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To cite this article: Wenqian Li *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **227** 052039

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Chitosan/cellulose sulfate mesoporus microspheres for the adsorptive removal of pollutants from water

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Abstract. The discharge of effluents is steadily increasing, resulting in serious damages to the environment. Considerable attentions have been paid to magnetic bioadsorbent technology to solve these environmental problems because of their low cost and high efficiency. A thermally induced sol-gel transition process in ionic liquid was conducted to produce microspheres from chitosan and cellulose sulfate in order to develop a novel bioasorbant. The developed adsorbents were characterized using Fourier transform infrared (FT-IR) spectra, scanning electron microscopy (SEM), and an Energy Dispersive Spectrometer (EDS). The adsorption performance was evaluated with a simulated waste water containing Congo red and heavy metals. Results indicated that the synthesized CHT-CS-Fe_3O_4 microspheres exhibited mesoporous property and a good sphericity with an approximate diameter of 20 µm. The composite microsphere showed an excellent performance in removing the anion dye Congo red with removal efficiency of 68% and adsorbing divalent lead with the maximum adsorption capacity q_m of 189 mg/g as well as removal efficiency of 93%. The material exhibited a highly selective property for the adsorption of different metals from the solution. These properties suggest that CHT-CS-Fe_3O_4 microspheres have the potential for application in water treatment.

1. Introduction

Water pollution is one of the greatest problems the world is facing today, increasing with every passing year and posing a bad threat to environment and public health. Various organic pollutants such as carbohydrate nutrient residues from industrial effluents constitute a great challenge on ecosystem health. Heavy metals are common contaminants in aqueous streams and are considered as priority pollutants since they are harmful to organisms even at very low trace levels. The removal of hazardous pollutants from wastewater has been an important issue for the environmental protection.

Currently, various methods such as oxidation [1], ultra-filtration [2], ion exchange [3] and so on, have been applied in the removal of chemical pollutants from water. Of all the methods, adsorption is one of the most effective technologies due to the advantages such as high efficiency, easy availability of media or materials for use as adsorbents, low cost and convenience [4]. Therefore, development of an effective adsorbent is essential for the adsorption process applied in the effluents treatment.

Chitosan (CHT) derived from the deacetylation of chitin, is a well-known biosorbent and has been extensively studied in the field of wastewater treatment due to existence of a high number of adsorption groups and thus possesses a high adsorption capability [5]. However, this material has some disadvantages, such as low solubility in common solvent, weak mechanical resistance and low stability in acidic solutions. To overcomethis problem, chitosan chains can be connected with other polymers to form an intense complex with improved properties. Recently, chitosan composites have

been developed to absorb heavy metals and dyes from effluent [6]. Thato et al. prepared a chitosan-lignin-titania nanocomposites for an efficient removal of brilliant black dye from aqueous solution [7]; Rathinam et al developed a bio-composite by conjugating chitosan to lysozyme using glutaraldehyde as a crosslinker and found the chitosan-lysozyme biocomposite showed excellent removal of Cr (VI) along with concurrent removal of other heavy metals such as Cd (II) and Ni (II) ions from aqueous mixtures [8]. These previous researches indicated that chitosan might serve as a promising composite material to remove dyes and heavy metals from effluents. Cellulose is a renewable polymer produced sustainably in large quantities. Nowadays, many cellulose derivative-based biosorbents have been successfully used to remove heavy metal ions from effluents, especially the biosorbents based on the modified cellulose with carboxyl and quaternary ammonium groups. They have shown better adsorption capabilities than native cellulose [9, 10]. Herein, a novel cellulose derivative, cellulose sulfate (CS) with a biocompatible and hydrophilic substituted group, is utilized for the modification of chitosan to improve its functions[11].

In this study, an environmental friendly adsorption microsphere was prepared from CHT and CS composite in an ionic liquid solution, containing ferroferric oxide (Fe_3O_4) nanoparticles for the benefit of subsequent separation. The adsorptive performance of the microsphere was evaluated for pollutants removal through batch experiments with a simulated wastewater containing bovine serum albumin (BSA), Congo red dye and heavy metals.

