Studies on Adsorption of Some Organic Dyes from Aqueous Solution onto Graphene Nanosheets

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ABSTRACT: *Graphene, a new member of the carbon family, was used as an adsorbent due to its exceptional capability to remove Rhodamine B (RB) and Malachite Green (MG), two organic dyes, from aqueous solutions. Adsorption kinetics of RB and MG onto graphene and adsorption capacity of the adsorbent were studied. Also the effects of parameters, including pH, contact time, temperature, and adsorbent dosage were studied. The adsorption process was followed using UV-visible spectroscopy. The isotherm analysis indicated that Freundlich and Langmuir isotherms are suitable for RB and MG, respectively. Pseudo-first- and pseudo-second-order models were considered to evaluate rate parameters. The kinetic experimental results fitted well the pseudo-second-order model for the two dyes, with correlation coefficients being greater than 0.99. Thermodynamic studies indicated that the adsorption processes is spontaneous for both the dyes, and exothermic for RB and endothermic for MG.*

KEY WORDS: *Graphene nanosheets, Adsorption, Rhodamine B, Malachite green, Isotherms, Kinetic.*

INTRODUCTION

Dyes are widely used in various industries such as textile, paper, rubber, plastic, leather, cosmetic, pharmaceutical, and food. Their discharge into water can cause environmental pollution, because most of the dyes used in industries are toxic and some are considered carcinogenic for human health [1]. Thus, treatment of

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1021-9986/15/2/51 *7/$/2.70*

dye-contaminated household wastewater and industrial effluents has become a challenging topic in environmental science and technology. Hence, removal of hazardous dyes from wastewater has attracted much attention in the last few years [2]. Rhodamine B (RB) and Malachite Green (MG) are organic cationic dyes used in various industries, but 20–40% of them remain in the effluent water, causing environmental pollution.

To remove dye pollutants from wastewater, many traditional physical methods have been used, such as adsorption, coagulation by chemical agents, reverse osmosis, precipitation, and ion exchange [3-6]. Among these methods, adsorption is most widely used because of its ease of operation and comparably low cost of application [7-9]. Various adsorbents, such as activated carbon derived from scrap tires [10], titania–silica mixed oxide xerogels [11], and graphene oxide [12], have been studied for adsorption of RB from aqueous solutions, and some of them showed good adsorption ability for this dye. In addition, different adsorbents such as carbon-based materials [13-15], minerals and biomaterials [16-19], modified clays [20], and hydrogels [21] have been used for removal of MG from aqueous solutions.

Carbon materials such as activated carbon [14, 15, 22], fullerenes, and Carbon NanoTubes (CNTs) are well known for their high adsorption capacity. They have been proved to possess great potential as adsorbents for removing many kinds of environmental pollutants [23-27].

Graphene, which is considered as the basic building block of all graphitic forms, is a single-atom-thick, two-dimensional carbon material. In comparison with other graphitic forms, graphene has extraordinary mechanical, thermal, and electronic properties such as ultrahigh specific surface area, good thermal conductivity, and fast mobility of charge carriers [28-31]. To date, graphene has attracted much attention due to its widespread potential applications in different fields of chemistry due to its unique structure. For example, graphene served as a sorbent for the solid-phase extraction [31-36] and also used as a modifier of electrodes in electrochemical detection [37]. Recent studies have shown that graphene has excellent adsorption capacity for inorganic and organic compounds. Heavy metal cations such as Pb^{2+},Cd^{2+}, and Zn^{2+} [38, 39] and anions such as F^- [40] have been removed from aqueous solutions using graphene as an adsorbent. Moreover, this carbon-based material has been used for removal of organic compounds such as phenol [41], 1-naphthol [42], and different dyes [12, 43] from aqueous solutions.

In this study, graphene due to its exceptional properties was used as an adsorbent to remove two organic dyes, RB and MG, from an aqueous solution. The effects of different parameters on the adsorption capacity were investigated in details. Finally, the thermodynamic and kinetic studies on the adsorption behavior of graphene were performed.

