Green approach of chemical immobilization of lead in metal-contaminated soils of NCT of Delhi using rock phosphate and coal fly ash

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ABSTRACT

Contaminated sites are the legacy of a long period of industrialization involving unconsidered production and handling of hazardous substances and unregulated dumping of wastes. Metal contamination need to be characterized on varying temporal and spatial scales. Keeping this object in mind, soil used for this study was collected from a Pb contaminated site in an industrial area of Naraina and Mayapuri in the NCT of Delhi. EPA Method 3051 is commonly regarded as a regulatory alternative to Method 3050. It is a rapid and accurate dissolution technique for soil metal ions. This technique is time saving and energy efficient. No acid fumes are generated. For all these reasons the above technique can be considered a green technique. Remedial measures required to clean up metal contaminated sites are often complex and economically unsustainable. Immobilization of the metal ions e.g., Pb, Zn and Cd by green amendments like rock phosphate and coal fly ash is promising and economically feasible technique. In this connection a bench scale investigation has been carried out to access the potential use of these amendments for immobilizing these metal ions in severely contaminated sites in Delhi. Parallel experiments have been carried out in columns with unamended and amended soil samples. Results have indicated that metal content in percolating waters are drastically diminished when amendments are admixed with soils.   © 2009 Trade Science Inc. - INDIA

INTRODUCTION

Green Chemistry is not a new branch of chemistry but is a pulling together of tools, techniques and technologies that can help chemists in research and production to develop more eco-friendly and efficient products and processes. The term, first defined by the US Environmental Protection Agency as 'the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products', is now widely accepted. Keeping this object in mind the current investigation has been undertaken.

Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems. Nevertheless, because of certain useful physical and chemical properties, some heavy metals, including mercury, lead, and cadmium are intentionally added to certain consumer and industrial products such as batteries, switches, circuit boards, and certain pigments. Usage patterns of heavy metals in products have varied over the years. The problems of soil pollution with heavy

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metals and organic pollutants are subject of investigation in all countries of Asia including India. Their correct solution requires the application of very precise analytical methods and reproducibility of the different pollutants determination in soil and the definition of reliable criteria for the estimation of the pollution degree that are compatible with the concrete conditions. Unfortunately, reliable analytical techniques and adequate sampling of media containing potential releases from waste disposal sites are only decades old, and so meaningful long term data on the fate of heavy metals in wastes do not exist. The rapid and accurate determination of heavy metals in environmental matrices such as soil has led to the development and continuous improvement of various analytical methods concerning both sample digestion and the choice of most appropriate instrumental techniques to obtain exhaustive chemical information in shortest time possible. At present, there are various official methods which are applying different acid mixtures and microwave heating systems. In this report we wish to compare these open flask hot plate and microwave assisted closed flasks methods when applied to Delhi soils.

The bioavailability of heavy metals in soil depends on their concentration in the soil solution and on the release of these ions from the solid soil phase[13]. Depending on sewage-sludge characteristics and heavy metal content, application of sewage sludge may increase or decrease the soluble heavy metal fraction in soil and may affect their transfer into the food chain[23]. Reducing the heavy metals solubility and bioavailability without removing them from contaminated soils is one measure that could weaken detrimental heavy metal impacts on the environment[17]. Immobilization can be achieved by adding natural and synthetic additives such as phosphate minerals, Fe and Mn oxides, aluminosilicates, and coal fly ash[20].

Within the frame of a comprehensive laboratory investigation aimed at identifying low cost metal immobilizing agents such as certain industrial waste products and certain industrial raw products, the authors explored the possibility of using coal fly ash and rock phosphate respectively. The effectiveness of green amendment, coal fly ash in immobilizing metals has been demonstrated for heavily contaminated soils lifted from industrial areas of Delhi by undertaking initial batch studies. Laboratory experiments have been underway for over a year now in columns containing soils mixed with CFA and the as received soil as controls. The Pb, Zn and Cd contents of the eluates are determined periodically as well as pH and conductivity. The results so far demonstrate that heavy metal content in the leachates drastically reduced upon addition of CFA[20].

Further the remediation of the metal contaminated soil using another green amendment such as rock phosphate has also been undertaken. Phosphate rock is the raw material used for phosphate fertilizer production. Hettiarachchi et al.[10] stated that phosphate rock was relatively insoluble compared to other sources of phosphate and should reduce P losses in runoff. Ma et al.[18] demonstrated that the use of phosphate rock was a cost effective way to remediate Pb- contaminated soils. Basta et al.[1] reported that phosphate rock immobilization products were more stable under acidification than other treatments, and that phosphate rock treatment would reduce bioavailability of Pb associated with the ingestion of contaminated soils by humans. Hettiarachchi et al.[10] reported that phosphate rock was equally or more effective than Triple Super Phosphate. The preliminary studies have revealed addition of rock phosphate results in formation of immobilization product, lead pyromorphite from compounds of lead in soluble contaminated form.

