Bull Environ Contam Toxicol (2011) 87:86–90
DOI 10.1007/s00128-011-0304-1

Fast and Considerable Adsorption of Methylene Blue Dye onto Graphene Oxide

Wenjie Zhang · Chunjiao Zhou · Weichang Zhou · Aihua Lei · Qinglin Zhang · Qiang Wan · Bingsuo Zou

Received: 27 December 2010 / Accepted: 3 May 2011 / Published online: 13 May 2011

Abstract The quite efficient adsorption of methylene blue dye from an aqueous solution by graphene oxide was studied. The favorable electrostatic attraction is the main interaction between methylene blue and graphene oxide. As graphene oxide has the special nanostructural properties and negatively charged surface, the positively charged methylene blue molecules can be easily adsorbed on it. In the aqueous solution of methylene blue at 293 K, the adsorption data could be fitted by the Langmuir equation with a maximum adsorption amount of 1.939 mg/mg and a Langmuir adsorption equilibrium constant of 18.486 mL/mg. The adsorption amount increased with the increase of the solution pH (3–11), was not affected significantly by KCl under the examined condition and the adsorption process was exothermic in nature. The fast and considerable adsorption of graphene oxide could be regarded as a potential adsorbent for cationic dye removal in wastewater treatment process.

Keywords Adsorption · Methylene blue · Graphene oxide · Electrostatic attraction · Langmuir model

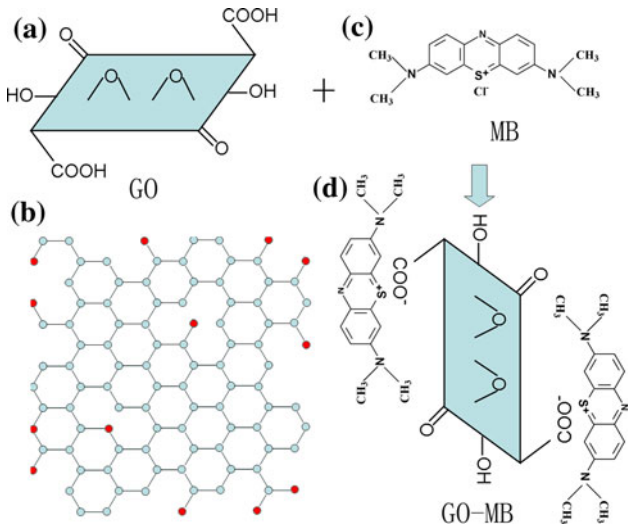
W. Zhang · W. Zhou · A. Lei · Q. Zhang · Q. Wan
School of Chemistry and Chemical Engineering, Micro-Nano Center, Hunan University, Changsha 410082, China

C. Zhou (✉)
College of Science, Hunan Agricultural University, Changsha 410128, China
e-mail: zcj69@163.com

B. Zou (✉)
Micro-nano Technology Center, School of MSE, Beijing Institute of Technology, Beijing 100081, China
e-mail: zoubs@bit.edu.cn

The effluents from textile plants contain portions of dyes, which are important water pollution sources. The dyes are deeply colored, multicomponent, and consume dissolved oxygen, and destroy aquatic life. Moreover, some dyes and their degradation products may be carcinogens and toxic (Mak and Chen 2004). Therefore, it is necessary to treat the dyes before disposal. Many methods have been used in wastewater treatment, such as biodegradation (Ong et al. 2005), ultra filtration (Zaghbani et al. 2007), photocatalytic degradation (Rauf et al. 2010), oxidation (Matsunaga and Inagaki 2006) and adsorption (Liu et al. 2010). Adsorption is a conventional but comparatively cheap and efficient technique for the treatment of these dye-bearing wastewaters (Yao et al. 2010). Usually, the effectiveness of any adsorption process largely depends on the physicochemical properties of the used adsorbent (Küçükosmanoğlu et al. 2006). So it is very important and meaningful to seek new adsorbents with large specific surface area, high adsorption capacity, fast adsorption rate and special surface reactivity (Zheng et al. 2009). There are a lot of reports about the adsorption of some dyes on various adsorbents such as fly ash (Wang et al. 2008), sand (Bukallah et al. 2007), rejected tea (Nasuha et al. 2010), polymers (Han et al. 2010); however, no such study is available on graphene oxide.

