Asian Journal of Chemistry; Vol. 23, No. 11 (2011), 4903-4906

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Kinetic Study of Biosorption of Methyl Orange from Aqueous Solution by Tail of Black Cherry as an Eco-friendly Biosorbent

MOHAMMAD MOMENHERAVI

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

*Corresponding author: Fax: +98 511 6228310; Tel: +98 511 8401750; E-mail: drmh45@yahoo.com

(*Received*: 19 October 2010; *Accepted*: 20 July 2011) AJC-10176

The preparation of activated carbon from tail of black cherry with diluted H_3PO_4 of chemical activated for removal a reactive dye methyl orange from aqueous solution were reported in present study. The effect of different experimental parameters, such as initial dye concentration, adsorbent dosage, agitation speed, contact time and temperature with pH controlled were investigated. The adsorption isotherms have been analyzed by the Langmuir, Freundlich and Linear models that the Langmuir isotherm has the highest correlation coefficients. Adsorption kinetics study of methyl orange onto tail of black cherry were carried out under dyeing conditions of pH controlled and an initial concentration 50 mg/L. Pseudo first-order and second-order kinetics models were used to determine the adsorption kinetics data. The data showed that the second-order model was the more appropriate with an activation energy 79.2 kJ/mol. Thermodynamic parameters were also evaluated. The values of enthalpy and entropy were -165 (kJ/mol) and -554.8 to -412.79 (J/mol.K) respectively, indicating that the process was spontaneous and exothermic. The results indicate that the highest percentage removal of methyl orange (97 %) can be achieved at 0.1 g of biosorbent, 10 mg/L concentration of methyl orange, contact time 18 h, agitation speed 400 rpm and temperature 25 ºC.

Key Words: Kinetics study, Adsorption, Methyl orange, Tail of black cherry.

INTRODUCTION

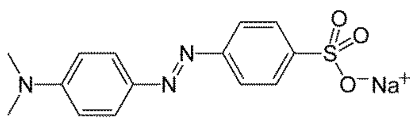
Synthetic dyes are extensively used in dyeing and printing process, paper, plastics, textiles, food, cosmetics, *etc.* in order to colour their products. Reactive dye and their breakdown products are toxic or mutagenic for life. Azo dye represents the largest class one or several azo bridges (N=N) linking substituted aromatic structures[1]. The methods of colour removal from industrials such as flocculation, hyper filtration, adsorption on activated carbon, ion exchange, oxidation, biological treatments[2-6].

Dye type, wastewaters compositions, operation costs and generated waste products determine feasibility of each method. Also dye strategies consist of a combination of different methods. Among these options, adsorption has been found to be higher to other methods[7]. Because of initial cost, ease of operation, simplicity design and preparing activated carbon from biological materials. Black cherry as natural fruit is available in around the world and in large quantities in different regions of Iran. It is widely use in processed as jams, juice and Iranian traditional foods.

Tail of black cherry as waste fruit is a new and low-cost adsorbent that composed of several compounds such as prussic acid, coumarine, amygdaline, *etc.* use for the removal of methyl orange from aqueous solution. While no study has been reported for the adsorption of dye and heavy metals on activated carbon prepared from tail of black cherry. The effect of different parameters such as initial dye concentration, contact time, adsorbent dosage, agitation speed and temperature were investigated. We have evaluated the isotherms, kinetic and some of thermodynamic parameters for adsorption of methyl orange onto activated carbon.

EXPERIMENTAL

Analytical grade reagents (methyl orange) were used in all experiments without any purification and water purified. The chemical structure of methyl orange is shown in **Scheme-I**. A stock solution of reactive methyl orange (1000 mg/L) was prepared and working solution of the desired concentration were obtained by successive dilutions of the stock solution. The concentration of the dye was determined at 470 nm, using UV-VIS spectrophotometer (Perkin Elmer Lambda 25).



Scheme-I Structure of methyl orange

Preparation of adsorbent: Tail of black cherry was obtained from Medicinal Research Center. It was washed several times with distilled water and dried in an oven at 150 ºC for 2 h. Then it was cut into small pieces. The raw materials were subject to chemical activation. The activation was carried out using diluted H_3PO_4 (28 %) solution for 24 h. After decantation the samples were dried in an oven at 150 ºC for 24 h, it was carbonized in a muffle furnace at 500 ºC for 1 h and then sieved to an average particle size.

