Journal of Geochemical Exploration xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

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

Evaluation of modified chitosan for remediation of zinc contaminated soils

Nimisha Tripathi Ph.D. [a,c,*,1], Girish Choppala Ph.D. [b], Raj S. Singh Ph.D. [a]

[a] Centre for Environmental Risk Assessment and Remediation, Building–X, University of South Australia, Mawson Lakes, South Australia 5095, Australia
[b] Southern Cross GeoScience, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia
[c] Central Institute of Mining and Fuel Research, Barwa Road, Dhanbad, Jharkhand, India

ARTICLE INFO

Article history:
Received 5 June 2016
Revised 9 August 2016
Accepted 17 August 2016
Available online xxxx

Keywords:
Chitosan
Zinc
Contamination
Soil
Immobilisation
Remediation

ABSTRACT

This study evaluated the effects of pure and modified chitosan beads on the remediation of zinc (Zn) polluted soils and estimated the bioavailability of Zn for Indian mustard plants. The soil was spiked with 0 to 400 mg kg^{-1} of Zn and subsequently amended with pure chitosan beads (PCB) and chitosan beads modified with molybdenum (MoCB), iron (ICB), single super phosphate (SSPCB) and mono calcium phosphate (MCPCB). Compared to the non-amended soils, chitosan bead amended soils had greater plant biomass, reduced plant metal uptake and increased immobilisation of Zn in soil and pore water. Shoot uptake of Zn decreased the most in MoCB amended soil, and least in PCB amended soil relative to unspiked soil. The decrease in plant Zn uptake and enhanced Zn immobilisation may be attributed to Zn complexation by modified chitosan beads with high surface area and cation exchange capacity (CEC). The application of modified chitosan beads to Zn contaminated soil could significantly decrease Zn bioavailability and toxicity.

1. Introduction

Industrial and mining activities release effluents that include toxic heavy metals. Unlike organic contaminants, heavy metals do not degrade, becoming a persistent threat to the terrestrial environment (Adriano, 2001). These metals pollute soil, sediments, surface and groundwater, and in serious cases bio-accumulate in living organisms and disrupting the food chain. Zinc is released to the environment from both geogenic and anthropogenic sources. Anthropogenic sources are greater than those from natural sources and represent a major management challenge. The primary anthropogenic sources of Zn in the environment are related to mining and metallurgic operations, discharges of smelter slags, coal and bottom fly ash and use of commercial products containing Zn (viz., coatings to prevent rust, dry-cell batteries, brass and bronze alloys).

Zinc does not volatilise from soil, but usually partially adsorbed to soil surfaces and partially leached to water bodies. Zinc and its salts cause acute and chronic toxicity to aquatic life in polluted waters (Milosavljević et al., 2011). Levels of Zn in excess of 500 mg kg^{-1} in soil interfere with the ability of plants to absorb other essential metals, such as iron and manganese (Emsley, 2011). The recommended threshold concentration for Zn (ecological investigation level) for soil and groundwater is 200 mg kg^{-1} as per the National Environment Protection (Assessment of Site Contamination) Measure (NEPC, 1999).

Chitosan, poly-β(1-4)-2-amino-2-deoxy-D-glucose, is derived from the deacetylation of chitin isolated from the exoskeletons of crustaceans. It is the world's second most abundant naturally occurring polysaccharide (Abdou et al., 2008). Chitosan consists of amino and hydroxyl groups that can act as binding sites for metal ion complexation. It is a powerful chelating agent and possesses high adsorption capacity for a variety of heavy metals including Zn, Cu and Hg (Chu, 2002; Dhakal et al., 2005). Chitosan has received considerable interest for its potential for removing metal ions from wastewaters. Since chitosan contains nearly 6.9% nitrogen and hence amino and hydroxyl groups on their chemical structures act as chelating sites for metal ions. It can adsorb heavy metals due to its excellent metal-binding capacities and is more cost effective than activated carbon (Babel and Kurniawan, 2003).

Earlier studies have investigated techniques for the removal of Zn from wastewater using a single gas-lift bioreactor, a biosorption technique using orange waste, separation of extractant-impregnated organogels and pH-sensitive chitosan based hydrogels (Milosavljević et al., 2011; Nii et al., 2010). Although several studies on the removal of heavy metals from waste waters have been carried out, there have been no studies on the remediation of Zn contaminated soils by chitosan. This work examines the potential of pure and modified chitosan beads to immobilise Zn in contaminated soils. Furthermore, the effectiveness of chitosan on reducing the bioavailability of Zn was investigated using Indian mustard plants.