Graphene Oxide (GO) (Scheme. 1(a) and (b)) is the oxidation product of graphene, which is a single sheet from graphite and has the ideal 2D structure with a monolayer of carbon atoms packed into a honeycomb crystal plane. Considerable attention has been drawn to both of them over the past several years because of their unique physical and chemical properties and potential applications in various research and industrial fields. There are a lot of successes in improvement of the preparative method and understanding of their chemical and physical properties. GO,



Scheme 1 Illustration of the reaction between GO and MB

which has a lot of oxygen-containing groups, such as hydroxyl, epoxide, carboxyl and carbonyl functional groups, is hydrophilic, negatively charged, and readily disperses in water to form a stable colloidal suspension.

Methylene blue (MB) has wide applications, including dyeing cottons and silks, coloring paper and so on. It is also used as an oxidation–reduction indicator, antiseptic and for other medicine purposes. In the present study, MB (Scheme. 1(c)) is selected as model compound to evaluate the efficiency of GO for the removal of dye from its aqueous solutions (Zaghbani et al. 2007). The influences of experimental conditions such as MB concentration, pH, temperature, adsorption rate, ionic strength and desorption solution were investigated in detail.

Materials and Methods

Methylene blue was obtained from Tianjin Damao Chemical Co. Graphite was supplied by Tianjin Guangfu Fine Chemical Research Institute. Persulfate and Phosphorus pentoxide were purchased from Tianjin Bodi Chemical Co and Shanghai Lingfeng Chemical Co, respectively. Potassium permanganate was the product of Changsha Xiangke Fine Chemical Co. The water used throughout this work was the reagent-grade water produced by Milli-Q SP ultrapure-water purification system of Nihon Millipore Ltd., Tokyo. All other chemicals were the analytic grade reagents commercially available and used without further purification.

Graphene oxide was prepared from natural graphite power by Hummers and Offeman (1958) as modified by Kovtyukhova et al. (1999).

Scheme 1 illustrates the interaction between GO and MB. The concentration of GO, which was used for adsorption in our experiment, was 2 mg/mL. The adsorption of MB onto GO was carried out in water at 293 K and pH 7. In general, 5 mL of 2 mg/mL GO was added to 25 mL of MB solution (0.4–4.0 mg/mL). After stirring by magnetic stirrer for 30 min to reach equilibrium, GO was centrifuged at 4,000 r/min for 5 min from MB solution and the final concentration of dye in the solution was analyzed by spectrophotometeric method at 664 nm (Beijing purkinje general instrument Co, TU1901UV/vis spectrophotometer). The amount of adsorption at equilibrium q_e (mg/mg) was calculated by the following equation.

$$q_e = \frac{C_0 V_{MB} - C_e(V_{MB} + V_{GO})}{W_{GO}} \quad (1)$$

where C_0 and C_e (mg/mL) are the initial and equilibrium concentration, V_{MB} and V_{GO}(mL) are the volume of the MB and GO solution, respectively. W_{GO}(mg) is the mass of GO in the solution.

Results and Discussion

The zeta potentials of GO were measured in water solutions at pH 2.7–11 (adjust by NaOH or HCl). As shown in Fig. 1, the Zeta-potential was negative and decreased with the increase of pH. This also confirmed that GO was negatively charged.

To determine proper equilibrium time of the adsorption progress, time intervals were assessed. It was noteworthy in Fig. 2 that the adsorption of MB (1.0 mg/mL) reached equilibrium within 5 min. Such a fast adsorption rate could be attributed to the absence of internal diffusion resistance and the good solubility of GO.

