



Preparation of Polyvinyl Alcohol/Graphene Oxide Composites and Their Adsorption Properties

Yanyan Dong*, Manuel J. Lis Arias**, Chengye Hu*, Wendan Wu*, Liping Liang*, Xinlan Mou* and Xu Meng*(***)†

*College of Textile and Garment, College of Life Science, Shaoxing University, Shaoxing, 312000, China

**Textile Research Institute of Terrassa (INTEXTER-UPC), 08222, Terrassa, Spain

***Key Laboratory of Clean Dyeing and Finishing Technology of Zhejiang Province, Shaoxing University, Shaoxing, 312000, China

†Corresponding author: Xu Meng

Nat. Env. & Poll. Tech.

Website: www.neptjournal.com

Received: 18-06-2019

Accepted: 30-08-2019

Key Words:

PVA/GO

Polymer

Composite material

Adsorption

ABSTRACT

The polyvinyl alcohol/graphene oxide (PVA/GO) hydrogel was prepared. It was confirmed that the adsorption performance of polyvinyl alcohol/graphene oxide hydrogel composite material was improved, and it does not cause secondary pollution. According to adsorption experiments, it was found that PVA/GO adsorbent with a content of 30 % graphene oxide has the best comprehensive performance. The suitable environment of adsorption was under 25°C, 12-18 h for adsorption time and acidic conditions. The suitable adsorbent dosage was 0.3g and the suitable concentration of the dye was 10 mg/L.

INTRODUCTION

With the development of industrial activities, a large amount of industrial wastewater has resulted in a number of environmental problems. Effective separation of wastewater is regarded as a potential solution for environmental protection (Gan et al. 2015, Nevárez et al. 2011, Sehaqui et al. 2015). There are various methods being used nowadays. Among them, adsorption has been confirmed to be a promising treatment because of its low cost and simple operation (Hameed et al. 2009, Adebajo et al. 2003, Gore et al. 2016). This method is especially suitable for printing and dyeing wastewater treatment. One of the most critical factors about the treatment is the properties of adsorbent, which determines the effect of adsorption. Graphene is the most widely used adsorbent in the adsorption. It has a large specific surface area as one of the structure features, but such as poor hydrophilicity, decreased adsorption effect in the later stage, and difficulty in removing after adsorption are its disadvantages (Kumar et al. 2016, Satti et al. 2010).

Compared to graphene's single molecular layer, GO has some advantages such as large number of hydrophilic groups, good dispersibility in water and easy surface modification (Russo et al. 2013). However, GO has tiny size and low cytotoxicity to normal cell. These cause the problem of secondary pollution if GO disperses in water. Researchers tried

to compound GO with other compounds to form membranes, pellets or fibres (Shen et al. 2015). But these methods rely on the other compounds to wrap GO for forming, which reduces the content of graphene oxide in the compound and hinders the advantage of specific surface area (Tiwari et al. 2013). In order to solve the above problems and ensure the adsorption effect at the same time, polyvinyl alcohol and GO will be combined into hydrogel materials in this experiment, and its adsorption properties will be explored further.

PVA is a kind of white, non-toxic and odourless solid, with a large number of hydrophilic groups on the molecular chain, which is the reason of its excellent water-solubility (Wahab et al. 2019). The intermolecular interaction force of polyvinyl alcohol molecules is large, which can form a high strength film in close contact. In the experiment, PVA/GO composite hydrogel was synthesized by using PVA as the carrier and fixing GO on the polyvinyl alcohol matrix to form a three-dimensional hydrogel adsorbent with network structure. This hydrogel can be deposited in water after adsorption and separated well without affecting the adsorption effect of GO. PVA/GO composite material is simple to prepare and easy to operate. It is also an excellent adsorption material due to which it not only guarantees the adsorption performance of adsorbent, but also overcomes the disadvantage of secondary pollution.

After the PVA/GO composites were successfully prepared, a series of batch adsorption experiments were designed to explore their adsorption properties. The influencing factors on the adsorption process were investigated, such as the content of GO in the composites, material dosage, initial concentration of dye solution, adsorption temperature, adsorption time and pH value.

MATERIALS AND METHODS

Preparation of graphene oxide: All the test specimens were prepared by adding 2 g graphene and 1 g sodium nitrate to 46 mL concentrated sulphuric acid in an ice bath, and stirring for 15 min. At the time of the specimens keeping at a temperature of 20°C, 6 g KMnO_4 was added slowly and stirred fully for 2 h, and then the specimens were placed at 35°C for 30 min. 92 mL of deionized water was added to them for diluting it. After standing about 15 min, 20 mL of 30% H_2O_2 was added after adding 280 g of water into the test specimens for further dilution. Then the samples reacted to bright yellow. After filtrating, the final product was washed in 5% diluted hydrochloric acid firstly and then washed in deionized water to neutral. Samples were dried under vacuum at 50°C. Finally, the samples were ground to a fine powder and stored for reserve.

