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An environment-friendly and multi-functional absorbent from chitosan for organic pollutants and heavy metal ion

Ang Li, Runjun Lin, Chong Lin, Bianyang He, Tingting Zheng, Lingbin Lu*, Yang Cao

Key Lab of Advanced Materials of Tropical Island Resources, Ministry of Education, College of Materials and Chemical Engineering, Hainan University, Haikou, 570228, Hainan, China

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A B S T R A C T

Developing environment-friendly green absorbents for disposal of wastewater remains to be studied. In this paper, the cross-linked chitosan aerogel (CsA) as an environment-friendly absorbent was obtained by a simple method involving cross-linked process and freeze drying technique. Compared with conventional absorbents, the porous chitosan aerogel was provided with unique properties such as low density (0.0283 g/cm^3), high porosity (97.98%) and outstanding adsorption performance. The chitosan aerogel also displayed good reusability and excellent elasticity with a maximal thickness recovery up to 96.8% of the original thickness. The as-prepared absorbent exhibited preferable adsorption capacities for crude oil, diesel and copper ion (41.07 g/g, 31.07 g/g and 21.38 mg/g, respectively). The aerogel can collect a wide range of organic solvents and oils with absorption capacities up to 40 times their own weight, depending on the density and viscosity of the liquids. The adsorption capacity for heavy metal ion was also considerable and the maximum adsorption capacity (q_m) of the aerogel for copper ion was 35.08 mg/g according to Langmuir isotherm model. Consequently, the chitosan aerogel with versatile adsorption properties has a good potential for wastewater treatment in environmental application.

1. Introduction

With the rapid development of economy and the modern industry, water pollution caused by oil spillage and industrial wastewater discharge (Mark, 2011; Dvořák, Svojitka, Wanner, & Wintgens, 2013) has drawn extensive attention, including heavy metal ions, organic dyes and other toxic pollutants. The harmful contaminants inflict great threat on environment and human being (Govers et al., 2014). Disposal of water contamination has always been a major environmental issue all over the world. Treatment methods have been continuously exploring for decade years, such as precipitation (Al-Harahsheh, Batiha, Kraishan, & Al-Zoubi, 2014; Mbamba, Batstone, Flores-Alsina, & Tait, 2015), flotation (Saththasivam, Loganathan, & Sarp, 2016; Silva, Chiavone-Filho, Neto, & Foletto, 2015), membrane technologies (Lin, Yang, Li, & Chen, 2015; Neoh, Noor, Mutamim, & Lim, 2015), oxidation-reduction (Sekaran et al., 2014; Li et al., 2014), photocatalytic degradation (Murgolo et al., 2015), adsorption (Bi et al., 2013), etc. Among these methods, adsorption has been wildly concerned by researchers in virtue of its simple operation, high removal rate, less secondary pollution, as well as low cost. Various absorbents were studied and applied in water treatment, from inorganic materials (e.g., clays (Bhattacharyya & Sen Gupta, 2011), zeolites (Wang & Peng, 2010), carbon nanotubes (Inyang, Gao, Zimmerman, Zhang, & Chen, 2014), exfoliated graphite (Huang et al., 2011)) to synthetic organic materials (including polyurethane (Li et al., 2015), polystyrene (Lee et al., 2013; Sun et al., 2012), polypropylene (Li & Wei, 2012), etc). However, most of inorganic absorbents remain in laboratory because of their expensive cost, low adsorption capacity and poor reusability. Likewise, the defects of synthetic organic absorbents (such as non-biodegradability and non-renewability) are still to be solved before their widespread application.

Chitosan (Cs, poly-β-(1 → 4)-2-amino-2-deoxy-D-glucose), produced by alkaline deacetylation of chitin, is one of the most abundant polysaccharides on the earth especially in coastal regions and well known for renewable, nontoxic, biocompatible and degradable (Bhatnagar & Sillanpää, 2009). As the only natural alkaline and cationic polysaccharide, chitosan has great potentials in wastewater treatment, because its amine and hydroxyl groups act as active sites for heavy metal and anionic organic pollutants (Crini & Badot, 2008). Owing to the functional groups, powdery chitosan can be dissolved and cross-linked to form the three-dimension network (Kadib & Bousmina, 2012). Compared with powdery and flake absorbents, porous chitosan aerogel obtained

* Corresponding author.
E-mail address: lulingbin@126.com (L. Lu).

