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Insights into the simultaneous removal of Cr^{6+} and Pb^{2+} by a novel sewage sludge-derived biochar immobilized nanoscale zero valent iron: Coexistence effect and mechanism

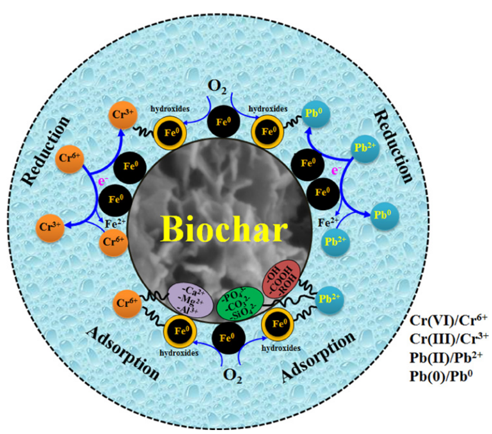
Zeng-Hui Diao [a,b,*], Jian-Jun Du [b], Dan Jiang [c], Ling-Jun Kong [d], Wen-Yi Huo [a], Cui-Mei Liu [a], Qi-Hang Wu [e], Xiang-Rong Xu [a,**]

[a] CAS Key Laboratory of Tropical Marine Bio-resources and Ecology, Guangdong Provincial Key Laboratory of Applied Marine Biology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
[b] School of Environmental Science and Engineering, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China
[c] Research Resources Center, South China Normal University, Guangzhou 510631, China
[d] School of Environmental Science and Engineering, Guangzhou University, Guangzhou 510006, China
[e] Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Center for Water Quality and Conservation of the Pearl River Delta, Guangzhou University, Guangzhou 510006, China

HIGHLIGHTS

- A novel biochar immobilized nanoscale zero-valent iron was firstly developed.
- A synergistic effect on the adsorption-coupled reduction was achieved.
- An acidic environment was favorable to the leaching of phosphate and total Fe.
- Removal of malachite green was due to the occurrence of Fenton reaction.
- A mechanism for the simultaneous removal of Cr^{6+} and Pb^{2+} was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Cr^{6+} and Pb^{2+} are both highly toxic pollutants and commonly co-exist in some industrial effluents and contaminated waters. In this study, simultaneous removal of Cr^{6+} and Pb^{2+} by a novel sewage sludge-derived biochar immobilized nanoscale zero-valent iron (SSB-nZVI) was systematically investigated. It was well demonstrated that a porous structure was successfully formed on the SSB-nZVI when the starch was used as an additive. A synergistic effect on the adsorption and reduction over the SSB-nZVI was achieved, resulting in nearly 90 and 82% of Cr^{6+} and Pb^{2+} removal within 30 min, respectively. Cr^{6+} was reduced prior to Pb^{2+}. A low pH could accelerate the corrosion of nZVI as well as phosphate leaching. When Malachite green was added as a coexisting organic pollutant, its effective removal was found due to the formation of a Fenton-like system. The SSB-nZVI could be run consecutively three times with a relatively satisfactory performance. Most of Cr^{6+} was converted into Cr_2O_3 and $Cr(OH)_3$ on the SSB-nZVI surface, whereas most of Pb^{2+} species existed as $Pb(OH)_2$ (or PbO). A possible reaction

* Correspondence to: Z.-H. Diao, School of Environmental Science and Engineering, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China.
** Corresponding author.
E-mail addresses: zenghuid86@scsio.ac.cn, (Z.-H. Diao), xuxr@scsio.ac.cn (X.-R. Xu).

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Cr^{6+}
Pb^{2+}
Malachite green

mechanism on the SSB-nZVI involved the adsorption, reduction and precipitation of both Cr^{6+} and Pb^{2+} over the particles. Present study sheds light on the insight of the fate and transport of Cr^{6+} and Pb^{2+} in aquatic environment, as well provides helpful guide for the remediation of coexistence of pollutants in real applications.

1. Introduction

In the last years, the utilization of biochar as a low-cost adsorbent for pollution remediation has received growing attention (Nunthaprechachan et al., 2013; Rajapaksha et al., 2016, 2018; Feng et al., 2018). Biochar and its composites are widely employed for the abatement of heavy metals and/or organic pollutants in water and sediment (Song et al., 2014; Kumar et al., 2017a, 2017b; P. Wang et al., 2017; S.S. Wang et al., 2017; Tang et al., 2018). Nowadays, the utilization of municipal sewage sludge produced abundantly from wastewater treatment plants has caught increasing attention (Smith et al., 2009; Feng et al., 2018; C.M. Liu et al., 2018; J.J. Liu et al., 2018; Tang et al., 2018). Among various utilizations, development of an efficient adsorbent biochar from sewage sludge has been proved to be a beneficial and feasible output (Smith et al., 2009; Hunsom and Autthanit, 2013; Feng et al., 2018). However, most of the biochar derived from sewage sludge had low surface areas due to the lack of porous structure. To overcome this drawback, $ZnCl_2$, often used as a chemically activating agent, was considered to be the most effective in improving the surface areas of biochar (Smith et al., 2009; Hunsom and Autthanit, 2013; Su et al., 2015; Feng et al., 2018). Nevertheless, the utilization of $ZnCl_2$ might bring the secondary pollution problem since $ZnCl_2$ is a kind of toxic substance. Recently, natural organic matter, such as starch, has been regarded as one of the most promising pore-forming agents for ceramic matrices due to its biodegradability, biocompatibility and non-toxicity (Sandoval et al., 2012; Lin et al., 2013; Dele-Afolabi et al., 2017). Thus a porous structure is estimated to form when starch is added into the biochar derived from the sewage sludge.

