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Utilization of waste Tunisian palm tree date as low-cost adsorbent for the removal of dyes from textile wastewater

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Abstract: The removal of dyes such, as methylene blue and Congo red, from an aqueous solution is studied by adsorption Tunisian palm tree date. The equilibrium isotherm for each dye-adsorbent system was determined. The experimental results have been fitted with Langmuir and Freundlich isotherms. The maximum adsorption capacities of palm tree date are found to be 200 and 90 mg/g at dyes of methylene blue and Congo red, respectively. A comparative cost study, based on the adsorption capacity alone, has shown that the costs of the required adsorbent are 1.1%, and 1,8%, respectively, compared with the case of commercial granular activated carbon. The Gibb's free energy values obtained confirm that the process is feasible and spontaneous $\Delta G < 0$. The negative values of ΔH indicate that an exothermic chemisorption took place. The negative values of ΔS suggest that the randomness decreases after adsorption.

Keywords: Adsorption, waste palm tree, methylene blue, Congo red, equilibrium isotherm.

Nomenclature

b	Parameter of Langmuir isotherm (l/mg)
C_0	Initial dye concentration in aqueous solution (mg/l)
C_e	Equilibrium dye concentration in liquid phase (mg/l)
K_F	Freundlich constant
$1/n$	Freundlich parameter
q_e	Equilibrium dye concentration in solid phase (mg/g)
q_{max}	Maximum dye adsorbed per unit mass of adsorbent (mg/g)
ΔG	Free energy of adsorption (J/mol).
ΔH	Change in enthalpy (J/mol)
ΔS	Change in entropy (J/mol K)
R	Gas universal constant (8,314 J/mol K)
K_L	Langmuir adsorption constant (l/mg)

Introduction

Dyes are, used by plastic, paper, tannery, textile, and many other industries in Tunisia to color their products. The discharged waste waters from these industries into river water make in water inhibitory to aquatic life. In addition to causing visible pollution, dyes have a tendency to sequester metals, cause microtoxicity to fishes and other aquatic organisms. It is difficult to remove dyes from the effluent, because they are stable to light and heat, and are biologically non-degradable. Hence, the conventional methods used in sewage treatment, such as the primary and secondary treatment systems, are unsuitable[1-7].

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It is therefore necessary, to use tertiary treatment to remove color before discharging the wastewater into natural streams.

Activated carbon is largely used in water treatment for its high capacity and wide applicability of adsorption and ready availability. However, the adsorption capacity is function of the pore size and structure of the carbon and the molecular size and chemical nature of solutes. On the other, large molecules, such as dye, are not treated with the common activated carbon do to its pore characteristics.

Various adsorbents, such as natural zeolites[8-12], mesoporous silica[13] and activated carbon from apricot waste have been used for the dye removal from water[14].

There is a growing interest in using low cost commercially available materials for the adsorption of dye colors. A wide variety of low cost materials, such as clay minerals[15,16], peat[17], cotton waste, rice husk, bark[18], palm fruit bunch[19], jackfruit peel[20], wood[21], castor seed shell[22] and Mansonia wood sawdust[23-25], etc., are being tried as viable substitutes for activated carbon to remove dyes from colored effluents.

The palm date in Tunisia is a sector in full expansion. The palm tree has a very important role in south Tunisia, both from the socio-economic and ecological viewpoint. It is the basis of the economy in the region of Djerid and Nefzaoua and it is in a privileged position in the national economy. Tunisian palm groves cover an area of 22,500 ha, with around 3,000,000 trees. They assure rather irregular production, but they are in good evolution. Their current production amounts range from 85 to 90,000 tons[26].

The present investigation is undertaken to test the use of a cellulosic waste, Tunisian palm tree date, for the removal of different types of dyes such as methylene blue (a cationic dye) and Congo red (anionic dye) from water. The equilibrium and kinetic data of the adsorption are then studied to understand the adsorption.

Experimental Section

Palm tree date

The palm tree date used in this study was collected from Gabès, Tunisia. It was sliced applying planning, crushed to the minimum possible size and sieved to a geometric mean size of 500µm. The material was not subjected to any form of pretreatment before use. The identification of waste Tunisian palm tree was carried out by IR spectroscopy (spectrometer Brunker-tensor 27) Figure 1.

