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Preparation of a new graphite oxide/chitosan composite membrane and its application in environmental protection engineering

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Novel magnetic graphene oxide-chitosan composite membranes (GO-Fe_3O_4-CS) have been prepared by solvothermal method. The properties of GO-Fe_3O_4-CS are studied by measuring its spectral characterization, hysteresis loop and dye adsorption performance. The results show that the morphology of the synthesized magnetic graphene oxide is about 100nm, and the Fe_3O_4 nanospheres grow uniformly on the graphene oxide surface. The hysteresis loop shows that GO-Fe_3O_4 has strong magnetism. GO-Fe_3O_4-CS complex has good adsorption effect on dye molecules such as methyl violet and methylene blue. In addition, the introduction of magnetism can simplify the process of recovering adsorbents and greatly reduce energy consumption. The magnetic graphene oxide/chitosan composite prepared is expected to be used in water treatment in real life.
Keywords: graphene oxide, chitosan, preparation of composite membranes

Сольватермическим методом получены новые магнитные композитные мембраны из оксида графена и хитозана (GO-Fe_3O_4-CS). Изучены их магнитные, спектральные свойства и характеристики адсорбции красителя. Результаты показывают, что морфология синтезированного магнитного оксида графена составляет около 100 нм, а наносферы Fe_3O_4 равномерно растут на поверхности оксида графена. Петля гистерезиса показывает, что GO-Fe_3O_4 обладает сильным магнетизмом. Комплекс GO-Fe_3O_4-CS обладает хорошим адсорбционным действием молекулы красителя, таких как метиловый фиолетовый и метиленовый синий. Кроме того, введение магнитных частиц может упростить процесс восстановления адсорбентов и значительно снизить энергопотребление. Предполагается, что полученный магнитный оксид оксида графена / хитозана будет использоваться для очистки воды.

Дослідженні нової композиційної мембрани з оксидною графікою та хітозану та її застосування в техніці захисту навколишнього середовища. *C. Li, Muhammad Aqeel Ashraf*

Сольватерміческім методом отримані нові магнітні композитні мембрани з оксиду графену і хітозану (GO-Fe_3O_4-CS). Вивчено їх магнітні, спектральні властивості та характеристики адсорбції барвника. Результати показують, що морфологія синтезованого магнітного оксиду графену становить близько 100 нм, а наносфери Fe_3O_4 поступово збільшуються на поверхні оксиду графену. Петля гістерезису показує, що GO-Fe_3O_4 володіє сильним магнетизмом. Комплекс GO-Fe_3O_4-CS володіє хорошим адсорбційним дією молекули барвника, таких як метиловий фіолетовий і метиленовий синій. Крім того, введення магнітних частинок може спростити процес відновлення адсорбентів і значно знизити енергоспоживання. Передбачається, що отриманий магнітний оксид оксиду графену / хітозану буде використовуватися для очищення води.

1. Introduction

Graphene and graphene oxide (GO) have unique two-dimensional nanostructures and excellent properties. Graphene-based materials have important applications in supercapacitors, energy absorption and storage, molecular sensing, catalysis, photothermal treatment, and environmental protection. Graphene oxide is the most convenient, fast and economical precursor for mass production of graphene-based materials. Chitosan (CS) is obtained by partial deacetylation of chitin, the second largest natural macromolecule. It has excellent biocompatibility, antimicrobial activity and biodegradability. Chitosan chain contains a large number of hydroxyl and amino groups, which can be combined with heavy metal ions, so as to achieve the purpose of adsorbing heavy metal ions. Its solubility in acidic aqueous solution shows positive electricity, and it can adsorb anionic dyes by electrostatic action. Magnetic materials can be controlled remotely and used for non-invasive monitoring. They are widely used in biomedicine, magnetic fluids, magnetic resonance imaging and environmental protection. The graphene oxide-chitosan complex is designed and prepared by using the advantages of chitosan and graphene-based materials and introducing magnetic nanoparticles. It is hoped that it will be of practical value in environmental protection.

Zhang and Shahbazi [1,2] have found that chitosan has excellent biocompatibility and good biodegradability. Especially in the field of wastewater treatment, a large number of amino groups in the molecular chain of chitosan make it have a large number of positive charges in dilute acid solution. It is a typical cationic flocculant, and the flocculation of chitosan has no toxic side effects and no secondary pollution [1,2]. In 2016, Rusu [3] found that chitosan can selectively adsorb metal ions in the absorption of heavy metal ions. Under acidic conditions, chitosan can form complex with metal ions to achieve the adsorption effect. In 2016, Salehi also found that chitosan had good adsorption for iodine and bromine after grafting with styrene [4]. These excellent properties of chitosan cannot be achieved by other adsorbents such as activated carbon. In 2016, Abou and Wang believed that it also had good film-forming properties, all of which made it a widely used and practical biomaterial [5,6]. Unfortunately, the mechanical and thermal properties of pure chitosan still have great defects, which cannot meet people's expectations, and also limit the use of this excellent material in all directions. Effective improvement of chitosan has become a major research direction.

