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Leaching Behaviour of Ca and Fe in Alkaline Soil: A Case Study of Kota, Rajasthan

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ABSTRACT

Soil is a major reservoir for contaminants as it has an ability to bind various chemicals. These chemicals can exist in various forms in soil and different forces keep them bound to soil particles. The transport mechanisms of metals through soil have long presented great interest to both environmental and soil scientists because of the possibility of groundwater contamination through metal leaching. In the present research work, the leaching of calcium and iron has been carried out in undisturbed columns of alkaline soil (pH=8.2) of Kota region of Rajasthan, India. $CaCl_2$ and $FeSO_4$ have been taken as the source of added calcium and iron. It has been observed that $[Ca^{2+}]_i$ and $[Fe^{+2}]_i$ increases with increase in$[Ca^{2+}]_{add}$ and $[Fe^{+2}]_{add}$ on addition of various concentrations of Ca and Fe in soil columns. Results indicate that $[Ca^{+2}]_{complexed}$ is increased on adding 120 and 360 mg/kg $CaCl_2$ but it is observed that this complexation is decreased on addition of 600 mg/kg $CaCl_2$, while most of the added Fe gets complexed in soil matter. The movement of Ca and Fe in soil profile is much affected by the mobility as well as other physicochemical properties of soil matrix.

INTRODUCTION

Soil, a complex heterogeneous system, possessing distinct morphological, mineralogical, physical, chemical and biological characteristics, is made up of minerals, organic matter (solid phase), water (liquid phase) and air (gaseous phase). The soil, through its components and properties, controls solubility, mobilization and deposition of toxic metals, resulted from anthropogenic sources [1-3]. In soil, various metals can be affected by processes of sorption/desorption, precipitation, dissolution, redox reaction and incorporation in the solid components of soil [4].

Crustal metals such as Ca and Fe originating dominantly from natural sources such as mainly earth crust compositions are released to the atmosphere in the form of or adsorbed onto particulate matter such as oxides (CaO and Fe_2O_3). In addition, these particles are emitted from smelters to the atmosphere in the form of sulfide, chloride and metallic forms.

Besides these sources, Ca and Fe are found in the soil of Kota city because of presence of Kota Super Thermal Power Station (KSTPS), a major coal based thermal power plant, where huge amount i.e. approximate 3000 metric tonne per day, of fly ash (homogeneous mixture of several metal oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, CuO, CdO, MnO_2, NiO_2, ZnO, PbO etc.) is produced and released in the atmosphere in and around Kota city. Nevertheless, few large scale industries including DCM Shriram Consolidated Limited (DSCL), Multimetals Limited, Samtel Glass Limited, Chambal Fertilizers and Chemicals Limited (CFCL), Shriram Fertilizers and Metal India, Shriram Rayons and a number of Kota stone cutting polishing units further enhance this metal burden of the city environment.

Calcium is necessary for good health, however, excessive intake causes hypercalcemia. As far as Fe is concerned the human body has the ability to store iron, however, too much iron in the body may be linked to heart diseases, cancer and diabetes.

The soil of the Kota district is characterized by deep, medium and black shallow alluvium soils. These soils range in depth from shallow to very deep with lime concretion or lime encrusted gravels at varying depths. The soils, in general, are clay loam to clay in texture and moderately to less permeable and developing cracks in dry season.

Availability of clay minerals with a high density of negative surface charges (high Cation Exchange Capacity values), high surface areas (small sizes) and also weak vander Waals forces between the structural layers have a great tendency for the absorption and migration of metal compounds in soil environments [5-6].

The various processes like low leaching of the salts, evaporation of soil water and different human activities contribute to the salt accumulation in soil [7]. The accumulated soluble salts are mainly chlorides and sulphates of Na, Ca, Fe and Mg. With increase in concentration of soil solution, the Ca and Mg salts are precipitated, resulting in the increased relative proportion of Na [8]. Thus, Na becomes the dominant exchangeable cation in the salt solution and plays a major role in the salinization of soil.

Keeping this view in mind, the present work is an effort to study the leaching behaviour of Ca and Fe metals in soil through column method which is used to ascertain effect of added salt solution ($CaCl_2$ and $FeSO_4$). The concentration of Fe was measured by Direct Air – Acetylene Flame method (Atomic Absorption Spectrophotometer - Shimadzu-6300) [9]. The Ca metal concentration was determined using Flame Photometer (Systronics -128) method. Certified standard solutions (CertiPUR* - MERCK) were used for calibrating the instruments.