2. Materials and methods

2.1. Materials
Chitosan (Molecular weight 140000 g/mol) with 90% deacetylation was purchased from Jinchun Biological Technology Co., Ltd. (Shanghai, China). Cellulose sulfate with different degrees of substitution (DS) were prepared by the heterogeneous reaction as described previously[12]. The ionic liquid (IL) used in this study was 1-ethyl-3-methylimidazolium acetate ([Emim]Ac), which was purchased from Chenjie Chemical Co., Ltd. (Shanghai, China). Nano Fe_3O_4 was purchased from Chenjie Co., Ltd. (Shanghai, China). Unless otherwise stated, all other reagents and chemicals were analytic grade.

2.2. Preparation of magnetic chitosan-cellulose sulfate composite microspheres
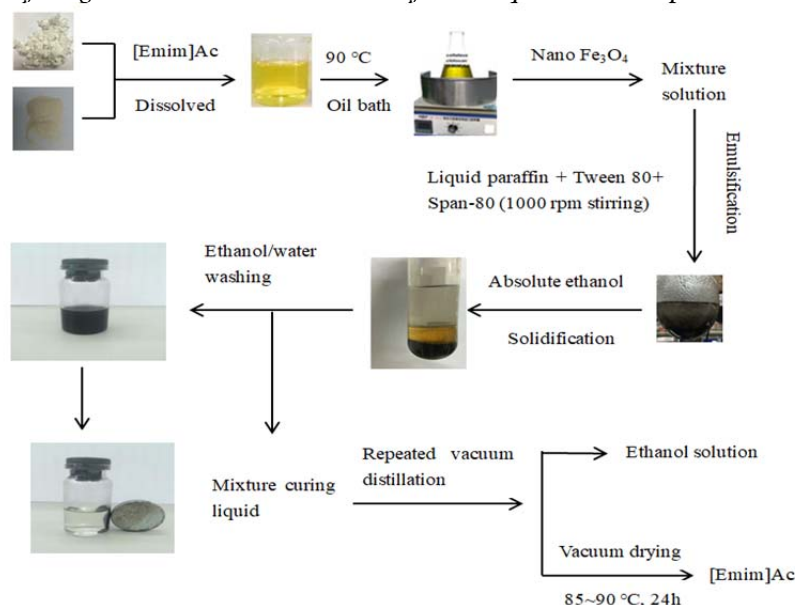

Figure 1. Scheme of the mesporous chitosan-cellulose sulfate microspheres preparation.

Mesoporous chitosan-cellulose sulfate composite microspheres were synthesized by sol-gel transition method as shown by the schematic representation in Figure 1. Chitosan (CHT) and cellulose sulfate (CS) were dried at 70 ˚C for 24 h in a vacuum oven before use. Then, 0.5 g CHT and CS were separately dissolved in 10 ml [Emim]Ac at 90˚C for 3 h and mixed together with varied volume ratio to obtain a series of CHT-CS mixture solutions. Subsequently, 30% (g/ml) nano Fe_3O_4 powder was added to CHT-CS mixture solution and vigorously agitated for 30 min. After that, the magnetic fluid (water phase) was immediately dispersed into a solution (oil phase) containing liquid paraffin, Tween 80 and Span 80 with different water/oil (w/o) volume ratios and agitation was carried out at 1000 rpm in a 90˚C oil bath for 2.5 h. By adding 2 times volume of absolute ethanol into the reaction solution and slowly cooling it down at the rate of 5˚C per 10 min to room temperature, the mesoporous microspheres were formed. The chitosan-cellulose sulfate-Fe_3O_4 microspheres products were separated from solution by external magnet and washed several times with 80% (v/v) ethanol/deionized (DI) water 3 times. Finally, magnetic microspheres were freeze-dried for the experiments, coded as chitosan-cellulose sulfate-Fe_3O_4 (CHT-CS-Fe_3O_4).