* Corresponding author at: Central Institute of Mining and Fuel Research, Barwa Road, Dhanbad, Jharkhand, India.
E-mail address: nymphaea7@gmail.com (N. Tripathi).
[1] Present address: Indo-UK Environment Centre, University of Greenwich, Chatham Maritime, Kent ME4 4TB, UK

http://dx.doi.org/10.1016/j.gexplo.2016.08.011
0375-6742/

2. Materials and methods

2.1. Preparation of chitosan gel beads

Chitosan with a deacetylation of nearly 88% was supplied by QingDao Yuanrun Chemical Co. (China) and was used without purification. Nearly 2.0 g of chitosan was dissolved with 50 mL of 5% (v/v) acetic acid solution and left overnight to form a yellow viscous chitosan acetate solution. Pure chitosan gel beads were prepared by phase inversion of chitosan acetate solution using 0.5 M NaOH solution. The wet chitosan gel beads were rinsed thoroughly with deionised water and dried at 60 °C. Molybdenum-impregnated chitosan beads (MoCB) were prepared by immersing known amounts of wet chitosan beads with 5 g L^{-1} Mo using ammonium heptamolybdate at pH 6 and stirred for 24 h at 200 rpm (Dambies et al., 2001). Iron-doped chitosan beads (ICB) were prepared by phase inversion of a mixture of 2 g of chitosan powder dissolved in 1 g of ferric chloride ($FeCl_3$) in 50 mL of 5% acetic acid (v/v).

The SSPCB was prepared by inversing a mixture of 2.5 g SSP, 2.0 g chitosan and 50 mL 5% acetic acid. Similarly MCPCB was prepared using a mixture of 2.0 g of MCP, 3.5 g of chitosan powder in 50 mL of 5% acetic acid (v/v). All mixtures were dripped into 3 M sodium hydroxide solution through a tube with 2 mm internal diameter. The ICB beads were collected after 30 min and then thoroughly washed with distilled water. Chitosan gel beads were oven dried at 60 °C to obtain a dry mass. Pure and modified chitosan beads were characterised with respect to the cation exchange capacity (CEC), Brunauer, Emmett and Feller (BET) surface area and pore size (Micromeritics, Gemini V, USA).

2.2. Soil sampling and characterization

Soil was collected from a non-contaminated site (0–10 cm depth) at Redland Bay, Queensland, and is classified as a Ferrosol. The air dried soil sample was mixed with Zn (ZnSO4) at a concentration of 50, 100 and 400 mg kg^{-1} and incubated at field capacity for two weeks. Soil suspensions were prepared in 50 mL polypropylene centrifuge tubes with 5 g of soil and 12.5 mL of 0.01 M CaCl2 shaken for 30 min in an end–over–end shaker. pH and EC were measured with a pH-EC analyser (TPS Smartchem–lab, Australia) and calibrated before measurements were taken. The particle size was determined by the weight percentages of sand, silt, and clay, calculated from the density of an aqueous soil suspension measured by hydrometer (Ashworth et al., 2001). Cation exchange capacity (CEC) and iron (Fe) and aluminium (Al) concentrations were determined by methods described in Rayment and Higginson (1992). Total organic matter was measured by the oxidisable dichromate method of Walkley and Black (1934).

2.3. Zinc immobilisation

Zn immobilisation was examined at known concentrations (50–500 mg kg^{-1}). Soil was amended with 0.8 g (0.4% w/w) of pure and modified chitosan beads and incubated at field capacity for one month. Following incubation, the soils were extracted with a 1 M NH4NO3 solution (1:2.5 w/v soil: NH4NO3) for 2 h and the concentration of Zn analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Agilent, Japan). The immobilisation of Zn was calculated using the following equation (Eq. (1)) (Park et al., 2011):

$$\text{Immobilized Zn}\,(\%) = \frac{(\text{NH4NO3 zinc for the control} - \text{NH4NO3 zinc for treated sample}) \times 100}{\text{NH4NO3 zinc for the control}} \quad (1)$$

2.4. Plant growth test

Plant growth dynamics were used to assess Zn bioavailability in the presence of modified chitosan beads. Plastic pots (500 mL capacity) were filled with 200 g of Zn-spiked-soil and amended with 0.8 g (0.4% w/w) of pure or modified chitosan beads. The chitosan amended soils were incubated for one week at field capacity. Ten seeds of Indian mustard (*Brassica juncea* L.) were sown per pot and the experiments carried out in a temperature-controlled greenhouse environment (25 ± 3 °C; 12 h light). Each treatment was studied in triplicate. After 3 days of germination, the seedlings were thinned to 4 per pot.

