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Fast removal of copper ions from aqueous solution using an eco–friendly fibrous adsorbent

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HIGHLIGHTS

- Fibrous adsorbents for metal ions remediation with easy recovery.
- Chitosan functional PET pretreated by plasma was used as an eco-friendly adsorbent.
- Adsorption capacity of 68.97 mg g^{-1} for Cu (II) by the PET-AA-CS.

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ABSTRACT

Functional PET fiber (PET–AA–CS) was prepared by oxygen–plasma pretreatment and grafting of acrylic acid (AA) and low–molecular–weight chitosan (LMCS) on the polyethylene glycol terephthalate (PET) substrate. This adsorbent was targeted for quick removal of metal ion in river pollutions with an easy recycling of the fiber after emergency processing. The fabricated PET–AA–CS was characterized by the scanning electron microscope (SEM), contact angle, fourier transform infrared (FTIR) spectra and X–ray photoelectron spectroscopy (XPS) to look into its morphology, surface functional groups, and adsorption mechanism of copper ions from the aqueous solution. The overall adsorption process of copper ions on the PET–AA–CS was pH–dependent with an optimal pH value of 5.0, at which a maximum capacity of 68.97 mg g^{-1} was obtained. The result of fitting also shows that adsorption process follows the Langmuir isotherm and pseudo–second–order model. Moreover, the material shows good stability during 5 cycles of adsorption and desorption, and also shows no significant effect of co–existing ions including Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, and et al. In general, PET–AA–CS developed in this study shows significant benefit of eco–friend and cost-efficiency for fast removal of copper ions in potential river metal pollutions comparing with traditional adsorbents.

1. Introduction

The contamination of industrial effluents containing toxic metal ions has become a serious problem environmentally and ecologically. It has shown a serious threat to human health and other living organisms (Liao et al., 2010; Crini, 2005). And for this reason, the treatment of toxic metal ions pollution in water has received an extensive concern and become a hot topic in environmental researches. Many methods, e.g. chemical precipitation (Fu and Wang, 2011; Kurniawan et al., 2006), ion exchange (Dabrowski et al., 2004), membrane separation (Zuo et al., 2005), oxidation/reduction, electrolysis (Su et al., 2011), solvent extraction (Serife et al., 2012), and adsorption (Babel and Kurniawan, 2003; Ihsanullah et al., 2016) have been used for the removal of toxic metal ions from water. Among these methods, adsorption has been one of the most promising techniques. Although the process is usually simple, suitable adsorbents for river emergency treatment are not always the same as it for industrial wastewater treatment. The well developed adsorbents for industrial wastewater include activated carbon (Mohan et al., 2006), resins (Florence and Batley, 1976), fly ash (Pehlivan et al., 2006), red mud (Gupta et al., 2001), grapheme (Yang et al., 2010), and chitosan (Gerente et al., 2007). However, most of these adsorbents do not show good balance between cost and ecological benefit, being either too expensive or poor eco-friendly during river water treatment. E.g., people used lime and activated carbon to treat contaminated water polluted by

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heavy metal ions in the past years. But lime causes serious ecological damage while activated carbon is too expensive for the large-scale application. Hereupon, it is urgent to develop a simple, efficient, and low-cost adsorbent for the removal of metal ions from river water.

Among these adsorption materials, chitosan is a well–known and cheap adsorbent for that it is rich in nature, non–toxic, biocompatible, biodegradable and eco-friendly (Wan Ngah et al., 2002; Wan Ngah et al., 2011). From the stand point of materials, chitosan is rich in functional groups including amino and hydroxyl groups which are the natural binding sites for metal ions through a series of processes/reactions of electrostatic interaction, ion–exchange, and coordinated complexation (Wan et al., 2004). However, the raw material of particle chitosan is usually difficult to recycle after adsorption reaction and shows poor stability especially in acidic aqueous solution. To overcome these disadvantages, chitosan composites need further development, e.g., cross-linked chitosan, thin-film (Nayak et al., 2015), core-shell (Dodi et al., 2012) adsorbents, and et al. There are at least two advantages for these composite chitosan adsorbents comparing with raw chitosan particles. Firstly, thin-film absorbents could significantly reduce the usage of chitosan, and therefore reduce the cost of the adsorbents. Secondly, the state-to-the-art material could be designed with different supporting substrates in order to obtain specific morphologies and functions, e.g. magnetically recycling (Ramalingam et al., 2015). Along with this strategy, many studies have focused on the improvement of the performance of raw chitosan by using crosslinking agents such as glutaraldehyde (GA) (Guibal et al., 1998), epichlorohydrin (ECH) (Miretzky and Cirelli, 2009), ethylene glycol ether (EGDE) (Chiou and Li, 2003) recently. Although crosslinking agents could improve mechanical properties of the chitosan and decrease the loss in the acid solution, the cross–linking reaction would also reduce the numbers of binding sites on the chitosan, leading to the decrease of the adsorption capacity. In addition, the cross–linking agents (eg. GA and EGDE) are harmful to people due to their physiological toxicity. A more candidate to fabricate chitosan-based adsorbent is to coat or graft chitosan on the supporting materials, especially on fibrous supporting materials. Usually, the composite fiber adsorbents usually have a higher adsorption rate and adsorption capacity comparing with adsorption resin. Moreover, the fibrous adsorbents can be used conveniently in the many forms: such as strips, rope or net. Particularly, the composite fibrous adsorbent can be easily pulled out from water in order to prohibit potential secondary pollution after usage. This composite of fibrous chains are installed in the sections of the polluted river, as shown in Fig. 1, which can capture metal ions along the river flow. The chains could be easily collected from the application system at regular intervals.

