Eurasian Journal of Environmental Research 1 (1)
www.cessciencegroup.com

Removal of Dyes from Wastewater by Adsorption Using Modified Boron Enrichment Waste: Thermodynamic Criteria

M. K. ÖDEN[1] and S. KÜÇÜKÇONGAR[2]

[1] Selcuk University, Sarayonu V.H.S., Department of Environmental Protect Technology, Sarayonu, Konya, Turkey
[2] Selcuk University, Eng. Fac., Department of Environmental Eng., Konya, Turkey
(Corresponding Author's E-mail: muhammedkoden@selcuk.edu.tr)

ABSTRACT

In this study, Methylene Blue (MB) and Malachite Green (MG) removal from synthetic wastewaters using modified boron enrichment waste by adsorption process were aimed. Boron enrichment waste was modified with acid and ultrasound together. The boron enrichment process waste could be used as an effective adsorbent due to its constituents including ulexite, calcite, dolomite, zeolite and some clays. About 84% MB and 80% MG removal were obtained by modified boron enrichment waste (MBEW) at optimum equilibrium conditions (Contact time: 20-10 min., adsorbent dose: 625-375 mg/L, pH: 11-10, shaking speed: 200 rpm and temperature: 25^0C) respectively. Besides, the thermodynamic parameters, such as ΔG°, ΔH° and ΔS° were also calculated. Thermodynamic (negative ΔG values) study indicates that the adsorption of dye is feasible, and spontaneous in nature. Thermodynamic study demonstrates the spontaneous and endothermic nature of sorption process due to negative values of free energy change and positive value of enthalpy change, respectively. All the studied results showed that the modified enrichment waste could be used as effective adsorption material for the removal of methylene blue and malachite green from aqueous solutions.

Keywords: Dyes, boron ore, boron enrichment waste, adsorption, colour removal.

INTRODUCTION

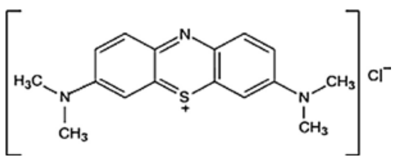
Many kinds of synthetic dyestuffs appear in the effluents of wastewater in A great number of industry such as dyestuff, pharmaceutics, food, coke, petroleum, pesticide, textiles, leather, paper, plastics, etc. Since a very small amount of dye in water is highly visible and can be toxic to creatures in water, the removal of color from process becomes environmentally important [1, 2]. Dyes may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life in them [2-4]. There are many different types of dyeing auxiliary. Such auxiliaries are extensively utilised in dyeing for all dye systems (eg disperse dyes/polyester, reactive dyes/cotton, acid dyes/wool, etc.) [5]. There are commonly used some paint types, for example, methylene blue (MB) and malachite green (MG) have wide applications which includes dyeing [6]. For the treatment of wastewater several investigations have been carried out to assess the potential of waste materials like fly ash, sawdust, bagasse ash and rice husk ash for their use as an effective alternative to activated carbon which is quite expensive. The properties of adsorbates and adsorbents are quite specific and depend upon their components. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater [7, 8]. Adsorption is between many methods (coagulation, flocculation, ion exchange, membrane separation, fenton, electrochemical oxidation etc.) is the most widely used In terms of efficiency, because of technical feasibility and easy [9, 10].

In this study, Modified Boron Enrichment Waste (MBEW or AUBEW) was used as adsorbent for removal of Methylene Blue (MB) and Malachite Green (MG) in synthetic color wastewater. The present study deals with the adsorption efficiency of modified leach waste for the removal of MB and MG from aqueous systems.

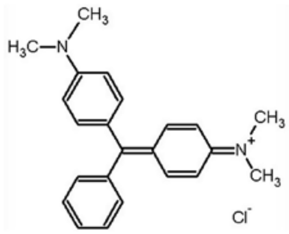
MATERIAL AND METHODS

Adsorption experiments and Adsorbates

Methylene blue (MB, Basic blue 9, C.I. 52015) is a basic dye, with the molecular formula $C_{16}H_{18}ClN_3S \cdot 3H_2O$ (molecular weight 373.90 g mol^{-1}) with CAS No. 61-73-4, was chosen as adsorbate [11] and Malachite Green (MG) is a cationic dye, with the molecular formula $C_{23}H_{25}N_2Cl$ (molecular weight 364.911g mol^{-1}) with λ_{max} (nm) 618, was chosen as adsorbate [12]. The chemical structure of the dye is shown in Fig. 1. A stock solution of methylene blue and malachite green were prepared (1000 mg/L) by dissolving required amount of dyes in distilled water. The stock solution was diluted with distilled water to obtain desired concentration.



