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Converting untreated waste office paper and chitosan into aerogel adsorbent for the removal of heavy metal ions

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ABSTRACT

The utilization of waste paper, an obsolete recyclable resource, helps to save resources and protect environment. In this paper, an aerogel was prepared to convert the waste paper into a useful material, which was used to adsorb heavy metal ions and handle water pollution. Combining waste office paper and chitosan, the aerogel obtained the enhanced mechanical strength, acid resistance and high adsorption capacity (up to 156.3 mg/g for Cu^{2+}). This adsorption process obeyed the pseudo-second order model and the Langmuir model. The research showed that a coordination compound was formed between amino group and Cu^{2+} during the adsorption process. The adsorbent could be regenerated well in 0.1 M H_2SO_4 with up to 98.3% desorption efficiency. The low cost, environmental friendliness, excellent adsorption capacity and regeneration ability made this novel aerogel a promising adsorbent for heavy metal ions. And this conversion is an effective reuse way of waste paper too.

1. Introduction

Recycling and utilization of waste paper can save resources and protect the environment (Hassanzadeh, Aminlashgari, & Hakkarainen, 2015; Pivnenko, Eriksson, & Astrup, 2015; Zhang et al., 2017). As an obsolete and recyclable resource, waste paper is mainly used for the preparation of paper pulp in paper-making industry (Ashrafi, Yerushalmi, & Haghighat, 2015; Rintala & Puhakka, 1994). However, it can only recycled 2.4 times (Zhang et al., 2015) on average in making new paper because of its gradual decrease in fiber strength during each cycle. Therefore, expanding the application and techniques, which can convert waste paper into valuable products, is beneficial to the recycling of waste paper. The potential applications can be alcohol (Nishimura et al., 2016) and methane (Baba, Tada, Fukuda, & Nakai, 2013) preparation, furniture (Yue, Liu, Lu, Lu, & Yang, 2012) and building materials (Aigbomian & Fan, 2013; Raut, Sedmake, Dhunde, Ralegaonkar, & Mandavgane, 2012). Waste paper can also be used as sorbent for adsorption of heavy metal ions and cleaning of spilled oil from water.

Aerogel made from waste paper can be used for oil spill cleanup and organic pollution. Carbon microbelt aerogel (Bi et al., 2014) made from waste office paper and carbon aerogel from waste newspaper (Han, Sun, Zheng, Li, & Jin, 2016) exhibited excellent hydrophobicity and high absorption capacity for oils and organic solvents. Recycled cellulose based aerogel (Feng, Nguyen, Fan, & Duong, 2015; Nguyen et al., 2013) from waste paper can also be used in oil sorption after hydrophobic modification. In addition to oil spills, heavy metal ions are also a significant source of water pollution (AlOthman, Alam, & Naushad, 2013; Naushad, ALOthman, Awual, Alam, & Eldesoky, 2015). Waste paper can also be made into adsorbent for the removal of metal ions from contaminated water. However, the adsorption capacity is low when waste paper is used as adsorbent directly. Therefore, many methods have been proposed by researchers to improve this property. Modification and compounding other materials are very effective ways to obtain higher adsorption capacity (Jabli, Saleh, Sebeia, Tka, & Khiari, 2017; Naushad, 2014; Tka, Jabli, Saleh, & Salman, 2018). Waste paper is rich in cellulose fibers, which products possess considerable adsorption capacity for metal ions through modification or compositing with other materials. Graft copolymers of cellulose with glycidyl methacrylate and some comonomers (Chauhan, Guleria, & Sharma, 2005) enhanced their sorption capacity for Cr^{6+}, Cu^{2+} and Fe^{2+}. The succinylated mercerized cellulose modified with triethylenetetramine (Gurgel & Gil, 2009) was used to adsorb metal ions. Its adsorption capacity for Cu^{2+}, Cd^{2+} and Pb^{2+} were up to 69.4 mg/g, 87.0 mg/g and 192.3 mg/g, respectively. Chitosan/cellulose film, beads or other composites (Li & Bai, 2005; Lima, Lazarin, & Airoldi, 2005; Luo, Zeng, Liu, & Zhang, 2015; Sun, Peng, Ji, Chen, & Li, 2009; Xiao & Hu, 2017) possessed efficient adsorption capacity for Cu^{2+} (27–122 mg/g) and some other metal ions. Meanwhile, the strength and homogeneity can be increased through compositing chitosan and cellulose.

