Int. J. Chem. Sci.: 12(4), 2014, 1273-1288
ISSN 0972-768X
www.sadgurupublications.com

ADSORPTION OF A CATIONIC DYE FROM AQUEOUS SOLUTIONS BY USING WASTE GLASS MATERIALS: ISOTHERM AND THERMODYNAMIC STUDIES

ZAINAB A. HADI, A. M. ALJEBOREE and A. F. ALKAIM[*]

Department of Chemistry, College of Science for Women, Babylon University, HILLA, IRAQ

ABSTRACT

Waste glass materials (WG), from Pepsi Cola solid wastes (PCSW), may be used as a sorbent for textile dyes removal from industrial wastewaters such as methylene blue (MB). In order to obtain the adsorption mechanism, adsorption processes were studied with Fourier transform infrared spectroscopy. The effect of various parameters like concentration, initial solution pH, particle size, mass dosage and temperature has been studied. Increasing the concentration of the adsorbent promoted an increase in the percentage of removal until saturation of the adsorbent. Also increase in pH of solution gives better adsorption. However, it is also observed that percent saturation of adsorption decreases with increase in particle size of adsorbent. The experimental isotherm data were analyzed using Langmuir, Freundlich, and Temkin models. Within the studied range of dye concentrations, the adsorption equilibrium was found to follow the Langmuir isotherm model well, with $R^2 > 0.99$. The dimensionless factor, R_L of the methylene blue, WG isotherm revealed that the adsorption process is favourable in nature. A full thermodynamic evaluation was carried out, calculating the parameters of enthalpy, free energy, and entropy (ΔH, ΔG, and ΔS). The thermodynamics of MB onto WG system indicates spontaneous and endothermic nature of the process. The efficiency of WG for the spontaneous and endothermic adsorption of MB dye is attributed to the copious availability of hydroxyl and other polar functional groups on the oxygen surface. The present adsorption studies of MB dye from aqueous solution revealed the potential of WG to be utilized as an alternative, inexpensive, and environmentally benign adsorbent for water purification.

Key words: Adsorption, Isotherms, Thermodynamics, Waste glass.

INTRODUCTION

Dye wastewater is mainly from textile, leather, paper, rubber, plastics, cosmetics, pharmaceutical, and food industries. Because dye wastewater always comes as large quantities,

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[*] Author for correspondence; E-mail: ayad_alkaim@yahoo.com; Ph.: + 964-7801-324986

complex composition, color depth, and high toxicity. It causes severe environmental pollution and human health hazards, if it is not treated properly before discharging into the natural water[1]. Some of the dyes also inhibit the growth of biota and importantly, they can be mutagenic and carcinogenic compounds[2]. The cationic dye of methylene blue is mostly used for dyeing of cotton, silk and wood[3]. MB can disturb human health as it causes the injury of eyes, breathing difficult, worming, profuse sweating, mental confusion and methemoglobinemia[3]. Therefore, an increased interest has been focused to find economic and effective methods for removing such dyes from the contaminated water[4,5].

Current treatment methods for dye wastewater include physical, chemical, and biological methods, and so on. Various removal methods have been studied by adsorption[6,7], chemical coagulation[8], liquid membrane separation[9], electrolysis[10], biological treatments[11], and oxidation[12]. However, these processes vary in their effectiveness, costs, and environmental impacts[13]. Among these processes, the adsorption process is much more competitive than other methods for its ready availability, lower cost, and wider range of applications[1]. In adsorption processes, a porous solid (adsorbent) is used to capture soluble substances present in aqueous solution (dyes for instance). Adsorption studies are generally focused on adsorbent selection, and articles, which evaluate its performance for dye removal can be commonly found on the literature: agro-industrial byproducts[14,15], chitosan[16,17], bacterial and fungal biomass[18,19], activated carbon[20-23], industrial waste[24,25] and minerals[26-28], among others has already been considered. The studies involving this material showed that it could be a more efficient and low-cost material for dye uptake.

Glass is a versatile material for its safe and durable use, which can be easily reused in the same and/or in related activities with minor (if any) medications[29]. Waste glass may be assumed as a secondary materials due to it is easy re-shaping in different forms. Therefore, main objective of this work was to perform methylene blue adsorption by a waste glass materials, which have a highest percentage of SiO_2[29] as adsorbent dependent and to obtain several information about the process, such as equilibrium and thermodynamics aspects.