(a)



(b)

Figure 1. Chemical structure of methylene blue (a) [11] and malachite green (b) [13]

Batch adsorption experiments were performed in 250 mL flasks with 100 mL of dye solutions containing adsorbents. The flasks were agitated on a shaker. Investigation the effect of different parameters on MB and MG adsorption was followed according to adsorbent dose, contact time, shaking speed and pH.

The dye concentrations in the solutions were determined at the beginning (C_0) and end (C_e) of the shaking period. The removal percentage (R (%)) of MG as well as the adsorbed quantity at the surface of waste materials (qe(mg/g)) were determined using Eqs. (1) and (2) respectively [6, 14].

$$R,\ \text{sorption}\ (\%) = \left[\frac{(Co - Ce)}{Co}\right] x\ 100 \quad (1)$$

The equilibrium amount of dye adsorbed from aqueous solution was determined by the following equation:

$$qe = \left[\frac{(Co - Ce)}{W} \text{ x V}\right] \quad (2)$$

where q_e is the amount of dye adsorbed at time t (mg $g^{-1}{}_{adsorbent}$); W is the adsorbent mass (g); C_0 and C_e are the initial and equilibrium solution concentrations of dye in aqueous solution (mg L^{-1}), respectively, and V is the volume of the solution (L)[1, 14].

Characterization Of Enrichment Waste

Modified Boron Enrichment Waste (MBEW or AUBEW) was used as adsorbents for dye removal from water in this study. MBEW formed during boron enrichment process was supplied from Etibor Colemanite and Ulexite Production Plant (Eti Mine Works General Directorate Bigadiç Boron Works Management Offices¸ Balıkesir, Turkey). Acid-ultrasound modified boron enrichment waste (MBEW) was treated with HCl and ultrasound for to increase the activated surface of adsorbent. The sono-modified process was performed by indirect sonication in an ultrasonic water bath, which was operated at a fixed 35-kHz frequency approximately 60 minutes.

The research was conducted with pH meter (Hach Multi-HQ40d Instruments) and a thermal stirrer (ZHWY-200B, Zhicheng Analytical Co., Ltd) was used for the batch adsorption experiments. The color solutions were filtered through 0.45-µm membrane filters (Millipore Corp., Bedford, Mass.) after settling. The exact concentration of basic dye was determined using a UV–Vis spectrometer (Hach Lange DR 2800) at a wavelength of maximum.

Optimizations and thermodynamics of adsorption

Methylene blue and malachite green removal efficiency from synthetic wastewater containing 100 mg/L and 50 mg/L stock dye solution, respectively, using MBEW as adsorbent was investigated. The results of experimental studies for to determine the optimum adsorption conditions at different initial contact time, adsorbent dose, pH, shaking speed and temperature were given in Fig.2 and 3.

Adsorption studies have focused on the adsorption thermodynamics to describe the adsorbent's adsorbate dependence. Thethermodynamic parameters reflect the feasibility and spontaneousnature of the process. These parameters include Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) and were calculated using Eqs. (3) and (4), as previously reported.

$$Ln\, K_D = \Delta S/R - \Delta H/(R * T) \quad (3)$$

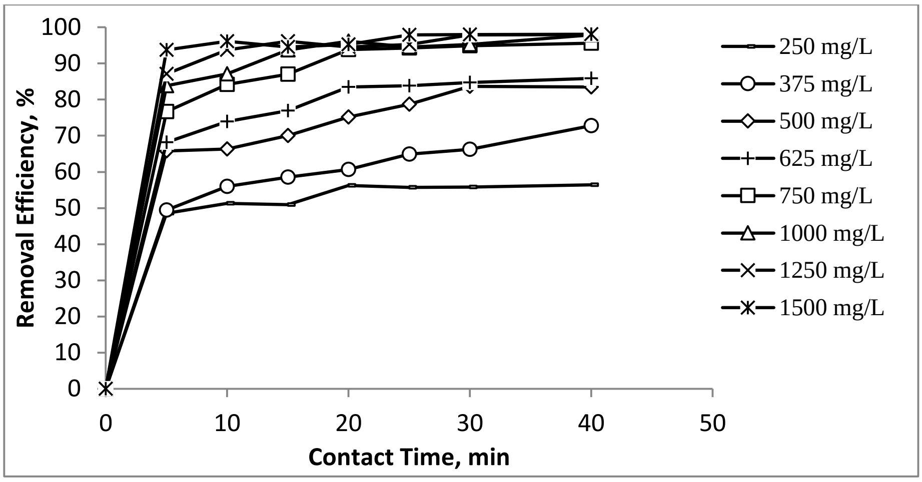
$$\Delta G = \Delta H - \Delta S * T) \quad (4)$$

