

Synthesis and properties of magnetic Fe₃O₄-activated carbon nanocomposite particles for dye removal

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Abstract

Magnetic Fe₃O₄-activated carbon nanocomposite was synthesized for the first time from rice husk based activated carbon. It was interesting to find the obtained composite still held a relatively large pore diameter of 3.1 nm, high surface area of 770 m²/g with 23 wt.% Fe₃O₄ coated, and a saturation magnetization (Ms) of 2.78 emu/g. The system demonstrated perfect magnetic separation performance and a high adsorption capacity of 321 mg/g for Methylene Blue (MB) from aqueous solution, both of which are significant for activated carbon's use as adsorbent.

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1. Introduction

Discharging of dyes into water resources even in a small amount can affect the aquatic life and food web. Most of these dyes are harmful when brought in contact with living tissues for a long time. The discharge of the dyes to the river stream without proper treatment causes irreparable damage to the crops and living beings. The sorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters [1,2]. Currently, the most widely used and effective physical method in industry is activated carbon [3–5].

Unfortunately, activated carbons are notoriously difficult to separate from solution. Attempts to use magnetic separation by applying an appropriate magnet have been reported for nanoparticles iron oxide or cobalt incorporated in mesoporous silica, such as MCM-41, MCM-48, and SBA-15 [6,7]. Generally, those ordered mesoporous materials are chosen as parent material, which can afford enough space for particles loading. However, the preparation of those parent materials were often complicated, thus these kinds of materials were not appropriate for industry. Rice husk is as feed to raise livestock and poultry and their yields are vastness. Therefore, rice husk based porous carbon can be as realistic parent materials for magnetic nanoparticles loading. If

one could combine the advantages of cheap activated carbon and magnetic particles to fabricate nanocomposite with high surface area, appropriate pore size, and magnetic separability, a promising novel adsorbent may be accessible. How to incorporate magnetic particles inside the pores while keeping a high surface area is the key point for the materials' use as adsorbent.

Herein, we report a simple method for fabricating magnetic Fe₃O₄-activated carbon nanocomposite from rice husk, with high surface area of 770 m²/g and large pore diameter of 3.1 nm. The adsorption capacity was investigated by adsorbing Methylene Blue (MB) from aqueous solution, which demonstrated an excellent adsorption capacity of 321 mg/g and perfect magnetic separation performance.

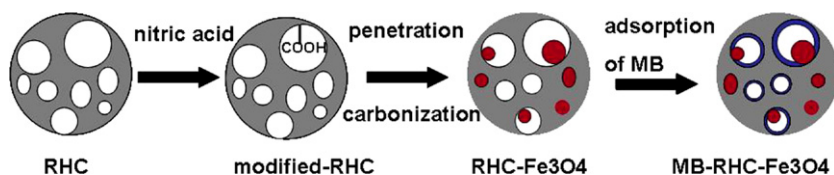
2. Experimental

2.1. The synthesis of Rice Husk based activated Carbon (RHC)

The porous carbon used in this study was prepared according to previous reports [8]. Firstly, the rice husk was washed and dried; secondly, the drying rice husk was carbonized at 450 °C in the presence of nitrogen. Then, the carbonized product was heated in the presence of sodium hydroxide (NaOH:C=3:1) at 400 °C for 25 min to dehydrate the mixture, thereafter the temperature was raised to 750 °C and this temperature was held for 90 min to activate the combination. Finally, the activated

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Scheme 1. The formation process of RHC-Fe₃O₄ and its application as adsorbent.

product was ground, washed with water and dried at 120 °C to get the activated carbon.

2.2. Magnetic Fe₃O₄-activated carbon nanocomposite

As described in Scheme 1: Firstly, the activated carbon from rice husk (RHC) were modified with nitric acid (63%) for 3 h at 80 °C to make it hydrophilic. Then 0.5 g of the modified RHC was dispersed in 20 ml aqueous solution containing 4 g Fe (NO₃)₃·9H₂O with the help of an ultrasonic bath, filtrated and dried. Thermal-treatment was conducted at 750 °C for 3 h in the presence of nitrogen to enable the formation of magnetic nanoparticles Fe₃O₄. The sample thus prepared was denoted as RHC-Fe₃O₄.