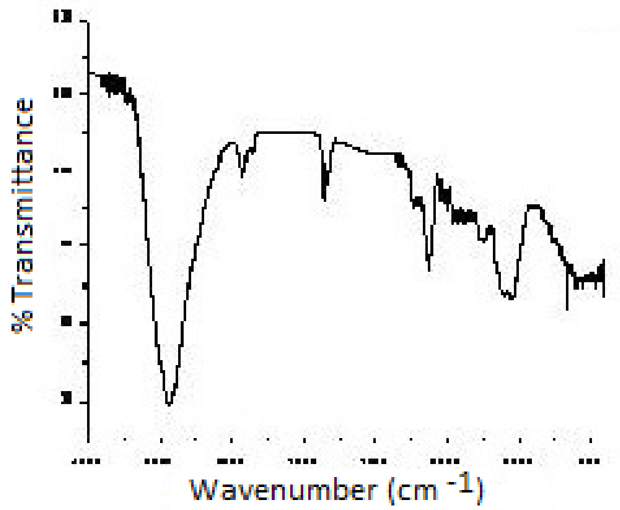
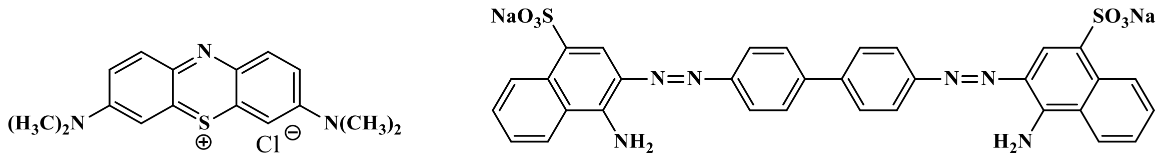


Figure 1. IR spectrum of the of waste Tunisian palm tree

The infrared spectrum shows three main bands: (i) a broad and intense band around 3434 cm^{-1} made of OH bonds that develop a hydrogen bond, (ii) band around 1631cm^{-1} showing the existence of C=C and (iii) a band around 1735 cm^{-1} representing C=O.

Dye characterization

Two dyes were used: methylene blue (MB) and Cong red (CR). The structure of each dye is listed in Fig. 2. The concentration of the dyestuff in the aqueous solution was determined employing a spectrophotometer. All the measurements were made at the wavelength that corresponds to the maximum absorbency, λ_{ma} = 630 nm for the methylene blue and λ_{max} = 500 nm for the Congo red[25]. Dilutions were undertaken when the absorbance exceeded a value of 0.6.



Methylene blue (MB) *Congo red (CR)*

Figure 2. Structure of different dyes used[27]

Methods

Batch adsorption experiments were conducted in a shaker bath at varying temperatures, using a constant amount of palm tree date particles with a series of 0.05 dm^3 dye solutions of different concentrations in sealed glass bottles. Equilibrium isotherms were constructed by shaking the bottles for a whole day. After that time, the samples were centrifuged and their equilibrium concentration C_e was determined using spectrophotometry. The amount of dye removed q_e was calculated using the relationship:

$$\mathbf{q_e = V\,(C_0 - C_e)\,/\,m_s}$$

Results and Discussion

Results

Plot of equilibrium dye loading q_e against the residual concentration of dye remaining in a solution after equilibrium, C_e, for different dyes is shown in Fig. 3 and Fig. 4.

