Investigating the use of synthetic humic-like acid as a soil washing treatment for metal contaminated soil

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HIGHLIGHTS

- A synthetic humic-like acid (SHLA) with a high COOH content was synthesized.
- Optimal soil washing conditions were determined.
- SHLA efficiently removed Cu, Zn, Ni, Pb, As from contaminated agricultural soils.
- SHLA effectively reduced the bioavailability and environmental risk of metals.
- SHLA shows great potential as a soil washing agent.

GRAPHICAL ABSTRACT
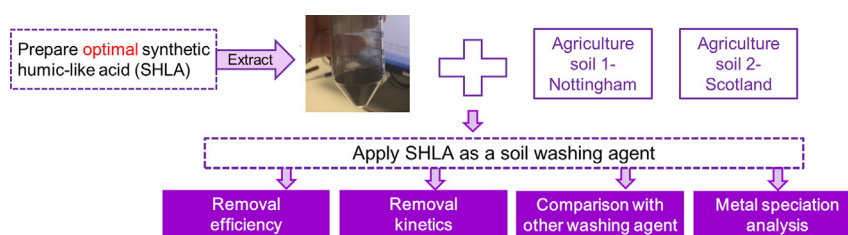
ABSTRACT

Humic acid can effectively bind several metals and is regarded as a promising soil washing agent. Previous studies indicate that carboxylic groups dominate metal binding to humic acid. In this study, a synthetic humic-like acid (SHLA) with high COOH content (5.03 mmol/g) was used as a washing agent to remove metals (Cu, Zn, Ni, Pb, As) from two contaminated agricultural soils (Soil 1 (pH: 6.17 ± 0.11; organic carbon: 5.91 ± 0.40%; Cu: 302.86 ± 3.97 mg/kg; Zn: 700.45 ± 14.30 mg/kg; Pb 323.56 ± 4.84 mg/kg; Ni: 140.16 ± 1.59 mg/kg) and Soil 2 (pH: 9.83 ± 0.01; organic carbon: 2.52% ± 0.25%; Cu: 242.81 ± 10.66 mg/kg; Zn: 841.00 ± 22.31 mg/kg, Pb $451.21 \pm 1,92$ mg/kg, As: 242.23 ± 5.24 mg/kg)). The effects of solution pH (4 to 11), liquid/solid ratio (L/S ratio, 5:1 (mL:g) to 80:1 (mL:g)), SHLA concentration (100 mg/L to 2000 mg/L), and contact time (0 to 1440 min) on % metal removal were investigated and optimum conditions identified: pH of 9, L/S ratio of 1:80, SHLA concentration of 1500 mg/L at 25 °C for 4 h. Under optimum conditions, a single washing removed 45.2% of Cu, 34.6% of Zn. 42.2% of Ni and 15.6% of Pb from Soil 1, and 30.6% of Cu, 28.1% of Zn. 14.6% of As and 18.1% of Pb from Soil 2. A modified BCR extraction of the two soils before and after washing indicated that the SHLA mainly removed metals in the exchangeable and acid soluble fraction and reducible fraction, which could effectively reduce bioavailability and environmental risk of metals. On a molar basis, SHLA was a more effective washing agent than commercial humic acid, Na_2EDTA, citric acid and tartaric acid. Overall, SHLA shows great potential for use as a soil washing agent.

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1. Introduction

Soil contamination by hazardous metals is currently a serious environmental issue worldwide. For example, hazardous metals are the most frequent contaminants (34.8%) affecting soil and groundwater in Europe and 82.8% of cases of soil contamination are caused by inorganic contaminants (mainly hazardous metals) in China (EEA, 2018; MEE, 2014). The original sources of excess hazardous metals in soils are various, including atmospheric deposition, sewage irrigation, waste disposal, mining activities, metal smelting, sewage sludge, pesticides and fertilizers (Lwin et al., 2018; Mahar et al., 2016; Su et al., 2014). Hazardous metals are of great concern because not only are they non-biodegradable, but they can enter the food chain and finally accumulate

in the human body, posing a great threat to both human health and the environment (Lesmana et al., 2009; Suanon et al., 2016). The most common metal contaminants include Cd, Cr, Hg, Pb, Cu, Zn, and As (Ashraf et al., 2017; Kumpiene et al., 2008).

