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ABSTRACT

Title	of	Thesis:	Adsorpt	ion	and	Descrption	of	Chromium	on
			Clayey	Soil	S				

- Ker-Shu Tan, Master of Science in Civil/Environmental Engineering
- Thesis directed by: Dr. Hsin-Neng Hsieh Associate Professor of Civil / Environmental Engineering

Chromium residue waste was produced during sixties in the chromium production process. It was used as construction fill. Problems associated with chromium waste sites include structure distress and surface and groundwater contamination.

The purpose of this study was to investigate the adsorption and desorption of chromium on soil. In order to achieve this purpose, experiments were conducted to study the effect of pH, type of chromium compound, and type of soil on adsorption and desorption.

Experiments were performed on kaolinite, bentonite and sand. In our study, it was found that sand had almost no adsorption for chromium. Kaolinite had less adsorption capacity compared with bentonite, which was consistent with the cation exchange capacity. Adsorption of chromium was related to the amount of the soil presented. It was found in this study that the amount of chromium adsorbed was proportional to the the concentration of chromium added to the soil. Trivalent chromium was highly attached to the soil, whereas hexavalent chromium was poorly adsorbed.

From our study, it seemed the sorption mechanisms were sorption of water causing the chromium being two: the adsorbed and the physical sorption between soil and chromium. The physical adsorption were caused by van der It was Waals force and ion exchange attraction force. found that clay would expand when there was a change of pH, the change of the concentration of the chemical or Swelling property made it very difficult to presented. separate the bentonite from supernatant. pH definitely had an impact on chromium adsorption. It was found that when the pH reached 4.5 to 5.0, trivalent chromium precipitated. Adsorption of trivalent chromiun increased as the pH also In the contrast, hexavalent chromium had a increased. higher adsorption capacity at lower pH values.

Several desorption processes were performed in this study. Pure water could remove chromium which was adsorbed due to van der Waals force. Other processes performed included oxidization of trivalent chromium to hexavalent chromium, change of pH. The above techniques could be oxidized trivalent chromium to hexavalent chromium, and change of pH, should be able to separate the chromium which was adsorbed due to ion exchange from clay. EDTA can also be used to extract chromium from soil.

Adsorption and Desorption of Chromium on Clayey Soils

by Ker-Shu Tan

Thesis Submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering

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CHAPTER 1 INTRODUCTION

Chromium was known to be used by human beings since the ancient time. The Hittites used chromium minerals in the fabrication of their hand weapons of "stainless steel". Medieval and Renaissance artists used chromium as pigments. From the time of discovery of crocoite, chromium salts were used in very limited industrial application until around the end of the nineteenth century. The process of manufacturing chromates by roasting chromite with lime and soda ash was discovered by 1800, and with it the chromium compounds became increasingly available commercially.[1]

Hudson County, New Jersey, one of the major areas for chromium production in the United States has generated over 2.75 million tons of alkaline waste before 1965. Some of this waste was used as fill and diking material. Recently, soil and groundwater pollution have been found at chromium waste sites. Investigated reports showed that contaminated sites contained 100 ppm to 10,000 ppm chromium salts in the soils. This concentration is far beyond the regulation of In the meanwhile, samples taken from a pond close E.C.R.A.. to a chromium contaminated site were found to have chromium concentration up to 8,000 mg/l. Chromate salts were also found to continue to leach out soluble chromium salts even years after disposal and created a serious problem in soil and groundwater.

Liquid Chromium wastes were produced by the industrial processes. The major industrial sources of chromium waste are wood treatment and tannery facilities, as well as chromium mining and milling operations. Typically, chromium-containing liquid wastes have been disposed of by discharging them to surface impoundments or lagoons. Chromium leaking from these sites into groundwater is relatively common.

Chromium contamination problems have been reported in the states of Texas, Maryland, Hawaii, and New Jersey in the United States and in Germany, England, and Japan. Thus, the problems addressed in this research are international in scope.[2]

Problems associated with chromium waste sites include distress and surface structure and ground water pollution.[2] Naturally occurring chromium also occurs at potentially harmful concentration, although such occurrences are thought to be rare. Robertson[3] reported that hexavalent chromium was found in the ground water in Paradise Valley, Maricopa County, Arizona. The concentration of hexavalent chromium exceed 0.05 mg/l, the U.S. Public Health Service's upper limit for hexavalent The present limit for dissolved chromium in chromium. drinking water is 10^{-6} M [4], a level that requires that some industrial waste solutions be treated to lower Cr(VI) concentrations before discharge to the environment.[5]

The main purpose of this study is a primary study to contribute the knowledge of soil washing to remove the chromium compounds from soil. Thus, the adsorption and desorption properties of chromium on clayey soils will be investigated in this study. In addition to this, factors affecting chromium adsorption and desorption upon soil physical and chemical properties will also be discussed in this study.

CHAPTER 2 LITERATURE REVIEW

2.1 Chromium Characteristics

There are two major types of chromium compounds in the nature: Cr(VI) and Cr(III). Hexavalent chromium is very mobile and could migrate considerable distances from its source.[1] Also, Hexavalent chromium is very toxic to animals and plants. Trivalent chromium is considered to be less toxic than hexavalent chromium. Some organic and inorganic compounds exist in the soils, such as manganese oxide and citric acid, which could oxidize the trivalent chromium to hexavalent chromium.

Bartlett et al.[6] reported that within the ranges of Eh and pH normally found in soils, chromium exists in four states: two trivalent forms, the Cr^{3+} cation and the $Cr0_2^{-}$ anion, and two hexavalent anion forms, $Cr_20_7^{-}$ and $Cr0_4^{-}$. They also indicated that the behavior of Cr(III) was quite similar to that of aluminum in response to varying amounts and sequences of applied lime and phosphorus.

They also reported that hexavalent chromium could be reduced by manure rapidly under the condition of low pH. Lowering the pH of the suspension below 3 brought about the reduction by manure of almost all of the added Cr(VI) within 24 hours. However, all of the Cr(VI) applied to the Marlo and Vergennes soils appears to have been reduced during the 5-week incubation period, even at natural pH's or above.[7]

These results indicated that some organic matter in the soil could reduce the Cr(VI) in the natural condition. Beside this, in the presence of Al in the solution, Cr(VI) was precipitated as the pH was increased above 4-5. The pHsolubility curve of the Cr(VI) anion in the presence of excess Al is quite similar in shape to that of phosphate with excess Al, and probably the Cr(VI) was coprecipitated with the Al. For the adsorption tests, they found most of soils could adsorb some Cr(VI), and Cr(VI) and phosphate were competing for the same adsorption sites.

Calder[1] has reported that a number of different chromium species could exist in groundwater environments. These species differ greatly in their solubility and in their tendency to be adsorbed by soil or aquifer materials. The concentration and mobility of chromium in groundwater are strongly dependent on its characteristics.