EXPERIMENTAL

Materials

Analytical grade MB supplied by Sigma-Aldrich, was used as adsorbate without further purification. The concentration of this dye was determined by a UV/spectrophotometer (Shimadzu 1650, Japan) at 663 nm wavelength.

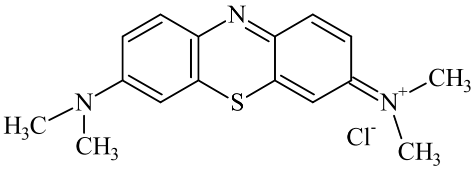


Fig. 1: Chemical structure of methylene blue

WG powder preparation

WG was recovered from Pepsi Cola solid wastes (PCSW). Preliminary, cleaned and crushed, then sieved and passed through different sizes (100-75 um, 75-50 µm, and less than 50 um). For preservation, they were kept in glass stopper bottles (containers) and to minimize contact with humidity, all these bottles were preserved in oven (60^oC) before the time of use.

Preparation of dye solutions

The stock solution was prepared by dissolving 1 g of analytical grade dye MB in 1000 mL of distilled water. All experiments were carried out at room temperature (25 ± 1^oC) using a constant agitation speed of 100 rpm.

At predetermined time (60 min.), the dispersion was drawn and separated immediately by centrifugation processing. Residual MB concentration in the supernatant was measured using a UV–vis spectrophotometer. The adsorption amount (q_e) and percentage removal (E%) are calculated based on the difference in the MB concentration in the aqueous solution before and after adsorption, according to the following equations:

$$q_e = \frac{(C_0 - C_e)\,V}{W} \quad \ldots(1)$$

$$E\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \ldots(2)$$

where C_0 (mg L^{-1}) is the initial MB concentration and C_e (mg L^{-1}) is the MB equilibrium concentration at time t (min), V (L) is volume of solution, and W (g) is the weight of WG sorbent.

Effect of different parameters on adsorption efficiency

Effect of waste glass mass

The effect of WG mass quantity was studied by varying the quantity of WG in the range of 0.05, 0.25, 0.5, and 1 g/100 mL whereas the parameters such as initial dye concentration, contact time, pH of the solution, stirring rate, particle size and temperature were all kept constant during the adsorption process.

The effect of WG mass was studied using a series of conical flasks each containing 100 mL of dye solutions with the initial concentration of 5 mg/L. The solution was shaken in a shaker for 1 h at 25°C. The residual concentration was measured to determine the optimum value of the adsorbent. Adsorption capacity and percentage of dye removal was calculated using the equations (1 and 2).

Effect of pH

A pH range of 2, 4, 6.4, and 9 was applied in order to investigate the pH effect in a batch set-up. The following procedure was followed to determine the optimum pH for MB. A series of conical flasks, each containing 100 mL of dye solution with an initial concentration of 10 mg/L was prepared by varying pH in the range of 2-9. The initial pH was adjusted using HCl (1 N) and NaOH (1 N) solutions. An amount of 0.5 g/100 mL of waste glass was added to each flask and was shaken for 1 hr at room temperature.

Effect of initial dye concentrations

The effect of initial dye concentration was studied by shaking the series of conical flasks containing 100 mL of dye solution with different concentrations in the range of 1-10 mg/L at room temperature. All the experiments were conducted at the natural pH (6.4) and the waste glass mass (0.5 g/100 mL).

Effect of particle size

The effect of particle size was studied by shaking the series of conical flasks containing 100 mL of dye solution (5 ppm) with different particle sizes in the range of 100-75, 75-50, and less than 50 µm at room temperature. All the experiments were conducted at the optimum values of pH (6.4) and the waste glass mass (0.5 g/100 mL).

Effect of solution temperature

The effect of solution temperatures was studied by shaking the series of conical flasks containing 100 mL of dye solution (10 ppm) with different solution temperature (10, 25, and 40°C). All the experiments were conducted at the optimum values of pH (6.4) and the waste glass mass (0.5 g/100 mL).

RESULTS AND DISCUSSION

FT-IR Analysis

The FT-IR spectra of WG performed before and after MB adsorption showed characteristic bands corresponding to various functional groups. It is clear from the Fig. 2 that after adsorption of MB, a significant change in intensity or shift of the present function groups has been observed. Fig. 2 shows new interactions formed between the functional groups of main composite of glass material SiO_2 and the positively charged dye molecules.

