Journal of Environmental Management xxx (2016) 1–8

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Enhancement of chromate reduction in soils by surface modified biochar

Sanchita Mandal [a, *], Binoy Sarkar [a], Nanthi Bolan [b, c, **], Yong Sik Ok [d], Ravi Naidu [b, c]

[a] Future Industries Institute (FII), University of South Australia, Mawson Lakes, SA 5095, Australia
[b] Cooperative Research Centre for Contaminant Assessment and Remediation of the Environment (CRC CARE), Callaghan, NSW 2308, Australia
[c] Global Center for Environmental Remediation, University of Newcastle, Callaghan, NSW 2308, Australia
[d] Korea Biochar Research Center & School of Natural Resources and Environmental Science, Kangwon National University, Chuncheon 24314, Republic of Korea

A R T I C L E I N F O

Article history:
Received 30 January 2016
Received in revised form
14 May 2016
Accepted 14 May 2016
Available online xxx

Keywords:
Black carbon
Charcoal
Engineered biochar
Designer biochar
Animal manure

A B S T R A C T

Chromium (Cr) is one of the common metals present in the soils and may have an extremely deleterious environmental impact depending on its redox state. Among two common forms, trivalent Cr(III) is less toxic than hexavalent Cr(VI) in soils. Carbon (C) based materials including biochar could be used to alleviate Cr toxicity through converting Cr(VI) to Cr(III). Incubation experiments were conducted to examine Cr(VI) reduction in different soils (Soil 1: pH 7.5 and Soil 2: pH 5.5) with three manures from poultry (PM), cow (CM) and sheep (SM), three respective manure-derived biochars (PM biochar (PM-BC), CM biochar (CM-BC) and SM biochar (SM-BC)) and two modified biochars (modified PM-BC (PM-BC-M) and modified SM-BC (SM-BC-M)). Modified biochar was synthesized by incorporating chitosan and zerovalent iron (ZVI) during pyrolysis. Among biochars, highest Cr(VI) reduction was observed with PM-BC application (5%; w/w) (up to 88.12 mg kg^{-1}; 45% reduction) in Soil 2 (pH 5.5). The modified biochars enhanced Cr(VI) reduction by 55% (SM-BC-M) compared to manure (29%, SM) and manure-derived biochars (40% reduction, SM-BC). Among the modified biochars, SM-BC-M showed a higher Cr(VI) reduction rate (55%) than PM-BC-M (48%) in Soil 2. Various oxygen-containing surface functional groups such as phenolic, carboxyl, carbonyl, etc. on biochar surface might act as a proton donor for Cr(VI) reduction and subsequent Cr(III) adsorption. This study underpins the immense potential of modified biochar in remediation of Cr(VI) contaminated soils.

1. Introduction

The production of solid and liquid wastes from industries is continuously increasing. The industries such as timber treatment, leather tanning, electroplating, mineral ore, and petroleum. Discharge huge amounts of wastes in landfill sites (Bolan et al., 2003; Di and Cameron, 2002; Rinklebe et al., 2016a, 2016b). Many of these wastes are enriched with a range of heavy metals, e.g., hexavalent chromium [Cr(VI)] which causes a detrimental effect on the environmental health. Chromium (Cr) is the 21st most abundant metallic element found in our environment (Choppala et al., 2012; Rajapaksha et al., 2013; Sarkar et al., 2013). The two most common species of Cr that include trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] can be found in most of the industrial waste materials (Van Ginkel et al., 2011). Among these two forms, Cr(VI) is more toxic than Cr(III). Since Cr(III) can be retained onto soil particles and less soluble, it is less subjected to leaching in the soil profile (Yang et al., 2007). On the other hand, by existing as an anion, Cr(VI) (known as chromate) is weakly adsorbed by soil particles and highly soluble, which enable plants to uptake it easily from soil, and also subject it to leaching into the groundwater (James and Bartlett, 1983; Rajapaksha et al., 2013). Chromate has a significant environmental concern due to carcinogenic, mutagenic and teratogenic effects on biological systems (Stearns et al., 1995). Chromate concentration in wastewater and drinking water are increasing alarmingly in the past decades. The USEPA maximum permissible limit of Cr(VI) in drinking water is

