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Studies on surface complexation modeling of Zn on soil and soil mixtures as a proposed liner material for waste containment facilities

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Abstract
The main aim of this paper is to model the behavior of red soil and black cotton soil along with lime mixture to sorption of zinc at different range of pH. Visual minteq version 3.0 was used, it was found that the model predicted the behavior accurately and this was compared with an experimental work done earlier. Surface complexation played an important role in the sorption process which gave a new impetus on the reactions taking place at various pH ranges. As most of the landfill leachates have a pH range of 3 to 8. It was concluded that this model generated data will help the landfill designers to take informed decision in dealing with hazardous waste.

Keywords: surface complexation, visual minteq, hydrous ferric oxide, landfills, liners

1 Introduction
Landfills have been the most economical and environmentally acceptable method for disposal of solid waste. However the Leachate generated in landfills migrate downwards and poses threat to ground water, unless properly controlled by barrier system. Percolating fluid will tend to migrate downward through the landfill as Leachate. Unless properly regulated, leachates generated by precipitation and other liquids within the waste, flows from the landfill into underlying ground water and thus potentially contaminate the drinking water aquifer. Industrial wastewaters generated from industrialization activities may contain various toxic heavy metals. The heavy metals, apart from being hazardous for living organisms when exceed the specific limits, have accumulating characteristics in nature as they cannot be biodegraded. Zn^{2+} being in the list of priority pollutants proposed by Environmental Protection Agency (EPA) give rise to serious poisoning cases. The main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness and lack of coordination in muscles [1-4]

1.1 Application of Adsorption Models:
A model is a theoretical construct, together with assignment of numerical values to model parameters, incorporating some prior observations drawn from field and laboratory data, and relating external inputs or forcing functions to system variable responses. Soil being a highly heterogeneous system it is difficult to model the adsorptive behavior using general models used for different types of sorbents. In this paper the surface complexation/ precipitation modeling has been successfully applied to describe the sorption of zinc on red soil of Bangalore and black cotton soil of Belgaum, of Karnataka state, India, and also adding lime. Only 3% lime was used based on the experimental results obtained in an earlier paper, it was found that by increasing the lime content to 6% the precipitated zinc in the form of zinc hydroxide was again converted back to zinc and the concentration of zinc in the solution started increasing, hence it was resolved to keep an optimum concentration of 3% lime. Model calculations are based on the diffuse layer model and a database of sorption constants for hydrous ferric oxide (HFO) which are incorporated in the Visual minteq version 3.0. The version 3.0 was launched on 28th October 2011and has been used in this study. The main aim of this work

is to understand the behavior of zinc at different pH conditions for adsorption on soil and soil mixtures. In our earlier work it has been found from experimental studies that zinc gets adsorbed at a pH of 7.7 Detailed sorption experiments were carried out and isotherm and kinetic modeling was done, it was found that most of these models failed to predict the adsorptive behavior of soils at different pH, also practically it was not feasible to run accurate experiments at varying pH. It was found that soil amended with lime significantly retarded Zn^{2+} migration. Sorption of zinc was mainly through surface precipitation along with complexation and ion exchange. It was not possible to determine which process was dominant at different pH, hence it is proposed to conduct simulation of these phenomenon to determine the dominant process at varying pH. Visual Minteq 3.0 predicts the complexation reactions of elements satisfactorily. Visual minteq is a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria, sorption etc. for natural waters. It combines state-of-the-art descriptions of sorption and complexation reactions with easy-to-use menus and options for importing and exporting data from/to Excel. Chemical equilibrium modeling has never been easier; Visual minteq was developed from the DOS program MINTEQA2, which was originally coded by the U.S. Environmental Protection Agency (EPA). Since 2000, when Visual MINTEQ was first published on the web, it has departed considerably from the original MINTEQA2 code, and therefore it is today a program on its own right. The aim of the program is to simulate equilibria and speciation of inorganic solutes in natural waters. The development of Visual minteq was supported by the Swedish Research Council (VR) and by the Foundation for Strategic Environmental Research (MISTRA). [5]

