

## Sorption behavior of nine chromium (III) organic complexes in soil

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**ABSTRACT:** Sorption data were obtained with a Matawan soil and the following chromium (III) organic complexes: chromium (III) ascorbate, chromium (III) glutamate, chromium (III) histidine, chromium (III) mandelate, chromium (III) citrate, chromium (III) cysteine, chromium (III) serine, chromium (III) pyruvate and chromium (III) oxalate. The influence of pH (2-12), ionic strength (0.005-1 M) and concentration of sorbate (1-10 mg/L) on the extent of sorption was evaluated. The pH value did not influence the percent sorption at environmentally relevant pH 7. Ionic strength between 0.005 and 0.01 M KNO<sub>3</sub> did not influence the sorption. Sorption and desorption data obtained at pH 7, 0.01 M KNO<sub>3</sub> and 1-10 mg/L for each chromium (III) organic complex were analyzed using Freundlich and Langmuir models. The Freundlich model provided good fits for all of the chromium (III) organic complexes. Sorption data for chromium (III) glutamate, chromium (III) pyruvate, chromium (III) oxalate, chromium (III) cysteine, chromium (III) ascorbate and chromium (III) citrate were described well by the Langmuir model. Estimates for the saturated sorption capacities were 141, 70.9, 36.5, 35.5, 28.6 and 4.4 µg/g, respectively. It was not possible to desorb significant amounts of the previously sorbed chromium (III) organic complexes. At the same pH, ionic strength and solid:liquid ratio, the order of the observed sorption to the Matawan soil from highest to lowest was chromium (III) mandelate, chromium (III) glutamate, chromium (III) histidine, chromium (III) cysteine, chromium (III) serine, chromium (III) pyruvate, chromium (III) oxalate, chromium (III) ascorbate and chromium (III) citrate.

**Keywords:** *Chromium (III) ascorbate; Chromium (III) histidine; Chromium (III) citrate; Chromium (III) cysteine; Chromium (III) serine; Desorption; Freundlich isotherm*

### INTRODUCTION

Chromium (Cr) exists in the natural environment primarily as the mineral chromite, FeOCr<sub>2</sub>O<sub>3</sub> (Vitale *et al.*, 1997). Mining activities and natural weathering cause Cr to be distributed as: 1) solid Cr (III) species: Cr(OH)<sub>3</sub>(s), (Fe, Cr) (OH)<sub>3</sub>(s) and Cr<sub>2</sub>O<sub>3</sub>, 2) dissolved Cr (III) species: CrOH<sup>2+</sup>, Cr(OH)<sub>2</sub><sup>+</sup> and Cr(OH)<sub>3</sub>, 3) dissolved Cr (VI) species: HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (Sass and Rai, 1987; Richard and Bourg, 1991; Shah *et al.*, 2009) and IV) elemental Cr (0). Past research has focused on behavior and removal mechanisms of Cr (VI) because of its relative high toxicity to aquatic organisms, (Ogundiran and Afolabi, 2008) which stems from its higher aqueous solubility and greater ability in comparison to Cr (III) to penetrate across the cell membrane (Oshida *et al.*, 1981; Holdway, 1988; Nieboer and Jusys, 1988; Wang *et al.*, 1997; Sivakumar

and Subbhuraam, 2005). Although Costa (2003) also suggests that Cr (III) not entering the cell might cause signaling pathways. This is a phenomenon which has been associated Cadmium and the induction of metallothionein (Huang *et al.*, 2001; Adams *et al.*, 2002). Growing evidence indicates that soluble Cr (III) organic complexes can form with natural organic matter in the environment (Nakayama *et al.*, 1981; Ahern *et al.*, 1985; Kaczynski and Kieber, 1994; Icopini and Long, 2002; Shrestha *et al.*, 2007) and become bioavailable (Davis *et al.*, 1994; Kaczynski and Kieber, 1994; Fukushima *et al.*, 1995; Mattuck and Nikolaidis, 1996; Walsh and O'Halloran, 1996; 1997; Howe *et al.*, 2003). For example, it was estimated that 60 % of the total dissolved chromium in the Sea of Japan exists as Cr organic complexes (Nakayama *et al.*, 1981) and the fraction of the total dissolved chromium in Australian coastal waters as Cr organic complexes ranged from 0

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to 90 % (Ahern *et al.*, 1985). Cr organic complexes, like other metal-organic complexes, are mobile in soil and recalcitrant to short term biodegradation processes. Cr (III) citrate showed little sorption to soil; Cr (III) malate had limited partitioning with soil; and Cr (III) histidine exhibited significant interaction with soil (Puzon *et al.*, 2008). The mobility appeared to vary depending on the organic ligand. Further, *Ralstonia eutropha* JMP 134 and *Pseudomonas aeruginosa* pAO1 readily degraded malate, citrate and histidine, but not the corresponding Cr (III) organic complexes (Puzon *et al.*, 2008). Icopipi and Long (2002) indicate that the elevated aqueous chromium concentrations in surface and pore water were induced from complexation with organic ligands. Considering the redox behavior of chromium and interaction with organic ligands in nature, the geochemical cycle of chromium is shown in Fig. 1. There is strong evidence that Cr (III) organic complexes exist in nature. Such Cr (III) organic complexes might be decomposed and became inorganic Cr (III), might be reoxidized to Cr (VI) and became toxic and might be sorbed by solid particles and became sequestered. Cr (III) organic complexes likely play an important role in the distribution and behavior of chromium in the natural environment, which in turn could influence Cr speciation and toxicity to organisms.