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In addition, chitosan was often used to adsorb Cu^{2+}, Fe^{2+}, Cr^{6+}, Zn^{2+}, Ni^{2+},Cd^{2+}, Pb^{2+} and other metal ions (Kanmani, Aravind, Kamaraj, Sureshbabu, & Karthikeyan, 2017; Wang & Chen, 2014) as the form of powder or flake (Zhu, Jiang, Xiao, & Li, 2010). But poor acid resistance, low mechanical strength and difficult separation restricted development of chitosan adsorbent (Tanhaei, Ayati, Lahtinen, & Sillanpää, 2015; Xiao & Hu, 2017).

In this paper, a new unbleached waste paper/chitosan aerogel was prepared through sol-gel process and freeze drying technique. The enhanced mechanical strength and acid resistance were expected because of hydrogen bonds between cellulose and chitosan. What is more, because the presence of ink has no obvious effect on adsorption, deinking (Franks & Page, 2003; Saxena & Singh Chauhan, 2017) for waste office paper was not necessary in this simplified process. Adsorption properties and mechanism of the aerogel for heavy metal ion Cu^{2+} were investigated in details. This work provided a potential application for waste office paper, and an economic way for removing heavy metal ions from contaminated water.

2. Materials and methods

2.1. Materials

Waste office paper (WP) was smashed mechanically into small pieces. Chitosan (CS) ($M_w = 3.0 \times 10^5$ with 90% deacetylation degree, bio-logical reagent) was purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol and sodium hydroxide (NaOH) were received from Xilong Chemical Co., Ltd., China. Urea was supplied by Guanghua Sci-Tech Co., Ltd., China. Copper sulfate ($CuSO_4$) supplied by Guanghua Sci-Tech Co., Ltd., China, was used as the source of Cu^{2+}. Ammonium hydroxide and ammonium chloride purchased from Sinopharm Chemical Reagent Co., Ltd., were used as buffer solution in the detection of copper. Bis(cyclohexanone)oxalyldihydrazone (BCO) from Aladdin Indus-trial Inc., was used as indicator in the detection of copper. All chemicals were analytic grade and used as received without further purification unless otherwise stated. Deionized water was used in the whole process of experiments.

2.2. Preparation of waste paper aerogel, chitosan aerogel and waste paper/chitosan aerogel

100 mL NaOH/urea aqueous solution (7 wt%/12 wt%) was kept in refrigerator at −18 °C for 1 h. Then, chitosan was instantly added to the solution and stirred at 1000 rpm at room temperature. After 30 s, waste office paper was added and stirred 10 min to form a homogeneous mixture. Stable hydrogel was obtained by standing at room temperature for 2 h, and then the hydrogel was washed with deionized water until pH = 7. Waste paper/chitosan aerogel (WP-CSA) was obtained after freeze drying for 48 h.

100 mL NaOH/urea aqueous solution (7 wt%/12 wt%) was kept in refrigerator at −18 °C for 1 h. Then, 4 g waste paper was instantly added to the solution and stirred for 10 min at 1000 rpm at room temperature. Hydrogel was obtained by adding 100 mL ethanol and keeping for 24 h at room temperature. Then the hydrogel was washed with deionized water until pH = 7. Waste paper (WPA) was obtained after freeze drying for 48 h.

Similar to the preparation of WPA, 4 g chitosan was instantly added to the same NaOH/urea aqueous solution and stirred for 10 min at 1000 rpm. Chitosan hydrogel was obtained by adding 100 mL ethanol and keeping for 24 h at room temperature. Then the hydrogel was washed with deionized water until pH = 7. Chitosan (CSA) was obtained after freeze drying for 48 h.