2. Materials and methods

2.1. Parameters for surface complexation model

The hydrous ferric oxide (HFO) content of red soil and black cotton soil and also mixture of redsoil and black cotton soil with lime was measured by ascorbate extraction method and the amorphous aluminum hydroxide content of the redsoil and black cotton soil was measured by oxalate extraction. Prior to chemical extractions the red soil was mixed with water until L/S = 2.5L/kg. These suspensions were subsequently equilibrated for 24 hr at four pH values of 4, 6.5, 8.5 and 10.5. The equilibrated suspensions were filtered over 0.2µm membrane filters, and the remaining solid material was extracted as below. HFO was extracted from 15g of soil with 300ml of ascorbic acid solution (20g/l) according to the method of Ferdelman described in Kostka and Luther. The extractions were performed at pH 8 and took 24 hr at room temperature. Amorphous aluminum hydroxide was extracted from 3g of soil with 300 ml of 0.2M of ammonium oxalate at pH 3 for 4 hr in the dark. All Fe and Al extracts were analysed by ICP – AES to obtain the concentrations of Fe and Al. The model development is based on the assumption that HFO is the primary sorbent mineral in soil, and second on the assumption that amorphous aluminum hydroxide also plays a role in the sorption process. For modeling purposes HFO was taken as surrogate sorbent for amorphous aluminum hydroxide. It can be justified that the use of HFO as a surrogate for aluminum hydroxide for the following reasons. The most reactive aluminum and iron hydroxides are $Fe(OH)_3$ (ferrihydrite /HFO) and $Al(OH)_3$. Iron(III) and Al(III) are known to substitute for each other in natural metal hydroxide. With respect to the input of sorbent mineral concentrations 1 mol of Al was assumed to be representative of 1mol of Fe. The molecular weight of 89g of HFO/mol of Fe recommended by Dzombak and Morel was used to calculate the concentration of HFO from the extracted Fe and Al. The resulting sorbent mineral concentrations are given in table 2. Specific surface area of HFO the general value of $600m^2/g$ recommended by Dzombak and Morel has been incorporated in the version 3.0 of visual minteq.

2.2. Input of data into Visual Minteq 3.0 and procedure to run the software:

From table 1 the concentrations of different elements used in this model are given, the ionic strength was fixed at 0.001M and the pH was fixed at 2. Component name and its concentration in molal were given in this case zinc and where ever necessary Al were added to the list of components. (In order to add a solid surface in the form of amorphous aluminum hydroxide, solid surfaces and excluded species were opened and specify finite solid phase was selected and amorphous $Al(OH)_3$ was selected from the list and its concentration in molal was added). Surface complexation reactions were chosen under adsorption and number of surfaces selected was 1 and HFO model given by Dzombik and Morel an upgrade of diffuse layer model was chosen. The concentration of Fe was added in g/l. The database feo-dlb_2008.vdb was selected and the sorption of Fe with Zn was chosen from database as $FeOZn^+$ species with id-number 16119500. Multi-problem menu was selected and a sweep of pH was done, adding components required to be monitored in the pH sweep. In our case the concentrations of FeO, $Fe(OH)_2$, $FeOZn^+$ and $Al(OH)_3$ were taken. After saving all these selections Minteq program was Run and output files were obtained. The output files can be obtained in excel and it was imported to origin and the data was plotted.

Table 1: Summary of sorbent and sorbate concentrations

Sl. No.	Name of sorbent	Fe concentration in g/l	Al concentration in Molal
1	Red soil	8.29	6.289E-04
2.	Red soil + 3%lime	8.72	6.8E-04
3.	Black cotton soil	8	4.4475E-04
4.	Black cotton soil + 3%lime	15	6.67E-04
5.	Sorbate / site concentrations of zinc 1.5293E-03 Molal		

3. Results and discussion

As per a previous experimental study by the same author the following results were obtained for Zinc with 3 % lime and 6 % lime content. The adsorption capacity was increasing, in soil lime system the pH of the system increases immediately due to this there is a possibility of formation of $ZnOH^+$ species and also to some extent precipitation of zinc onto the surface of the soil. The $ZnOH^+$ species get adsorbed onto the soil surface along with Zinc ions, in addition to Zinc retention through ion exchange and adsorption mechanism. This leads to an increase in the total capacity of soil to retain more amount of Zinc.

The pH at the surface of the particle is 0.5 to 1 unit higher than the ambient pH. Hence the precipitation of the metal ions can still occur onto the surfaces of the material at pH values 0.5 to 1.0 unit lower than the pH at which solution precipitation occurs. For only soil, since Red soil is acidic with a pH of 4 to 6 at low pH conditions the concentration of the H^+ ions is more , hence these H^+ ions are also competing with Zinc ions for the available exchangeable positions as well as adsorption sites leading to low retention of Zinc ions at low pH conditions. It is observed that Zn adsorption increases with pH in soil lime system and reaches equilibrium condition. There is a possibility of formation of $ZnOH^+$ and the hydrolysed species are strongly adsorbed to soil surfaces. And hence precipitation is not a major mechanism of retention of Zinc in soils because of the relatively high solubility of Zinc compounds.