Cr (III) forms strong complexes with amine and carboxylate Lewis Base groups (Pearson, 1963), which are common constituents of natural organic matter in the environment. Complexation with these multidentate aminocarboxylate ligands has been shown to cause dissolution of amorphous Cr (OH)<sub>3</sub>(s), thereby increasing the mobility and bioavailability of Cr (III) in aquatic environments (Carbonaro and Stone, 2005; Shrestha *et al.*, 2007). The fate of these mobile and bioavailable Cr (III) organic complexes in the environment is not well understood. Questions remain as to whether chromium mobility is increased when present as soluble Cr (III) organic complexes or decreased by being combined as macromolecular complexes. This work focused on determining the extent of sorption of Cr (III) organic complexes to solid particles.

Sorption of Cr (III) organic complexes onto Current literature suggests that natural organic ligands influence the transport of heavy metals in soils and infiltration into groundwater systems (von Gunten and Kull, 1986; Stumm and Morgan, 1996; Buerge-

Weirich *et al.*, 2003) due to their complexation and sorption properties. For the soluble Cr (III) organic complexes, can they be sorbed by soil or sediment particles? How easily can they be desorbed? In this work, the influence of varying pH and ionic strength on sorption of model Cr (III) organic complexes to a Matawan soil is examined. The organic ligands used to form Cr (III) organic complexes include glutamic acid (glu), histidine (his), cysteine (cys), serine (ser), mandelic acid (mand), ascorbic acid (asc), citrate (cit), pyruvic acid (pyr) and oxalate (oxa). These ligands were chosen because they are common in the natural environment and can form complexes with Cr (III).

This research was carried in the lab of the Department of Geography and Environmental Engineering, G.W.C Whiting School of Engineering, the Johns Hopkins University, Baltimore, Maryland, USA from May, 2005 to September, 2006.

## MATERIALS AND METHODS

### Chemical reagents

All chemicals were reagent grade or better and were used without further purification. Ascorbic acid, glutamic acid, cysteine and serine were purchased from Sigma (St. Louis, MO). Sodium hydroxide (NaOH), chromium chloride (CrCl<sub>3</sub>·6H<sub>2</sub>O), disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>), sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>), potassium hydrogen phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), sodium borate decahydrate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) and sodium bicarbonate (NaHCO<sub>3</sub>) were purchased from J. T. Baker (Phillipsburg, NJ). L-histidine, sodium citrate, sodium oxalate, potassium nitrate (KNO<sub>3</sub>) and sodium azide (NaN<sub>3</sub>) were purchased from Fisher (Fair Lawn, NJ). Mandelic acid, pyruvate acid sodium, and nitric acid (HNO<sub>3</sub>) were purchased from Acros (Fair Lawn, NJ), Kodak (Rochester, NY) and Fluka (France), respectively. All solutions were prepared with Milli-Q (18 MΩ-cm) water (Millipore Corp., Milford, MA). The Cr (III) stock solution (1,000 mg/L, 19.23 mM) was prepared by dissolving CrCl<sub>3</sub>·6H<sub>2</sub>O in a 0.01 M HNO<sub>3</sub> (Fisher Scientific) solution.

### Soil

The soil used in this study was a Matawan soil obtained from the USDA Agricultural Research Center in Beltsville, Maryland. The characteristics of this test soil are summarized in Table 1. The information was obtained in part from the USDA and in part from



measurements in the same laboratory mentioned here-above.

### Methods

Cr (III) organic complexes were prepared by mixing 250 mLs of a 20 mM solution of each organic ligand with 250 mLs of a 5 mM Cr (III) solution. The 5 mM Cr (III) solution was prepared by diluting the stock Cr (III) solution at pH 3-4. The combined solutions were mixed on a rotator for 12 days at  $30 \pm 2$  °C. At the end of the mixing period, the uncomplexed Cr (III) was precipitated out from the solution as Cr (OH)<sub>3</sub>(s) by raising the pH to 8.1 with 10 M NaOH and filtering the solution using a 0.20 µm filter (SFCA/PF, Corning, Germany). A pH meter (Fisher Accumet Model 15) with Ross combination Electrode (Fisher, Accumet) was used to monitor the solution pH.

