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硕 士 学 位 论 文

磁性壳聚糖材料制备新方法研究

Praparation and Characterization of Novel Magnetic Chitosan Materials

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摘　要

壳聚糖分子中含有大量的官能基团如氨基、羟基，从而具有良好的吸附性能。若在壳聚糖中引入磁性物质，则壳聚糖材料在外加磁场条件下易于同介质分离，并且所得磁性材料还能保留壳聚糖自身的特性。本论文以此为出发点，选用铁离子溶液为磁性 Fe_3O_4 源并将其与壳聚糖溶液混合，以氨水为沉淀剂，通过一步沉淀法制备磁性壳聚糖微球(magnetic chitosan sphere, MCSS)；采用反相乳液法，将氨水溶液首先分散，再加入上述混合溶液制备微米级的中空磁性壳聚糖微球(hollow magnetic chitosan sphere, H-MCSS)；利用壳聚糖络合铁离子的性能，用氨气熏蒸法制备磁性壳聚糖杂化材料(hybrid magnetic chitosan material, H-MCSM)；另外，本论文还考察了所制备磁性壳聚糖材料对重金属离子和有机污染物的吸附应用。具体内容如下：

1. 将溶解于醋酸的壳聚糖溶液与铁离子溶液均匀混合，并逐滴滴加入沉淀剂氨水中，通过一步沉淀法制备磁性壳聚糖微球。详细研究了铁离子浓度、壳聚糖浓度对微球制备的影响。采用傅立叶红外光谱(FT-IR)、X-射线衍射(XRD)对微球进行物相结构分析，证实微球由壳聚糖和 Fe_3O_4 组成。热重(TG)分析结果表明，随着铁离子加入量的增加，微球中的 Fe_3O_4 含量也逐渐增加。扫描电镜(SEM)观察发现，微球表面紧实有褶皱和条纹状结构，内部为多层结构且无明显相分离。上述结果表明，Fe_3O_4 与壳聚糖存在相互作用，Fe_3O_4 以纳米尺度分散在壳聚糖基质中。电子探针(EPMA)能谱(EDS)结果显示，Fe 元素含量在微球径向由外至里分布逐渐降低，表明纳米 Fe_3O_4 粒子在磁性微球中也遵循相同的分布。通过振动样品磁强计 (VSM) 分析微球的磁学性能，发现磁性壳聚糖微球具有超顺磁性，其饱和磁化强度(M_s)与 Fe_3O_4 含量呈 M_s/(emu) = -4.6 + 80.7 w_{Fe3O4} 的线性关系。由此，通过改变铁离子起始浓度、壳聚糖与铁离子浓度配比可容易地制备所需 M_s 的磁性微球。并且，由于纳米 Fe_3O_4 在微球表面的富积，可通过煅烧去除壳聚糖得到空心结构的微球。

2. 以 Cu^{2+}和甲基橙(MO)为重金属离子和有机污染物代表，采用静态吸附法研究了上述磁性微球(MCSS1)在水处理方面的应用。通过改变磁性壳聚糖微球的用量、吸附时间、温度、pH 值和吸附溶液初始浓度，研究磁性微球对 Cu^{2+}和甲基

橙吸附的影响。结果表明，MCSS1 对 Cu^{2+}的饱和吸附容量为 1.69mg/g，达到饱和吸附的时间为 150min；MCSS1 对 MO 的饱和吸附容量为 0.614mg/g，达到饱和吸附的时间为 100min。温度对 Cu^{2+}和 MO 吸附率影响不大。pH 的改变对二者吸附有较大影响，其中，对铜离子吸附的最佳 pH 约为 5，对 MO 吸附的最佳 pH 约为 4。由此，这种壳聚糖磁性微球将在污水处理方面具有潜在的应用。

3. 采用反相乳液法和上述一步沉淀法相结合，制备空心的壳聚糖磁性微球。首先，将氨水在搅拌下分散在液体石蜡中制得 W/O 的氨水微滴；再将壳聚糖与铁离子混合溶液滴加上述 W/O 体系，继续反应 30min，即可制得粒径在 100 ~200 μm 的空心壳聚糖磁性微球。采用光学显微镜观察，发现微球球形结构良好、表面光滑，但干燥过程容易使微球塌陷。上述空心微球经交联反应后，尺寸稳定性能得到提高。同时，所制备的微球经煅烧后为中空结构的无机微球。此外，还通过 FT-IR、XRD 、TG 和 SEM 研究了所制备磁性微球的组成和微观结构。结果表明，所得微球为空心壳聚糖磁性微球，微球尺寸受搅拌速度影响，煅烧后微球壁厚在 50nm~1μm 之间。由此，本部分工作提供了一种制备空心杂化微球材料的简便方法，将在载药、靶向释放以及作为催化剂载体方面具有潜在的用途。

4. 将摩尔比为 2：1 的 $NH_4Fe(SO_4)_2$ 与 $(NH_4)_2Fe(SO_4)_2$ 混合溶液直接滴加入壳聚糖溶液中得到絮状沉淀物，过滤后再将其置于氨水蒸气气氛中反应 6h，即可制得磁性壳聚糖杂化材料。FT-IR、TG 结果表明，杂化材料由壳聚糖和 Fe_3O_4 组成，其中 Fe_3O_4 的含量为 40%。SEM 结果表明，杂化材料在纳米~微米尺度，具有巨大的比表面积。这种具有壳聚糖自身性能的杂化材料对 Cu^{2+}很好的吸附性能，能在 1h 内快速吸附脱色，且容易通过简单的磁过程与吸附体系分离。因而，该方法将极大简化用于污水处理的磁性壳聚糖材料的制备，有利于工业化生产制备和应用。

