REMOVAL OF HEAVY METALS FROM CONTAMINATED SOIL BY WASHING $CACL_2$ AND EFFECT OF pH

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Introduction

Surveys of the concentrations of heavy metals in river Yamuna water, aquatic plants and soils showed that contain elevated concentration of heavy metals upstream to down stream Okhla to Wazirabad [1]. The remediation/ or immobilization of heavy metals in contaminated soil to compost [2] washing with mineral acids, this effect being frequently associated with soil pH in increase in acidic soil (e.g., HCl, HNO_3), chelate [e.g., ethylenediamine tetraacetic acid (EDTA), diethylenetriamine pentaacetic acide (DTPA) determine their efficacy for removal of heavy metals from soils [2]. The river Yamuna covers a 22 km stretch between Wazirabad and Okhla barrage in Delhi which is only 2% of its catchment area, but it contributes about 80% of the river's total pollution load. The 19 major drains from Delhi dispose untreated municipal wastewater, approximately 2 270 million litres per day, into the Yamuna, in which approximately 355million litres per day are from the industrial effluents [3]. This contamination in the Yamuna water might be due to untreated sewage and industrial waste. The toxic components and heavy metals in river Yamuna are a major cause of extinction of its fauna and flora [4]. In recent years pollution of freshwaters in third world countries has reached an alarming point where it might extend to a point of irreparable damage with implicating consequences [5]. The concentration levels are relatively low in areas of high pH and low organic matter content concentration. The limiting pH level and the release edge for all heavy metal contaminants are characterized to facilitate the selection of appropriate acid strength for remediation of heavy metal contaminated soils. Because of the difference in the affinities of heavy metals with soil and soil constituents [6], the effective pH level is likely to vary depending on the type of heavy metal and its bonding strengths with soil. The current information for some coarse-textured soils shows minor variation in the threshold pH value among Zn (pH = 4.6 ± 0.4), Pb (pH = 4.1 ± 0.1) and Cu (pH = 4.1 ± 0.1) [7]. The information will enable the selection of appropriate acid strength for remediating heavy metal-contaminated soils [8].

The objectives of this research were to determine: (1) This study has its importance for determining and fluxes of heavy metals in river Yamuna to aquatic plants and bed soils (2) the effective threshold pH values for the release and fraction of several metals including Cd, Zn, Ni, Pb from river Yamuna contaminated soils (3) if soil washing with 0.1 M HCl reduces the heavy metal concentrations of the soils below the trigger levels.

Materials and Methods

Soil properties

The pH was measured immediately after samples were brought to the laboratory and the concentration of heavy metals in river Yamuna water was estimated using a certified MERCK standards solution using atomic absorption spectrometry (AAS-Auto sampler) with a 100 Perkin Elmer instrument. Heavy metals in soil were calibrated using certified reference soil materials. Samples were brought to room temperature before analysis for heavy metals by air–acetylene flame hollow cathode lamp AAS. A deviation of ¡5–10% was observed from certified values of heavy metals. The detection limits by the AAS Graphite-100 instrument for heavy metals were as follows: Cd 0.01, Zn 0.01 ppm, Ni 0.04 ppm and Pb 0.01 ppm.

The metal contamination resulted from industrial effluents with water laden with heavy metals from illegal discharge of industrial wastewater. Soil samples were collected from three sites to a depth of about 20 cm, air dried, and crushed to pass through a 2-mm sieve. They were analyzed for selected physical and chemical properties including pH (1:2 soil:water ratio), soluble salts by saturation extract, organic matter by the Walkley and Black procedure, particle size distribution by the pipette method, cation exchange capacity by displacement with a saturating salt solution, and total concentration of various metals. In addition to the total Cd, Zn, Ni and Pb for the Okhla and wazirabad soil were analyzed by digesting 1.0 g of soil in 8 mL of aqua regia at 95 °C for 16 h. This was followed by the analysis of all heavy metals by atomic absorption spectrophotometry (AAS – 100, Perkin Elmer USA). Since Pb in the Wazirabad soil was the only heavy metal exceeding the national cleanup standards, it was the only heavy metal investigated for this soil. All analyses were done in triplicate.

