Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

http://chemeng.hust.edu.vn/jca/

Study on the adsorption of Rhodamine B on MoS_2/RGO composite

Phan Thi Thuy Trang[1*], Truong Thanh Tam[1], Vo Vien[1,2], Nguyen Hong Lien[3*]

[1]Faculty of Natural Science – Quy Nhon University*
[2] Applied Research Institute for Science and Technology, Quy Nhon University
[3]School of Chemical Engineering – Hanoi University of Science and Technology*
**Email: phanthithuytrang@qnu.edu.vn, lien.nguyenhong@hust.edu.vn*

ARTICLE INFO

Received: 15/6/2020
Accepted: 30/8/2020

Keywords:
graphene, reduced graphene oxide, MoS_2/RGO composite, adsorption, rhodamine B

ABSTRACT

In this study, MoS_2/RGO (reduced graphene oxide) composite material was synthesized and tested for adsorption of RhB in water. The adsorption studies were carried out at room temperature and the effects of pH, amount of adsorbents, concentration of adsorbate and time of adsorption on the adsorption were measured. In addition, the dynamics of the adsorption process was also investigated. The results showed that the MoS_2/RGO composite displayed toward RhB with maximum adsorption capacity reaching q = 57.79 mg/g at pH = 3.54 and the adsorption process follows the Langmuir adsorption isotherm with the pseudo-second-order model. Findings from this research indicated that the graphene based semiconductor MoS_2/RGO composite could be considered a promising adsorbent for removal of organic dyes from waste waters.

Introduction

As one of the most commonly used dyes, Rhodamine B (RhB) is widely used in different industries such as textile, paper, paints, leathers, and etc. However, when released, this organic dye will cause serious environmental and biological problems, even capable of causing irritation to the human skin, eyes and respiratory tract [1]. Thus, the removal of this dye from waste waters is always at high demand. Different treatment methods have been studied for removal of RhB from water such as coagulation-flocculation [2], adsorption [3], chemical oxidation [4], biological [5], and photocatalyst [6]. Among these, adsorption is considered a widely applicable and superior technique owing to the low cost of treatment, the ease of design and operation, and high effeciency [7].

Various types of adsorbents have been used for RhB adsorption, including carbon and carbon based materials, thanks to their large surface area, chemical and thermal stablity [4]. Recently, increasing attention of material scientists has been paid to graphene, one of the carbon based materials because of its outstanding properties such as large specific surface area (2630 m^2/g), high mechanical strength, good heat resistance and good optical property. As reported in [8], graphene is a promising adsorbent for removal of heavy metals, dyes and flouride ions from aqueous solutions.

In order to exploit special properties of graphene, this material has been combined with other semiconductors, such as Cu_2O [9], SnO_2 [10], ZnO [11] and applied as adsorbents in water treatment. In this study, MoS_2 is selected to composited with graphene because it has a similar graphene-like layer structure

http://doi.org/10.51316/jca.2020.070

with layers bonding together by weak interactions of Vanderwaals, good adsorbability and enviromentally friendly [12]. This semiconductor has been applied for charge storage, catalysis the hydrogen separation and adsorption of RhB [12,13]. Particularly, the MoS_2/RGO composite has been used to remove Pb(II) ion from waste water by adsorption with excellent adsorption capacity of 384.16 mg/g at pH = 5.0 and in the presence of humic acid (HA) [14]. The adsorption of Pb(II) on MoS_2/RGO well followed the pseudo-second-order kinetic model. Besides, Jiang et al [15] has also synthesized MoS_2/RGO composite and applied for adsorption of Cr(VI) in water. High adsorption capacities of 268.82 mg/g (at pH = 2) and 192.63 mg/g (at pH = 4.6) of this composite have been reported. However, the removal of persistent organic colorants from waste waters using MoS_2/RGO as an adsorbent has not been studied yet. Therefore, this research will focus on synthesis of MoS_2/RGO composite and application for removal of RhB from waste waters by adsorption method. This may widen the application of MoS_2/RGO composite as an adsorbent in the treatment of environments polluted with organic dyes.