In this paper red soil, black cotton soil and with lime mixtures were considered, since the database of visual minteq has only HFO and other database of aluminum hydroxide is not available. Hence for each mixture Fe and Fe with Al were taken as input data into the model and an ionic strength of 0.001 M was set for all the calculations. [6-13]

3.1 Behaviour of soil and lime:

In the figure 1 it can be seen that the speciation of hydrous ferric oxide over different pH is as shown the SOH represents the solid oxide/ hydroxide – water interface. FeO represents ferrous oxide and $Fe(OH)_2$ ferrous hydroxide, $FeOZn^+$ iron zinc complex. The solids hydroxide water interface represents the physical adsorption taking place it can be seen that this phase is predominant at pH 4 and 11. The interaction of FeO and $Fe(OH)_2$ is quite opposite and the point of zero surface charge is at a pH of 6, below this pH $Fe(OH)_2$ is predominant and above pH 6 FeO is dominant. $Fe(OH)_2$ forms a stable precipitate at pH of 6. It can be seen that the complexation of zinc takes place from pH 4 to 11. Comparing the sorption of zinc between red soil and red soil lime mixture, it can be seen clearly that there is a 14% jump in sorption of zinc from red soil lime mixture than only red soil. It might be due to the presence of calcium in excess quantities in lime than redsoil. Since Ca is good in precipitation and hydrolysis of zinc takes place effectively. Protonation of H^+ ions takes place therefore $Fe(OH)_2$ is dominant at acidic pH and after reaching neutral pH FeO becomes dominant, which can be seen in figure 1. It can also be seen in figure 1 that the speciation of black cotton soil (BCS) with lime is similar with that of black cotton soil but the magnitude of sorption is higher than that of red soil. There is a jump of 62.5% for BCS with lime than only with BCS.The reason for this behavior is same as enumerated above.The sorption of BCS is higher than red soil the reason might be specifically due to a higher cation ion exchange capacity (CEC) and specific surface area which cannot be considered in this model.