The stability of Cr (III) organic complexes (working solution was 10 mL and about 190 µM Cr (III) organic) as a function of pH was assessed in batch tests before the soil sorption experiment. All buffer stock solutions were prepared first at 50 mM. Then reaction solutions were added: 2.5 mLs of the 0.8 mM Cr (III) organic bulk complex solution and 1 mL of the 50 mM pH buffer solution, diluted to 10 mLs with MW. The pH was measured. The mixtures were reacted for 48 h. A KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub> buffer was used for pH 4 and pH 5, a NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> buffer for pH 6.8, a NaH<sub>2</sub>PO<sub>4</sub> buffer for pH 7.4, a Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O buffer for pH 9.1 and a NaHCO<sub>3</sub> buffer for pH 10.0 (Clesceri *et al.*, 1989). For batches with pHs below 4.0 and above 11.0, no buffers were used; the pH was adjusted by adding HNO<sub>3</sub> and NaOH, respectively. The phosphate was chosen as a pH buffer according to the literature (Puzon *et al.*, 2005). 48 h later, the samples were filtered (0.2 µm, SFCA/PF, Corning, Germany) and tested by atomic absorption spectrometry (AAS).

The sorption of Cr (III) organic complexes to the Matawan soil was evaluated in a series of batch experiments. One gram of soil was placed in a series of 15 mL disposable polypropylene centrifuge tubes (Falcon, NJ), with 3 mM of NaN<sub>3</sub> to inhibit bacterial growth. An appropriate volume of each Cr (III) organic solution was added to each tube. The influence of pH on sorption of the Cr (III) organic complexes was examined by setting up tubes to span a range of pHs. Each tube consisted of 5 mM pH buffer, 10 mg/L Cr (III) organic complex and 1:10 soil solid:liquid ratio. The same pH buffers described above were used.

The effect of ionic strength on Cr (III) organic sorption was examined by setting up a series of tubes containing 10 mg/L of the Cr (III) organic and 1 M, 0.1 M, 0.05 M, 0.01 M and 0.005 M KNO<sub>3</sub>. The pH of all these batches was adjusted to 7.0 using 5 mM NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> buffer. 3 mM NaN<sub>3</sub> was also added.

Another set of tubes was prepared to examine the influence of Cr (III) organic concentration on sorption behavior. Tubes were prepared containing 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 mg/L of each Cr (III) organic, 5 mM of a NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> buffer (pH 7), 10 mM KNO<sub>3</sub> and 3 mM NaN<sub>3</sub>. Each tube was mixed at  $30 \pm 2$  °C on a rotator (4609C ROTATOR, Glass-Col Model 099A-RD-4512 Rotator) for 10 day. After culmination of the sorption mixing period, each tube was centrifuged at 4000 g for 40 min and the supernatant was filtered (0.2 µm, SFCA/PF, Corning, Germany) and tested by AAS. The amount of Cr (III) organic that could be subsequently desorbed from soil was determined by adding 10 mL DI water with 5 mM pH buffer, 10 mM KNO<sub>3</sub> and 3 mM NaN<sub>3</sub>, to the soil remaining in the batch tubes after centrifugation. The mixture in each tube was mixed for 10 day and centrifuged at 4000 g for 40 min. The supernatant was filtered (0.2 µm,

Table 1: Characteristics of the Matawan Soil (dwt., average±standard deviation)

Characteristics*	Concentration	Methods**	Metals	Concentration* µg/g	Methods
Clay	2-10 %	USDA sampling	Cr	6.3 ± 0.1	EPA method 3051 ICP-MS with dynamic reaction cell
pH	4.5-5.5	USDA sampling	Pb	21.8 ± 0.7	
OC	2 %	USDA sampling	Zn	63.4 ± 2.1	
pH	6.89 ± 0.05	Soil/water 1:10	Cu	12.0 ± 2.2	
DOC	0.53 ± 0.04	UV-persulfate TOC	Cd	0.25 ± 0.01	
	mg C/g soil	Analyzer (Dohrmann)			
Surface area	3.62 ± 0.13	B.E.T.N <sub>2</sub> adsorption	Ni	3.4 ± 0.08	
	m <sup>2</sup> /g soil		Co	1.37 ± 0.05	

\*OC = organic carbon; DOC = dissolved organic carbon

\*\*Data provided from the USDA Agricultural Research Center in Beltsville, MD.



SFCA/PF, Corning, Germany) and tested for chromium by AAS.

The percent sorption and the distribution coefficient were calculated by computing a mass balance for each batch test. The amount sorbed was determined from the difference between the initial and the equilibrium concentrations of the sorbate. To reduce error in the sorption calculations, all batches were designed so that the equilibrium solution concentrations fell between 15 % and 85 % of the initial Cr (III) organic concentration. If not otherwise stated the all the experiment were performed in triplicate and calculated the average.

