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Study on Effect of HCl and $CaCl_2$ on Extraction of Heavy Metals From Contaminated Soils

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The efficiencies of hydrochloric acid and calcium chloride were tested for extracting metals from contaminated soils. The selectivity of the acids and $CaCl_2$ toward soil adsorption sites, the lower the pH in the extracts and the more soil metals Pb, Cd and Zn, Ni could be extracted. The concentration of heavy metals observed was in Yamuna river were, Cd 0.18, Zn 1.3, Ni 1.6, Pb 1.38 mg/L and in submerged plants were, Cd 0.3, Zn 1.19, Ni 0.8, Pb 0.97 mg kg^{-1} in Okhla and in Yamuna river Cd 0.09, Zn 0.98, Ni 1.02 and Pb 0.95 mg/L and in submerged plants Cd 0.0 9, Zn 0.9, Ni 1.9 and Pb 0.3 mg kg^{-1}, respectively in Wazirabad. This indicates that industry effluents could be one of the cause pollution and point sources of metals pollution in the Yamuna river. The Okhla point have low pH compare to Wazirabad (pH 6.2-7.2 and 7.2-9.0) and Okhla soil releases more heavy metals like Cd, Pb, Zn and Ni in site Okhla > Wazirabad. The correlation analysis revealed that Cd and Pb fraction of metals in soil with pH and salt was highly correlated ($p < 0.001$), whereas the Zn and Ni fraction was not better correlated ($p < 0.001$).

Key Words: Soil fractionation, Yamuna river, Extraction of heavy metals, Wastewater, Submerged plants.

INTRODUCTION

The Yamuna river covers a 22 km stretch between Okhla and Wazirabad 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, *ca.* 2270 million liters per day, into the Yamuna river, in which *ca.* 355 million liters per day are from the industrial effluents[1]. This contamination in the Yamuna river might be due to untreated sewage and industrial waste. The toxic components and heavy metals in Yamuna river are a major cause of extinction of its fauna and flora[2,3]. 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. Increased concentrations of heavy metals have occurred in many ground water, aquatic plants and agricultural soils as a result of anthropogenic activities such as smelting, land disposal of hazardous chemical-contaminated effluents, industrial solid wastes and waste waters and use of pesticides containing metals and metalloids such as cadmium, lead, zinc and nickel. To improve underground water, soil quality and agricultural field and to minimize the transfer of heavy metals from soil to water and crops, subsequently to humans, a number of nations have established a maximum loading limit for each heavy metal. Remediation action is applicable if soil metal concentration exceeds the standard limit[4-6].

Surveys of the concentrations of heavy metals in Yamuna river, submerged plants and soils showed that they contain high concentration of heavy metals from downstream to Okhla upstream to Wazirabad[4]. These soils have to be remediated to bring the heavy metal concentrations below the effective limit. The remediation or immobilization of heavy metals in contaminated soil by compost, chelate, washing with mineral acids, this effect being frequently associated with soil pH in increase in acidic soil (*e.g.*, HCl, HNO_3), determine their efficacy for removal of heavy metals from soils[7-11].

In the extraction of heavy metals with acid solution, the release of heavy metals into solution as a function of pH should be known. The release can involve exchange reactions and/or dissolution depending on acid strength and heavy metals involved. The concentrations of heavy metals are relatively low in areas of high pH and low organic matter content concentrations[12,13]. The effective 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 metals from contaminated soils. Because of the difference in the affinities of heavy metals with soil and soil constituents[14-16], the effective pH levels is likely to vary depending on the type of heavy metals and its bonding strengths with soil. The current information for some coarse-textured soils shows minor variation in the threshold pH value among Zn ($pH = 4.6 \pm 0.4$), Pb ($pH = 4.1 \pm 0.1$) and Cd ($pH = 4.1 \pm 0.1$)[16]. The information will enable the selection of appropriate acid strength for remediating heavy metal-contaminated soils[9,17].

The objectives of this research were to determine fluxes and release of heavy metals in two soils and levels of heavy metals in Yamuna river, submerged plants and soils and to study the effect of pH and $CaCl_2$ of different concentration on removal or extraction of heavy metals from two contaminated soil.