Batch adsorption experiments: The effect of experimental parameters such as initial dye concentration (10-200 mg/L), adsorbent dosage (0.1 g) and temperature (20, 30, 40, 60 ºC) on the dye adsorption were studied in the batch mode of operation for a contact time. Dye samples were prepared by dissolving a known quantity of the dye in double distilled water and used as stock solution and diluted to the required initial concentration. Dye solution (250 mL) of certain concentration and a known amount of adsorbent were agitated in thermostat rotary shaker at speed of 400 rpm at 25 ºC temperature. At various time intervals the remaining concentration of dye in solution was measured spectrophotometrically at 470 nm and after equilibrium, adsorption capacity was calculated from the relationship:

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where, q_0 (mg/g) 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. The percentage of dye removal (R %) from solution was calculated from the relationship:

$$R\ \% = (C_0 - C_t)/C_0 \times 100 \quad (2)$$

where C_0 and C_i (mg/L) are the initial concentration and concentration at time t, respectively.

RESULTS AND DISCUSSION

Effect of initial concentration of dye: The adsorption capacity of tail of black cherry for reactive methyl orange was determined at concentration ranging from 10-200 mg/L. The results represented that the amount of dye adsorbed increase with increasing dye concentration but the percentage of removal decrease. This increase initial concentration is to the decrease in resistance to the uptake of solute from dye solution. Similar results have already been reported[8]. The results show that the percentage removal of dye decrease from 97 to 77 % as the initial dye concentration increase from 10 to 200 mg/L (Fig. 1).

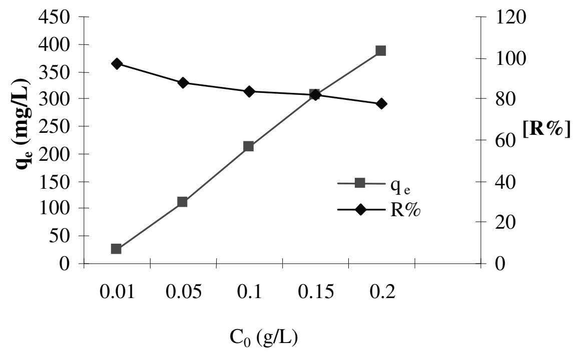


Fig. 1. Effect of initial concentrations on the removal of reactive dye methyl orange onto activated carbon (tail of black cherry)

Effect of contact time: Effect of contact time for removal of reactive dye methyl orange onto activated carbon prepared from tail of black cherry is shown in Fig. 2. This effect on the percentage removal of dye was investigated at initial dye concentration (10, 100, 200 mg/L). At the beginning adsorption rate was rapid but higher in the beginning due to the large surface are available of biosorbent. When the adsorption of the exterior surface reached saturation, the dye ions exerted onto the pores of the adsorbent particles and were adsorbed by the interior surface of the particles[9-11].

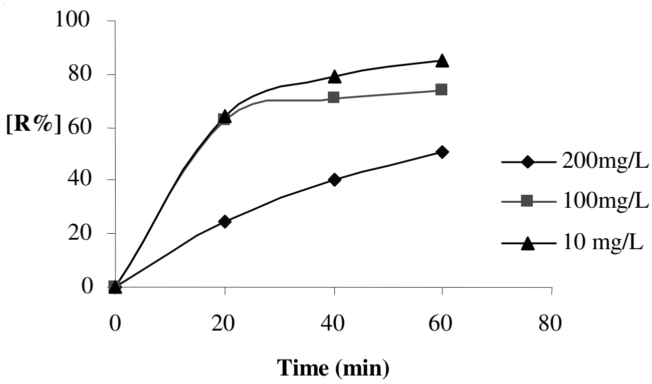


Fig. 2. Effect of contact time on the removal of reactive dye at different initial concentrations onto tail of black cherry. Conditions: adsorbent 0.1g; contact time 1 h

Effect of dose of adsorbent: The percentage colour removal increased from 62 to 83.2 % with an increase in adsorbent dosage from 0.1 to 2 g. The effect of dose of biosorbent on the percentage removal of reactive dye is shown in Fig. 3.

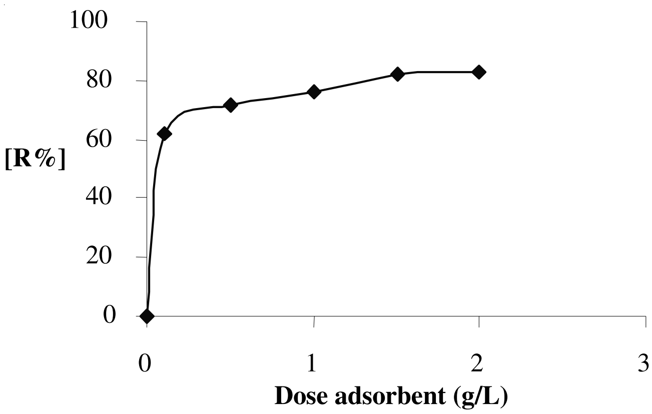


Fig. 3. Effect of biosorbent dose tail of black cherry on the removal of reactive dye methyl orange. Conditions: initial concentration 50 mg/L; temperature 25 ºC; contact time 1 h.