Effects of dilute HCl and $CaCl_2$ on metal extraction

The effect of acid strength on the release of various heavy metals for these soils was studied by shaking 5 g of soil with 45 mL of HCl solution for 16 h on a platform shaker. The HCl concentrations used were

0, 0.001, 0.005, 0.01, 0.05, 0.1 and 0.2 M, which created a broad range of pH to facilitate the determination of the limiting pH level for the release of heavy metals. At the end of the shaking period, the suspensions were analyzed for pH before being transferred to centrifuge tubes and centrifuged at 10,000 rpm for 3 min. The supernatant in each centrifuge tube was filtered through a 0.45-μ membrane filter, and the filtrate was subsequently analyzed for the concentration of the Cd, Zn, Ni and Pb metals by AAS. The extraction was repeated successively three times. After each extraction, a fresh solution (45 mL) of the same HCl concentration was used to transfer the soil from the centrifuge tube back to the flask for the next extraction. All glassware was washed with HCl solution (5%) and rinsed repeatedly with deionized water before use. The effect of $CaCl_2$ on the release of the heavy metals was studied at low acid strengths up to 0.01 M HCl. The concentrations of the salt solution used ranged from 0 to 0.2 M. The salt solution was added with HCl to bring the final HCl concentration up to 0.01 M.

The limiting pH levels for the target metals were determined by regression technique. The regression equations were developed based on the response of metal concentrations to declining solution pH. From the equations, we calculated the pH at which the concentration of each metal was zero was calculated. This pH was assumed to be the limiting pH value. The limiting pH value as the pH value at which the solubility of the metal was five times greater than the solubility of that metal at some higher pH level ([7].

Results and Discussion

The Okhla site slightly acidic and Wazirabad site soils were neutral acidic and as with soils had high clay contents (>33%) (Table1). The soil analysis confirmed that the Okhla site soil was highly contaminated with Cd, Zn, Ni, and Pb, and the Wazirabad soil with Zn and Pb. (Table. 1)). The Pb concentration in the Okhla soil was more than three times higher than the standard limits (500 mg Pb kg^{-1}) established by the Environmental Protection Agency EPA. While Cd concentration in the Okhla aquatic plants and soil have exceed the concentration level (5 mg kg^{-1}), it exceeded the permissible level (2.5 mg kg^{-1}) for living and soils. The Pb and Cd contamination of the okhla soil resulted when wastewater from a battery, steel, chemical and plating processing plant was directly discharged into the river Yamuna. Improper and untreated disposal of industrial wastewater often contributes to heavy metal contamination of soils in Delhi river Yamuna [3]. Since the concentrations of Cd, Zn, Ni, and Pb in the Okhla soil and Pb in the Wazirabad soil well exceeded the trigger levels, food crop production is prohibited on both soils until after they have been remediated.

Table 1: Physical chemical properties of Okhla and Wazirabad soils in Delhi

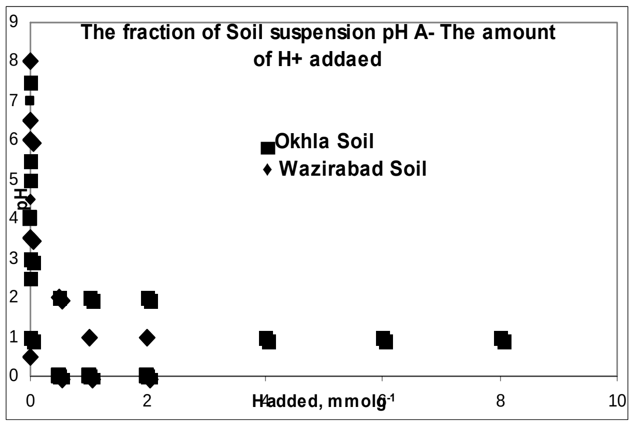
Soil	pH	Organic matter	Metal content					
			CEC	Clay	Cd	Zn	Ni	Pb
			cmole kg^{-1}	%	mg kg^{-1}			
Okhla	6.2	4.75	25.82	36	109.7	1473	587	597
Wazirabad	7.2	3.70	20.46	33	36.67	1027	149	149

