Research Paper

Remediation of metal contaminated soil by aluminium pillared bentonite: Synthesis, characterisation, equilibrium study and plant growth experiment

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ARTICLE INFO

ABSTRACT

In order to enhance the efficiency of metal immobilisation, bentonite clay was pillared with polyhydroxy aluminium complexes. The pillared bentonite was systematically characterised by multiple techniques including x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The clay product was assessed for its metal removal efficiency from aqueous systems through batch experiments with variables in pH, amount of adsorbent and initial metal concentration. The adsorption data were fitted with Langmuir and Freundlich isotherm models. The maximum monolayer adsorption capacity of pillared bentonite was 61.4, 32.3 and 50.3 mg g^{-1} for Cu (II), Zn (II) and Ni (II), respectively. The immobilisation efficiency of pillared bentonite was assessed by greenhouse pot culture experiment with amaranth as the test crop. Amendment of soil with pillared bentonite at 2.5% significantly improved the plant growth as well as reduced the bioavailable metals in the metal spiked soils. The study demonstrated that pillared bentonite could potentially be used for addressing heavy metal pollutions by immobilising the metals in the contaminated soil.

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1. Introduction

Heavy metals contamination of the environment has emerged as a serious problem due to the rapid industrialisation and urbanisation of the society. The wastes or by-products generated through these activities are discharged into the environment, which directly contaminates the water bodies and soils. Inorganic wastes containing heavy metals pose a great threat to human being because of their non-degradability and biomagnifications (Mapanda et al., 2005; Kurniawan et al., 2006; Singh et al., 2010). Additionally, due to the paucity of good quality waters, industrial and/or municipal wastewaters are commonly used for irrigation purposes in peri-urban areas across the developing countries. The excessive accumulation of heavy metals in agricultural soils by repeated applications of polluted waters may cause soil contamination, and seriously impact the food quality and safety by imposing the risk of bioaccumulation in the food chain (Pescod, 1992; Rattan et al., 2009). For example, in the peri-urban Keshopur area near New Delhi in India, the concentrations of heavy metals, specially Zn, Cu and Ni, were respectively 208, 170 and 83% greater in soils irrigated with

sewage treatment water over tube well water for 20 years (Datta et al., 2000; Rattan et al., 2005).

Since heavy metals are non biodegradable, an ecofriendly, economically viable and comprehensive remediation technique is the need of the hour. Among many remediation approaches, the risk-based land management aims to manage the contaminated soils through reduction of the risks to an acceptable level instead of complete removal of the contaminants from the system which otherwise incurs prohibitively high costs of ex-situ and in-situ clean up (Naidu, 2013). Stabilisation of metals in soil by amendments is a rational method which can effectively reduce the bioavailability of contaminants and thus the risks below the level of concern (Hettiarachchi and Pierzynsk, 2002; Bolan et al., 2014; Shaheen et al., 2015). For stabilising metals in the soil, the quantity and quality of colloid- forming adsorptive complexes is the most important factor which determines the bioavailability of the metals. The high metal adsorption capacity of clay minerals (because of their large specific surface area and reactive functional groups) makes them one of the most common amendments for metal adsorption/stabilisation (Lothenbach et al., 1999; Prost and Yaron, 2001; Saha et al., 2002; Kim et al., 2005; Fu and Wang, 2011). Furthermore, the metal loading capacity of clay minerals can be improved significantly through various modifications (Cooper et al., 2002; War et al., 2006; Sarkar et al., 2012). One such modification is the pillaring process where a guest metal species is inserted without changing the layered

structure of the clay mineral (Schoonheydt et al., 1999). Few studies previously investigated the adsorption of heavy metals by pillared clay minerals mainly from aqueous solutions (Bhattacharya and Gupta, 2006; Manohar et al., 2006; Perelomov et al., 2015). Nevertheless, additional information are needed on the use of functionalised clays for the immobilisation of heavy metals and their effect on the health risk assessment of vegetable crops grown in metal contaminated soils. Therefore, in the present study, an aluminium-pillared bentonite was evaluated as the immobilising agent for the remediation of a metal spiked soil. Bioconcentration factor and hazard quotient were calculated to assess the efficiency of the pillared bentonite in reducing the metal uptake by a leafy vegetable crop (*Amaranthus viridis*) which was grown in the contaminated soil.

2. Materials and methods

2.1. Materials

A bentonite sample was procured from Minerals Limited, New Delhi, India, and the clay size (<2 μm) bentonite particles were isolated by employing the sedimentation procedure. All chemicals supplied by Sisco Research Laboratories Pvt. Ltd. (SRL), India, were of analytical grade and used without further purification. Bentonite was pillared with $AlCl_3.6H_2O$. Stock solutions of metals (Zn, Cu and Ni) containing 1000 mg L^{-1} metal ion was separately prepared by dissolving appropriate amount of analytical reagent grade nitrate [$Ni(NO_3)_2.6H_2O$] and sulphate [$Cu(SO_4)_2.5H_2O$; $Zn(SO_4)_2.7H_2O$] salts of the heavy metals in double distilled water. The working standard solutions of the metals were prepared from the stock solution by appropriate dilution in double distilled water. The soil for the greenhouse pot culture experiment was collected from the top 10 cm of the agricultural farm of Indian Agricultural Research Institute (IARI), New Delhi. Selected physico-chemical properties of the experimental soil are listed in Table 1. The soil was spiked with 250 mg kg^{-1} of Zn and 100 mg kg^{-1} each of Cu and Ni by addition of dissolved metal solution and mixing it thoroughly with the soil. Among other heavy metals, Zn, Cu and Ni concentrations were alarmingly high in the sewage irrigated soils in the peri-urban area of New Delhi (Datta et al., 2000; Rattan et al., 2005). For this reason, these three heavy metals were selected in the current study.