This was due to the fact that as the dosage of adsorbent was increased, there was less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the biosorbent and increase in availability of surface active sites resulting from the increased dose and conglomeration of the biosorbent[7,11,12].

Effect of agitation speed: Fig. 4 shows the effect of agitation speed on the adsorption of methyl orange onto biosorbent tail of black cherry. Adsorption of methyl orange increases by with agitation speed 100 to 400 rpm for an initial concentration of 50 mg/L for 3 h.

TABLE-1
LANGMUIR, FREUNDLICH AND LINEAR ISOTHERM CONSTANTS AND CORRELATION COEFFICIENTS

Temperature (K)	Langmuir isotherm			Freundlich isotherm			Linear isotherm	
	q_o (mg/g)	K_L (L/g)	R^2	K_F	n	R^2	K (L/g)	R^2
293	555.5	43×10^{-2}	0.994	26.7	1.32	0.9866	7725.8	0.9487
303	2500	26×10^{-4}	0.995	13.0	1.103	0.8340	6.73	0.9998
313	625	20×10^{-4}	0.973	8.31	1.39	0.8461	2.94	0.4687
333	-10000	10×10^{-5}	0.999	6.19	0.99	0.7574	2.92	0.4814

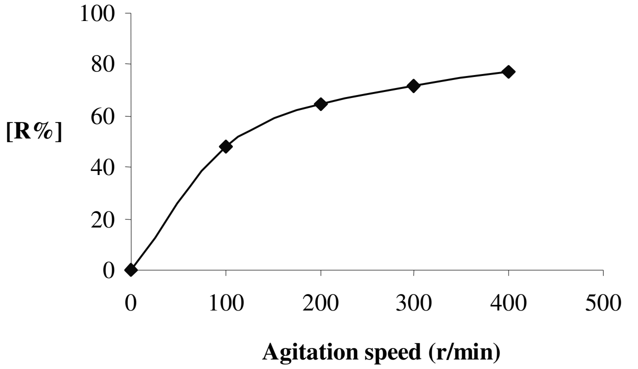


Fig. 4. Effect of agitation speed on the adsorption reactive dye methyl orange onto tail of black cherry. Conditions: initial concentration 50 mg/L; adsorbent 0.1 g; contact time 3 h

Effect of temperature on the adsorption: Adsorption of methyl orange dye was studied at different temperatures (20, 30, 40, 60 ºC). The results show that the adsorption of methyl orange decrease with increasing of temperature (Fig. 5). A similar result also reported for adsorption of dyes onto biosorbent[13,14]. This can be explained by the exothermic process. These results were used to determine the adsorption isotherms and thermodynamic parameters. Three most common isotherm equations, Langmuir, Freundlich and Linear were calculated in this study. Table-1 displayed the results of the calculated isotherm constants at different temperatures. Langmuir isotherm model were found to best fit the experimental data. The values Langmuir constants decrease with increasing temperature (Fig. 6).

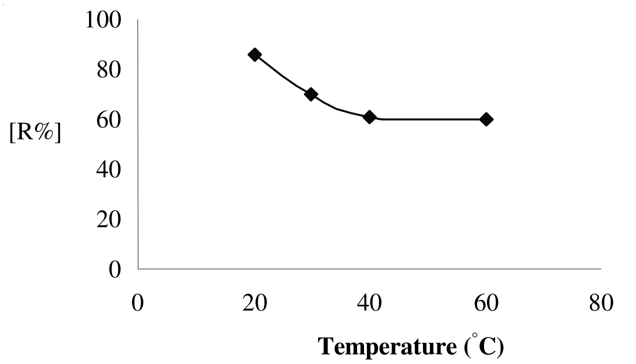


Fig. 5. Effect of temperature on the removal of methyl orange onto biosorbent tail of black cherry. Conditions: initial concentration 150 mg/L; adsorbent 0.1g; temperatures (20, 30, 40, 60 ºC)

Kinetics approach: In order to study the adsorption rates of reactive dye by biosorbent (tail of black cherry), the pseudo first-order and pseudo second-order rates models were investigated. The Lagregren equation describes pseudo first-order model[14], gives:

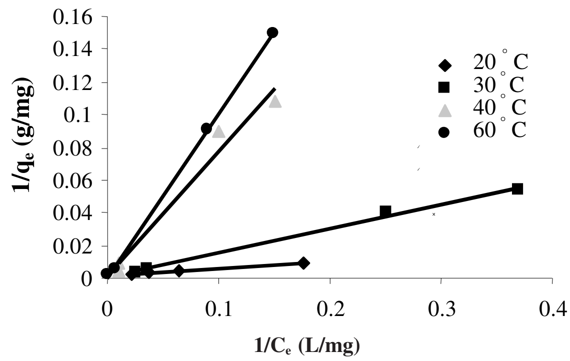


Fig. 6. Plot of Langmuir for the adsorption of the reactive dye methyl orange onto activated carbon tail of black cherry at different temperatures.

$$dq_t/dt = k_1(q_e - q_t) \tag{3}$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t respectively, k_1 is the rate constant of pseudo first-order adsorption process (1/min). After integration of eqn. (3) for the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

By ploting of $\ln(q_e - q_t)$ *versus* t first-order rate constant k_1 and equilibrium adsorption density q_e were calculated from slope and intercept of plot. The pseudo second-order model[15], gives:

$$dq_t/q_t = k_2 (q_e - q_t) \tag{5}$$

where k_2 is the equilibrium rate constant for pseudo second-order adsorption (g/mg.min). After integration of eqn. (5) and applying boundary conditions t = 0 to t and $q_t = 0$ to q, gives:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{6}$$

$$h_i = k_2 q_e^2 \tag{7}$$

where h_i is the initial dye adsorption[13] (mg/g.min). The slope and intercept of plot of (t/q_t *versus* t) were used to calculated the pseudo second-order rate constant k_2 and q_e (cal) (Fig. 7). The results are listed in Table-2.

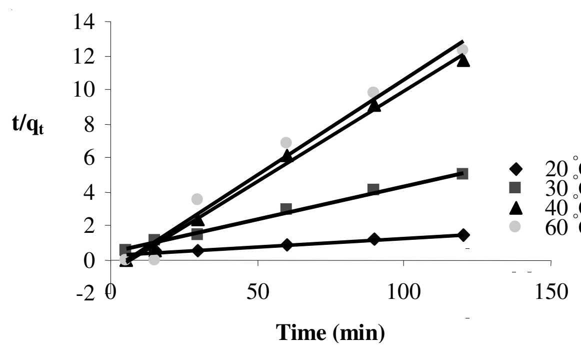


Fig. 7. Plot of pseudo second-order models to reactive dye methyl orange sorption onto tail of black cherry in an initial concentration at different temperatures. Conditions: initial concentration 50mg/L; adsorbent 0.1g; contact time 2 h

TABLE-2
KINETIC PARAMETERS FOR METHYL ORANGE ADSORPTION ONTO TAIL OF BLACK CHERRY AT DIFFERENT TEMPERATURE (CONDITIONS: INITIAL CONCENTRATION 50 mg/L; ADSORBENT 0.1 g; CONTACT TIME 2 h)

Temperature (K)	Pseudo second-order model				
	$q_{e,exp(mg/g)}$	$k_2 \times 10^{-4}$ (g/mg.min)	h_i	$q_{e,cal(mg/g)}$	R^2
293	110.75	3	3.3	105.3	0.9913
303	25.00	37	2.3	24.44	0.9949
313	10.25	165	-1.4	9.42	0.9949
333	9.75	216	-1.7	8.93	0.984

The correlation coefficients of all examined data were found very high. It showed a good compliance with the pseudo second-order equation. These results determined that the experimental data for the adsorption kinetics of reactive dye on biosorbent were fitted by the pseudo second-order kinetic model. Similar phenomenon was observed for the adsorption of basic dyes onto pomegranate peel[9], cotton[14] and apricot stone[15].

Thermodynamics approach: The activation energy (E_a) for the adsorption of reactive dye onto biosorbent prepared from tail of black cherry was determined from the rate constants k_2 and by using the Arrhenius equation[16].

$$\ln k = \ln A - E_a/RT \quad (8)$$

where, E_a, R and A refer to the Arrhenius activation energy, the gas constants and the Arrhenuis factor respectively. The plot of Arrhenuis (ln k *versus* 1/T) for the adsorption of methyl orange onto biosorbent (tail of black cherry) is shown in Fig. 8.