In 2017, when Mokhtar e.a. [7] studied GO, it was found that because of its unique nature and potential value, it attracted wide attention. GO has many hydrophilic oxygen-containing functional groups. Under appropriate conditions, GO can be completely stripped in water to obtain a stable suspension. At this time, almost all GO exists as a single layer flake. In this state, the lamellae can be functionalized, dispersed into polymers, or deoxidized to form new complexes. In 2018, Zhao found that functionalized GO has good application prospects in molecular sensing, catalysis, photothermal therapy, energy storage, and environmental protection [8]. The research of Teng [9] shows that graphene oxide is the precursor of chemical synthesis of graphene. There are many oxygen-containing functional groups in the lamellae, such as hydroxyl, carboxyl, epoxy and so on. It is a good active reinforcement material. Wu [10] believed that these groups can improve the interface interaction between graphene oxide and matrix materials, and improve the mechanical properties of nanocomposites.

Ferrous chloride hexahydrate and graphene oxide are synthesized by solvothermal method, then mixed with chitosan and lyophilized to obtain complex for dye adsorption. The magnetic graphene oxide and its chitosan complexes are characterized. The adsorbability of the complexes to methyl violet, methylene blue, rhodamine B and Congo red is studied.

2. Experimental

2.1 Materials and methodsLaboratory drugs and methods

Chitosan (CS) was purchased from Aladdin Reagent Company. Its degree of deacetylation is more than 90%, its viscosity is less than 200 mPa-s, and its molecular weight is 20.25 million. Graphite powder (purity> 99%, analytical purity) was obtained from Brilliant Chemical Reagent Company. Ethylene glycol, diethylene glycol, oncentrated sulfuric acid, sodium nitrate, potassium permanganate, hydrogen peroxide, hydrochloric acid, and other products were analytically pure. Methyl Violet and Methyl Orange dyes, Rhodamine B and Methylene Blue were additionally refined when used. Ultrapure water for solution preparation and dialysis in this experiment was manufactured by an ultrapure water meter UPH-IV (China) with specific resistance of 18.25 mK p cm. HC1 was diluted at 40°C to remove metal ions. Then the GO powder is washed and filtered repeatedly to near neutrality. Finally, vacuum drying is carried out at 40°C for 24 hours. The GO synthesized is peeled off by ultrasound at room temperature and dialyzed in 0.025% ammonia water for 48 hours to prevent agglomeration and freeze-drying.

2.2 Synthesis of magnetic graphlte oxide

Magnetic graphene oxide ($GO\text{-}Fe_3O_4$) is synthesized by solvothermal method. Specific steps are as follows: 60mg of freeze-dried GO is weighed and dissolved in a mixture of 7.5ml ethylene glycol and 22.5ml diethylene glycol to make it completely dissolved by ultrasound. In turn, 0.81g $FeCl_3$-$6H_20$, 0.75g sodium acrylate and 2.25g sodium acetate are added, and stirred overnight to make it completely dissolved. Finally, a brown solution is obtained. The mixture is put into a PTFE reactor and reacted for 12 hours at 200°C. Then, it is cooled to room temperature, washed three times with ethanol and water, separated magnet, removed supernatant, and dried at 50°C for 24 hours.

2.3 Preparation of $GO\text{-}Fe_3O_4\text{-}CS$ complex

4g CS is weighed, and 156g water and 2ml acetic acid are added in turn and stirred to dissolve completely to obtain 2.5wt% CS solution. The dried $GO\text{-}Fe_3O_4$ solid is ground in a mortar. The 0.01g $GO\text{-}Fe_3O_4$ sample is dispersed in 1ml water by ultrasonic wave for 30 minutes. The $GO\text{-}Fe_3O_4\text{-}CS$ complex is obtained by adding 1g 2.5wt% CS solution, scrolling, ultrasonic for 30 minutes, adding 0.1MNaOH solution to adjust the ph to 7, freezing-drying after fixing with liquid nitrogen.

2.4 Adsorption testing of $GO\text{-}Fe_3O_4\text{-}CS$ complex

The $GO\text{-}Fe_3O_4\text{-}CS$ composite is crushed into powder to increase its specific surface area. Then it is added into methyl violet, methylene blue, rhodamine B, Congo red, chrome azure S, acid chrome blue K and methyl orange solutions of 5ml 0.01mgml in turn, and shaken on a shaking bed for 12 hours. After adsorption, the adsorbent is separated and removed by a magnet. The crushed $GO\text{-}Fe_3O_4\text{-}CS$ complex is added to 10ml 0.005mg/ml Rhodamine B solution and shaken on a shaking table. After separating the complex with magnet at a certain interval, the supernatant is absorbed for the determination of UV-vis spectra. After each determination, the solution is put back into the original bottle.