2.3. Characterization of chitosan-cellulose sulfate-Fe_3O_4 microspheres

Fourier transform infrared (FT-IR) spectra of the microspheres and raw materials were measured by the KBr disk method on a **VEXTEX70 FTIR** spectrophotometer **(Bruker Co.Ltd., Germany).**The morphology and structure of the microspheres were observed by the scanning electron microscopy (SEM, LEO1530 VP, Zeiss, Germany) with an accelerating voltage of 10 kV, equipped with a secondary electron detector and energy dispersive X-ray microanalysis (EDS). Samples were freeze-dried and coated with gold before observation. The Horiba model LA-920S laser light-scattering particle size distribution analyzer (Horiba Instrument, Japan) was used to measure the particle size distribution. The magnetic properties were analyzed with Physical Property Measurement System (PPMS, Quantum Design PPMS-9, America).

2.4. Adsorption equilibrium experiments of CHT-CS-Fe_3O_4 microspheres

The adsorption behaviors for Congo red and heavy metals by the microspheres were carried out as follows. The experiment was conducted by placing 4 mg CHT-CS-Fe_3O_4 microspheres were placed into 20 mL aqueous solution containing a concentration of 1.0 mg/L of Congo red and heavy metals respectively. The dispersion mixtures were shaken at a speed of 250 rpm to equilibrate at 25˚C for 24 h. The concentration of the supernatant was measured at predetermined time intervals. The concentrations of heavy metals were measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES, HORIBA-Jobin Yvon ULTIMA 2), while Congo red concentration was assayed by UV-Vis spectrometer at 498 nm. The amount of adsorption, q_t (mg/g), was calculated according to the following equation:

$$q_t = (c_0 - c_t) \, V/W \qquad (1)$$

The percentage removal of the adsorbate was calculated using the following equation:

$$\%Removal = (c_0 - c_t)/c_0 \times 100\% \qquad (2)$$

Where c_0 and c_t (in mg /L) denote the initial concentration and concentration of the adsorbate after time t, W is the weight of the adsorbent used (g), and V is the volume of the adsorbate solution (L).

3. Results and discussion

3.1. Synthesis of CHT-CS-Fe_3O_4 microsphere

The CHT-CS microspheres integrated with Fe_3O_4 nanoparticles were obtained by the gel-sol transition methods. The mesoporous microsphere has a magnetic susceptibility of 16 emu/g and can be easily removed from wastewater by applying external magnets. According to our pre-test, the appropriate concentration of CHT-CS mixture was fixed at 5 mg/ml for the fact that lower concentration made the microspheres disrupted and higher concentration led to a block on the pores of the mesoporous

microsphere. CHT: CS (w/w) is critical for CHT-CS microspheres preparation. As shown in Table 1, the obtained microsphere tended to swell or even collapse when CHT: CS was lower than 1:2 although a narrow distribution and mall average diameter was obtained at this ratio. When CHT: CS was reduced from 1:1 to 1:8, the surface of the microsphere becomes significantly smoother, and the particle size is more uniform. Meanwhile, the ratio of CHT: CS mixture and the emulsion solvent, namely water: oil (v/v), was found to impact the size and its distribution. With the increase of water: oil with a fixed CHT: CS of 1:1, the average diameter of uniform microdroplets decreased sharply. In consideration of both the stability and diameter of the microsphere, water: oil of 1:6 was selected during the followed preparation.

Table 1. Percentage size distribution and the average size of CHT-CS-Fe$_3$O$_4$ microspheres prepared under different conditions.

Conditions	Percentage size distribution (%)				Ave.size
CHT:CS(w/w) [a]	5-10μm	10-50μm	50-100μm	100-200μm	(μm)
1:2	0.9±0.1	99.1±0.1	0	0	13.7±0.05
1:1	6.6±0.3	79.6±0.6	13.3±0.5	0.6±0.1	20.0±0.3
4:1	2.7±0.1	90.2±0.2	6.9±0.1	0.2±0.07	20.8±0.1
8:1	2.4±0.1	94.0±0.15	3.6±0.1	0	19.7±0.1
water:oil (v/v) [b]					
1:2	2.2±0.15	86.9±0.5	8.8±0.6	2.1±0.1	25.3±0.2
1:4	2.1±0.1	89.8±0.3	7.7±0.2	0.4±0.1	24.2±0.2
1:6	2.3±0.15	91.4±0.2	6.1±0.1	0.1±0.05	21.8±0.1
1:8	1.1±0.1	95.0±0.1	3.9±0.7	0	17.7±0.1

[a] water:oil (v/v) was 1:6.
[b] CHT:CS (w/w) was 1:1.