## RESULTS AND DISCUSSION

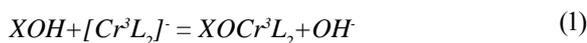
### *Effect of pH on Cr (III) organic complexes and its sorption*

The influence of pH on the stability of Cr (III) organic complexes is shown in Fig. 2. Most Cr (III) organic were independent of pH except for Cr (III) cys. Cr (III) cys complex was not stable as pH value below 7.0 and became precipitated at pH value below 3.9. After filtering, the soluble Cr (III) concentration was decreased from 9.88 mg/L (pH > 7.0) to 1.35 mg/L (pH < 3.9). Cr (III) mand complex show a wave from pH 5.0 to 7.0 due to the measurement error.

The effect of pH on percent sorption of each Cr (III) organic complex to the Matawan soil is shown in Fig. 3. For all of the Cr (III) organic complexes except Cr (III) glu, Cr (III) cys, Cr (III) mand and Cr cit, the percent sorption to the Matawan soil was independent of the pH over the pH range 2 to 12. The Cr (III) mand complex showed greater sorption at pH less than 5 than at pH 7 and above 7. Cr (III) glut, Cr (III) his, Cr (III) mand and Cr (III) ser complexes were sorbed less at pH 12 than at pH below 12. The sorption of Cr (III) asc and Cr (III) pyr complexes tended to remain constant over the entire pH range studied. The Cr (III) oxa complex sorbed the most at pH 12. The Cr (III) cys and Cr (III) glu complex was stable at pH from 7 to 10. Cr-III cit exhibited higher sorption at pH less than 3. Above pH 3, the percent sorption decreased with increasing pH.

In general, the pH dependence of soil sorption results from surface complexation, ligand exchange, the electrostatic interactions induced from surface charge, and the hydrophobic or hydrophilic interactions between the sorbate and soil at different pHs condition. The Matawan soil in this study had 2

- 10% clay content and 2% organic carbon (Table 1). Ge and Hendershot (2004) suggested that such a soil has a low anion exchange capacity and carries mostly a negative surface charge. The surface reactions for such a soil involve only neutral ( $\equiv\text{SiOH}$ ) or negatively ( $\text{SiO}^-$ ) charged surface functional groups. The ion-exchange reaction of soil and anionic complexes, such as Cr (III) glutamate with  $\text{OH}^-$  of  $\text{XOH}$ , may occur through the following equilibrium reaction:



According to Eq. 1, increasing the pH may reduce the ion-exchange competition of the anion Cr (III) organic complex with the  $\text{OH}^-$  of  $\text{XOH}$  and decrease the possibility of Cr (III) organic sorbing onto the soil. In addition, with decreasing pH, the fraction of the neutral Cr (III) organic complex such as Cr (III) mand may increase, which enhances the hydrophobic effect of the complex from the bulk solution, leading to increased sorption.

In addition, pH could change sorbate charges and molecular structures. For example, Cr (III) cit complex might decompose at pH less than 3 since it was prepared by  $\text{CrCl}_3$  and organic compounds. The dominant forms of Cr (III) are likely to be  $[\text{Cr}^3(\text{H}_2\text{O})\text{Cl}_2]^+$ ,  $[\text{Cr}^3(\text{H}_2\text{O})_5\text{Cl}]^{2+}$  and  $[\text{Cr}^3(\text{H}_2\text{O})_6]^{3+}$  (Gaspar and Buglyo, 2000) and be sorbed onto the soil surface. A similar reaction might be applied to the other complexes. The percent of sorption onto the soil was low and all around 17 %. At extremely high pH, such as 11 to 12, Cr (III) glu, Cr (III) ser, Cr (III) his and Cr (III) mand complexes showed lower percent of sorption, possibly due to zero or negative charges on the molecules.

### *Influence of ionic strength on Cr (III) organic sorption*

This batch experiment consisted of 5 mM pH buffer, 3 mM  $\text{NaN}_3$  and 10 mg/L of the Cr (III) organic.

The ionic strength for the solution conditions was nearly 0.01 M, therefore, the influence of increasing the ionic strength above 0.01 M on Cr (III) organic sorption is shown in Fig. 4. Sorption of Cr (III) asc, Cr (III) cit and Cr (III) oxa remained fairly unchanged whereas that of Cr (III) glu, Cr (III) mand and Cr (III) pyr increased with increasing ionic strength. This increase in the sorption was likely due to changes in the soil surface charge at higher ionic strengths. The sorption of Cr (III) his decreased with increasing ionic strength



in the range of 0.01-1.0 M KNO<sub>3</sub>. The Cr (III) his complex is cationic, so increasing ionic strength leads to an increase in soil cation exchange capacity. Cr (III) cys and Cr (III) ser complexes precipitated at ionic strengths greater than 0.01 M KNO<sub>3</sub> and Cr (III) mand precipitated at an ionic strength of 1.0 M KNO<sub>3</sub>. However, sorption data are not available for the precipitated complexes. Based on these data, sorption with an ionic strength of 0.01 M KNO<sub>3</sub> provided the best overall results for

the subsequent experiments.

