ISSN 1027-5495. Functional Materials, 26, No.2 (2019), p. 262-266.
doi:https://doi.org/10.15407/fm26.02.262

Analysis of adsorption properties of magnetic composites: preparation of multi-walled carbon nanotubes

Chengwen Zhang

School of Electrical Engineering, Tongling University, Tongling, Anhui 244000, China

Received May 5, 2019

Magnetic carbon nanotube composites have great adsorption performance and have been applied in many fields including sewage treatment and separation. In this study, the Multi-walled Carbon Nanotubes (MWCNTs) were taken as an example to analyze its absorption performance, and the magnetic MWCNTs composite was obtained by the preparation of Fe_3O_4 and SiO_2 and combination with MWCNTs. The adsorption experiment of the magnetic MWCNTs composite was performed with Congo red (CR). The results showed that magnetic MWCNTs had great adsorption properties to CR, and its adsorption effects increased with the increase of the concentration and temperature of solution and was better under low pH value. The experimental results shows that the magnetic MWCNTs has good adsorption properties, which provides some theoretical support for its further application in sewage treatment.

Keywords: magnetic material, multi-walled carbon nanotube, adsorption performance, composite

Проанализированы адсорбционные свойства магнитных многостенных углеродных нанотрубок (MWCNT). Магнитный композит MWCNTs получен путем использования Fe_3O_4 и SiO_2 в комбинации с MWCNT. Эксперимент по адсорбции магнитного композита с многостенными углеродными нанотрубками проведен с конго красным (CR). Результаты показали, что магнитные MWCNT обладают хорошими адсорбционными свойствами по отношению к CR и их адсорбционный эффект увеличивался с увеличением концентрации и температуры раствора. Результаты эксперимента показывают, что магнитные MWCNTs имеют хорошие адсорбционные свойства, что обеспечивает его дальнейшее применение для очистки сточных вод.

Аналіз адсорбційних властивостей магнітних композитів: підготовка багатостінних вуглецевих нанотрубок. *Chengwen Zhang*

Проаналізовано адсорбційні властивості магнітних багатостіних углеродних нанотрубок (MWCNT). Магнітний композит MWCNT отримано за допомогою Fe_3O_4 і SiO_2 у комбінації з MWCNT. Експеримент по адсорбції магнітного складу з багатокомпонентними нанотрубками перевірено конго червоним (CR). Результати показали, що магнітні MWCNT володіють хорошими адсорбційними властивостями у відношенні до CR і їх адсорбційний ефект збільшується зі збільшенням концентрації і температури розчину. Результати експерименту показують, що магнітні MWCNT мають хороші адсорбційні властивості, що забезпечує його подальше застосування для очищення сточних вод.

1. Introduction

Carbon nanotubes (CNTs) are high-quality nanomaterials that have received extensive attention from researchers in the fields of industry, biology and materials [1]. They can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) carbon nanotubes according to the number of layers. The diameter of CNTs is small, the wall of each layer is controlled by Van der Waals' force, and their electroconductivity and thermal conductivity are better [2]. It also has good adsorption performance [3], optical performance, field emission performance [4], etc. However, it also has some defects. Due to its own structure, CNTs has poor magnetism and super-hydrophobicity. The original synthesized CNTs are easy to agglomerate and difficult to be uniformly dissolved in water and other solvents. Therefore, a certain method is needed to modify its properties. Due to the good adsorption capacity of CNTs, its application as an adsorbent in sewage treatment has received extensive attention [5]. Inyang et al. [6] modified the properties by Sodium Dodecyl Benzene Sulphonate (SDBS)-assisted and dip-coated pecan or bagasse biomass in CNTs and found that SDBS could promote the distribution of CNTs on the surface of charcoal and had strong adsorption capacity of pollutants to be used as a sustainable alternative to sewage treatment. Wang et al. [7] combined graphene, MWCNTs and Fe_3O_4 to form a composite material. The adsorption properties of the material were analyzed by dye methylene blue. The maximum adsorption capacity of the material was 65.79 mg/g, and the cost of the material was relatively low to be recyclable. Thus, it was an excellent adsorbent. Yang et al. [8] synthesized CNTs and Mg(Al)O nanoparticles into a composite material. The adsorption experiment was carried out by taking Congo red as an example. It was found that the initial PH value of the solution and the amount of adsorbent had a certain impact on the adsorption of the material. The maximum adsorption capacity of the material reached 1250 mg/g, which proved the application prospect of the material in sewage treatment. Ansari et al. [9] prepared CNTS and graphene oxide composites for the removal of two pollutants, Cr (IV) and Congo red (CR). The adsorption properties were found to be related to solution PH, contact time and temperature. It provided a new way for CNTs composites to adsorb various pollutants in aqueous solution. In this study, multi-walled carbon nanotubes (MWCNTs) were as an example, and $Fe_3O_4@SiO_2$ were prepared with magnetic material Fe_3O_4. Then, the $Fe_3O_4@ SiO_2$ was combined with MWCNTs to form magnetic MWCNTs composites. The adsorption performance of the material was confirmed by adsorption experiments on Congo red. It is conducive to its promotion and application in the fields of industry, etc., and also contributes to the modification of MWCNTs by magnetic materials.

