Potential of surface complexation and redox modeling for chromium(VI) adsorption on local materials as liners for waste containment facilities

Syed Abu Sayeed MOHAMMED[*]

Faculty of Civil Engineering, HKBK College of Engineering, #22/1, Nagawara, Bangalore 560045, India

Abstract: The main aim of this paper was to model the behavior of red soil and black cotton soil along with fly ash mixture to sorption of chromium at different ranges 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. By conducting this simulation study, it was found that surface complexation and reduction played an important role in the sorption process, which gave a new impetus for 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 these model-generated data will help landfill designers make informed decisions in dealing with hazardous waste.

Key words: Surface complexation, Visual MINTEQ, hydrous ferric oxide, landfills, liners

1. Introduction

There is a growing emphasis on the problems of Cr pollution with the development of modern industry. Chromium has been used on a large scale in many different industries, including metallurgy, electroplating, production of paints and pigments, tanning, wood preservation, Cr chemical production, and pulp and paper production These industrial processes discharge large quantities of Cr compounds in liquid, solid, and gaseous wastes into the environment and can ultimately have significant adverse biological and ecological effects. Most of these end up as solid wastes in landfills and over a period of time might enter the ground water as leachates (Mohammed and Naik, 2011a). Cr is present naturally at background concentrations and hence the US Environmental Protection Agency specifies some standards. An average concentration of 100 mg/kg of Cr is found in soils and the range can vary from 1 to 1000 mg/kg as safe in ordinary soils; in drinking water, it should be less than or equal to 0.1 mg/L.

1.1. Behavior of Cr^{6+} at different pH levels

By conducting an extensive survey of the literature available on the behavior of Cr^{6+} at different pH levels, the following unique properties were hereby enumerated. The speciation of Cr^{6+} species, as shown in Table 1, gives details of different forms of Cr^{6+} species at different pH levels. When the pH is over a range of 0 to 2, it gives rise to the Cr^{3+} species (trivalent chromium ion), which is very stable, while from pH 2 to 6 it changes to $CrOH^{2+}$ (chromium monohydroxide), and as the pH rises to over 6 to 8, it gives rise to $Cr(OH)_2^+$ (chromium dihydroxide). As the pH starts moving towards the highly alkaline range from 8 to 10, it gives rise to a neutrally

[*]Correspondence: abubms@gmail.com

charged $Cr(OH)_3^0$ (chromium trihydroxide). This is a transition phase from here and at a pH of 10 to 14, it converts from cation to anion $Cr(OH)_4^-$ (chromium tetrahydroxide). Because of this behavior of Cr^{6+} species, it is a challenge to find methods to attenuate chromium. As most of the adsorbents are anionic in nature and sorb cationic ions, the transition of Cr^{6+} species from cationic to anionic at alkaline pH mars the efficiency of sorption (George and Vaclavikova, 2008).

Table 1. Speciation reactions of chromium at different pH levels.

Type of ion	pH	Reaction	Name of product formed
Cation	0–2	$Cr^{6+} + 3e^- \rightarrow Cr^{3+}$	Trivalent chromium ion
Cation	2–6	$Cr^{3+} + OH^- \rightarrow [CrOH]^{2+}$	Chromium monohydroxide
Cation	6–8	$[CrOH]^{2+} + OH^{-Æ} \rightarrow [Cr(OH)_2]^+$	Chromium dihydroxide
Neutral charge	8–10	$[Cr(OH)_2]^+ + OH^- \rightarrow Cr(OH)_3^0$	Chromium trihydroxide
Anion	10–14	$Cr(OH)_3 + OH^- \rightarrow [Cr(OH)_4]^-$	Chromium tetrahydroxide