### Sorption isotherms

The experimental data obtained in this study were analyzed by the following three sorption isotherm models, Linear isotherm, Langmuir isotherm (Langmuir, 1918) and Freundlich isotherm (Freundlich, 1926).

The sorption data for the Langmuir and Freundlich

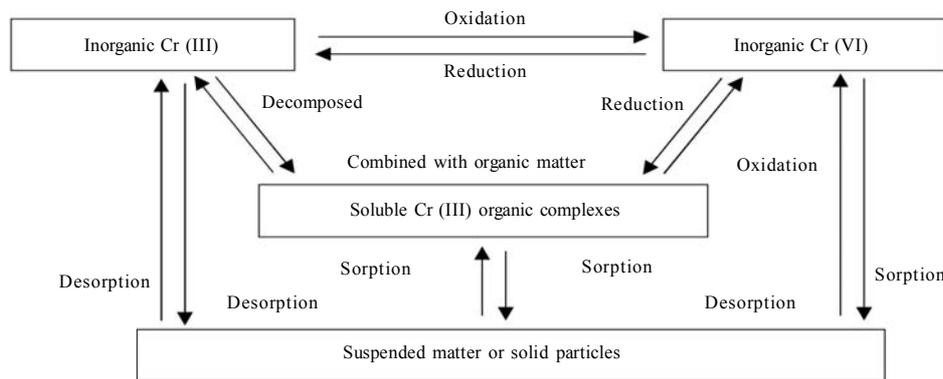


Fig. 1: The geochemical cycle of Cr in nature (Puzon *et al.*, 2005)

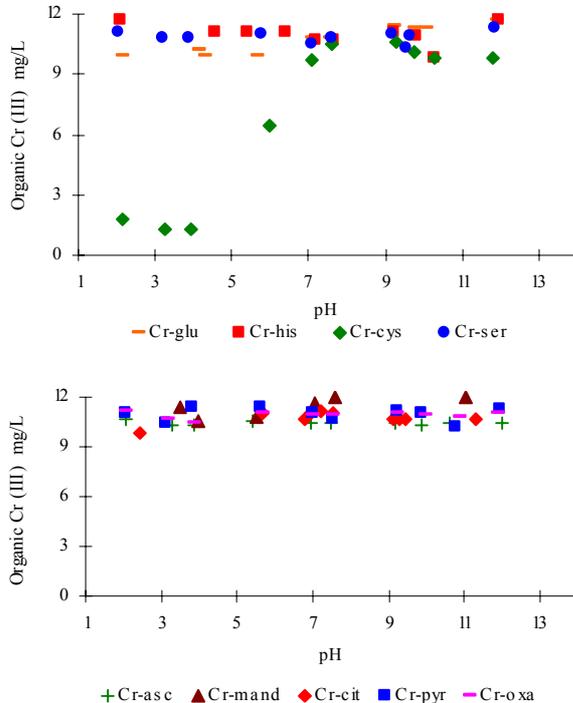


Fig. 2: Stability of organic Cr (III) complexes as a function of pH at 30 ± 2 °C and contact time of 48 h

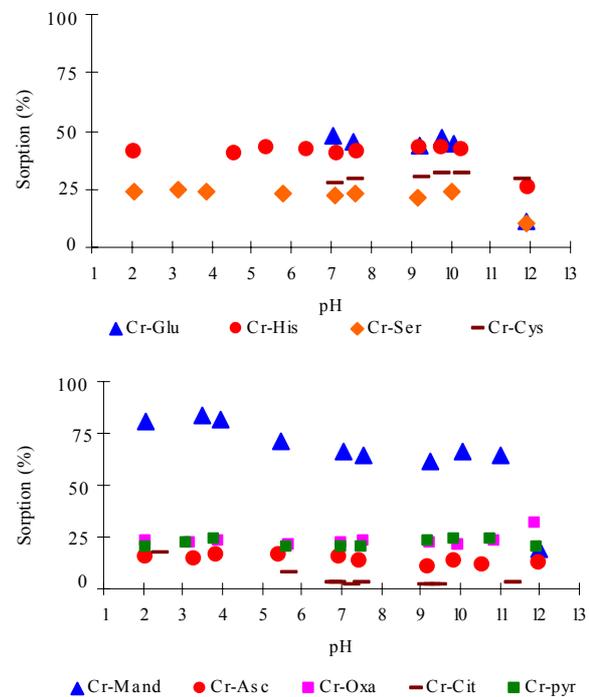


Fig. 3: Percent of each Cr (III) organic complex sorbed onto the Matawan soil as a function of pH at 30 ± 2 °C and contact time of 10 days