The pH of the solution, which can change the surface charge of adsorbent (GO) and adsorbate (MB), is a very important factor in our work. To study the effect of pH on

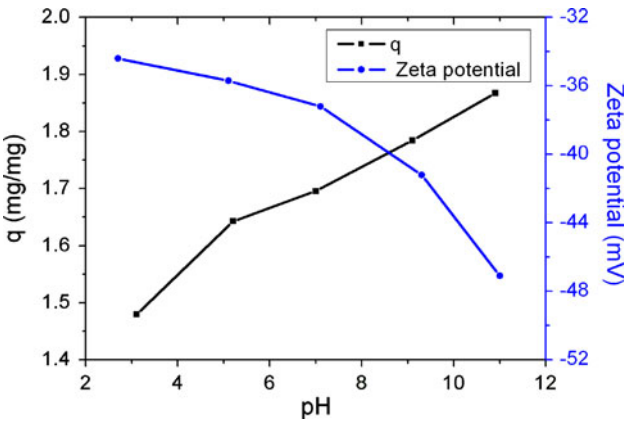


Fig. 1 Zeta potentials of GO at different pH (*filled circle*). Adsorption of MB on GO as a function of pH, Conditions: (GO: 0.33 mg/mL; MB: 1.0 mg/mL; temperature: 293 K; time: 2 h) (*filled square*)

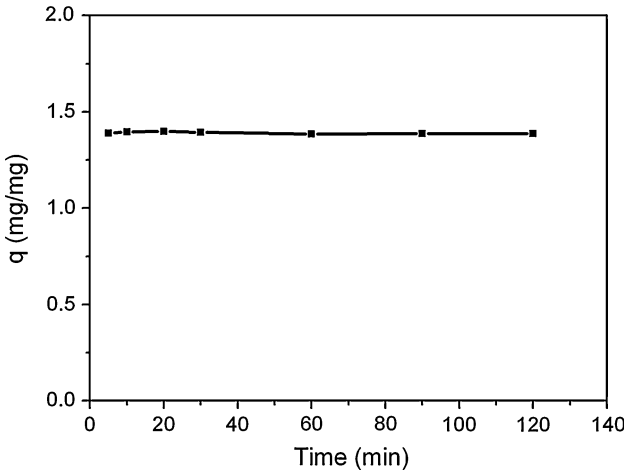


Fig. 2 Adsorption of MB on GO as a function of time. Conditions: (GO: 0.33 mg/mL; MB: 1.0 mg/mL; temperature: 293 K; pH: 7)

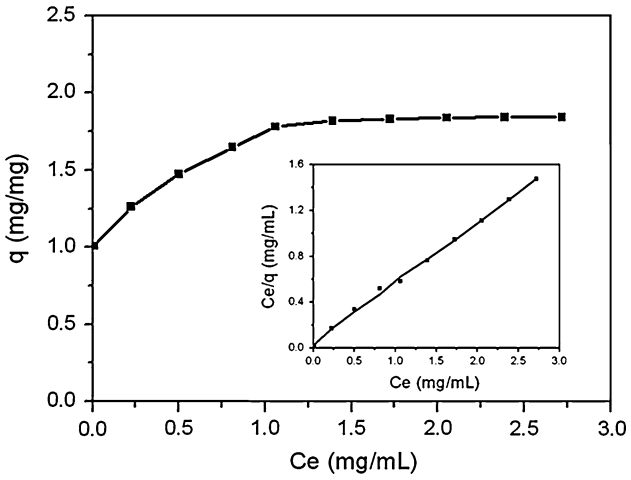


Fig. 3 Adsorption isotherm of MB on GO. Conditions: (GO: 0.33 mg/mL; MB: 0.33–3.3 mg/mL; temperature: 293 K; pH: 7; time: 2 h). The inset illustrates the linear dependence of C_e/q on C_e