EXPERIMENTAL SECTION

Materials

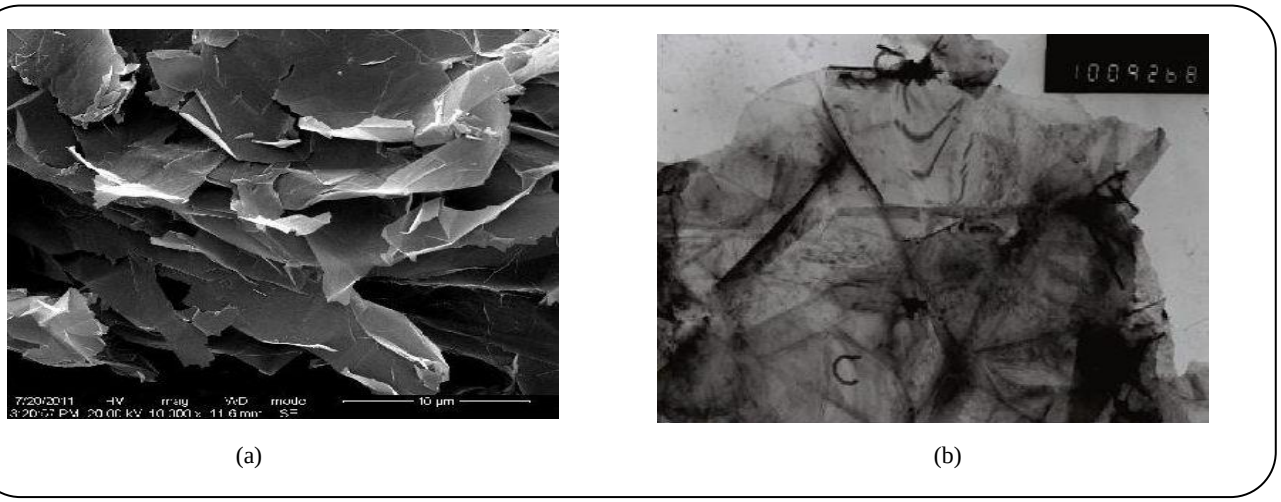
All chemicals used in this study were of analytical reagent grade and were used without further purification. Analytical reagent grade RB and MG were purchased from Merck Co. (Germany). Stock solutions of RB and MG were prepared by dissolving an accurately weighed amount of each dye in distilled water to achieve a concentration of 500 mg/L and subsequently diluted to the required concentrations. Graphene was obtained from Neutrino Company (Iran), with the following specifications: purity>99.5%, thickness 4–20nm, layers<30, diameter 5-10μm, and volume resistivity 4×10^{-4} ohm cm. Fig. 1 shows the SEM and TEM spectra of obtained graphene. The figure exhibits SEM images of graphene, consisting of almost transparent carbon nanosheets with a thin wrinkled structure intrinsic to graphene.

Apparatuses and Software

Absorption measurements were carried out on a Shimadzu UV-2550 PC spectrophotometer, using 1.0 cm quartz cells. Measurements of pH were performed with a Metrohm 827 pH-meter, using a combined glass electrode. A shaker (Behdad, Iran) was used to shake the solution during the experiments. A JENWAY heater was used to control the temperature of solution. Data were handled using Microsoft excel 2007.

Procedure

A definite amount of graphene (0.02 g) was added to 10 mL of dye solutions of known concentrations. The pH of the dye solutions was adjusted with 0.1 M HCl or 0.1 M NaOH. The solution was stirred to get adsorption equilibrium. After centrifuging the solution, the remained dyes were determined spectrophotometrically



(a) (b)

Fig. 1: SEM spectrum (a) and TEM(b) spectrum of graphene nanosheets.

at a suitable wavelength, using a calibration curve. The amount of adsorbed dye at equilibrium was calculated using Eq. (1):

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

Here, C_0 and C_e are the initial and equilibrium concentrations of dyes (mg/L), respectively; m is the mass of graphene (g), and V is the volume of the solution (L).

Experimental data analysis

In order to find the best kinetic model that fits the adsorption experimental data, the pseudo-first-order and the pseudo-second-order models were examined. Linear forms of the first-and second-order models can be described using Eqs. (2) and (3), respectively:

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}q_e - \frac{K_1}{2.303}t \quad (2)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (3)$$

Where q_e is the amount of the adsorbed dye at equilibrium per unit mass of the adsorbent (mg/g), and K_1 (1/min) and K_2 (g/ mg min) are the rate constants of the adsorption in pseudo-first- (Eq. (2)) and pseudo-second-order (Eq. (3)) reactions, respectively.

Two famous adsorption isotherm models, Langmuir and Freundlich isotherms, were used in this work to simulate the adsorption isotherms. They differ in the basic assumptions, shape of the isotherm, and nature of the adsorbent surface. The Langmuir isotherm can be described using Eq. (4):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (4)$$

Where C_e is the equilibrium concentration of the solution (mg/L), q_{max} is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant related to the affinity of the bonding sites and adsorption energy (L/g). The Freundlich isotherm model has the following form:

$$\mathrm{Ln}q_e = \mathrm{Ln}K_F + \frac{1}{n}\mathrm{Ln}C_e \quad (5)$$

Where K_F and n are Freundlich constant characteristics of the system indicating the adsorption capacity and adsorption intensity, respectively.

RESULTS AND DISCUSSIONS

Effect of parameters on adsorption

Effect of pH

The pH of adsorption medium is one of the most important parameters to determine the adsorption property of an adsorbent. Fig. 2 shows the effect of initial pH on the adsorption of MG and RB, which were studied in the pH range of 3–9. It can be seen that RB removal is independent of pH in the studied range. On the other hand, MG removal is 11% at pH=3 and increases to 67% at pH=5, which may be attributed to the formation of more functional groups on the surface of graphene,

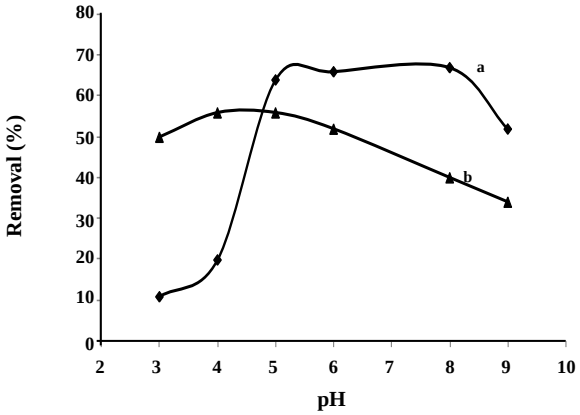


Fig. 2: Effect of parameter pH on dyes adsorbed by graphene, (a) MG (2mg/L) , (b) RB(10 mg/L).