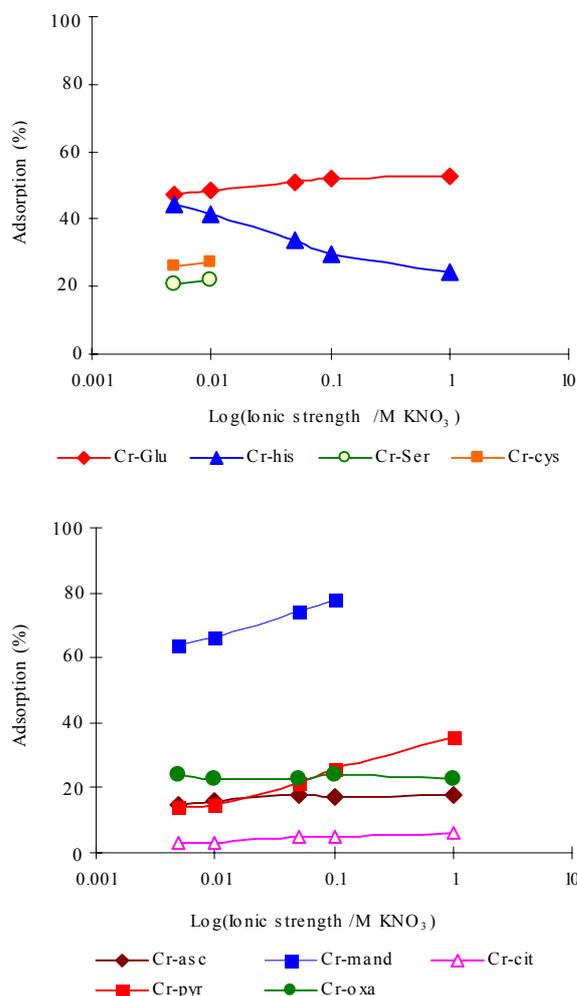


Fig. 4: Percent of each Cr (III) organic complex sorbed onto the Matawan soil as a function of ionic strength at  $30 \pm 2$  °C and contact time of 10 d. The ionic strength was controlled with  $\text{KNO}_3$

isotherms are shown in Fig. 5. The best fit coefficients for the isotherms are summarized in Table 2. The sorption of Cr (III) asc, Cr (III) glu, Cr (III) cit, Cr (III) cys, Cr (III) pyr and Cr (III) oxa complexes were described well by both the Langmuir and the Freundlich models. The sorption data for the Cr (III) cit complex were described better by the Freundlich isotherm in comparison to the Langmuir isotherm. The good fits to the Freundlich model might be because the Langmuir isotherm has more restrictive assumptions (i.e., single layer sorption, homogeneous surface and bonding energies and no interaction among the compound and the surface) than the Freundlich isotherm in explaining adsorption phenomena (Petruzzelli *et al.*, 1985).

Even though Cr (III) glu, Cr (III) pyr, Cr (III) oxa, Cr (III) cys, Cr (III) asc and Cr (III) cit complexes are negatively charged at neutral pH (data to be published in a follow-on paper), their sorption capacities with the Matawan soil differed (Table 2). The properties of the different ligands are likely contributing to the observed differences in sorption behavior.

The sorption data for the Cr (III) his, Cr (III) mand and Cr (III) ser complexes were described only by the Freundlich model with values of  $n$  being 1.33, 1.78 and 1.20, respectively. These values of  $n$  are greater than one, suggesting that cooperative sorption was involved. The cooperative sorption behavior for the Cr (III) his, Cr (III) mand and Cr (III) ser complexes likely stems from their existence as more than one species (the data will be published in a subsequent manuscript). For the Cr (III) cys complex, both the Langmuir and the Freundlich models showed poor fits with the sorption data

Table 2: Fitted sorption and desorption parameters for the Langmuir and Freundlich models at  $30 \pm 2$  °C

Cr (III) organic complex	Langmuir model					Freundlich model				
	$K_1$	sorption $Q_0$ ( $\mu\text{g/g}$ )	$r^*$	desorption $K_1'$	$r^*$	$n$	sorption $K_2$	$r^*$	desorption $N'$	$r^*$
Cr (III) asc	0.22	28.57	0.99	0.03	0.98	0.64	4.47	0.99	0.62	0.97
Cr (III) glu	0.05	140.85	1			0.65	19.67	1		
Cr (III) his						1.33	3.72	1	1.04	0.99
Cr (III) mand						1.78	45.65	0.98		
Cr (III) cit	0.41	4.4	0.93	0.05	0.96	0.37	1.75	0.94	0.47	0.94
Cr (III) cys	0.10	35.46	0.86			0.40	10.70	0.77		
Cr (III) ser						1.20	1.85	0.96		
Cr (III) pyr	0.30	70.92	0.99	0.02	0.99	0.89	3.21	0.99	0.729	0.99
Cr (III) oxa	0.17	36.5	0.97	0.003	0.96	0.69	5.34	0.96	0.56	0.97

