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Polyethyleneimine-bacterial cellulose bioadsorbent for effective removal of copper and lead ions from aqueous solution

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ABSTRACT

Bacterial cellulose (BC) is a green biopolymer suitable for heavy metal ion removal from aqueous solution due to its nano-porous microstructure. Polyethyleneimine-bacterial cellulose (PEI-BC) was prepared by reductive amination of dialdehyde BC with polyethyleneimine. The capacity of PEI-BC in Cu(II) and Pb(II) adsorption from aqueous solution was investigated. The adsorption kinetics could be well expressed by pseudo-second-order model and the adsorption isotherm data were well fitted with Freundlich model. Adsorption processes of Cu(II) and Pb(II) by PEI-BC reached equilibrium very rapid in 30 and 60 min, respectively. The maximum adsorption capacity of PEI-BC on Cu(II) and Pb(II) was found to be 148 and 141 mg/g, respectively, which was higher than that of unmodified BC and other modified BC reported. PEI-BC also showed good reusability in the adsorption of Cu(II) and Pb(II). This study demonstrates that polyethyleneimine modification makes BC a potential bioadsorbent for heavy metal ion removal in waste water.

1. Introduction

The heavy metal pollution from industrial waste water is a severe problem. How to deal with and recycle the toxic heavy metal contaminated water has attracted extensive attention of researchers. Different methods of removing heavy metal ions from polluted wastewater have been developed, including chemical precipitation, ion exchange, flocculation, membrane filtration (Yuan and He, 2015), electrochemical treatment (Tran et al., 2017), adsorption (O'Connell et al., 2008), etc. Among these methods, adsorption is considered as a very promising and effective method, since many of the natural materials that can be used for adsorption are green, renewable, and prone to chemical modifications. Cellulose and cellulose-based materials including some agro-industrial wastes such as crop straws/stalks, bagasse, crop/fruit/nut shells, etc. have been applied for heavy metal ion removal (Wang et al., 2017; Suhas et al., 2016; De Luna et al., 2015).

The oxygen, nitrogen, and sulphur atoms in some functional groups such as amines, carboxylic acids and thiols can easily form strong chelation with metal ions (He et al., 2014). Therefore, the grafting of cellulose-based materials with those functional groups could enhance its adsorption ability and efficiency for heavy metal ions. For example, acrylic acid (Hajeeth et al., 2013) and maleic anhydride (Zhou et al., 2012) were used to modify cellulose with carboxylic acid groups; diethylenetriamine (Gurgel and Gil, 2009) and acrylonitrile N,N-methylenebisacrylamide (Zheng et al., 2010) were used to modify cellulose with amine groups; thioglycolic acid (Wu et al., 2012) was used to modify cellulose with thiol groups. These modifications produced cellulose or cellulose-based materials with enhanced adsorption ability for heavy metal ions.

Bacterial cellulose (BC) is a type of extracellular cellulose mainly produced *in vitro* by Acetobacter bacteria (Cheng et al., 2017). There is no essential difference in chemical structure between BC and cellulose from higher plant. They are both cellulose molecules made up of glucose molecules linked by β-1, 4 glycosidic bonds. However, compared to conventional plant based cellulosic materials, bacterial cellulose has a high degree of purity, near 100% of cellulose content and without other common components in plant fiber. Similar to cellulose from other primitive organisms such as algal cellulose, BC microfibril diameter is 10–100 nm, about one tenth of the ordinary plant fiber filament (Xiang et al., 2016; Yan et al., 2008). The microfibrils of BC interlock with each other, forming a unique network structure (Xiang et al., 2017). Therefore, it has good tensile strength, water bonding ability and excellent shape maintenance ability (Xiang et al., 2017; Cacicedo et al., 2016). Because of the unique advantages of BC, the commercial applications of BC are becoming common, such as temporary skin tissue substitutes, separation membranes, low calorie foods such as coconut Nata, paper strengthening agent, etc. (Cacicedo et al., 2016).

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Due to its three-dimensional nano-reticular microstructure, BC may be better than regular cellulose in the adsorption of heavy metal ions (Chen et al., 2009 a). In order to further enhance the absorption ability to heavy metal ions, different functional groups can also be applied to BC through its abundant hydroxyls. The studies about the application of functionalized BC to ion adsorption have often been reported (Chen et al., 2009a,b; Lu et al., 2014; Oshima et al., 2008; Shen et al., 2009). For example, diethylenetriamine can be grafted onto BC to improve the metal ions adsorption because of the chelation of nitrogen element with metal ions (Shen et al., 2009). However, in previous reports, the ionic adsorption capacity of these modified materials needs to be further improved. Therefore, it is necessary to modify BC with new methods to increase its metal ion adsorption capacity.

Compared with the previous study of ion adsorption material from BC, this paper is devoted to the study of a novel polyethyleneimine modified BC (PEI-BC) adsorbent. Polyethyleneimine is a highly branched molecule containing a large amount of primary and secondary amine side groups, facilitating its adsorption to heavy metal ions. The capability of amines forming chelation with metal ions has an order of primary > secondary > tertiary amines, due to the steric hindrance effects (Boyd et al., 1947). Additionally, the large amount branched groups of polyethyleneimine may contribute to the formation of highly entangled structures with BC, so that heavy metal ions can be trapped more easily. Along with the three-dimensional nano-network structure of BC, PEI-BC is expected to demonstrate a great adsorption capacity for heavy metal ions. This article also studied the effects of pH, ion concentration, adsorption time and other factors on the adsorption of heavy metal ions by PEI-BC. The adsorption kinetics of the first- and second-order kinetics and Langmuir and Freundlich isotherms were used to evaluate the adsorption process.