EXPERIMENTAL

Soil properties: The metal contamination resulted from industrial effluents laden with heavy metals from illegal discharge of industrial wastewater. The Yamuna river sample collected form Okhla and Wazirabad site, pH was measured immediately after samples were brought to the laboratory and the concentration of heavy metals in Yamuna river was estimated using a certified Merck standards solution according to APHA[18], using atomic absorption spectrometry (AAS-Auto sampler-100) Perkin-Elmer instrument. Heavy metals in suspended aquatic plants and soil were calibrated using reference soil samples. Soil samples were brought to room temperature before analysis for heavy metals. A deviation of 15-10 % was observed from certified values of heavy metals. The detection limits by the AAS-Autosampler 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 submerged aquatic plants showed signs of phytotoxicity, curling of veins and leaves before the harvest age. Above water and inside the water, living plant tissue were collected, washed in a mild sodium lauryl sulfate solution, double rinsed in deionized water and dried for 48 h at 70 °C. Metal analysis was completed in accordance with standard procedures in APHA[18]. The filtered extracts were analyzed for metal concentrations *via* AAS-100. Duplicate samples, blanks and internal standards of plant samples were routinely included in plant analysis for data quality control.

Soil samples collected from the 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 with some modified procedure[19], 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 spectrophotometer (AAS-100, Perkin-Elmer USA). All analyses were done in triplicate.

Metal extraction with dilute HCl and $CaCl_2$: The effect of acid strength on the release of various heavy metals from 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 0.005, 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 extraction procedures were the same as described above and each extraction was repeated successively three times. Concentrations of the heavy metals were analyzed using the procedures described above.

The effective limit of 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. The starting point for the regression was the pH at which the concentration of the metals began to rise and the ending point for the regression was the pH at which the release of the metals. From the equations, we calculated the pH at which the concentrations of each metal become zero was calculated. This pH was assumed to be the effective pH value. The effective pH value is the pH value at which the solubility of the metal was five times greater than the solubility of that metal at higher pH level[16]. The pH level was set at 5.5 for Cd and at 4.5 for Pb. The effective pH value defined here avoids the problem of having to prescribe different pH values for different metals. The regression analysis was also performed for the determination of $CaCl_2$ effects on the release of the heavy metals.

RESULTS AND DISCUSSION

Heavy metal concentrations in the soils: Okhla site soil was found in acidic nature and while Wazirabad soil were slightly acidic neutral as reference sample and as with soils had high clay contents (> 33 %) (Table-1). The soil analysis confirmed that the Okhla site soil was highly contaminated with Cd, Zn, Ni and Pb and the Wazirabad soil with Ni and Pb (Table-1). The Pb concentration in Okhla soil was more than three times higher than the standard limits (459 mg Pb kg^{-1}) established by the Environmental Protection Agency[20]. While Cd concentration in Okhla in submerged plants (0.3 mg kg^{-1}) and soil have exceed the concentration level (5 mg kg^{-1}), it exceeded the permissible level (2.5 mg kg^{-1}) for living matter 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 Yamuna river. Improper and untreated disposal of industrial wastewater often contributes to heavy metal contamination of soils in Yamuna river[4]. Since, the concentrations of Cd, Zn, Ni and Pb in the Okhla soil and Pb in the Wazirabad soil exceeded with the trigger levels and food crop production is not safe on both soils until after they have been remediated.

TABLE-1
ANALYSIS RESULTS OF THE TWO SOILS

Soil	pH	Organic matter	CEC (cmol kg^{-1})	Clay (%)
Okhla	6.2	4.75	25.82	36
Wazirabad	7.2	3.70	20.46	33
Heavy metals (mg kg^{-1})	Cd	Zn	Ni	Pb
Okhla	109.7	1473	587	459
Wazirabad	36.67	1027	149	149

Effects of HCl concentration on metal extractability: The pH of both the soils declined sharply from near neutral to about pH 2.2 by the addition of 4000 μmol H^+ g^{-1} (Fig. 1A) with 0.01 M HCl. It further declined to pH 1.2 by the addition of 1000 μmol H^+ g^{-1} with 0.1 M HCl. Increasing to 2000 μmol 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, presu-mably as a result of sorption of protons or hydroxylation of surface sites, was accom-panied 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 and 1B).