2. Experimental

In an earlier work of the author, experiments were conducted on red soil of Bangalore and black cotton soil of Belgaum with additives like lime, cement, and fly ash used to study the sorption and leaching behavior of chromium. Sorption and leaching test data were applied to adsorption isotherms and kinetic models. The Langmuir isotherm was found to be more suitable than the Freundlich isotherm for both soils. Correlation coefficients obtained from all models fitted well in the following ranking: Elovich >intraparticle diffusion >pseudo-second-order >pseudo-first-order. The standard error of estimate proved pseudo-second-order to be more accurate than first-order. The intraparticle diffusion model proved that surface adsorption and intraparticle diffusion operate concurrently during adsorbent and adsorbate interaction. Scanning electron microscopy (SEM) images and electron dispersive spectroscopy (EDS) showed distinct adsorption of chromium. Soils with fly ash mixture were found to be a better material to attenuate chromium. It was found that the conventional models did not define clearly the actual phenomenon involved in the retention of chromium; hence, it was resolved to use an advance model in the form of Visual MINTEQ (Mohammed and Naik, 2010).

2.1. Application to surface complexation models

As per Thormann and Muellar (1985), 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 for different types of sorbents. In this paper, the surface complexation/precipitation modeling has been successfully applied to describe the sorption of chromium on red soil of Bangalore and black cotton soil of Belgaum, while also adding fly ash obtained from the Raichur thermal power station, Karnataka state, India, to this soil. Model calculations are based on the diffuse layer model and a database of sorption constants for hydrous ferric oxide (HFO), which were incorporated in Visual MINTEQ version 3.0. The latest version 3.0, which was launched on 28 October 2011, was used in this study. The main aim of this work was to understand the behavior of chromium at different pH conditions for adsorption on soil and soil mixtures. In the author's earlier work, it was found from experimental studies that chromium is reduced at low pH. 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, which was also confirmed by the works of Oladoja et al. (2008).

It was found that fly ash contains free iron and manganese and aluminum oxides, which significantly retard Cr^{6+} migration. Chromium adsorption increases with decreasing pH due to protonation of the hydroxyl groups, and this reaction can be described as a surface complexation reaction between the Cr^{6+} species and the surface hydroxyl sites. Hence, it was proposed to use soil fly ash mixture as a better material to retain chromium. Its behavior at low pH levels is difficult to study; hence, the use of speciation modeling helps us to predict its behavior, and within this pH, complexation reactions are predominant. 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, and so on 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 US Environmental Protection Agency. Since 2000, when Visual MINTEQ was first published, 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 and by the Foundation for Strategic Environmental Research (Mohammed et al., 2009).

2.2. Parameters for surface complexation model

The HFO content of red soil and black cotton soil, and also of the mixture of red soil and black cotton soil with fly ash, was measured by the ascorbate extraction method, and the amorphous aluminum hydroxide content of the red soil and black cotton soil was measured by oxalate extraction. Prior to chemical extractions, the red soil was mixed with water until L/S = 2.5 L/kg. These suspensions were subsequently equilibrated for 24 h at 4 pH values of 4, 6.5, 8.5, and 10.5. The equilibrated suspensions were filtered over 0.2-μ m membrane filters, and the remaining solid material was extracted as below. HFO was extracted from 15 g of soil with 300 mL of ascorbic acid solution (20 g/L) according to the method of Ferdelman as described by Kostka and Luther (1994). The extractions were performed at pH 8 and took 24 h at room temperature. Amorphous aluminum hydroxide was extracted from 3 g of soil with 300 mL of 0.2 M of ammonium oxalate at pH 3 for 4 h in the dark. All Fe and Al extracts were analyzed by ICP–AES to obtain the concentrations of Fe and Al, as per procedures given in the work of Meima and Comans (1998).

The model development is based first on the assumption that HFO is the primary sorbent mineral in soil, and secondly on the assumption that amorphous aluminum hydroxide also plays a role in the sorption process. For modeling purposes, HFO was taken as the surrogate sorbent for amorphous aluminum hydroxide. The use of HFO as a surrogate for aluminum hydroxide is justified 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)

Table 2. Summary of sorbent and sorbate concentrations.