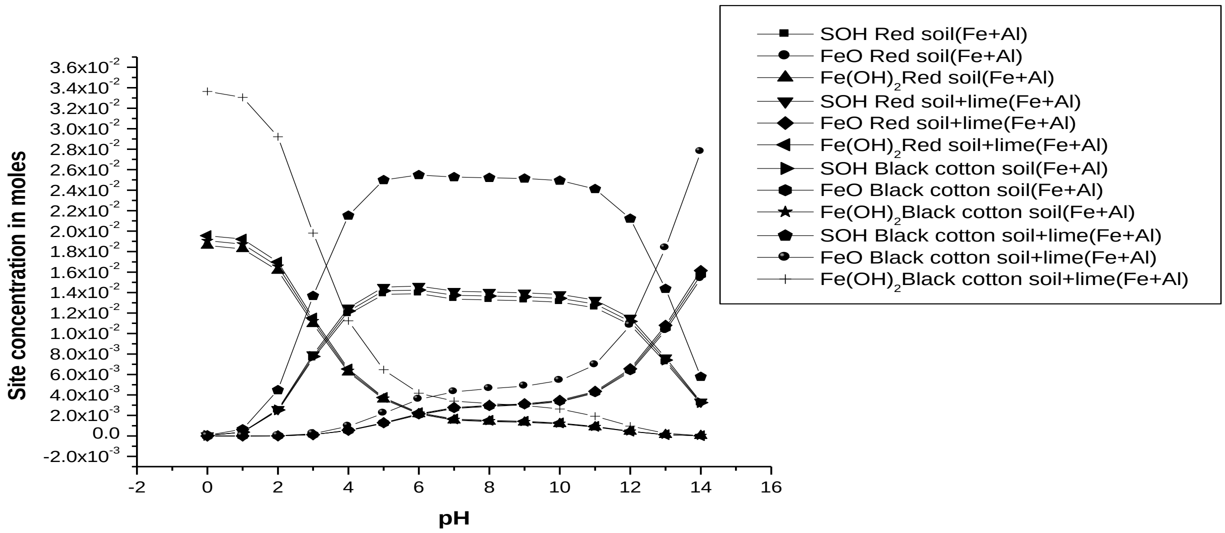

Figure 1: Speciation of Zn at different pH for various soil mixtures

3.2 Surface complexation of Zn^{2+} for mixtures of red soil, black cotton soil with lime

As shown in figure 2, an attempt has been made to understand the behavior of Zn^{2+} for surface complexation reactions. The data obtained through the model was plotted only for iron zinc complex (FeOZn) and it has been found that the complexation reaction is almost similar for all the mixtures taken and the order of sorption is BCS lime >redsoil lime>BCS >redsoil. The reactions are dominant at pH range of 5 to 13; this is the optimum pH where most of the reactions are found to be dominant for other chemical elements considered in this model.

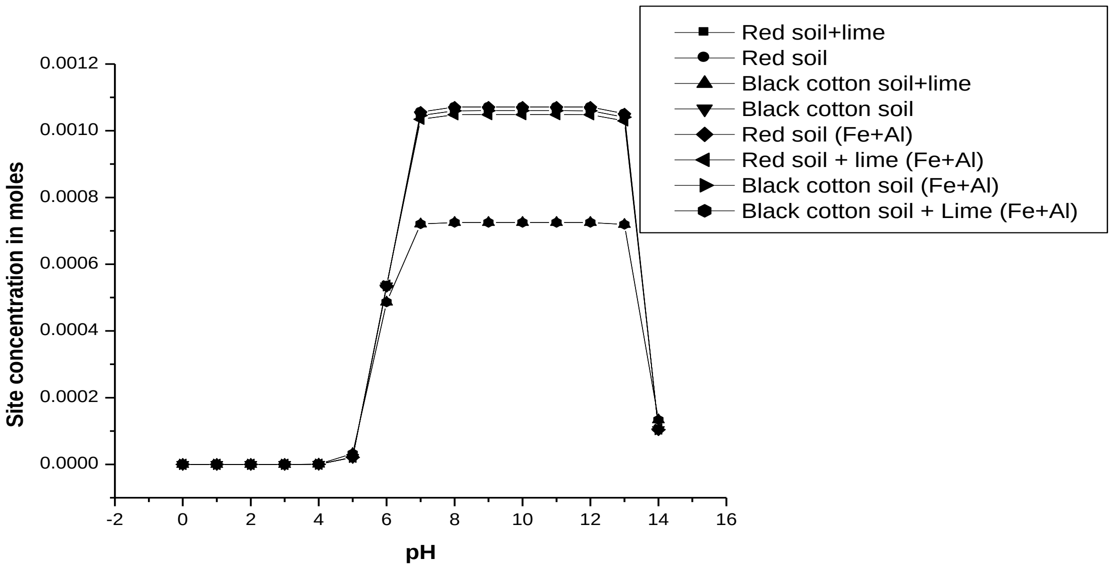

Figure 2: Variation of surface complexation of Zn at different pH

3.3 Speciation of amorphous aluminum hydroxide for sorption of zinc

From figure 3, it can be seen that the data generated using visual minteq for different mixtures of red soil, black cotton soil and with lime mixtures are taken and only the speciation of amorphous aluminum hydroxide for sorption of zinc is taken and discussed. It can be seen that the distribution of $Al(OH)_3$ is quite effective only at a pH range of 5 to 8. This is the range where maximum sorption of zinc takes place and forms a stable complex. It can also be seen that the presence of $Al(OH)_3$ plays a dominant role as the site concentration of $Al(OH)_3$ is more than Fe which is because the initial concentration of alumina in all these mixtures is much higher than Fe (refer table 2). Also it can be observed from figure 3 that due to the presence of calcium in different forms in lime the sorption follows the order BCS lime> BCS> redsoil lime > redsoil. It can be concluded that $Al(OH)_3$ plays a very important role in sorption. Unfortunately Visual Minteq does not provide any database for $Al(OH)_3$ sorption instead the database of Fe is taken as a surrogate and calculations are done. Even with this assumption this model satisfactorily predicts the sorption behavior of $Al(OH)_3$ for different sorbents which is proved through figure3. This has been possible because the version 3.0 has incorporated a number of upgrades for the database.

