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An overview of carbothermal synthesis of metal–biochar composites for the removal of oxyanion contaminants from aqueous solution

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ABSTRACT

Biochar shows promise as a potential low–cost sorbent for removing oxyanions from wastewater. However, this generic material exhibits a very wide range in porosity, surface area and surface chemical properties that depend on the starting biomass composition and the conditions under which it is converted to char. Without dosing either reactant biomass or product biochar with certain metals (in elemental, oxide/hydroxide or layered double hydroxide form), the capacity of biochar to remove oxyanions is usually low. This review compiles the recent research on modifications of biochar to produce metal-biochar composites that exhibit high oxyanion removal capacities. The general effect of the added metal is first established and then an overview of the several syntheses used to make metal–biochar composites is presented. Effects of chemical activation and of the addition of single metallic elements, single and binary oxides/hydroxides, and layered double hydroxides on removal of AsO_4^{3-}, AsO_3^{3-}, CrO_4^{2-}, NO_3^- and PO_4^{3-} are next summarized. The effects of metal dosing and pyrolysis conditions on the surface chemistry and environmental stability of the composite are discussed. Finally, a summary of the research needed to maximize and/or target removal of specific oxyanions, address issues of long–term ecotoxicity of metal–biochar composites, and verify performance with field-testing is presented.

Contents

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1. Introduction

1.1. Oxyanion contamination in water

Widespread surface and groundwater pollution is a serious threat to environmental quality [1]. The most common contaminants are microorganisms, suspended particles, colloidal materials, pesticides, and various dissolved metallic and non–metallic substances [2]. Inorganic oxyanions such as arsenate (AsO_4^{3-}), arsenite (AsO_3^{3-}), chromate (CrO_4^{2-}), nitrate (NO_3^-), phosphate (PO_4^{3-}) and others are of particular concern because of their high solubility and mobility in water, and their direct toxicity or negative impacts on the environment [3].

High levels of AsO_4^{3-}, AsO_3^{3-}, CrO_4^{2-}, NO_3^- and PO_4^{3-} in groundwater have been reported world–wide [4]. Long–term exposure to low levels of As is associated with skin, lung, bladder, urinary tract, kidney and liver cancer, and noncancerous illnesses [5]. Somewhat higher levels of exposure to CrO_4^{2-} may cause liver damage, pulmonary congestion, vomiting and severe diarrhea [6]. Consequently, the World Health Organization has designated 10 and 50 μg/L as maximum contaminant levels (MCLs) in drinking water for As and CrO_4^{2-}, respectively [4]. Although NO_3^- and PO_4^{3-} are nutrient species, their discharge into surface water may cause eutrophication, leading to an overgrowth of phytoplankton, disruption of the aquatic ecosystem, and even disease in animals and humans [7]. Therefore, these oxyanions must be removed from wastewater before they are released into the environment.

Various methods including coagulation–filtration, membrane separation, and ion sorption have been used to remove oxyanion contaminants from wastewater. The effectiveness of these methods depends in part on the physical and chemical properties of the oxyanion [8,9]. Among these methods, sorption offers several advantages including high efficiency, low cost and simple operation. Further, since no reagents are required, it is considered to be environmentally friendly [10]. Accordingly, there is keen interest in further developing this methodology, including the use of biochar [11].

1.2. Biochar from carbothermal treatment of biomass

Biochar is a carbon–rich, stable, porous solid derived from the thermal conversion of biomass under limited or no oxygen conditions [12]. Many different biological materials (or feedstocks) such as animal waste, microbial and plant residue, sludge and tire waste can be converted to biochar by carbonization, pyrolysis, gasification, hydrothermal treatment and other thermal methods. However, the feedstock and conversion process affect the properties of the biochar and its suitability for specific uses [13–15]. Biochar may be added to soil to mitigate greenhouse gas emission and promote carbon sequestration [16–18], enhance soil fertility for agricultural production [19,20], and improve composting [21].

While the main practical uses of biochar to date have been as a soil amendment to promote carbon sequestration [22,23] and for contaminant remediation [24,25], the growing literature on biochar includes numerous other avenues of research for which reviews are available: method of preparation [14,26,29–32], physicochemical properties [29,33], environmental stability [14,34,35], economic benefits [28,36,37], and future challenges [27,28,38]. Due to several properties of biochar, including its stable carbon matrix, porosity and large specific surface area containing various functional groups, it is a promising sorbent for the removal of pollutants from water. Unlike traditional, high–cost activated carbon, biochar is an effective, yet low–cost sorbent. Activated carbon is generally prepared at temperatures ≥800 °C, thus requires high energy besides activation with steam, CO_2 or dehydrating chemicals such as $ZnCl_2$ and H_3PO_4 [39]. In contrast, biochar is produced at < 800 °C from low–cost and abundant feedstocks, mainly agricultural biomass waste [40]. Further, conversion of such organic solid wastes to biochar eliminates disposal and therefore helps protect the environment. Thus, there is increasing interest in biochar as a sorbent for treating contaminated water. Biochar has been studied as a sorbent for persistent organic pollutants, heavy metals and nutrients in water [41–44]. Reviews on the use of biochar for the removal of organic pollutants and microorganisms [45], and heavy metal cations [24,46–51] are also available.

1.3. Purpose of this review

Recently a series of so–called "engineered/modified" biochars produced either by changes to the production process or by loading the feedstock with chemical agents designed to increase the removal capacity for oxyanions have been introduced [11,44,52–61]. A comprehensive review presented by Tan et al. [51] summarized the various techniques by which biochar-based nano-composites are synthesized and their effectiveness in removing pollutants (methylene blue, arsenic, phosphate, chromate, cadium, and lead, etc.) from solution. However, the effectiveness of these materials specifically for the removal of oxyanion contaminants (e.g. AsO_4^{3-}, AsO_3^{3-}, CrO_4^{2-}, NO_3^- and PO_4^{3-}) from water has not been exhaustively reviewed and summarized [62], and there is limited knowledge on their performance in actual wastewater treatment [63]. Given the seeming potential of engineered/modified biochars for removal of oxyanions, it is important to summarize all relevant work, and thus help guide future research. This review: (1) compares oxyanion removal by biochars with that obtained by metal oxides and metal oxide-biochar composites prepared by different carbothermal processes; (2) examines the mechanisms of oxyanion removal by metal–biochar composites; (3) discusses carbothermal synthesis of metal–biochar composites; and (4) presents possible future developments and challenges.

2. Oxyanion removal by pristine biochar and modified biochar

The chemical and physical properties of biochar vary widely depending on the feedstock and conditions under which it is