Chapter 5
Conclusions

5.1 Introduction

Soils are one of the most important pathways for metal transport to ground water and surface water resources. Study of soil-metal interaction for specific site, metal and soil conditions has been strongly recommended due to wide variation in characteristics affecting the mobility of metals through soils. Chhattisgarh has many metal-based industries due to its huge mineral resources, making possibility of metal-based waste contaminating the soils a strong reality. To understand the behavior of various soils available in the state vis-a-vis metal sorption and desorption, and to investigate the suitability of local soils as low cost adsorbent of metals and as landfill liner material, a thorough and systematic study of various parameters affecting soil-metal interaction was required, as no such study has been done on sorption of metal cations on local soils. The present work addresses this gap in the existing knowledge. The conclusions from the experimental findings have been presented sequentially through the following sections.

5.2 Soil characteristics

Four soils, representing the majority of soils of Chhattisgarh — Kanhar (Vertisol), Dorsa (Alfisol), Matasi (Inceptisol), and Bhata (Entisol) were selected for the study. The aim of the present work was to investigate the removal of cadmium, copper, and chromium (III). These has been designated as Class A (Cd) and Class B (Cr and Cu) waste with permissible concentration limits of 50 mg Kg\(^{-1}\) and 5000 mg Kg\(^{-1}\) respectively, in the Schedule I of Government of India Hazardous Waste (Management and Handling) Rules, 2003. Further, Cr(III) and Cu have also been reported as amongst the most sorbed, and Cd as amongst the least sorbed of the metals by soils, in several reported works.

The experimental results revealed that the favorable sorption parameters — natural pH, clay content, dominating minerals, carbonate content, organic carbon content, cation exchange capacity, and the total specific surface area most prominent in Kanhar, followed by Dorsa, Matasi, and Bhata, respectively. Bhata has the highest Fe and Mn concentration that might influence its sorption behavior favorably and might overcome lack of other constituents influencing metal sorption behavior. With reference to the dominating mineral in soils — Kanhar, Dorsa and Matasi appear to be
the soils carrying permanent negative charge independent of the pH values in natural conditions, as they contain mineral montmorillonite and illite respectively, having 2:1 clay structure. Whereas Bhata is having pH dependent variable charge due to the dominating presence of kaolinite having 1:1 clay structure. Interestingly, the various parameters in soils are closely related to their position on the landscape, changing gradually down the slope, there is increase in clay content, cation exchange capacity, carbonates, organic carbon, and calcium and magnesium ions on exchange sites. Along the same direction, there is gradual change in colour from red to darker gray brown, in texture from sandy loam to clayey, in consistency from non-sticky to very sticky, in mineralogical make up towards decrease in kaolinite and illite, and concurrent increase in montmorillonite, and in organic carbon and calcium carbonate from almost none to abundant.

5.3 Sorption experiments

5.3.1 Sorption kinetics

Sorption kinetics experiments exhibit that for all three metals and for all the four soils maximum sorption (about > 60 to 90%) occurs within 240 minutes under the experimental conditions and after equilibration for two days the metals seem to reach constant concentration for the applied dose (copper 98%, cadmium 99%, and chromium 100% removal).

5.3.2 Effect of pH on sorption edge

Sorption edge experiments to study effect of pH reveal that the sorption of copper increases between pH of 4.5 and 6, with pH near 5.5 exhibiting sharp increase in sorption. For cadmium the sorption edge is not as sharp as copper or chromium but the substantial increase in sorption pH is observed between 5.5 and 7.5, the pH value near 7.0 exhibiting sharp increase in cadmium sorption. Sorption edge for chromium is between pH 4.5 and 6.0, with maximum chromium sorption around pH value of 5.5 (98%). The trends of the results are similar to all the four soils.

5.3.3 Sorption isotherm studies

The sorption isotherm experiments reveal that sorption is very good for all the four soils at the lower applied concentration of metals (up to 50 mg L⁻¹) as indicated by the H-type isotherm curve for initial lower metal concentration range. However, at higher concentrations (>50 mg L⁻¹) the soils exhibit dissimilarity in sorption of different metals, manifested from transition to L-type shape of the isotherms. Both, Freundlich and Langmuir isotherms models fit well, with Freundlich showing better fit for all the soil-metal combinations. Based on the sorption capacities (q in mg Kg⁻¹) the
order of soils on the basis of metal-sorption performance is established as Kanhar > Dorsa > Matasi > Bhata. Kanhar shows good sorption capacities even at higher metal loading. The sequence of metals in decreasing order of sorption is observed as Cr > Cu > Cd.