Sl. No.	Name of sorbent	Fe concentration in g/L	Al concentration in mol
1	Red soil	8.29	4.8293×10^{-4}
2.	Red soil + fly ash	8.59	6.289×10^{-4}
3.	Black cotton soil	8	4.4475×10^{-4}
4.	Black cotton soil + fly ash	6.5	1.4958×10^{-3}
5.	Sorbate/site concentrations of chromium 1.9232×10^{-3} mol		

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 1 mol of Fe. The molecular weight of 89 g 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. The specific surface area of HFO of a general value of 600 m^2/g as recommended by Dzombak and Morel was incorporated in version 3.0 of Visual MINTEQ, as described in the work of Meima and Comans (1998).

2.3. Input of data into Visual MINTEQ 3.0 and procedure to run the software

In Table 2, the concentrations of different elements used in this model are given. The ionic strength was fixed at 0.001 M and the pH was fixed at 2. Component names and its concentrations in mol were given for chromium, and wherever necessary, Al was 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, the specified finite solid phase was selected, and amorphous Al(OH)$_3$ was selected from the list and its concentration in mol was added. Surface complexation reactions were chosen under adsorption, the number of surfaces selected was 1, and the HFO model given by Dzombak and Morel, an upgrade of the 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 Cr was chosen from the database as FeCrO$_4^-$ species with id-number 16112120. The multiproblem menu was selected and a sweep of pH was done, adding components required to be monitored in the pH sweep. In this case, the concentrations of FeO, Fe(OH)$_2$, FeCrO$_4^-$, and Al(OH)$_3$ were taken. After saving all these selections, the MINTEQ program was run and output files were obtained. The output files can be obtained in Excel and were imported to origin, and the data were plotted (Barakat, 2008; Said, 2010; Mohammed and Naik, 2011b).

3. Results and discussion

In this paper, red soil, black cotton soil, and the 2 with fly ash mixtures were considered, since the database of Visual MINTEQ has only HFO and other databases of aluminum hydroxide are 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 calculations (Kermani et al., 2006).

3.1. Behavior of red soil and fly ash

In Figure 1 the speciation of HFO over different pH levels is as shown, and SOH represents the solid oxide/hydroxide–water interface. FeO represents ferrous oxide and Fe(OH)$_2$ ferrous hydroxide, while FeCrO$_4^-$ represents ferrous chromate and iron chromium complex. The solid hydroxide–water interface represents the physical adsorption taking place, and it can be seen that this phase is predominant at pH 3 and 10. The interaction of FeO and Fe(OH)$_2$ is quite opposite and the point of zero surface charge is at a pH of 9; below this pH, Fe(OH)$_2$ is predominant, and above pH 9, FeO is dominant. Fe(OH)$_2$ forms a stable precipitate at a pH of 9 and remains constant; this is in confirmation with the speciation of Cr^{6+} as given in Table 1. It can be seen that the complexation of chromium takes place from pH 4 to 8. Comparing the sorption of chromium between red soil and red soil fly ash mixture, it can be seen clearly that there is a 133% jump in sorption of chromium with fly ash as compared to only red soil. This might be due to the presence of iron and alumina in excess quantities in fly ash compared to red soil. Since Fe is a good reducing agent and chromium is a highly reactive element, the reduction of Cr takes place effectively. Protonation of H$^+$ ions takes place; therefore, Fe(OH)$_2$