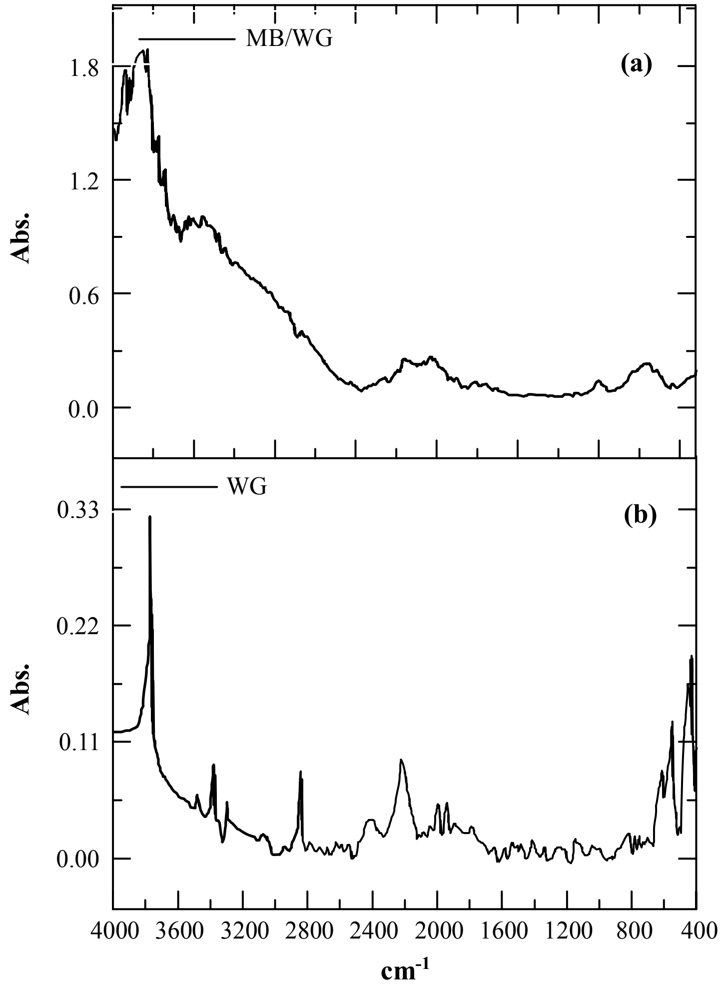


Fig. 2: FT-IR spectra of WG (a) before, (b) after MB adsorption (adsorbent dosage = 0.5 g, contact time = 60 min, temperature = 298 K, shaking rate = 100 rpm and pH = 6.4, and contact time 1 hr)

Effect of operational factors on adsorption

Effect of initial MB concentration

The initial concentration of the MB dye solution has a significant effect on color removal. It can be seen from Fig. 3 that the color removal of MB dye solution onto WG by adsorption rose rapidly at the beginning and then gradually slowed down until equilibrium was reached. It might be explained that a large number of vacant surface sites were available for adsorption during the initial stage. However, with a lapse of adsorption time, the remaining vacant surface sites were difficult to be occupied due to steric barrier between MB adsorbed on the surface of WG and solution phase[1,30]. The results can be attributed to an increase in the driving force of concentration gradient with the increase in the initial concentration[1].

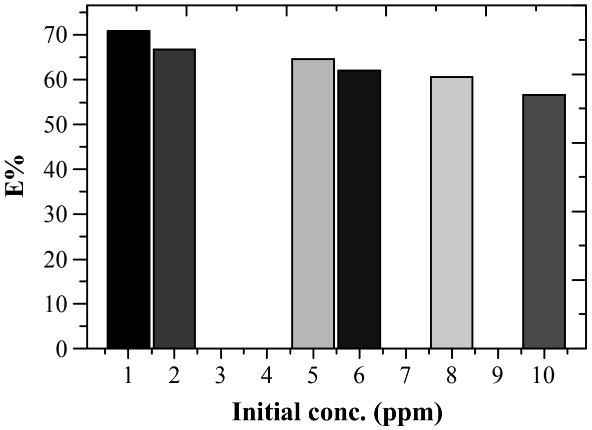


Fig. 3: Effect of initial MB dye concentration on the removal of MB onto WG (T = 298 K; adsorbent dosage = 5 g L^{-1}; shaking speed = 100 rpm; natural pH = 6.4)

Effect of waste glass mass

From an economic point of view, the study of adsorbent mass is useful for selecting the appropriate amount of adsorbent for industrial applications. The effect of adsorbent dose on the MB removal was studied by varying dosage of WG from (0.5 to 10 g L^{-1}) at initial concentration of dye (5 mg L^{-1}). The results are shown in Fig. 4.