Chromium speciation in groundwater is affected by pE (redox) and pH conditions. Chromium(VI) predominates under oxidizing (high redox) conditions, whereas Cr(III) predominates under more reducing(low redox) conditions. At total chromium concentrations below 500 mgL⁻¹(0.01M), the dominant Cr(VI) species are the oxyanions $HCrO_4^{-1}$ and $CrO_4^{2^{-1}}$. Equilibrium between the two species is dependent on pH:

 $HCrO_4^- = CrO_4^- + H^+$

At Cr(VI) concentrations above 500 mgL⁻¹, the $Cr_2O_7^{2-1}$ ion predominates in acidic environments.[8]

$$Cr_2O_7^{2-} + H_2O = 2HCrO_4^{-}$$
 K = $10^{-2.2}$

The dominant Cr(III) species occurring in groundwater also depend on pH. The governing reaction are:

$$Cr^{3+} + H_2O === CrOH^{2+} + H^+$$

 $CrOH^{2+} + H_2O === Cr(OH)_2^+ + H^+$
 $Cr(OH)_2^+ + H_2O === Cr(OH)_3 + H^+$
 $Cr(OH)_3 + H_2O === Cr(OH_4)^- + H^+$

 $CrOH^{2+}$ and Cr^{3+} predominate in more acidic, waters and $Cr(OH)_3$ and $Cr(OH)_4^-$ predominate in more alkaline water.

Eary et al.[9] has studied that the trivalent chromium oxidizes to hexavalent chromium by reaction with manganese dioxide. They indicated that the oxidation of aqueous Cr(III) does not occur by surface-catalyzed reactions with dissolved oxygen but by direct reaction with B-MnO₂(s). This reaction was limited probably by anionic Cr(VI)adsorption in acidic solution and by $Cr(OH)_3(s)$ precipitation in neutral to alkaline solution.

Another study of oxidation-reduction reaction of chromium were carried out by James et al.[10] They used the following four different chromium(III) compounds to perform this study. 1. Freshly-precipitated $Cr(OH)_3$. 2. Crcitrate. 3. aged $Cr(OH)_3$ in citrate. 4. aged $Cr(OH)_3$. These compounds produced different amounts of Cr(VI) in the

same condition. They are numerically labelled in the order of the amount of Cr(VI) produced. Compound listed under item 1. above produced the most amount and that listed under item 4. produces the lest. Reaction time was another major factor in their study. They indicated that adding citric acid with Cr(VI) increased the quantity of Cr(VI) removed by the soil at both pH values and during both equilibration times. Also, increasing the level of citric acid increased the rate of reduction of Cr(VI).

Oxidation-reduction method can be used to removed aqueous Cr(VI) from waste water. Eary et al.[5] found that the most efficient method for removing aqueous Cr(VI) from waste waters is by the simple addition of Fe(II) salts. The reduction of aqueous Cr(VI) by aqueous Fe(II) can be described by the overall reaction:

$$Cr(VI)(aq) + 3Fe(II)(aq) \longrightarrow Cr(III)(aq) + 3Fe(III)(aq)$$

The reduction of aqueous Cr(VI) by aqueous Fe(II) not only removes the toxic Cr(VI) species from solution but also results in the precipitation of $(Cr_xFe_{1-x})(OH)_{3(s)}$. The solubility of this solid limits Cr(III) concentrations, over the pH range of approximately 5.0-11.0, to less than the drinking water standard of 10^{-6} M Cr.

Stollenwerk and Grove[11] reported that chromium(VI) could be reduced to Cr(III) by acidification, using NO_2 , and some organic carbon. The rate of reduction of Cr(VI) to

Cr(III) increased with increasing NO_2 , DOC, H^+ , and temperature. Reduction of Cr(VI) by organic matter occured in some samples even though the samples were unacidified. Reduction of Cr(VI) is inhibited to an extent by storing the sample at 4^oC. Several reduction mechanism can be summarized by

$$HCrO_{4}^{-} + 7H^{+} + 3e^{-} == Cr^{3+} + 4H_{2}O$$
$$HCrO_{4}^{-} + 3NO_{2} + H^{+} == 3NO_{3}^{-} + Cr^{3+} + H_{2}O$$
$$4HCrO^{4-} + 16H^{+} == 4Cr^{3+} + 3O_{2} + 10H_{2}O$$

The last equation shows that Cr(VI) can be reduced to Cr(III), even in deionized water, at the pH values of less than 2. They also indicated that water samples collected for the determination of Cr(VI) should be filtered (0.45-um membrance), refrigerated, and analyzed as quickly as possible. Water samples should not be acidified.

Amacher and Baker[12] reported that chromium from organic sources such as sewage sludge remained in soil in a reduced state associated with the organic matter or perhaps organo-Cr complexes sorbed to iron oxides and was not oxidized by manganese oxides. Inorganic sources of Cr $(CrCl_3, Cr(OH)_3, and Cr_2O_3)$ were oxidized in soil, but only a few percent of the added Cr was oxidized while the remainder was sorbed by the various soil components (organic matter and iron oxides, etc.) and apparently was unavailable for oxidation. They also indicated that not all the

solution Cr(III) easy oxidized because the Mn(IV) at the surfaces of the manganese oxide minerals was "used up" and access of Cr(III) to Mn(IV) beneath the mineral surface was blocked by Mn(II) remaining sorbed to the mineral.

2.1.1 Toxicity of Chromium

Chromium as a metal is biological inert and does not produce toxic or other harmful effects in man or laboratory animal. Compounds of Cr(III) have no established toxicity. However, it is known that in an excessive concentration, trivalent chromium, in an aquatic environment, inhibits the growth of certain algae and can result in the death of shellfish or fish. The chief health problems associated with chromium are related to Cr(VI) compounds, which are irritant and corrosive and may be adsorbed by ingestion, through the skin, and by inhalation. Acute systemic poisoning is rare and usually may result from absorption through the skin.[13]

For plants, hexavalent chromium compounds are also more toxic than trivalent chromium compounds. A wheat plant was killed by 64 mg/l sodium dichromate.[14] Hunter and Vergnano[15] reported that slight chlorosis is produced in oat plants grown in nutrient solution with 10 mg/l of chromium.

Chromium has also been reported to be a carcinogen. Workers who are exposed to chromium in a variety of different forms and occupational settings have been linked to increased respiratory cancer risk. Extensive reviews on the carcinogenicity of chromium have been published by government bodies, international organizations, academic institutions[16,17,18,19], and by individuals[20]; the U.S.EPA[21] has also prepared a reappraisal of the literature.

2.2 Adsorption and Desorption of Chromium on Soil

Zachara et al. [22] had found that major groundwater anions bind to the surface of amorphous Fe₂O₃·H₂O, reduce positive charge, and compete directly with Cro_4^{-} as sites become limited. The surface reaction of these anions reduces $CrO_4^{=}$ adsorption. Cations have little influence on CrO_4^{-} adsorption, indicating that ion pair formation in on the surface is not of consequence. solution or Chromium(VI) adsorption on iron oxyhydroxide was significantly reduced by the presence of SO_4^{2-} , HCO_3^{-} , and They also indicated that surface complexation HASiOA. constants along with diffuse double-layer models of adsorption can estimate the extent of suppression anticipated under various subsurface chemical regimes.

also reported that chromate adsorption They by kaolinite increased with decreasing pH because of protonation of chromate and/or variable charge sites on kaolinite. The amount of $CrO_{4}^{=}$ adsorbed, however, varied as much as four-fold depending on the pretreatment method. The DCB (dithionite-citrate-bicarbonate)-treated kaolinite adsorbed the most $CrO_A^{=}$, whereas the kaolinite treated with acidified NaClO₄ adsorbed the least. In the presence at equal concentration of CrO_4^{-} and SO_4^{-} , the two solutes sorbed independently, suggesting binding to separate sites. However, it would increase the adsorption in the presence of excess SO_4^{-1} . The adsorption of both chromate and sulfate can be described in terms of a site-binding model of kaolinite edge, in which the edge is viewed as composite layers of Al and Si oxide. Surface complexation constants for CrO_4^{-} on kaolinite were similar to those for alumina, pointing to the importance of Al-OH edge sites in chromate adsorption.[23]

According to the cation-exchange of the soil, Komarneni et al.[24] used cesium to exchange tobermorites. From their experiment, natural tobermorite exhibited little exchange for alkali cations. But for (Al + Na)-substituted synthetic tobermorites, high cation-exchange capacity were obtained from their results.