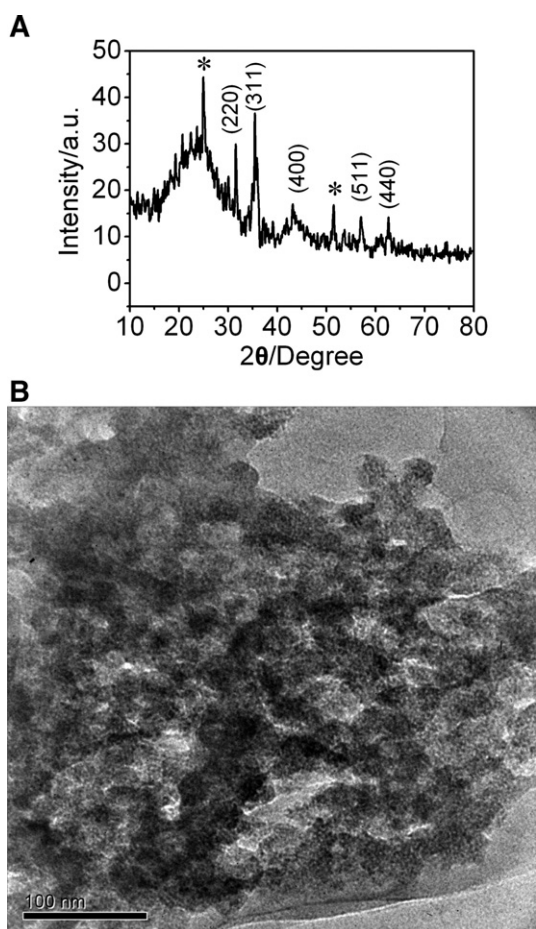


Fig. 1. A) The powder X-ray diffraction pattern of the RHC-Fe₃O₄ (JDCS: 85-1436), the peaks denoted as * are from graphitic carbon); B) TEM image of RHC-Fe₃O₄.

2.3. The adsorption of MB on RHC-Fe₃O₄

10 mg RHC-Fe₃O₄ and 30 ml MB stock solutions of different concentration were mixed and shaken in distilled water at 25 °C. The mixture was filtered and the residual MB concentration in the filtrate was measured using a spectrophotometer at wavelength 662 nm.

3. Results and discussion

In order to validate the compound of Fe and O inside porous carbon to be Fe₃O₄, the samples were measured by powder X-ray diffraction. As demonstrated in Fig. 1A), a number of prominent Bragg reflections could be indexed as the face-centered cubic (fcc) structure of Fe₃O₄ with the corresponding diffraction peaks of (220), (311), (400), (511), and (440) planes. The reflection peaks appear broader indicating as-prepared Fe₃O₄ nanoparticles with small dimensions. TEM image is showed in Fig. 1B), almost uniform nanocomposite was observed in a large scale. No obvious large size of iron oxide was detected. This conclusion was evidenced by the high surface area of the resultant nanocomposite RHC-Fe₃O₄ (770 m²/g).

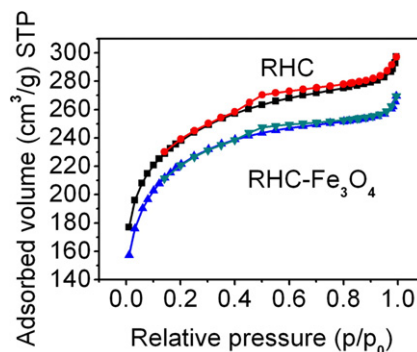


Fig. 2. Nitrogen adsorption isotherms of RHC and RHC-Fe₃O₄ at 77 K.

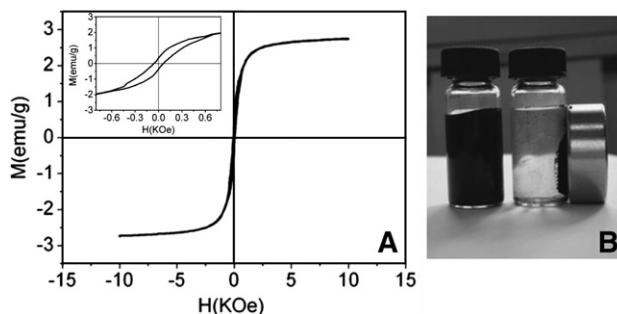


Fig. 3. (A) Magnetic hysteresis cycles for the RHC-Fe₃O₄, (B) Separation of RHC-Fe₃O₄ from solution by a magnet.

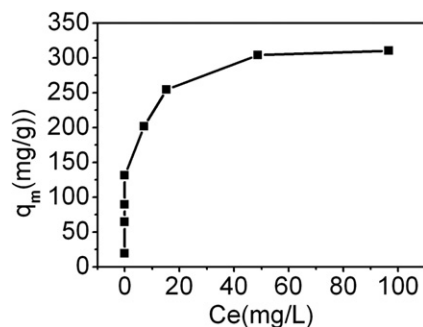


Fig. 4. Equilibrium adsorption of MB onto the RHC-Fe₃O₄ at 298 K.

The pore structures of RHC and RHC-Fe₃O₄ were studied by N₂ adsorption/desorption analysis (Fig. 2). Compared with the original RHC, the surface area of the resultant RHC-Fe₃O₄ was observed reduce from 826 m²/g to 770 m²/g, attributing to the formation of nanoparticles Fe₃O₄ inside the pores. The average pore size of RHC-Fe₃O₄ decreases from 3.4 nm to 3.1 nm further confirmed the conclusion. Characteristics of thermogravimetric analysis (TGA) of the sample RHC-Fe₃O₄ indicated that there was about 23 wt.% of Fe₃O₄ inside the obtained nanocomposite. It was noteworthy that the Fe₃O₄ loading resulted in a slight decrease in the surface area, which would benefit for adsorbing other molecules.