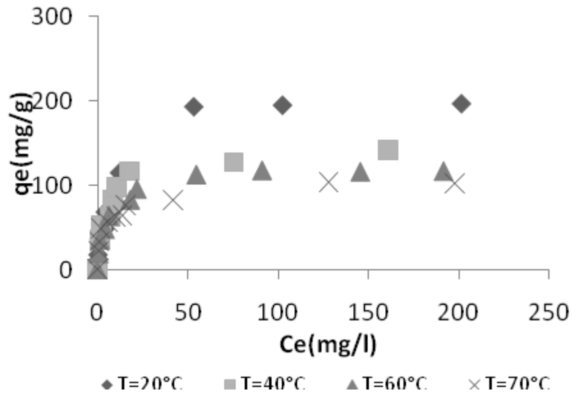


Figure 3. Adsorption isotherms for methylene blue dye

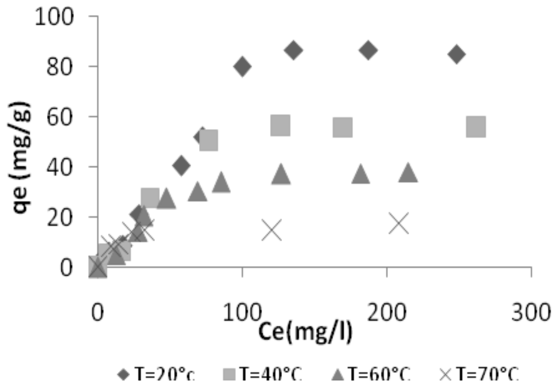


Figure 4. Adsorption isotherms for Congo Red dye

The data show that while the methylene blue can be easily removed from the solution, the Congo red cannot be easily adsorbed on palm tree date particles. The affinities of the cationic and anionic dyes to the adsorbent are methylene blue, Congo red. The structure of waste Tunisian palm tree is cellulose based, and the surface of cellulose in contact with water is negatively charged[28]. Most dyes are ionized in solution, many being salts or sulphonic or carboxylic acids while others contain acidic phenolic groups. The Congo red is an example of dye which ionizes to an anionic colored component D^- and a cation of Na^+. The approach of an acidic dye anion will suffer coulombic repulsion due to the presence of the strong anionic groups in waste Tunisian palm tree. Methylene blue is an example of a dye, which will be ionized to give the colored cationic dye base. This latter will undergo attraction on approaching the anionic waste Tunisian palm tree structure. The approach of an acidic dye molecule to cellulose is shown in the following scheme Figure 5.

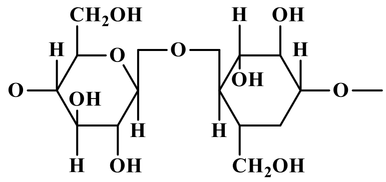


Figure 5. Waste Tunisian palm tree structure

Composed of up to 60% and 20% lignin[29], the lignins in waste palm tree are mainly derived from coniferly alcohol. The hydroxyle groups in lignin do not possess the same degree of activity as the phenolic and carboxylic groups in the humic and fulvic acids[30]. Nevertheless, they will exert a considerable repulsive force on approaching anions. On this basis, it is to be expected that a basic dye will have a strong adsorption affinity for waste palm tree. This can be observed by comparing the relative magnitudes of equilibrium uptake for the dyes shown in Table 1 as q_m values.

Analysis of adsorption isotherms for different dyes is important for developing an equation that can represent the results that can be used design purposes. The model forms of the Langmuir and Freundlich equations can be respectively represented as:

$$q_e = \frac{b.q_m.C_e}{1+b.C_e} \qquad \text{.........................(1)}$$

$$q_e = k_F\, C_e^{1/n} \qquad (2)$$

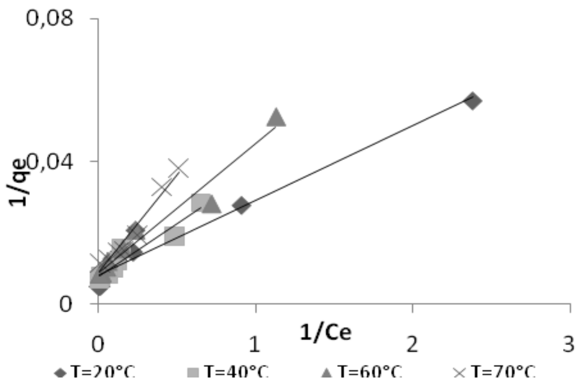


Figure 6. Langmuir plots corresponding to the adsorption of methylene blue

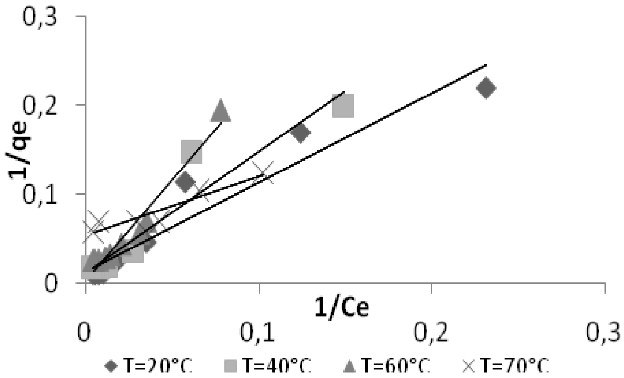


Figure 7. Langmuir plots corresponding to the adsorption of Congo red

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined as[31]:

$$\mathbf{R_L = 1/(1+a_L*C_0)} \qquad (3)$$

The isotherm parameters along with the regression coefficients are given in Table 1.