In addition, nanoscale zero-valent iron (nZVI) is regarded as one of the most promising materials for the abatement of various pollutants (T. Wang et al., 2014; L. Wang et al., 2014; Diao et al., 2016a, 2016b, 2017; Mu et al., 2017; Sun et al., 2018). However, nZVI easily tends to aggregate so that its reactivity will significantly decrease (Guan et al., 2015; Huang et al., 2016; Gong et al., 2017; Sun et al., 2018). Thus, several materials such as biochar, kaolinite, sepiolite, bentonite and sodium alginate have been widely used as a carrier for the nZVI particle (Fu et al., 2015; Guan et al., 2015; Su et al., 2015; Diao et al., 2016a; Huang et al., 2016; Bhattacharjee et al., 2016; P. Wang et al., 2017; S.S. Wang et al., 2017; C.M. Liu et al., 2018; J.J. Liu et al., 2018). The immobilized nZVI has been successfully proved to be efficient in removing various kinds of pollutants such as organic compounds and heavy metals, with a better performance compared with the bare nZVI (Fu et al., 2015; Diao et al., 2016a; Huang et al., 2016; Gong et al., 2017). However, to date, there is no report on the application of a biochar produced from the combination of sewage sludge and the starch as the carrier of nZVI for the removals of various heavy metals in solutions. It is still unclear how the coexistence effect of different heavy metals does over the biochar/nZVI composite. Actually, the presence of as-obtained biochar might decline the nZVI aggregation and thus remain the high reactivity of nZVI. Furthermore, heavy metals might be effectively removed via a synergistic effect on the adsorption of the biochar and the reduction of the nZVI. Additionally, organic compounds like dyes are often found as accompanying contaminants in the real heavy metal-contaminated environment (Liu et al., 2014; Diao et al., 2015). Thus it would be more motivated to investigate the coexistence effect of dyes on the removals of various heavy metals by the biochar/nZVI composite.

In this study, a biochar/nZVI composite (named as SSB-nZVI) was synthesized using the sewage sludge and the starch by a facile two-step method. Actually, Cr^{6+} is highly soluble and mobile in environment, resulting in carcinogenicity and toxicity to aquatic systems (Ponder et al., 2000; Peng et al., 2017). Pb^{2+} is also a toxic metal which can cause damage to the brain, red blood cells and kidneys (Zhang et al., 2013; Wan et al., 2018). Additionally, the United States Environmental Protection Agency has set the maximum contaminant levels in drinking water at 0.015 mg L^{-1} for Pb^{2+} and 0.1 mg L^{-1} for Cr^{6+} (Kumari et al., 2015). Thus, Cr^{6+} and Pb^{2+} were selected as the representative heavy metals. The main objectives were to: (1) assess the feasibility of the biochar derived from the combination of sewage sludge with starch; (2) evaluate the removal of Cr^{6+} and/or Pb^{2+} under different conditions; (3) test reusability of the SSB-nZVI; (4) clarify the fates of Cr^{6+} and Pb^{2+} on the SSB-nZVI; and (5) explore the possible reaction mechanism on the SSB-nZVI for the simultaneous removal of Cr^{6+} and Pb^{2+} in water.

2. Material and methods

2.1. Materials

Sewage sludge sample was obtained from an activated sludge, a wastewater treatment plant located at Guangzhou, Guangdong, China. The collected sludge was subjected to the following pretreatment. The sample was washed using double distilled water and dried at 100–110 °C overnight. Subsequently it was ground and sieved through a 100 mesh sieve, and finally stored in a closed bottles until use. The principal compositions of the sewage sludge sample were obtained by an energy dispersive X-ray spectroscopy. Result indicates that the main compositions were C, O, Si, Al, Fe, Zn, Mg, Na and P, whereas heavy metals including Cr and Pb were not detected (Table S1). The spin trapping reagent 5,5 dimethyl pyrroline oxide (DMPO) was obtained from Aladdin Chemistry Co., Ltd. The chemicals used in the experiments such as $Pb(NO_3)_2$, $K_2Cr_2O_7$, Malachite green (MG), $FeCl_3 \cdot 6H_2O$, $NaBH_4$ and starch were of the analytical reagent grade.

2.2. Synthesis process

The synthesis procedure of sewage sludge-derived biochar (SSB) was as follows: 2.0 g of starch was added into 30 mL of solution containing ethanol and double distilled water (40%, v/v) in a conical flask with stirring. Afterward, 50.0 g of the pretreated sewage sludge was added into the above solution for 480 min to ensure completely uniform immersion. The mixture was dried and put into a crucible, then heated at a rate of 10 °C min^{-1} to 600 °C for 180 min under N_2 atmosphere. The as-obtained solid was washed quickly with ethanol and double distilled water. Finally, the solid was dried under N_2 atmosphere. The solid without the addition of starch (named as SSB-0) was prepared under the identical conditions.

The procedure of sewage sludge-derived biochar immobilized nanoscale zero-valent iron (SSB-nZVI) composite was similarly prepared by a conventional liquid-phase reduction process (Diao et al., 2016a). Briefly, 10 g of the above SSB was mixed with 9.66 g ferric chloride, ethanol and double distilled water (80%, v/v) to a final volume of 50 mL in a three-necked flask. The 50 mL mixture was mechanically stirred to form a uniform mixture for 20 min under N_2 atmosphere. Then excess amount of $NaBH_4$ solution was added to produce a solid, which was then separated and quickly washed using ethanol. Finally, the above solid was dried and sealed to save. The bare nZVI was prepared without SSB under the identical conditions.