is dominant at acidic pH levels and after reaching a neutral pH FeO becomes dominant, which can be seen in Figures 1 and 2. It can be seen in Figure 2 that the speciation of black cotton soil (BCS) with fly ash is similar with that of red soil, but the magnitude of sorption is higher than that of red soil. There is a jump of only 40% for BCS with fly ash as compared to only BCS, and the magnitude of sorption of Cr^{6+} by BCS is higher by a magnitude of almost 83% as compared to red soil. This is generally due to a higher concentration of Fe in BCS than in red soil. Specifically, it is due to a higher cation ion exchange capacity (CEC) and the specific surface area, which cannot be considered in this model. During this process, many compounds are formed, and it can be seen that $FeCrO_4^-$ is one such compound that forms and remains constant through a wide range of pH levels.
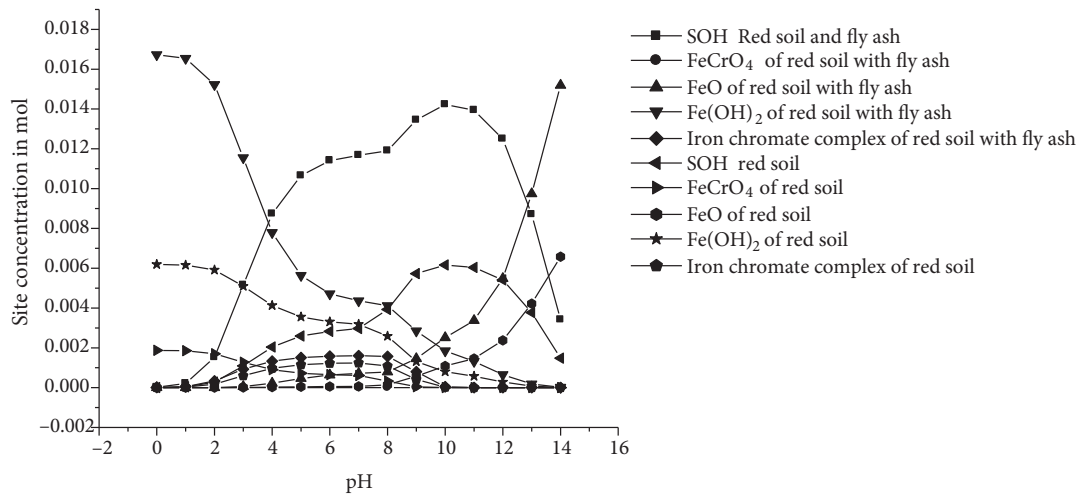

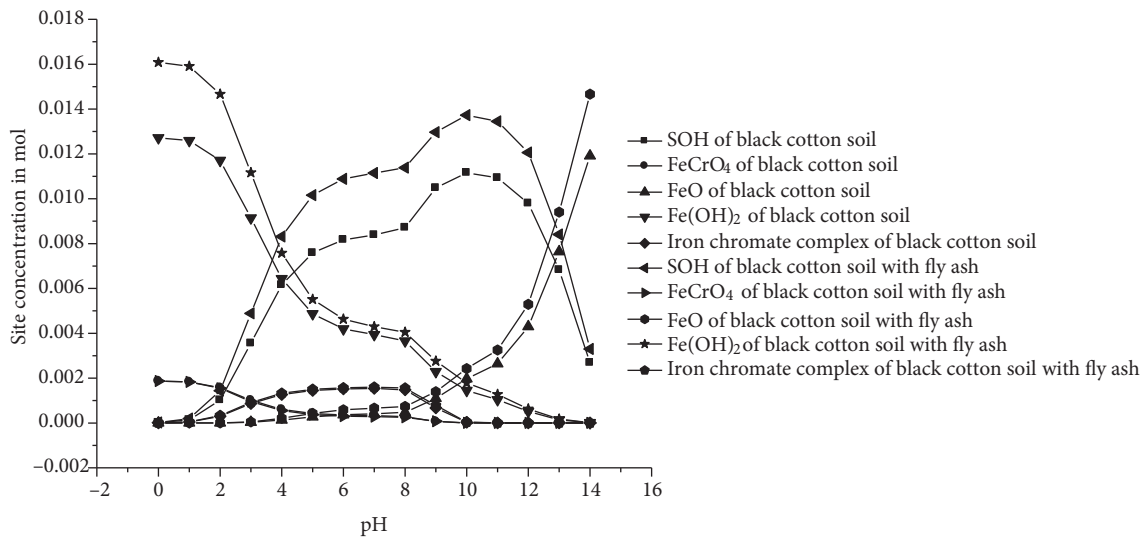**Figure 1.** Speciation of red soil and fly ash with Cr^{6+}.