The increase in percentage removal (E%) of MB was due to an increase in surface area and adsorption sites for a fixed initial dye concentration[31,32]. While, the adsorption capacity (mg g^{-1}) decreased with increasing adsorbent mass. This may be attributed to aggregation or overlapping of sorption sites. Therefore, the total number of binding sites and effective surface area of WG decreases and the diffusion path length increased, resulting in adsorption capacity decrease[1,31].

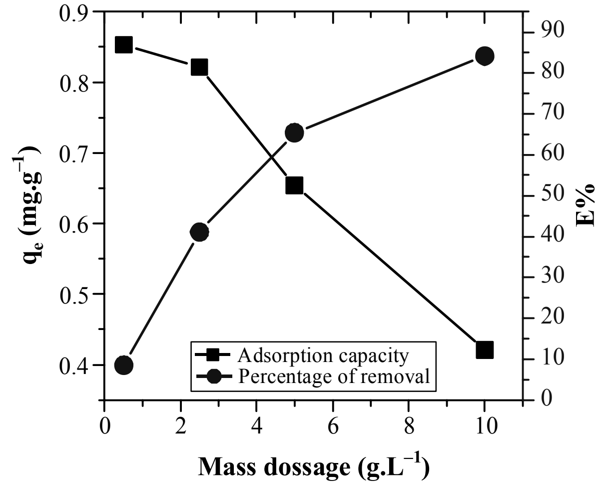


Fig. 4: Effect of adsorbent dosage on the removal of MB onto WG (*T* = 298 K; initial MB concentration = 5.0 mg L^{-1}; shaking speed = 100 rpm; natural pH = 6.4)

Effect of initial solution pH

The pH value, which can control the protonation of the functional groups, is an important factor for the adsorption process. The adsorption experiments were carried out by varying pH range from 2 to 9, and the results are illustrated in Fig. 5. Previous studies have shown that the high pH may cause the hydrolysis of the reactive groups in the dye[33]. Therefore, a study of the hydrolysis of MB was carried out. It can be observed the peak (663 nm) decreased with increasing pH of the dye solution (Figure not shown). Thus, the hydrolysis reaction did not promote significant alteration in the chromophoric groups, which took place after the hydrolysis[34].

The adsorption quality at equilibrium (q_e), and percentage of removal (E%) was found to increase obviously with an increase in pH from 2 to 9. So the increase of pH value is conducive to the adsorption process of MB on the WG. With lower pH value, the surface charge became positively charged; thus, making H^+ ions compete effectively with dye cations causing a decrease in the adsorption capacity[1]. However, at higher pH value, more negatively charged surface of the adsorbent was available; thus, facilitating greater dye cations removal.

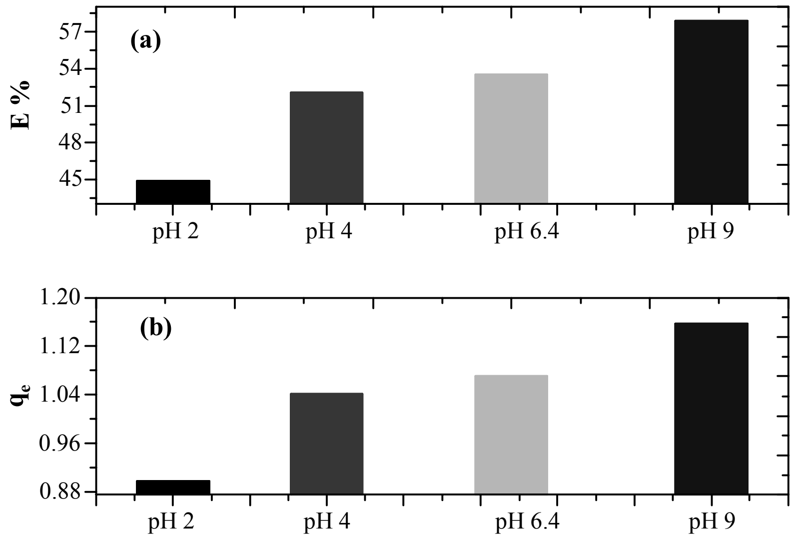
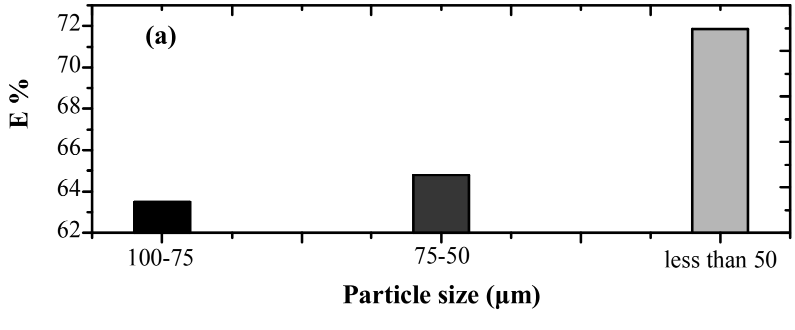