Soil in Kota City

Results of physicochemical analysis of a sample collected from the surface layer of soil from a reference sampling site are given in Table 1.

Table 1: Some physicochemical characteristics of soil.

S. No.	Soil properties	Values
1	pH	7.5
2	ECe (dSm^{-1})	0.67
3	Bulk density (mg mg^{-3})	1.35
4	Colour	Brownish-black
5	Sp-gravity	2.57
6	Type	Clay-clay loam
7	Sand (%)	25
8	Silt (%)	26.2
9	Clay (%)	48
10	Cation Exchange Capacity (meq/100g)	46.01
11	Organic Carrbon (g/kg)	6.5

***** The physicochemical analysis of soil is performed by soil and water laboratory, Chambal Krishi Kendra, CAD, Nanta Farm, Kota (Raj.).

The geological quantitative composition of above mentioned soil sample analyzed through WD-XRF is shown in Table 2.

Table 2: Geological quantitative composition of surface soil sample at the reference sampling site as determined by WD-XRF.

Metal	Composition	Metal	Composition	Metal	Composition
CaO	60954 ppm	Sc	9 ppm	Rb	56 ppm
TiO_2	1.04 %	V	105 ppm	Sr	172 ppm
MnO	0.09 %	Cr	158 ppm	Y	36 ppm
Fe_2O_3	4.12 %	Co	102 ppm	Zr	626 ppm
Zn	149 ppm	Ni	42 ppm	Nb	16 ppm
Pb	68 ppm	Ga	10 ppm	Th	13 ppm
Cu	48 ppm	Sn	7 ppm	La	43 ppm
Ba	373 ppm	Sb	3 ppm	Cs	4 ppm
As	33 ppm	Ce	138 ppm	Compton	76.03 %

It is evident from Table 2 that sample contains high % of Compton followed by CaO, Fe_2O_3, TiO_2 & MnO since they exist in the environment as crustal ingredients (dust, soil, sand etc.). Other inorganic oxides (heavy metals such as Zn, Pb & Cu) present in low % could have originated through emissions from coal based Thermal Power Plant.

Thus, the agricultural land of Kota region has been cursed with heavy metal contamination by various anthropogenic activities such as mining activities, vehicular emission & industrial activities.

MATERIALS AND METHODS

The clay loam soil collected from a reference sampling site (closest to Kota Super Thermal Power Station) Kota was sun dried and sieved for uniform particle size (< 53 µm). Columns of 60 x 3 cm^2 were prepared surrounded by glass jacket of continuously flowing thermostated water. 60 g soil was filled in the column and was gently packed at water filled porosity of 0.11 cm^3 cm^{-3}. Lower end of column is packed with glass wool. A fixed volume of aqueous salt solution with desired metal concentration (Ca and Fe) is added at the top of the soil column in each experiment. Salt solution is allowed to get adsorbed uniformly in the column for 24 hours after which the column is continuously leached with deionised water. The leaching is carried out till the soluble metals are completely removed from the soil column.

The flow rate of column is 2±1 mL leachate per 5 minutes. After completely removing the soluble metal ions from column, the soil of column is transferred into a beaker and a suspension is obtained in a known volume of water. This soil suspension is stirred for 2 hours. The metal ion concentration is further determined in the filtrate of the soil suspension to ensure the complete removal of soluble metal ions from the soil column. The treatment of data is based on the calculation of the parameters as defined below:

$[M^{2+}]_s$ = Leachable metal present in soil column, mg/kg.

$[M^{2+}]_{add}$ = M^{2+} concentration introduced in the experimental soil column, mg/kg.

$[M^{2+}]_i$ = Total leachable metal content present initially, mg/kg.

$[M^{2+}]_{comp}$ = Complexed M i.e. M^{2+} concentration retained in column.

$[M^{2+}]_s + [M^{2+}]_{add} - [M^{2+}]_i$

Where: M = Metal i.e. Ca or Fe.

RESULTS AND DISCUSSION

Leaching of Ca in Undisturbed Soil Columns

In experimental soil columns, leaching of Ca^{2+} incorporates $[Ca^{2+}]_{comp}$ and $[Ca^{2+}]_i$. The values of $[Ca^{2+}]_i$ and $[Ca^{2+}]_{comp}$ for $CaCl_2$ are given in Table 3.

