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Preparation and Adsorption Properties of Magnetic CoFe$_2$O$_4$–Chitosan Composite Microspheres[1]

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Abstract—Magnetic chitosan microspheres made from novel polymer materials show outstanding applied characteristics. Magnetic chitosan microspheres are rather cheap, non-toxic, tasteless, alkali resistant, corrosion resistant, easily degradable, easily recyclable, and so on. It can be widely used in many fields. In this paper, magnetic CoFe$_2$O$_4$/chitosan core-shell microspheres are prepared by means of emulsification cross-linking technique using CoFe$_2$O$_4$ as core and glutaric dialdehyde as crosslinking agent. The results demonstrated that the different calcining temperature of magnetic (CoFe$_2$O$_4$) particles, CoFe$_2$O$_4$/chitosan ratio and stirring time of the suspension medium are the most effective parameters that control the size, size distribution, morphology and magnetism of the described microspheres. Finally, the size, morphology and chemical structure of the prepared materials are studied by different methods. The results show that the optimal calcination temperature of magnetic particles is 700°C, the optimal ratio of CoFe$_2$O$_4$/chitosan is 1 : 1, ultrasonic dispersion time is 30 min. The prepared chitosan magnetic microspheres have small size and are well dispersed when the stirring time is 3 h. The prepared magnetic chitosan microspheres are well shaped spheres with a diameter from 1 to 50 μm, in which CoFe$_2$O$_4$ particles are dispersed uniformly. The magnetic chitosan microspheres show excellent magnetic response and have good adsorption characteristics.
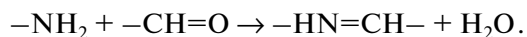
Keywords: chitosan magnetic microsphere, magnetic response, adsorption.

1. INTRODUCTION

Chitosan is the deacetylated derivative of chitin [1–5], the most abundant natural polymer on earth after cellulose [6–8], obtained from crustaceans [9–12], such as shrimps, squids, and crabs. Chitosan is the only basic polysaccharide in nature. It can be used as a drug carrier due to can be non-toxicity [13]. Owing to its biocompatibility and biodegradation, chitosan has wide application in many fields, such as wastewater treatment [14–16], medicine, food, drug, environmental protection, light industry and agriculture [16–22].

The amino group of chitosan can interact with aldehydes or ketones with formation of Schiff bases (aldimines and ketimines). The reaction is as follows:

$$-NH_2 + -CH=O \rightarrow -HN=CH- + H_2O.$$

The structural schematic diagram of cross-linking chitosan is as follows:
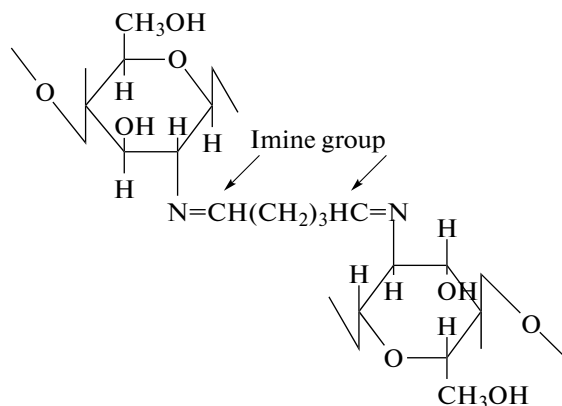
With the rapid development of nanotechnology, magnetic nanoparticles are currently being widely studied [23]. Superparamagnetic iron oxide nanoparticles have attracted researchers in various fields such as physics [24], medicine [25], biology [26], and materials science [27] due to their multifunctional properties

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such as small size, superparamagnetism and low toxicity [28]. However, the nanoparticles tend to aggregate due to strong magnetic dipole-dipole attraction between particles [29]. At the same time, acid [30], alkali [31], and salt [32] resistance of magnetic nanoparticles is low. Recently, the combination of organic and inorganic components at nano-sized level has attracted considerable attention because of the potential applications in many field [33].