Fig. 5: Effect of pH on the removal of MB onto WG: (a) percentage of removal, (b) adsorption capacity (T = 298 K; adsorbent dosage = 5.0 g L^{-1}; initial MB concentration = 10.0 mg L^{-1}; shaking speed = 100 rpm)

Effect of particle size

Adsorption process is related with surface area of adsorbent directly because it determines the time required for transport within the pore to adsorption sites so particle size is very important factor affecting adsorption capacity[35].

The effect of particle size on removal of methylene blue was studied with different sizes (100-75, 75-50, and less than 50 µm). The results are shown in Fig. 6. The removal efficiency of methylene blue by WG increases from 63.5 to 71.8% as the particle size decreases from 100-75 to less than 50 µm for an initial concentration of 5.0 mg/L.



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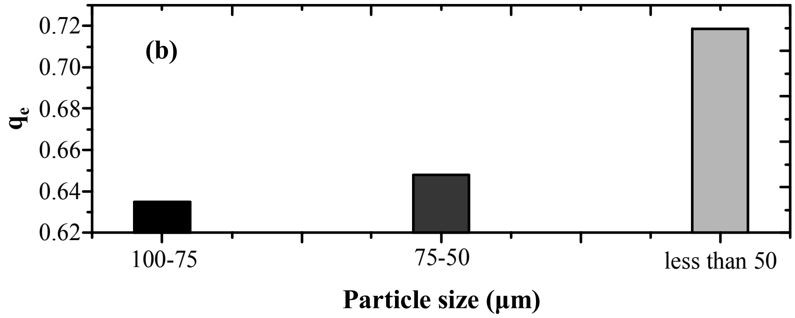

Fig. 6: Effect of particle size on the removal of MB onto WG: (a) percentage of removal, (b) adsorption capacity (T = 298 K; adsorbent dosage = 5.0 g L^{-1}; initial MB concentration = 10.0 mg L^{-1}; shaking speed = 100 rpm, and pH 6.4)

The extent of the adsorption process increases with increased specific surface area. The specific surface available for adsorption will be greater for smaller particles, and hence, adsorption efficiency of methylene blue increases as particle size decreases. For larger particles, the diffusion resistance to mass transport is higher, and most of the internal surface of the particle may not be utilized for adsorption[36].

Thermodynamic parameters

The thermodynamic parameters provide in-depth information about the energetic changes associated with adsorption process. The thermodynamic parameters, namely, the standard Gibbs energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) of the adsorption of the methylene blue onto the WG were determined by using the following equations[37].

$$K_d = \frac{q_e}{C_e} \quad \ldots(3)$$

$$\Delta G^o = -\,RT \ln K_d \quad \ldots(4)$$

$$\ln K_d = \frac{\Delta S^o}{R} + \frac{\Delta H^o}{RT} \quad \ldots(5)$$

where K_d is the distribution coefficient, T is the temperature, and R is the gas constant, respectively. $\Delta H°$ and $\Delta S°$ are calculated from the slope and intercept of van't Hoff plots of ln K_d vs T^{-1} (Fig. 7).

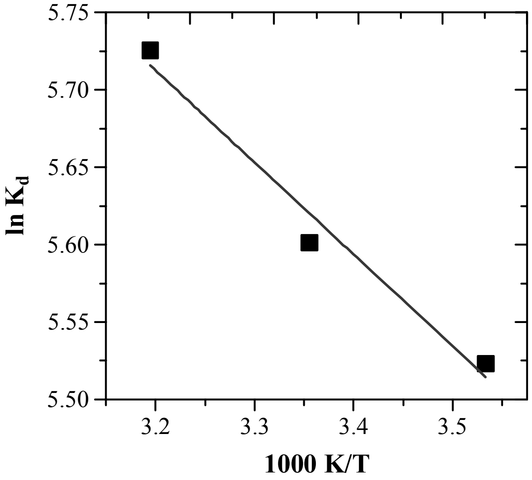

Fig. 7: Linearized form of Van Hoff's equation

The calculated values of thermodynamic parameters of the MB/WG system are given in Table 1. The negative Δ*G* values at different temperatures indicate the spontaneous nature of the adsorption of MB onto the WG. The calculated Δ*H* value from Van't Hoff plots was found to be 4.9399 KJ·mol^{-1}, which indicates the adsorption process is endothermic and physical interaction in nature[38].