Preparation of PVA/GO composites: All the working solutions were prepared by adding 90 g deionized water in a beaker with 10 g PVA and stirred to dissolve PVA at 90°C. 9.2 g NaOH and 6 mL epichlorohydrin were added and stirred in the beaker. Samples were reacted over 6 h in the oven at 35°C. After forming gel material, freeze dryer was used to dry the material until its weight is constant. Finally, PVA

hydrogel without graphene oxide was obtained. According to the above method and on the basis of the above steps, new samples were prepared by adding 0.1 g and 0.2 g, 0.3 g and 0.4 g of graphene oxide powder into the hydrogel, and reacted over 6 h at 35°C in the oven until forming gelatinous material. With the help of the freeze dryer, the material was dried until its weight became constant. Then the gel composite was cut up and labelled for storage.

Pre-experimental treatment: The standard navy-blue dye was configured with a concentration of 1 g/L. The absorbance of the standard navy-blue dye was measured at different concentrations (10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L, 70 mg/L), and the standard curve was obtained. According to the curve equation, $R^2 = 0.999$, which proved that the prepared solution could meet the standard.

Diluting part of the standard dye solution and five groups of dye solution with a concentration of 10 mg/L (200 mL in each group) were obtained. Some dye was kept before adsorption, and then adsorbed with 0.5 g composite materials with different contents of graphene oxide. Soaking the samples over 12 h at the constant temperature of 25°C, it was observed that the colour of dye became shallow after the reaction, and the adsorbent was adhered with navy-blue, which proved that composite material has good adsorption effect and deserved the follow-up study.

Batch adsorption experiments: To explore the adsorption effect of different contents of graphene oxide, 0.3 g PVA/GO composite hydrogel was taken separately which contains 0, 10%, 20%, 30%, 40% of graphene oxide and these samples were added to 200 mL navy-blue dye solution, whose initial concentration was 10 mg/L. The samples were placed in an

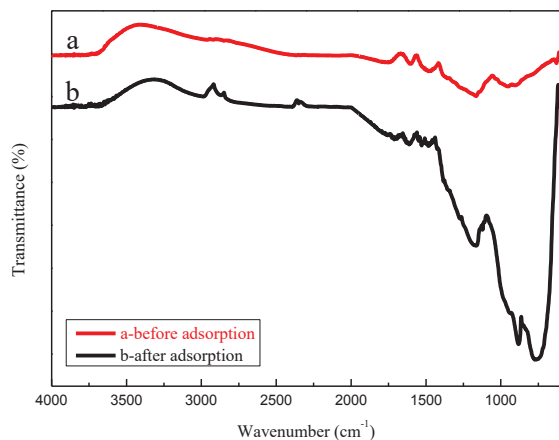


Fig. 1: Infrared spectra of PVA/GO composite before and after adsorption.

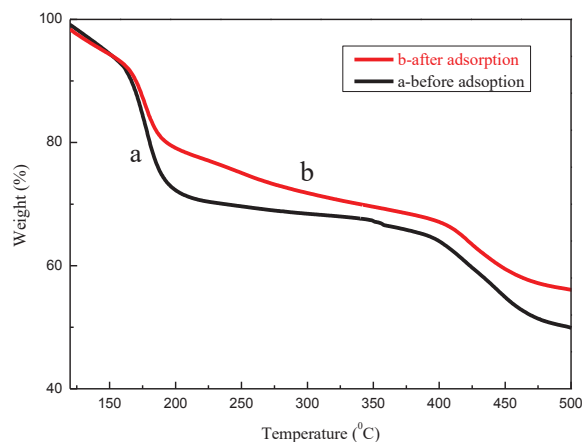


Fig. 2: Thermo gravimetric characterization of PVA/GO composite before and after adsorption.

oscillator with a constant temperature and oscillated for about 15 h until adsorption saturation. The absorbance of the dye was measured before and after adsorption.

To explore the effect of the adsorbent dosage on the adsorption, different doses (0.1 g, 0.3 g, 0.5 g, 0.7 g, 0.9 g) of the PVA/GO composite hydrogel (containing 30 % GO) respectively were taken and added to 200 mL navy-blue dye with an initial concentration of 10 mg/L. The samples were placed in an oscillator with a constant temperature and oscillated for about 15 h until the adsorption saturation. The absorbance of the dye was measured before and after adsorption.

To explore adsorption effect of adsorbent on different concentrations of the dye, 200 mL navy-blue dye with concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L respectively was prepared. 0.3 g PVA/GO composite hydrogel (containing 30 % graphene oxide) was added into these samples. The samples were placed in an oscillator with a constant temperature and oscillated for about 15 h until adsorption saturation. The absorbance of the dye was measured by ultraviolet spectrophotometer before and after adsorption.