Plant biomass was harvested after one month and the shoots and roots were collected, washed carefully with Milli-Q water to remove soil, oven dried (60 °C for 4 days) and weighed for dry mass determination. Zinc concentration in plant material was determined after digestion in Conc. HNO3. Plant material (0.1–0.5 g) was weighed into 75 mL digestion tubes and cold digested overnight with 5 mL of concentrated nitric acid. The samples were heated using a temperature controlled digestion block (AI Scientific Block Digestion System AIM500, Australia) programmed to slowly increase the temperature to 140 °C until approximately 1 mL of plant digest remained in the tube. After the extraction, the samples were centrifuged at 4000 rpm for 20 min, filtered through 0.45-μm membrane filters and aqueous phase was analysed using ICP-OES (Perkin–Elmer Optima–5300, Japan).

3. Results and discussion

3.1. Properties of the materials

Physico-chemical properties of soils and chitosan beads are provided in Table 1. The pH of soil was 5.02, the EC 36 μS cm^{-1} and moisture content 8.29%. Soil particle size was dominated by silt (44%), followed by clay (35%) and sand (21%). Organic carbon content and CEC were 3.92% and 10.9 cmol kg^{-1}, respectively. Molybdenum, Fe, SSP and MCP loadings on chitosan beads were 10.25, 0.96, 0.4 and 0.14 g 100 g^{-1} dry bead, respectively. Cation exchange capacity of modified chitosan beads were given in Table 1.

Based on earlier studies (Chen et al., 2007; Guibal et al., 1998), on heavy metal removal from water using modified chitosan, we selected molybdenum, single super phosphate and mono calcium phosphate for modifying chitosan. It was hypothesized that these modification materials can also serve as a slow release nutrients in nutrient deficient soils.

Greater CEC values for all impregnated chitosan beads compared to PCB may be due to introduction of more anions (molybdate, hydrogen phosphate and phosphate) to the chitosan bead structure. Iron-impregnated beads were lower in CEC value than chitosan beads, possibly due to iron saturation of the negative-charged chitosan surface.

The BET surface areas of the modified chitosan beads were higher than the pure chitosan bead. The MoCB had the largest surface area (6.63 m^2 g^{-1}), followed by SSPCB (4.67 m^2 g^{-1}), MCPCB (2.00 m^2 g^{-1}), PCB (0.186 m^2 g^{-1}) and ICB (0.141 m^2 g^{-1}). Pore size was greatest for MoCB (17.94 Å), followed by SSPCB (17.38 Å), MCPCB (16.59 Å), ICB (11.72 Å) and PCB (8.34 Å). The intercalation of the chitosan structure by their respective anions (molybdate, phosphate

Table 1
Physico-chemical properties of soil and chitosan beads.

Samples	pH	EC (μs cm^{-1})	OC (%)	Sand (%)	Silt (%)	Clay (%)	CEC (cmol kg^{-1})	BET surface area (m^2 g^{-1})
Soil	5.02	36	3.92	21	44	35	10.9	–
PCB	–	–	–	–	–	–	21.01	0.186
MoCB	–	–	–	–	–	–	34.02	6.63
ICB	–	–	–	–	–	–	15.75	0.141
SSPCB	–	–	–	–	–	–	24.03	4.67
MCPCB	–	–	–	–	–	–	32.63	2.0

PCB = pure chitosan beads, MoCB = molybdenum chitosan beads, ICB = iron chitosan beads, SSPCB = single super phosphate chitosan beads, MCPCB = monocalcium phosphate chitosan beads.

Please cite this article as: Tripathi, N., et al., Evaluation of modified chitosan for remediation of zinc contaminated soils, J. Geochem. Explor. (2016), http://dx.doi.org/10.1016/j.gexplo.2016.08.011