Experimental

Materials

Graphite powder (Merck, German), ascorbic acid ($C_6H_8O_6$, vitamine C) (Indian), hexaamonium heptamolipdat tetrahydrat ($[NH_4]_6Mo_7O_{24}.4H_2O$), sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), dehydrat etanol (C_2H_5OH), hydrochloric acid (HCl), thiourea, rhodamine B (China) were used as original without purification.

Preparation of GO and RGO

Graphene oxide (GO) was synthesized from the graphite powder using Hummers method [16]. Reduced graphene oxide (RGO) was reduced from GO using ascorbic acid as reducing agent [17].

Preparation of MoS_2 and MoS_2/RGO composite

MoS_2 was prepared via a simple calcination method with a mixture of hexaammonium heptamolypdate tetrahydrate ($[NH_4]_6Mo_7O_{24}.4H_2O$) and thiourea. For the preparation of the MoS_2/RGO composite, the mixture of MoS_2 and RGO in water and ethanol were treated under ultrasonication in 1 hour to reach the good dispersion. After that, the mixture were stirred for 5 hours to make a homogeneous solution. In the next step, the solution was transfered to an autoclave and heated to 180 ^oC for 10 hours. After naturally cooled down to room temperature, the solution in the vessel was centrifuged to obtain a black solid, which was then washed with water and absolute ethanol three times. Finally, the obtained composite was dried at 80 ^oC for 10 hours. Details were described in our previous study [17].

RhB adsorption on MoS_2/RGO composite

Rhodamine B was dissolved in water at the concentration of 20 mg/L for the adsorption test. A mixture of 5 mg catalyst (MoS_2/RGO composite) was added in 20 mL RhB solution. The mixture was stirred in dark environment and at certain periods, an aliquot of supernatant solution was taken out to measure the dye concentration using an UV-Vis spectrophotometer (CE - 2011).

The amount of dye adsorbed onto the MoS_2/RGO composite (q_t, mg/g) at time t (minute) was calculated by the following equation:

$$q_t = \frac{(C_o - C_t).V}{m} \qquad (1)$$

where C_o is the initial RhB concentrtion (mg/l), C_t is the RhB concentration (mg/l) at t (minute). V is the volume (l) the RhB solution and m is mass (g) of the MoS_2/RGO composite used for the adsorption test.

Results and Discussion

Effect of contact time

The effect of contact time on the adsorption of RhB on MoS_2/RGO composite is shown in Figure 1.

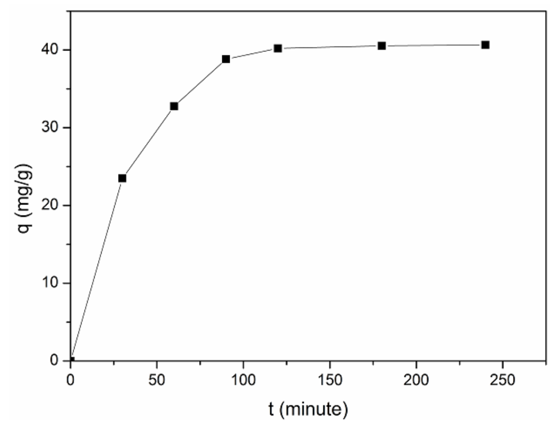

Figure 1: Effect of contact time on the adsorption of RhB on MoS_2/RGO composite (the RhB initial concentration C_0=20 mg/L)

The results showed that during the first 30 minutes, the adsorption rapidly increased due to large availability of adsorption sites in the MoS_2/RGO composite. After that, the rate of RhB adsorption slowly increased and reached the equilibrium after 120 minutes. Therefore, the following experiments on adsorption will be done with the contact time of 120 minutes.

Effect of pH

The pH of solution is an important factor affecting the adsorption. Meanwhile, the pH of waste waters change significantly depending on discharges. Therefore, the effect of pH on the adsorption capacity of the MoS_2/RGO composite was investigated at different pH conditions, ranged from 2 to 10. The results are shown in Figure 2.