Griffin et al.[25] have shown that adsorption of Cr(VI) by kaolinite and montmorillonite clay increased with

decreasing pH. And the adsorption of Cr(III) increased as the pH of the suspensions increased. Above pH 5, Cr(III) should be immobile because of precipitation. Below pH 4, Cr(III) species were strongly adsorbed by both kaolinite and montmorillonite and would therefore have a relatively low mobility through soils or clay minerals used as landfill liners. Between pH 4, and 5, the combination of adsorption and precipitation should render Cr(III) quite immobile. They also investaged that in the pH range 1.5 to 4.0, 30 to 300 times more Cr(III) than Cr(VI) was adsorbed by the clay minerals; and at higher pH values the ratio (Cr(III) removed)/(Cr(VI) removed) became even larger because of increased Cr(III) removal and decreased adsorption of The adsorption of Cr(VI) was low relative to Cr(VI). Cr(III), even at very low pH values where Cr(VI) adsorption was highest.

Bartlett et al.[6] investigated that only HCl and $Na_AP_2O_7$ extracted significant quantities of the Cr(III) added from soil. At best, these quantities were not good representations of total soil Cr(III). The NH,OAc and NaF removed very small fractions of the amounts present. Further KH2PO4 the more, was best extractant for characterizing Cr(VI) in soils for the following reasons:[6] (i) orthophosphate has a strong affinity for Cr(VI) adsorption sites; (ii) unlike pyrophosphate, it does not remove organic compounds that interfere with the colorimetric determination of Cr(VI); (iii) unlike HCl, it

does not lower the pH enough to reduce Cr(VI) during the extraction process; and (iV) KH_2PO_4 extracted more Cr(VI) than did NH_4OAc , HCl, $Na_4P_2O_7$, NaF, KCl, or $KCl \cdot KHCO_3$, regardless of pH.[6] They also reported that sodium hydroxide extracted all the Cr(VI) at pH 12. However, it was still not suitable for extracting anions for exchangeable Cr(VI) in most soils. Because at pH 12, humic and fulvic acids are dispersed. They interfere in the colorimetric analysis of Cr(VI) and may reduce desorbed Cr(VI).[16]

James and Bartlett [26] had reported that divalent $CrO_4^{=}$ may be adsorbed in similar fashion to $SO_4^{=}$ and $HPO_4^{=}$, forming binuclear, bridged complexes on goethite, Fe·OCr(OO)O·Fe, or on Al oxides and other soil colloids with positively charged surfaces. They also indicated that liming the soils decreased both the exchangeable Cr(VI) and that removed in nonexchangeable form. This effect is probably due to a decrease in positive charge on soil colloids as pH increased.

2.3 Remedy for Contaminated Sites

Several remedial options could be considered for cleaning the chromium contaminated sites. The first option is excavation and disposal of soil at a R.C.R.A. approved site. This option is expensive. Presently, the minimum

costs for excavation, transport, and disposal in "secured landfill" is about \$240 per ton for the hazardous waste in Billions of dollars will be needed to handle New Jersey. the chromium wastes generated in the past. In addition, the capacity of existing secured landfills is not sufficient to large handle such amounts of waste. Also. the transportation of large quantities of waste from one place to another is a hazard.

The second option is on-site fixation. It would stabilize the contaminated soil through a chemical or physical fixation. The chemically fixated soil would be replaced on-site and then covered with a clean soils cap. So far, no satisfactory analysis has been obtained on the fixation of chromium contaminated soils. It is also uncertain as to whether the site would be usable following the chemical fixation process. Questions such as long term stablity and integrity of the cap have also been considered.

Fitzpatrick et al.[27] they used in situ vitrification to stablize the contaminated soil. In situ vitrification is a thermal treatment process that converts contaminated soil into a chemically inert, stable glass and crystalline product. The process is showed in Figure 2-1. The vitrified waste form showed a low leach rate for heavy metals of about $1 * 10^{-4} \ 1b/ft^2/day$ or lower. And the cost effectiveness was \$100 to \$250/ton for soils.



Figure 2-1 The In Situ Vitrification Process

The last option is soil washing. Soil washing process can be carried out in the contaminated site. In this case, the soil can be put back where it came from and without transportation and other relative problems.

Shirk and Farrell[28] had carried out a serious tests by using twenty potential "lixiviants", or leaching substances, to extract the chromium from contaminated soil. In their report, sodium hypochlorite (5%) was the best reagent which can reach higher efficiency than others. The extraction mechanism is:

 $2FeCr_{2}O_{4} + 7Clo^{-} + 8OH^{-} == 4CrO_{4}^{+} + 2Fe(OH)_{3} + 7Cl^{-} + H_{2}O$

They also reported that, after extraction, the metal can be removed from the lixiviant by using anion exchange resin. Barium chloride were used to precipitate barium chromate. This recovery production can reduce or eliminate the cost of the former process.

Ellis et al[29] performed a series of tests of soil washing. The tests demonstrated that sequential treatment of soil with ethylenediaminetetraacetic acid (EDTA), hydroxylamine hydrochloride, and citrate buffer was effective in removing metals from soil, and all were necessary for good cleanup. The EDTA chelated and solubilized all of the metals to some degree; the hydroxylamine hydrochloride reduced the soil iron oxidemanganese oxide matrix, releasing bound metals, and also

reduced chromium and additional acid-labile metals. The best removals observed were: cadium, 98 percent; lead, 96 percent; copper, 73 percent; chromium, 52 percent; and nickel, 23 percent.

Dugan et al.[30] investigated that hexavalent chromium in the soil sample could be readily leached to the concentration less than 5 mq/l by using water. They used a pilot plant to perform four different methods of soil leaching (downflow, continuous upflow, continuous upflow with air, and batch mixing) in the laboratory soil column. The initial chromium concentration in the soil sample were 15.8 mg/l and 12.4 mg/l. They reported that after the entire washing cycle was completed, the downflow method leached the Cr^{+6} to 1.84 mg/l, while the continuous upflow (without air) method decreased the Cr^{+6} to 1.55 mg/l. And the soil residue Cr^{+6} was only leached to approximately 2.7 mg/l for the continuous flow-with-air method. The hydraulic detention time was determined after the soil was leached to a Cr^{+6} concentration of <3.5 mg/l. Under these condition, the hydraulic detention time was respectively 36, 20, 12, and 16 min for the laboratory bench downflow, continuous upflow, continuous upflow with air, and batch mixing methods.