Figure 2. Speciation of black cotton soil and fly ash with Cr^{6+}.

3.2. Comparison of speciation with red soil, black cotton soil, and with fly ash

In Figure 3, a comparison of speciation of red soil, black cotton soil, and the 2 with fly ash mixtures is made. It can be observed that the sorption is of the order BCS–fly ash >red soil–fly ash >BCS >red soil. For all

4 mixtures, the interaction of FeO and $Fe(OH)_2$ is similar and the point of zero surface charge is at a pH of 9, while below this pH $Fe(OH)_2$ is predominant and above pH 9 FeO is dominant. $Fe(OH)_2$ forms a stable precipitate at a pH of 9 and remains constant; this is in confirmation with the speciation of Cr^{6+} as given in Table 1. It can also be observed that complexation reactions have taken place and a stable iron chromate complex is formed. It can be concluded that the main criteria of sorption is reduction and complexation for these mixtures, which has been proven true through experimental works in an earlier paper of the author (Atmani et al., 2009; Mohammed and Naik, 2011c).

3.3. Surface complexation of Cr^{6+} for mixtures of red soil, black cotton soil, and the 2 with fly ash

As shown in Figure 4, an attempt was made to understand the behavior of Cr^{6+} for surface complexation reactions. The data obtained through the model were plotted only for iron chromate complex and it was found that the complexation reaction was almost similar for all the mixtures taken, with order of sorption of BCS–fly ash >red soil–fly ash>BCS >red soil. The reactions are dominant at the pH range of 4 to 8; this is the optimum pH range, where most of the reactions are found to be dominant for other chemical elements considered in this model (Mohammed et al., 2010).
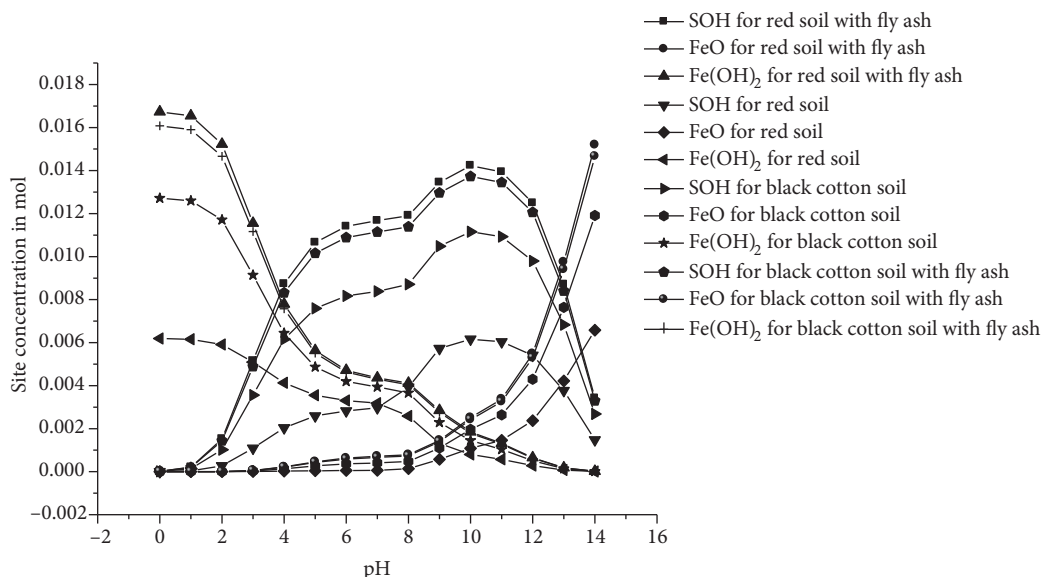

Figure 3. Comparison of speciation of red soil, black cotton soil, and the 2 with fly ash.