2.3. Cu^{2+} adsorption

Cu^{2+} (from $CuSO_4$) concentration was determined by BCO-Spectrophotometry method (Li et al., 2016; Yang et al., 2010). Briefly, 1 mL Cu^{2+} solution, 5 mL BCO solution (the concentration is 2 g/L, the solution is the mixture of water and ethanol with a volume ratio of 1:1) and 10 mL buffer solution were added into a 50 mL volumetric flask. After bringing to volume with deionized water and keeping for 10 min, the absorbance was measured at 600 nm. And the Cu^{2+}concentration was calculated by the standard curve, which was measured by Cu^{2+} solution with known concentration. All adsorption experiments were carried out at room temperature (25 ± 1 °C).

Kinetic studies for Cu^{2+} were conducted through placing 0.5 g WP-CSA in 500 mL 100 mg/L Cu^{2+} solution and shaking the solution at 150 rpm. The adsorption capacity (Q_t, mg/g) was calculated according to the following formula (1) (Saleh & Danmaliki, 2016):

$$Q_t = V(C_0 - C_t)/m_0 \quad (1)$$

where V (L) is volume of Cu^{2+} solution and m_0 (g) is weight of adsorbent. C_0 (mg/L) and C_t (mg/L) are Cu^{2+} concentration at initial time and given time t, respectively. The Cu^{2+} adsorption kinetics of WP-CSA were evaluated by the pseudo-first order kinetic equation (as shown in formula (2)) and the pseudo-second order kinetic equation (as shown in formula (3)) (Ho & McKay, 1999; Saleh, 2015).

$$Q_t = Q_e(1 - \exp(-k_1 t)) \quad (2)$$

$$Q_t = (k_2 Q_e^2 t)/(1 + k_2 Q_e t) \quad (3)$$

In these two formulas, Q_e (mg/g) is the fitting value of equilibrium adsorption capacity, t (h) is the adsorption time, Q_t (mg/g) is the adsorption capacity at time t, k_1 and k_2 are adsorption rate constants of the pseudo-first order kinetic equation and the pseudo-second order kinetic equation, respectively.

Isothermal adsorption for Cu^{2+} was tested by placing 0.1 g WP-CSA in 100 mL 10–500 mg/L Cu^{2+} solution and shaking at 150 rpm for 24 h. The data was fitted by both the Langmuir model (as shown in formula (4)) and the Freundlich model (as shown in formula (5)) (Kenawy et al., 2017; Li et al., 2016). The saturated adsorption capacity (Q_s) was obtained from the Langmuir model.

$$1/Q_e = 1/Q_s + 1/(aQ_sC_e) \quad (4)$$

$$\ln Q_e = \ln K_f + (1/n)\ln C_e \quad (5)$$

In the two models, Q_e (mg/g) is equilibrium adsorption capacity, C_e (mg/L) is equilibrium concentration, a is Langmuir adsorption constant, K_f and $1/n$ are Freundlich adsorption constant.

Influence of pH of aqueous solution on Cu^{2+} adsorption was tested by placing 0.1 g WP-CSA in 100 mL 100 mg/L Cu^{2+} solution with different initial pH (1.86–5.52) and shaking the solution at 150 rpm for 24 h. And the pH of the solution was controlled by appropriately adding 10 μL dilute sulfuric acid (0.1%) with a pipette every 30 min.

2.4. Desorption

The desorption study was done using different acid solvents (0.1 M HCl, H_2SO_4 and HNO_3) (Alqadami, Naushad, Alothman, & Ghfar, 2017). 0.1 g WP-CSA was added to a conical flask containing 100 mL Cu^{2+} solution (100 mg/L) and shaking the solution at 150 rpm for 24 h. After that, WP-CSA was taken out and cleaned the surface with filter paper. And the adsorption capacity was measured as the above mentioned method. Then the Cu^{2+}-loaded WP-CSA was placed in a conical flask containing 100 mL 0.1 M acid solution (HCl, H_2SO_4 and HNO_3) and shaken at 150 rpm for 1 h. After that, the solution was separated and the Cu^{2+} concentration in solution was determined by the method described above. The desorption capacity Q_d was calculated according to the following Eq. (6).

$$Q_d = (C_s V)/m_0 \quad (6)$$

In this equation, Q_d (mg/g) is the desorption capacity. C_S and V are the Cu^{2+} concentration and the volume of acid solution. And m_0 is the