To explore the influence of temperature on the adsorption process, 0.3 g PVA/GO composite hydrogel (containing 30 % graphene oxide) was added to 200 mL navy-blue dye (initial concentration of 10 mg/L) at different temperatures of 25°C, 35°C, 45°C, 55°C and 65°C, respectively. The samples were

placed in an oscillator with a constant temperature and oscillated for about 15 h until adsorption saturation. The absorbance of the dye was measured before and after adsorption.

To explore the influence of reaction time on adsorption, 0.3 g PVA/GO composite hydrogel (containing 30 % graphene oxide) was added to 200 mL navy-blue dye with the initial concentration of the dye at 10mg/L. The adsorption time was 6 h, 9 h, 12 h, 18 h and 24 h. The absorbance of the dye was measured by ultraviolet spectrophotometer before and after adsorption.

To explore the effect of pH on adsorption, pH of the solutions was adjusted to 1, 3, 5, 7, 9, 11, and 13 by adding HCl or NaOH. 0.3 g PVA/GO composite hydrogel (containing 30 % graphene oxide) was added to 200 mL navy-dye with initial concentration of 10 mg/L at different pH values. The samples were oscillated for about 15 h until adsorption saturation. The absorbance of the dye was measured before and after adsorption.

RESULTS AND DISCUSSION

Infrared Spectroscopy

In Fig.1, curve a is the infrared spectrum of the adsorbent before adsorption. 3420 cm^{-1} is the stretching vibration peak of the hydroxyl group, and such strong peaks also appear at

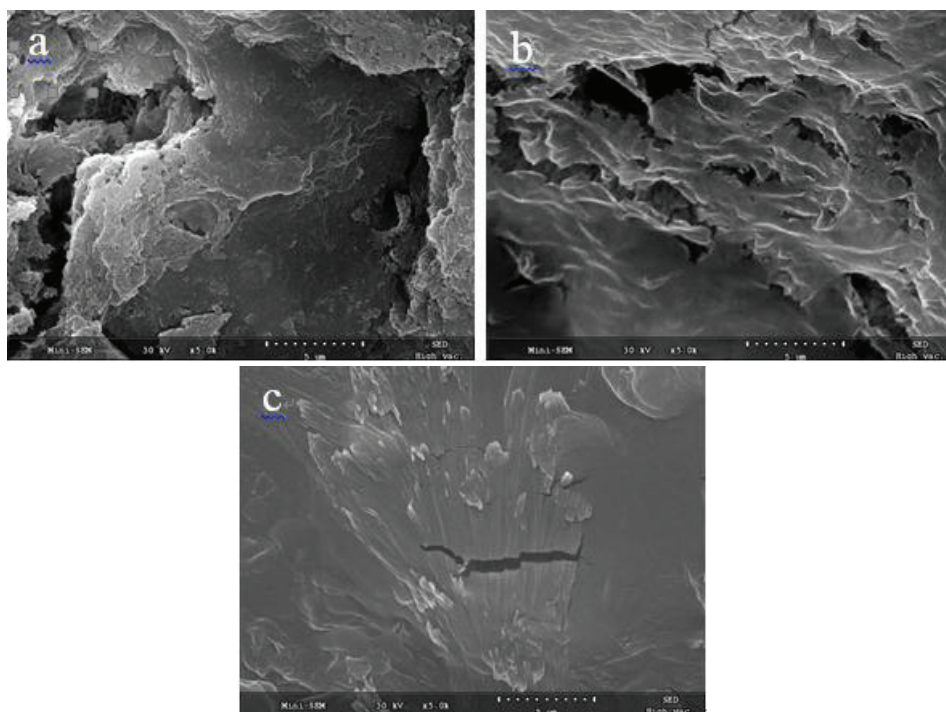


Fig. 3: a. SEM image of PVA hydrogel; b. SEM image of PVA/GO composite before adsorption; c. SEM image of PVA/GO composite after adsorption.

1400 cm^{-1} and 1630 cm^{-1} , which indicated the symmetric and asymmetric stretching vibration peaks of the carbonyl group. This indicated that GO was fixed on the substrate of PVA, the hydroxyl group of PVA, and the carboxyl group of GO were esterified. The two formed a three-dimensional network structure through covalent cross-linking. Curve b is the infrared spectra of the adsorbent after adsorption. It found that strong peak appeared in the front position obviously. The adsorption mechanism depends on hydrogen bonding, electrostatic effect, and molecular inter-atomic forces between the adsorbent and dye molecules. Contrasting with the images, the adsorbent adsorbing on dye made polymer material structure to change, and proved that adsorbent's success for the efficiency of dye adsorption.

