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Kinetic and Thermodynamic Study on the Removal of Methyl Orange From Aqueous Solution by Adsorption onto Camel Thorn Plant

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The use of cheap, high efficiency and ecofriendly adsorbent has been studied as an alternative source of activated carbon for the removal of dyes from wastewater. This study investigates the use of activated carbon prepared from Camel thorn plant for the removal of methyl orange dye from aqueous solution. The effect of various experimental parameters such as contact time, temperature, initial dye concentration and dose of adsorbent were studied. The results showed that the adsorption of methyl orange as the amount of adsorbent increased, the percentage of dye removal increased accordingly but it decreased with the increase in initial dye concentration and solution temperature. The adsorption kinetics was found to follow pseudo-second-order rate kinetic model, ($R^2 > 0.99$). Langmuir and Freundlich isotherms were used to analyze the equilibrium data at different temperatures. The apparent thermodynamic parameters were calculated and the adsorption process was found to be spontaneous and exothermic.

Key Words: Methylene orange, Removal, Adsorption, Isotherm, Kinetic, Thermodynamic, Activated carbon, Camel thorn.

INTRODUCTION

In textile industries large amounts of water and chemicals are used for dyeing process. The wastewaters of this process usually consist of a number of contaminants including acids, bases, dissolved solids, toxic compounds and organic dyes. The dye compounds not only esthetically are displeasing, but also impede light penetration in the plants, thus upsetting the biological treatment process within the treatment plant. In addition, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities[1].

Wastewaters commonly contain moderate concentrations (10-200 mg L^{-1}) of dyestuffs, contributing significantly to the pollution of aquatic ecosystems. The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, *i.e.*, molecules with one or several azo (N=N) bridges linking substituted aromatic structures. These dyes are designed to be chemically

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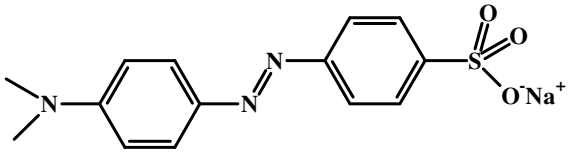
and photolytically stable. They exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life[2,3].

Conventionally, chemical coagulation/flocculation, ozonation, adsorption, oxidation, electrochemical treatment, filtration and floatation *etc*., are all means used for the removal of dyestuffs. Although they can remove dyes partially, their initial investment and operational costs are so high that they can be widely used in dyeing and finishing industries, especially in developing countries[4-6]. Among these processes, adsorption has been found to be superior to other techniques for waste-water treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity, but its use is limited due to its high-cost, has led to a search for cheaper substitutes. Natural materials that are available in large quantities may have potential as inexpensive sorbents. Due to their low-cost, after these materials have been expended, they can be discarded without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Material such as rice bran, sugarcane bagasse pith, bagasse fly ash, pomegranate peel, coconut shell, *Ulva lactuca* and *Sargassum*, *Azadirachta indica* leaf, hazelnut shell, Coir pith, orange peel, walnut shells, *etc*., as adsorbents for the removal of dyes from wastewaters[1,5-17].

In the present study activated carbon was prepared from low-cost adsorbent (Camel thorn plant) as a new adsorbent for the removal of methyl orange dye from aqueous solutions. The effect of different parameters such as temperature, contact time, adsorbent dose and initial dye concentration were investigated. The kinetic data and equilibrium data on batch adsorption studies were carried out to understand the adsorption process.

EXPERIMENTAL

Reactive methyl orange ($C_{14}H_{14}N_3NaO_3S$) is an anionic dye (**Scheme-I**). It was used as received without further purification. A stock solution of methyl orange (1000 mg L^{-1}) was prepared and suitably diluted to the required initial concentration. The concentration of the dye was determined at 470 nm, using UV/vis spectrophotometer (Perkin-Elmer Lambda 25).



Scheme-I: Structure of methyl orange (MO)

Adsorbent preparation: The Camel thorn plant collected from agriculture solid waste were washed several times with distilled water and dried in air and soaked for 24 h in a solution of phosphoric acid (28 %). After decantation, the sample was washed with distilled water and then was dried in an oven at 150 °C, overnight. The dried material thus obtained was then stored in desiccators for subsequent studies.