Table 3: The values of $[Ca^{2+}]_i$ and $[Ca^{2+}]_{comp}$ at different $[Ca^{2+}]_{add}$ for $CaCl_2$ at 30^0C; Soil = 60 gm.

$[Ca^{2+}]_{add}$ (mg/kg)	$[Ca^{2+}]_i$ (mg/kg)	$[Ca^{2+}]_{comp}$ (mg/kg)
0	4350.23	-
120	4412.17	58.06
360	4601.44	108.79
600	4850.16	100.07

For $CaCl_2$ added columns (Table 3), $[Ca^{2+}]_i$ is increased with increase in $[Ca^{2+}]_{add}$ (Figure 1). Plot of $[Ca^{+2}]_{add}$ vs $[Ca^{+2}]_{comp}$ (Figure 2) shows that $[Ca^{+2}]_{comp}$ is increased on adding 120 and 360 mg/kg $CaCl_2$ but we notice that on addition of 600 mg/kg $CaCl_2$ complexation is decreased. The movement of Ca in soil profile is much affected by the mobility as well as properties of co-anions. Cl^- is highly mobile, hence does not get adsorbed at anion exchange sites of clay minerals and moves downward along with Ca, thus enhances the leaching of Ca in natural soil profile [10].

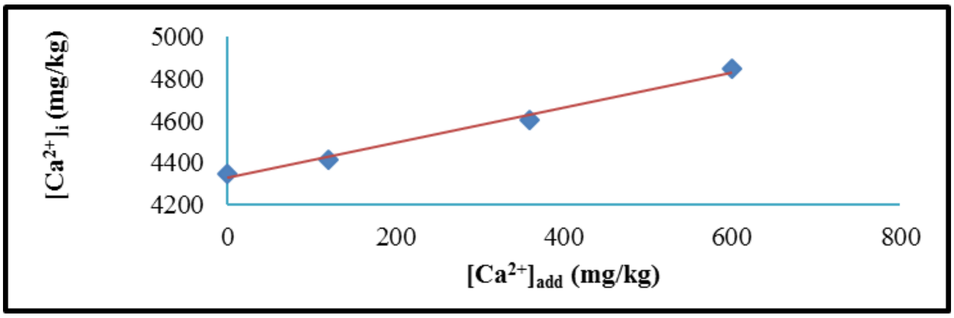

Figure 1: Variation of $[Ca^{2+}]_i$ with$[Ca^{2+}]_{add}$ for leaching of Ca salt studied at 30^0C; Soil = 60 gm.

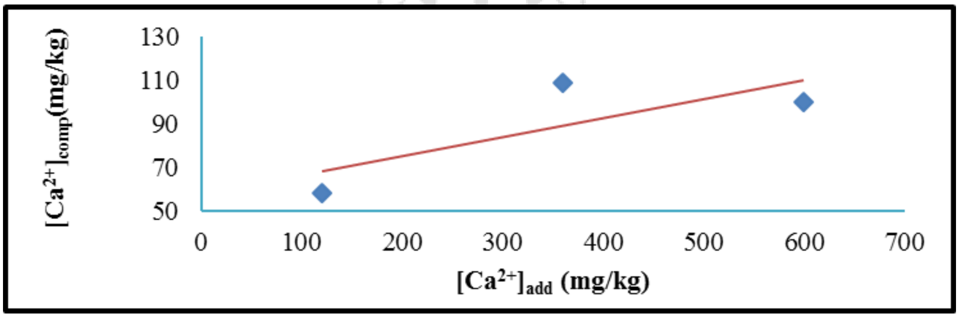

Figure 2: Variation of $[Ca^{2+}]_{comp}$ with $[Ca^{2+}]_{add}$ for leaching of Ca salt studied at 30^0C; Soil = 60 gm.

Leaching of Fe in Undisturbed Soil Columns

To study the leaching kinetics of Fe^{+2}, various concentrations of $FeSO_4$ are added as a source of Fe in experimental soil columns. The values of $[Fe^{+2}]_i$ and $[Fe^{+2}]_{comp}$, are given in Table 4.

Table 4: The values of $[Fe^{2+}]_i$ and $[Fe^{2+}]_{comp}$ at different $[Fe^{2+}]_{add}$ for $FeSO_4$ at 30^0C; Soil = 60 gm.