Thermo Gravimetric Characterization

Fig. 2 shows the thermo gravimetric characterizations of PVA/GO composite material with 30 % GO before and after the adsorption. Curve b is the thermo gravimetric characterization of the composite after adsorption, and the results show that the weight loss occurs between 100°C to 200°C, and the main reason for this change is the thermal decomposition of functional groups. Compared to curve a, the thermal decomposition temperature increases after adsorption, which proved the successful adsorption of the dye by the adsorbent.

SEM Characterization

Fig. 3a is the SEM image of PVA without GO, and sparse holes are observed on the material surface. Fig. 3b is the SEM image of PVA/GO with a content of 30 % graphene oxide, showing a more regular layered porous structure. This is due

to the covalent cross-linking reaction between PVA and GO, and forming a three-dimensional network structure. At the same time, during the preparation of hydrogel composites, some pores appeared by water evaporation during drying. Fig. 3c is the SEM image of the composite after adsorption. There are no empty holes and the texture is flat. This is because the dye molecules are attached to the composite during the adsorption process and the water grains appeared during the oscillation adsorption.

Langmuir, Freundlich and Temkin Adsorption Isotherm Fitting

The adsorption isotherm can be used to evaluate the adsorption capacity of the adsorbent ($Q_e = V \times (C_0 - C_e) / m$). Fig. 4 shows the adsorption performance of PVA/GO with 30 % GO with the blue dye. It was found that higher the initial concentration, higher the adsorption capacity. Because the dye molecules with high concentration distribution have greater diffusion driving force, they overcome more mass transfer resistance of solid phase and water phase, and more dye molecules combine with adsorbent molecules fully to play a role. Langmuir equation is as below:

$$\frac{C_e}{q_m} = \frac{1}{q_m b} + \frac{C_e}{q_e}$$

Where, q_e is the equilibrium adsorption capacity and q_m is the limit adsorption capacity. C_e is the equilibrium concentration, and b is the adsorption equilibrium constant.

The above adsorption isotherm data were fitted by the Langmuir isotherm equation, and the curve in Fig. 5 was obtained. The curve equation $y = 0.5031x + 0.0062$ ($R^2 = 0.9894$) indicated that the adsorption of navy blue dye by the com-

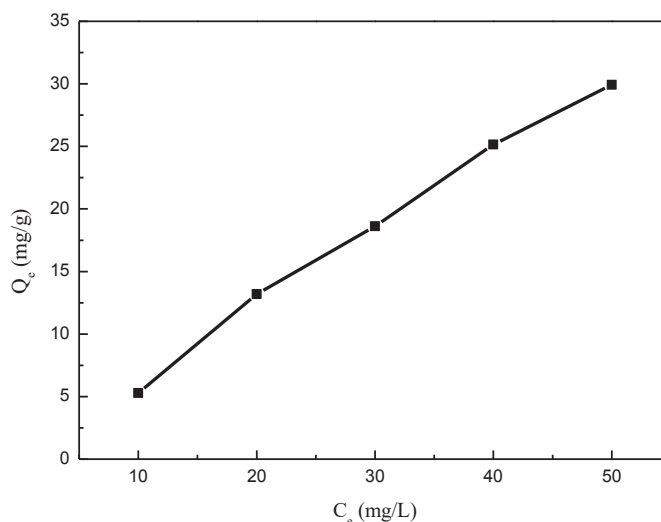


Fig. 4: Adsorption isotherm of PVA/GO composites with a content of 30% GO.

posite material was consistent with the Langmuir isotherm adsorption model, indicating that the composite material had excellent adsorption performance.

In addition, in the Langmuir isothermal model, the dimensionless equilibrium parameter $RL = 1/(1+KL \times C_0)$ was used to obtain the RL values of different initial concentrations of the colourant. When $RL = 0$, the adsorption process is irreversible; when $0 < RL < 1$, the adsorption process is favourable; when $RL = 1$, the adsorption process is linear; when $RL > 1$, the adsorption process is unfavourable. When the RL values ranged from 0.19 to 0.32, the adsorption process was favourable.

Freundlich's isothermal equation is as follows:

$$\log q_e = \log K_F + \log C_e$$

Where, K_F and n are the adsorption empirical constants, C_e is the adsorption equilibrium concentration (mg/L), and q_e is the equilibrium adsorption quantity (mg/g). The curve in Fig. 6 was obtained, and the equation of the curve was $y = 1.0749x - 0.324$, $R^2 = 0.9899$.

The equation of Temkin is as follows:

$$q_e = A + B \log C_e$$

The Temkin equation describes the energy relation of adsorption heat decreasing linearly with adsorption amount, and the curve in Fig. 7 is obtained. The curve equation is $y = 50.266x - 30.21$, $R^2 = 0.8986$, which does not conform to the Temkin isothermal equation.

Based on the above three isothermal adsorption equations, the data in Table 1 are obtained. It can be known that the adsorption of PVA/GO composite on navy dye conforms to Langmuir and Freundlich equations, but not to Temkin equation. In addition, the isothermal adsorption model proves

that PVA/GO composite has a good adsorption effect.