2. Methods and materials

Magnetic material refers to a material that can generate a continuous magnetic field by itself. It has different properties such as paramagnetic and diamagnetic properties. Combined with CNTs, it can significantly improve material properties, and the method for preparing magnetic CNTs composite is relatively simple. Fe_3O_4 is a kind of magnetic material, which is low in cost and can be prepared by coprecipitation method [10] and solvothermal method [11]. It can improve the hydrophilicity of CNTs, enhance solubility and facilitate the formation of high quality composite materials. SiO_2 has high hardness and hydrophilicity, which is beneficial to reduce the Van der Waals' force of CNTs, making it easier to mix with solvents. Thus, it is an excellent additive. Therefore, MWCNTs was used as an example, and its properties were modified with Fe_3O_4 and SiO_2 in this study.

2.1. Experimental materials and equipment

Experimental materials included $FeCl_3{\cdot}6H_2O$ (Sinopharm Group, China; analytical reagent), $Na_3C_6H_5O_7{\cdot}H_2O$ (Beijing Chemical Works, China; analytical reagent), ethylene glycol (Beijing Chemical Works, China; analytical reagent), ethanol alcohol (Yongda Reagent, China; analytical reagent), sodium acetate (Tianjin Regent, China; analytical reagent), ammonia hydroxide (Liaoning Quanrui, China; analytical reagent), TEOS (Beijing Chemical Works, China; TEOS: Beijing Chemical Works, analytical reagent), MWCNTs (Beijing Boyu Hi-Tech Material Technology Effective Company, Chian; 95% reagent) and Congo red (Tianjin North Glass Shopping Center, China; analytical reagent).

Experimental equipment included KQ-100B ultrasonic cleaner (Kunshan Ultrasonic Instrument, China), KH-100 teflon reactor (Beijing Xingda Hengxin, China), EP115 air drying oven (Pentax, Germany), DZF-6051vacuum drying oven (Shanghai Yiheng, China), JJ-1 power basic stirrer (Jintan Jiangnan Instrument Factory, China) and JA2003 electronic analysis balance (Shanghai Shunyu Hengping, China).

2.2. Preparation of $Fe_3O_4@SiO_2$

1.95 g of $FeCl_3{\cdot}6H_2O$ and 0.57g of $Na_3C_6H_5O_7{\cdot}2H_2O$ were dissolved in 4 ml of ethylene glycol under ultrasound to prepare a transparent solution.

6.6 g of sodium acetate was dissolved in 40 ml of ethylene glycol to prepare a transparent solution.

The above two solutions were mixed, stirred for 30 min, and placed in a 100 ml teflon-lined reactor.

The solution was heated in a reaction kettle at 200 °C for 10 h.

After the solution was naturally cooled to room temperature, Fe_3O_4 particles were obtained by magnetic precipitation cleaning.

480 ml of ethanol was mixed with 96 ml of distilled water was prepared.

The nano-Fe_3O_4 particles were added to the mixed liquid and stirred.

6 ml of aqueous ammonia and 0.72 ml of TEOS were added, and the mixture was stirred at room temperature for 8 hours.

After magnetic cleaning, Fe_3O_4@SiO_2 was obtained.