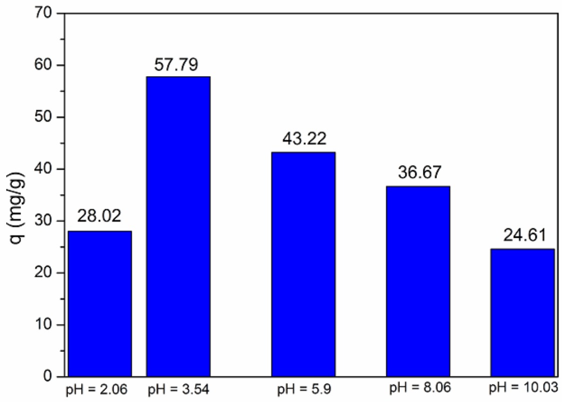

Figure 2: Effect of pH on the RhB adsorption onto MoS_2/RGO composite (C_0 = 20 mg/L, t = 120 min)

The results showed that as the pH increased from 2 to 4, the adsorption capacity of the material was increased with the highest level of 57.79 mg/g at pH = 3.54. However, as the pH continued to increase, the adsorption capacity of the MoS_2/RGO composite decreased. In order to explain this phenomenon, the zero charge point (pH_{pzc}) of adsorbent was determined. The results are shown in Figure 3.

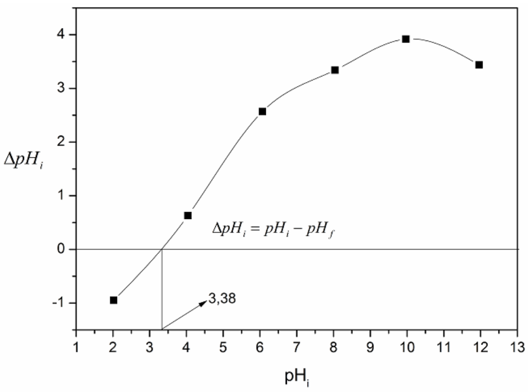

Figure 3: The zero charge point of the MoS_2/RGO composite

From Figure 3, it could be seen that the zero charge point of MoS_2/RGO was pH_{pzc} = 3.38, indicating positively charged surface when pH was lower than 3.38, and negatively charged surface when pH was larger than this point. Besides, RhB often exists in two principal forms in water, cationic (RhB^+) at pH < 7 and zwitter ionic ($RhB^{\pm}$) at pH > 7 [18]. Therefore, at the tested pH = 3.54 (pH > pH_{pzc}), the surface charge of MoS_2/RGO composite is negative, while the RhB is in cationic form (RhB^+), then facilitating the adsorption of RhB. At pH less than pH_{pzc}, both of the composite and RhB are positively charged, then electrostatic repulsive forces prevent the adsorption of RhB on the adsorbent surface, reducing the adsorption efficiency. At pH greater than 7, the adsorption capacity of the MoS_2/RGO is also low, because RhB exists in the zwitter ion form while the material is negatively charge, decreasing the attraction between RhB and composite surface.

Effect of initial concentration of RhB

To study the effect of the initial RhB concentration on the rate of adsorption on MoS_2/RGO composite, different experiments were carried out in the range of C_o = 20 to 50 mg/L. The results are shown in Figure 4.

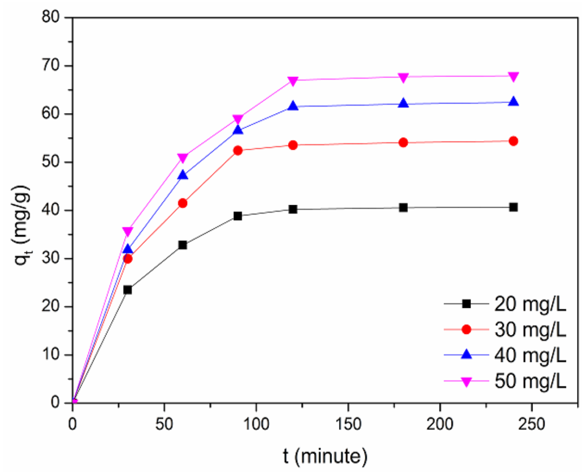

Figure 4: Effect of initial concentration (C_0) on the RhB adsorption on MoS_2/RGO composite