where $K_D = {q_e}/{C_e}$ is the MB/MG concentration at equilibrium adsorbed at the surface of waste materials (mg/L), R is the universal constant of gas (8.314 J/mol K), and C_e is the MB/MG concentration at equilibrium (mg/L) [14-16].

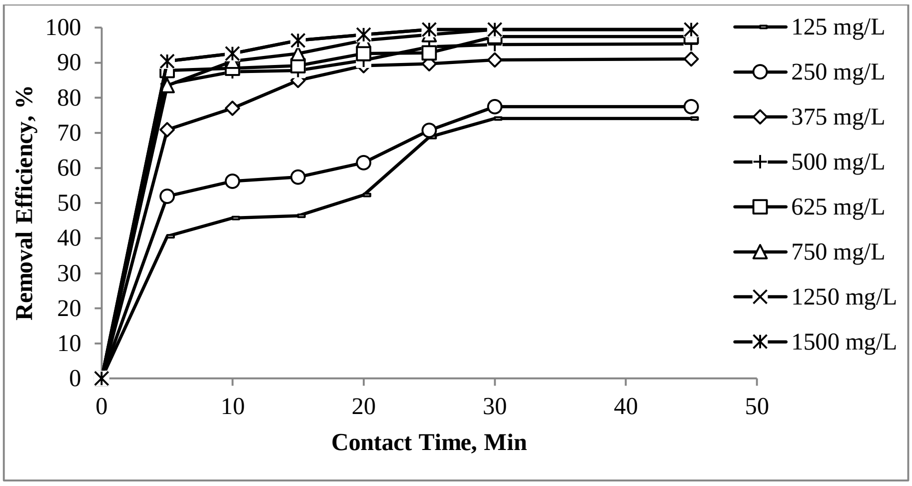
RESULTS AND DISCUSSION

Optimizationof adsorption

Dyes removal was studied using MBEW as adsorbents from synthetic wastewaters at initial adsorbent dose between 125-2000 mg/L, temperature 25^0 C, original pH value 5-6.5 range for MB and pH value 9 for MG, shaking speed 200 rpm and contact time 0-150 minutes at two dyes.



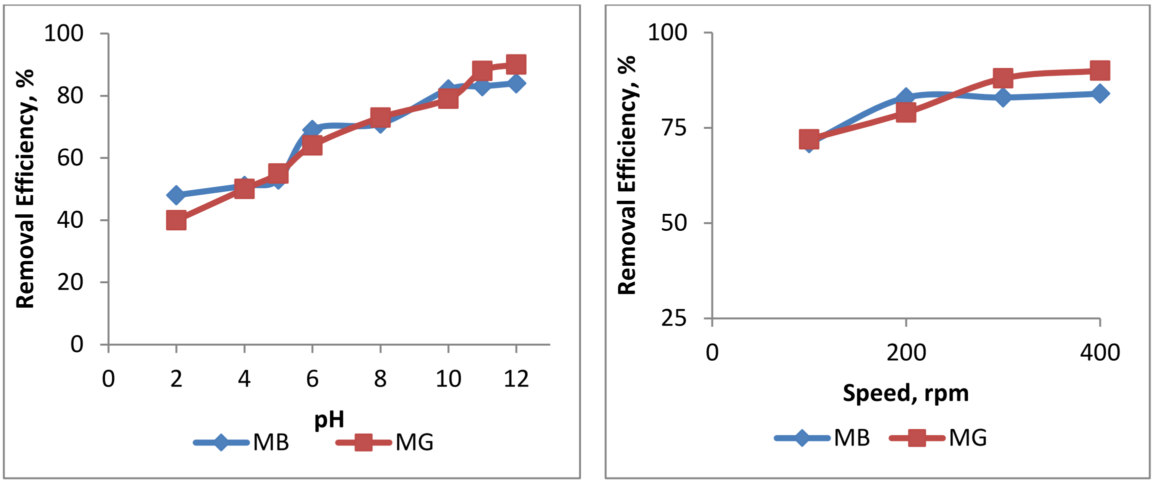
(a)



(b)

Figure 2. Effects of contact time on color removal efficiency with MBEW a) Methylene blue b) Malachite green (Initial Conditions = pH:5-6, 9 Temperature: 298 Kelvin, Dye Concentration: 100 and 50 mg/L, shaking speed: 200 rpm).