* Corresponding author.
** Corresponding author. Cooperative Research Centre for Contaminant Assessment and Remediation of the Environmental (CRC CARE), Callaghan, NSW 2308, Australia.
E-mail addresses: mansy043@mymail.unisa.edu.au (S. Mandal), Nanthi.Bolan@newcastle.edu.au (N. Bolan).

http://dx.doi.org/10.1016/j.jenvman.2016.05.034
0301-4797/

Please cite this article in press as: Mandal, S., et al., Enhancement of chromate reduction in soils by surface modified biochar, Journal of Environmental Management (2016), http://dx.doi.org/10.1016/j.jenvman.2016.05.034

0.05 mg L^{-1} and in landfill discharge is 0.1 mg L^{-1}, but extremely high concentrations up to 3950 mg L^{-1} in tannery wastewater has also been detected, which is a serious threat to our environment (EPA, 1990; Herath et al., 2015; Owlad et al., 2009).

Highly toxic Cr(VI) can be reduced to less toxic Cr(III) by using various biowastes such as poultry manure, dairy manure, and biosolids (Park et al., 2008; Singh and Rattan, 2014). Such reaction can be accelerated by using carbon (C) rich materials like biochar (30–70% C), which act as a proton donor for the reduction and the subsequent immobilization sink of Cr(III). Biochar is generally produced as a by-product of the thermal decomposition of organic biomass at low temperature and a limited supply of oxygen (Ahmad et al., 2014; Joseph and Lehmann, 2009; Rajapaksha et al., 2013). In recent days, biochar attracts much interest because of its unique capacity of remediating contaminants in soil and water. The multi-functionality of biochar includes: a) potential carbon sequestration agent in soil, b) adsorbent of heavy metals in soil and aqueous solution, c) nutrient (macro and micro) sink in soil, thereby reducing their leaching losses, and d) soil fertility and productivity enhancer (Clough et al., 2013; Knowles et al., 2011; Mandal et al., 2015; Novak et al., 2016; Woolf et al., 2010).

Biochars produced from manures could be an effective tool for reducing Cr(VI) in soils. Biochar can stimulate soil microbial community and enhance production of dissolved organic carbon (DOC) which can then act as a proton donor for Cr(VI) reduction reaction (Schindler et al., 1992). For example, Bolan et al. (2003) found that application of organic amendments like farmyard manure and biosolids could alleviate Cr(VI) toxicity and reduce its plant availability. Biochar properties, such as its high surface area, and the presence of effective surface functional groups (containing oxygen), are also responsible for this reduction reaction (Choppala et al., 2012; Hsu et al., 2009a, 2009b; Inyang et al., 2015; Mohan et al., 2014).

Biochar characteristics could be modified by incorporating zerovalent iron (ZVI) to further enhance the Cr(VI) reduction reaction. The contaminant remediation efficiency of ZVI is well known, and it is an inexpensive and environmentally safe material (Chekli et al., 2016; Stefaniuk et al., 2016). Zhou et al. (2014) found that ZVI modified biochar increased Cr(VI) removal up to 27.8% from aqueous solution compared to unmodified biochar. Chitosan is another renewable biomaterial which could also be used to modify biochar (Zhou et al., 2013). Chitosan is a transformed polysaccharide which is sourced from natural chitin and it is the 2nd most abundant polysaccharide in the environment (Tharanathan and Kittur, 2003; Zhou et al., 2013). It also acts as a remediation agent because of its high affinity to contaminants, nontoxic nature, and biodegradability (Gerente et al., 2007; Pontoni and Fabbricino, 2012).

