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Fast microwave-assisted preparation of a low-cost and recyclable carboxyl modified lignocellulose-biomass jute fiber for enhanced heavy metal removal from water

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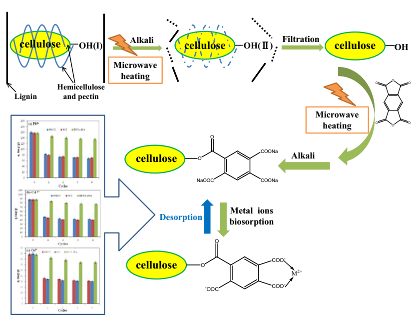
HIGHLIGHTS

- The low-cost and recyclable jute was modified for enhanced heavy metal removal.
- Microwave heating was innovatively explored in pretreatment and graft reaction.
- The tensile performance of biomass was firstly investigated.
- Adsorption equilibrium was achieved sharply in 20 min with high metal uptake.
- $CMJF_{MH}$ can be easily and effectively regenerated with EDTA-2Na solution.

GRAPHICAL ABSTRACT



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ABSTRACT

A low-cost and recyclable biosorbent derived from jute fiber was developed for high efficient adsorption of Pb(II), Cd(II) and Cu(II) from water. The jute fiber was rapidly pretreated and grafted with metal binding groups (—COOH) under microwave heating (MH). The adsorption behavior of carboxyl-modified jute fiber under MH treatment ($CMJF_{MH}$) toward heavy metal ions followed Langmuir isotherm model ($R^2 > 0.99$) with remarkably high adsorption capacity (157.21, 88.98 and 43.98 mg/g for Pb(II), Cd(II) and Cu(II), respectively). Also, $CMJF_{MH}$ showed fast removal ability for heavy metals in a highly significant correlation with pseudo second-order kinetics model. Besides, $CMJF_{MH}$ can be easily regenerated with EDTA-2Na solution and reused up to at least four times with equivalent high adsorption capacity. Overall, cheap and abundant production, rapid and facile preparation, fast and efficient adsorption of heavy metals and high regeneration ability can make the $CMJF_{MH}$ a preferred biosorbent for heavy metal removal from water.

1. Introduction

Water pollution caused by heavy metal ions such as Pb(II), Cd (II) and Cu(II) is one of the major environmental problems in many countries (Bogusz et al., 2015; Liu and Lee, 2014; Luo et al., 2015; Sargın et al., 2015; Wang and Chen, 2014) due to the non-biodegradable characteristic of heavy metal, and they tend to accumulate in the vital organs of humans and animals (He and Chen, 2014). Therefore, it is of great importance to remove heavy metals from aqueous solution rapidly and effectively. Among many techniques available for heavy metals removal from water, adsorption method is considered to be advantageous owing to the minimization of chemical sludge (Kim et al., 2015; Wang et al., 2015), ease of

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construction and operation, and low cost of promotion (Loo et al., 2012; Tran et al., 2015).

It has been a trend that lignocellulose biomass is explored as the novel biosorbents for the remediation of water contaminated with heavy metal ions (Abdolali et al., 2013; Karnitz Júnior et al., 2010; Karthik and Meenakshi, 2015) owing to their advantages of abundant production, low cost, and environmental friendliness. Despite various advantages, novel biosorbents in their native form lacked high adsorption capacities toward metallic contaminants when compared with commercial adsorbents (e.g., activated alumina or zeolite). With the aim of enhancing the adsorption performance, the original lignocellulose biomass needs to be chemically modified. In fact, the presence of three hydroxyl groups at the C2, C3, and C6 atoms of the anhydroglucose units of the cellulose backbone in the biomass has provided the possibility of introducing different types of new functionalities (e.g. such as esters (Júnior et al., 2009), amines (Wahab et al., 2010) and succinic anhydride (Gurgel et al., 2008), etc.).

In the study, jute fiber was chosen as a promising raw material owing to its low cost, renewable characteristic and abundant production (Rombaldo et al., 2014). Owing to the variable morphology and high tensile strength of jute fiber, it could be used to spin, which is more convenient to apply in the water remediation than granular absorbents. Above all, the jute fiber is rich in cellulose which can be grafted with some functional groups to enhance heavy metal removal (Chanda et al., 2015). Remarkably, considering that the cellulose of raw jute is inaccessible to the chemical modification reagents since non-cellulosic components existed (Júnior et al., 2009; Shukla and Pai, 2005), the pretreatment process is necessary and essential to improve the accessibility of hydroxyl groups in the cellulose (Dong et al., 2015; Hassan, 2015).