5.3.4 Effect of various parameters on metal sorption

5.3.4.1 Effect of ionic strength

Experiments to study effects of various parameters on sorption exhibit variation in results for different soil-metal combinations. Increase in ionic strength results in decreased metal sorption for all the soils and for all the metals. The effect is more pronounced for Bhata amongst soils and cadmium amongst metals and least on sorption on Kanhar amongst soils and chromium amongst metals.

5.3.4.2 Effect of competing anions

Presence of anions other than the background electrolyte 0.01 M NaNO₃, affects the sorption. The effect is different for various soil-metal combinations. Presence of chloride reduces sorption of all the metals for all the soils. The effect of sulfate is mixed, for Kanhar and Dorsa the sorption of all the metals is slightly reduced, while for Matasi and Bhata either it is slightly improved or remains similar. However, presence of phosphate improves the metal sorption in all the cases except for sorption of copper on Kanhar and Dorsa where the reduced sorption has been observed. This has important bearing on various management practices adopted in field. Particularly in agricultural practices phosphate as fertilizer is liberally applied. Phosphate is also present in domestic wastewater due to cloth washing detergents. Industrial wastewaters and municipal wastewaters may contain higher concentration of chlorides and sulfates. Once reaching the soil with metal contaminated waste the effect on metal sorption or mobility will depend on these characteristics and may result in different scenarios.

5.3.4.3 Effect of competing cations (calcium)

Experiments conducted to study the effect of competing cations in the form of calcium, reveal reduced sorption for all the metals-soils combinations but to various extents — the soils in the sequence of reduction in sorption are Bhata > Matasi > Dorsa > Kanhar and metals are Cd > Cu > Cr. These results have important bearing on the common approach of raising the pH using lime to remove most of the metals as an effective step in wastewater treatment and liming of acidic soils for agriculture, as presence of increased concentration of calcium in soil might improve the metal leaching.

5.3.4.4 Effect of organic matter
Removal of organic matter native to the soil reduces sorption of metals on Kanhar, Dorsa, and Matasi, whereas sorption of copper and chromium on Bhata is improved. This might be due to exposure of additional Fe and Mn sites present in the highest concentration in Bhata. However, across all the soils the impact of organic matter is not pronounced, might be due to low concentration of organic carbon in all the soils (2.3 to 6.8 g Kg\(^{-1}\)).

5.3.4.5 **Effect of Fe-Mn oxides**

Removal of hydrous-oxyhydroxides of Fe-Mn results in reduction in sorption of heavy metals by all the soils. Results match with the relative abundance of Fe-Mn in soils, with the most affected soil sequence of Bhata > Matasi > Dorsa > Kanhar.

5.3.4.6 **Effect of strong chelating agent EDTA**

Study on effect of complexation with anthropogenically introduced strong chelating agent EDTA revealed reduction in sorption of metals particularly severe at pH of 7.0. At pH 5.5 the effect is drastically reduced owing to the reduced strength of EDTA complexation in acidic environment. However, sorption of cadmium on Bhata exhibits anomalous behavior of improvement in sorption in presence of EDTA, sorption being more at pH 5.5 than pH 7.0. The reason might be related to strong presence of iron in Bhata which has stronger stability (formation) constant with EDTA than cadmium. However, overall, the chelation effect of EDTA is much pronounced particularly at higher pH causing maximum movement of metals to solution.

5.3.4.7 **Effect of compost application**

To study the effect of compost application on soils, and to simulate the addition of well-digested organic matter by sludge solids applications to soils, well-digested cow-dung compost was added to the soils and effects on metal sorption were monitored. Compost-added-Kanhar shows reduction in sorption of all three metals — copper, cadmium, and chromium. Other soils — Dorsa, Matasi, and Bhata, exhibit improved sorption of metals — copper, cadmium, and chromium after the compost application. Mixed results have been reported by various researchers on different soils and metals due to application of organic matter in the form of compost, biosolids, and dissolved organic matter [(Kalbitz and Wennrich (1998); Amrhein, et al. (1992); Zhou and Wong (2001); Bloomfield, 1981; Temminghoff *et al.*, 1997; Tills and Alloway (1983); Bolan *et al.* (2003); and Li *et al.* (2001)]. These mixed observations require that thorough study of metal-soil-organic matter interaction shall be done for the specific situation before deriving conclusion from the available data.