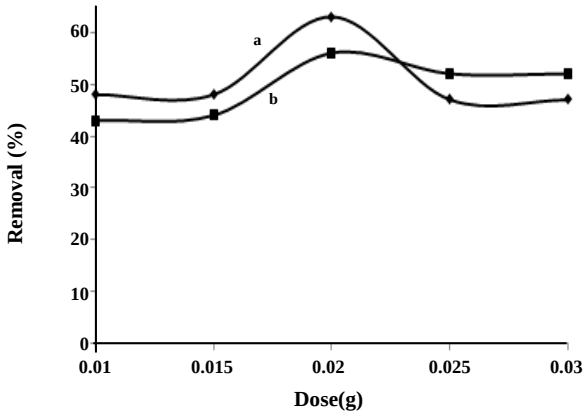


Fig. 3: Effect of parameter dose on dyes adsorbed by graphene. (a) MG(2mg/L), (b) RB(10 mg/L).

increasing their surface complexation capability [43]. It seems that the adsorption efficiency of MG, which is a cationic dye, increases with an increase in the negative charge on the dye, which has been attained by increasing the pH. This reason is similar to that reported in the literature [10].

Effect of dosage

Effect of adsorbent dosages on the percentage removal of RB and MG is shown in Fig. 3. As can be seen in the figure, the percentage removal of RB and MG increases with an increase in the adsorbent dosage from 0.01 to 0.02 g, which can be attributed to the increases in the surface area and the number of active sites [43].

Effect of temperature

Effect of temperature on the adsorption of RB and MG onto graphene was investigated at 298, 313, and 333 K. Adsorption of RB decreased with increasing temperature (Fig.4A). However, adsorption of MG appeared to increase with increasing temperature (Fig.4B). This might be attributed to the increase in the rate of diffusion of MG molecules across the external boundary layer and the number of active sites available for adsorption on the internal pore surfaces of graphene particles [42, 44].

Effect of contact time

Effect of contact time on the adsorption of RB and MG was studied at room temperature by adding 0.02 g of graphene into their solutions (10 mL) at two different concentrations (10 and 15 mg/L for RB and 2 and 5 mg/L for MG). The results showed that (not shown here) adsorption gradually increased with the increase in contact time for both dyes. The time required to reach the equilibrium was 45 min for the studied concentrations of both dyes.

Adsorption isotherms

Several mathematical models are available for describing equilibrium studies of the adsorption of dyes on solid surfaces. Langmuir and Freundlich models are frequently applied to calculate the adsorption isotherms that can fit the experimental data. The Langmuir model assumes that adsorption occurs on a homogenous surface and there is no interaction between adsorbents in the plane of the surface. The Langmuir isotherm follows Eq.(4). The Freundlich model follows an empirical equation related to adsorption on a heterogeneous surface. This isotherm follows Eq. (5).

In this work, both models were used to describe the experimental data obtained at three temperatures (298, 313, and 333 K). To evaluate the adsorption capacity and adsorption isotherms, 0.02 g graphene was added to 10 mL solution of RB or MG, with their concentrations ranging from 6 to 25 mg/L and from 2 to12 mg/L, respectively.

In order to check the Langmuir model, C_e/q_e was plotted against C_e for RB and MG; q_{max} and k_L were evaluated, respectively, from the slope and the intercept (Tables 1 & 2) for both dyes.

As can be seen in Tables 1 & 2, the maximum adsorption capacity of graphene is 111.11 mg/g for RB and 3.86 mg/g

Table 1: Isotherm parameters for the adsorption of RB onto graphene.

T(K)	Langmuir				Freundlich		
	q_{max}(mg/g)	K_L(L/g)	R^2	R_L	1/n	K_F(L/g)	R^2
298	111.11	26×10^{-5}	0. 977	0.323	1.258	2.764	0.985
313	85.87	2×10^{-5}	0. 989	0.147	1.131	1.698	0. 995
333	43.47	96×10^{-5}	0.981	0. 23	1.015	1.083	0. 992

Table 2: Isotherm parameters for the adsorption of MG onto graphene

T(K)	Langmuir				Freundlich		
	q_{max}(mg/g)	K_L(L/g)	R^2	R_L	1/n	K_F(L/g)	R^2
298	3.654	1.000	0. 998	0. 333	2.241	1.000	0. 939
313	3.863	1.113	0. 992	0. 309	1.422	0. 999	0.978
333	3.883	1.287	0.989	0. 279	1.697	0.915	0.901