Effects of HCl concentration on metal extractability

Solution pH of both soils declined sharply from near neutral to about 2.2 by the addition of 400 μmole H^+g^{-1} (Fig. 1A) with 0.01 M HCl. It further declined to 1.2 by the addition of 1000 μmole H^+g^{-1} with 0.1 M HCl. Increasing to 2000 μmole H^+g^{-1} with 0.2 M HCl depressed the solution pH to about 1 at which point a sharp increase in the loss of H^+ from solution occurred (Fig. 1B). At pH > 2.2, the small loss of H^+ from solution, presumably as a result of sorption of protons or hydroxylation of surface sites, was accompanied by a sharp drop in solution pH. At pH < 2.2, a small reduction in solution pH was accompanied by a steep rise in the loss of H^+ from solution as H^+ was used in the dissolution of mineral components in the soils. The response of solution pH to increased H^+ addition appeared to be the same for both soils containing more than 30% clay Fig. 1A & IB. While the concentration released was highest for Zn and lowest for Cd reflecting their totals in the soil, the total concentration across all heavy metals was not a good indicator of their extractability. Despite having a concentration comparable to Zn, both and Ni were far less extractable than Zn across the pH range studied. The release edge showed the extractability of the heavy metals in the Okhla soil generally decreased in the order of Cd > Pb> Zn > Ni at pH about 2.2 or higher.

The order for all but Ni in general reflects the strength of their affinities with soils. Comparing the response of the fraction of Pb extracted to pH for the Wazirabad soil with that of other heavy metals in the Okhla soil. The limiting pH value and the slope of the response curve should characterize heavy metal release from the soils as solution pH declines. The limiting pH value determined based on the regression equations developed from the response of the fraction of the heavy metals extracted to pH (Table 2) was lowest for Pb (pH = 3.1), Ni (pH = 4.3), and highest for Cd (pH = 4.8) and Zn (pH = 4.9) [7]. The value for Pb for the Wazirabad soil is lower compared with the value (pH = 4.1). The wazirabad soils in the study are sandy and contain far lower heavy metal concentrations than the contaminated soils used in our study.The heavy metals studied also differed markedly in the slope of the response of extractability to declining pH at pH below the effective values. The slope for the heavy metals followed the order: Pb(0.379) > Cd(0.225) > Zn(0.179) > Ni(0.096). With a high response slope, Pb contamination in the Okhla, Wazirabad soil and other contaminated soils could be remediated with washing or flushing with 0.1 M HCl, provided that the Pb contamination is not too excessive. This also was generally true for Cd, and Zn. The low pH value, coupled with a low response slope, make Ni rather stable in the soil and will be very difficult to remediate without extensive dissolution. This difficulty will also be encountered for Zn, though to a lesser degree. The low response slope for Ni will require an acid strength greater than 0.2 M HCl to effectively remove Ni from the soil.

The fraction of the total metal Cd, Pb, Zn and Ni in Okhla soil by the effect of pH and conct. Of $CaCl_2$