5.4 **Sequential extraction**
Studies on sequential extraction of metals sorbed on the soils following BCR protocol have been done to get an idea about metal fractions bound to various phases in soils. For all the soils, in their natural state, the sequence of easiness of metal desorption is in the order of Cd>Cu>Cr, which is just opposite to the sorption sequence of Cr>Cu>Cd. In natural soils — for Kanhar, most of the copper (51%) is bound to reducible fraction attached to iron and manganese oxyhydroxides, while most of the cadmium (68%) is in residual fraction, and chromium (42%) is primarily attached to organic matter and sulfide fraction. For Dorsa, most of the copper (43%) is bound to reducible fraction attached to iron and manganese oxyhydroxides, most of the cadmium (65%) is in residual fraction, and chromium (32 and 41%) is primarily attached to respective fractions attached to iron and manganese oxyhydroxides, organic matter, and sulfides. For Matasi, most of the copper (56%), cadmium (61%), and chromium (62%) is bound to residual fraction removable only by strong leachant (aqua regia). Similarly, Bhata, in its natural form, contains most of the copper (56%), cadmium (61%), and chromium (62%) in the residual fraction removable only by strong leachant (aqua regia).

For soils loaded with metals, the metal desorption sequence is quite different from their natural behavior. In case of Kanhar, major portion of copper (56 - 72%) and chromium (52 - 64%) is observed to be fractionated in reducible part seemingly attached to iron and manganese oxyhydroxides. Cadmium is primarily fractionated in exchangeable portion (water and acid soluble) associated with the soluble species, carbonates, and cation exchange sites; and reducible fraction attached to iron and manganese oxyhydroxides, for metal loading of 50 and 200 mg L⁻¹. At 5 mg L⁻¹ it is about equally distributed in all the four fractions. For Dorsa, maximum concentration of copper (71 - 78%) and chromium (55 - 68%) are fractionated in reducible part, seemingly attached to iron and manganese oxyhydroxides, while for metal loading of 50 and 200 mg L⁻¹ cadmium is primarily fractionated in exchangeable, water and acid soluble fraction associated with the soluble species, carbonates, and cation exchange sites. Matasi has copper, 42-51% and 10-42%, respectively fractionated in exchangeable, water and acid soluble fraction; and in reducible fraction attached to iron and manganese oxyhydroxides; cadmium is fractioned (62-76%) in exchangeable, water and acid soluble fraction; and Chromium (47 - 61%) is fractionated in reducible fraction seemingly attached to iron and manganese oxyhydroxides. Similarly, for Bhata, maximum concentration of copper, 42-51% and 10-42% is fractionated in exchangeable, water and acid soluble fraction; and in reducible fraction attached to
iron and manganese oxyhydroxides, respectively; cadmium is found fractioned (62–76%) in exchangeable, water and acid soluble fraction; and Chromium (47 – 61%) is fractionated in reducible fraction seemingly attached to iron and manganese oxyhydroxides.

For increasing metal loading more and more metal is found in exchangeable fraction. The sequential extraction studies reconfirm the sorption findings that at lower applied concentrations metals are mostly fractionated at several strongly sorbed permanent sites in soils, making their movement to solution phase difficult. However, with increasing applied metal concentration these permanent sites are saturated and metal tend to sorbed at exchangeable phase making their movement to soil solution feasible. This shows limitation of soil as a strong adsorbent at very high metal concentration. The sequence of soils Kanhar > Dorsa > Matasi > Bhata, according to the sorption capacity for metals is also confirmed by the sequential extraction experiments.

5.5 Effect of simultaneous competitive sorption of heavy metals on soils

The effect on sorption of competitive behavior of metals has been studied to simulate the mixed metal matrix effect the soil might be exposed to in real life. Due to competition among the metal cations, plots of the concentration of metal adsorbed versus equilibrium concentration of metal in solution, for all the metals, do not yield a straight line. Also, the sorption data do not fit well for both the Freundlich and Langmuir isotherms models. On the basis of values of distribution coefficients the strength of sorption sequence for the metals can be listed as Cr>Cu>Cd; and for soils Kanhar>Dorsa>Matasi>Bhata for multiple competitive sorption as well.

