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Stabilization of cationic and anionic metal species in contaminated soils using sludge-derived biochar

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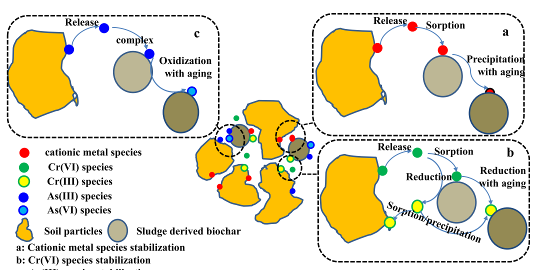
HIGHLIGHTS

- SDBC can effectively stabilize Pb, Cd, Ni, Cr and As in soils.
- A higher temperature and a longer aging favor the stabilization process.
- Sharp temperature drop may release the immobilized As(III) and Cr(VI) species.
- SDBC can enhance Cr(VI) reduction and As(III) oxidation in soil for a long term.
- Adding SDBC as a separate layer is unfavorable as it raises metal release peak.

GRAPHICAL ABSTRACT



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ABSTRACT

Currently, sludge pyrolysis has been considered as a promising technology to solve disposal problem of municipal sewage sludge, recover sludge heating value, sequester carbon and replenish nutrients in farmland soils. The resultant sludge-derived biochar (SDBC) is potentially an excellent stabilizing agent for metal species. This study applied the SDBC into four soils that had been contaminated in field with cationic Pb(II) and Cd(II)/Ni(II), and anionic Cr(VI) and As(III), respectively. The performance of metal stabilization under various operational and environmental conditions was evaluated with acid batch extraction and column leaching tests. Results indicated the SDBC could effectively stabilize these metals, which was favored by elevated temperature and longer aging. Periodic temperature decrease from 45 to 4 °C resulted in the release of immobilized Cr(VI) and As(III) but not Pb(II). However, a longer aging time offset such metal remobilization. This was possibly because more Pb was strongly bound and even formed stable precipitates, as shown by XRD and sequential extraction results. With increasing time, Cr(VI) was sorbed and partly reduced to Cr(III), while immobilized As(III) was co-oxidized to As(V) as indicated by XPS spectra. Column tests revealed that adding SDBC as a separate layer was unfavorable because the concentrated Cd(II) and Ni(II) in localized positions increased the peak levels of metal release under continuous acid leaching. In contrast, uniformly mixed SDBC could effectively delay the metal breakthrough and reduce their released amounts. Yet, a long-term monitoring may be required for evaluating the potential leaching risks and bioavailability/toxicity of these immobilized and transformed species in the SDBC-amended soils.

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1. Introduction

The widespread soil contamination by heavy metals is attracting extensive concerns of scientists and engineers, due to the adverse effects of heavy metals on food quality, soil health and ecological system. The available remediation technologies for these soils are mainly divided to two groups: namely separation and concentration (e. g. soil excavation and disposal, ex situ soil washing, in situ soil flushing, phytoremediation, electro-kinetic remediation, etc.) and immobilization (e.g. in situ chemical stabilization) (Zhang et al., 2010; Bolan et al., 2014; Tsang and Yip, 2014). While the extraction approach may be susceptible to potential leaching and enhanced bioavailability of mobilized heavy metals (Lo et al., 2011; Zhang and Tsang, 2013), the immobilization technology seems to be more cost-effective and less destructive, and thus more suitable for lightly to moderately contaminated soils. Most immobilization techniques aim at minimizing the mobile, soluble, bioavailable and bioaccessible metal fractions that can pose major environmental risks while preserving the soil functionality. For example, Lee et al. (2013) applied calcined oyster shell and coal mine drainage sludge to effectively stabilize the As, Pb and Cu in the contaminated soil.

The most widely used materials to immobilize and stabilize heavy metals in soils can be classified into two groups: inorganic minerals/byproducts (such as oxides/hydroxides, carbonates, phosphates, fly ash, and waste sludge/shell) (Lee et al., 2009; Komárek et al., 2013; Tsang et al., 2013; Michaljevic et al., 2014; Tsang and Yip, 2014) and organic components (including plant-derived biochar, green/food waste compost, natural humic substances, etc) (Ahmad et al., 2014a; Bian et al., 2014; Tsang et al., 2014; Rajapaksha et al., 2015). These soil amendments may raise alkalinity in environment (Gray et al., 2006; Ahmad et al., 2014a; Rees et al., 2014), facilitate metals to precipitate or co-precipitate with (hydro)oxides, carbonates and/or phosphates (Cao et al., 2003; Kumpiene et al., 2008; Wang and Tsang, 2013; Ahmad et al., 2014b), and/or form outer-/inner-sphere complexes with hydroxyl, carboxyl, and phenolic groups on their surface (Bradl, 2004; Uchimiya et al., 2011, 2012; Komárek et al., 2013).