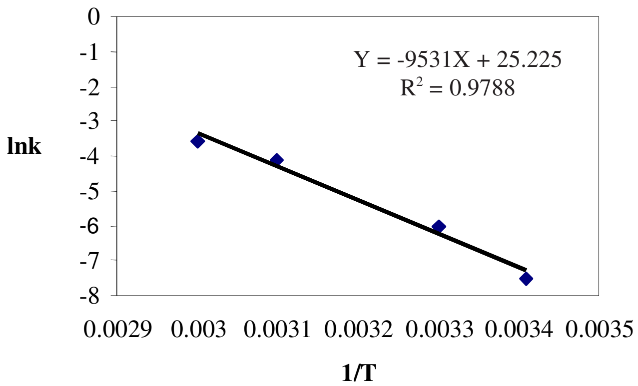


Fig. 8. Plot of Arrhenuis for the adsorption of reactive dye methyl orange onto biosorbent (tail of black cherry)

Using the values of binding Langmuir constants (K_L) and following relationships were determined enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°).

$$\ln K_L = -\Delta H^o / RT + \text{Constant} \quad (9)$$

$$\Delta S^o = (\Delta H^o - \Delta G^o) / T \quad (10)$$

$$\Delta G^o = -RT \ln K_L \quad (11)$$

The calculated values are listed in Table-3. The negative values of the entropy (ΔS°) were supportive of an interaction between dye and adsorbent.

TABLE-3
THERMODYNAMIC PARAMETERS FOR METHYL ORANGE ADSORPTION ONTO TAIL OF BLACK CHERRY AT DIFFERENT TEMPERATURES (CONDITIONS:INITIAL CONCENTRATION 50 mg/L; ADSORBENT 0.1 g)

Temperature (K)	E_a (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)
293	79.24	-137.6	-500.00	-7.64
303	–	–	-503.30	-12.59
313	–	–	-473.48	-16.91
333	–	–	-412.70	-27.68

Conclusion

The present study showed that the activated carbon prepared from chemically treated tail of black cherry is an effective and low-cost biosorbent for removal of methyl orange from aqueous solution. In this investigation, adsorption capacity of tail of black cherry was examined. It was a function of adsorbate concentration and temperature. The adsorption isotherms could be well fitted by the Langmuir equation. The adsorption process could be best described by the second order-equation. The thermodynamic parameters (ΔG°, ΔH°, ΔS°) indicate that adsorption process is spontaneous and exothermic. From the presented study, it may be concluded that the removal of azo dyes (methyl orange) from aqueous solutions by adsorption onto tail of black cherry has been found to be useful means for controlling the water pollution due to dyes. Undoubtedly, cheap adsorbents offer a lot of promising benefits for commercial purposes in the future.

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Chemistry IAUM for supporting and providing the laboratory facilities.

REFERENCES

1. D. Suteu and D. Bilba, *Acta Chem. Slov.*, **52**, 73 (2005).
2. M. Pollock, *Am. Dyestuff Reporter*, **62**, 21 (1973).
3. A. Mishra and M. Bajpai, *Bioresour. Technol.*, **97**, 1055 (2006).
4. N. Kurtoglu and D. Senol, *Asian J. Chem.*, **20**, 1986 (2008).
5. G. Annadurai, R.S. Juang and D.J. Lee, *J. Hazard. Mater.*, **92**, 263 (2002).
6. S. Yenidogan, M. Oktav and M. Ulgen, *Asian J. Chem.*, **22**, 3705 (2008).
7. N. Kannan and M.M. Sundaram, *Dyes Pigments*, **51**, 25 (2001).
8. N.K. Amin, *J. Hazard. Mater.*, **125**, 261 (2010).
9. N.K. Amin, *Disalination*, **223**, 152 (2008).
10. I.D. Mall, V.C. Srivastava, N.K. Agrawal and I.M. Mishra, *Chemosphere*, **61**, 492 (2005).
11. P.K. Malik, *Dyes Pigments*, **56**, 239 (2001).
12. S.E. Bailey, T.J. Bricka and M. Adrian, *Water. Res.*, **33**, 2469 (1999).
13. E. Demirbas, M. Kobya and M.T. Sulak, *Bioresour. Technol.*, **99**, 5368 (2000).
14. M. Chairat, S. Rattanaphani, J.B. Bremner and V. Rattanaphani, *Dyes Pigments*, **76**, 435 (2008).
15. N. Yeddou and A. Bensmaili, *Desalination*, **185**, 499 (2005).
16. M. Dogan and M. Alkan, *Chemosphere*, **50**, 517 (2003).