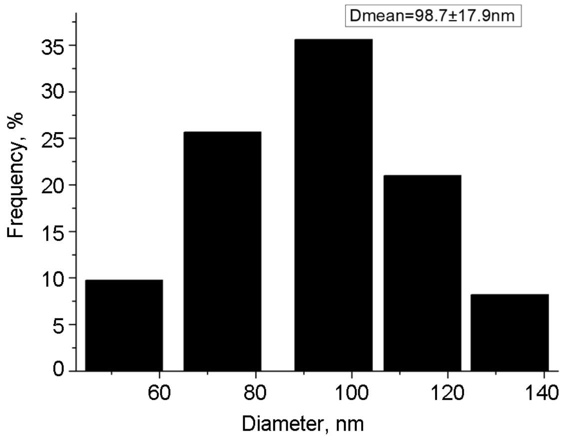

Fig. 1. Particle size distribution of Fe_3O_4.

2.5 Spectroscopic characterization

The infrared spectrum is determined by PerkinElmer Spectrum Two infrared spectrometer, and the scanning range is 4000-400cm^{-1}. Ultraviolet spectroscopy is determined by U-4100 spectrophotometer. All samples are measured with pure water as reference. Raman spectra are measured on Lab-RAMHR800. The excitation wavelength is 473nm and the scanning range is 1000-3000 cm^{-1}. XRD test is carried out on D/MAX-2200PC diffractometer with copper target, incident wavelength of 0.154nm, film testing range of 8-80°C, graphite powder and graphene oxide testing range of 5-40°C.

2.6 Hysteresis loop

Dry $GO\text{-}Fe_3O_4$ samples and freeze-dried $GO\text{-}Fe_3O_4\text{-}CS$ samples are placed in sealed polypropylene test tubes and packaged into plastic pipettes. The samples are detected in magnetometers equipped with MPMSXL (Quantum Design, USA) and RSO (Sample Reciprocating Oscillation Device). Samples are measured at room temperature and data are collected.

3. Results and discussion

3.1 Synthesis and characterization of $GO\text{-}Fe_3O_4$

The GO synthesized in aqueous solution can be well dispersed, smooth and has a certain folded two-dimensional structure. Fe_3O_4 nanoparticles almost grow on GO sheets without obvious agglomeration. Fe_3O_4 nanoparticles are formed by aggregation of smaller particles. Moreover, the par-

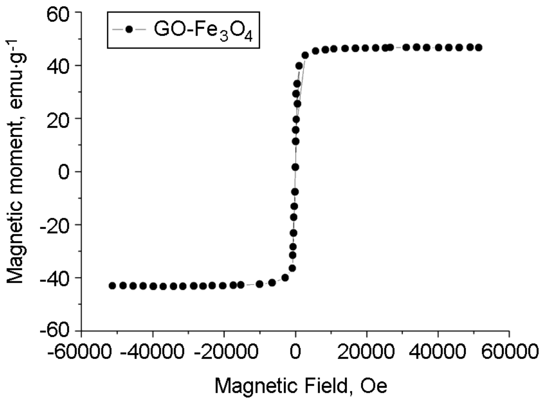

Fig. 2. Magnetization curve of $GO\text{-}Fe_3O_4$.

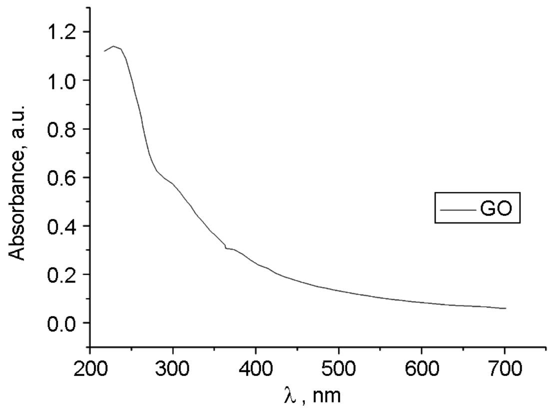

Fig. 3. UV-vis spectra of GO aqueous solution.