In this paper, magnetic $CoFe_2O_4$/chitosan core-shell microspheres are prepared by means of emulsification cross-linking technique using $CoFe_2O_4$ as core and glutaric dialdehyde as crosslinking agent for chitosan. The prepared microspheres have small size and are well dispersed when the stirring time is 3 h. The prepared microspheres are well shaped spheres with a diameter from 1 to 50 μm, in which $CoFe_2O_4$ particles are dispersed uniformly. The magnetic chitosan microspheres show excellent magnetic response and good adsorption characteristics.

2. EXPERIMENTAL

2.1. Materials

Glutaraldehyde solution (50%), liquid paraffin, petroleum ether, ethanol, glacial acetic acid, sodium hydroxide, Span-80, $CoCl_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ were purchased from Kemel Chemical Reagent Co. All the chemicals were of reagent grade and were purified before use. Chitosan ($M_w = 1.0 \times 10^5$, deacetylation degree 95.5%) was purchased from YuHuan Chemical Company, Zhejiang Province, China. Deionized water was re-deionized (electrical resistivity ≥18.9 MΩ cm, 25°C) and deoxygenated by boiling for 1 hour before used.

2.2. Synthesis of Magnetite

$CoFe_2O_4$ was prepared without any additional stabilizer by controlled coprecipitation approach that could be found elsewhere. In a typical synthesis, an aqueous solution containing $CoCl_2$ and $Fe(NO_3)_3$ in stoichiometric ratio was placed into the three-necked flask and heated to 90°C under mechanical stirring (500 rpm). NaOH solution (0.1 mol/L) was added to adjust pH to 11 and the mixture was refluxed for 1 h. When a light black sediment appeared, the crystal growth was allowed to proceed for 2 h with constant stirring (200 rpm) to produce a stable suspension. The product was isolated from the solvent by an external magnetic field followed by redispersing in deionized water, and then dried at room temperature.

2.3. Preparation of Magnetic Chitosan Nanoparticles

According to mass ratio of $CoFe_2O_4$ and chitosan is 1 : 4, 0.5 g $CoFe_2O_4$ magnetic particles were quickly added into the 40 mL acetic acid solution (5 vol %)

containing 2 g of chitosan. The solution was placed in the ultrasonic reactor (22 kHz, 1000 W) for 10 min to disperse the chitosan and the magnetic particles uniformly. After that, 40 mL of liquid paraffin and 10 drops of Span-80 were added. Then the solution is placed in the ultrasonic reactor (22 kHz, 500 W) for 30 min. To active $CoFe_2O_4$ to get better magnetic properties, the reaction systems were kept at 60°C for 5 h in a water bath. The cross-linked magnetic chitosan nanoparticles were formed by adding 2 mL of glutaraldehyde and by keeping the same condition for 5 h. After reaction, the prepared nanoparticles was precipitated with centrifugation (8000 rpm for 1 h) and rinsed with ethanol and deionized water for four times. Finally, the prepared nanoparticles were freeze dried for 24 h.

2.4. Characterizations of Magnetic Chitosan Nanoparticles

X-ray power diffraction (XRD) measurement was performed using a Bruker D8 diffractometer with monochromatized CuK_α radiation (λ = 1.5426 Å), 40 kV, 30 mA. Fourier transform infrared spectroscopy (FTIR, IR Prestige-2I, Shimadzu) was used to confirm the structure of the magnetic $CoFe_2O_4$-chitosan nanoparticles. The nanoparticles were studied by transmission electron microscopy (TEM, H-7650, Hitachi) to evaluate their size and morphology. The sample of $CoFe_2O_4$-chitosan nanoparticles for TEM analysis was obtained by placing a drop of the nanoparticles dispersion in ethanol onto a copper micro-grid and evaporation at 20°C. The surface of the magnetic particles was studied by scanning electron microscopy (SEM, Kyky-2800, Kyky Technology Co.). The elemental composition of the particles was analyzed by elemental analyzer (Vario EL III, Elementar Inc.). Magnetic measurements were done in a vibrating sample magnetometer (VSM, PPMS-9, Quantum Design). The sample powder was placed in a Teflon-coated sample holder and the mass was accurately measured.