Due to the high levels of heavy metal contents (especially Cd) (Wang et al., 2005; Liu and Sun, 2013), huge amounts of municipal wastewater treatment sludge in some regions of China, such as Pearl River Delta, are not suitable for the land application even after sludge digestion or composting, if without any prior metal removal/stabilization process. Therefore, the sludge-derived biochar (SDBC) prepared through sludge pyrolysis has aroused increasing interests, as this can stabilize most heavy metals in sludge-derived biochar and permit a safer sludge application for replenishing nutrients to farmland soils (Liu et al., 2014; Song et al., 2014; Wesenbeeck et al., 2014). In view of a lower level of organic matter and a higher content of mineral oxides in ash, the corresponding metal stabilization performance of SDBC may be different from carbon-rich biochars produced from plant/crop residuals and poultry manure (Cao et al., 2009, 2011; Rajapaksha et al., 2014). The SDBC was found to be a good sorbent to remove both cationic and anionic metal ions from aqueous phase (such as Pb^{2+}, AsO_2^-, and CrO_4^{2-}) (Zhang et al., 2013a, 2015a). This is because SDBC accommodates more alkaline groups than acidic ones, thus raising solution pH for metal precipitation and complexation of cationic metals on the solid surface (Lu et al., 2012), while it also supplies abundant active sites and amorphous iron/aluminum oxides for immobilization of anionic metals (Zhang et al., 2015a, 2015b). Therefore, SDBC may be a promising agent to immobilize heavy metals in the soil matrixes for realizing low-impact and cost-effective remediation.

The limited available studies about soil amendment using SDBC mainly evaluated the metal accumulation in crops (Liu et al., 2014; Song et al., 2014; Wesenbeeck et al., 2014) and/or immobilization of cationic metals only (Hossain et al., 2010; Méndez et al., 2012). Its stabilization efficacy of anionic toxic species, such as Cr(VI) and As(III), has not been addressed at all. More importantly, the long-term stability of the immobilized heavy metals and metalloids should be monitored (Bolan et al., 2014). Recent findings revealed that soil amendments with biochars, compost, dewatered sludge, or coal fly ash could not indefinitely immobilize the target metals under continuous acid leaching (Houben et al., 2013; Tsang et al., 2013, 2014). Therefore, it is important to assess the influence of environmental factors (e.g., temperature change and aging time) as well as biochar deployment method, which are very critical for the fate of immobilized metals and long-term effectiveness of SDBC application as a soil amendment agent.

This study aimed to investigate metal immobilization by SDBC in four soils collected from the field-contaminated sites, which were contaminated with cationic metals as well as Cr(VI) and As(III) species, respectively. The significant roles of operational conditions and environmental factors in the SDBC-amended soils were probed by means of batch extraction and column leaching tests.

2. Materials and methods

2.1. SDBC preparation

SDBCs were prepared in an LTKC-6-12 pipe oven (Lantian Instrument limited Corp., Hangzhou, China) at 400 °C for 2 h retention, which were the optimal conditions based on our previous studies (Zhang et al., 2013, 2015a). The raw sewage sludge used herein was collected from Lijiao Sewage Treatment Plant in Guangzhou (23°20′N, 113°30′E), where an oxidation ditch process (average hydraulic retention time of 18 h) was employed to remove BOD_5, nitrogen and phosphorus nutrients without the primary sedimentation. The properties of SDBCs were given in Table 1 and our previous studies (Zhang et al., 2013, 2015a).

2.2. Metal stabilization in contaminated soils by SDBCs

Four field contaminated soil samples were used herein. Two of them were primarily contaminated by cationic metals (Pb, Cd and Ni), which were collected from the Dabaoshan mining site in Shaoguan (Soil 1#) and a battery manufacturing waste site near Guangzhou (Soil 2#), respectively. The third soil contained Cr(III) and Cr(VI) species from an electroplating site in Guangdong (Soil 3#), and the last one was contaminated with considerable anionic As(III) species from an industrial waste disposal site in Jiangxi (Soil 4#). More than 5 kg of surface soils (less than 20 cm below ground) were collected from the contaminated sites and air-dried at room temperature. The soils were crushed and pulverized to pass through 2-mm sieve to remove stones and coarse particles, and the resulting samples were ready for soil characterization and subsequent metal stabilization experiments. The soil characteristics and metal concentrations are listed in Table 1.

To immobilize and stabilize cationic and anionic metals in these soil samples, the contaminated soils were uniformly mixed with varying amounts of SBDC for different periods of contact time (0–100 d) in the laboratory. The mixed soil samples were placed in a glass dish and exposed to ambient air at a moisture content of 50% (monitored and regulated by spraying deionized water every 5 d). The operational and environmental conditions varied including the amount of SDBC addition (1–5% by dry mass) and soil temperature (4, 25 and 45 °C). Recent literature usually applied 1–5% biochar in field as otherwise the required amount and volume increase of biochar would arouse concerns, yet a few experiments used SDBC dosage beyond 5% for elucidating their roles in this study. In Pearl