2.3 Preparation of magnetic MWCNTs

MWCNTs were prone to generate impurities such as amorphous carbon in the preparation process, which could affect the performance analysis of CNTs. Therefore, it was necessary to purify the composites before preparation and then purified MWCNTs was used. The steps are as follows: 3 g of MWCNTs was placed in a 250 ml flask, and 100 ml of 65% to 68% nitric acid was added.

The solution was stirred in a stirrer, then heated to 110 °C, refluxed for 4 h and cooled to room temperature to remove.

The solution was repeatedly filtered with deionized water until it was washed to neutral.

The obtained black solid was placed in an evaporating dish and dried in a dry box at 60 °C for 8 hours to obtain purified MWCNTs.

0.004 g of Fe_3O_4@SiO_2 and 0.016 g of MWCNTs were weighed and added to deionized water.

The two materials were mixed uniformly for 30 min to obtain a black liquid, which was magnetic MWCNTs composite.

2.4 Adsorption experiment of magnetic MWCNTs

CR is a widely used organic dye. The dye waste water containing CR produced by textiles, rubber, plastics and other industries brings very serious environmental pollution problems. In this study, the prepared magnetic MWCNTs was used for the adsorption of CR in dye waste water, and the effects of initial dye concentration and temperature on the adsorption performance of waste water were researched.

0.02 g of magnetic MWCNTs was added to the 100 ml of configured CR solution, and the mixture was evenly stirred to ensure that the device could fully function. The adsorption performance of the material was expressed by the amount of adsorption. The calculation equation of the amount of adsorption is:

$$X = \frac{V(C_0 - C_t)}{m},$$

where V is the volume of the CR solution, C_0 is the initial concentration of the solution, C_t is the instantaneous concentration at the time t, and m is the mass of the magnetic MWCNTs.

3. Experimental results

3.1. The absorption characterization of magnetic MWCNTs

The Scanning electron micrographs of MWCNTs and magnetic MWCNTs are shown in Fig. 1. A represents MWCNTs, and B represents magnetic MWCNTs. Many long and thin tubular MWCNTs were observed in Fig. 1A. After the preparation of magnetic materials, iron oxide particles adhered to the surface of MWCNTs, forming magnetic MWCNTs.

3.2. Effect of initial concentration on adsorption properties of magnetic MWCNTs

The adsorption experiments were carried out with CR solutions, the concentrations of which were respectively 40 mg/l, 60 mg/l and 80 mg/l, and the adsorption properties of the magnetic MWCNTs are shown in Table 1.

It could be found from Table 1 that the higher the concentration of the solution was, the better the adsorption performance of the magnetic MWCNTs was. When the concentration of the solution was 40 mg/l, the adsorption amount increased from 56.7 mg/g to 75.6 mg/g. When the solution concentration was 80 mg/l, the adsorption amount increased from 63.8 mg/g to 92.8 mg/g, which was significantly higher than the amount of adsorption at the concentration of 40 mg/l. It indicated that the higher the initial concentration of the solution was, the better the adsorption performance was. It might be because the increase of the concentration of the solution caused the driving force to rise and overcame the resistance between CR and the material, thereby achieving a higher adsorption effect.