Various remedial approaches for metal-contaminated soil have been investigated in the past decades, including soil washing, solidification/ stabilization, soil amendment, phytoremediation, electrokinetic processes, and bioremediation (Bolan et al., 2014; Leštan et al., 2008; Liu et al., 2017; Rosestolato et al., 2015; Wan et al., 2016; Xia et al., 2017). Of these, soil washing is regarded as one of the most efficient, rapid and cost-effective techniques (Wuana and Okieimen, 2011). Washing agents, which are the key to soil washing techniques, can be classified into four types: 1) inorganic acid (e.g. HCl, H_2SO_4, HNO_3); 2) synthetic organic chelating agents (e.g., EDTA, DTPA, EDDS); 3) surfactants (e.g. humic acid, saponin, rhamnolipid) and 4) low-molecular-weight organic acids (e.g., oxalic acid, citric acid, tartaric acid) (Ferraro et al., 2016; Gusiatin and Radziemska, 2018; Jiang et al., 2017; Kulikowska et al., 2015; Meng et al., 2017; Yoo et al., 2017). However, although inorganic acid and synthetic organic chelating agents have high metal removal efficiencies, inorganic acid will acidify soil, change soil structure and decrease soil fertility and microorganism activity; while synthetic chelating agents have low biodegradability and can have adverse effects on groundwater quality and soil microorganism health (Gusiatin and Klimiuk, 2012; Meng et al., 2017; Yang et al., 2017). Thus, using environmentally friendly and cost-effective washing agents is encouraged to reduce risks to ecosystems and human health.

Humic acid (HA) is a natural surfactant (Conte et al., 2005) that can not only effectively complex many different metals due to its abundant oxygen-containing functional groups especially carboxylic group and phenolic-OH group, but also improve soil properties (Meng et al., 2017; Perminova and Hatfield, 2005; Sparks, 1995). Thus, humic acid has been regarded as a promising soil washing agent (Hartley et al., 2014; Kulikowska et al., 2015; Meng et al., 2017; Tsang and Hartley, 2014). In addition to occurring naturally, humic acid can be synthesized by abiotic humification processes, that is the transformation of humic precursors (e.g., polyphenol, amino acids, and reducing sugars) to humic substances catalyzed by materials containing metallic oxide (e.g., pure MnO_2, zeolite, and steel slag). Humic acid synthesized by abiotic humification is called synthetic humic-like acid (SHLA) (Fukushima et al., 2009; Hardie et al., 2009; Qi et al., 2012; Zhang et al., 2017; Zhang et al., 2015). Compared with natural humic acid, SHLA has the advantage that its structural characteristics can be controlled to some extent by changing the abiotic humification conditions, such as the species of precursors, pH, temperature and the ratio of catalyst (Fukuchi et al., 2012; Jokic et al., 2004; Yang and Hodson, 2018a, 2018b; Zhang et al., 2017; Zhang et al., 2015). Recently, we have reported a SHLA which was optimized to complex Cu^{2+} and can be used as an adsorbent for removing several metal ions from metal-contaminated water (Yang and Hodson, 2018a; Yang and Hodson, 2018b). However, studies on how to apply SHLA as part of the soil washing process are still rare. The novelty of our study lies in the application of a SHLA that has been synthesized to optimize its metal removal efficiency for soil washing.

In this study, we examined the use of aqueous SHLA as a soil washing agent. Previous studies indicate that carboxylic groups dominate metal ion binding to humic acid (Gondar et al., 2006; Xu et al., 2016; Yang et al., 2015). An optimal SHLA with a high COOH content was produced using synthesis conditions informed by our previous experiments and characterized by elemental analysis, acidic functional group content, FTIR and UV-VIS absorbance. A series of batch removal experiments were carried out to determine the effect of initial SHLA concentration (100–2000 mg/L), pH (4–9), liquid/soil ratio (L/S ratio, 5:1 to 80:1 (mL:g)) and reaction time (0–1440 min) on % metal removal in two agricultural soils (Soil 1 and Soil 2); optimum extraction conditions were determined. Using the BCR sequential extraction method (Zhang et al., 2017), I_R (reduced partition index) and M_F (metal bioavailability factor) parameters, metal speciation distribution before and after SHLA

washing and the influence on metal stability and mobility in two soils were also investigated. Finally, a comparison of metal washing efficiency between SHLA and four other washing agents (CHA, Na_2EDTA, citric acid and tartaric acid) was conducted.