The Effect of PVA/GO Composites with Different GO Content

The (0) bottle in Fig. 8 is the navy blue dye with a concentration of 10 mg/L before adsorption, and the (a) - (e) bottles are 0.3 g dye which were fully adsorbed by PVA/GO composites containing 0, 10 %, 20 %, 30 % and 40 % GO respectively. It was found that the composites containing 30 % and 40 % GO have better adsorption effect. The absorbance of the solution was further measured. The concentration of the solution was calculated according to the standard curve of the dye, and then the adsorption rates were obtained, which were used to draw the graph as shown in Fig. 8. According to the data analysis, the adsorbent containing 30 % graphene oxide can be selected.

The Effect of PVA/GO Composites with Different Dosage

No. 0 bottle in Fig. 9 is navy blue dye with a concentration of 10 mg/L, while Nos. 1-5 bottles are PVA/GO composite hydrogel (containing 30 % graphene oxide) with dosages of 0.1 g, 0.3 g, 0.5 g, 0.7 g and 0.9 g, respectively, and the colour is a result of the full adsorption with the dye. It was observed that more the dosage, better the adsorption effect, but with the increase of the dosage, the adsorption effect did not change much. The absorbance of the solution was further measured, and the solution concentration was calculated according to the standard curve of the dye. According to the data analysis, the selection of 0.3 g adsorbent is fine to adsorb on 200 mL navy blue dye with a concentration of 10 mg/L.

The effect of PVA/GO Composites with Different Dye Concentrations

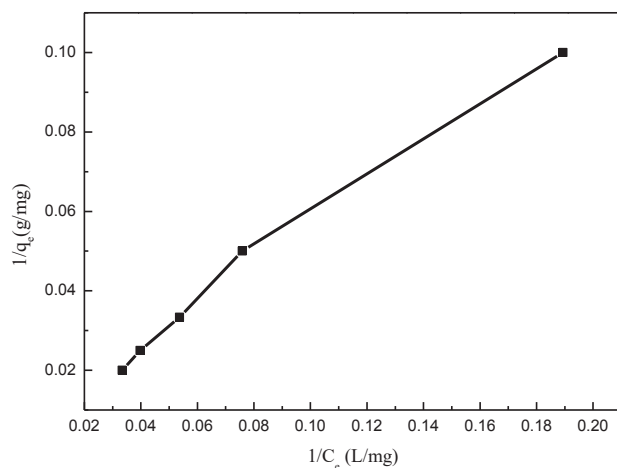


Fig. 5: Adsorption isotherm of Langmuir.

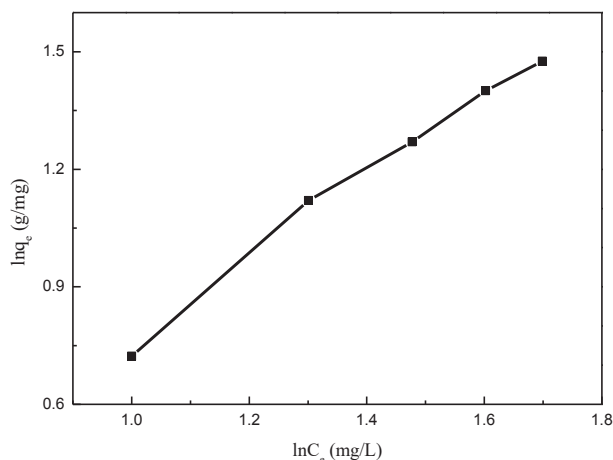


Fig. 6: Adsorption isotherm of Freundlich.

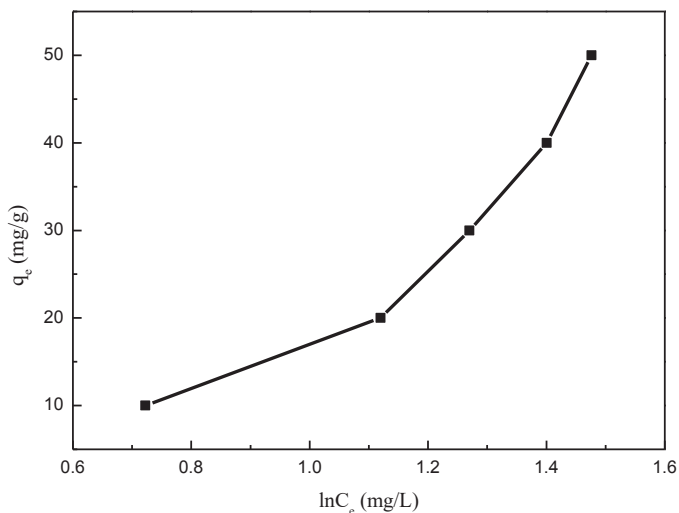


Fig. 7: Adsorption isotherm of Temkin.