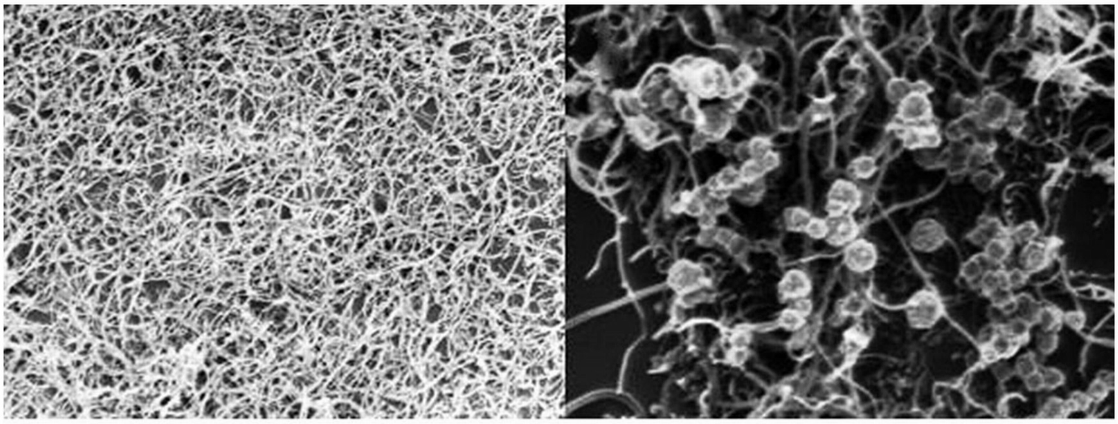

Fig. 1. The scanning electron micrograph

3.3. Effect of temperature on adsorption properties of magnetic MWCNTs

The adsorption experiments were carried out in an environment of 20 °C, 40 °C and 60 °C, and the adsorption properties of the magnetic MWCNTs are shown in Table 2.

It could be found from Table 2 that in the environment of 20 °C, the adsorption amount of CR by magnetic MWCNTs increased from 62.7 mg/g to 85.1 mg/g. In the environment of 60 °C, the adsorption amount after 20 min of experimentation has exceeded the adsorption amount after 2 h at 20 °C. After 2 h, the adsorption amount reached 94.5 mg/g. It indicated that the adsorption effect of magnetic MWCNTs increased with increasing temperature.

3.4. Effects of PH value on the absorption properties of magnetic MWCNTs

Solutions with PH values of 5, 6, 7, 8 and 9 were taken for absorption experiment. The absorption properties of magnetic MWCNTs is shown in Fig. 2.

It can be seen from Figure 2 that the absorption properties of magnetic MWCNTs decreased with the increase of PH value, and the absorption amount was 119.7 mg/g when the PH value was 5 and 80.7 mg/g when the PH value was 9. It indicated that magnetic MWCNTs had better absorption properties under environment with low PH value.

4. Discussion

CNTs, also known as bucky tubes, are composed of single-layer or multi-layer graphene. They have excellent properties and can be prepared by arc discharge, laser casting, etc. But they are difficult to dissolve in water and other solvents due to limitations of high molecular weight, Van der Waals' force, etc. Thus, they are difficult to handle. Therefore, they need to be modified to improve performance. The dispersion of CNTs can be achieved by adding solvents or dispersants, chemical oxidation, etc., helping CNTs to be better promoted and applied in various industries. Wrapped metal oxide is a good CNTs modification method [12], which can increase the function of CNTs without destroying the original structure of CNTs, reduce its dispersibility in solution and improve adsorption.

CNTs composites with Fe_3O_4 have good superparamagnet [13] and good separation [14], and SiO_2 has high hydrophilicity, high viscosity and hardness and is a good additives in the preparation of materials. Thus, $Fe_3O_4@SiO_2$ was used to modify the properties of CNTs in this study. Firstly, magnetic Fe_3O_4 nanoparticles were prepared, then $Fe_3O_4@SiO_2$ particles were prepared and uniformly mixed with MWCNTs to obtain magnetic MWCNTs composites. In order to analyze its adsorption performance, organic dye CR was taken as an example, and magnetic MWCNTs were used as adsorp-

Table 1. Effect of initial concentration on adsorption properties

Concentration	20 min	40 min	60 min	80 min	100 min	120 min
40 mg/l	56.7 mg/g	62.7 mg/g	63.4 mg/g	67.8 mg/g	72.3 mg/g	75.6 mg/g
60 mg/l	62.7 mg/g	65.6 mg/g	83.2 mg/g	84.6 mg/g	85.1 mg/g	87.8 mg/g
80 mg/l	63.8 mg/g	67.2 mg/g	85.6 mg/g	87.4 mg/g	89.7 mg/g	92.8 mg/g

Table 2. Effect of temperature on adsorption properties

Temperature	20 min	40 min	60 min	80 min	100 min	120 min
20 °C	62.7 mg/g	65.4 mg/g	79.2 mg/g	81.3 mg/g	83.9 mg/g	85.1 mg/g
40°C	78.2 mg/g	79.6 mg/g	83.4 mg/g	86.7 mg/g	87.9 mg/g	88.6 mg/g
60°C	87.6 mg/g	89.7 mg/g	91.2 mg/g	92.3 mg/g	93.4 mg/g	94.5 mg/g

tion materials to study the effects of initial dye concentration, temperature and PH value on the adsorption properties of the materials.