adsorption, the experiments were carried out at 1.0 mg/mL MB with 0.33 mg/mL GO concentration. The initial pH value ranging from 1.5 to 11 was controlled by adding dilute chloride acid or sodium hydroxide solutions. The result was illustrated in Fig. 1. It was found that the adsorption capacity of GO increased with increasing the solution pH. According to the acid–base equilibrium isotherm, there are two equilibriums of MB and GO followed by $MBH^{2+} \longleftrightarrow MB^{+} + H^{+}$ and GO-H $\longleftrightarrow GO^{-} + H^{+}$. At lower pH values, hydrogen ion competes with MB cation, and most of GO exist in the form of GO-H, which reduced the adsorption amount of MB. At higher pH values, more GO^{-} occur, which may enhance electrostatic attraction and the adsorption amount for MB (Liu et al. 2010).

To determine the influence of initial MB concentration, the initial MB concentration varied from 0.33 to 3.3 mg/mL at pH 7 and 293 K. The result is shown in Fig. 3. It showed that the initial concentration of dye solution affected the adsorption capacity greatly. Owing to the adsorption sites of the adsorbent getting diminished, the adsorption capacity reached a plateau until the concentration of dye solution increased up to 1.66 mg/mL, indicating that the removal of MB highly depended on the initial dye concentration. This could be attributed to the increase in driving force of concentration gradient, because the increase of dye concentration could accelerate the diffusion of dye molecules onto the adsorbent.

The adsorption isotherm indicates the relationship between the absorbent and the adsorbate when the adsorption process reaches an equilibrium state. Several models have been used to describe the adsorption isotherms. In this paper, the Langmuir model was used to describe the relationship between the absorption amount of dye and its equilibrium concentration.

The equilibrium isotherm of MB adsorption by GO at pH 7 and 293 K is shown in Fig. 3. The Langmuir isotherms equation is represented by the following equation.

$$\frac{C_e}{q} = \frac{1}{Kq_m} + \frac{C_e}{q_m} \quad (2)$$

where q is the equilibrium adsorption amount of MB (mg/mg), C_e is the equilibrium MB concentration in the aqueous solution (mg/mL), q_m is the maximum adsorption amount of MB per mg of adsorbent (mg/mg) and K is the Langmuir adsorption equilibrium constant (mL/mg). Langmuir isotherm was given in the inset in Fig. 3, which shows the plot of C_e/q *vs.* C_e yielded a straight line. From the obtained results, it was deduced that the adsorption of MB was well fitted to the Langmuirean behavior. From the slope and intercept, the values of q_m and K could be estimated to be 1.939 mg/mg and 18.486 mL/mg, respectively.

Usually, temperature has two major effects on the adsorption process. That is increasing the temperature could increase the rate of diffusion of adsorbate and decrease the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent of a particular adsorbate. The effect of temperature on the adsorption of MB (1.0 mg/mL) by GO in water at pH 7 was illustrated in Fig. 4. As can be seen, the adsorption amount of MB showed a contrary trend with temperature. Higher temperature resulted in less adsorption indicating that the adsorption was an exothermic process.

As we all know, effluents from textile and dyeing industries contain not only dyes but also high concentrations of salts which may affect the removal of dye. So the effect of the ionic strength in solution was also studied. The effect of KCl concentration on the adsorption amount of MB (1.0 mg/mL) by GO (0.33 mg/mL) was given in