$[Fe^{2+}]_{add}$ (mg/kg)	$[Fe^{2+}]_i$ (mg/kg)	$[Fe^{2+}]_{comp}$ (mg/kg)
0	163.92	-
83.93	166.54	81.31
268.58	170.22	262.28
470.0	175.78	458.14

Our experimental soil inherently possesses 163.92 mg/kg of Fe. On addition of various concentrations of Fe in soil columns, it is seen that $[Fe^{+2}]_i$ increases with increase in $[Fe^{+2}]_{add}$ (Figure 3). It is evident from the Table 4 that most of the added Fe gets complexed in soil matter [11-12]. Plot of $[Fe^{+2}]_{add}$ vs $[Fe^{+2}]_{comp}$ (Figure 4) shows an exactly linear trend which proves that both the above terms are in proportional linear relation. The solubility of Fe is strongly dependent on soil pH. The activity of Fe^{3+} decreases 1000-fold for each unit increase in soil pH, while its solubility is lowest in a pH range of 7.4-8.5 [13]. Therefore, the Fe deficiency is greatest in calcareous and alkaline soils in Kota city.

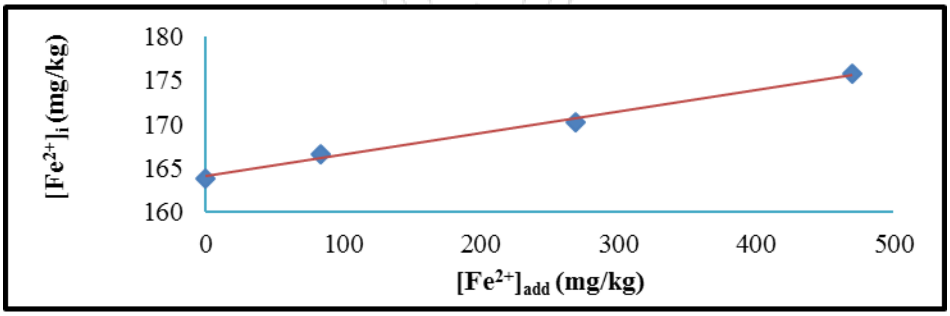

Figure 3: Variation of $[Fe^{2+}]_i$ with$[Fe^{2+}]_{add}$ for leaching of Fe salt studied at 30^0C; Soil = 60 gm.

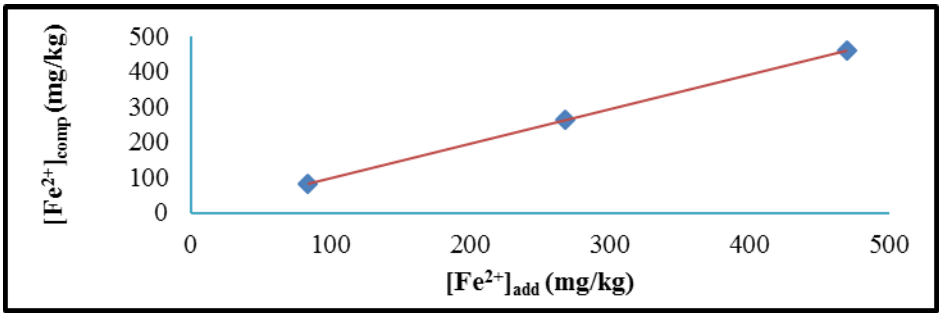

Figure 4: Variation of $[Fe^{2+}]_{comp}$ with $[Fe^{2+}]_{add}$ for leaching of Fe salt studied at 30^0C; Soil = 60 gm.

As evident from the results, stabilizing the alkaline soil by calcium ion initially increased the complexation thereby decreasing the leached amount upto certain added amount. On its further addition, complexed form was decreased hence slight leaching was found to occur. As far as Fe^{2+} is concerned we find that it remains in complexed state till the end indicating its stabilizations and hence effective reduced leaching. It is concluded from these results that under identical experimental conditions, other toxic metals will also behave in the similar manner depending upon the individual properties of a particular metal and the accompanying anion.

CONCLUSION

Results from the above leaching experiments indicate the potential of alkaline soil of Kota region for contamination of water system as the soil of Kota region are exposed to heavy metals contamination resulting from increased anthropogenic activities such as mining activities, vehicular emission & industrial activities besides fly ash emission from KSTPS. Hence, treatment of alkaline soil of Kota City using lime may reduce this leaching of metals from contaminated soil. Stabilizing metal contaminated agricultural land is an economical and feasible way to reduce pollutants in and around Kota City. It is to be noted that the extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated soil matrix.

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