of adsorbents (tea and charcoal) at different temperatures. The dye uptake on both of adsorbents was determined by the equation 3.

$$Q_e = (C_o - C_e) V / wt \tag{3}$$

Where: Q_e (mg/g) adsorption capacity, C_o (mg/L) in the initial concentration of dye, C_e (mg/L) is adsorbed concentration at equilibrium, V (L) is solution volume of dye and wt (g) is the amount of adsorbent.

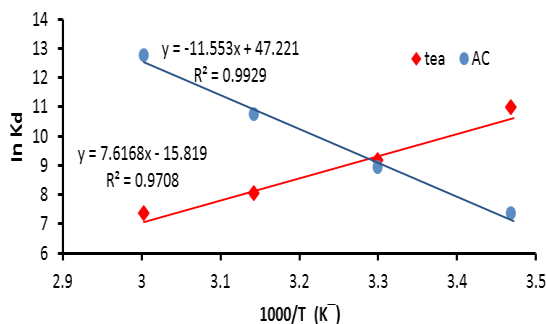


Fig. 7. Arrhenius plot for safranin O dye sorption on the both of adsorbents (tea waste and AC) at different temperatures

Table 1: Thermodynamic parameters at different temperatures

T(K)	Tea leaves			Activated carbon		
	ΔH^o (KJ/mok)	ΔG^o (KJ/mok)	ΔS^o (KJ/mok)	ΔH^o (KJ/mok)	ΔG^o (KJ/mok)	ΔS^o (KJ/mok)
288	-63.326	-26.013	-131.519	96.051	-17.381	392.595
303		-22.659			-22.536	
318		-21.177			-28.307	
333		-20.083			-35.196	

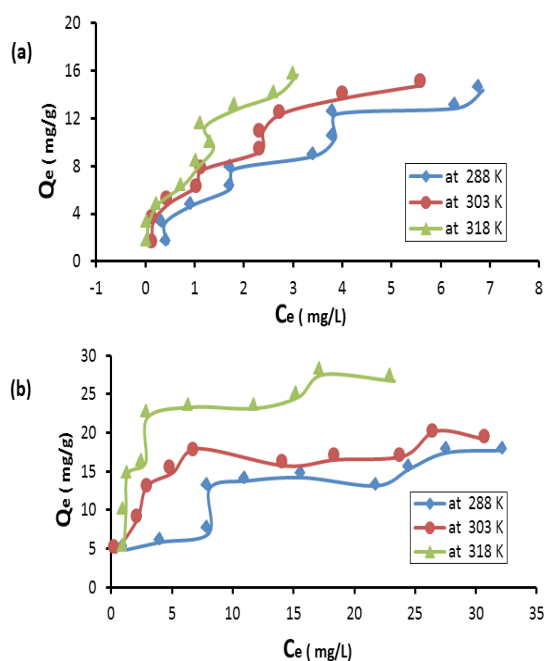


Fig. 8. Adsorption isotherms of safranin O dye onto (a- tea waste and b- AC) surface at different temperatures

The Langmuir isotherm assuming that the uptake of molecules of dye happens onto a homogenous surface formed monolayer adsorption, and the linear equation²¹ of this isotherm is.

$$\frac{1}{Q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \tag{4}$$

Where the Q_o is equilibrium capacity (mg/g); C_e is equilibrium adsorbed concentration(mg/L); Q_o is maximum equilibrium adsorbed per unit adsorbent mass (mg/g) and K_L the Langmuir isotherm constant (L/mg). By plotting values of $1/Q_e$ versus values of $1/C_e$, the values of K_L and Q_o was calculated from the slop and the intercept, see Fig.(9). The separation factors(R_L) is an important feature of the Langmuir isotherm is explained according to the following equation and calculations are listed in the Table 2²².

$$R_L = \frac{1}{1 + K C_o} \tag{5}$$

That the K is constant of Langmuir and the C_o initial dye concentration. The Langmuir constant is designate the nature of adsorption nature as, thus, according to the adsorption isotherm, when $R_L > 1$ the adsorption is unfavorable, $R_L = 1$ the adsorption is linear and $0 < R_L < 1$ the adsorption is favorable¹³⁻¹⁶.

