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Preparation of iminodiacetic acid-modified magnetic biochar by carbonization, magnetization and functional modification for Cd(II) removal in water

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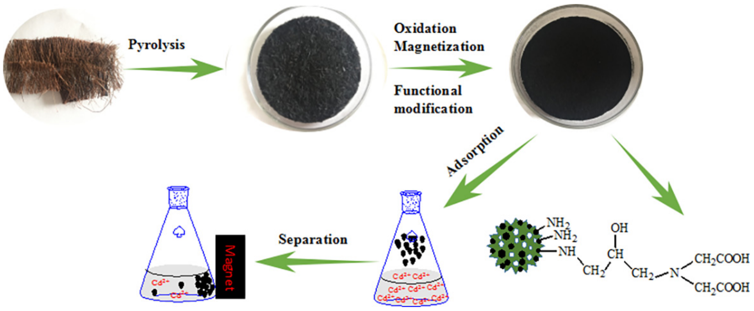
GRAPHICAL ABSTRACT



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ABSTRACT

A novel iminodiacetic acid magnetic biochar (MBCI) was prepared, characterized and evaluated its adsorption performance for the removal of Cd(II) from aqueous solution. The biochar (BC) derived from palm fiber was served as a novel matrix, first oxidized by hydrogen peroxide (BCO) and loaded of Fe_3O_4 nano-particles (MBCO), followed by a coupling reaction and functional modification (MBCI). The characterization results showed that the Fe_3O_4 nano-particles were successfully loaded on the surface of biochar and the carboxyl groups of MBCI were obviously more than that of the pristine BC. The mass ratio for magnetization was well determined to be 1.8:1–2.3:1, which could guarantee high removal and recovery efficiency. The adsorption kinetics could be well fitted by the pseudo-second-order model and adsorption isotherm was well described by the Langmuir model. The surface complexation model was established to illustrate the adsorption process and adsorption of Cd (II) on MBCI was controlled by the surface complexation mechanism between functional groups in MBCI and Cd (II). MBCI possessed high adsorption capacity (197.96 mg/g at 323 K), reusability (retained 82.18% after five successive cycles) and sharing magnetic property (16.88 emu/g), which guaranteed it readily and efficient separation from the aqueous solution.

1. Introduction

Water pollution by heavy metals has caught extensive attention owing to its high toxicity and non-biodegradability [1]. Long-time of drinking water contaminated by heavy metals such as copper, lead, cadmium would result in pulmonary, immunological, cardiovascular, neurological, and endocrine disorders and cancers [2–4]. Heavy metals are widely used in mining operations, leather tanning, battery

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manufactures, power generation facilities, metal plating, etc. [5,6]. Thus, removal of heavy metals is more prior from wastewater to avoid contamination to the ecosystem. Several methods for removal of heavy metals have been investigated, including chemical precipitation, ultrafiltration, membrane separation and electrochemical deposition [7–9]. However, these techniques suffer from several advantages such as low removal efficiency, high reagent and energy requirements and generation of secondary pollution [10,11]. Adsorption is one of the most popular and cost-effective methods for removal contaminates from aqueous solution. With increasing emphasis on the sustainable development, the economic feasible and environmentally friendly adsorbents have become a research hotspot.

At present, the studies of the adsorbents were focused on the relatively cheap biochar. Biochar is a carbonaceous material prepared from forestry wastes, agricultural waste and industrial organic wastes [12,13]. Biochar has been extensively studied and widely applied in the fields of contaminate removal and wastewater purification owing to its porous structure, high surface area, rich functional groups and acid, alkali corrosion resistance [14,15]. However, owing to the small particle sizes and low density, the powdered biochars are difficult to be separated from solution after treatment. A large number of contaminates are adsorbed in the biochar particles. If these particles were not removed in time, the secondary pollution will be generated, affecting the regeneration and reuse of the biochar, which restricted its further application in wastewater treatment [16].

It is well known that Fe_3O_4 nanoparticle possesses rapidly magnetic response in an external magnetic field, so the biochar was magnetized by introducing the magnetic Fe_3O_4 to the biochar matrix, which would be an excellent idea to overcome this disadvantage [17]. Son prepared a engineered magnetic biochar derived from marine macro-algal biomass for removal of copper, zinc and cadmium from aqueous solution, which exhibited a high adsorption capacity and could be easily collected from the aqueous solution as a magnetic force was imposed [18]. Trakal discussed the cadmium and lead adsorption efficiency of biochars modified by impregnation with magnetic particles [19]. Nevertheless, naked Fe_3O_4 nanoparticles tend to be unstable since it was prone to fall out from the biochar matrix. Thus, it is a challenge to fix the Fe_3O_4 nanoparticles to the biochar matrix. The amino-terminated 3-Triethoxysilylpropylamine (TSA) with like-hand structure is considered as a coupling reagent to link with biochar and Fe_3O_4 particles, which could guarantee the nanoparticles could be encapsulated on the surface of biochar.