2.5. Adsorption Performance Analysis

Magnetic chitosan nanoparticles were added into methylene blue solution of certain concentration, followed by sampling of 5 mL of above solution at regular intervals and measuring their absorbance value, the adsorption performance was measured according to the change of methylene blue solution absorbance by the formula as follows.

$$\eta/\% = \frac{C_0 - C}{C_0} \times 100\%,$$

where C_0 is the original concentration of methylene blue solution, mg/g; C is after concentration of adsorbed methylene blue solution, mg/g; h is adsorption efficiency, %.
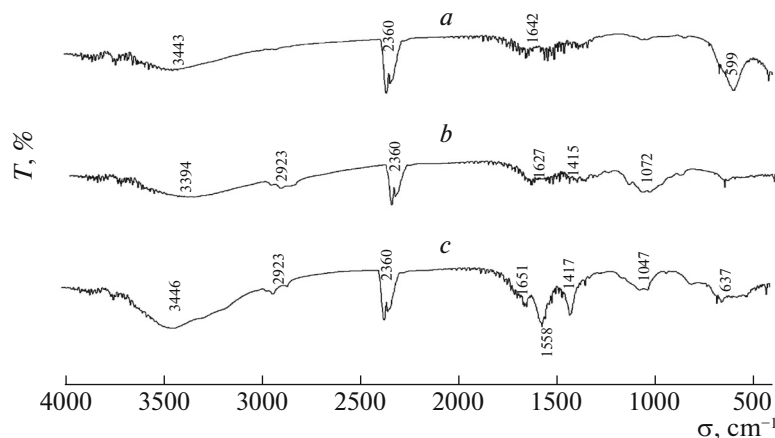
Fig. 1. FTIR spectra of the chitosan (*a*), magnetic CoFe$_2$O$_4$ particles (*b*), and magnetic chitosan (*c*).

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

The curves *a*, *b*, and *c* in Fig. 1 correspond to the IR spectra of the CoFe$_2$O$_4$ particles, chitosan particles and CoFe$_2$O$_4$-chitosan nanoparticles. In the curve *a*, 3443 and 1642 cm^{-1} bands correspond to residual water in KBr used for preparing the pellets. The absorption peak located at 599 cm^{-1} was attributed to the Fe−O−Co stretching vibration. Bands at 1627, 1415, and 1072 cm^{-1} are attributed to the bending vibration of N−H bond, bending vibration of C−H with alcohol hydroxyl groups in chitosan, and the symmetric stretching vibration of C−O bond, respectively. In the curve of *b* and *c*, strong and broad absorption band at 3400 cm^{-1} can be attributed to overlap vibration of −NH and −OH. Compared with *a* and *c*, we can see that the bending vibration peaks at 1627 cm^{-1} of N−H was red shifted to the absorption peak at 1558 cm^{-1}, and a new absorption peak at 1651 cm^{-1} appeared, which can be attributed to Schiff base formed by cross-linking reaction between the −NH$_2$ groups of chitosan and the C=O groups of glutaraldehyde. From the spectrum *c*, we also can see that a new peak appeared at 637 cm^{-1}, which was attributed to the metal −Co−, showed that CoFe$_2$O$_4$ magnetic particles effectively crosslinked chitosan particles.

3.2. X-ray Diffraction Analysis (XRD)

Figure 2 showed the XRD spectra of CoFe$_2$O$_4$ nanoparticles (Fig. 2a) and the magnetic CoFe$_2$O$_4$-chitosan (Fig. 2b), respectively. As can be seen from the figure, the peak of main crystalline phase was attributed to CoFe$_2$O$_4$. Seven peaks (1, 1, 1), (2, 2, 0), (3, 1, 1), (4, 0, 0), (4, 2, 2), (5, 1, 1), and (4, 4, 0) of CoFe$_2$O$_4$ can be observed in the two samples, which coincide exactly with the JCPDS card. As can be seen that chitosan-coating did not lead to the changes in the crystalline phase of CoFe$_2$O$_4$ magnetic core. The analysis of XRD data indicated that target product contain microcrystalline CoFe$_2$O$_4$. Due to the presence of chitosan, baseline XRD peaks of CoFe$_2$O$_4$ were raised, it also showed where the chitosan wrapped CoFe$_2$O$_4$.