3.1 Theory of Adsorption

Adsorption is a surface phenomenon that is defined as the increase in concentration of a particular component at the surface or interface between two phases.[31] The process can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquidsolid interfaces.

In this study, clays are the adsorbate, and the chromium solution is the adsorbent. Thus, the adsorption could occur because dissolved ionic species are attracted to mineral surface that have a net electrical charge due to imperfections or substitutions in the crystal lattice or chemical dissociation reactions at the particle surface.

Adsorption of the first type falls within the realm of ion-exchange and is often referred to as exchange adsorption. Exchange adsorption is a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface.

There are two major determining factors for exchange adsorption. One is the charge on the ion, the other is the molecular size (hydrated radius) of the adsorbate. In a system containing a monovalent ion and a trivalent ion under the stated conditions, the influence of kinetic energy to remain in solution phase is the same for each. But the

trivalent ion is attracted much more strongly toward a site of opposite charge on the surface than a monovalent ion of the adsorbent. For ions of equal charge, the smaller ion is able to accomplish closer approach to the adsorption site and thus it will be favored.

Clays contain both cation and anion exchange sites. Cation exchange in clays can be attributed to the negative charge by clay surfaces. Clays also contain anion exchange sites, although little is known about them. For example, in low pH systems where particle edges are charged positively, anion adsorption would be expected. Another example is the tannate anions adsorbed at particle edges by complexing with the exposed octahedral alumina ions. This leads to a reversal in edge charge from positive to negative and prevents edge-to-face flocculation.

The second type of adsorption is termed "physical adsorption". It occur as a result of van der Waals forces. The adsorbed molecule is not affixed to a specific site at the surface but is, rather, free to undergo translational movement within the interface.

The last type of adsorption is "chemical adsorption". The adsorbate undergoes chemical interaction with the adsorbent. This process exhibits high energies of adsorption, because the adsorbate forms strong localized bonds at active centers on the adsorbent. In this case, molecules are considered not to be free to move on the

surface, or within the interface.[32]

3.2 Double Layer Theory

Double layer theory was first develped by Gouy and Chapman and will not be presented here. In this theory, ions were considered as point charges. The colloidal stability of suspensions, osmotic swelling and ion exchange are governed by the structure of the diffuse electrical double layers on the particles in the suspension.[33] Clay surface carry negative charge. The cations would be attracted near the clay surfaces when the clay is placed in solution. And there is a tendency for them to diffuse away in order to equalize concentrations throughout. Anions, however, are excluded from the negative force fields of the Figure 3-1 shows the cations and the anions particles. distribution adjacent to a clay surface. The negative surface and the distributed charge in the adjacent phase are together termed the diffuse double layer.[34]

For the double layer's model, the stern model presented the relationship between the electric potential and the charge distance from surface. Stern's model considers the actual size of the ions, and he developed the model of a molecular condenser in series with a diffuse double layer as sketched in Figure 3-2.

There are many factors that could affect the double layers, such as the the surface charge density or surface



Figure 3-1 Distribution of ions adjacent to a clay surface according to the concept of the diffuse double laye



Total charge = v1 + v

Figure 3-2 Stern's model of the potential distribution in the electrical double layer
potential, electrolyte concentration, cation valence, dielectric constant, and temperature.

3.3 Equiliburium Isotherm

aqueous solutions involves Adsorption from concentration of the solute on the solid surface. As the adsorption process proceeds, the sorbed solute tends to desorb into the solution. Equal amounts of solute eventually are being adsorbed and desorbed simultaneously. Consequently, the rates of adsorption and desorption will attain an equilibrium state, called adsorption equilibrium. The presentation of the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration in bulk solution, at constant temperature, is termed the adsorption isortherm.

The Freundlich equation has been used in this research for studying adsorption isotherm and the general form of the Freundlich equation is shown below:

 $q_e = X/m = K_F C^{1/n} ------ (3-1)$ where X = weight of chromium adsorbed (mg) $= V(C_i - C_e) ------- (3-2)$ V = volume of chromium solution added (ml) $C_i = \text{initial concentration of chromium (mg/1)}$ $C_e = \text{equilibrium concentration of chromium (mg/1)}$ m = weight of soil $k_d, n = \text{empirical constants}$

The Freundlich equation is an empirical expression that

encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the data, the Freundlich equation is written in logarithmic form. Substituting equation (3-2) into equation (3-1), and taking logarithm on both sides.

$$C_0 - C$$

log------ =log K_f + 1/n log C ----- (3-3)
m

 K_{d} and 1/n are determined by applying linear regression to the logarithmic form of the equation, where log x/m and log C_p can be determined from experiment.

3.4 Mass Balance

The adsorptive capacity of clay can be estimated by using the following equation:

Cr mg/g soil =
$$[C_i(mg/1) * V_i - C_e(mg/1) * V_e] / W_s --(3-4)$$

where C_i = the initial concentration
 C_e = the equilibrium concentration
 V_i = the initial volume in ml
 V_e = the equilibrium volume in ml
 W_s = the weight of added soil in gram

Equation 3-4 shows that the adsorption capacity of soils depends on the difference of the initial and the equilibrium concentration. It also varies with the volume of the solution.

3.5 Chromate Speciation

The chromate salts exist in different species in different situation. The following section will discuss the chromium species in concentration(%)-pH diagram.

An analysis was performed to arrived at a distribution diagram for various Cr(VI) species as function of pH. The details are presented in Appeddix. Results of these analysis are shown in Figure 3-3. The total chromium concentration varies from concentration 0.05 mg/l to 52 mg/l

Figure 3-3 indicates that Cr_{4}^{-2} predominates in basic condition; and $\text{Cr}_{2}\text{O}_{7}^{=}$ and HCr_{4}^{-} predominate in acidic condition. It also indicates that the $\text{Cr}_{2}\text{O}_{7}^{-2}$ ions become the major ions as the concentration increased.

Chromium speciation in water is also affected by pE (redox) and pH conditions. Figure 3-4 shows the relationship between the pE and pH at equilibrium in the system $Cr + H_2O + O_2$ at $25^{O}C$ and 1 atm. Chromium(VI) predominates under oxidizing (high redox) conditions, whereas Cr(III) predominates under more reducing (low redox) conditions.[35]

Another Eh and pH diagram was calculated by Garrels and Christ.[36] Within the ranges of Eh and pH normally found in soils, Chromium has the capability of existing in four states-two trivalent forms, the Cr+3 cation and the $\text{CrO}_2^$ anion, and two hexavalent anion forms, $\text{Cr}_2\text{O}_7^{-2}$ and CrO_4^{-2} .



Figure 3-3 Chromium species present in water as a function of pH



Figure 3-5 shows the chromium speciation in different Eh and pH.

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CHAPTER 4 METHODS AND MATERIALS

Two types of soils, sands and clays, were used for this study. Bentonite and kaolinite clays were utilized for this study. Potassium dichromate and potassium chromate were used as Cr(VI) in this research, since these are the species that are normally found in soils as already mentioned in chapter 2. Chromium nitrate was used as Cr(III) for this study.