MATERIALS AND METHODS

Site characterization

The soil used for this study was collected from a Pb contaminated site in an industrial area of Naraina and Mayapuri in the NCT of Delhi. Industrial activities, which included a recycling operation for lead batteries, industrial activities, which included paints and recycling operation for lead batteries, have all contributed to the contamination of this site.

The total Pb concentrations in the soil ranged from 1875 to 6625 mg kg^{-1}. Lead concentration decreased with soil depth, with the majority of the Pb present near the soil surface (0-20 cm).

Soil analysis

Experimental procedures

Soil samples were collected from the top 20 cm at the industrial sites at Mayapuri. They were collected from a location where high concentrations of Pb are present. They were air-dried, sieved through a 2-mm

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stainless steel sieve and stored at room temperature. The soil sample was thoroughly mixed to ensure uniformity.

Metal concentration

They were then digested using the microwave digestion procedure (USEPA Method 3051) for total Pb concentration using Scientific microwave Anton Paar Multiwave 3000. The clean soil sample was collected from Himalayan region. Concentrations of Pb, in the extracts were analyzed with AAS (acetylene air flame) (Perking Elmer A Analyst -100) with addition calibration.

Electrochemical properties

Electric conductivity (EC) and pH were measured in water suspensions and in 0.01 M $CaCl_2$. (*Elico CM* 180 and *Elico LI* 127)

The Pb contents and pH in the clean and contaminated soils were 165 and 6625 mg kg^{-1}, and 7.5 and 8.11, respectively.

Clay content

The clay content was determined by sedimentation analysis using a hydrometer after dispersion in sodium polyphosphate.

The Toxicity Characteristics Leaching Procedure (TCLP) was used to evaluate the efficiency of P amendments on lead toxicity[24,26].

Analytical procedures for remediation

Bench test for phosphate amendment

In our preliminary laboratory experiments these soil samples were subjected to Pb immobilization optimization by testing P sources and application rates using bench experiments.

In this investigation, column tests were used to evaluate the effectiveness of selected treatments for further detailed evaluation. A total of 25 g air-dry soil was mixed with $Ca(H_2PO_4)_2$ H2O salt at an application rate equivalent to 22.5 ton per acre for the contaminated soil. After uniform mixing, mixture was placed in 60-mL syringes containing 0.5 g coarse washed-sand to prevent soil loss during leaching. Mixed solution of 0.005 M H_3PO_4 and 0.001 M $CaCl_2$ was added to bring soil to near field capacity. Each column was covered with polyurethane film to avoid moisture loss but allow adequate air exchange. It was incubated at room temperature. After one week of incubation, 25 mL of deionized water was leached through columns under gravity and samples were returned for continued incubation and were extracted after 4 week.

Leachate was filtered through 0.45 μm membrane filters. The supernatant was analyzed for dissolved organic carbon (DOC), phosphate, and metals as described above. The TCLP test was used to evaluate the effectiveness of applied treatment by taking soil sample from one of the column replicates.

Batch test leaching for CFA amendment

10 g air dried soil was mixed with the amendment (for CA1, 1g CFA and for CA2, 2.5g CFA) according to the factorial design and left at room temperature for two weeks to equilibrate at humidity level corresponding to 50% of the soil water holding capacity. Such samples were prepared in triplicate along with samples without amendment. These samples were then filled into 250 mL PE bottle and mixed with 110 mL and water acidified to pH 4 using HNO_3 at a liquid to solid ratio (L/S) 10L kg^{-1}. Samples were shaken for 24 h using an orbital shaker. pH and conductance were measured in unfiltered samples. The treated and untreated samples were leached with 400-500 ml (560-750 mm annual rainfall) of artificial rain water under a saturated flow regime, collecting successive leach fractions of 25 ml using a fraction collector. Leachates were filtered through 0.45 μm membrane filters. The supernatant was analyzed for metals as described above.

RESULT AND DISCUSSION

Green analytical technique

To adequately protect or restore soil ecosystems there is a great need to characterize soils suspected or presumed to be contaminated with heavy metals. Metal contamination need to be characterized on varying temporal and spatial scales. Keeping this object in mind, soil used for this study was collected from a Pb contaminated site in an industrial area of Naraina and Mayapuri in the NCT of Delhi. To properly assess metal health hazard in soils, several sample preparation methods have been evaluated in the past to calculate soil screening levels for the soil-plant-human pathways. Acid digestion and thermal decomposition steps can result in analyte losses, incomplete recoveries, and/or sample contamination. EPA digestion method 3051a (microwave, HNO_3-HCl, total-recoverable) widely applicable