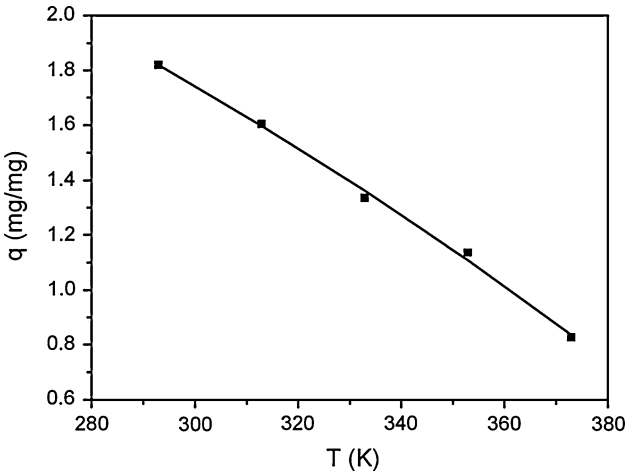


Fig. 4 Adsorption of MB on GO as a function of temperature. Conditions: (GO: 0.33 mg/mL; MB: 1.0 mg/mL; pH: 7; time: 2 h)

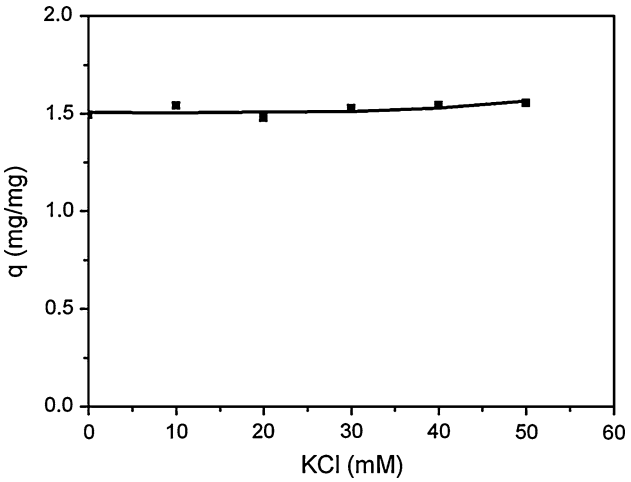


Fig. 5 Adsorption of MB on GO as a function of KCl concentration. Conditions: (GO: 0.33 mg/mL; MB: 1.0 mg/mL; temperature: 293 K; pH: 7; time: 2 h)

Fig. 5. It was found that the adsorption amount of MB remained almost constant with the increase of KCl concentration up to 50 mM. This implied that the electrostatic attraction between the negatively charged GO and the positively charged MB molecules was not affected significantly by KCl under the examined condition.

As shown in Fig. 6, the concentration of acetic acid did not significantly affected the desorption of MB, about 37% of MB could be desorbed. At the same time, we used a methanol solution of NH_4OH (CH_3OH:NH_4OH = 24:1, V/V), the percentage of MB desorption was about 30%. The result of the desorption progress of MB was not as good as the others' report, which was achieved by using a methanol solution containing acetic acid or ammonia. The low desorption percentage might be attributed to the special structure of GO. GO is a single sheet and the area of the surface is very large. MB molecular is smaller than GO,

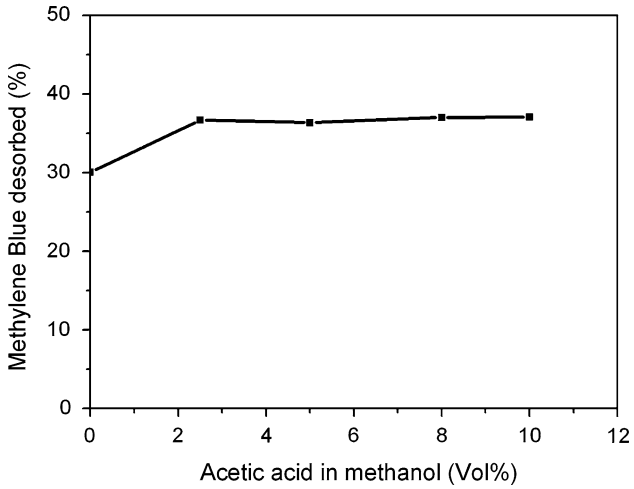


Fig. 6 Desorption of MB from GO as a function of acetic acid concentration in methanol. Adsorption conditions: (GO: 0.47 mg/mL; MB: 0.33 mg/mL; temperature: 293 K; time: 5 min)

it is easily absorbed on and packaged into GO. At the same time, the complex of GO and MB assembled seriously, so the desorption progress was very difficult.