Adsorption studies: Batch adsorption experiments were carried out at room temperature (20 ± 2 ºC). Exactly 200 mL of reactive dye solution of known initial concentration (10-80 mg L^{-1}) was shaken at the constant agitation speed (700 rpm) with a required dose of adsorbents (0.1-1.5 g L^{-1}) for a specific period of contact time (10-240 min) in a mechanical shaker. After equilibrium, the final concentration (C_e) was measured. The percentage removals of dye were calculated using the eqn. 1:

$$\text{Removal of dye (\%)} = (C_0 - C_e)\ 100/C_0 \quad (1)$$

where C_0 and C_e are the initial and final (equilibrium) concentrations of dye (mg L^{-1}), respectively. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different concentrations (20-80 mg L^{-1}), at different temperatures (20-40 °C) were agitated with known amounts of adsorbents until the equilibrium was achieved. Equilibrium adsorption capacity was calculated from the eqn. 2:

$$q_e = (C_0 - C_e)\cdot V/W \quad (2)$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e is the dye concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent.

RESULTS AND DISCUSSION

Investigation of sorption parameters

Effect of initial concentration of dye and temperature on adsorption of methyl orange dye: The effect of initial concentration of dye on the removal of methyl orange (in terms of percentage removal) on adsorbent was studied as shown in Fig. 1. The percentage removal of the dye was found to decrease with the increase in initial dye concentration. This indicates that there exist reductions in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of methyl orange. Similar results have been reported in literature[5].

Fig. 2 illustrates the effect of temperature on adsorption for different initial concentration of dye. It is shown that the adsorption of methyl orange dye on activated carbon decreases as the solution temperature increases. Similar results were obtained by various authors for the adsorption of dyes on various adsorbents[7]. This can be explained by the exothermic spontaneity of the adsorption process and by the weakening of bonds between dye molecules and active sites of adsorbents at high temperatures.

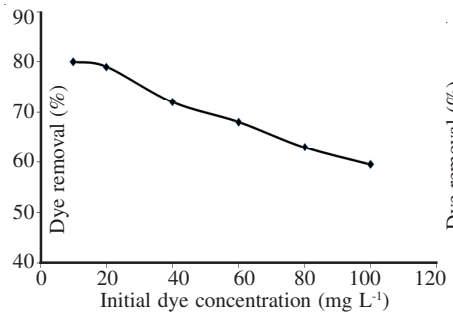


Fig. 1. Effect of initial concentration on methyl orange dye removal by activated carbon (dose of adsorbent = 0.5 g)

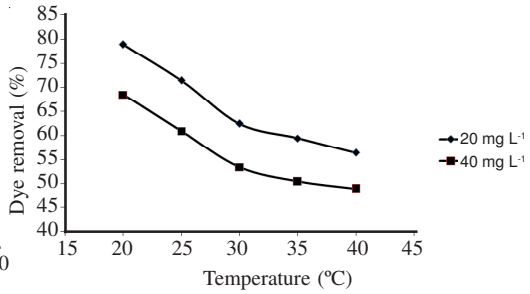


Fig. 2. Effect of temperature on methyl orange dye removal by activated carbon (dose of adsorbent = 0.5 g)

Effect of contact time: The effect of contact time on the percentage removal of methyl orange dye was investigated at initial dye concentration (10-80 mg L^{-1}) as shown in Fig. 3. The percentage removal of dye by activated carbon was rapid in the beginning but it gradually decreased with time until it reached equilibrium. The plots reveal that the maximum per cent removal of the dye after 90 min of shaking. The rate of removal is higher in the beginning due to larger surface area available of adsorbent. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles[1,5-6].

Effect of dose of adsorbent: The percentage removal of methyl orange increased with the increase in dose of adsorbent (Fig. 4). This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent[5].