Table 1. Langmuir constants for methylene blue (BM) and Congo red (CR).

T(°C)	Dye	q_m (mg/g)	b (l/mg)	R^2	$R_L.10^2$
20	BM	122	0,392	0,954	2,05
	RC	73,53	0,013	0,925	49,9
40	BM	121	0,27	0,922	2,87
	RC	72,12	0,009	0,906	57,66
60	BM	112,036	0,25	0,960	3,44
	RC	30,03	0,001	0,954	95,85
70	BM	109,89	0,166	0,958	5,2
	RC	18,41	0,001	0,899	97,14

The results indicate that the adsorption capacity of palm tree date particles is high for the methylene blue and low for Congo red dye. The R_L values dictate favorable adsorption for $0 < R_L < 1$. The data in Table 1 show that the R_L values ranged between 0.02 and 0.95, indicating that palm tree date bunch particles are favorable for different dyes.

The experimental equilibrium data for the adsorption of different dyes on palm tree date particles have been analyzed using the linear form derived from the Freundlich isotherm (3). Figure 8 and Figure 9 present the plots of the Freundlich isotherms for the adsorption of methylene blue and Congo red respectively.

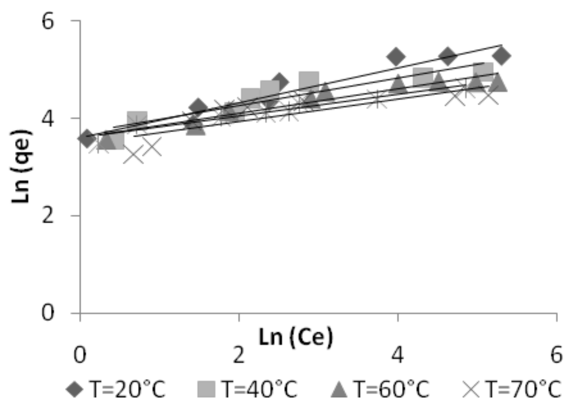


Figure 8. Freundlich plots corresponding to the adsorption of methylene blue.

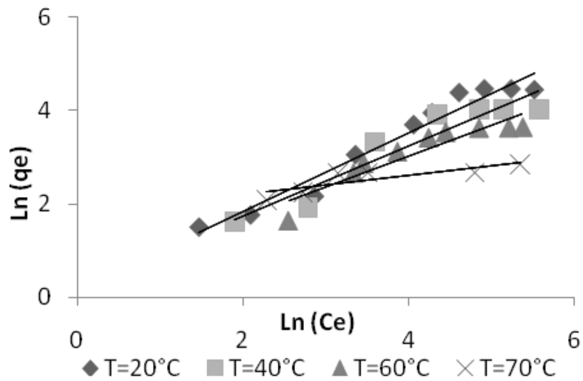


Figure 9. Freundlich plots corresponding to the adsorption of Congo red

The isotherm parameters along with the regression coefficients are given in Table 2.

Table 2. Freundlich constants for methylene blue (BM) and Congo red (CR).

T(°C)	Dye	K	n	R^2
20	BM	36 2	2,76	0,9235
	RC	1,149	1,179	0,9572
40	BM	407	3,58	0,8573
	RC	1,28	1,57	0,8084
60	BM	36 8	3,99	0,9217
	RC	1,2 6	1,36	0,8006
70	BM	32,38	4,31	0,6829
	RC	1,27	1,33	0,8955

The value of n, the Freundlich parameter, which was between 1 and 10 also confirmed that adsorption, was favorable.

Comparative costs of dye removal

To assess the economic feasibility of the new adsorbent, a cost comparison between activated carbon and palm tree date bunch particles was carried out. The equilibrium experiments were carried at 20°C using a uniform particle size of 500 µm. The maximum values of the adsorption capacity q_{max} were determined and the values were used as basis for estimating the adsorption process. Activated carbon was taken as a reference, having a comparative cost of one currency unit per kilogram. Table 3 shows the relative cost of palm tree date together with the adsorption costs for removing 1kg of dye. Results revealed that the relative cost to remove 1kg of dye are respectively 1,1% and 1,8% for methylene blue, and Congo red compared with activated carbon.