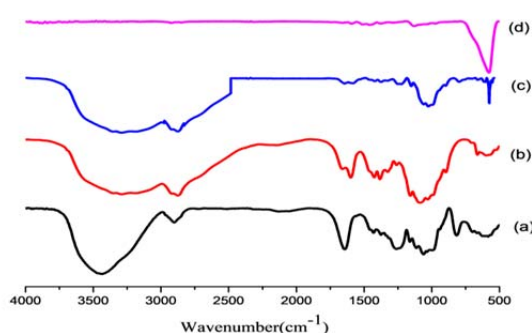### 3.2. Characterization of CHT-CS-Fe$_3$O$_4$ microsphere

Figure 2. The FT-IR spectrum of CS (a), CHT (b), CHT-CS-Fe$_3$O$_4$ microspheres (c) and Fe$_3$O$_4$ (d).

As can be observed in Figure 2, FT-IR spectrum showed 4000~3000 cm^{-1} region stands for the stretching vibration of the unreacted OH groups in CS and the band at 2874 cm^{-1} is due to C-H stretching vibration and band at 1652 c^{-1} confirming the presence of carbonyl group. The absorbance bands at 818 cm^{-1} and 1260 cm^{-1} corresponded to symmetric and asymmetric stretching vibrations of the sulfate group. In CHT, the existence of amino-group (NH^2) on the chitosan was manifested through double peaks at 3355 cm^{-1} and 3288 cm^{-1}, which were attributable to the symmetric and asymmetric stretching vibrations of the two N-H bonds. The peak of 1648 cm^{-1} was attributed to the

bending vibration of N-H. For pure Fe_3O_4, the peak at 560 cm^{-1} corresponds to FeO group, which was also found in the microsphere, indicating the successful entrapment of nano Fe_3O_4 in the composite material. The adsorption peak of the microsphere at 3446 cm^{-1} significantly decreased compared to that of CS, indicating the cross-linking between the hydroxyl groups of CS and chitosan through hydrogen bonds. However, no obvious new absorbance band occurred in the microsphere, suggesting a bending instead of chemical reaction happened during the CHT-CS microsphere preparation.
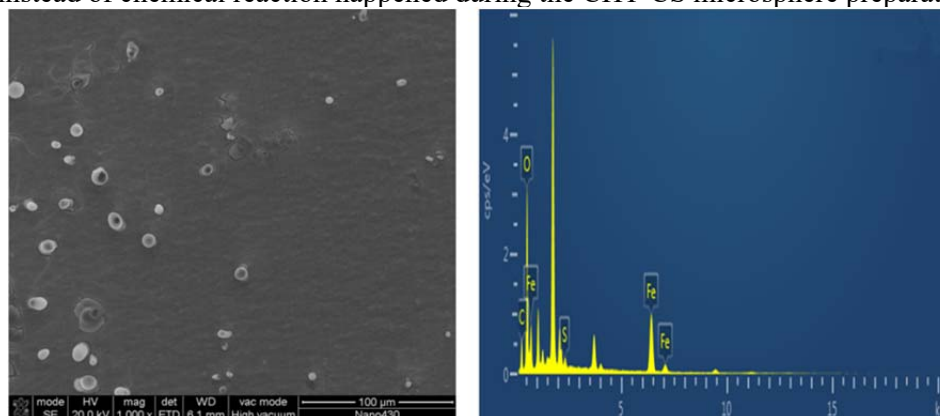

Figure 3. EDS from SEM of CHT-CS-Fe_3O_4 microspheres (weight ratio of CHT: CS was 4:1).