Table 1: The Langmuir, Freundlich and Temkin isothermal adsorption model constants and their correlations for the adsorption of colorants by composites.

Isothermal equation of Langmuir			Isothermal equation of Freundlich			Isothermal equation of Temkin		
R^2	Q_m	k	R^2	k	N	R^2	A	B
0.9894	0.5031	0.0062	0.9899	1.0749	0.324	0.8986	50.266	30.21

The above figure in Fig. 10 shows the navy blue dye before adsorption with concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L. The below figure in Fig. 10 is the effect picture which shows the full adsorption of 200 mL navy blue dye and 0.3 g PVA/GO composite hydrogel (containing 30 % graphene oxide). The absorbance of the

solution was further measured. The solution concentration was calculated according to the standard curve of the dye, and then the adsorption rates were obtained. According to the data analysis, 0.3 g adsorbent (containing 30 % graphene oxide) has the best adsorption effect on 200 mL dye with a concentration of 10 mg/L.

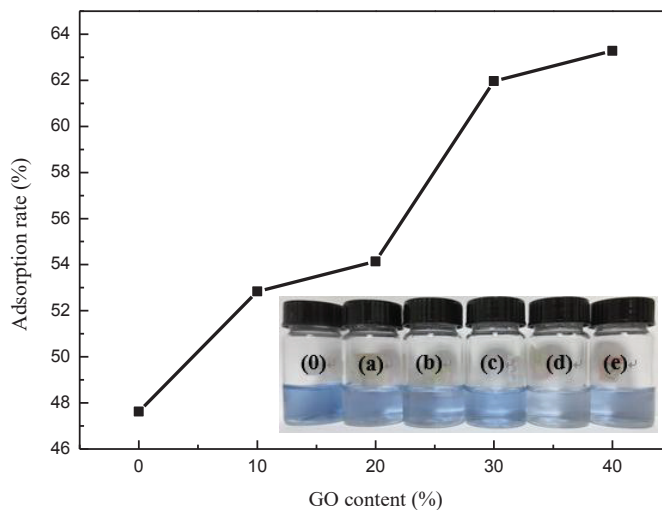


Fig. 8: Adsorption curves of composite materials with different GO contents.

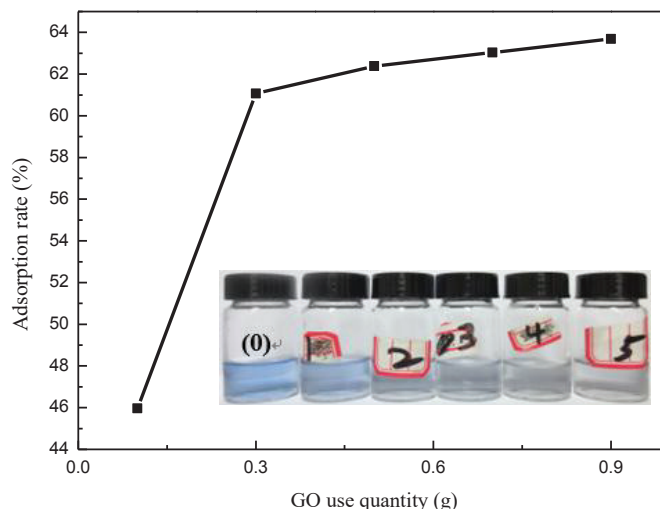


Fig. 9: Adsorption curves of composites with different dosage.

The Adsorption Rates of PVA/GO Composite at Different Temperatures

In Fig. 11, No. 0 bottle is dye with a concentration of 10 g/L before adsorption and Nos. (a)-(e) bottles are adsorbed fully by 0.3 g PVA/GO composite hydrogel (containing 30% graphene oxide) at the temperature of 25°C, 35°C, 45°C and 55°C, 65°C respectively. It was observed that the adsorption effect decreased when the temperature was too high. The absorbance of the solution was further measured. The solution concentration was calculated according to the standard curve of the dye, and then the adsorption rates were obtained, which were used to draw the graph shown in Fig. 11. According to the data analysis, the adsorption effect is

suitable under 25°C.