2. Materials and methods

2.1. Materials

Catechol ($C_6H_6O_2$, >99% purity), glycine ($C_2H_5NO_2$, >99% purity), glucose ($C_6H_{12}O_6$, >99% purity), thimerosal ($C_9H_9HgNaO_2S$, >97% purity), manganese oxide (MnO_2, >99% purity), ethylenediaminetetraacetic acid disodium salt dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, 98.5–101.5% purity), citric acid ($C_4H_8O_7$, >99% purity), tartaric acid ($C_4H_8O_7$, >99% purity) and commercial humic acid (CHA) were purchased from Sigma-Aldrich. Sodium phosphate dibasic dihydrate ($Na_2HPO_4 \cdot 2H_2O$, >99% purity), sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot H_2O$, >99% purity) and hydrogen peroxide (H_2O_2, 30% purity) were purchased from ACROS Organics. Calcium chloride ($CaCl_2$, >99% purity), acetic acid (CH_3COOH, >99% purity) and ammonium acetate (CH_3COONH_4, >99% purity) were purchased from Fisher Chemical. Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, >99% purity) were purchased from Alfa Aesar. Ultra-pure water was prepared using a PURELAB Classic ultra-pure system (ELGA, UK) from deionized water.

2.2. Soil sampling and characterization

Two agricultural soils with similar bulk metal concentrations above permitted levels for agricultural use (see below) but different pH and organic matter contents that could result in differing performances of the SHLA washing agent were sampled for this study. Soil 1 in this study was collected from a farm located on the Stoke Bardolph Estate (GR 52.97104, −1.05515; Nottingham, UK). Soil 1 has been treated with sewage sludge for several decades and is used for growing corn for the Stoke Bardolph Energy Crop Plant (Riddell-Black, 1994; Severn Trent Water, 2016). Soil 2 was obtained from an upland farm near Laurencekirk (GR 56.89450, −2.54512; Aberdeenshire, UK) and was previously treated with metal(loid) rich wood ash arising from waste wood combustion, applied in controlled experiments at 10% vol (Trakal et al., 2017; Mitchell et al., 2018). The soils were air dried ar room temperature and sieved to 2 mm. Soil pH was measured in a 1:2.5 (w/v) soil/ultrapure water mixture (Rowell, 1994). Soil organic carbon was determined using a vario MACRO C/N analyzer (Elementary, Germany). Cation exchange capacity (CEC) of soil was measured following the method of Hendersot and Duquette (Hendershot and Duquette, 1986). Soil texture was determined using a Malvern Laser granulometer (Malvern Instruments, UK). Methodological details are provided in the Supplementary materials. Total metals in soil and the concentration of metals in the BCR residual fraction (see below) were measured following the International Standard Organization (ISO)-method BS7755 (British, 1995).

2.3. Preparation and characterization of optimal synthetic humic-like acid

In preliminary experiments, 11 synthetic humic-like acids (SHLAs) were synthesized under varying abiotic humification conditions (different temperatures, pH, precursor species and initial concentrations, and masses of catalyst) to determine optimal synthesis conditions to produce a SHLA with a high COOH content (Yang and Hodson, 2018a). Subsequent to these preliminary investigations, the SHLA used in this study was synthesized using these conditions: a pH 8, 0.25 M glycine: 0.25 M catechol mixture at 25 °C with 2.5 wt% MnO_2 as a catalyst. In detail, all glassware and pure water were autoclaved (121 °C for 27 min, 0.12 MPa) prior to use to ensure that the humification was abiotic. An 1 L aliquot of autoclaved phosphate buffer (pH 8, 0.2 M Na_2HPO_4/ NaH_2PO_4 autoclaved at 121 °C for 27 min, 0.12 MPa) containing 0.02%