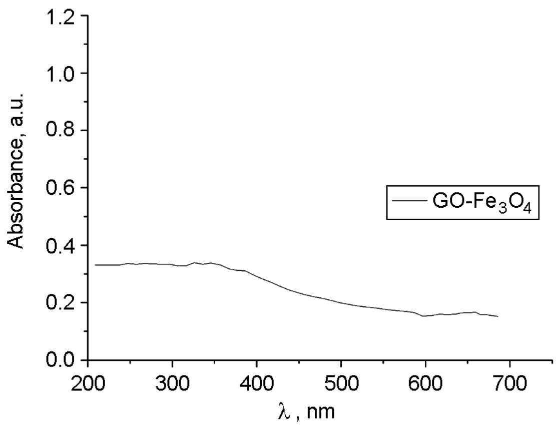

Fig. 4. UV-vis spectra of $GO\text{-}Fe_3O_4$ aqueous solution.

ticle size of Fe_3O_4 nanoparticles is relatively uniform. Figure 1 shows the particle size distribution of Fe_3O_4 nanoparticles, with an average particle size of about 100nm.

The magnetic properties of the prepared magnetic graphene oxide are measured, as shown in Figure 2. The hysteresis loops are typical S-shaped, and the samples show super paramagnetism without coercivity and remanence, which means when the magnetic field is removed, there is no magnetism. The saturation magnetization is 44.37emu·g^{-1}, which has strong magnetism and can be separated directly by magnet. Therefore, it is possible to separate pollutants after adsorption.

Figure 3 and 4 are ultraviolet-visible absorption spectra of GO and $GO\text{-}Fe_3O_4$ aqueous solutions. The aqueous solution of GO has two characteristic absorption peaks at 230nm and 300nm. $GO\text{-}Fe_3O_4$ absorbs at ultraviolet because it produces the peak of charge-hole, which means the d-d transition of Fe. The energy of ultraviolet light is enough to excite excitons with enough energy to cause hole-charge separation, while the energy of visible light is too low to excite.

3.2 Characterization of $GO\text{-}Fe_3O_4\text{-}CS$ complexes

The magnetic nanoparticles of $GO\text{-}Fe_3O_4$ and $GO\text{-}Fe_3O_4\text{-}CS$ composites are distributed on GO sheets. The size distribution of these nanoparticles is uniform, and the diameter of these nanoparticles is about 100 nm. These nanoparticles are formed by the accumulation of smaller nanoparticles. Cracks appear on the surface of GO, which indicates that GO has been destroyed by reaction at high temperature. Figure 5 shows the magnetic properties of the $GO\text{-}Fe_3O_4\text{-}CS$ composite. The hysteresis loop still shows a typical S-type. The sample shows no coercivity and remanence and is super paramagnetic. The saturation magnetization is 10.14emupg-1, which has strong magnetism and can be separated directly by magnet. Moreover, the separation time of the complex and the solution is greatly shortened by magnets, which only takes about 30 sec.

3.3 Adsorption test results of $GO\text{-}Fe_3O_4\text{-}CS$ complexes

It can be found that the prepared complex has good adsorption effect on dyes methyl violet, methylene blue, rhodamine B and Congo red, and has good adsorption effect on chrome azure S and acid chrome blue K. The adsorption performance for methyl orange is general. In the process of adsorption, the complex adsorbed methyl violet fastest. After about 10 minutes, the water solution of methyl violet became colorless and clarified. The adsorption rate of methylene blue is faster, and it can be completely absorbed for about 2-3 h, but the adsorption efficiency of other dyes is slower. The mechanism of adsorption here is the interaction of chitosan and GO.

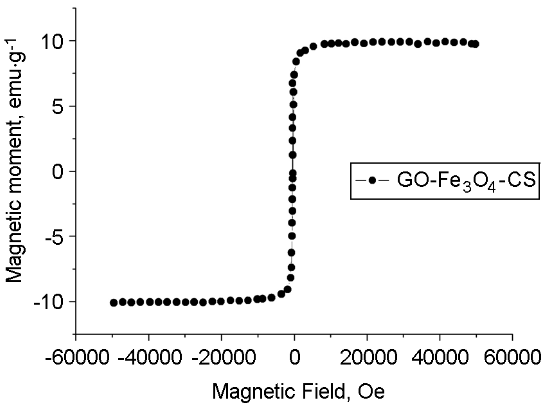

Fig. 5. Magnetization curve of GO-Fe_3O_4-CS.

4. Conclusion

The morphology of the magnetic graphene oxide synthesized by us is that the Fe_3O_4 nanospheres grow uniformly on the graphene oxide surface at about 100 nm. The hysteresis loop shows that GO-Fe_3O_4-CS has strong magnetic properties. The results show that GO-Fe_3O_4-CS complex has a good adsorption effect on methyl violet, methylene blue, rhodamine B, Congo red and other dye molecules. Moreover, magnetic nanoparticles grow on GO sheets. CS and GO-Fe_3O_4can be covalently crosslinked to prevent the oxidation of Fe_3O_4 nanoparticles and the leakage caused by the diffusion of magnetic nanoparticles from the composite during the adsorption process. It has the advantages of simple operation and low energy consumption. Therefore, the magnetic graphene oxide/chitosan complexes designed and prepared by us are expected to be applied to the environmental protection in real life.

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