4.1 Soil Properties

Sand used was New Brounswick Sand. Kaolinite (Standard Air Floated Kaolinite) was obtained from the Georgia Kaolinite Company Inc. Table 4-1 and 4-2 show the physical and chemical properties of bentonite and kaolinite. From Table 4-1, it indicates that bentonite is a very highly plastic, colloidal, and expansive clay. The cation exchange capacity (CEC) shows that kaolinite carries less negative charge than bentonite.

Figure 4-1 shows the schematic diagram of kaolinite and bentonite. Kaolinite consists of a layer of gibbsite on top of a layer of silicate, this mineral is called a "two-layer" mineral. Bentonite is the three-layer sheet mineral. Figure 4-1 shows the bentonite made of a gibbsite sandwiched between two silica sheets.

TRATA A T THISTORY CHA CHARTORY ITORCTOTOD OF DOTT	Table	4-1	Physical	and	Chemical	Properties	of	Soils
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Physical property	kaolinite	bentonite
Optimum moisture Content	21.5%	33.8%
Maximum dry density (g/cm ³)	1.64	1.37
Specific gravity	2.55	2.78
Organic Carbon Content	12.48	7.23
Liquid limit	48%	275%
Plastic limit	32%	107%
Shrinkage limit	na	15%
pH in water	5.0	9.3
pH in Cacl ₂	4.9	9.2
Moisture content of Air Dried samples	0.30 %	7.5 %
Cation - exchange Capacity (in meg per 100 g)	3 - 15	80 - 150

Chemical property	kaolinite	bentonite
Fe203	0.6%	.83%
Al ₂ 0 ₃	38.1%	19.76%
sio ₂	45.1%	51.1%
Na ₂ 0	0.3%	0.04%
TiO2	1.4%	-
к ₂ 0	0.1%	0.11%
MgO	0.2%	3.22%
CaO	very little	1.62%

Table 4-2 Chemical Composition of Soils

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4.2 Adsorption Test Procedure

In order to determine the adsorption capacity of chromium on soil, the batch technique was used to evaluate the equilibrium conditions. This study was conducted in a series of 50 ml screw cap test tubes. Accurately measured quantities of soils were placed in each test tube and 45 ml of different concentrations of chromate salts were added.

Sulfuric acid or sodium hydroxide was added to adjust the pH. The test tubes were sealed by Teflon-lined caps and placed on an electrically operated shaker and shaken at 250 rpm for at least 24 hours at room temperature.

The test tubes were then centrifuged at 1,000 rpm for about 50 minutes to allow the soil to settle. The solutions were filtrated by 0.45 um filter and diluted in order to fit for sensitive range of atomic the absorption Concentrations spectrophotometer. of supernatant were measured using Parkin Elmer Model 305B atomic absorption spectrophotomer. Tubes containing 0 g of soil, serving as blank, were used to check the initial concentration of chromium added and the amount of precipitated in the solution during the adjustment of pH.

4.3 Chromium Desorption

4.3.1 Sample Preparation

In order to carry out the desorption test, soil samples were prepared first. The detection limit of Atomic Absorption Spectrometer is lower than 5 mg/l. In order to work within this limit, it was decided to use in 20 mg/l of Cr^{+3} and 4 mg/l of Cr^{+6} solution. The amount of soil used in each tube was 3 gram. After twenty-four hours shaking, 37 ml of supernatant were removed from the test tube. The residual chromium in the tube was treated as the initial contaminated condition for desorption tests.

4.3.2 Desorption Test Procedure

Pure water, oxidizing agent and acid solution were used to extract the chromium. MnO_2 was used as oxidizing agent. Sulfuric acid was used to prepare the acid solution. Thirty-seven ml of solvent were added into the test tube at the first desorption cycle. After first desorption cycle, thirty-seven ml sovlent were replaced in the following each desorption cycle. The concentrations of supernatant were measured by the adsorption test whose procedure is stated in section 4.2

CHAPTER 5 RESULTS AND DISCUSSION

In this chapter, the effects of the soil weight, pH, chromium concentration, and chromium compound on adsorptive capacity of different soils are discussed in the first part. The second part presents the effects of desorption of chromium by using different solution.

5.1 Tests on Sand

The adsorption capacity of sand was observed in these tests. Different concentration of Cr(VI) and Cr(III) were added into the tube which contained 10 gm sand. Table 5-1 shows the relationship between the inital concentration and the equilibrium concentration of chromium. The adsorption capacity of sand was also obtained by using Equation 3-4. The volume of Ve was 41 ml.

Chromium Compound	Initial Conc. (mg/l)	Equili. Conc. (mg/l)	Adsorp. Capacity (ug/g)
Cr ⁺³	31.5	31.0	14.65
Cr ⁺³	15.0	15.2	5.18
Cr ⁺³	5.0	5.0	2.50
Cr ⁺⁶	19.0	19.5	5.55
Cr ⁺⁶	10.5	10.2	5.43
Cr ⁺⁶	5.0	4.9	2.41
Cr ⁺⁶	1.0	1.0	0.50

Table 5-1 Adsorption Capacity of Sand

It is seen from table 5-1 that the adsorption capacity of sand can be obtained by using Equation 3-4. This table shows that the adsorption capacity of sand increases as the concentration of chromium increased. However, by inspection of the difference between the initial and the equilibrium concentration, it is obvious that sand adsorbed no chromium. All the adsorption capacity showed in Table 5-1 represented the residual amount of chromium which could not be removed from the tube. Because of this, the difference between the initial and the equilibrium volume (Vi-Ve) can be neglected during the calculation of adsorption capacity. Thus, equation 3-4 can be rewritten as follow:

Cr mg/g soil = [Ci(mg/l) - C.e(mg/l)]* V/ Ws ----(5-1)
where V= the addition volume of chromate solution

Equation 5-1 indicates that the adsorption capacity of soil is equal to the difference of the initial and equilibrium concentration times the total volume of solution. It also implies that the residual chromium can be removed by water.

Based on thees results, all the following experiments used the Equation 5-1 to calculate the adsorption capacity of soils.

5.2 Time effect:

In this report, all the data were obtained under the equilibrium condition. Thus, the time to reach equilibrium was studied first.

5.2.1 Hexavalent Chromium

This study was performed using potassium chromate as absorbate and 3 grams of bentonite and kaolinite as absorbent. The concentration of the solution was measured every thirty minutes. Figures 5-1 and 5-2 show that the concentration of the chromium decreases as adsorption time increases. After about 180 minutes, the concentration of solutions approached a constant. These results indicate that after 180 minutes, the reaction between soils and solutions reached equilibrium conditions.

5.2.2 Trivalent Chromium

Tests similiar to those conducted for hexavalent chromium were performed by replacing Cr(VI) with Cr(III). $Cr(NO_3)_3$ was used as Cr(III). Figure 5-3 shows the results. The chromium concentration reduced quickly for the first 30 minutes. After one hour, the chromium concentration reached a constant value. Unlike hexavalent chromium, trivalent chromium reached to equilibrium condition ealier.













5.3 Soil Weight Effect

In order to obtain the maximum adsorption capacity of unit soil weight in this study, different soil weights (bentonite and kaolinite) were added into each tube. Same amounts of chromium concentrations were also added into each tube.