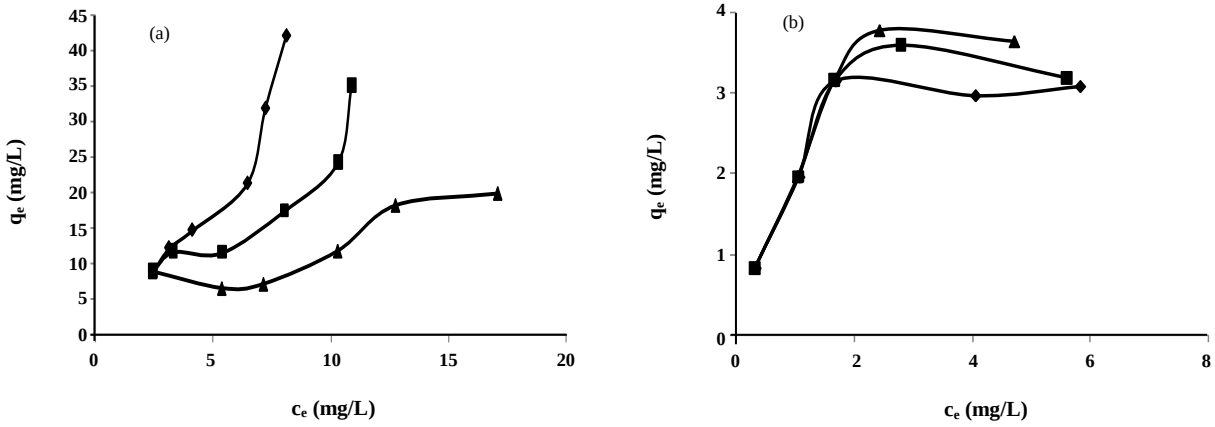


Fig. 4: Effect of parameter temperature(♦298■ 313 ▲333K) on dyes adsorbed by graphene for (a) RB (10 mg/L) and (b) MG (2mg/L).

for MG, indicating that graphene is a good adsorbent for removal of dyes from aqueous solutions.

In addition, the Freundlich model was checked for both dyes. From the slope and intercept of the straight portion of the linear obtained by plotting Lnq_e against LnC_e (figure not shown), the values of Freundlich parameters were calculated and listed in Tables 1 and 2 for RB and MG, respectively. The Freundlich isotherm model has higher determination coefficients (R^2>0.98) for RB, and the Langmuir isotherm model has higher determination coefficients (R^2>0.99) for MG. This indicates that the Freundlich model fit the experimental data well for RB and the Langmuir model for MG. It is clear the k_F and n decrease as the temperature increases in each of the two dyes, indicating that adsorption is favorable at lower temperatures.

Another parameter, R_L, a dimensionless equilibrium parameter that is defined as follows [45]:

$$R_L = \frac{1}{1+K_L C_0} \quad (6)$$

Where K_L is the Langmuir constant (L/g) and C_0 is the highest initial dye concentration (mg/L). This parameter indicates whether the isotherm is unfavorable (R_L>1), favorable (R_L<1), linear (R_L=1), or irreversible (R_L=0) [45, 46]. In this work, the value of R was between 0 and 1

Table 3: Parameters of pseudo-second-order kinetic models of MG and RB.

Dye	C (mg/L)	$q_{e,exp}$ (mg/g)	K_2 (1/min)	$q_{e,cal}$ (mg/g)	R^2
MG	15	21.666	62×10^{-4}	23.255	0.9984
	10	15.71	73×10^{-4}	16.949	0.9992
RB	5	0.222	75×10^{-3}	0.229	0.9973
	2	0.908	225×10^{-3}	0.943	0.9985

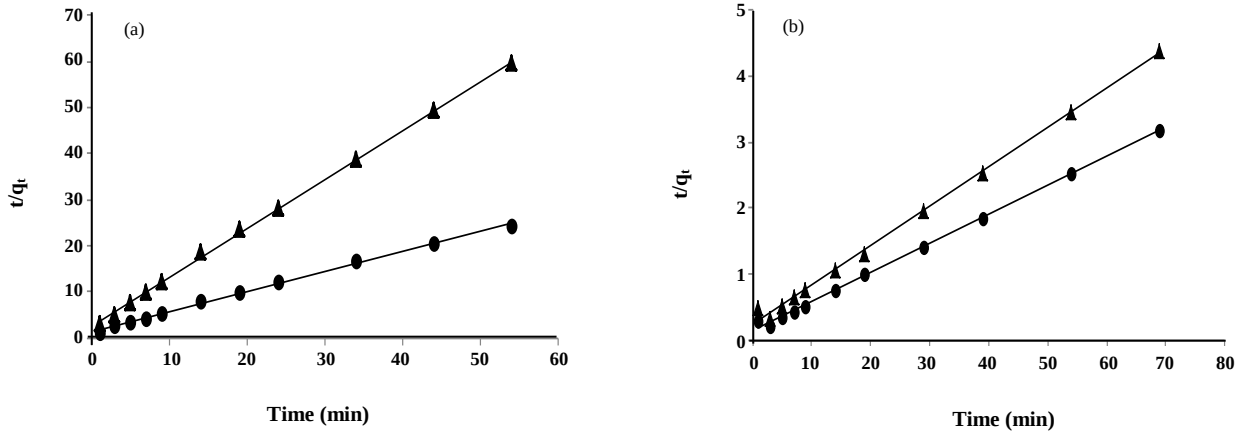


Fig. 5: Kinetic pseudo-second order model of A:MG and B:RB adsorbed by graphene, ca (▲:2 ppm ●:5ppm) and RB, b (▲:10 ppm ●:15ppm).

for RB and MG, indicating that the respective isotherms used for the adsorption of RB and MG onto graphene was appropriate and favorable (Tables 1 and 2).