The synthetic mechanism of Fe_3O_4 nanoparticles were expressed as following:

$$2Fe^{3+} + Fe^{2+} + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4^+ + 4H_2O \tag{1}$$

Since the magnetic medium might hinder the pores of the biochar, resulting in lower surface area and less developed porous structure. Functional modification could increase the functional groups of biochar and further increase the adsorption capacity and selectivity to certain heavy metals. Some functional groups including sulfonyl, sulfhydryl, carboxyl, hydroxyl, amino and amide groups can chelate with metal ions, which generally contains some coordinate atoms, e.g., S, O or N [20]. Among these functional groups, carboxyl group shows much strong capacity to coordinate with metal ions owing to the ion exchange, electrostatic interaction and complexation: (1) Due to the strong electronegativity of O atom, the electron pair on –OH bond shift to oxygen, which facilitates the ionization of hydrogen, consequently, the coordination complex of $-COO^{-}$-M^{2+}(M^{2+}, metal ions) is easily generated through ion exchange; (2) Electrostatic interaction also coexists between the negatively charged carboxyl anion and the positively charged metal cation during the adsorption process; (3) The formation of the coordination complex is ascribe to the sharing of lone-pair electron on the O of the carboxyl with metal ions which could provide for empty orbital [21]. Therefore, the modification of biochar with carboxyl is an effective method to enhance the adsorption capacity and selectivity to certain metal ions.

In this study, a novel modified biochar (MBCI) was prepared via coupling reaction and functional modification and evaluated its adsorption performance for removal of Cd(II) from aqueous solution. First, the biochar (BC) derived from palm fiber was oxidized by hydrogen peroxide (BCO). Next, the BCO was mixed with Fe_3O_4 nanoparticle to impart magnetism by the silane coupling agent (MBCO). Finally, the MBCO was functionally modified with iminodiacetic acid (MBCI), by which carboxyl could be introduced to the magnetic biochar. Consequently, the presence of magnetic nanoparticles endows the MBCI with strong magnetic response, which improves separation efficiency. Additionally, the effects of pH, initial concentration of Cd(II), adsorption time and temperature were discussed to evaluate the adsorption performance of MBCI. The study results provided a scientific basis for the application of MBCI in the treatment of heavy metals in wastewater.

2. Materials and methods

2.1. Materials

All chemicals and reagents utilized in this study were of analytical grade, Milli-Q water was utilized throughout the experiments for solution preparation and glassware cleaning. Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. 3-Triethoxysilylpropylamine (TSA), Iminodiacetic acid (IDA), epichlorohydrin (EC), N,N-Dimethylformamide (DMF) and other chemicals were purchased from Honghua Reagent Co. Ltd. (Changsha, China). Palm fiber was cut and washed with tap water to clear the dust and other adhering impurities, soaked in 1 mol/L NaOH for 12 h, washed with Milli-Q water for several times and then dried at 323 K.

2.2. Preparation of the modified biochar

The pristine biochar (BC) was produced through pyrolysis the palm fiber in a muffle furnace at 400 °C with a heating rate of 10 °C /min under the protection of N_2 and maintained for 2 h. The pyrolysed products were cooled down to room temperature under the same N_2 flow and the resulting biochar was ground, sieved, and successively washed with 0.01 mol NaOH, 0.01 mol HCl, Milli-Q water and oven-dried at 323 K overnight. The synthesis of Fe_3O_4 nano-particles by chemical co-precipitation of in Fe^{3+}/Fe^{2+} solution was based on a previous study by Zhou et al. [22]. As shown in Scheme 1, about 20.0 g BC weighted accurately was added into 200 mL hydrogen peroxide (20%). The oxidation reaction was performed under N_2 atmosphere at 343 K for 3 h. The oxidized biochar was named as BCO.

To prepare the MBCO, a certain mass ratio (1:0, 3:1, 2.5:1, 2:1, 1.5:1, 1:1, 0:1) of BCO and Fe_3O_4 nano-particles was mixed and stirred in 100 mL Milli-Q water under the protection of N_2 for 1 h, then 5 mL of 3-Triethoxysilylpropylamine (TSA) was added to the mixture solution. The magnetic biochar was obtained by stirring the mixture at 323 K for 8 h. So, the magnetic property was introduced to the biochar. After being separated by a magnet, the resulting biochar washed with ethanol and Milli-Q water several times, then oven-dried at 323 K overnight.

Next, a medium of 100 mL mixed solvent with DMF/distilled water (V:V = 1:1) was prepared, then 2.0 g of MBCO and 10 mL epichlorohydrin (EC) were added in the medium for cross-linking. The mixture was stirred for 12 h at 303 K under the protection of N_2. Next, 8.0 g of iminodiacetic acid (IDA) and 100 mL of 1 mol/L NaOH were added into mixture and stirred in an oil bath at 343 K for 12 h. After being separated with magnet, the modified biochar was subsequently washed with acetone, ethanol and Milli-Q water and finally oven-dried at 323 K overnight. Hence, the iminodiacetic acid modified magnetic biochar (MBCI) was obtained.