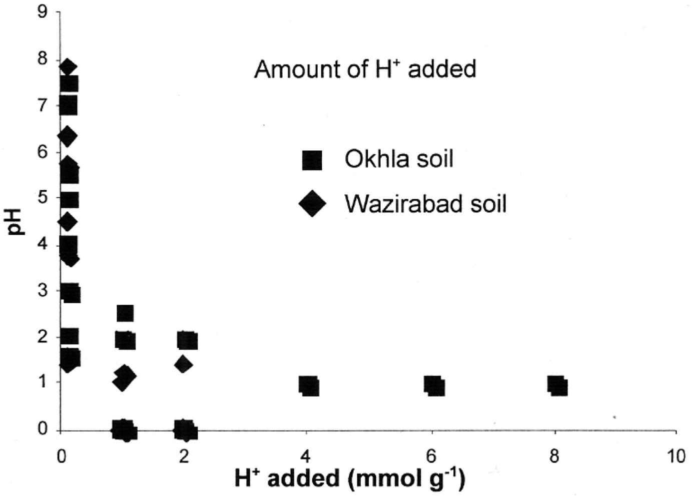

Fig. 1A. Relation of soil suspension pH

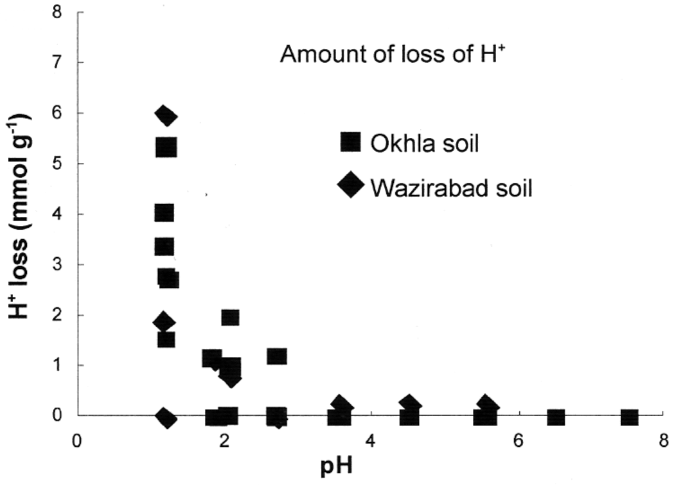

Fig. 1B. Relation of soil suspension pH

The concentration released was highest for Cd, Pb and lowest for Ni reflecting their totals in the soil, the total concentration across all heavy metals was not a good indicator of their extractability (Fig. 2). Despite having a concentration comparable to Zn, Ni was less extractable than Cd and Pb 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[21]. Comparing the response of the fraction of Pb extracted to pH for the Wazirabad soil with same that of other heavy metals in the Okhla soil (Fig. 2).

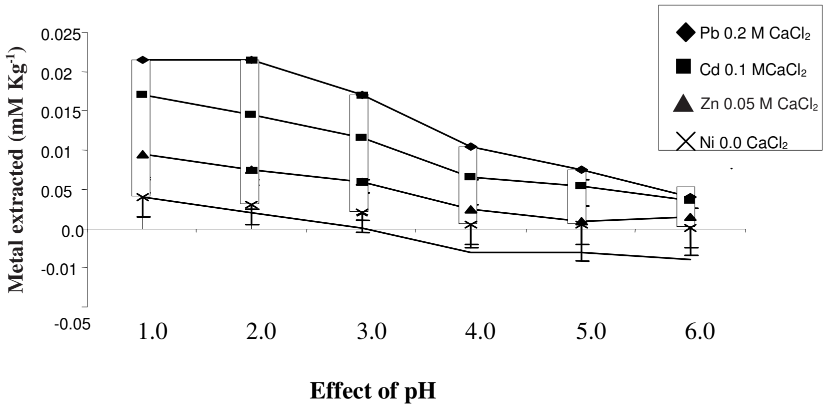

Fig. 2. The fraction of the total metal Cd, Pb, Zn and Ni in Okhla soil by the effect of pH and concentration of $CaCl_2$

The effective pH value and the slope of the response curve should characterize heavy metal release from the soils as solution pH declines. The effective 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)[16]. The value for Pb for the Wazirabad soil is lower compared with the value (pH = 4.1). Wazirabad soils in the study are sandy and contain far lower heavy metal concentrations than the contaminated Okhla soils used in present study.