In this work, the fibrous adsorbent was prepared by grafting low–molecular–weight chitosan (LMCS) on polyethylene glycol terephthalate (PET) fibers. PET fiber was chosen as a substrate for its excellent thermal stability, low density, non–toxicity, and easy and reliable supply. However, as the supporting material, PET is high–crystalline, chemically inert, and hydrophobic, and therefore it is unfavorable for the grafting LMCS on its surface. Further surface modification is required before the grafting LMCS molecules. There are many methods, e.g., physic–chemical and chemical methods include alkaline treatment for surface ester hydrolysis (Brueckner et al., 2008), gamma irradiation (Kumar et al., 2012), plasma (Lai et al., 2006) etc. to do this modification. We developed the method of using plasma pretreatment because that plasma treatment (Zhang et al., 2014) is a time–efficient, versatile, low–cost and eco–friendly technology. By this plasma pretreatment, free radicals, electrons, and ions during the plasma discharging process would activated the surface chemical states of the fiber. Therefore, the surface after modification could have excessive active sites for grafting functional groups in the next step (Chan et al., 1996; Zhu et al., 2014). However, the reactive surface could not last for a long time, and we use acrylic acid (AA) as the protecting layer to obtain the PET-AA (Li et al., 2013). Then low–molecular–weight chitosan was grafted on the PET-AA fibers. Copper ions were used as the model pollutant and the adsorption experiments were carried out to evaluate the adsorption capacity of copper ions on the PET–AA–CS. The isotherms, thermodynamics, and kinetics of the adsorption process were also investigated. Results showed that the PET–AA–CS could be a good candidate as cost-effective and environment-friendly adsorbent for the separation and removal of copper ions from water, especially for the emergency treatment of toxic metal pollution.

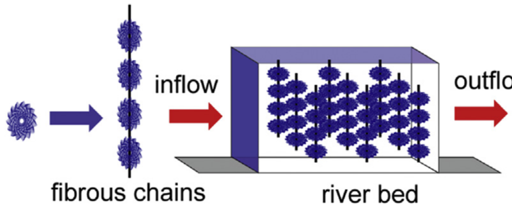

Fig. 1. The installation diagram of fibrous adsorbents for removal of heavy metal ions from river water. The composite fibrous chains are installed in the sections of the polluted river which captures metal ions along the river flow. The chains could be easily collected after the remediation via reinstallation operation at regular intervals.

2. Experimental

2.1. Materials

Small pieces of PET samples were cut from commercial PET fibers used as substrates in this study. Chitosan, N–Hydroxysuccinimide (NHS), 2–(morpholino) ethanesulfonic acid (MES) and 1–(3–dimethylaminopropyl)–3–ethylcarbodiimide Hydrochloride (EDC) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). All the other chemicals were of analytical grade and purchased from the Sinopharm Chemical Reagent Co., Ltd. (China). Stock solutions (1000 mg L^{-1}) were prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ in deionized water and further diluted to the proper concentration.

2.2. Preparation of the low–molecular–weight chitosan (LMCS)

Chitosan was pretreated by hydrogen peroxide degradation in order to obtain LMCS before grafting with the PET–AA according to a previously reported method (Huang et al., 2008). 3 g chitosan (CS) was dissolved in 150 mL of 0.1 M acetic acid solution (HAc) at room temperature under magnetic stirring for 30 min. Subsequently, H_2O_2 (12%) was added slowly to the chitosan solution, the mixture was stirred continuously and the temperature was increased to 60 °C for 3 h. At the end of reaction process, the solution was cooled down to room temperature and vacuum filtered to remove the insoluble impurities. The filtrate was added with ethanol, and the pH value was adjusted to 7.0 for the precipitation of LMCS.

2.3. Preparation of the PET–AA–CS fibers

The PET samples were cleaned in an ultrasonic cleaner (Kun Shan Ultrasonic Instruments Co., Ltd, KQ–250B) using ethanol and DI water, respectively. They were then dried and kept in vacuum (Shanghai Sumsung Laboratory Instrument Co., Ltd, DZG–6050). The PET fibers were pretreated by the plasma system (100 W,