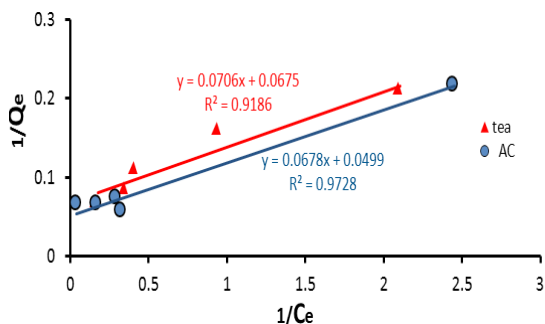
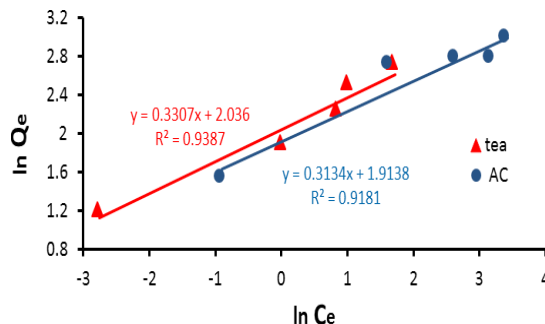


Fig. 9. Langmuir isotherm of safranin O dye onto (tea waste and AC) surface at 298 K

The model of Freundlich isotherm explains adsorption of the adsorbate on the adsorbent surface. It is usually employed for investigate the heterogeneity and the surface energies. The Freundlich isotherm expression follows equation 6²³.

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

Thus, K_f is adsorption constant which is the total capacity of adsorption (mg/g); $1/n$ is heterogeneity of the surface (dimensionless). The plot of $\ln Q_e$ against $\ln C_e$ for the adsorption data of dye is shown in Fig.10, which allows to calculate the Freundlich constant values, n^{-1} and K_f from slope and intercept, respectively. As show in the Table 2. The Adsorption equilibrium isotherms were studied according to the linear Freundlich and Langmuir isotherms, and the parameters K_L , K_f , n , and R_L were listed in the Table 2. The result showed that, the model of Langmuir isotherm and Freundlich isotherm acceptably explains experimental data. The correlation coefficient were higher for both utilized adsorbents $R^2= 0.938, 0.918$ for tea and charcoal respectively (Freundlich isotherm), and $R^2= 0.918, 0.972$ for tea and charcoal respectively (Langmuir isotherm), These results display a useful linearity. Moreover the suitable illustration of the Freundlich module possibly signifies adsorption of safranin-O on the charcoal was multilayer adsorption²⁴⁻²⁶. The findings display that the n value is more than one ($n=3.03$, and 3.19 for tea and charcoal respectively) representing that the dye adsorbed onto both adsorbents are favorable. This agree with the results value of R_L , the heterogeneity value in the Table 2, signify that the each the adsorbent particles have a heterogeneous structure²⁷⁻³⁰.



Figure(10): Freundlich isotherm of safranin O dye onto (tea waste and AC) surface at 298K

Table 2: Parameters of Freundlich and Langmuir Isotherm for the adsorption of safranin O dye onto (tea and charcoal) surface at 298 K

Isotherm models	Parameters	Surface	
		Tea leaves	Activated carbon
Freundlich	K_f (mg/g)	7.659	6.778
	$1/n$	0.33	0.313
	n	3.03	3.194
	R^2	0.938	0.918
Langmuir	Q_0 (mg/g)	14.814	20.04
	K_L (L/mg)	0.956	0.735
	R_L	0.094	0.119
	R^2	0.918	0.972

CONCLUSION

In this study, low-cost tea wastes were compared with active carbon prepared from dates' stones as adsorbent to remove Safranin O dye . The results were very convergent between tea wastes and active carbon as adsorbent for all studied parameters (the adsorbent dosage were 0.15 g of tea wastes and 0.05 g of active carbon). The results also showed that, the adsorption equilibrium is very short in time for both of adsorbents (10 min for activated carbon, 12 min for tea leaves). From the results above, we conclude that low-cost tea waste can be used as highly efficient adsorbent to remove dyes from Wastewaters.

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Conflict of interest

None to declare.

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