Kinetic studies

In order to investigate the controlling mechanism of the adsorption process, the pseudo-first-order equation (Eq. (2)) and the pseudo-second-order rate equation (Eq. (3)) were applied to analyze the experimental data at two different initial concentrations for RB and MG (10 and 15 mg/L, and 2 and 5 mg/L, respectively). As can be seen in Table 3, the determination coefficient (R^2<0.96) obtained from the pseudo-first-order model is very low for RB and MG. Therefore, plots of $\log(q_e-q_t)$ against time (t) do not give a straight line, indicating that adsorption of these two dyes onto graphene does not fit the pseudo-first-order model.

Validity of the pseudo-second-order model was checked by the fitted straight line presented in Fig. 5. The corresponding kinetic parameters and determination coefficients are summarized in Table 3. The high correlation coefficients were obtained for pseudo-second-order model of both dyes (R^2>0.99). Also high correlation coefficients were obtained by plotting experimental capacities at equilibrium ($q_{e,exp}$) versus the calculated capacities ($q_{e,cal}$). These results show that the pseudo-second-order model fits the experimental kinetic adsorption data better than the pseudo-first-order model.

Thermodynamic study

Thermodynamic parameters were used to define the effect of temperature on the adsorption process of RB and MG onto graphene at 298, 313, and 333 K. Thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were calculated using the Eqs.(7) and (8):

$$\Delta G^0 = -RT\ln k_L \quad (7)$$

$$\ln k_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

Here, R is the universal gas constant (8.314J/mol K), K_L is the Langmuir constant (L/g), and T is the absolute temperature (K). ΔS^0 and ΔH^0 were calculated, respectively, from the intercept and slope of the plot of

Table .4: Thermodynamic parameters for MG and RB adsorbed by graphene.

Dye	T (K)	ΔG^0 (KJ/mol)	ΔS^0 (J/mol)	ΔH^0 (KJ/mol)
MG	298	-0.0018	19.997	5.960
	313	-0.280		
	333	-0.700		
RB	298	-2.519	-65.225	-21.898
	313	-1.278		
	333	-0.222		

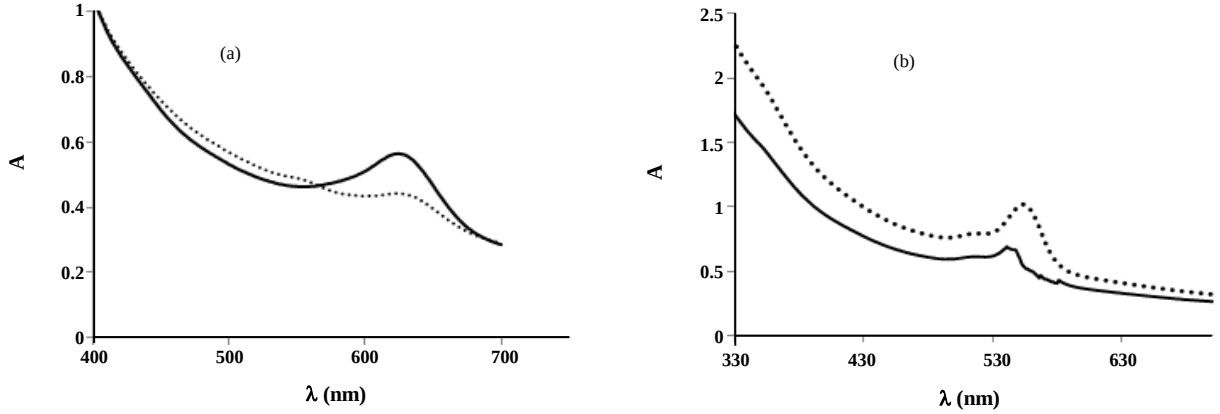


Fig. 6: Visible spectra of spiked real samples forMG (a) and RB (b) Before(dotted line) and after (solid line) adsorption treatment.