3.3. SEM Analysis

Figure 3 showed the SEM picture of magnetic CoFe$_2$O$_4$−chitosan composite. As can be seen from the Fig. 3, the surface of magnetic CoFe$_2$O$_4$−chitosan was relatively smooth, the size of the particles was uniform, and their diameter was about 30−40 μm.

3.4. TEM Analysis

TEM image of magnetic CoFe$_2$O$_4$−chitosan composite is shown in Fig. 4. It can be seen that the dispersibility of magnetic microspheres was not particularly good. The reason may probably due to the small volume of the particles, the magnetic field had a strong influence on the particles. Another reason was the presence of agglomeration of nanoparticles in solution. However, it can be seen that microspheres were spherical and have regular sizes and relatively smooth surface. The diameter of the microspheres was about 1 μm.

3.5. Elemental Analysis

The data of elemental analysis of the magnetic composite are shown in the table. The atomic ratio of Fe and Co was about 2 : 1 and it indicated that CoFe$_2$O$_4$ magnetic particles were encapsulated by chitosan particles integrally.
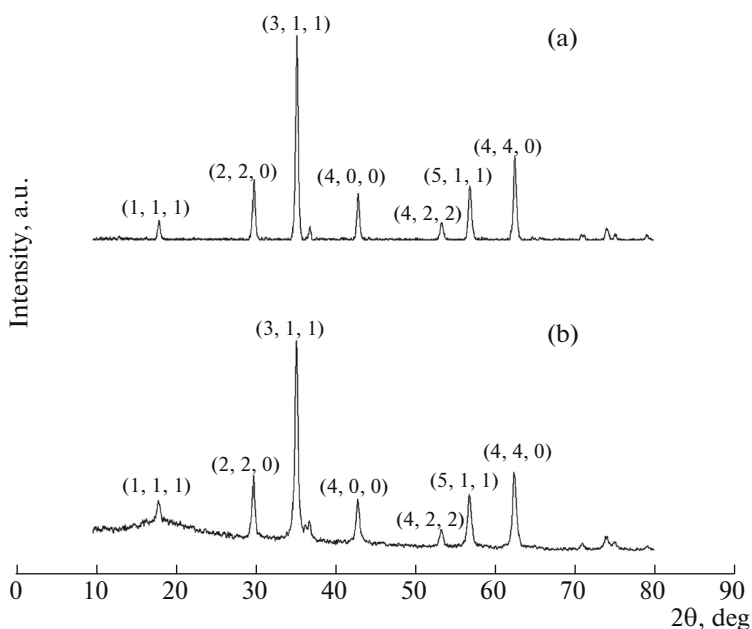
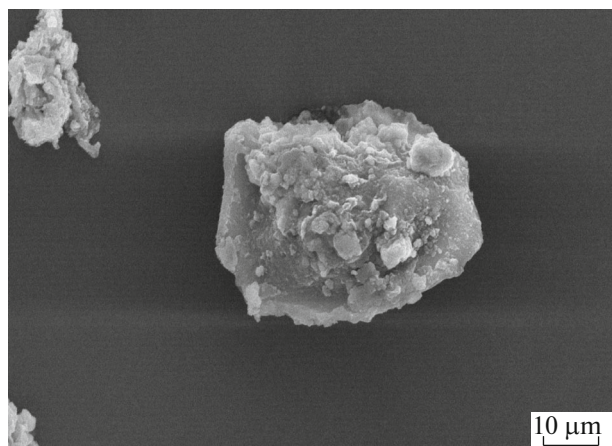**Fig. 2.** XRD patterns of magnetic $CoFe_2O_4$ particles (a) and their composite with chitosan (b).