\*Correlation coefficients



(correlation coefficient values of 0.862 and 0.767, respectively). A contributing factor is the Cr (III) cys complex with its -SH group was not stable as it is subject to oxidation upon exposure to air to form a cysteine complex. Sorption of all the Cr (III) organic complexes with the Matawan soil were described well by the Freundlich model, with the Cr (III) asc, Cr (III) glu, Cr (III) cit, Cr (III) cys and Cr (III) oxa complexes

having nonlinear sorption isotherms ( $n = 0.37-0.69$ ) and the Cr (III) pyr complex having a nearly linear isotherm ( $n = 0.89$ ).

The desorption data are presented in Fig. 6 and the behavior of the Cr organic complexes provided insight into the bioavailable fraction and mobility. Desorption of the Cr (III) organic complexes was essentially irreversible. Since limited desorption was

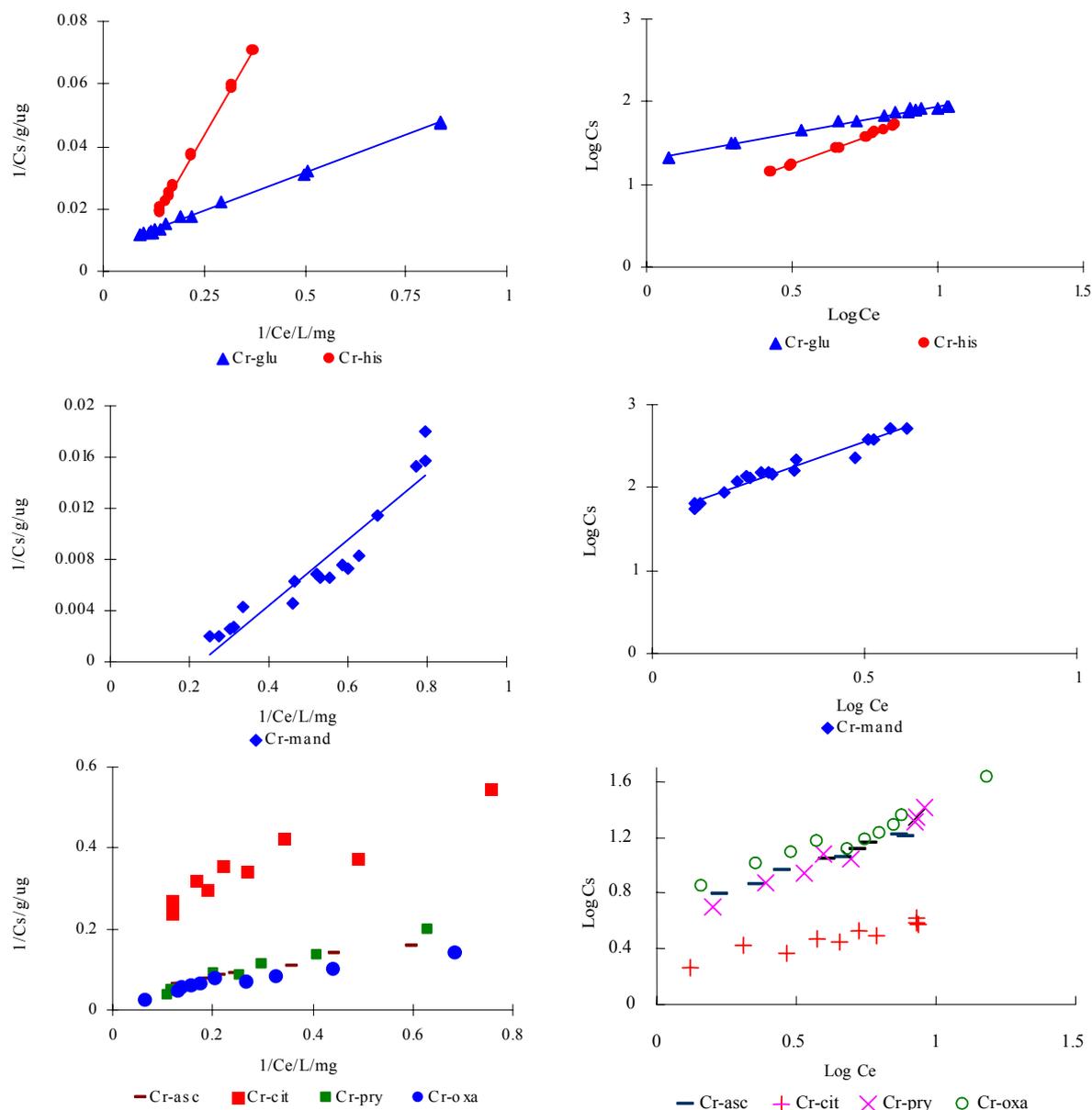


Fig. 5: Langmuir and Freundlich sorption isotherms for each Cr (III) organic complex at  $30 \pm 2$  °C, 0.01 M  $KNO_3$ , 5 mM pH 7 buffer, 3 mM  $NaN_3$  and contact time of 10 days