The dye removal percent increased with the increase in dose of adsorbents. The optimum removal efficiencies were obtained at adsorbent dosages 83%, and 77% for methylene blue and malachite green, respectively. The optimum adsorption dosage was 625 mg/L and 375 mg/L for MB and MG, respectively



(a) (b)

Figure 3. Effects of pH and stirrer speed on color removal efficiency with MBEW a) pH b) Speed (Initial Conditions = Temperature: 298 Kelvin, Dye Concentration: 100 and 50 mg/L, contact time: 20 (MB) and 10 (MG) minutes, dosage: 625 (MB) and 375 (MG) mg/L).

Thermodynamics of adsorption

For to determine the adsorption thermodynamic; ln K_c and 1/T relations of equilibrium data at different temperature (25 ^{0}C, 35 ^{0}C and 45 ^{0}C) were investigated. The results of the experiments were given in Fig.4 and Table 2.

The thermodynamic parameters of the adsorption system are Gibb's energy change (ΔG°), enthalpy change (ΔH°), entropy change (ΔS°), and the equilibrium constant (K). The adsorption process can occur spontaneously at the normal and high temperatures, because of $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} > 0$.

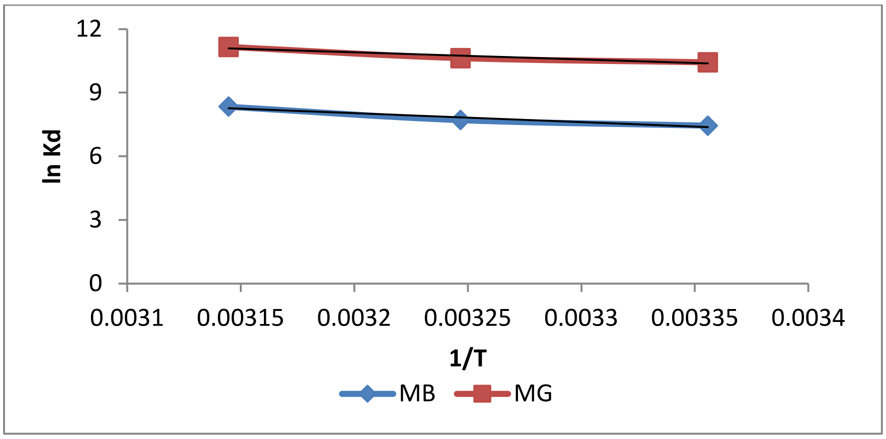


Figure 4. Thermodynamic parameters for the adsorption of dyes onto MBEW for MB and MG

Table 2. Thermodynamic parameters for the adsorption of MB and MG onto MBEW.

Dyes	Adsorbent	T (K)	lnb	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
Methylene Blue	MBEW	298	1,536	-18,271	35,217	0,179
		308	1,571	-20,065		
		318	1,650	-21,860		
Malachite Green	MBEW	298	1,363	-25,704	28,187	0,180
		308	1,382	-27,512		
		318	1,430	-29,321		

Thermodynamic (negative ΔG values) study indicates that the adsorption of dye is feasible, and spontaneous in nature. The results indicated that the boron enrichment process waste could be a promising adsorbent for removal of MB from aqueous solution. Thermodynamic study demonstrates the spontaneous and endothermic nature of sorption process due to negative values of free energy change and positive value of enthalpy change, respectively.