MB could be adsorbed fast and considerably from an aqueous solution by GO due to its large specific surface area providing available adsorption sites and the absence of internal diffusion resistance. The electrostatic attractions between the positively charged MB and negatively charged GO play an important role in the adsorption. The equilibrium data fitted well in the Langmuir model of adsorption, and the adsorption amount of MB increased with the increase of the solution pH, on the contrary, decreased with the increase of temperature, and was not affected significantly by KCl. The desorption was difficult because of the special structure of GO. Both the adsorption and desorption reached equilibrium within 5 min. The present study indicated that GO could be employed for the removal of MB from water and wastewater.

Acknowledgments This work was supported by the NSFC funds of China (No. 20873039, No. 90606001 and No. 20903038) and HNSF funds of Hunan province (No. 07JJ4002).

References

Bukallah SB, Rauf MA, AlAli SS (2007) Removal of methylene blue from aqueous solution by adsorption on sand. Dyes Pigm 74:85–87

Han RP, Zhang LJ, Song C, Zhang MM, Zhu HM, Zhang LJ (2010) Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. Carbohydr Polym 79:1140–1149

Hummers WS, Offeman RE (1958) Preparation of graphitic oxide. J Am Chem Soc 80:1339–1340

Kovtyukhova NI, Ollivier PJ, Martin BR, Mallouk TE, Chizhik SA, Buzaneva EV, Gorchinskiy AD (1999) Layer-by-layer assembly

of ultrathin composite films from micron-sized graphite oxide sheets and polycations. Chem Mater 11:771–778

Küçükosmanoğlu M, Gezici O, Ayar A (2006) The adsorption behaviors of methylene blue and methyl orange in a diaminoethane sporopollenin-mediated column system. Sep Purif Technol 52:280–287

Liu Y, Zheng Y, Wang AQ (2010) Enhanced adsorption of methylene blue from aqueous solution by chitosan-g-poly (acrylic acid)/vermiculite hydrogel composites. J Environ Sci 22(4):486–493

Mak SY, Chen DH (2004) Fast adsorption of methylene blue on polyacrylic acid-bound iron oxide magnetic nanoparticles. Dyes Pigm 61:93–98

Matsunaga T, Inagaki M (2006) Carbon-coated anatase for oxidation of methylene blue and NO. Appl Catal B 64:9–12

Nasuha N, Hameed BH, Mohd Din AT (2010) Rejected tea as a potential low-cost adsorbent for the removal of methylene blue. J Hazard Mater 175:126–132

Ong SA, Toorisaka E, Hirata M, Hano T (2005) Biodegradation of redox dye methylene blue by up-flow anaerobic sludge blanket reactor. J Hazard Mater B124:88–94

Rauf MA, Meetani M, Khaleel A, Ahmed A (2010) Photocatalytic degradation of methylene blue using a mixed catalyst and product analysis by LC/MS. Chem Eng J 157:373–378

Wang SB, Ma Q, Zhu ZH (2008) Characteristics of coal fly ash and adsorption application. Fuel 87:3469–3473

Yao YJ, Xu FF, Chen M, Xu ZX, Zhu ZW (2010) Adsorption behavior of methylene blue on carbon nanotubes. Bioresour Technol 101:3040–3046

Zaghbani N, Hafiane A, Dhahbi M (2007) Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration. Sep Purif Technol 55:117–124

Zheng LL, Su YL, Wang LJ, Jiang ZJ (2009) Adsorption and recovery of methylene blue from aqueous solution through ultrafiltration technique. Sep Purif Technol 68:244–249