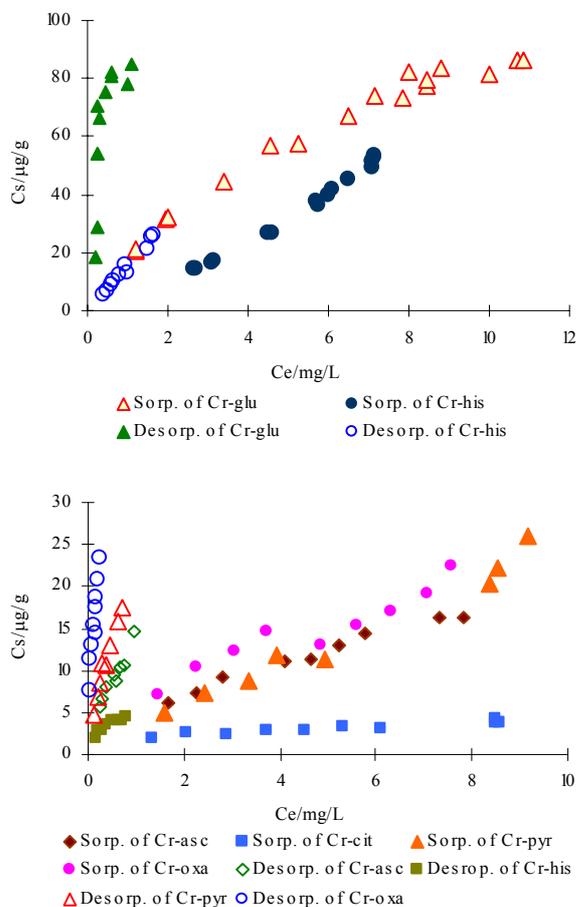


Fig. 6: Sorption and desorption data for selected Cr (III) organic complexes with the Matawan soil at  $30 \pm 2$  °C, 0.01 M  $\text{KNO}_3$ , 5 mM pH 7 buffer, 3 mM  $\text{NaN}_3$  and contact time of 10 days

observed, the desorption data could not be fitted to an isotherm model. Consequently, Cr (III) organic complexes remain sorbed to soil or sediment particles and would not exhibit high mobility.

Sorption and desorption of Cr (III) cys and Cr (III) serine with the Matawan soil was not reproducible; their data were not considered in this study. Cr (III) cys complexes have the  $-\text{SH}$  group which could be oxidized by  $\text{MnO}_2(\text{s})$  or other oxidants in this soil, changing the composition of this complex. The other plausible reason for the instability with both complexes is they exist as several species with different charges. The Cr (III) ser complex existed predominantly as a cationic species exhibiting

complex sorption and desorption behavior. Additional research is needed to evaluate their sorption and desorption behavior.

## CONCLUSION

At pHs of most natural environments (pH 5 to 9), a constant percent sorption was observed for each Cr (III) organic complex. Varying the ionic strength between 0.005 and 0.01 M  $\text{KNO}_3$  did not influence the sorption of each Cr (III) organic complex. The sorption data with pH 7, 0.01 M  $\text{KNO}_3$  and 1-10 mg/L Cr (III) organic complex exhibited good fits with the Freundlich model. In addition, Cr (III) glut, Cr (III) pyr, Cr (III) oxa, Cr (III) cys, Cr (III) asc and Cr (III) cit could be fit with a Langmuir model. Estimates for the saturated sorption capacities were 141, 70.9, 36.5, 35.5, 28.6 and 4.4  $\mu\text{g/g}$ , respectively. It was not possible to desorb significant amounts of the previously sorbed Cr (III) organic complexes. At the same pH, ionic strength and solid:liquid ratio, the order of the observed sorption to the Matawan soil from highest to lowest is Cr (III) mand, Cr (III) glu, Cr (III) his, Cr (III) cys, Cr (III) ser, Cr (III) pyr, Cr (III) oxa, Cr (III) asc and Cr (III) cit. The highest percent of sorption is around 75 % for the Cr (III) mand complex and the lowest percent of sorption is around 2 % for the Cr (III) cit complex.

In fact, natural organic matters are more complicated than those ligands researched in this paper. The natural Cr (III) organic complexes are also complicated and varied. Although, those ligands are part of natural organic matters and have some similar function groups; this study can help to understand the behavior of sorption on soil particles. The mechanism and the possible transformation will be carried in the next study about natural organic Cr (III) complexes in soil.

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