The Adsorption of PVA/GO Composites at Different Adsorption Time

In Fig. 12, bottle (0) was the dye before adsorption, and bottle (a)-(e) were the navy blue dye, which were prepared by adding 0.3 g (graphene oxide content was 30%) PVA/GO composite hydrogel to 200 mL dye with the initial concentration of 10 mg/L and being adsorbed for 6 h, 9 h, 12 h and 24 h. The absorbance of the solution was further measured. The solution concentration was calculated according to the standard curve of the dye, and then the adsorption rates were calculated, which were used to draw the

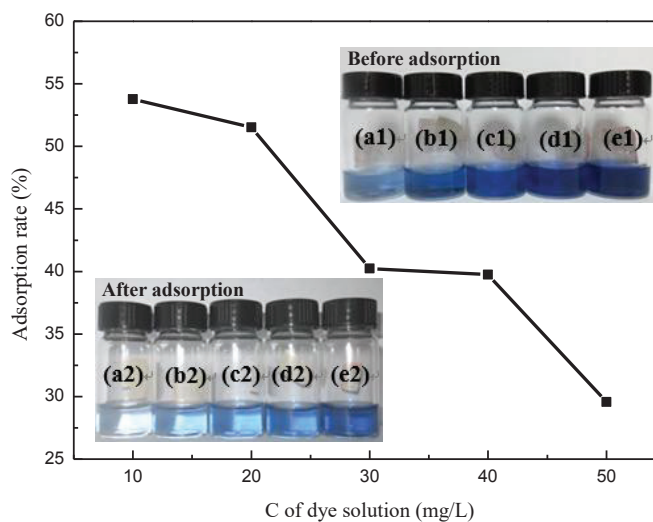


Fig. 10: The adsorption rate of PVA/GO composite for different concentrations of dye.

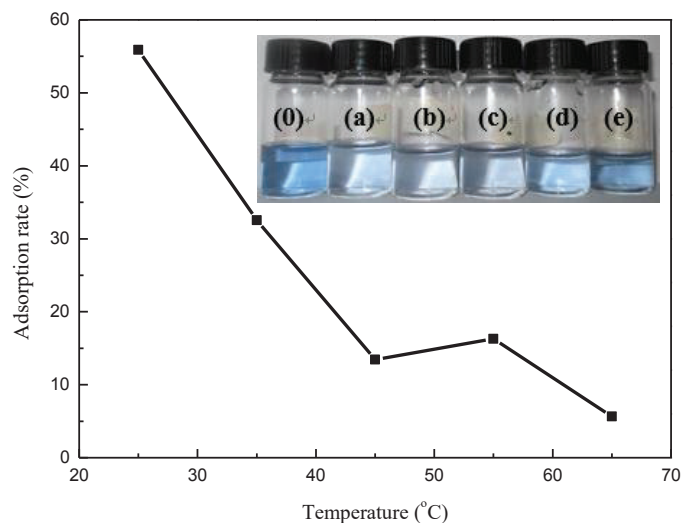


Fig. 11: Adsorption rates of PVA/GO composite at different temperatures.

following graph. According to the data analysis, the longer the adsorption time, the better the effect.

The Adsorption Rates of PVA/GO Composites at Different pH

In Fig. 13, (a1)-(g1) were the solutions before adsorption with pH values of 1, 3, 5, 7, 9, 11 and 13 respectively. In the figure, (a2)-(g2) were the navy blue dye, which was prepared by adding 0.3 g PVA/GO composite hydrogel (containing 30 % graphene oxide) and adsorbing on the 200 mL dye with initial concentration of 10 mg/L at pH values of 1, 3, 5, 7, 9, 11 and 13 respectively. The absorbance of the solution was

further measured. The solution concentration was calculated according to the standard curve of the dye, and then the adsorption rates were obtained. According to the data analysis, the adsorption effect of the adsorbent is the best under acidic conditions, moderate under the neutral environment, and the worst under the alkaline environment.

CONCLUSION

The polyvinyl alcohol/graphene oxide (PVA/GO) hydrogel as adsorbent was prepared, and the adsorption performance was investigated. The results showed that the GO content, dosage, dye concentrations, temperatures, adsorption time,

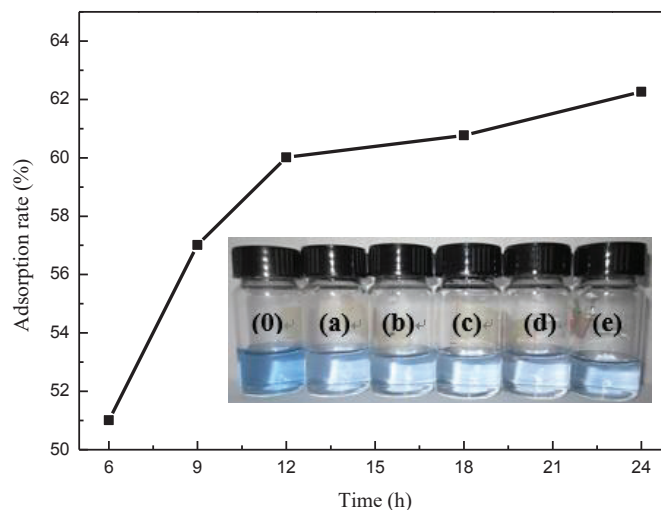


Fig. 12: The adsorption rates of PVA/GO composite for different adsorption time.