Table 1: Thermodynamic parameters for the adsorption of MB onto WG

ΔS (J.K^{-1}.mol^{-1})	ΔH (kJ.mol^{-1})	ΔG (kJ.mol^{-1})	T (K)
63.302	**4.9399**	-12.995471	**283**
		-13.877765	**298**
		- 14.899197	**313**

Adsorption isotherms

Equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems for practical applications, as the isotherms can be used to interpret the specific relationship between the concentration of adsorbate and its extent of adsorption onto the adsorbent surface at a constant temperature.

Adsorption data are most commonly represented by the equilibrium isotherm value, which is a plot of the quantity of the sorbate removed per unit sorbent (q_e) as the solid phase concentration of the sorbent against the concentration of the sorbate in the liquid phase (C_e).

Several isotherm models have been used to predict validity of the experimental data. In the present study, three of the most commonly used models, namely the Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium.

The non-linear form of the Langmuir isotherm model[39] is given as –

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \qquad \ldots(6)$$

where K_L (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, q_{max} and q_e (mg/g) are the maximum and equilibrium adsorption capacity, respectively. Langmuir constants generated from adsorption data plot of q_e against C_e (Fig. 8) are summarized in Table 2.

The Freundlich isotherm is based on the premise that adsorption occurs on rare heterogeneous surfaces sites with different energy of adsorption and are also non-identical. The non-linear form of the Freundlich isotherm was used to investigate the adsorption process adherence to the model[40]:

$$q_e = K_f C_e^{1/n} \qquad \ldots(7)$$

K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favorable physical process[41]. The values of the model parameters obtained from the plot of q_e against C_e (Fig. 8) are presented in Table 2.

The non-linearized form of Temkin isotherm[42] is represented by Eq. (8):

$$q_e = \frac{RT}{b} \log (K_T C_e) \qquad \ldots(8)$$

where Tempkin constant (b) is related to the heat of adsorption (kJ/mol), R = Gas constant (8.314 J/mol.K), T = Temperature (K), and K_T = Emprical Temkin constant related to the equilibrium binding constant related to the maximum binding energy (L/mg), (L/mol)

The adsorption data can be analyzed according to the Eq. (8). Results are shown in Fig. 8 and the isotherm constants K_T and b are shown in Table 2. The best fit of isotherm was selected based on the highest correlation coefficient (R^2) value (closest to unity), which describe the fitness of the isotherm to the experimental data.

Table 2: Langmuir, Freundlich and Temkin model isotherms parameters for MB adsorbed on the surface of WG

SE	Value	Parameters	Isotherm models
0.24087	2.64687	q_m (mg.g^{-1})	*Langmuir*
0.02455	0.17608	K_L(L.mg^{-1})	
	0.99705	R^2	
0.02675	0.39779	K_F	Freundlich
0.05636	0.73891	1/n	
	0.98569	R^2	
5.9040	24.665	B/J.mole^{-1}	Temkin
0.02994	0.39772	K_T	
	0.97757	R^2	

q_{max} = Maximum adsorption capacity; K_L = Langmuir constant; K_F, 1/n = Freundlich constants; b, k_T = Tempkin constants; R = Universal gas constant (8.314 J.K^{-1}.mol^{-1})

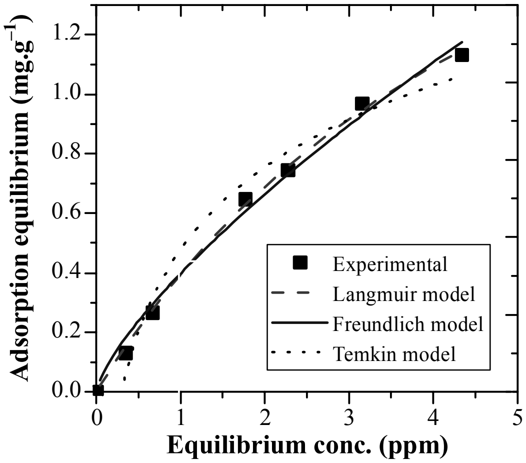

Fig. 8: Langmuir, Freundlich and Tempkin isotherms plot (pH 6.4, agitation speed 100 rpm, mass dosage 5 g/L)