From the view of results, magnetic MWCNTs had a good adsorption effect on CR. First, from the perspective of initial concentration, under the three different concentrations of experiments, when the concentration was relatively low, at 40 mg/l, the adsorption capacity of magnetic MWCNTs reached 75.6 mg/g after two hours of experiment. When the concentration was higher at 80 mg/l, the adsorption amount reached 92.8 mg/g after two hours, and the adsorption effect was significantly better. As the concentration of the solution increased, the driving force was improved, and the resistance between the dye and the adsorbent was reduced. Therefore, the magnetic MWCNTs could sufficiently achieve the adsorption of CR. From the view of temperature, the adsorption effect of magnetic MWCNTs was better at high temperature. At 60 °C, the adsorption amount at the 20th minute of the experiment reached 87.6 mg/g, which exceeded the adsorption amount at the 2nd h at 40 °C. Under an environment with low PH value, magnetic MWCNTs had better absorption properties.

5. Conclusions

In this study, the properties of MWCNTs were modified by magnetic material $Fe_3O_4@SiO_2$ to obtain magnetic MWCNTs composites. Then the adsorption performance of the material was analyzed by taking the adsorption of CR as an example. The good adsorption performance of the material was proved by adsorption experiments. The adsorption effect was better under the conditions of high temperature and concentration, which is beneficial to the further development of CNTs materials and provides some experience for the practice of magnetic MWCNTs in the field of sewage treatment.

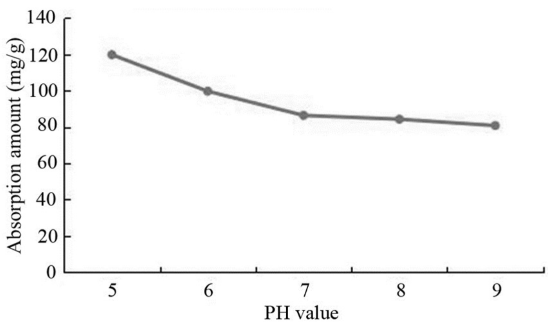

Fig. 2. Effect of PH value on the absorption properties of magnetic MWCNTs

References

1. M. A. Azam, F. M. Alias, L. W. Tack, et al., *J. Mol. Graph. Model.*, **75**, 85 (2017).
2. L. Sun, W. Kong, M. Li, et al., *Nanotechnology*, **27**, 075401 (2016).
3. W. Wang, C. Jiang, L. Zhu, et al., Int. *J. Mol. Sci.*, **15**, 15981 (2014).
4. Y. D. Lim, D. Grapov, L. Hu, et al., *Nanotechnology*, **29**, 075205 (2017).
5. Y. Xie, C. He, L. Liu, et al., *RSC Adv.*, **5**, 82503 (2015).
6. M. Inyang, B. Gao, A. Zimmerman, et al., *Environ. Sci. Pollut. Res.*, **22**, 1868 (2015).
7. P. Wang, M. Cao, C. Wang, et al., *Appl. Surf. Sci.*, **290**, 116 (2014).
8. S. Yang, L. Wang, X. Zhang, et al., C*hem. Eng. J.*, **275**, 315 (2015).
9. M. O. Ansari, R. Kumar, S. A. Ansari, et al., *J. Colloid Interf. Sci.*, **496**, 407 (2017).
10. H. Chen, Z. Chen, G. Zhao, et al., J. Hazard. *Mater.*, **347**, 67 (2017).
11. Y. Yang, L. Ge, V. Rudolph, Z. Zhu, *Dalton Trans*, **43**, 7028 (2014).
12. K. Nemeth, K. Nemeth, L. Kovacs, et al., *J. Nanosci. Nanotechno.*, **17**, 5445 (2017).
13. S. S. Bayazit, Desalin. *Water Treat.*, **52**, 6966 (2014).
14. D. L. Xiao, H. Li, H. He, et al., *Carbon*, **71**, 343 (2014).