The typical SEM image and EDS analysis of CHT-CS-Fe_3O_4 composite are shown in Figure 3. It can observe from the SEM image that the uniform spherical particles were separately distributed. The pore size of the obtained particles were in mesoporous range. The surface and cross sections (data not shown) were found full of numerous holes and ravines structures which could provide a large number of adsorption sites. Therefore, it allowed fast channel and diffusion of pollutants into the internal pores for contact with the adsorption sites on the microsphere. EDS analysis of CHT-CS-Fe_3O_4 microspheres indicating the elemental composition clearly showed the existence of Fe partially on the surface and mostly in the core of the microsphere, confirming the successful entrapment of nano Fe_3O_4 in the CHT-CS composite.
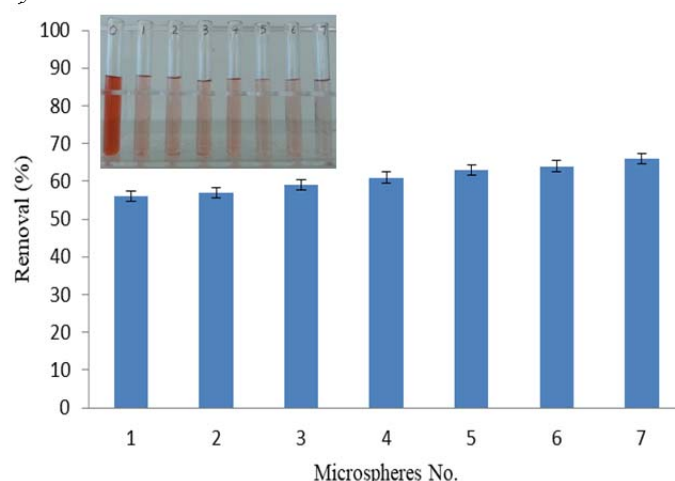
3.3. Adsorptive capacity

Figure 4. The removal efficiency of Congo red of CTH-CS Fe_3O_4 microsphere prepared by different raw material ratio. No.1~7 represents for microsphere made from CHT: CS (w/w) 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1.

Figure 4 showed the absorption of CHT-CS microsphere for the dye Congo red. As can be seen, the color of the solution rapidly changed within 5 minutes and became nearly colorless and transparent, which showed their excellent adsorption properties. The removal efficiency increased from 56% to 66% with the increasing of the portion of CHT in the composite microsphere. Microsphere No.7 with CHT: CS of 1:6 showed the highest removal efficiency of 68%, which indicated that the CHT with cation functional groups played a more important role in removing the anion dye Congo red through electrostatic interaction. However, a higher CHT: CS ratio was impossible because the microsphere would become less uniform and the whole morphology will disrupt. Therefore, in the following study, microsphere with CHT: CS ratio of 6:1 was chosen for further adsorption test.
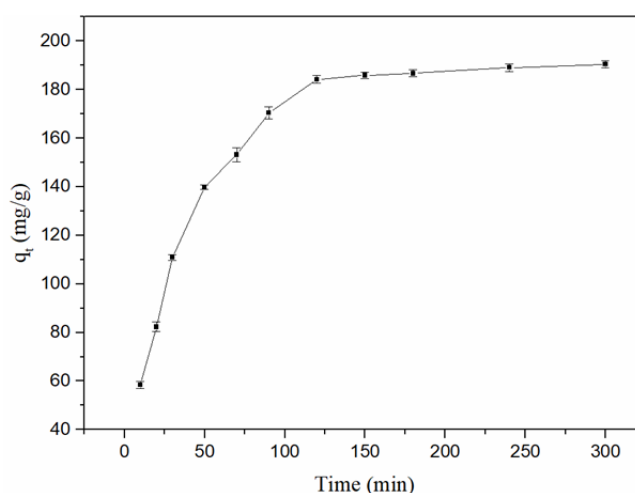

Figure 5. The adsorption capacity of Pb^{2+} by CTH-CS-Fe_3O_4 microsphere. (T = 25±0.5˚C; pH=5.0; adsorbent dosage = 4.0 g/L).