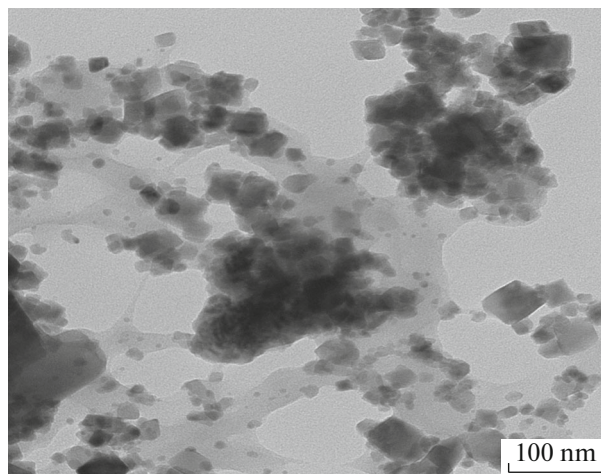**Fig. 3.** SEM of magnetic $CoFe_2O_4$–chitosan.

Fig. 4. TEM of magnetic $CoFe_2O_4$–chitosan.

3.6. Adsorption of Methylene Blue

The change of the optical density of methylene blue solution with time in the adsorption experiments is shown in Fig. 5. With the increase of time, the adsorbed dye quantity increased, and the solution was near to colorless at the end of the experiment. If the increase of adsorption time, composite microspheres of methylene blue absorption curve will be straight. The desorption efficiency is $\eta = 92.85\%$ which is important in to many fields, such as wastewater treatment, etc.

Experimental results show that magnetic $CoFe_2O_4$-chitosan nanoparticles have good adsorption effect to the methylene blue, which was a kind of application prospect of dye wastewater treatment agent. Also they can be used in absorbing Ca^{2+}, Cd^{2+}, Mo^{6+}, Bi^{3+}, Cu^{2+}, which are present in industrial wastewater.

Elemental analysis of the magnetic chitosan particles

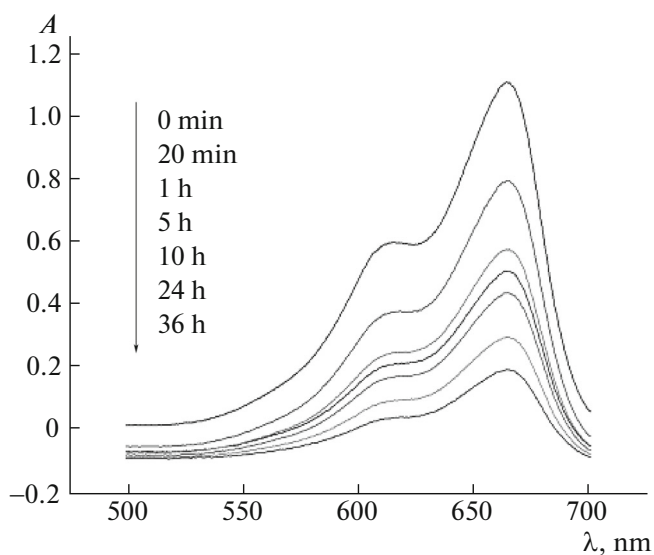| Element	C, %	O, %	N, %	Co, %	Fe, %
Content	53.42	27.52	2.31	4.91	9.94

Fig. 5. Absorption curve of methylene blue solution with magnetic $CoFe_2O_4$–chitosan nanoparticles.

4. CONCLUSIONS

Magnetic $CoFe_2O_4$/chitosan core-shell microspheres are prepared by means of emulsification crosslinking technique using $CoFe_2O_4$ as core and glutaric dialdehyde as chitosan crosslinking agent. The optimum reaction conditions was as follows: the calcination temperature of magnetic $CoFe_2O_4$ particles is 700°C, the optimal ratio of $CoFe_2O_4$/chitosan is 1 : 1, ultrasonic dispersion time is 30 min. The prepared chitosan magnetic microspheres have small size and well dispersed when the stirring time is 3 h. The prepared magnetic chitosan microspheres are well shaped spheres with a diameter from 1 to 50 μm, in which $CoFe_2O_4$ particles are dispersed uniformly. The magnetic chitosan microspheres show excellent magnetic response and good adsorption characteristics, and can be applied to many fields, such as wastewater treatment, etc.