The heavy metals studied also differed markedly in the slope of the response of extractability to declining 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[22,23]. This was also generally true for Cd and Zn. The low pH value, coupled with a low response slope, make Ni rather stable in the soil and difficult to remediate without extensive dissolution. This difficulty also encountered for Zn, though to lesser degree. The low response slope for Ni will require an acid strength greater than 0.2 M HCl

TABLE-2
RELATIONSHIP BETWEEN THE RISES IN FRACTION OF Cd, Zn, Ni AND Pb EXTRACTED AND DECLINING pH

Soil	Element	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 + 0.163	0.96
Wazirabad	Cd	y = - 0.0159 + 0.163	0.56
	Ni	y = - 0.061x + 0.156	0.59
	Zn	y = - 0.156x + 0.320	0.52
	Pb	y = - 0.379x + 1.182	0.94

Y = Fraction of the metals extracted; x = pH.

to effectively remove Ni from the soil. Forms of heavy metal Pb could have some bearing on its extractability[24]. Soil environmental factors could affect heavy metal form and extractability in soil.

Washing of 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, Pb, Zn and Ni) from contaminated soils[25]. This technique is considered viable for remediating metal-contaminated soils in Yamuna river and agricultural crops. 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, 0.39 for Ni and 0.87 for Pb in Okhla soil and 0.80 for Pb in the Wazirabad soil[25], 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 Makino *et al.*[20]. Extraction of heavy metals from contaminated soils with increasing acid strength proceeds from exchange process involving protonation of oxide surface sites and/or exchange with sorbed metals on the permanent charge sites to dissolution process in which the reactive surfaces of the oxides and chlorides are dissolved. The pH level at which the metal removal process shifts from exchange to dissolution was near pH 2, which was attained following the second cycle of the four successive extractions with 0.01 M HCl. For Cd, Zn, Ni and Pb, the percentages of the total Cd, Zn, Ni and Pb extracted in the Okhla soils at these stages were 0.67, 0.55, 0.23 and 0.60, respectively. Successive soil washings with 0.01 M HCl to bring soil pH to near 2 could be considered as an alternative to the more acidic 0.1 M HCl, particularly for soils moderately contaminated with Cd, Zn and Pb. Washing soil at pH 2 was found effective in removing sorbed Pb from contaminated soil[24]. 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. The applicability of the dilute acid to and the number of successive extractions required for metal-contaminated calcareous soils needs to be examined[26-28].

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 Wazirabad soil increased with increasing HCl concentration, as expected. The effective pH values of the release for Cd, Zn and Pb were higher than Ni. Within the pH range studied (from about 1.0 to 6.5), the release of Ni was not but Cd, Pb were more highly correlated. While 4 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 still capable of extracting more than 60 % of the total Cd and *ca.* 50 % of total Zn in the Okhla soil and total Pb in the Wazirabad soil. However, the applicability of this technique to metal-contaminated soils containing high $CaCO_3$ needs to be tested. Addition of $CaCl_2$ to dilute acid solution markedly enhanced the extractability of Cd and Pb in the Okhla soil. The efficacy of 0.001 M HCl containing 0.1 M $CaCl_2$ was the same as that of 0.01 M HCl in extracting Cd from the soil. The $CaCl_2$ increased the efficiency of dilute HCl (< 0.01 M) to remove Cd and Pb from the soil[19,29-32]. The present study useful to extractions of heavy metals from contaminated soils and this technique controlled soil heavy metals, amendments with dilute HCl and combination of $CaCl_2$.

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