$\ln(K_L)$ versus 1/T. Thermodynamic parameters for MG and RB are listed in Table 4. The negative value of ΔG^0 suggests the feasibility and spontaneous nature of the adsorption processes for both dyes. The decrease in ΔG^0 value with increasing temperature reveals that adsorption of MG onto graphene becomes more favorable at higher temperatures, but RB shows a completely opposite trend to that of MG. In general, the values of ΔG^0 between 0 and –20 KJ/mol indicate that the adsorption process is physisorption, while the values between –80 and –400 KJ/mol correspond to chemisorptions [47, 48]. Therefore, in this work, the adsorption process was physisorption in nature, for both dyes. The positive and negative values of ΔH^0 for MG and RB indicate that the adsorption reaction is endothermic for MG and exothermic for RB, respectively. The positive valueof ΔS^0 demonstrates increased randomness at the solid–solute interface and the affinity of the adsorbent for MG.

Application of the proposed method

The proposed method was applied to remove RB and MG from real sample. Real sample was wastewater of paper-making factory (Tabriz-Iran). This sample was spiked with different amount of two dyes. These solutions were treated under optimum conditions purposed for the removal of RB and MG. The spectra of solutions were recorded before and after of adsorption treatment using UV-vis spectrophotometer. Fig. 6 shows the visible spectra of real sample spiked with MG and RB before and after treatment. It is clear from the visible spectrum that absorbance of dyes reduced by treatment. Absorbance of compound was measured before and after adsorption treatment at their λ_{max} and the removal yields of 35 and 25 % were obtained for RB and MG, respectively. Results indicate that the proposed method can be applied for the removal of RB and MG from real sample.

CONCLUSIONS

Results of this study showed that graphene is an effective adsorbent for removal of RB and MG from aqueous solutions. Batch adsorption experiments showed that the adsorption of MG and RB onto graphene was dependent on pH, adsorbent dosage, contact time, and temperature. The experimental data fitted well the Freundlich isotherm equation for RB and the Langmuir isotherm equation for MG. The pseudo-second-order rate model was applied to study the kinetics of adsorption. The results showed that adsorption of RB and MG onto graphene fitted the pseudo-second-order model. Thermodynamic investigations indicated that the adsorption reactions of RB and MG were exothermic and endothermic, respectively, and were spontaneous processes.

Acknowledgments

This work was financially supported by the Iran National Science Foundation, INSF (Research proposal No.: 91042596).

Received : Jun. 21, 2014 ; Accepted : Apr. 21, 2015

REFERENCES

[1] Ambashta R.D., Sillanpää M., Water Purification using Magnetic Assistance: A Review, *Journal of Hazardous Materials*, **180**: 38-49 (2010).

[2] Crini G., Non-Conventional Low-Cost Adsorbents for Dye Removal: A Review, *Bioresource Technology*, **97**: 1061-1085 (2006).

[3] Wang S., Zhu Z.H., Characterisation and Environmental Application of an Australian Natural Zeolite for Basic Dye Removal from Aqueous Solution, *Journal of Hazardous Materials*, **136**: 946-952 (2006).

[4] Azami M., Bahram M., Nouri S., Naseri A., A Central Composite Design for the Optimization of the Removal of the Azo Dye, Methyl Orange, from Waste Water using the Fenton Reaction, *Journal of the Serbian Chemical Society*, **77**: 235-246 (2012).

[5] Naseri A., Ayadi-Anzabi H., Monitoring of Decolorization of a Two Dyes Mixture using Spectrophotometric Data and Multivariate Curve Resolution: Modeling the Removal Process Using an Experimental Design Method, *Analytical Methods*, **4**: 153-161 (2012).

[6] Khataee A.R., Safarpour M., Naseri A., Zarei M., Photoelectro- Fenton / Nanophotocatalysis Decolorization of Three Textile Dyes Mixture: Response Surface Modeling and Multivariate Calibration Procedure for Simultaneous Determination, *Journal of Electroanalytical Chemistry*, **672**: 53-62 (2012).

[7] Molashahi M., Hashemipour H., Experimental Study and Artificial Neural Network Simulation of Methane Adsorption on Activated Carbon, *Korean Journal of Chemical Engineering*, **29**: 601-605 (2012).

[8] Chen C., Ting C., Yisu S., Tian, Y., Adsorption of Cu (II) from Aqueous Solution on Fly Ash Based Linde F (K) Zeolite, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **33**: 29-35 (2014).

[9] Panahi H.A., Zadeh M.S., Tavangari S., Moniri E., Ghassemi J., Nickel Adsorption from Environmental Samples by Ion Imprinted Aniline -Formaldehyde Polymer, *Iranian Journal of Chemisry and Chemical Engineering (IJCCE)*, **31**(3): 35-44 (2012).

[10] Li L., Liu S., Zhu T., Application of Activated Carbon Derived from Scrap Tires for Adsorption of Rhodamine B, *Journal of Environmental Sciences*, **22**: 1273-1280 (2010).

[11] Rasalingam S., Peng R., Koodali R.T., An Investigation into the Effect of Porosities on the Adsorption of Rhodamine B Using Titania–Silica Mixed Oxide Xerogels, *Journal of Environmental Management*, **128**: 530-539 (2013).

[12] Ramesha G.K., Vijaya Kumara A., Muralidhara H.B., Sampath S., Graphene and Graphene Oxide as Effective Adsorbents Toward Anionic and Cationic Dyes, *Journal of Colloid and Interface Science*, **361**: 270-277 (2011).