TABLE 1: Selected physicochemical properties of the contaminated and control soil samples*

Reference soil	pH [a]	Conductance (µS)	OM [b]	Sand	Silt	Clay	Pb$_T$ [c] (mg kg^{-1})	Zn$_T$ [c] (mg kg^{-1})	Cd$_T$ [c] (mg kg^{-1})
Contaminated sample MAYA	8.11	0.39	2.63	77.5	5	17.5	4925 1530	16650 5535	356 152
Controlled sample HIM	7.55	0.23	3.51	77.5	7.5	15	165 63	704 352	15 3.5

*Data represent an average of twelve replicates with a standard deviation, [a]pH was determined with a 1:1 ratio of soil/water, [b]Organic matter, [c]Total concentration, Concentrations given in red colored font have been determined using hot plate method

for adapting the prescription-based method to create a performance-based method and permit newer technological implementations such as microwave heating[16]. The technique provides rapid, safe, and efficient digestion and is not susceptible to losses of volatile metals[11]. It has thus been adopted by the EPA (EPA Methods 3051 and 3051a) to extract metals from sludge, soil or sediment[24]. EPA Method 3051 is commonly regarded as a regulatory alternative to Method 3050[16,24]. It is a rapid and accurate dissolution technique for soil metal ions. This technique is time saving and energy efficient. No acid fumes are generated. For all these reasons the above technique can be considered a green technique.

Selected chemical properties of the collected surface soil (0-20 cm) are listed in TABLE 1. The soil is very sandy, with a pH of 8.11, which is within the range typical of Delhi soils. Lead was the main contaminant with a concentration of 4925 mg kg^{-1}, which exceeds the critical level for industrial soils (1,400 mg kg^{-1}). Generally, Pb, was concentrated on the surface soil (0-20 cm) and their concentrations decreased with soil depth. However, a substantial amount of Pb (>2,000 mg kg^{-1}) was found at depths below 30 cm. In the long run, it is possible that the metals may leach downward to the subsurface soil[3,4,5,7,8]. For comparison the lead concentration using conventional hot plate method has also been given in the TABLE 1. Results indicate that the conventional hot plate methods do not give a complete estimation of metal ions in soil.

Green amendments for soil remediation

For the soil stabilization to be successful, amendments that can adsorb, complex, (co)precipitate contaminants, or a combination thereof, should be selected. Soil treatment application *in situ* also requires that chosen amendments have no reverse effects on soil properties and biota. Soil amelioration with materials similar to natural soil constituents (e.g. oxides, organic matter) can reduce metal mobility, while contributing to the recovery of soil quality. Soluble contaminants are subject to migration with soil water, uptake by plants or aquatic organisms, or loss due to volatilization into the atmosphere. In recent years, attention has focused on the development of *in situ* (in place) immobilization methods that are generally less expensive and disruptive to the natural landscape, hydrology, and ecosystems than are conventional excavation, treatment, and disposal methods. *In situ* immobilization of metals using inexpensive amendments such as minerals (e.g., rock phosphate) or waste by-products (e.g., coal fly ash) are promising alternatives to current remediation methods. This technique relies on a fundamental understanding of the natural geochemical processes governing the speciation, migration, and bioavailability of metals in the environment. In polluted soils, metals can be dissolved in solution, held on inorganic soil particles, complexed with organic soil components, or precipitated as pure or mixed solids. Metals in soil may be associated with various phases that are reactive, semi-reactive or non-reactive. The risk to the environment from contaminated soil cannot be assessed by simply considering the total amount of potentially toxic metals within the soil because these metals are not necessarily completely mobile or bioavailable. The main goal of *in situ* remediation techniques is to reduce the fraction of toxic elements that is potentially mobile or bioavailable. Environmental mobility is the capacity for toxic elements to move from contaminated materials to any compartment of the soil or groundwater. Bioavailability refers to the fraction of a contaminant that can be taken into any biological entity, be it plant, earthworm, or human. Depending on the chemical form in which a contaminant occurs, it may range from being totally bioavailable to less bioavailable. All additives in this case caused a reduction in the heavy metal ions lability, ranging from 95% to 100% compared to the control.