The results indicated that, in the study range, as the initial RhB concentration increased, the adsorption capacity of MoS_2/RGO composite increased too. This is originated from the larger RhB molecules available for adsorption. However, the diference in the adsorption capacity slowly increased as the initial RhB concentration reached 50mg/L due to the limitation of adsorption sites in the adsorbent. Especially, one common point could be observed is that, the adsorption capacity remains constant (reaching equilibrium) after a period of 120 minutes, independing on the initial RhB concentration.

http://doi.org/10.51316/jca.2020.070

Adsorption isotherms study

To determine the best fit isothermal model for the RhB adsorption over MoS_2/RGO composite, the Langmuir and Freundlich models were tested. The Langmuir isotherm models can be expressed as the following equations [19]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (2)$$

Where q_e (mg/g) is the amount of RhB adsorbed on MoS_2/RGO at equilibrium, q_m (mg/g) is the maximum adsorption capacity and K_L is the Langmuir constant related to the free energy of adsorption. q_e can be expressed as follow:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \qquad (3)$$

In addition, a dimensionless separarion constant R_L an be expressed as follow:

$$R_L = \frac{1}{1 + K_L C_o} \qquad (4)$$

Where the value of R_L indicates the type of isotherm that is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm assumes a heterogeneous adsorption surface during the adsorption process. The Freundlich isotherm model is represented by the following equation [20]:

$$lnq_e = \frac{1}{n} lnC_e + lnK_F \qquad (5)$$

Where $\frac{1}{n}$ and K_F are the constant related to the intensity of adsorption and capacity of adsorption, respectively.

The experimental results on application of these two models are shown in Figure 5 and Figure 6.

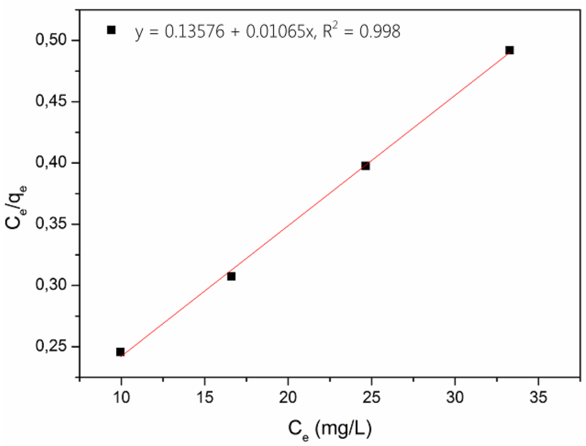

Figure 5: The Langmuir isotherm model for the adsorption of RhB over MoS_2/RGO composite

From Fig 5, it can be seen that the caculated maximum adsorption capacity q_{max} is 93.9 mg/g and the correlation coefficient R^2 = 0.998. The value of K_L = 0.078 and 0 < R_L < 1 confirm that the pattern of Langmuir isothermal adsorption is favorable for RhB adsorption over MoS_2/RGO.

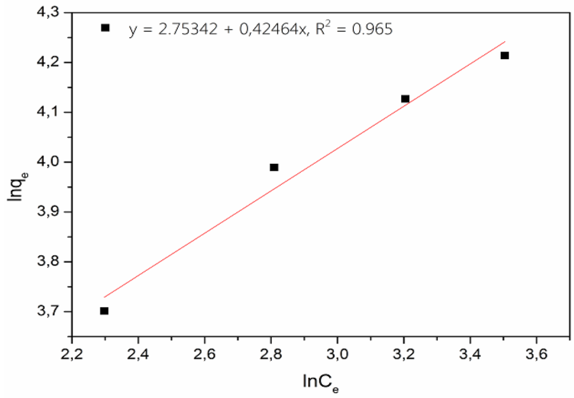

Figure 6: The Freundlich isotherm model for the adsorption of RhB over MoS_2/RGO composite

From Figure 6 it can be determined that, the correlation coefficient R^2 = 0.965, K_F = 15.6 [(mg/g)(L/mg)$^{1/n}$] and value of constant 1/n = 0.42. Compared to the results caculated using Langmuir model, the correlation coefficient R^2 of the Langmuir isotherm model (R^2 = 0.998) is higher than the one of Freundlich isotherm model (R^2 = 0.965). Thus, the Langmuir isotherm model is better description of RhB adsorption over MoS_2/RGO composite.