本论文磁性壳聚糖材料的制备与表征研究均属于原创性探索研究。

关键词：壳聚糖 磁性微球 杂化材料 制备与表征

Abstract

Chitosan (CS) has excellent adsorption performance because of the large amount of functional groups such as amino and hydroxyl groups of the macromolecule. If magnetic component was introduced into chitosan material, the composite material could not only retain the characteristics of chitosan, but also be easily isolated from the adsorption medium under a magnetic field. Therefore, Fe^{2+} and Fe^{3+} were chosen as precursors of magnetic Fe_3O_4 to mix with CS solution, and then were co-precipitated in one step by ammonia aqueous solution to prepare magnetic chitosan spheres (MCSS). By combining inversed micro-emulsion and the above mentioned co-precipitation, ammonia aqueous solution was firstly dispersed, and then iron ions/CS mixture solution was added to fabricate a hollow magnetic chitosan sphere (H-MCSS). Hybrid magnetic chitosan material (H-MCSM) was prepared by firstly CS adsorption of iron ions, then by ammonia vapor treatment. In addition, the removal of heavy metal ion and organic pollutant by adsorption of the obtained magnetic materials has been carried out in order to investigate their applications. The main contents of the work are following:

1. A facile and robust approach is presented to prepare superparamagnetic chitosan spheres by simply dropping iron and chitosan mixture solution to ammonia aqueous solution. Fourier transforms infrared spectra (FT-IR), X-ray diffractions (XRD) and thermogravimetric (TG) analyses of the obtained spheres indicate that the composite spheres consisted of chitosan and Fe_3O_4. The microstructures of the surface and the inner part of the sphere were observed by scanning electron microscope (SEM) to indicate nano scale of the Fe_3O_4 component. The results suggest that the nano sized Fe_3O_4 particles can be stabilized by CS molecules in the matrix of sphere to avoid aggregating based on their binding interaction. Because of the nano scale distributed Fe_3O_4 particles, the composite spheres show superparamagnetic properties, and the saturation magnetization of the composite sphere increases linearly with the Fe_3O_4 content. An electron probe microanalyzer was employed to measure the energy dispersive spectra of the magnetic sphere, through which the element contents at different points along the radius of MCSS1 have been obtained. It has been found that the Fe_3O_4 content decreased gradually from outer surface to its inner core. Moreover,

the composite sphere was calcined in air at 700 °C in order to prepare spherical hollow sphere.

2. Cu^{2+} and methyl orange (MO) were used as representative heavy metal ion and organic pollutant to test the adsorption behavior of the above obtained MCSS1. The adsorption performance of MCSS1 was studied by static adsorption, and the influences of the amount of MCSS1, adsorption time, temperature, pH, initial concentrations of pollutants were investigated in detail. The results show that the saturation adsorption capability of MCSS1 for Cu^{2+} is 1.69mg/g and the time to reach saturation adsorption is 150min; the saturation adsorption of MCSS1 for MO is 0.614mg/g and the time to reach saturation adsorption is 100min. The temperature has little effect on the adsorption of both Cu^{2+} and MO, but pH variation greatly influences their adsorptions, The best pH for Cu^{2+}adsorption was measured to be about 5 and the optimal pH for MO adsorption was measured to be about 4. So the magnetic chitosan sphere reveals potential applications in the field of the water treatment.

3. Inversed micro-emulsion and the co-precipitation were combined to prepare the H-MCSS. Firstly, micro-droplets of ammonia solution in the manner of W/O were obtained by dispersing ammonia solution in liquid paraffin, and then iron ions/CS mixture solution were dropped into the W/O system to react for 30min with stirring. After filtration, the H-MCSS was obtained with the diameter ranging from 100μm to 200μm. The H-MCSS revealed spherical shape and smooth surface, but easily shrinked and collapsed during drying. The dimensional stability of the H-MCSS was improved by cross-linking. Inorganic hollow microspheres were obtained by calcination of the H-MCSS. The microstructure of the H-MCSS was analyzed by FT-IR, XRD, TG and SEM. The results indicate that the size of the H-MCSS is mainly affected by stirring rate, and the thickness of the H-MCSS is in the range of 50 nm to 1μm after calcination. Therefore, this part provides a facile way to prepare hollow magnetic microspheres, which have potential applications as drug carrier for targeted release, catalyst carrier, and so on.

4. Mixture solution of $NH_4Fe(SO_4)_2$ and $(NH_4)_2Fe(SO_4)_2$ (mole ratio of 2:1) was directly added into the chitosan solution to obtain a loccular precipitate, which was filtrated to be positioned in an ammonia vapor atmosphere to react 6h to prepare hybrid magnetic chitosan material (H-MCSM). FT-IR, TG results show that the H-

MCSM is formed by chitosan and Fe_3O_4, and the Fe_3O_4 content is about 40%. SEM results show that the H-MCSM is in the scale between nanometer and micrometer indicating a huge surface area of the obtained H-MCSM. Therefore, the H-MCSM showed good adsorption on Cu^{2+} to rapidly destain the solution in 1 hour and could be separated easily by a simple magnetic process. This method has greatly simplified the preparation of hybrid magnetic chitosan materials, which was thought to be versatile for industrial production.

In this thesis, the preparation and characterization of the magnetic chitosan materials are original researches.

Keywords: Chitosan; Magnetic microspheres; Hybrid material; Preparation and Characterization

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