Remediation using phosphate rocks

Phosphate rocks have been also tested to remediate soils polluted with zinc, cadmium or copper (TABLE

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TABLE 2 : Pb, Zn and Cd concentrations in bench leachates after phosphate amendment after 2 weeks

Treatment	Leachate concentration (μg L^{-1})		
	Pb(μg L^{-1})	Zn(μg L^{-1})	Cd(μg L^{-1})
RP0	15.9	1955.5	55.8
RP1	13.4	1678.6	46.7
RP2	12.8	1687.1	49.9

TABLE 3: Pb, Zn and Cd concentrations in bench leachates after CFA amendment after 2 weeks

Treatment	Leachate concentration		
	Pb(μg L^{-1})	Zn(mg L^{-1})	Cd(mg L^{-1})
CA1	ND	2497.5	40.5
CA2	ND	2382.6	35.1

2). These treatments, although generally effective for zinc as well as cadmium, do not attain the level of immobilization shown for lead. Phosphate rock has the highest affinity for Pb (99%), followed by Cd (97%) and Zn (90%). In general, these treatments lessen the risk of polluted soils limiting metal leaching and bioavailability. In addition to Pb, phosphate rock can also remove Zn and Cd from aqueous solutions. Lead is present in various oxidation states in soil. The solubility of the Pb compounds (lead acetate > $PbSO_4$ > $PbCO_3$ > PbS ~ pyromorphite) followed trends based on known solubility data. Geochemically stable and less bioavailable pyromorphite is expected to get formed. Phosphate has been shown to effectively immobilize Pb from contaminated soils [2,10,17,7,14,15,18,19]. It is well documented that lead phosphates are the most insoluble and stable forms of Pb in soils, and they can form rapidly in the presence of adequate Pb and P.

The possible mechanisms for metal retention by phosphate minerals included: (1) ion exchange processes at the surface of PR[22,28]; (2) surface complexation[28]; (3) precipitation of some amorphous to poorly crystalline, mixed metal phosphates[18]; and (4) substitution of Ca in PR by other metals during recrystallization (coprecipitation)[28,4,5,12]. However, it is difficult to quantify the relative contribution from each mechanism that is responsible for metal removal and it appears that all four mechanisms may work together. As such, estimating the extent of each mechanism contributing to metal retention by PR has not been reported. In addition, contaminated soils commonly encountered multi-metals including Pb, Cu, Zn, Cr, Cd and Ni[18]. Competitive retention of these metals onto phosphate minerals has not been well studied, and individual metal immobilization mechanisms are still not fully understood.

Remediation using CFA

The results of the bench scale studies have been tabulated in TABLE 3. Several studies have demonstrated coal fly ash (CFA) to efficiently reduce trace element mobility in soil[6,9]. Coal fly ash is capable of immobilizing Pb, Cd, Cu and Zn effectively from aqueous solutions. Among the three metals studied, the metals sorbed by the ash decreased in the order: Pb > Cd > Zn. Significant reductions in the leaching of Cd by 89% and Pb by 100% were observed in the soil treated with CFA alone. 85% reduction was observed for Zn. Although an exact mechanism of element retention by CFA is unclear, the main reasons are believed to be (I) an increase in pH causing the precipitation of insoluble phases and (II) an increase in a specific surface area, promoting metal sorption via surface complexation, cation exchange reactions or both. This suggests that immobilization is fundamentally related to the neutralization of the soils and to a decreased aggressivity of the leach solution by strongly alkaline fly ash. The initial attack of the leach solution solution is able to solublize the metals that once in solution precipitate in the form of hydroxides in as the liquid phase becomes alkaline. Metal sorption by the ash was probably due to ion exchange between metal ions in the aqueous solutions and Ca^{2+} on the surfaces of calcite and gypsum in the ash, which resulted in the formation of calcite-gypsum-like minerals.

CONCLUSION

To properly assess metal health hazard in soils, out of the several sample preparation methods evaluated to calculate soil screening levels for the soil-plant-human pathways, EPA method 3051b is commonly regarded as a regulatory alternative to Method 3050. It is a green analytical procedure as very less amounts of reactants are required. It is less time consuming, energy saving and no acid fumes are generated.

The stabilization of soils contaminated with Pb, Zn and Cd (soil MAYA) as assessed by the bench experiment significantly reduced the leaching of all analyzed elements. The treatment efficiency decreased in the following order: Pb >Cd > Zn in soil. Even if stabilization does not alter the contamination level of soil, it reduces the risk contaminants pose to human health and the environment by modifying the element mobility and availability, and thus allowing a step towards a non-toxic

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environment. By reducing contaminant mobility (migration potential) the risk class of a site is also reduced. Our results strongly demonstrate that rock phosphate was effective in reducing Pb solubility and bioavailability through dissolution of phosphate rocks and precipitation of pyromorphite. The effective and rapid Pb^{2+} immobilization from solution and contaminated soils by phosphate rock, the limited effects from other minerals, anions, and cations, the apparent environmental stability of the reaction products, along with the ready availability and low cost of hydroxyapatite or phosphate rock suggest that this approach might have great merit for cost-effective in situ immobilization of Pb contaminated water, soils, and wastes. The stabilization method applied at moderately contaminated sites offers a considerably lower cost alternative to conventional remediation techniques while delivering environmentally acceptable results and should therefore be more appealing to the public.

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