Although some researchers around the world have conducted the modification of cellulose (Dong et al., 2015; Gurgel et al., 2008; Shukla and Pai, 2005), there are some limitations in the literature reports: firstly, there are very few works on graft modification of jute fiber for adsorption toward heavy metal ions, and these adsorption capacities were not very high (e.g. only 8.4 mg/g for Cu (II) (Shukla and Pai, 2005)). The researchers rarely considered the potential competitive adsorption between heavy metal ions and co-ions (Na(I), K(I), Mg(II) and Ca(II)) which usually exist at much higher concentration in the natural aqueous solution. Secondly, long time for pretreatment (Melo et al., 2014) (e.g. more than 2 h for the pretreatment of jute fibers (Gao et al., 2015)) and graft modification (e.g. about 24 h for the graft modification of cellulose (Gurgel et al., 2008)) may be difficult to meet the requirements of practical application such as emergency water treatment. Besides, little attention was paid to the tensile performance of fibrous materials which could affect the spinning effect and applicability of fibrous biosorbents in the water treatment.

To solve these problems, 1,2,4,5-benzenetetracarboxylic anhydride (PMDA), a widely applicable chemical agent containing two anhydride groups per molecule, was used to react with hydroxyl groups of cellulose molecules in the jute fiber to introduce carboxylic groups via formation of ester functions for higher adsorption capacities of heavy metal ions.

Microwave heating (MH) as an alternative heat source has been proved to be more rapid and homogeneous than traditional conductive heating. Besides, the advantages of MH over other types of radiation, such as plasma irradiation, for the preparation of adsorbents are in terms of energy savings (Liao et al., 2012). It is generally considered that electromagnetic energy of MH can easily penetrate inside the particles, interact simultaneously with polar substances at the molecular level, and then is converted to heat through the motion of molecules (Deng et al., 2015; Hashem et al., 2014; Liao et al., 2012), which can lead to significantly faster reaction rates. However, few works have been mentioned in the literature describing the feasibility of MH application in the pretreatment or graft reaction of lignocellulose biomass like jute fiber. Moreover, jute fiber and chemical reagents in the study are the good microwave absorbers. Thus, it provides possibility to pretreat and modify the jute fiber by microwave heating efficiently.

In this study, we presented a fast, environment-friendly and facile method for preparation of the carboxyl-modified jute fiber under MH treatment ($CMJF_{MH}$) and evaluated its adsorption performance toward Pb(II), Cd(II) and Cu(II) ions from aqueous solutions. Basically, the initial alkaline pretreatment of raw jute was conducted under MH treatment rapidly. Then, more carboxylic groups were quickly introduced on the pretreated jute surface via formation of ester functions following MH treatment as well. The characterization tests of FTIR, SEM, EDX and tensile performance were conducted to investigate the chemical and morphological changes of the biomass. The adsorption behavior of the $CMJF_{MH}$ toward Pb(II), Cd(II) and Cu(II) from their aqueous solutions including pH-dependence, adsorption kinetics, isotherm and thermodynamic was studied, and the competitive adsorption of the three metal ions in the presence of each ion: Na(I), K(I), Mg(II) and Ca(II) at different concentrations were investigated. And the regenerative abilities of modified biomass were assessed. Finally, the adsorption mechanism for Pb(II), Cd(II) and Cu(II) ions was studied based on the above experimental and characterization results.

2. Experimental

2.1. Materials and reagents

Jute fiber was collected from a local industry, then cleaned, dried and cut into 5 cm in length to avoid getting twined while stirring in the synthesis process. $Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H_2O$ and $CuSO_4{\cdot}5H_2O$ were purchased from Tianjin Bodi Chemical Reagent Co., Ltd., China. The solution of Pb(II), Cd(II) and Cu(II) were prepared by dissolving weighted amounts of the above chemicals in deionized water. Pyromellitic dianhydride (PMDA) (AR quality) and Dimethylformamide (DMF) (AR quality) used in the synthesis process were supplied by Aladdin Corporation of China. NaOH solution (0.1 and 0.01 mol/L) and HNO_3 solution (0.1 and 0.01 mol/L) were prepared using sodium hydroxide (AR quality) and nitric acid (AR quality) to adjust the pH of aqueous media.

2.2. Synthesis of carboxyl-modified jute fiber by microwave heating

The synthesis route was mainly divided in two steps: (1) the microwave-assisted pretreatment of jute fiber was conducted to remove non-cellulose substances and obtain mercerized cellulose for the enhanced graft reaction process; (2) the carboxyl groups were rapidly introduced into the pretreated jute under microwave treatment. The detailed operation steps are as follows.

2.2.1. Pretreatment of jute fiber by microwave heating

Jute fiber (20 g/L) was initially pretreated with NaOH solution (15 wt%) for 10 min at 368 K under microwave heating with constant stirring. Then, the microwave-pretreated biomass was filtered, washed with distilled water up to pH = 7.0, then dried in a vacuum oven at 338 K for about 4 h and stored in a desiccator.

2.2.2. Grafting carboxyl groups onto jute fiber by microwave heating

The above microwave-pretreated jute fiber was grafted with carboxyl groups via esterification reaction. Initially, PMDA (20 g/L) was dissolved in the DMF solution in a 250 mL three neck flask to make PMDA readily accessible to the pretreated jute. Jute fiber (10 g/L) was added in the three neck flask. Next, the flask was