Although the equilibrium data fitted well to the Langmuir, Freundlich and Tempkin adsorption isotherm models (as observed from Table 2), the Langmuir model exhibited better fit to the adsorption data than the other models. The favorability of the adsorption (R_L) was evaluated from parameters of Langmuir adsorption isotherm model. The R_L can calculate from the following equation[43]:

$$R_L = \frac{1}{1+K_L C_o} \quad \ldots(9)$$

where K_L is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration of dye. The R_L can vary: for $R_L > 1$ the adsorption is unfavorable; $R_L = 1$ the adsorption is in linear condition; the adsorption is favorable when $0 < R_L < 1$; and $R_L = 0$ is for irreversible conditions. The value of R_L for the sorption of MB onto WG is shown in Fig. 9, which indicates that sorption of MB on WG was "favourable".

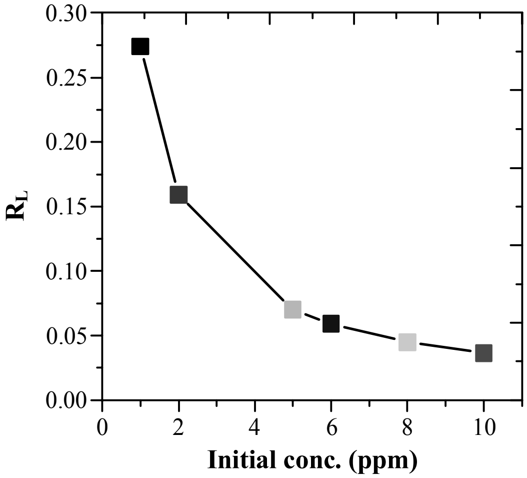

Fig. 9: Value of separation factor R_L for adsorption of MB by WG at the same conditions of results found in Fig. 8

CONCLUSION

Encouraging results were obtained with WG tested as adsorbent of MB dye, currently used in paper making and textile industries. The obtained results indicate that whole WG can be successfully used as adsorbent of MB dye in aqueous solution without needing any previous treatments such as chemical modification. The adsorption isotherms from aqueous solutions onto WG were also determined. The equilibrium data were fitted to the Langmuir, Freundlich and Temkin isotherm models.

The study of influence of pH revealed that the adsorbent exhibited better adsorption performance under basic conditions. The adsorbent dose inversely affected the adsorption capacity of WG, whereas the adsorption capacity increased with increasing initial dye concentration. The negative ΔG values and positive ΔH value, as obtained from the thermodynamic study, established the spontaneous and endothermic nature of MB adsorption. The adsorption equilibrium data were fitted very well by the Langmuir isotherm model, with $R^2 > 0.99$. Thus, the present investigation has provided a new efficient, low-cost, economical, and environmentally safe adsorbent with potential for practical application in the treatment of dye-contaminated wastewater.

REFERENCES

1. H. Shi, W. Li, L. Zhong and C. Xu, Ind. Eng. Chem. Res., **53**, 1108 (2014).
2. M. Berrios, M. A. Martın and A. Martın, J. Ind. Eng. Chem., **18**, 780 (2012).
3. A. Hassani, F. Vafaei, S. Karaca and A. R. Khataee, J. Ind. Eng. Chem., **20**, 2615 (2014).
4. A. N. Fernandes, C. P. Almeida, N. A. Debacher and M. M. de S. Sierra, J. Mol. Struct., **982**, 62 (2010).
5. S. Cengiz and L. Cavas, Bioresour. Technol., **99**, 2357 (2008).
6. A. M. Aljeboree, A. N. Alshirifi and A. F. Alkaim, Arabian J. Chem., (in Press).
7. A. M. Aljeboree, A. F. Alkaim and A. H. Al-Dujaili, Desalin. Water Treat., (in Press).
8. F. El-Gohary and A. Tawfik, Desalination, **249**, 1159 (2009).
9. A. Dâas and O. Hamdaoui, J. Hazard. Mater., **178**, 973 (2010).
10. L. Wang, J. Hazard. Mater., **171**, 577 (2009).
11. M. H. El-Naas, S. A. Al-Muhtaseb and S. Makhlouf, J. Hazard. Mater., **164**, 720 (2009).
12. H. T. Gomes, B. F. Machado, A. Ribeiro, I. Moreira, M. Rosario, A. M. T. Silva, J. L. Figueiredo and J. L. Faria, J. Hazard. Mater., **159**, 420 (2008).
13. S. Chakraborty, M. K. Purkait, S. Das Gupta, S. De and J. K. Basu, Sep. Purif. Technol., **31**, 141 (2003).
14. Y. Hamzeh, A. Ashori, E. Azadeh and A. Abdulkhani, Mater. Sci. Eng., C, **32**, 1394 (2012).