Figure 5-4 shows the adsorption capacity of kaolinite vs. different soil weight. It is shown that the adsorption capacity of unit soil weight was a constant for chromium nitrate. Thus, the adsorption capacity is proportional to soil weight.

Experiments for higher concentrations, 216.5 ppm, 2100 ppm, and 80,000 ppm of potassium chromate solution were performed different soil weights. Data are shown in Table 5-2. At the concentration of 216.5 ppm, the adsorption capacity is not proportional to soil weight. The adsorption capacity of unit soil weight decreased as the soil weight increased. Less amount of Cr(VI) were adsorbed. This phenomenon indicates that the adsorption capacity has reached a maximum condition at a certain unit soil weight.

Some negative values of adsorption capacity were observed for the concentration of 2,100 ppm and 80,000 ppm. An attempt will be made to furnish this probable explanation for this behavior in the following section. Bentonite tends



Figure 5-4 The effect of soil weight on the adsorption on kaolinite

to swell, thereby pulling the water from the supernatant into it. This has the effect of increasing the concentration of the supertant. The high chromium concentration in the supernatant can be attributed to this phenomena

Table 5-2 The Effect of Soil Weight on the Adsorption on Kaolinite

initial conc. (ppm)	conc.after adsorption (ppm)	Soil Wt. (g)	Reduction in conc. (ppm)	Reduction % remov.	adsorption per gram(ppm)		
216.5	210.0	1	6.5	3.0	6.5		
216.5	215.5	2	1.0	0.5	0.5		
216.5	210.0	3	6.5	3.0	2.2		
216.5	209.0	4	7.5	3.5	1.9		
216.5	200.0	б	16.5	7.6	2.7		
	1156 Alle Anno 1176 Anno 406 Alle Anno 1166 Anno 1166 Anno 1166						
2100.0	2165.0	1	-65.0	0.0	-65.0		
2100.0	2120.0	2	-20.0	0.0	-10.0		
2100.0	2165.0	3	-65.0	0.0	-21.7		
2100.0	2050.0	4	50.0	2.4	12.5		
2100.0	2040.0	6	60.0	2.9	10.0		
80000.0	79500.0		500 0	0.6	500 0		
80000 0	80000 0	2	0.0	0.0	0.0		
80000.0	80000.0	C	0.0	0.0	0.0		
80000.0	78500.0	4	1500.0	1.9	375.0		
80000.0	78550.0	5	1450.0	1.8	290.0		
80000.0	77575.0	6	2425.0	3.0	808.3		
* soil t	* soil type : kaolinite chromium compound : K ₂ CrO ₄						

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initial conc. (ppm)	conc.after adsorption (ppm)	Soil Wt. (g)	Reduction in conc. (ppm)	Reduction % remov.	adsorption per gram(ppm)
216.5	185.0	1	31.5	14.5	31.5
216.5	195.0	2	21.5	9.9	10.8
216.5	205.0	3	11.5	5.3	9.8
216.5	207.5	4	9.0	4.2	2.3
216.5	207.5	6	9.0	4.2	1.5
2100.0	2100.0	1	0.0	0.0	0.0
2100.0	2150.0	2	-50.0	0.0	-25.0
2100.0	2125.0	3	-25.0	0.0	- 8.3
2100.0	2125.0	4	-25.0	0.0	- 6.3
2100.0	2100.0	6	0.0	0.0	0.0
76750	69250	2	7500	9.8	3750
76750	73500	4	3250	4.2	813
76750	76250	6	500	0.7	83
76750	79100	8	-2350	0.0	- 294

Table 5-3 The Effect of Soil Weight on the Adsorption on Bentonite

Bentonite was used to perform the same test. Table 5-3 shows the data. The total adsorption capacity of soil decreased as the soil weight increased for the concentration of 216.5. No consistent tend can be observed in the higher concentration. So far, no reasonable explanation can be

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offered to explain this except that the expansion of soil was observed. Under this kind of condition, it was hard to separate the supernatant from soil.

5.4 pH Effect

In these experiments, the pH value of chromium solution was adjusted by the addition of sulfuric acid and sodium hydroxide. Then, different pH value of solutions were added into different tubes which contained the same amount of soil.

5.4.1 Hexavalent Chromium

For these investigations shown in figure 5-5, pH value of $K_2Cr_2O_7$ solution varied from 1 to 12. The initial pH was around 4. The adsorption capacity of kaolinite decreased as the pH increased from 1 to 4. After pH rose above 5, the adsorption capacity increased to abound 4 times that for pH below 5. But around pH 11, the adsorption capacity dropped. Two possible reasons can be offered for the tendency of Cr^{+6} adsorption to increase with decreasing pH. The first probable explanation can be attributed to anion exchange in soils. Under acidic conditions, the hydrogen ion concentration increases around soil edges. This result in the formation of a positively charged region around the



Figure 5-5 The effect of pH on the adsorption of potassium dichromate on kaolinite

edges of clay particles. Anions such as Cr^{+6} are adsorbed in this positively charged region.

Another factor contributing to adsorption of Cr^{+6} is the effect of SO_4^{-} in soil. These ions compete with $Cr_2O_7^{-}$ ions, replacing each other. This could result in decreased adsorption with increased presence of SO_4^{-} .

Second, in consideration of the ion species in the basic condition, $CrO_4^{=}$, Na^+ , K^+ , and OH^- were the major ions in the solution. Theoretically, only positive charge could be adsorbed by kaolinite. But in practical, the soil adsorbed $CrO_4^{=}$ and the adsorption capacity was higher than that in acidic condition. This result might be caused by the isophormous replacement. In basic condition, less hydrogen ions could be attached on the soil's surface. Thus, isophormous replacement might be carried out more easier than in acidic condition.

Another prediction is that when in basic condition, sodium ions attached to the soil surface was very stable. They also can form the positive charge layer. Comparison of the difference between basic and the acidic condition, somdium ions seemed play a important role during the adsorption process.

Another group of tests were carried out using potassium chromate to replace potassium dichromate. The initial pH value of potassium chromate solution was around 8. Sodium

hydroxide was added to adjust the pH over 8. The adsorption capacity increased as the pH decreased until pH reached around 2. Same reasons described earlier can be used to explain the result. The difference is that under strong acidic condition $SO_4^{=}$ might play a important role. Figure 5-6 showed this result.

Comparing the results of these two groups of tests, it can be inferred that the ions species existed in the solution controlled the adsorption capacity of soil, and kaolinite adsorbed very small amount of chromate salts.

5.4.2 Trivalent Chromium

In this section, chromium nitrate was used as chromium (III). As mentioned before, trivalent chromium would precipitate when sodium carbonate is added. The formation of precipitate limits the adsorption studies of pH values. Chromium(III) would precipitate with a pH value around 4.5 to 5.5. This pH value depends on the concentration of the trivalent chromium. The higher the concentration of chromium(III), the lower the pH value would cause the precipition.

From Figure 5-7, the adsorption capacity of kaolinite increased as the pH increased. In the low pH, more negative charge on the soil's surface were occupied by the hydrogen ions. This caused the adsorption capacity became lower in



Figure 5-6 The effect of pH on the adsorption of potassium chromate on kaolinite



Figure 5-7 The effect of pH on the adsorption of chromium nitrate on kaolinite



Figure 5-8 The effect of pH on the adsorption of chromium nitrate on bentonite

the strong acidic condition. Similiar tests were performed with bentonite. When the pH reduced to around 2, the adsorbed Cr^{3+} began to release to the solution. Fig 5-8 shows the result.

