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Amino modification of biochar for enhanced adsorption of copper ions from synthetic wastewater

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ABSTRACT

Biochar was modified as a high efficient and selective absorbent for copper ions (Cu(II)) by nitration and reduction. Results of X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analyses indicated that the amino groups were chemically bound to the functional groups on the biochar surface. Kinetics, thermal dynamics, and adsorption and desorption of Cu(II) in fixed-bed were investigated. The results demonstrated that the amino-modified biochar exhibited excellent adsorption performance for Cu(II). The adsorption capacity and bed volume of the modified biochar are five- and eight- folds of the pristine biochar, respectively. The Cu(II) combined with the amino groups through strong complexation based on the comparison of XPS and ATR-FTIR analyses before and after adsorption, which endows it with the high pH stability and ion selectivity.

1. Introduction

Heavy metal ions in water pose a potential threat to aquatic lives and human beings due to their accumulation in the food chains (Wang et al., 2012). Copper, one of the ubiquitous heavy metals, belongs to one of the priority pollutants categorized by US EPA. Compared to the redox and chemical precipitation, adsorption of Cu(II) is a cost-effective method. Recently, emerging materials, such as polyethyleneimine nanoclusters (Chen et al., 2010), Fe_3O_4 magnetic nano-particles (Liu et al., 2013), and biosorbents (Kim et al., 2012), were developed for removal of Cu(II) from solution.

Carbon materials, such as activated carbon, fullerene, and graphene, have been widely used in pollution control because of their stability and large surface area. For example, activated carbon can act as an adsorbent for heavy metals, and graphene can function as a support of metallic catalyst to degrade the organic pollutants (Hanigan et al., 2012; Zhang et al., 2012; Kadirvelu et al., 2001). However, these carbon materials are hard to selectively adsorb pollutants (Kadirvelu et al., 2001). To enhance their capacity and selectivity for pollutant removal or stability for carbon-supported metallic catalysts, modification of carbon materials has attracted many attentions in recent years (Chen et al., 2003; Wang et al., 2011). For example, citric-acid-modified activated carbon showed remarkably higher adsorption performance than the unmodified carbon due to the introduction of carboxyl groups. Alves et al. (2001) anchored organic molecules with amine groups onto activated carbons. However, such techniques require strict pretreatment for the successful anchoring of

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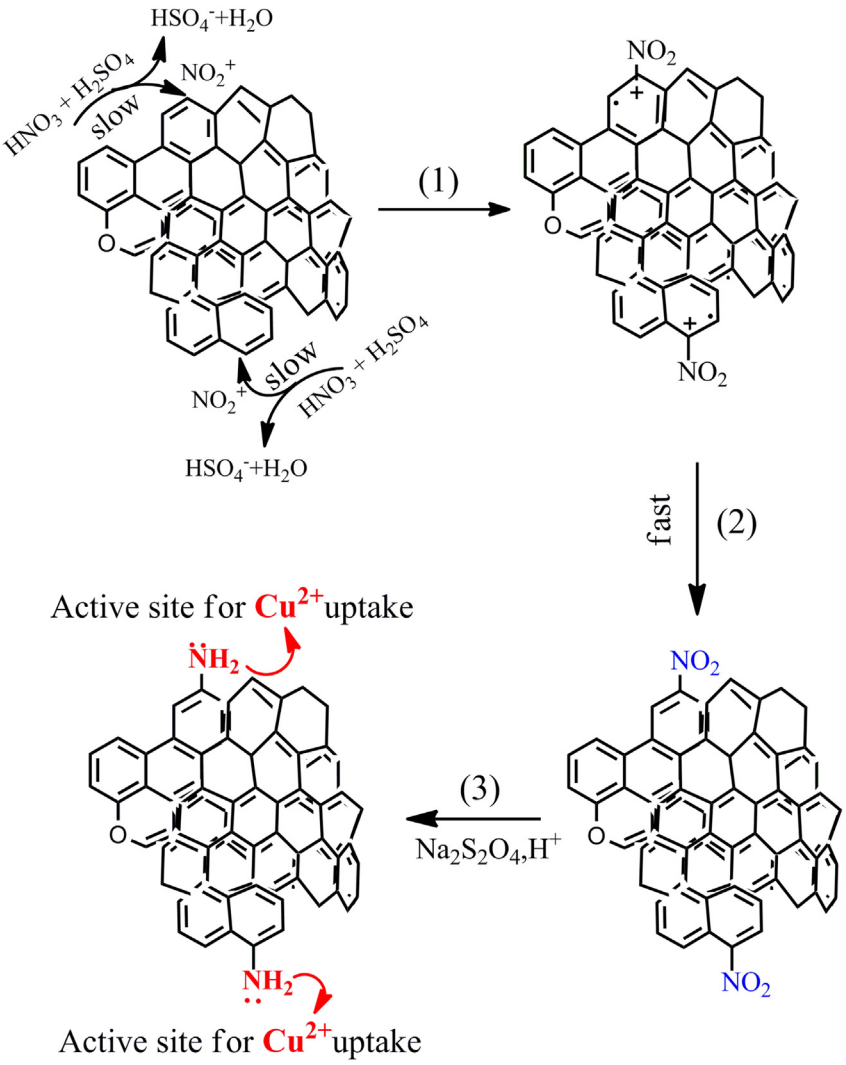

Fig. 1 – The schematic of amino-modification of biochar.

organic molecules. Biochar, a byproduct of biomass pyrolysis, is obtained from fast thermochemical decomposition of lignocellulosic biomass at relatively low temperatures (<973 K) and contains many functional groups (e.g., amino, carboxyl, and hydroxyl groups) (Cao et al., 2009; Hsu et al., 2009). Such groups may not only favor the adsorption of pollutants, but also facilitate the anchor of other functional groups. Several methods (acid and alkali modification, oxidation, and chemical graft) have been used to modify biochar and improve its adsorption performance of heavy metals (Liu et al., 2012; Xue et al., 2012; Gutiérrez-Valero et al., 2007). In general, these techniques modify the interfacial region of biochar by increasing the specific surface area or the chemical reactivity by forming surface functional groups that can chemically bond with the heavy metals.

Amino modification is a promising method for enhancing the adsorption efficiency of metal ions on biochar since the amino moiety is a powerful complexing functional group that efficiently complexes with heavy metals due to the high stability constants of the metal complexes (Denney and Mendham, 1989; Buttry et al., 1999). Therefore, amino modification made biochar very useful to selectively adsorb metal ions. Nitration is an effective method for introducing nitrogen functional groups on aromatic rings by electrophilic aromatic substitution. The obtained nitro compounds can be reduced readily to the corresponding amino derivatives using various reducing agents (Carey and Sundberg, 2007; Yantasee et al., 2004). Considering that biochar generally has a large amount of condensed aromatic C which is characterized by rings of six C atoms linked together (Liang et al., 2008; Lehmann and Joseph, 2009), it is well-founded that biochar may undergo nitration reaction by electrophilic aromatic substitution. To our best knowledge, research on the modification of biochar with amino as well as the adsorption mechanism involving both complexation and ion-exchange has not been reported.

This work aims to demonstrate a simple and cost-effective method for the preparation of amino-modified biochar with significantly improved adsorptive performance to heavy metals. To this end, we 1) prepared amino-modified biochar by electrophilic aromatic substitution and reduction reactions, 2) demonstrated the chemical bonding between the