Multiple metal sorption results show that competition is weaker in soils with higher capacity to adsorb cations, since there are available sites for almost all the metal cations in the adsorption complex. On the other hand, competition among heavy metals is very strong in soils with lower capacity to hold metal cations, where more Cd are dislocated from the adsorption complex and substituted by Cr and Cu. In a field situation, this could impose a much higher risk of contamination of aquifers, creeks, groundwater, etc., through leaching of these heavy metals in the soil profile and also a much higher risk of making them available for uptake by plants.

5.6 Column sorption and leaching

To simulate the condition of heavy metal contaminated wastewater percolating through the soil strata in field, a column flow through experiment has been conducted with Kanhar as the soil media as it demonstrated maximum sorption for all the metals.
To simulate the percolation of rainwater in soil mass, contaminant solution (rain water spiked with metals) was ponded on the soil column surface and the flow was allowed to percolate from top under gravity. Results show much better sorption of metals than in batch experiments, probably due to solution pH being higher, retardation in flow due to filling up of the pores leading to increased empty bed contact time, resulting in more time, and hence more opportunities for sorption. Further, removal of competitively desorbed exchanged species is there in column, improving the sorption. The multiple effect of filtration mechanism — mechanical straining of colloids larger than pore space (for clayey soil such as Kanhar this is a possibility particularly at the later stages of column run); and sedimentation by the continuous voids of the soil media acting as the ‘tube settlers’, might also be responsible for this improvement. First metal to show detectable concentration in the effluent was cadmium, but for copper and chromium even after 68 bed volumes the removal remained very high.

Leaching of the soil column by rain water reveals initial high concentration of all the metals in the effluent — probably due to leaching of metals stored in soil void pools and precipitated metal ions retained in the pores — the metal concentration dropped quickly and after about 25 bed volumes remained below the detection limit. The leachant (natural rain water) is not able to desorb much of the sorbed metals, but the situation might change if the pH of the water or wastewater percolating through the soil is acidic and contains strong leachant like EDTA or dissolved organic acids.

Out of all the soils of Chhattisgarh, the Kanhar emerges as the most promising sorbent for removal of Cr (III), Cu, and Cd. Its use as sorbent as the finishing treatment of wastewater for metal removal or as landfill liner material shows potential, however, detailed studies specific to a particular situation must be undertaken. Its suitability for other toxic pollutants, particularly pesticides shall also be investigated, before putting it to use.

Attempt has been made in this thesis to provide a study of some of the parameters affecting the soil-metal sorption in context of major soils of Chhattisgarh. The present work can be useful to various researchers and agencies involved in managing metal waste disposal on soils. However, within the limited scope of the study it was not possible to simultaneously investigate and monitor all the parameters affecting soil-metal interaction. Further studies are required to comprehensively explore this multifaceted research area.
5.7 Future scope of the work

Study of soil-metal interaction is a developing research area in Indian context and it can be considerably improved by future research. Some of the aspects that may be incorporated in future work are:

1. The various parameters identified in the present work can be studied in further details by concentrating on one or two parameters and study their effect on more samples of similar type of soil.

2. Similarly, one soil type can be taken and its behavior with variations in different parameters can be studies to find relative importance and correlation of these.

3. Field experiments on soils can be attempted to study the real-life scenario.

4. Industrial and municipal waste dumpsites can be taken for study to investigate the correlation between the dumped waste characteristics, the behavior of immediate soil and soil in vicinity and landfill leachate characteristics, to arrive at better understanding of metal movement through soils.

5. Several models by the different researchers have been attempted to analyze soil-metal interaction, however there is dearth of data for Indian conditions. Attempts can be made to apply various models and select best one for Indian soils and conditions.

6. Soil-metal interaction being surface phenomenon, studies at molecular level using molecular spectroscopy techniques will be very useful. Specifically, molecular-scale techniques such as near-edge (XANES) and extended-fine structure (EXAFS) X-ray absorption spectroscopy (XAS) which are possible only at most advanced synchrotron facilities, can be undertaken to have real picture at the solid solution interface.