5.5 The Effect of Concentration

In order to study the effect of concentration and the maximum sorptional capacity, a series experiments were carried out.

Figure 5-9 shows the effect of concentration on adsorption capacity of bentonite. The horizontal axis equilibrium concentration of chromium. represents the Different chromium compounds were used in these tests. The initial concentration of trivalent chromium was varied from 44.4 mg/l to 1040 mg/l. As the chromium concentration increased, the adsorption capacity increased sharply till the adsorption capacity reached to around 9,000 ug/g. After a certain amount of concentration increased, the adsorption capacity increased again. For hexavalent chromium, the initial concentration was varied from 4 mg/l to 100 mg/l. The adsorption capacity of bentonite increased smoothly as also the chromium concentration increased. Comparison of these three different chromium compounds, indicates that trivalent chromium was adsorbed more than hexavalent



Figure 5-9 The effect of concentration on adsorption in bentonite

chromium. Only small quantities of hexavalent chromium were adsorbed.

Figure 5-10 shows the removal percentage of chromium. With a initial concentration of trivalent chromium less than 200 mg/l, the removal percentage reached to 100%. This means all the chromium was adsorbed by the soil. But for hexavalent chromium, even when the initial concentration reduced from 250 mg/l to 4.1 mg/l, the removal percentage was still below 25%. These phenomena might indicate that positive charge sites existing on bentonite surface affected chromium adsorption.

Same phenomena were observed when bentonite was replaced by kaolinite. Figure 5-11 and Figure 5-12 show the results. Comparison of these figures indicates that kaolinite has a tendency to adsorb more potassium dichromate than potassium chromate. This could be because potassium dichromate is acidic in solution.

Inspection of Figure 5-9 and Figure 5-11 reveals that bentonite adsorbed more chromium than kaolinite. This because bentonite carries more negative charge than kaolinite. This is related to properties of clays which have been discussed in chapter 4.



Figure 5-10 The removal percentage of chromium on adsorption on bentonite at equilibrium concentration

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Figure 5-11 The effect of concentration on adsorption in kaolinite



Figure 5-12 The removal percentage of chromium on adsorption in kaolinite at equilibrium concentration

5.6 The Sorption Isotherm

The coefficients of adsorption isotherm equation can be derived from equation 3-3. Freundlich adsorption isotherms for Cr(III) and Cr(VI) are shown in Figures 5-13 and 5-14. Table 5-3 lists k_d and n for different chromium compounds on kaolinite and bentolinite.

Table 5-4 Kinetic Constant for Clay Adsorption

Chromium	Kaolinite		Bentoni	te	
Compound	^K d	n	K _d	n	
$Cr(NO_3)_3$	285.1	4.468	3396.25	4.115	
K ₂ Cr ₂ O ₇	1.812	0.989	1.953	0.818	
K ₂ CrO ₄	1.282	1.369	8.33	1.535	

From above data, The Freundlich equations of the clays for different chromium compounds can be expressed as follow:

 $q_e = X/m = 285.1 * c^{1/4.468} ----(5-2)$ $q_e = X/m = 1.812 * c^{1/0.989} ----(5-3)$ $q_e = X/m = 1.282 * c^{1/1.369} ----(5-4)$

Equations 5-2, 5-3, and 5-4 represent the Freundlich equations of kaolinite for different chromium compounds.

$$q_{e} = X/m = 3396.25 * c^{1/4.115} ---(5-5)$$

$$q_{e} = X/m = 1.953 * c^{1/0.818} ----(5-6)$$

$$q_{e} = X/m = 8.33 * c^{1/1.535} ----(5-7)$$

Equations 5-5, 5-6, and 5-7 represent the Freudlish equations of bentonite for different chromium compounds.


Figure 5-13 Adsorption isotherms for kaolinite



Figure 5-14 Adsorption isotherms for bentonite

5.7 Desorption

Based on the previous studies, several methods for chromium desorption tested are discussed in the following section. Before the desorption test, the contaminated soil samples was prepared first. This process have been described in chapter 4.

5.7.1 Pure Water

The first solution for desorption was performed by using distilled water. As mentioned in chapter 4, there are three types of adsorption reactions. Distilled water can remove the chromium attached to the soil surface by the van der Waals force. Table 5-5 shows the efficiency of distilled water for different chromium compounds on kaolinite.

From Table 5-5, it appears that distilled water can remove over 80% hexavalent chromium from kaolinite. But only 1.4% trivalent chromium was removed by distilled water. It indicated that most trivalent chromium was adsorbed and this is probably by the ion-exchange and chemical adsorption. Since a large percentage (82%) was desorped by pure water, it can be stated that for hexavalent chromium,

van der Waals force plays the major role in the adsorption reaction.

chromium compound	chromium amount in the soil (ug/g)		efficiency	washing
	initial	final	(3)	сусте
Cr(NO ₃) ₃	271.46	267.87	1.32	3
Cr(NO ₃) ₃	267.02	262.91	1.51	3
$Cr(NO_3)_3$	270.60	266.87	1.38	3
Average :	269.69	265.88	1.40	
 К ₂ Сг0 ₄	14.10	1.76	87.52	2
K ₂ CrO ₄	15.33	3.00	80.43	2
K ₂ CrO ₄	15.33	3.00	80.43	2
Average :	14.92	2.59	82.79	

Table 5-5 The Efficiency of Desorption with Distilled Water

5.7.2 Acid Extraction

From previous studies, it seems that kaolinite and bentonite can adsorb trivalent chromium because of the soil's surface charge. And they adsorbed less trivalent chromium at low pH. The second reagent tested in this study was to use acid to extract Cr^{+3} from kaolinite. The

contaminated soil was prepared by following the procedure which had been described in chapter 4.3. Sulfuric acid was used.

Figure 5-15 shows the relationship between chromium concentration in the kaolinite and the desorption cycle. The pH value of this system was controlled under 1.7 at the first twelve desorption cycle. After the 12th desorption cycle, pH value was reduced to around 1.5. Each desorption cycle period was 24 hours. Thus, Figure 5-15 also indicates the time effect for this study.

According to Figure 5-15, chromium was removed rapidly at the first five desorption cycle. After this, a little amount of chromium was removed until more sulfuric acid was added. These phenomena indicated that the chromium removed depends on the pH and the washing cycle. Besides this, the volume of the solution is probably another factor affecting the removal efficiency.

5.7.3 Oxidation Method

According to the preliminary laboratory study, kaolinite and bentonite adsorbed little hexavalent chromium than trivalent chromium. Thus, most trivalent chromium would leach into solution after being oxidized. Based on this knowledge, this method was performed by using oxidation reagent to oxidize trivalent chromium to hexavalent



Figure 5-15 Desorption of chromium (III) from kaolinite in acidic solution

chromium. MnO₂ was used as oxidation reagent in this experiment.