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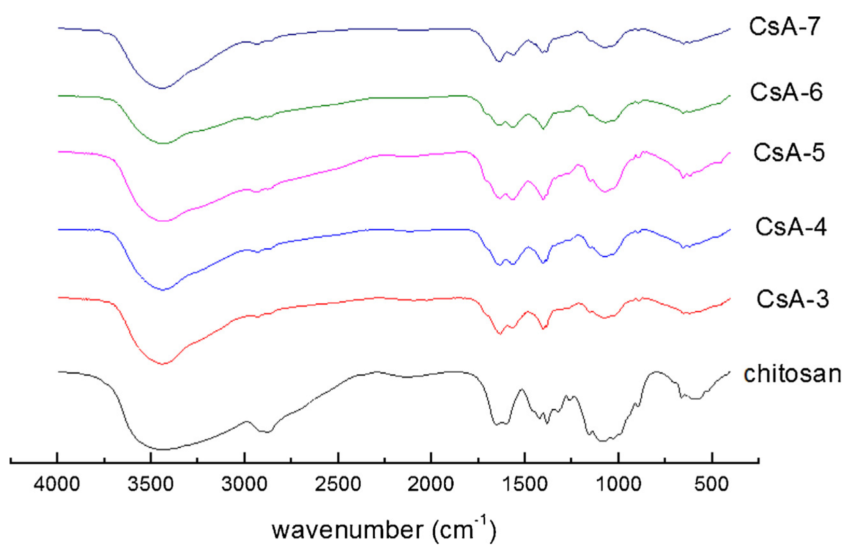

Fig. 1. FT-IR spectra of chitosan and chitosan aerogels with glutaraldehyde concentration varying from 3 wt% to7 wt%.

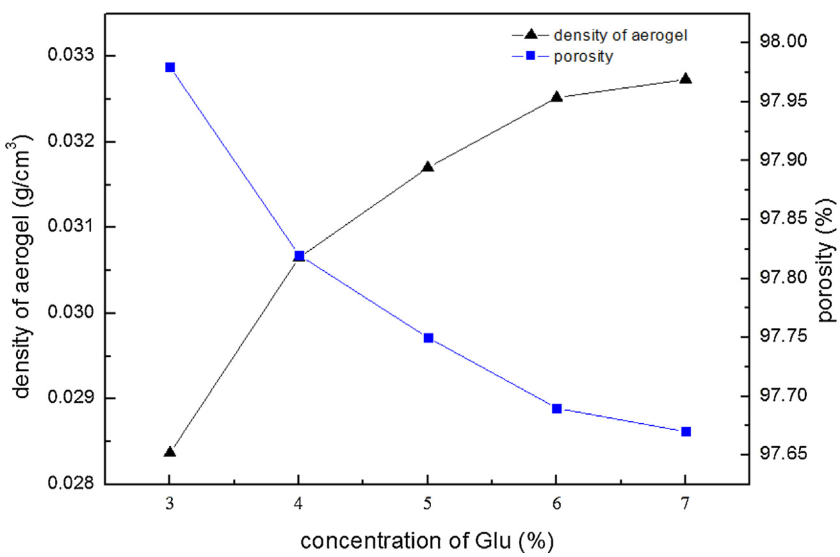

Fig. 2. Effect of glutaraldehyde concentration on density and porosity of chitosan aerogel.

by extracting liquid solvent in the hydrogel possesses unique properties such as higher adsorption capacity, easier separation process and environment-friendly (Sokker, El-Sawy, Hassan, & El-Anadouli, 2011). As the lightest solid material, aerogel has been reported to be high porosity, low density, large specific surface area, low heat conductivity coefficient, and low dielectric constant (Nguyen et al., 2013; Aulin, Netrval, Wågberg, & Lindström, 2010). Currently, most researchers pay attention to chitosan aerogel beads or aerogel films for metal and dye adsorption (Ennajiha, Bouhfid, Essassi, Bousmina, & Kadib, 2012; Kadib & Bousmina, 2012; Mututuvari & Tran, 2013), while few of them notice that bulk chitosan aerogels have great advantages for multiple pollutants adsorption. Actually, the multi-functionality is also a significant parameter to estimate absorbents (Kyzas, Kostoglou, Lazaridis, & Bikiaris, 2013).

In this work, chitosan aerogel monolith as a versatile absorbent for oils, organic pollutants and heavy metal ions adsorption was prepared by cross-linked and freeze-drying technique. Copper ion and a wide range of oils and organic solvents were used as adsorbates to investigate the multi-functional adsorbability of the chitosan aerogel. The effects of cross-linking degree on adsorption property and elastic property of the aerogel were discussed. The bulk shape solid aerogel could be easily separated from environment during the recycling process.

2. Materials and methods

2.1. Materials

Chitosan ($M_w = 3.0 \times 10^5$ with 90% deacetylation degree, biological reagent) and ammonium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. and glutaraldehyde was obtained from Tianjin Fu Chen Chemical Reagents Factory. Glacial acetic acid and ammonia solution (25–28%) were received from Xilong Chemical Co., Ltd., China. Carbon tetrachloride and absolute ethanol were supplied by Guanghua Sci-Tech Co., Ltd., China. Copper chloride from Tianjin Yongda Chemical Reagent Co., Ltd., and bis(cyclohexanone) oxalyldihydrazone (BCO) from Aladdin Industrial Inc., were used as metal adsorbate and indicator, respectively. All chemicals and solvents were analytic grade and used as received without further purification unless otherwise stated. Deionized water was used in all experiments.