In this study, biochar was modified with ZVI and chitosan in order to obtain an effective material for soil Cr(VI) remediation. Chitosan was used as a glue substance to attach ZVI particles on the surface of biochar. The main objective of this study was to quantify and compare the effect of manure, manure derived biochar and modified biochars on Cr(VI) reduction in two contrasting soils.

2. Materials and methods

2.1. Soil and manure samples

Uncontaminated surface (0–10 cm depth) were collected from two different agricultural field's sites in South Australia (termed as Soil 1- Port Sunny vale soil; and Soil 2 - Mount Lofty soil). Soil samples were air dried and ground to pass through 2 mm sieve (stainless steel). These two soils markedly varied in their pH values, which is an important property that would influence the Cr(VI) reduction reaction. Three different manure samples were used in this study; poultry manure (PM), cow manure (CM) and sheep manure (SM). Cow manure and sheep manure were obtained from Bunnings warehouse, South Australia, and poultry manure from manure supplies, Mannum, South Australia. Selected physico-chemical properties of the soil and manure samples are given in Table 1.

2.2. Biochar production

Biochars (BC) were prepared from the three manure samples and termed as PM-BC, CM-BC, and SM-BC. Manure samples were combusted at 450 °C for 1 h in a specially designed pyrolyzer unit (Tube furnace, OTF-1200X). Nitrogen environment was maintained throughout the pyrolysis process and the temperature was raised at a rate 10 °C min^{-1}. Pyrolyzed material was allowed to cool inside the pyrolyzer unit in N_2 environment, the fine powder was collected and passed through a 1 mm sieve prior to use.

2.3. Biochar modification

Chitosan powder (100,000–300,000 g mol^{-1} molecular weight) and ZVI (<800 μm) were purchased from Fisher Scientific, Australia. Biochars (PM-BC and SM-BC) were modified according to a previously described method (Zhou et al., 2013, 2014) and termed as PM-BC-M and SM-BC-M. In brief, chitosan (1.5 g) was dissolved in 90 ml of 2% acetic acid followed by addition of 1.5 g ZVI and 1.5 g biochar into the mixture. The mixture was stirred magnetically for 1 h to obtain a homogeneous suspension. Then a 1.2% sodium hydroxide (NaOH) (450 ml) solution was added dropwise to the above suspension. The resulting mixture was kept undisturbed for the overnight following which the solid portion was separated by centrifugation at 4500 rpm for 20 min. The modified biochar sample was washed repeatedly with Milli-Q (18.2 Ω) water in order to remove any free NaOH. After decantation, the solid portion was freeze dried at −40 °C. Cow manure biochar was omitted because it showed less Cr(VI) reduction compared to PM-BC and SM-BC from both soils.

2.4. Chemical analysis

The pH of soils, manures, biochars and modified biochars was measured by a pH meter (smartCHEM-LAB Laboratory Analyser) in Milli-Q water (1:10 w/v) by employing an hour of agitation (200 rpm) followed by 5 min standing. Electrical conductivity (EC) was also measured using the above suspensions on an EX electrode (smartCHEM-LAB Laboratory Analyser) following after allowing the sediment to settle. Total C, N and S content of soils, manures, biochars and modified biochars were determined using Leco TruMac CNS Analyser (LECO Corporation, USA).

Specific surface area and pore volume of the manures, biochars, and modified biochars were determined from the N_2 adsorption isotherms obtained at −196 °C using a Gemini 2380 Surface Area Analyser. Surface functional groups of the samples were investigated by Fourier Transform Infrared (FTIR) spectroscopy on an Agilent Cary 660 FTIR Analyser. Prior to spectra collection, the samples were homogenously mixed with dry potassium bromide (KBr) (0.01% w/w) in an agate mortar and pressed into composite pellets using a hydraulic press.

2.5. Chromate reduction

Soil samples spiked with 100 mg kg^{-1} of Cr(VI) as potassium dichromate ($K_2Cr_2O_7$), were used for the incubation experiment. The metal was added to soil at field capacity level, mixed uniformly