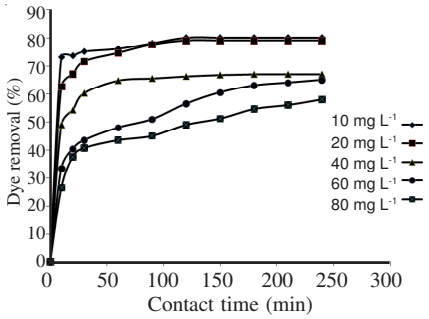


Fig. 3. Effect of contact time on methyl orange dye removal by adsorbent at different initial concentration

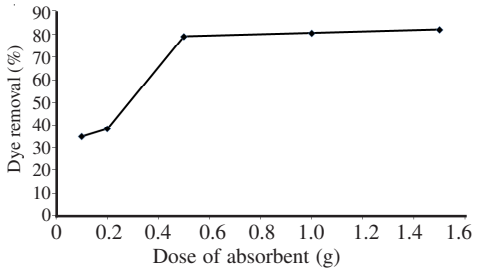


Fig. 4. Effect of dose adsorbent C_0 = 20 mg L^{-1}, contact time = 2 h

Adsorption kinetic study: The adsorption of a solute by a solid in aqueous solution is a phenomenon with often complex kinetics.

Pseudo-first-order model: The pseudo-first-order model was described by eqn. 3[2,7]:

$$\log (q_e - q_t) = \log (q_e) - k_1 t/2.303 \quad (3)$$

where q_e and q_t refer to the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}).

Pseudo-second-order model: The pseudo-second-order model[2,7] is represented by eqn. 4:

$$t/q_t = 1/k_2 qe^2 + t/q_e \quad (4)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). Experimental kinetic data were adjusted according to the indicated models (Fig. 5). The results of Table-1 showed that the second order equation model provided the best correlation with experimental results. This fact indicates that the sorption of methyl orange dye on adsorbent follows the pseudo-second order kinetic model[2,7].

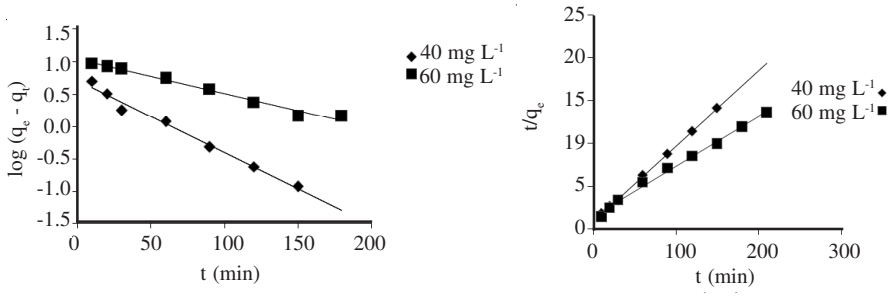


Fig. 5. (a) Pseudo-first-order and (b) pseudo-second-order kinetic models for methyl orange dye onto adsorbent

TABLE-1
RATE CONSTANTS FOR DIFFERENT KINETIC MODELS

Dye concentration (mg L^{-1})	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	R^2
40	0.025	0.986	0.0087	0.999
60	0.011	0.981	0.0021	0.993

Adsorption equilibrium study: Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. In order to discover the adsorption capacity of activated carbon prepared from Camel thorn, the experimental data points were fitted to the Langmuir and Freundlich isotherm eqns. 5 and 6 and the constant parameters of these equations were calculated (Fig. 6). Langmuir model[1,7]:

$$C_e/q_e = 1/Q_0K_L + C_e/Q_0 \quad (5)$$

where K_L is the Langmuir adsorption constant (L mg^{-1}) and Q_0 is the theoretical maximum adsorption capacity (mg g^{-1}) and in Freundlich model[4]:

$$\log q_e = \log K_F + 1/n \log C_e \quad (6)$$

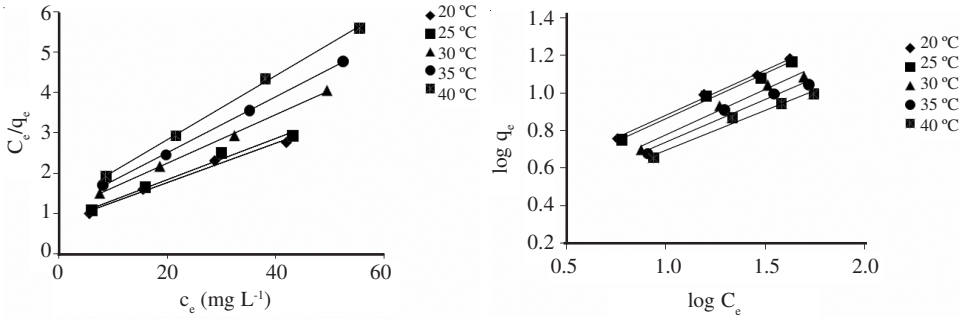


Fig. 6. (a) Langmuir and (b) Freundlish plots for the adsorption of the methyl orange dye onto adsorbent

where K_F (L mg^{-1}) and n are isotherm constant the capacity and intensity of the adsorption, respectively.

The values in Table-2 show that the experimental data were more suitable to the Langmuir model than to the Freundlich model. Corresponding to monolayer coverage of the binding sites availed in the adsorbent[2].

TABLE-2
FREUNDLISH AND LANGMUIR ADSORPTION
CONSTANTS AT DIFFERENT TRMPRATURES

T (K)	Freundlich isotherm			Langmuir isotherm		
	K_F	1/n	R^2	K_L	Q_0	R^2
293	2.496	0.484	0.997	0.0607	20.83	0.985
298	2.421	0.479	0.991	0.0618	19.61	0.984
303	1.959	0.484	0.977	0.0619	16.67	0.998
308	1.932	0.452	0.971	0.0620	14.49	0.999
313	2.042	0.399	0.982	0.0630	12.66	0.998

Thermodynamic study: Thermodynamic parameters were evaluated to confirm the adsorption nature and the inherent energetic changes involved during sorption. The thermodynamic constants, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. Therefore, the thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant K_0 with the change in temperature.

The constant K_0 for the adsorption reaction can be defined as:

$$K_0 = a_s/a_e = v_s\, q_e/v_e\, C_e \quad (7)$$

where a_s is the activity of adsorbed dye, a_e is the activity of dye in solution at equilibrium, q_e is the surface concentration of dye on adsorbent (mg g^{-1}), C_e is the concentration of dye at equilibrium solution (mg L^{-1}), v_s is the activity coefficient of the adsorbed dye and v_e is the activity coefficient of dye in solution. As the concentration of dye in the solution approaches zero, the activity coefficient approaches unity, reducing eqn. 7 to the following form:

$$K_0 = a_s/a_e = q_e/C_e \quad (8)$$

Values of K_0 were therefore obtained by plotting ln (q_e/C_e) *versus* q_e and extrapolating q_e to zero. Its intercept give the values of ln K_0.

Therefore, the thermodynamic constants can be obtained from the following equations:

$$\Delta G = -RT \ln K_0 \quad (9)$$

$$\ln K_0 = -\Delta H/RT + \Delta S/R \quad (10)$$

ΔH and ΔG can be obtained form the slope and intercept of Van't Hoff plot of ln K_0 *versus* 1 /T[7,18,19]. The data are presented in Fig. 7 and Table-3.

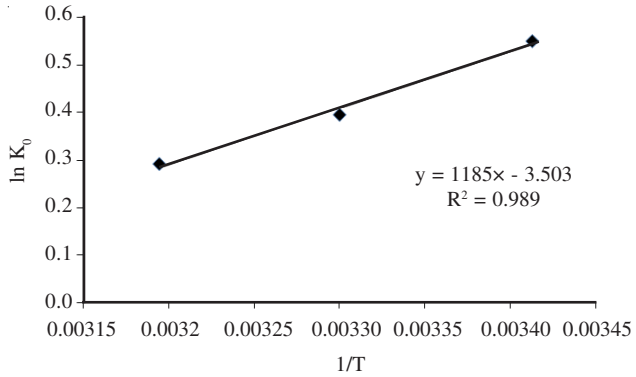


Fig. 7. Plot of Van't Hoff equation for adsorption methyl orange onto activated carbon

TABLE-3
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF MO DYE ONTO ACTIVATED CARBON

T(K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
293	-1.337	–	–
308	-0.990	-9.88	-29.12
313	-0.757	–	–

The negative ΔG values confirm the spontaneous nature and feasibility of the adsorption process. The negative values of ΔH further confirm the exothermic nature of the adsorption process, while the negative ΔS values suggest the decrease in adsorbate concentration in solid-liquid interface indicating thereby the increase in adsorbate concentration onto the solid phase. It also confirms the decreased randomness at the solid-liquid interface during adsorption.