The magnetic characterization by a vibrating sample magnetometer (USM, ToeiVSM-5, USA) was depicted in Fig. 3A. From the plot of magnetization (M) and magnetic field (H) and its enlargement near the origin, the very weak hysteresis revealed the resultant magnetic nanoparticles were nearly superparamagnetic with a saturation magnetization (Ms) of 2.78 emu/g at room temperature. Which confirm most of the magnetic particles remain nanoscale in the composite RHC-Fe₃O₄. As displayed in Fig. 3B, after dispersion of RHC-Fe₃O₄ in water, there was a change from black to colorless within few minutes by placing a conventional laboratory magnet near the glass bottle. That is to say the black particles of RHC-Fe₃O₄ were attracted toward the magnet, and the clear solution could be easily decanted off or removed by pipette. This simple experiment proved that RHC-Fe₃O₄ possessed magnetism and could be potentially used as a magnetic adsorbent to remove compounds in liquid phase. It was interesting to find that RHC-Fe₃O₄ still had a perfect performance even after stirred in water for two months. This magnetic separation is an attractive alternative to filtration or centrifugation.

The adsorption capacity of RHC-Fe₃O₄ was investigated by adsorbing Methylene Blue from its aqueous solutions. The adsorption isotherm of MB onto the RHC-Fe₃O₄ at 25 °C is displayed in Fig. 4, the knee of the isotherm is sharp and the plateau is fairly horizontal. The sorption isotherm reflects that the MB uptake on the carbon surface is of the Langmuir type [9]. That could attribute to the strong interaction between the heteroatom-containing groups on the carbon surface and the positive charges on the MB molecules [10]. It is reasonable to suggest that the adsorption is site-specific and thus a monolayer is formed.

Langmuir constant, q_m represents the monolayer saturation at equilibrium. The other mono-component Langmuir constant, K_L , indicates the affinity for the binding of MB. A high K_L value indicates a high affinity. Values of q_m and K_L at 25 °C were calculated from the Langmuir plots. The value of q_m and K_L obtained at 298 K is 321 mg/g and 0.225, respectively. Compared with those activated carbons with almost the same surface area reported by others, with the values of 227 mg/g and 0.13 [11], the materials we prepared showed a higher adsorption capacity and high affinity even with 23 wt.% of Fe₃O₄ inside.

4. Conclusions

In summary, the magnetic activated carbon with a high adsorption capacity and perfect magnetic separation performance was prepared for the first time. Surface modification of RHC to become hydrophilic make it easy for Fe(NO₃)₃·9H₂O to access the pores of RHC and enable the formation of Fe₃O₄ nanoparticles inside the pores, leaving a high surface area and large pore size. It is expected that the obtained magnetic RHC-Fe₃O₄ can be used as potential sorbents for the removal of various toxic pollutants from wastewater.

Acknowledgements

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References

- [1] V. Vadivelan, K. Vasanth Kumar, J. Colloid Interface Sci. 286 (2005) 90.
- [2] M. Bjelopavlic, G. Newcombe, R. Hayes, J. Colloid Interface Sci. 210 (2) (1999) 271.
- [3] Y. Guo, S. Yang, W. Fu, J. Qi, Z. Wang, H. Xu, Dyes Pigm. 56 (2) (2003) 19.
- [4] C. Namasivayam, D. Kavitha, Dyes Pigm. 54 (2002) 47.
- [5] P.K. Malik, Dyes Pigm. 56 (2) (2003) 39.
- [6] A.H. Lu, W.C. Li, A. Kiefer, W. Schmidt, E. Bill, G. Fink, F.S. Angew, J. Am. Chem. Soc. 126 (2004) 8616.
- [7] A.H. Lu, S. Wolfgang, M. Nina, B. Helmut, S. Bernd, T. Bernd, B. Eckhard, K. Wolfgang, F.S. Angew, Chem. Int. Ed. Engl. 43 (2004) 4303.
- [8] Y.P. Guo, J.Z. Zhao, H. Zhang, S.F. Yang, J.R. Qi, Z.C. Wang, H.D. Xu, Dyes Pigm. 66 (2005) 1–23.
- [9] J. Avom, J.K. Mbadcam, C. Noubactep, P. Germain, Carbon 35 (1997) 365.
- [10] P.T. Hang, G.W. Brindley, Clay. Clay Miner. 18 (1970) 203.
- [11] Y.R. Lin, H. Teng, Microporous Mesoporous Mater 54 (2002) 167.