3.4. Behavior of chromate at different pH

In Figure 5, a graph of the concentration of chromate at different pH levels is plotted. Three oxides of chromate were considered: chromate, dichromate, and perchromate. This was done to understand the reduction reactions taking place. It can be observed that concentration of perchromate is highest at acidic pH levels and remains constant from 2 to 5, whereas at the same pH range the concentration of chromate is lowest and slowly increases from pH 5. At the neutral pH of 7, there is point of zero charge and a transition of $HCrO_4^-$ to CrO_4^{-2} takes place. Deprotonation of $HCrO_4^-$ takes place and it is converted to CrO_4^{-2}. This speciation of chromate proves that the redox reaction is very prominent in sorption of Cr^{6+}. The concentration of dichromate is constant through all the pH ranges, proving it to be very stable.
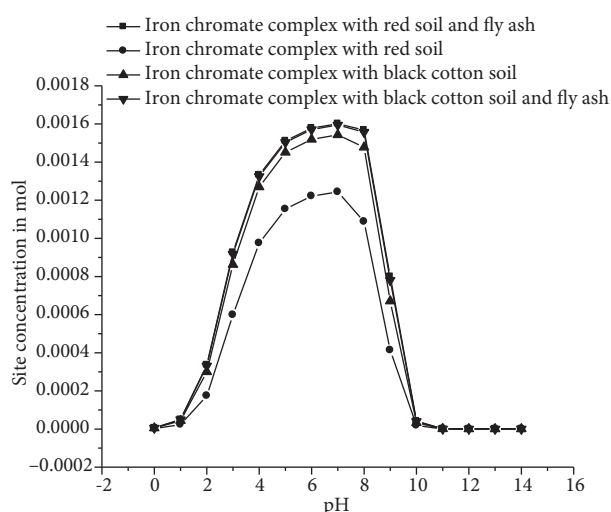
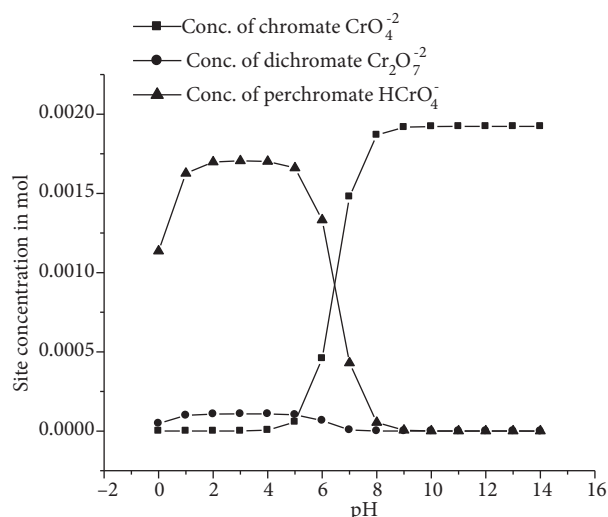**Figure 4.** Variation of surface complexation model.

Figure 5. Behavior of chromate at different pH levels.

3.5. Behavior of Fe and Al with chromium

In order to observe the interaction of Fe and Al, it was proposed to model the behavior of Al for mixtures of red soil, black cotton soil, and the 2 with fly ash. The concentration of Al present was put into the model and Visual MINTEQ was run as described earlier. The data obtained were plotted as shown in Figure 6. It can be observed that there are marked differences in the way the model projected the system. It was found that Al is a very reactive element and its interaction with chromium in reducing it into a stable compound is much higher than that with only with Fe, as stated above. Al acts as a competing ion and hence the values are much lower. It was also found that the model failed to predict a number of parameters with combinations of Fe and Al, the reason being that there is no database for Al in Visual MINTEQ, and it was assumed that Al acts as a surrogate to Fe in modeling and that we invariably use the same database as for Fe. This gives us a rough estimate of the sorption process taking place in presence of Al. It can be observed from Figure 6 that the SOH has slightly shifted into a purely alkaline environment for sorption, which be due to the presence of a competing ion like Al, which increases the magnitude of ions getting reduced rather than being complexed. The behavior of $Fe(OH)_2$ and FeO is similar to what was observed above.