Conclusion

In this work, Camel thorn plant has been used successfully as an adsorbent for the removal of reactive methyl orange dye from aqueous solutions. Adsorption was influenced by various parameters such as initial dye concentration, dose of adsorbent, contact time and temperature. Removal efficiency increased with decreasing the

dye concentration and increasing dose of adsorbent. The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption equilibrium of methyl orange dye onto adsorbent. The data were in good agreement with Langmuir isotherms. The results were shown that the adsorption of methyl orange onto camel thorn best fitted by pseudo second order model.

The determination of the thermodynamic parameters (ΔG, ΔH and ΔS) indicates the spontaneous and exothermic nature of the adsorption process. The negative sign of ΔS indicates that the adsorption process takes place through electrostatic interaction between adsorbent surface and adsorbate species in solution. Since camel thorn, an agriculture solid waste, used in this study, locally available, the adsorption process is expected to be economically viable for wastewater treatment.

REFERENCES

1. S. Hashemian, S. Dadfarnia, M.R. Nateghi and F. Gafoori, *African J. Biotech*., **7**, 600 (2008).
2. D. Suteu and D. Bilba, *Acta Chim. Slov*., **52**, 73 (2005).
3. A. Maximova and B. Koumanova, *J. Univ. Chem. Tech. Metall.*, **43**, 101 (2008).
4. Y. Wang, M. Yang, B.Z. Quan and Y. Han Qing, *Sep. Purif. Technol*., **50**, 1 (2006).
5. A. Nevine Kamal, *Desalination*, **223**, 152 (2008).
6. M. Rachakornkij, S. Ruangchuay and S. Teachakulwiroj, *J. Sci. Technol*., **26**, 13 (2004).
7. N.K. Amin, *J. Hazard. Mater*., *J. Hazard. Mater*., **165**, 52 (2009).
8. N. Gupta, S.S. Amritphale and N. Chandra, *J. Hazard. Mater*., **163**, 1194 (2009).
9. Y. Yasin, M. Zobir and H. Hj Ahmad, *Malaysian J. Anal. Sci*., **11**, 400 (2007).
10. S.S. Azhar, A.G Liew, D. Suhardy, K.F. Hafiz and M.D.I Hatim, *Am. J. Appl. Sci.*, **2**, 1499 (2005).
11. H. Tahir, M. Sultan and Q. Jahanzeb, *African J. Biotech.*, **7**, 2649 (2008).
12. H. Tahir, U. Hammed, Q. Jahanzeb and M. Sultan, *African J. Biotech*., **7**, 3906 (2008).
13. E. Demirba, M. Kobya, S. Oncel and S. Encan, *Chem. Eng. J*., **91**, 317 (2004).
14. R.N. Prasad, S. Viswanathan and J. Renuka Devi, *Am.-Eur. J. Sci. Res*., **3**, 123 (2008).
15. C. Namasivayam, N. Muniasami, K. Gayathri, M. Rani and K. Rananathan, *Biores. Technol*., **57**, 37 (1998).
16. S. Kaur and M. Kaur, *J. Environ. Poll*., **6**, 173 (1999).
17. Sumanjit, T.P.S. Walia and R. Kaur, *Online J. Health Allied Sci.*, **6** (2007).
18. A. Gurney, E. Arslankaya and I. Tosun, *J. Hazard. Mater*., **146**, 362 (2007).
19. X.-E. Shen, X.-Q. Shan, D.-M. Dong, X.-Y. Hua and G. Owens, *J. Colloid. Interface Sci*., **330**, 1 (2009).

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