Adsorption kinetics study

The pseudo-first order model and the pseudo-second order model were applied to better understand the nature of the adsorption process. Those models are expressed in the following equations [21,22]:

$$\ln(q_e - q_t) = lnq_e - K_1 t \qquad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 . q_e^2} + \frac{t}{q_e} \qquad (7)$$

where q_e is the amount adsorbed at equilibrium (mg/g), q_t is the amount adsorbed at time t (mg/g) and K_1, K_2 are the pseudo-first constant order and the pseudo-second constant order, respectively.

Fig 7 and Fig 8 indicate the linear representation of the pseudo-first order model and the pseudo-second order model. The results showed that the correlation coefficient of pseudo-first order model (R^2 = 0.961) was lower than the coefficient of pseudo-second order model (R^2 = 0.993). This confirms again that the RhB adsorption process on the MoS_2/RGO well fit with the pseudo-second order model.

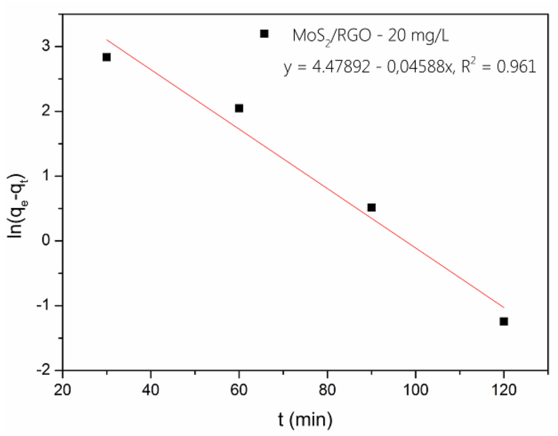

Figure 7: The pseudo-first order kinetics model for the adsorption of RhB by MoS_2/RGO

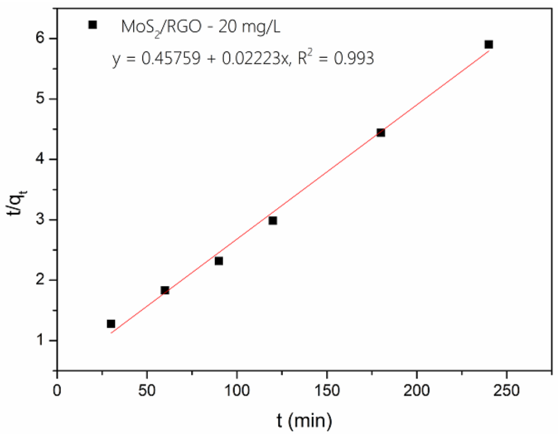

Figure 8: The pseudo-second order kinetics model for the adsorption of RhB by MoS_2/RGO

Conclusion

The MoS_2/RGO composite was synthesized via the hydrothermal method and firstly applied for removal of RhB from water by adsorption. The time needed for reaching adsorption equilibrium of MoS_2/RGO was 120 minutes. The maximum adsorption capacity of the composite was 57.79 mg/g at pH = 3.54. The Langmuir isotherm was found to better describe the adsorption of RhB on MoS_2/RGO composite than the Freundlich one, with a regression coefficient R^2 = 0.998 and an K_L = 0.078. The adsorption kinetics of RhB on MoS_2/RGO composite fitted better to a pseudo-second order model than a pseudo-first order model, with the correlation coefficient R^2 = 0.993. These results confirmed that, the combination of MoS_2 with RGO resulted a good adsorbent for the removal of organic dyes like RhB from water environments.

Acknowledgements

This work was done in the framework of the project 9.52.03.01 at the Natural Science Department Laboratory (Quy Nhon University) and Department of Petrochemical Organic Technology (Hanoi University of Science and Technology).

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