3.6. Speciation of amorphous aluminum hydroxide for sorption of chromium

In Figure 7, data generated using Visual MINTEQ for different mixtures of red soil, black cotton soil, and the 2 with fly ash mixtures are reflected with the speciation of amorphous aluminum hydroxide for sorption of chromium 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 the maximum sorption of chromium takes place and it 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 greater than Fe because the initial concentration of alumina in all these mixtures is much higher than that of Fe (refer to Table 2). It can also be observed from Figure 7 that due to the presence of alumina in different forms in fly ash, the sorption follows the order of BCS–fly ash >red soil–fly ash >BCS >red soil. 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 for 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 as proven in Figure 7. This is possible because the latest version, 3.0, has incorporated a number of upgrades for the database.
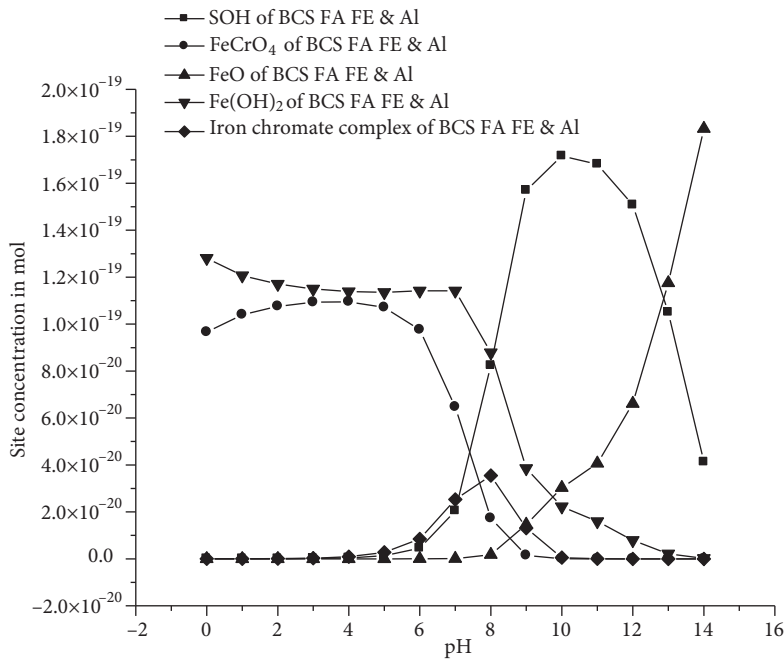

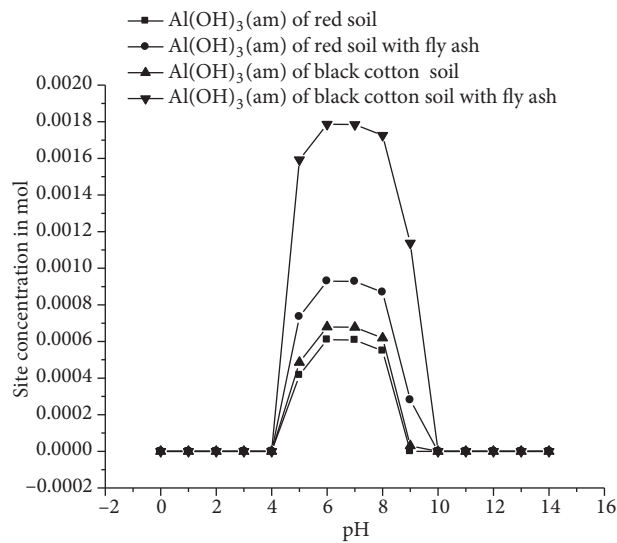**Figure 6.** Speciation of Cr^{6+} for Fe and Al.

Figure 7. Speciation of amorphous aluminum hydroxide for sorption of chromium.