CONCLUSION

In this study, different adsorbents show promising adsorption capacity for methylene blue removal and malachite green. The ability of modified of boron enrichment waste as an adsorbent to remove MB and MG from aqueous solutions was investigated. The operating criterions for the maximum color removal were dye solution concentration (0.1 and 0.05g/L), MBEW sorbent dosage (0.125 g/200 mL and 0.075 g/200 mL), contact time (20 min and 10 min) for MB and MG respectively, speed (200 rpm) and temperature (298 K). Removal of methylene blue and malachite green dyes are pH dependent and the maximum removal was attained at pH 11 and 10, respectively. Thermodynamic (negative ΔG values) study indicates that the adsorption of dye is feasible, and spontaneous in nature. It was found that MBEW developed can effectively remove dyes, in their competition also behaves as a good adsorbent. It is believed that the results of this study will contribute to use of boron enrichment waste released from boron mineral processing plant in different disciplines.

ACKNOWLEDGMENT

This study was financially supported by Selcuk University Scientific Research Coordinating Office under grant no 13101005. We also gratefully thank to Assoc. Prof. Dr. Celalettin OZDEMİR for supporting of this study. This study was presented at 2nd International Conference on Civil and Environmental Engineering (ICOCEE - Cappadocia) as oral presentation. It selected by ICOCEE Scientific Committee for publish at EJERE.

REFERENCES

1. Chiou, M.-S., P.-Y. Ho, and H.-Y. Li, *Adsorption of anionic dyes in acid solutions using*

chemically cross-linked chitosan beads. Dyes and Pigments, 2004. **60**(1): p. 69-84.

2. Aksu, Z., *Application of biosorption for the removal of organic pollutants: a review.* Process Biochemistry, 2005. **40**(3): p. 997-1026.
3. Robinson, T., et al., *Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative.* Bioresource Technology, 2001. **77**(3): p. 247-255.
4. Clarke, E. and R. Anliker, *Organic dyes and pigments. In: Handbook of environmental chemistry, anthropogenic compounds,.* New York: Springer-Verlag,, 1980. **3**(part A.): p. 181–215.
5. Burkinshaw, S.M. and G. Salihu, *The role of auxiliaries in the immersion dyeing of textile fibres: Part 1 an overview.* Dyes and Pigments, 2017.
6. Kushwaha, A.K., N. Gupta, and M.C. Chattopadhyaya, *Removal of cationic methylene blue and malachite green dyes from aqueous solution by waste materials of Daucus carota.* Journal of Saudi Chemical Society, 2014. **18**(3): p. 200-207.
7. Khattri, S.D. and M.K. Singh, *Adsorption of basic dyes from aqueous solution by natural absorbent.* Indian J. Chem. Technol., 1999. **6**(2): p. 112–116.
8. Khattri, S.D. and M.K. Singh, *Removal of malachite green from dye wastewater using neem sawdust by adsorption.* Journal of Hazardous Materials, 2009. **167**(1): p. 1089-1094.
9. Oei, B.C., et al., *Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution.* Bioresource Technology, 2009. **100**(18): p. 4292-4295.
10. Gupta, V.K., et al., *De-coloration of hazardous dye from water system using chemically modified Ficus carica adsorbent.* Journal of Molecular Liquids, 2012. **174**: p. 86-94.
11. Khosravi, I. and M. Eftekhar, *Na 0.5 Li 0.5 CoO 2 nanopowders: Facile synthesis, characterization and their application for the removal of methylene blue dye from aqueous solution.* Advanced Powder Technology, 2014. **25**(6): p. 1721-1727.
12. Bouaziz, F., et al., *Adsorptive removal of malachite green from aqueous solutions by almond gum: Kinetic study and equilibrium isotherms.* International Journal of Biological Macromolecules, 2017.
13. Ghaedi, M., et al., *Isotherm and kinetics study of malachite green adsorption onto copper nanowires loaded on activated carbon: Artificial neural network modeling and genetic algorithm optimization.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015. **142**: p. 135-149.
14. Uma, S. Banerjee, and Y.C. Sharma, *Equilibrium and kinetic studies for removal of malachite green from aqueous solution by a low cost activated carbon.* Journal of Industrial and Engineering Chemistry, 2013. **19**(4): p. 1099-1105.
15. El-Zahhar, A.A. and N.S. Awwad, *Removal of malachite green dye from aqueous solutions using organically modified hydroxyapatite.* Journal of Environmental Chemical Engineering, 2016. **4**(1): p. 633-638.
16. Agarwal, S., et al., *Kinetics and thermodynamics of Malachite Green dye removal from aqueous phase using iron nanoparticles loaded on ash.* Journal of Molecular Liquids, 2016. **223**(Supplement C): p. 1340-1347.