2.2. Synthesis of pillared bentonite

Bentonite (<2 μm) was pillared with aluminium according to a previously published method (Lothenbach et al., 1999) with some minor

Table 1
Selected physico-chemical properties of the experimental soil.

Soil properties	Values
Mechanical composition	
Sand %	76.3
Silt %	11.6
Clay %	12.1
Soil texture	Sandy loam
pH (1:2 Soil:water)	8.32
EC (1:2) (dS m^{-1})	0.45
CEC (cmol (p^+)) kg^{-1}	11.4
Soil organic carbon (g kg^{-1})	5.42
Available soil N (mg kg^{-1})	156
Available soil P (mg kg^{-1})	9.1
Available soil K (mg kg^{-1})	218
DTPA extractable metals	
Zn (mg kg^{-1})	1.12
Cu (mg kg^{-1})	1.11
Ni (mg kg^{-1})	nd
Total metal content	
Zn (mg kg^{-1})	85
Cu (mg kg^{-1})	28
Ni (mg kg^{-1})	2

modifications. Sodium saturated bentonite was first prepared by adding 10 mL of sodium chloride solution (0.25 M) drop-wise to a 10% (w/v) bentonite suspension in double distilled water. The mixture was continuously stirred on a magnetic stirrer for 16 h. Following separation through centrifugation (5000 rpm for 10 min), the sodium saturated bentonite particles were washed with double distilled water until the supernatant became chloride free. The product was then dried in an oven for 2 h and grinded to powder. The pillaring solution was prepared by drop-wise addition of 0.2 M sodium hydroxide to 0.2 M aluminium chloride solution under continuous stirring to reach the OH/Al ratio of 2. The pillaring solution was prepared and kept at room temperature (25 °C) for 5 days for the purpose of aging. The pillaring solution was added at a rate of 3–4 mL min^{-1} to 10% (w/v) sodium saturated bentonite suspension under continuous stirring on a magnetic stirrer and the reaction mixture was aged at 25 °C for 16 h after the pillaring process. The final product was washed with distilled water to remove the excess precipitate, dried at 80 °C, calcined at 300 °C for 2 h in a hot-air oven, grinded, sieved through 100 mesh, and kept in a desiccator until further use.

2.3. Characterisation of pillared bentonite

In order to determine the changes in crystallinity, X-ray diffraction (XRD) patterns of the pillared bentonite was recorded with a Philips model PW1710 diffractometer, fitted with a Cu tube ($\lambda = 1.5418$ Å, 40 kV and 20 mA, scanning from 3° to 15° 2θ at a step angle of 0.1°, 5 s/step). The XRD was performed at room temperature at 21–26% relative humidity without adding any saturating cation to the samples.

Fourier transform infrared (FTIR) analyses were performed at room temperature in the spectral range of 4000–600 cm^{-1} using a FTIR spectrometer (model SPECTRUM-1000, Perkin Elmer). The pillared bentonite along with dehydrated KBr (0.02% (w/w)) was ground and mixed thoroughly, and the mixture was made into pellet by a hydraulic press. The spectra were collected with 64 scans of accumulation at a resolution of 4 cm^{-1}.

The surface morphology of the pillared clay was observed under a Scanning Electron Microscope (Zeiss Evoma10) at up to 20 keV primary electron beam energy. Finely powdered sample was mounted on a double-sided tape placed on an aluminium stub with industrial glue and coated by 20 nm thick palladium layers in vaccum prior to analysis. Images were acquired using the Secondary Electron (SE) signals (Everhart-Thornley detector).

Specific surface area (SSA) and cation exchange capacity (CEC) of the pillared bentonite were determined by EGME (ethylene glycol monoethyl ether) method (Carter et al., 1965) and Ca—Mg exchange method (Jackson, 1973), respectively.

2.4. Adsorption experiments

All the adsorption equilibrium experiments were conducted by batch method in triplicate. Our previous reports already demonstrated that the Al-bentonite adsorbed significantly greater quantity of heavy metals than the raw bentonite (Kumararaja et al., 2014; Kumararaja and Manjaiah, 2015). The current study therefore focussed on some specific reaction parameters for the adsorption of multiple heavy metals by the pillared clay and its ability to immobilise heavy metals in contaminated soils. To examine the effect of adsorbent dose on metal adsorption, 50 mL of 25 mg L^{-1} metal solution with different concentration of pillared bentonite (0.01, 0.025, 0.05, 0.1, and 0.2 g) in polypropylene bottles was shaken for 24 h on an end to end shaker. Preliminary experiments showed that a 24 h agitation was sufficient to reach the adsorption equilibrium. The pH of the metal solution was adjusted with 0.01 M HCl or NaOH to 6, 7 and 8 for Cu, Zn and Ni, respectively. Following agitation the solution was filtered through Whatman No. 42 filter paper. The initial and equilibrium concentrations of metal in the aqueous solutions were analysed by Atomic Absorption