[13] Önal Y., Akmil-Başar C., Eren D., Sarıcı-Özdemir Ç., Depci T., Adsorption Kinetics of Malachite Green onto Activated Carbon Prepared from Tunçbilek Lignite, *Journal of Hazardous Materials*, **128**: 150-157 (2006).

[14] Önal Y., Akmil-Başar C., Sarıcı-Özdemir Ç., Investigation Kinetics Mechanisms of Adsorption Malachite Green onto Activated Carbon, *Journal of Hazardous Materials*, **146**: 194-203 (2007).

[15] Rahman I.A., Saad B., Shaidan S., Sya Rizal E.S., Adsorption Characteristics of Malachite Green on Activated Carbon Derived from Rice Husks Produced by Chemical-Thermal Process, *Bioresource Technology*, **96**: 1578-1583 (2005).

[16] Ahmad R., Kumar R., Adsorption Studies of Hazardous Malachite Green onto Treated Ginger Waste, *Journal of Environmental Management*, **91**: 1032-1038 (2010).

[17] Kiani G., Dostali M., Rostami A., Khataee A.R., Adsorption Studies on the Removal of Malachite Green from Aqueous Solutions onto Halloysite Nanotubes, *Applied Clay Science*, **54**: 34-39 (2011).

[18] Ghaedi M., Mosallanejad N., Study of Competitive Adsorption of Malachite Green and Sunset Yellow Dyes on Cadmium Hydroxide Nanowires Loaded on Activated Carbon, *Journal of Industrial and Engineering Chemistry*, **20**: 1085-1096 (2014).

[19] Ghaedi M., Ansari A., Habibi M.H., Asghari A.R., Removal of Malachite Green from Aqueous Solution by Zinc Oxide Nanoparticle Loaded on Activated Carbon: Kinetics and Isotherm Study, *Journal of Industrial and Engineering Chemistry*, **20**: 17-28 (2014).

[20] Arellano-Cárdenas S., López-Cortez S., Cornejo-Mazón M., Mares-Gutiérrez J.C., Study of Malachite Green Adsorption by Organically Modified clay using a Batch Method, *Applied Surface Science*, **280**: 74-78 (2013).

[21] Tang H., Zhou W., Zhang L., Adsorption Isotherms and Kinetics Studies of Malachite Green on Chitin Hydrogels, *Journal of Hazardous Materials*, **209-210**: 218-225 (2012).

[22] Nekoo S.H., Fatemi Sh., Experimental Study and Adsorption Modeling of COD Reduction by Activated Carbon for Wastewater Treatment of Oil Refinery *Iranian Journal of Chemistry and Chmical Engineering (IJCCE):*, **32**(3): 81-89 (2013).

[23] Gupta V.K., Kumar R., Nayak A., Saleh T.A., Barakat M.A., Adsorptive Removal of Dyes from Aqueous Solution onto Carbon Nanotubes: A Review, *Advances in Colloid and Interface Science*, **193-194**: 24-34 (2013).

[24] Arasteh R., Masoumi M., Rashidi A.M., Moradi L., Samimi V., Mostafavi S.T., Adsorption of 2-Nitrophenol by Multi-Wall Carbon Nanotubes from Aqueous Solutions, *Applied Surface Science*, **256**: 4447-4455 (2010).

[25] Moradi O., Applicability Comparison of Different Models for Ammonium Ion Adsorption by Multi-Walled Carbon Nanotube, *Arabian Journal of Chemistry*, Inpress (2011).

[26] Moradi O., Fakhri A., Adami S., Adami S., Isotherm, Thermodynamic, Kinetics, and Adsorption Mechanism Studies of Ethidium Bromide by Single-Walled Carbon Nanotube and Carboxylate Group Functionalized Single-walled Carbon Nanotube, *Journal of Colloid and Interface Science*, **395**: 224-229 (2013).

[27] Liu F., Zhang H., Zhu L., Liao Y., Nawaz F., Meng X., Xiao F.-S., High-Temperature Hydrothermal Synthesis of Magnetically Active, Ordered Msoporous Resin and Carbon Monoliths with Rusable Adsorption for Organic Dye, *Adsorption*, **19**: 39-47 (2013).

[28] Liu Y., Xie B., Zhang Z., Zheng Q., Xu Z., Mechanical Properties of Graphene Papers, *Journal of the Mechanics and Physics of Solids*, **60**: 591-605 (2012).

[29] Ionita M., Pandele M.A., Iovu H., Sodium Alginate/Graphene Oxide Composite Films with Enhanced Thermal and Mechanical Properties, *Carbohydrate Polymers*, **94**: 339-344 (2013).

[30] Terrones M., Botello-Méndez A.R., Campos-Delgado J., López-Urías F., Vega-Cantú Y.I., Rodríguez-Macías F.J., Elías A.L., Muñoz-Sandoval E., Cano-Márquez A.G., Charlier J.-C., Terrones H., Graphene and Graphite Nanoribbons: Morphology, Properties, Synthesis, Defects and Applications, *Nano Today*, **5**: 351-372 (2010).