4. Conclusions

In this paper an attempt has been made to use the latest version of Visual MINTEQ to model the sorption behavior of red soil, black cotton soil, and the 2 with fly ash mixture on chromium. It has been found that the model accurately predicts the behavior of these mixtures, and it can be concluded that the order of sorption of Cr^{6+} is black cotton soil–fly ash >red soil–fly ash >black cotton soil >red soil, as was proven experimentally

in an earlier paper. The advantage of using this model was the ability to study the behavior over a range of pH levels, which was not possible experimentally. This model gave a new impetus for the complexation and redox reactions taking place at various pH ranges. As most of the landfill leachates have a pH range of 3 to 8, these data can be used in the design of hazardous waste landfills as designers would have a firsthand knowledge of the behavior of these liner materials toward a heavy metal like chromium.

References

Atmani, F., Bensmaili, A. and Mezenner. N.Y., "Synthetic Textile Effluent Removal by Skin Almonds Waste", Journal of Environmental Science and Technology, 2, 153–169, 2009.

Barakat, M.A., "Adsorption of Heavy Metals from Aqueous Solutions on Synthetic Zeolite", Research Journal of Environmental Sciences, 2, 13–22, 2008.

George, P. and Vaclavikova, G.M., "Removal of Chromium (VI) from Water Streams: A Thermodynamic Study", Environmental Chemical Letters, 6, 235–240, 2008.

Kermani, M.H., Pourmoghaddas, B., and Khazaei, Z., "Removal of Phenol from Aqueous Solutions by Rice Husk Ash and Activated Carbon", Pakistan Journal of Biological Sciences, 9, 1905–1910, 2006.

Kosta, J.E. and Luther, G.W. 3rd, "Partioning and Speciation of Solid Phase Iron in Saltmarsh Sediments", Geochimica et Cosmochimica Acta, 58, 1701–1710, 1994.

Meima, J.A. and Comans, R.N., "Application of Surface Complexation/Precipitation Modeling to Contaminant Leaching from Weathered Municipal Solid Waste Incinerator Bottom Ash", Journal of Environmental Science and Technology, 32, 688–693, 1998.

Mohammed, S.A.S. and Naik, M., "Adsorption Characteristics of Metals in Aqueous Solution by Local Materials with Additives as Liners for Waste Containment Facilities", Journal of Water and Environment Technology, 8, 29–50, 2010.

Mohammed, S.A.S. and Naik, M., "Potential Use of Black Cotton Soil with Additives as a Liner Material to Retain Zinc: Isotherm and Kinetic Studies", International Journal of Ecology and Development, 19, 15–29, 2011a.

Mohammed, S.A.S. and Naik, M., "Utilization of Red Soils and Amended Soils as a Liner Material for Attenuation of Copper from Aqueous Solution: Isotherm and Kinetic Studies", Journal of Environmental Science and Technology, 4, 504–519, 2011b.

Mohammed, S.A.S. and Naik, M., "A Review and Evaluation of Selected Kinetic Models and Sorption Processes in Amended Soils", International Journal of Research in Chemistry and Environment, 1(2), 1–14, 2011c.

Mohammed, S.A.S., Naik, M. and Tanveeruddin, S., "Influence of Additives on the Retention of Metal Ions in a Soil of Bangalore, India", Ambiente Agua - An Interdisciplinary Journal of Applied Sciences, 4, 20–36, 2009.

Oladoja, N.A., Aboluwoye, C.O. and Olademeji, Y.B., "Kinetics and Isotherm Studies on Methylene Blue Adsorption onto Ground Palm Kernel Coat", Turkish Journal of Engineering and Environmental Science, 32, 303–312, 2008.

Thomann, R.V. and Muellar, J.A., Principles of Surface Water Quality Modeling and Control, Harper & Row, London, 1985.

Said, E.L., "Selecting Kaolinite Clay for Copper Removal in Batch and Fixed Bed Column Systems", International Journal of Chemical Technology, 2, 88–93, 2010.