15. A. P. Vieira, S. A. Santana, C. B. Bezerra, H. S. Silva, J. P. Chaves, J. P. de-Melo, F. da-Silva, C. Edson and C. Airoldi, J. Hazard. Mater., **166**, 1272 (2009).
16. A. Chen and Y. Huang, J. Hazard. Mater., **177**, 668 (2010).
17. C. Chen, J. Chang and A. Chen, J. Hazard. Mater., **185**, 430 (2011).
18. X. Xiong, X. Meng and T. Zheng, J. Hazard. Mater., **175**, 241 (2010).
19. C. Yenikaya, E. Atar, A. Olgun, N. Atar, S. Ilhan and F. Colak, Eng. Life Sci., **10**, 233 (2010).
20. R. Baccar, P. Blánquez, J. Bouzid, M. Feki, H. Attiya and M. Sarrà, Fuel Process. Technol., **106**, 408 (2013).
21. L. T. Prola, F. M. Machado, C. P. Bergmann, F. E. de Souza, C. R. Gally, E. C. Lima, M. A. Adebayo, S. L. P. Dias and T. Calvete, J. Environ. Manage., **130**, 166 (2013).
22. A. F. Alkaim and M. B. Alqaragully, Int. J. Chem. Sci., **11**, 797 (2013).
23. A. F. Alkaim, A. H. Elywe and Z. S. Abdalameer, Iraqi National J. Chem., **51**, 301 (2013).
24. B. Qiu, X. Cheng and D. Sun, Bioresour. Technol., **113**, 102 (2012).
25. C. A. Demarchi, A. Debrassi and C. A. Rodrigues, Color. Technol., **128**, 208 (2012).
26. M. M. Nassar, M. S. El-Geundi and A. A. Al-Wahbi, Desalin. Water Treat, **44**, 340 (2012).
27. S. Arellano-Cardenas, S. L´pez-Cortez, M. Cornejo-Mazon and J. C. Mares-Gutiérrez, Appl. Surf. Sci., **280**, 74 (2013).
28. S. Karaca, A. Gürses, Ö. Açışlı, A. Hassani, M. Kıranşan and K. Yıkılmaz, Desalin. Water Treat., **51**, 2726 (2013).
29. H. S. Ibrahim, N. S. Ammar, H. H. Abdel Ghafar and M. Farahat, Desalin. Water Treat., **48**, 320 (2012).
30. S. Senthilkumaar, P. R. Varadarajan, K. Porkodi and C. V. Subbhuraam, J. Colloid Interface Sci., 2854, 78 (2005).
31. R. Kumar, M. O. Ansari and M. A. Barakat, Ind. Eng. Chem. Res., **53**, 7167 (2014).
32. M. Ghaedi, A. Ansari, M. H. Habibi and A. R. Asghari, J. Ind. Eng. Chem., **20**, 17 (2014).
33. C. C. Guaratini, A. G. Fogg and M. B. Zanoni, Dyes Pigments, **50**, 211 (2001).

34. M. A. Al-Ghouti, M. A. M. Khraisheh, S. J. Allen and M. N. Ahmad, J. Environ. Manage., **69**, 229 (2003).

35. D. Özer, G. Dursun and A. Özer, J. Hazard. Mater., **144**, 171 (2007).

36. M. Gouamid, M. R. Ouahrani and M. B. Bensaci, Energy Procedia, **36**, 898 (2013).

37. L. Ai, M. Li and L. Li, J. Chem. Eng. Data, **56**, 3475 (2011).

38. W. Zou, K. Li, H. Bai, X. Shi and R. Han, J. Chem. Eng. Data., **56**, 1882 (2011).

39. O. Redlich and D. L. Peterson, J. Phys. Chem., **63**, 1024 (1959).

40. Y. Ho, W. Chiu and C. Wang, Bioresour. Technol., **96**, 1285 (2005).

41. P. S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi and S. Sivanesan, Desalination, **261**, 52 (2010).

42. M. J. Tempkin and V. Pyzhev, Acta Physicochim. URSS, **12**, 217 (1940).

43. M. Auta and B. H. Hameed, Chem. Eng. J., **171**, 502 (2011).

Accepted : 17.07.2014