Table 3. Relative costs of methylene blue and Congo red removal.

Dye	Adsorbent	q (mg/g)	AMR	RCK	RCR
MB	Carbon	233	4.48	1.00	1.00
	PTD	200	5.00	0.01	0.0011
CR	Carbon	170	5.88	1.00	1.00
	PTD	90	11.11	0.01	0.018

PTD: Palm Tree Date.

AMR: Adsorption mass required to remove 1kg dye.

RCK: Relative cost per kilogram of adsorbent.

RCR: Relative cost to remove 1kg dye.

Thermodynamic analysis

The Langmuir isotherm constant, K_L, was used to estimate the thermodynamic parameters Gibbs free energy ΔG, change in enthalpy ΔH, and change in entropy ΔS. The free energy of adsorption ΔG can be related to the Langmuir adsorption constant by the following expression:

$$\Delta G = -RT \ln k_L \qquad (4)$$

Also, enthalpy and entropy changes are related to the Langmuir equilibrium constant by the following expression:

$$\ln k_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (5)$$

Thus, a plot of Ln $K_L$vs.1/T should be a straight line. ΔH and ΔS values could be obtained from the slope and intercept of this plot (Figure 10).

The values of ΔG were calculated using equation (4). A plot of Ln K_L versus 1/T was a straight line (Figure 10).

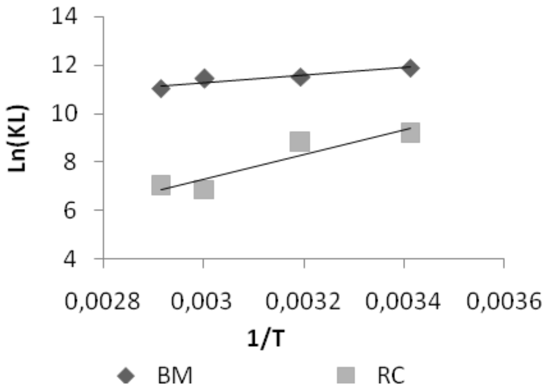


Figure 10. Van'tHoff plot for methylene blue and Congo red adsorption onto waste Tunisian palm tree date

From the slope and intercept, ΔH and ΔS were calculated. Results are shown in Table 4.

Table 4. Thermodynamic parameters

Dye	T (°K)	ΔG°	ΔH° (kJ/mol)	ΔS°
MB	293	-28,98	-12,48	-56,29
	313	-30,10		
	333	-31,23		
	343	-30,63		
CR	293	-22,81	-41,53	-63,88
	313	-21,54		
	333	-20,26		
	343	-19,62		

Gibbs free energy values were found to be between (-28, 98; -31, 23 kJ/mol) and (-19, 62; -22, 81 kJ/mol) for the methylene blue and Congo red respectively. Negative values of ΔG indicated that the adsorption process was spontaneous. The results show that the enthalpy of adsorption ΔH for methylene blue and Congo red was -12, 48, and -41, 53 kJ/mol, respectively, which was in the range of chemisorptions. The negative value of ΔH also indicated that the adsorption process is exothermic. Values of q_m for methylene blue were predicted to be 122; 121; 112; 36 and 109, 89 mg/g at 293; 313; 336 and 343 K respectively. The decrease in q_m with increase in temperature also confirms that methylene blue adsorption on waste palm is exothermic process. Meanwhile, the ΔS value was found to be negative -55.26 and -63.88 kJ/mol respectively for methylene blue and Congo red. The negative value of S indicated that the methylene blue and Congo red molecules are more regularly arranged on the adsorbent surface respectively for methylene blue and Congo red.

The negative value of ΔS indicated that the methylene blue and Congo red molecules are more regularly arranged on the adsorbent surface.

Conclusion

The experimental results proved that palm tree date particles have considerable potential for the removal of cationic dye from waste waters over a wide range of concentrations. The equilibrium isotherms determined were found to fit Langmuir and Freundlich isotherms. The current study also reveals that palm tree date can be fruitfully employed as industrial adsorbent for methylene blue and Congo red. The palm tree date is cheaper than the commercially available carbons while their performance is comparable. The thermodynamic analysis indicated that the adsorption of methylene blue and Congo red onto waste palm was: (i) exothermic; (ii) chemisorptions; (iii) feasible and spontaneous and (iv) decreased randomness on the solid surface.

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