Figure 5-16 shows that the chromium concentration reduced as desorption cycle increased. This result is similar to that shown in Fig 5-15. The difference between these two tests is: In the tests shown in Fig 5-15, sulfuric acid was added in each cycle to keep the pH in constant. But for the tests shown in Fig 5-16, MnO₂ were added in the first cycle and the 7th cycle. The reaction time between 13th and 14th cycle was ten days, and the amount reduced was significantly increased. It can be indicated that time effect is the major factor for oxidation reaction.

5.7.4 EDTA Extraction

In this study, 0.1 M EDTA $(C_{10}H_{14}N_2Na_2O_8\cdot 2H_2O)$ solution was used to extract the chromium from kaolinite. Figure 5-17 shows the relationship between chromium concentration in the soil and the desorption times. The samples were prepared in the manner described in chapter 4. After shaking 24 hours, the samples were stored for 60 days.

The samples contained around 90 ug chromium in 3 gm of kaolinite. After 3 cycles of desorption, chromium concentration in the samples reduced to around 10 ug and reached to a constant. The desorption efficiency reach to 88%.



Figure 5-16 Desorption of chromium (III) from kaolinite with oxidant



Figure 5-17 Desorption of chromium (VI) from kaolinite with EDTA

Comparison this result with the initial concentration in the samples revealed, chromium concentration was higher than the samples which were used to study in the section 5.7.1. The difference between these samples was the storage time. The samples were stored for 60 days in this study. More than twice the amount of hexavalent chromium was absorbed by kaolinite. This result indicates that kaolinite adsorbed more hexavalent chromium after a long reaction time.

5.8 Conclusion

Based on the results obtained the following conclusions may be drawn.

- 1. Trivalent chromium began to precipitate at pH over 4.5 whereas hexavalent chromium did precipitate at any pH.
- 2. pH would affect the adsorption capacity. For trivalent chromium, high hydrogen ion concentration would reduce the adsorption capacity. However for hexavalent chromium, high hydrogen ion concentration would increase the adsorption capacity.
- 3. Any kind of ions (cation or anion) would affect the adsorption capacity of soil. Cations would increase the amount hexavalent chromium adsorbed and reduce the trivalent chromium adsorbed. Anions would increase the

trivalent chromium adsorbed and reduce the hexavalent chromium adsorbed.

- 4. Bentonite adsorbs more chromium than kaolinite.
- 5. Trivalent chromium is much easier to be adsorbed than hexavalent chromium on clayey soil.
- 6. 83% hexavalent chromium can be removed from kaolinite by water, whereas only 1.4% trivalent chromium was removed by distilled water.
- 7. Concentration of hydrogen ion and the volume of acidic solution are the major factors affecting acid extraction.
- 8. Not all the trivalent chromium adsorbed by clay can be oxidized by MnO₂. The amount of hexavalent oxidized chromium is a function of time.

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APPENDIX

The distribution diagram for the various Cr(VI) species as function of pH at $Cr_T = 5$ ppm

Equilibra :

$$CrO_4^{-2} + H^+ == HCrO_4^- logK_1 = 6.5 K_1 = 3162277.66$$

 $HCrO_4^- + H^+ == H_2CrO_4 logK_2 = -0.8 K_2 = 0.1585$
 $2HCrO_4^- == Cr_2O_7^{-2} + H_2O logK_3 = 1.52 K_3 = 33.1131$
 $Cr_2O_7^{-2} + H^+ == HCr_2O_7^- logK_4 = 0.07 K_4 = 1.175$

$$Cr_{T} = [CrO_{4}^{-}] + [HCrO_{4}^{-}] + 2[Cr_{2}O_{7}^{-}] + 2[HCr_{2}O_{7}^{-}]$$

$$Cr_{T} = [HCrO_{4}^{-}]/[H^{+}]K_{1} + [HCrO_{4}^{-}] + 2K_{3}[HCrO_{4}^{-}]^{2}$$

$$+ K_{4}[Cr_{2}O_{7}^{-2}][H^{+}]$$

$$= [HCrO_{4}^{-}] (1/[H^{+}]K_{1} + 1 + 2K_{3}[HCrO_{4}^{-}]]$$

$$+ 2K_{2}K_{4}[HCrO_{4}^{-}][H^{+}] \}$$

let
$$L_0 = [Cr0_4^{-2}]/Cr_T$$
 $L_1 = [HCr0_4^{-1}]/Cr_T$
 $L_{22} = 2[Cr_20_7^{-2}]/Cr_T$ $L_{23} = 2[HCr_20_7^{-1}]/Cr_T$

 $=> L_{1} = (1/[H^{+}]K_{1} + 1 + 2K_{3}[HCrO_{4}] + 2K_{3}K_{4}[HCrO_{4}][H^{+}])^{-1}$ $=> L_{1}/[H^{+}]K_{1} + L_{1} + 2L_{1}K_{3}[HCrO_{4}] + 2L_{1}K_{3}K_{4}[HCrO_{4}][H^{+}] = 1$

$$L_{1}/[H^{+}]K_{1} = L_{0}$$
 $2L_{1}K_{3}[HCrO_{4}] = 2L_{1}^{2}K_{3}Cr_{T} = L_{22}$
 $2L_{1}K_{3}K_{4}[HCrO_{4}][H^{+}] = 2L_{1}^{2}K_{3}K_{4}Cr_{T}[H^{+}] = L_{23}$

For $Cr_T = 5 \text{ ppm} = 0.0962 \text{ M}$

$$L_1/[H^+]K_1 + L_1 + 2L_1^2K_3K_4Cr_T[H^+] + 2L_1^2K_3Cr_T = 1...(1)$$

*>
$$pH = 7 \implies [H^+] = 10^{-7}$$

Substitute $[H^+]$, K_1 , K_3 , K_4 , Cr_T into Eq.(1)
 $L_1 = 0.186827$
 $[HCr_4^-] = 0.186827 * 0.0962 = 0.01797 M$
 $[Cro_4^{-2}] = 0.05683 M$
 $[Cr_2o_7^{-2}] = 0.01070 M$
 $[HCr_2o_7^-] = 1.257 * 10^{-9}$*

PH	[HCr0 ₄ ⁻]	[Cr04 ⁻²]	[Cr ₂ 07 ⁻²]*2	[HCr ₂ 0 ₇ ⁻]*2
1	0.02992	0.0	0.05930	0.00697
2	0.03116	0.0	0.06429	0.00076
3	0.03129	0.00001	0.06483	0.00001
4	0.03128	0.00010	0.06481	0.00001
5	0.03111	0.00057	0.06406	0.0
6	0.02945	0.00931	0.05744	0.0
7	0.01797	0.05684	0.02139	0.0
8	0.00293	0.09270	0.00057	0.0
9	0.00030	0.09589	0.0	0.0
10	0.00003	0.09615	0.0	0.0

• .

рĦ	[HCrO ₄ -]%	[cro ₄ ⁻²]%	[Cr ₂ 07 ⁻²]8	[HCr207 ⁻]%
1	31.18	0.0	61.64	7.24
2	32 39	0.0	66.83	0.78
3	32.52	0.0	67.39	0.0
4	32.52	0.1	67.37	0.0
5	32.34	0.6	66.59	0.0
6	30.61	9.68	59.71	0.0
7	18.68	59.08	22.24	0.0
8	3.05	96.36	0.59	0.0
9	0.31	99.68	0.0	0.0
10	0.0	100.0	0.0	0.0