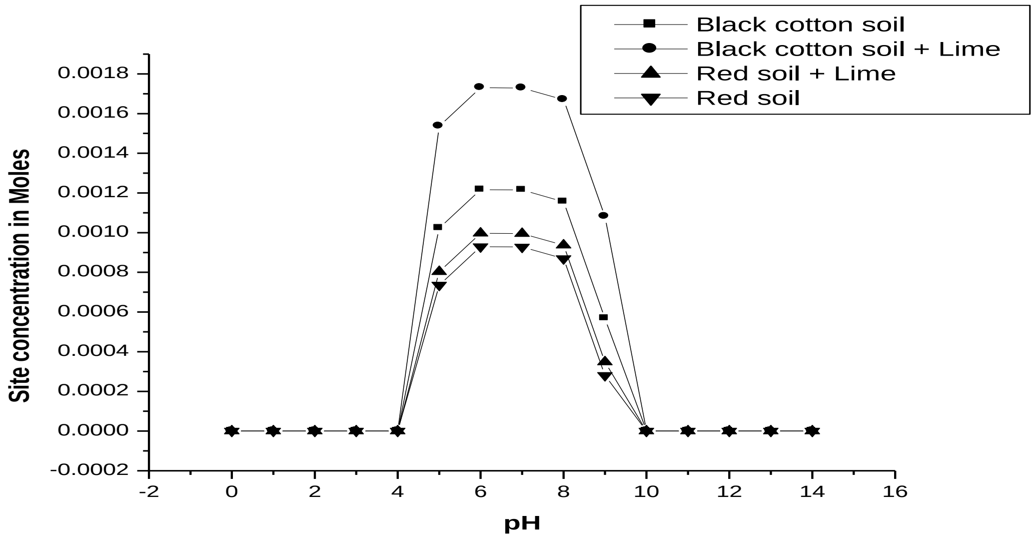

Figure 3: Variation of $Al(OH)_3$ at different pH

3.4 Speciation of zinc at varying pH

In figure 4 it can be seen that zinc adsorption takes place effectively at a pH range of 4 to 7. Also it can be seen that maximum adsorption of zinc has taken place and the behavior of zinc is almost similar for all mixtures considered, the reason might be formation of a stable precipitate of zinc hydroxide at a pH of 7 where in all the metal gets converted and hence the concentration of zinc is zero in the solution.

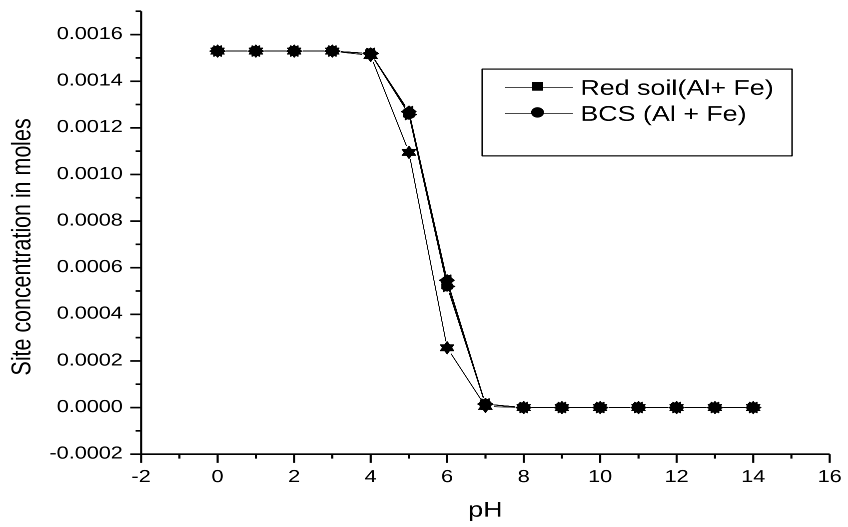

Figure 4: Speciation of Zinc at varying pH

Conclusion

In this paper an attempt has been made to use the latest version of Visual Minteq 3.0 to model the sorption behaviour of redsoil ,black cotton soil and with lime mixture on zinc. It has been found that the model accurately predicts the behavior of these mixtures, it can be concluded that the order of sorption of Zn^{2+} is Black cotton soil lime>Red soil lime >Black cotton soil > Red soil this was also proved experimentally through an earlier paper. The advantage of using this model was to study the behavior over a range of pH which was not possible experimentally. This model gave a new impetus on the complexation reactions taking place at various pH ranges. As most of the landfill leachates have a pH range of 3 to 8. This data can be used in the design of hazardous waste landfills as the designers would have a firsthand knowledge of behavior of these liner materials for a heavy metal like zinc.

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