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Review

Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater

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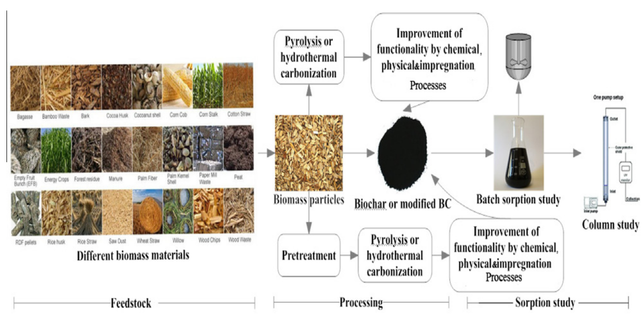
HIGHLIGHTS

- Biochar modifications and subsequent functionality improvement are summarized.
- Modified biochar has shown enhanced sorptive capacity for contaminants.
- Continuous column applications for contaminant removal have been examined.
- Regeneration methods for modified biochar have been evaluated.
- Future research directions using modified biochar have been proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Modified biochar (BC) is reviewed in its preparation, functionality, applications and regeneration. The nature of precursor materials, preparatory conditions and modification methods are key factors influencing BC properties. Steam activation is unsuitable for improving BC surface functionality compared with chemical modifications. Alkali-treated BC possesses the highest surface functionality. Both alkali modified BC and nanomaterial impregnated BC composites are highly favorable for enhancing the adsorption of different contaminants from wastewater. Acidic treatment provides more oxygenated functional groups on BC surfaces. The Langmuir isotherm model provides the best fit for sorption equilibria of heavy metals and anionic contaminants, while the Freundlich isotherm model is the best fit for emerging contaminants. The pseudo 2^{nd} order is the most appropriate model of sorption kinetics for all contaminants. Future research should focus on industry-scale applications and hybrid systems for contaminant removal due to scarcity of data.

Contents

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1. Introduction

Biochar is a stable carbon dominant material which is obtained by thermal or hydrothermal processes when biomass is heated at elevated temperature with little or no oxygen (Ahmed et al., 2015; Klinar, 2016). Modified BCs are obtained when BCs are further activated to improve their pore structure, surface area and functionality (Kwiatkowski, 2008). Raw BCs may have limited ability to selectively adsorb contaminants of high concentrations (Ma et al., 2014). Modified BCs with enriched surface functional groups enhanced sorption capacity, e.g. hydrous manganese oxide modification of peeled pine wood BCs exhibited 5-fold higher Pb(II) sorption capacity than parent BCs (Gan et al., 2015; Wang et al., 2015b). Consequently, various modification methods including surface oxidation, impregnation of metal oxides and functionalization have been applied to improve their performance in environmental remediation (Xue et al., 2012; Zhang et al., 2015). Thus modified BCs can be used as effective sorbents for removing organic and inorganic contaminants from water (Tan et al., 2015; Zhang et al., 2015). BCs and modified BCS can also play a role in carbon sequestration and sludge conditioning, hence increasing soil fertility and agricultural productivity (Hu et al., 2016).

The functional groups such as hydroxyl, carboxyl, ether, amide, amine, alkayl, alkyne, alkine and carbonyl are responsible for accumulating contaminants from water and wastewater. The atomic ratios such as H/C (aliphatic), O/C and N/C (polar index) are related to the specific properties of the BCs. Improvements in those functional groups can be done via steam activation, chemical modification, impregnation and heat treatment (Shen et al., 2008). Moreover, nano-composite sorbents with nano-sized metal oxyhydrates are attached onto carbonaceous surfaces within BCs matrix and increase the sorption of contaminants. Modified BCs can be used as an alternative sorbents compared to AC, graphene and carbon nanotubes (CNT), and have similar removal capacity for many contaminants. Thus, the aim of this review is to critically examine recently published studies on modified BCs for the removal of heavy metals, anions and organic contaminants including emerging contaminants from aqueous solutions. Specifically this review covers preparation methodologies for modified BCs; improved properties of modified BCs; sorption isotherms, kinetics, mechanism and continuous operations for the removal of inorganic and organic contaminants; and suggestions for future studies of modified BCs.

2. Biochar surface modification methodologies

Modification of the BC surface can be realized in different ways as presented in following sections. Different modification of BCs is summarized in Supplementary Table S1.

2.1. Steam activation

Steam activation is commonly used to introduce porous structure and oxygen-containing functional groups (e.g. carboxylic, carbonyl, ether and phenolic hydroxyl groups) onto BC surfaces; hence increasing the hydrophilicity of BCs despite steam being a weaker oxidant. In this method, feed material is first pyrolyzed at a temperature from 300 to 700 °C for 1–2 h under a limited supply of air, or nitrogen or sometimes ambient air flow. Then, the pyrolyzed sample is steam activated at a temperature of 800–900 °C for 30 min to 3 h with 2.2 to 5 mL min^{-1} steam pass (Ippolito et al., 2012; Rajapaksha et al., 2015) (Fig. 1a). Steam changes the properties of BCs by removing the trapped products of incomplete combustion during pyrolysis, and oxidizes the carbon surface by generating mainly H_2, CO and CO_2.

2.2. Heat treatment

Heat treatment provides more basic surface functional groups to BCs which are mostly used for sorbing hydrocarbons (Shen et al., 2008). BCs are placed heated to the desired temperature (800–900 °C) for 1–2 h (Li et al., 2014), subsequently hydrogen, air or argon is introduced for forming new functional groups on BC surfaces, e.g. basic pyrone-type groups resulting from carbonyl and ether-type groups (Fig. 1b). Heat treatment of BCs increases surface hydrophobicity by removing hydrophilic groups such as carbonyl and ether groups. In general, large number of acidic