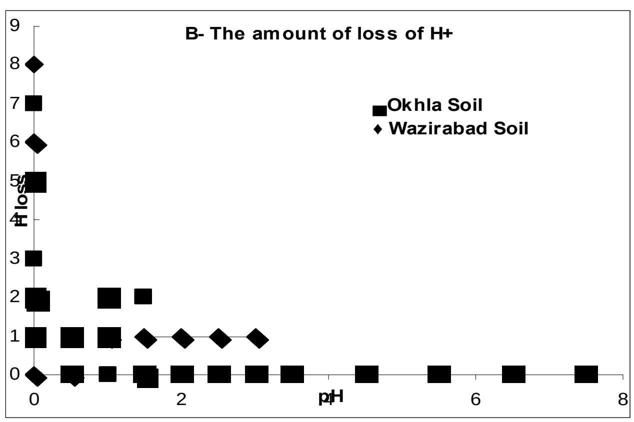
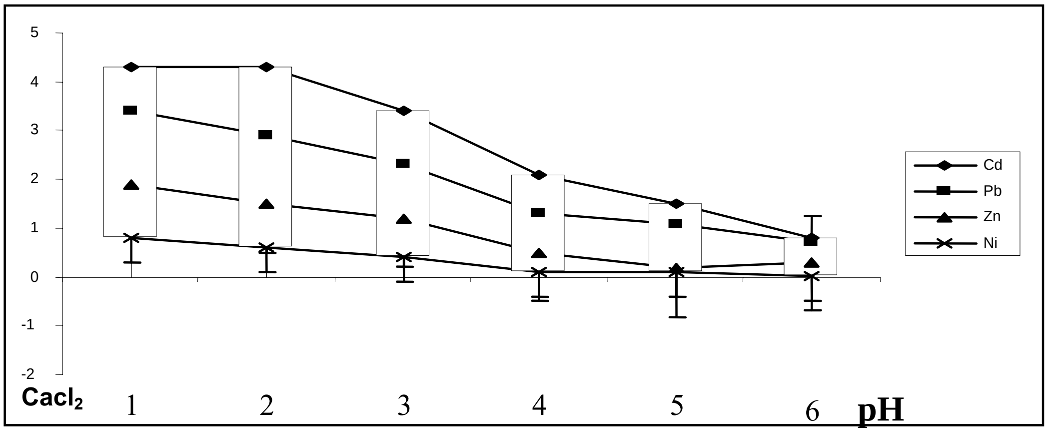


Table 2.The relationship between the rise in fraction of Cd, Zn, Ni, and Pb extracted and declining pH

Soil	Metal	Equation	r^2
Okhla	Cd	y = − 0.225x + 1.071	0.96
	Ni	y = − 0.096x + 0.414	0.95
	Zn	y = − 0.179x + 0.875	0.96
	Pb	y = − 0.374x + 1.89	0.96
Wazirabad	Ni	y = − 0.156x + 0.320	0.52
	Pb	y = − 0.379x + 1.182	0.94

y = fraction of the metals extracted; x = pH.



Washing metal-contaminated soils with 0.1 M HCl showed some promise as a remediation technique as it rapidly and effectively removes some heavy metals (e.g., Cd, Zn, Ni and Pb) from contaminated soils. The fractions of the heavy metals extracted with four successive extractions of Okhla and Wazirabad soils with this acid solution were 0.68 for Cd, 0.74 for Zn, 0.72, 0.39 for Ni, and 0.87 for Pb in Okhla soil and 0.80 for Pb in the Wazirabad soil. While the result in general agrees with the finding of that the acid solution is moderately effective in removing Zn, Cd, and Pb from contaminated soils, this technique failed to sufficiently reduce Ni in the Okhla soil to levels below the trigger levels established by the EPA. Washing soil at pH 2 was found effective in removing sorbed Pb from contaminated soil. While successive washing with 0.01 M HCl sacrifices some efficiency in the extraction of Cd, Zn, Ni and Pb from the acidic soils, it would generate far less quantity of toxic oxide residue than does 0.1 M HCl [8, 9]

Conclusion

The release of Cd, Zn, Ni and Pb from an Okhla soil highly contaminated with these heavy metals and the release of Pb from a Pb-contaminated The limiting pH values of the release for Cd, Zn and Pb were higher than Ni it was lower. Within the pH range studied (from about 1.0 to 6.5), the release of Ni was more highly correlated. While four successive extractions of the soils with 0.1 M HCl succeeded in reducing Pb concentration of the Wazirabad soil to below the trigger level, it failed to substantially remove Ni or Cd from the Okhla soil. The strength of the acid solution could be lowered to 0.01 M as this solution was still capable of extracting more than 60% of the total Cd, 70% of the total Pb and approximately 50% of total Zn in the Okhla soil and total Pb in the Wazirabad soil.

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