Figure 5 showed the adsorption of Pb^{2+} by CHT-CS-Fe_3O_4 microsphere. As can be seen, the absorption capacity of Pb^{2+} increased rapidly during the first 120 min and reached equilibrium with the highest adsorption capacity of 189 mg/g, and thus the maximum Pb^{2+} removal efficiency reached 93%, showing the mesoporous microsphere exhibited an excellent adsorption for Pb^{2+} in the simulated waste water containing Pb^{2+}. However, in most practical application, the pollutants are more complex containing multiple contaminants other than a single Pb^{2+} contaminant. Thus more pollutants were considered simultaneously in the next study.
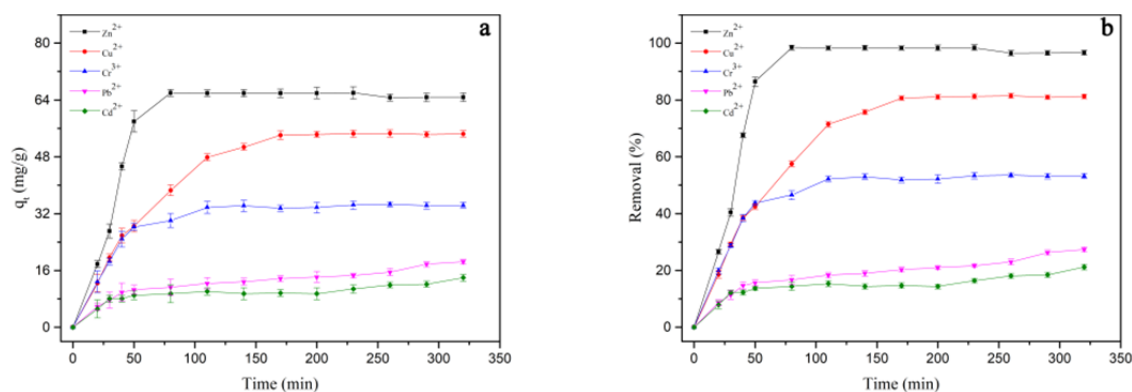

Figure 6. Time profile of q_t (a) and removal (b) of Zn^{2+}, Cu^{2+}, Cr^{3+}, Pb^{2+} and Cd^{2+} with CHT-CS microspheres (T = 25±0.5 ˚C; pH=5.0; adsorbent dosage = 4.0 g/L).

The adsorption selectivity for different heavy metal ions by CHT-CS microsphere was also studied using the mixed solution containing Zn^{2+}、Cu^{2+}、Cr^{3+}、Pb^{2+} and Cd^{2+}. As shown in Figure 6, the equilibrium adsorption capacity for Zn^{2+}、Cu^{2+}、Cr^{3+}、Pb^{2+} and Cd^{2+} was 64.8 mg/g, 54.5 mg/g, 34.3 mg/g, 18.5 mg/g and 14.0 mg/g, respectively. It is notable that the adsorption capacity for Pb^{2+} decreased significantly compared to using a solution containing Pb^{2+} only. The removal rate followed the order of $Zn^{2+} > Cu^{2+} > Cr^{3+} > Pb^{2+} > Cd^{2+}$ with the highest removal of Zn^{2+} 96.6%, which was similar with previous report [13]. Such a difference demonstrated that the porous microspheres have very different adsorption abilities for different ions, which was related to the radius of the hydrate ions, the free energy of hydration, and the activity of the ions as well, and could be explained from the proton exchange mechanism [6].

4. Conclusions

A mesoporous microsphere was developed with a natural polymer CHS and a cellulose derivative CS in an ionic liquid Solution by gel-sol transition methods. The obtained CHT-CS-Fe_3O_4 microsphere exhibited excellent performances in adsorbing and removing both the ionic dye and cationic heavy metals in water. Additionally the used mesoporous absorbents can be easily removed from wastewater by applying an external magnetic field. CHT-CS-Fe_3O_4 microsphere showed great potential in waste water treatment for adsorption and removal of the toxic and hazardous substances.

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