REFERENCES

1. R. A. A. Muzzarelli, Carbohydr. Polym. **29**, 309 (1996).
2. R. A. A. Muzzarelli, Natural Chelating Polymers (Pergamon Press, Oxford, 1973).
3. H. I. Bolker, Natural and Synthetic Polymer: An Introduction (Marcel Dekker, New York, 1974).
4. J. D. Dee, O. Rhode, and R. Wachter, Cosmet. Toilet. **116**, 39 (2001).
5. A. K. Singla and M. Chawla, J. Pharm. Pharmacol. **53**, 1047 (2001).
6. H. K. No and S. P. Meyers, J. Agric. Food Chem. **37**, 580 (1989).
7. K. Kurita, Polym. Degrad. Stabil. **59**, 117 (1998).
8. S. E. Baily, T. J. Olin, R. M. Bricka, and D. D. Adrian, Water Res. **33**, 2469 (1999).
9. Y. Sawayanagi, N. Nambu, and T. Nagai, Chem. Pharmacol. Bull. **31**, 2064 (1983).
10. T. C. Yang and R. R. Zull, Ind. Eng. Chem. Prod. Res. Dev. **23**, 168 (1984).
11. J.-K. Yanga, I.-L. Shibb, Y.-M. Tzengc, and S.-L. Wang, Enzyme Microb. Technol. **26**, 406 (2000).
12. T. A. Khan, K. K. Peh, and H. S. Ch'ng, J. Pharm. Sci. **5**, 205 (2002).
13. T. D. Jiang, Chitosan (Huaxue Gongye Chubanshe, Beijing, 2001).
14. X. B. Li and H. Zhu, Yaoxue Jinzhan 29, 166 (2005).
15. S. M. Ding, X. H. Feng, Y. T. Wang, et al., Fenxi Kexue Xuebao **21**, 127 (2005).
16. O. Pillai and R. Panchagnula, Curr. Opin. Chem. Biol. **5**, 447 (2001).
17. E. Khor and L. Y. Lim, Biomater. **24**, 2339 (2003).
18. S. Yuan and T. Wei, J. Bioact. Compat. Polym. **19**, 467 (2004).
19. G. Crini, Bioresour. Technol. **97**, 1061 (2006).
20. M. Kerec, M. Bogataj, P. Veranic, et al., Eur. J. Pharmaceut. Sci. **25**, 113 (2005).
21. L. Y. Chen, Z. G. Tian, and Y. M. Du, Biomaterials **25**, 3725 (2004).
22. Y. H. Lin, H. F. Liang, C. K. Chung, et al., Biomaterials **26**, 2105 (2005).
23. J. D. Van Hamme, A. Singh, and O. P. Ward, Biotechnol. Adv. **24**, 604 (2006).
24. R. S. Makkar, S. S. Cameotra, and I. M. Banat, AMB Express **1**, 5 (2011).
25. Hp. Meyer, Org Process Res. Dev. **15**, 180 (2011).
26. S. L. Fox and G. A. Bala, Bioresour. Technol. **75**, 235 (2000).
27. L. R. Rodrigues, J. A. Teixeira, and R. Oliveira, Biochem. Eng. J. **32**, 135 (2006).
28. J. Roger, J. N. Pons, R. Massart, A. Halbreich, and J. Bacri, Eur. Phys. J.: Appl. Phys. **5**, 321 (1999).
29. I. M. Banat, R. S. Makkar, and S. S. Cameotra, Appl. Microbiol. Biotechnol. **53**, 495 (2000).
30. A. Sing, J. D. van Hamme, and O. P. Ward, Biotechnol. Adv. **25**, 99 (2007).
31. J. D. Desai and I. M. Banat, Microbiol. Mol. Biol. Rev. **61**, 47 (1997).
32. E. Carrero, N. V. Queipo, and S. Pintos, J. Petrol. Sci. Eng. **58**, 30 (2007).
33. M. Nitschke, S. G. V. A. O. Costa, and J. Contiero, Biotechnol. Progr. **21**, 1593 (2005).