[31] Wang Y., Gao S., Zang X., Li J., Ma J., Graphene-Based Solid-Phase Extraction Combined with Flame Atomic Absorption Spectrometry for a Sensitive Determination of Trace Amounts of Lead in Environmental Water and Vegetable Samples, *Analytica Chimica Acta*, **716**: 112-118 (2012).

[32] Wang Y., Ke X., Zhou X., Li J., Ma J., Graphene for Separation and Preconcentration of Trace Amounts of Cobalt in Water Samples Prior to Flame Atomic Absorption Spectrometry, *Journal of Saudi Chemical Society*, Ipress (2012).

[33] Huang K.-J., Jing Q.-S., Wei C.-Y., Wu Y.-Y., Spectrofluorimetric Determination of Glutathione in Human Plasma by Solid-Phase Extraction using Graphene asAdsorbent, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **79**: 1860-1865 (2011).

[34] Chen L., Lu Y., Li S., Lin X., Xu Z., Dai Z., Application of Graphene-Based Solid-Phase Extraction for Ultra-Fast Determination of Malachite Green and Its Metabolite in Fish Tissues, *Food Chemistry*, **141**: 1383-1389 (2013).

[35] Wu X., Hong H., Liu X., Guan W., Meng L., Ye Y., Ma Y., Graphene-Dispersive Solid-Phase Extraction of Phthalate Acid Esters from Environmental Water, *Science of The Total Environment*, **444**: 224-230 (2013).

[36] Liu Q., Shi J., Zeng L., Wang T., Cai Y., Jiang G., Evaluation of Graphene as an Advantageous Adsorbent for Solid-Phase Extraction with Chlorophenols as Model Analytes, *Journal of Chromatography A*, **1218**: 197-204 (2011).

[37] Chakrabarti M.H., Low C.T.J., Brandon N.P., Yufit V., Hashim M.A., Irfan M.F., Akhtar J., Ruiz-Trejo E., Hussain M.A., Progress in the Electrochemical Modification of Graphene-Based Materials and Their Applications, *Electrochimica Acta*, **107**: 425-440 (2013).

[38] Wang H., Yuan X., Wu Y., Huang H., Zeng G., Liu Y., Wang X., Lin N., Qi Y., Adsorption Characteristics and Behaviors of Graphene Oxide for Zn(II) Removal from Aqueous Solution, *Applied Surface Science*, **279**: 432-440 (2013).

[39] Deng X., Lü L., Li H., Luo F., The Adsorption Properties of Pb(II) and Cd(II) on Functionalized Graphene Prepared by Electrolysis Method, *Journal of Hazardous Materials*, **183**: 923-930 (2010).

[40] Li Y., Zhang P., Du Q., Peng X., Liu T., Wang Z., Xia Y., Zhang W., Wang K., Zhu H., Wu D., Adsorption of Fluoride from Aqueous Solution by Graphene, *Journal of Colloid and Interface Science*, **363**: 348-354 (2011).

[41] Li Y., Du Q., Liu T., Sun J., Jiao Y., Xia Y., Xia L., Wang Z., Zhang W., Wang K., Zhu H., Wu D., Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption of Phenol onto Graphene, *Materials Research Bulletin*, **47**: 1898-1904 (2012).

[42] Zhao G., Li J., Wang X., Kinetic and Thermodynamic Study of 1-Naphthol Adsorption from Aqueous Solution to Sulfonated Graphene Nanosheets, *Chemical Engineering Journal*, **173**: 185-190 (2011).

[43] Liu T., Li Y., Du Q., Sun J., Jiao Y., Yang G., Wang Z., Xia Y., Zhang W., Wang K., Zhu H., Wu D., Adsorption of Methylene Blue from Aqueous Solution by Graphene, *Colloids and Surfaces B: Biointerfaces*, **90**: 197-203 (2012).

[44] Gao Y., Li Y., Zhang L., Huang H., Hu J., Shah S.M., Su X., Adsorption and Removal of Tetracycline Antibiotics from Aqueous Solution by Graphene Oxide, *Journal of Colloid and Interface Science*, **368**: 540-546 (2012).

[45] Weber T.W., Chakravorti R.K., Pore and Solid Diffusion Models for Fixed-Bed Adsorbers, *AIChE Journal*, **20**: 228-238 (1974).

[46] Chen M., Chen Y., Diao G., Adsorption Kinetics and Thermodynamics of Methylene Blue onto p-tert-Butyl-calix[4,6,8]arene-Bonded Silica Gel, *Journal of Chemical & Engineering Data*, **55**: 5109-5116 (2010).

[47] Fernandes A.N., Almeida C.A.P., Debacher N.A., Sierra M.M.d.S., Isotherm and Thermodynamic Data of Adsorption of Methylene Blue from Aqueous Solution Onto Peat, *Journal of Molecular Structure*, **982**: 62-65 (2010).

[48] Weng C.-H., Lin Y.-T., Tzeng T.-W., Removal of Methylene Blue from Aqueous Solution by Adsorption Onto Pineapple Leaf Powder, *Journal of Hazardous Materials*, **170**: 417-424 (2009).