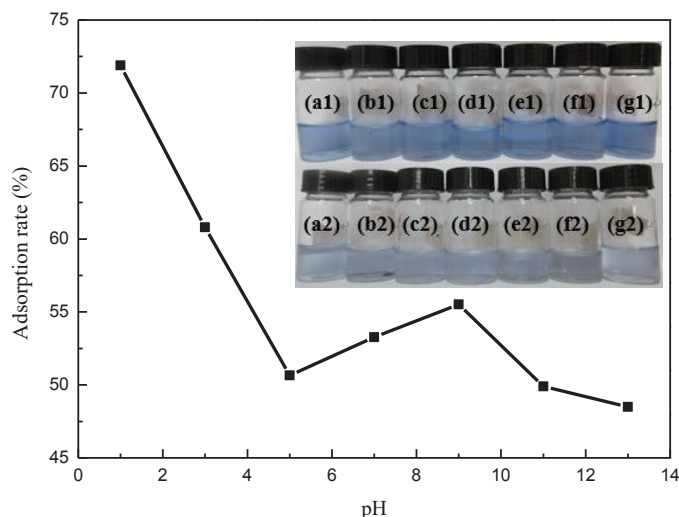


Fig. 13: Adsorption rates of PVA/GO composites in different pH environments.

and pH value have an influence on the removal rate of the dye from wastewater. It was confirmed that PVA/GO adsorbent with a content of 30 % graphene oxide had the best comprehensive performance. The suitable environment of adsorption is at 25°C, 12-18 h for adsorption time and acidic conditions. The suitable adsorbent dosage is 0.3 g and the suitable concentration of the dye is 10 mg/L.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Shaoxing Public Welfare Project (Grant No. 2017B70042), and the International Science and Technology Cooperation Project of Shaoxing University (Grant No. 2019LGGH1004).

REFERENCES

- Adebajo, M.O., Frost, R.L., Klopogge, J.T., Carmody, O. and Kokot, S. 2003. Porous materials for oil spill cleanup: A review of synthesis and absorbing properties. *Journal of Porous Materials*, 10: 159-170.
- Gan, L., Shang, S., Hu, E., Yuen, C.W.M. and Jiang, S.X. 2015. Konjac glucomannan/graphene oxide hydrogel with enhanced dyes adsorption capability for methyl blue and methyl orange. *Applied Surface Science*, 357: 866-872.
- Gore, P.M., Dhanshetty, M. and Balasubramanian, K. 2016. Bionic creation of nano-engineered Janus fabric for selective oil/organic solvent absorption. *Rsc Advances*, 6: 111250-111260.
- Hameed, B., Ahmad, A. and Aziz, N. 2009. Adsorption of reactive dye on palm-oil industry waste: Equilibrium, kinetic and thermodynamic studies. *Desalination*, 247: 551-560.
- Kumar, A.S.K. and Jiang, S.J. 2016. Chitosan-functionalized graphene oxide: A novel adsorbent an efficient adsorption of arsenic from aqueous solution. *Journal of Environmental Chemical Engineering*, 4: 1698-1713.
- Nevárez, L.M., Casarrubias, L.B., Canto, O.S., Celzard, A., Fierro, V., Gómez, R.I. and Sánchez, G.G. 2011. Biopolymers-based nanocomposites: Membranes from propionated lignin and cellulose for water purification. *Carbohydrate Polymers*, 86: 732-741.
- Russo, P. and Hu, A.G. 2013. Compagnini, Synthesis, properties and potential applications of porous graphene: A review. *Nano-micro Letters*, 5: 260-273.
- Satti, A., Larpent, P. and Gun'ko, Y. 2010. Improvement of mechanical properties of graphene oxide/poly (allylamine) composites by chemical crosslinking. *Carbon*, 48: 3376-3381.
- Sehaqui, H., de Larraya, U.P., Tingaut, P. and Zimmermann, T. 2015. Humic acid adsorption onto cationic cellulose nanofibers for bioinspired removal of copper(II) and a positively charged dye. *Soft Matter*, 11: 5294-5300.
- Shen, Y. and Chen, B. 2015. Sulfonated graphene nanosheets as a superb adsorbent for various environmental pollutants in water. *Environmental Science & Technology*, 49: 7364-7372.
- Tiwari, J.N., Mahesh, K., Le, N.H., Kemp, K.C., Timilsina, R., Tiwari, R.N. and Kim, K.S. 2013. Reduced graphene oxide-based hydrogels for the efficient capture of dye pollutants from aqueous solutions. *Carbon*, 56: 173-182.
- Wahab, A.H.A., Saad, A.P.M., Harun, M.N., Syahrom, A., Ramlee, M.H., Sulong, M.A. and Kadir, M.R.A. 2019. Developing functionally graded PVA hydrogel using simple freeze-thaw method for artificial glenoid labrum. *Journal of the Mechanical Behavior of Biomedical Materials*, 91: 406-415.