2. Experimental

2.1. Materials

Gluconacetobacterxylinus ATCC23767 was obtained from Nanjing High Tech University Biological Technology Research Institute Co., Ltd. (Nanjing, China) and used to produce the bacterial cellulose (BC) pellicles. BC pellicles were prepared through the static fermentation method according to Xiang et al., (2017). Polyethyleneimine (M_w = ~600), sodium periodate, sodium cyanoborohydride, sodium hydroxide, ethylenedinitrilo tetraacetic acid disodium salt (Na_2EDTA), $CuSO_4{\cdot}5H_2O$ and $PbCl_2$ were purchased from Shanghai Macklin Biochemical Co., Ltd. All other chemicals used are of analytical grade.

2.2. Preparation of PEI-BC

Approximately 30 g of wet BC pellicles (moisture content = 98.5%) were cut into 1 cm × 1 cm strips and then disintegrated by a lab blender (SKG 1246, China) at instant mode for 3 times.

The disintegrated BC, 90 mL distilled water and 0.21 g Na_2IO_4 were mixed into a conical flask with magnetic stirring at 350 rpm. The reaction was carried out at room temperature and light absent condition for 2 days. After completion of the reaction, the dialdehyde BC were filtered and washed with distilled water several times until pH became neutral.

With the dialdehyde BC, 5.6 g polyethyleneimine and 80 mL distilled water were mixed into a conical flask. As a catalyst, 0.21 g sodium cyanoborohydride was also added. The pH of the mixture was adjusted to 5.8–6 with 0.1 M hydrochloric acid. The reaction was conducted with magnetic stirring at 350 rpm and room temperature for 6 h. After reaction, the polyethyleneimine modified BC (PEI-BC) were filtered and washed with distilled water several times to remove impurities.

2.3. Characterization of PEI-BC

Surface morphologies were evaluated on undisintegrated BC using a scanning electron microscope (SEM) (Evo-18, Carl Zeiss). The BC and PEI-BC were disintegrated by the lab blender for 2 min and dried on a glass plate in 105 °C to form a film. The films were used for Fourier Transform Infrared (FT-IR) analysis. FT-IR spectra were recorded on a Vector 33 equipped with a MCT detector in the absorption mode with a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}. The nitrogen content of the PEI-BC was analyzed on the films through an Elemental Analyzer (Vario EL cube, Elementar, Germany).

2.4. Adsorption experiments

For the adsorption experiment, PEI-BC (with oven dried weight of 0.03 g) was added to 30 mL $CuSO_4$ or $PbCl_2$ solutions at room temperature. The metal ion initial concentrations, pH values and adsorption times varied according to different situations.

To investigate the effects of pH on heavy metal ion adsorption, a series of $CuSO_4$ and $PbCl_2$ solutions with different pH values were configured by 0.1 M HCl and 0.1 M NaOH. The initial concentration for both metal ion solutions was 100 mg/L. The pH values of $CuSO_4$ solutions were set to 2, 3, 3.5, 4, 4.5 and 5; the pH values of $PbCl_2$ solutions were set to 3, 3.5, 4, 4.5, 5, 5.5 and 6. The adsorption time was 3 h.

For kinetic adsorption experiments the adsorption time was set to 3, 7.5, 15, 30, 60 and 90 min. The initial concentration for both metal ion solutions was 100 mg/L. The pH of $CuSO_4$ solution was controlled at 4.5, and the pH of $PbCl_2$ solution was controlled at 5.5.

For adsorption isotherm experiments, the pH of $CuSO_4$ and $PbCl_2$ solutions were controlled at 4.5 and 5.5, respectively. The adsorption time was 3 h. The initial concentrations of Cu(II) or Pb(II) were set to 100, 200, 400, 600, 800, 1000, 1200 and 1400 mg/L.

The concentration of Cu(II) or Pb(II) ions in the aqueous solution was measured by an atomic absorption spectrophotometer (Z-2000, Hitachi, Japan).

The amount of metal ions adsorbed from the solution was calculated by the following equation (Eq. (1)):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e represent the initial metal ion concentration and adsorption equilibrium mental ion concentration (mg/L), respectively, while the V represents the volume of the solution (L) and m is the absolute dry mass of the PEI-BC used (g).

2.5. Regeneration of PEI-BC

Desorption of metal ions from PEI-BC was examined in a 0.05 M Na_2EDTA solution. PEI-BC from the adsorption experiments (initial ion concentration of 100 mg/L at pH 4.5 for Cu^{2+} and pH 5.5 for Pb^{2+}) with metal ions adsorbed was added into 30 mL of the 0.05 M Na_2EDTA solution. The mixtures were stirred on a magnetic stirrer at 350 rpm and room temperature for 1 h, and samples were taken from the solution to monitor the amount of metal ions desorbed into the solution. After the desorption test, the PEI-BC were separated and washed with 0.05 M NaOH solution followed by DI water, and reused in the next cycle of adsorption experiment. The adsorption–desorption experiments were conducted for four cycles.

3. Results and discussion

3.1. Characterization of PEI-BC

Selective oxidation by sodium periodates on anhydroglucose units of BC opens the C2-C3 position to form dialdehyde cellulose (Coseria et al., 2013). In the Schiff base reaction mechanism, the amine groups