

INFLUENCES OF SOIL PROPERTIES ON CHROMIUM (III) SORPTION

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ABSTRACT

Soil adsorbing properties reduce sorption ability of the metal, which in turn may influence decision for remediation at contaminated sites. The objective of this study is presentation of a model based on soil properties to estimate the sorption of Cr(III) in chromium contaminated soils. Twenty uncontaminated soil samples, with properties similar to the contaminated soils were selected from around of city of Tabriz and treated with Cr as CrCl₃. A multiple regression analysis with statgraph software was used to drive an expression that related Cr sorption to common soil properties. The results showed that four soil properties were important in determining the amount of Cr adsorbed by the soils including pH, cation exchange capacity, total inorganic carbon and clay content with nearly 80% variability in Cr sorption and a reasonable level of confidence by this model. The obtained model suggested that Cr(III) sorption was enhanced by higher soil pH, more total inorganic carbon, more clay, and higher cation exchange capacity.

Key words: Chromium, soil properties, sorption model, contaminated soil

INTRODUCTION

The presence of chromium in the environment is widespread due to its usage in many industrial processes. The metallurgic, tanning and plating industries are just a few examples of applications which use chromium on a daily basis (Nriagu and Nieboer, 1988). Chromium is stable in 2 oxidation states: cationic Cr with a valence of 3 and anionic with a valence of 6. Chromium (III) is often considered to be mobile in the environment while the more environmentally stable, Cr(VI), is considered less mobile (Chung, 1998). There are several factors that contribute to the decreased mobility of Cr (III) in soil: strong adsorption onto negative soil surfaces, the ability to form complex molecules with organics found in soil, and formation of oxides and hydroxides and other insoluble materials in soil (Endorf and Zasoski, 1992). Chromium (VI) is considered the most harmful of oxidation states since it is both a mutagen and a carcinogen at low sub-ppm levels (Levis, 1982). Although Cr (III) is generally

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considered less harmful to human health than its oxidized state, it may be of concern due to its potential to oxidize Cr(VI) and its ability to accumulate to very high solid phase concentrations in some soils (Endorf and Sparks, 1992). Typically calculated health risks are incorporated based on a reference soil dose derived from studies that use soluble aqueous metal species. The metal-sequestering of soil may significantly lower bioavailability of Cr, which in turn may influence the decision for remediation at contaminated sites. Thus, action levels set by state regulators concerning the bioavailability of Cr in soil may need to consider specific soil properties instead of using guidelines (Proctor, 1997).

There is a leather factory in the west of Tabriz city located in north west of Iran. Wastes from the Industrial Zone of Tabriz, Charmshahr, are disposed in the surrounding soils. Because of sludge-borne Cr of these wastewaters, that is a question that whether these exposed soils can adsorb Cr from these wastes, and thereby control groundwater pollution and plant uptake of Cr in this area. The

purpose of this work was to study the sorption capacity of soils in this region, which in turn influences its availability for leaching in soil and plant uptake. Simple statistical model was developed based on measured soil properties to estimate the sorption of Cr by the proposed soils.

MATERIALS AND METHODS

Twenty uncontaminated soil samples which their properties were similar to the contaminated soils were selected from Charmshahr (a small town around Tabriz). Selected soils did not receive sludge but were in adjacent to sludge received soils.

Some of physico-chemical properties of the soils were determined in laboratory (Table 1). Soil pH was determined using deionized water in a 2:1 solution/solid ratio with a Perkin Elmer pH meter. Total organic and inorganic carbons (TOC and TIC) were measured by combustion in furnace. Soil TOC was determined on pretreated samples to remove TIC, which involved a near boiling, 3 M HCL extraction method on agitated samples. Soil TIC was computed from difference between total soil carbon (no pretreatment) and TOC. Clay and silt percentages were determined by hydrometric method (Klute *et al.*, 1965). Determination of the soil cation exchange capacity was carried on by Baver method (Page *et al.*, 1965, Klute *et al.*, 1965). Because obtaining actual contaminated soil from these sites was difficult, the collected soil samples were treated with Cr

(III). For this, 10 g of soil was placed in a centrifuge vessel along with 100 mL of 500 ppm Cr (III) as CrCl_3 with pH=4. The slurry was agitated on a reciprocal shaker for 2 d, centrifuged, and decanted for analysis. This was repeated for 3 more times. After the fourth addition of Cr, the soils were washed 3 times with deionized water (DI) water and allowed to air dry. Once the soils were dry, they were gently crushed, homogenized and then wetted with DI water to achieve a 30% moisture content. The soils were kept in containers for study. For determination of Cr (III) and Cr (VI), the soil samples were digested in nitric and fulvic acids (Bartlett and James, 1979). Cr (VI) and total Cr (Cr_T) in the filtered samples were measured using a colorimetric method and atomic absorption instrument, respectively. Cr (III) was calculated as the difference between Cr_T and Cr (VI). For statistical analyses, a multiple regression technique in statgraph software was used to drive an expression that related Cr (III) sorption to common soil properties. The model was run using stepwise regression to determine the most soil properties for calculating sorption. Multiple linear regression was then employed to determine the linear equation to use when computing the Cr (III) sorption based on important soil properties previously determined.

RESULTS

In Table 1, some physico-chemical properties of the soil samples are shown. As the Table shows,

Table 1: Selective soil chemical and physical properties*

Soil No.	TOC (%)	TIC (%)	Clay (%)	Silt (%)	CEC (cmol/kg)	PH (DI)
1	1.55	0.56	8.7	29.5	7.7	5.0
2	0.19	0.09	14.9	28.4	4.7	1.3
3	1.64	0.39	10.2	23.0	4.4	5.8
4	0.29	0.21	44.8	15.5	4.4	1.6
5	1.89	0.99	6.1	59.0	6.0	6.6
6	0.10	0.07	23.6	44.2	4.0	5.1
7	0.91	0.59	19.5	48.5	5.8	5.2
8	0.11	0.10	25.8	38.3	3.7	4.9
9	0.55	0.39	22.5	75.8	5.6	6.8
10	0.21	0.13	30.9	67.2	5.4	5.6
11	3.41	1.01	49.1	44.5	44.5	6.0
12	0.36	0.25	64.7	29.5	5.5	4.7
13	3.54	1.49	12.4	34.8	10.6	3.9
14	0.21	0.18	12.6	32.1	3.7	4.4
15	3.97	2.37	24.4	56.2	13.3	4.7
16	2.01	1.15	23.9	54.3	8.0	4.6
17	3.55	0.62	6.0	69.0	8.0	7.1
18	0.42	0.26	19.0	42.2	14.0	4.8
19	0.72	0.52	26.9	68.0	6.8	6.7
20	0.28	0.08	10.8	24.8	6.9	7.4

* TOC, total organic carbon; TIC, total inorganic carbon; CEC, cation exchange capacity; DI, deionized

selected soils had different properties. pH ranged from 1.3 to 7.4. Ranges of clay and silt contents are 6% to 64.9% and 15.5% to 75.8%, respectively. As a result, the soils have various textures, from heavy to light ones. The soils have good CEC: 44.5 to 69 mol/kg. Percentages of TIC and TOC were 0.07 to

2.37 and 0.1 to 3.97, respectively. In Fig. 1 Cr(III) concentrations on the various soils (mg/kg) are presented. Chromium sorption by the 20 soils varied markedly with values ranging from 0.736 g/kg to 0.817 g/kg, with mean of 0.340 g/kg and standard deviation of 0.210 g/kg. The majority of the soils adsorbed

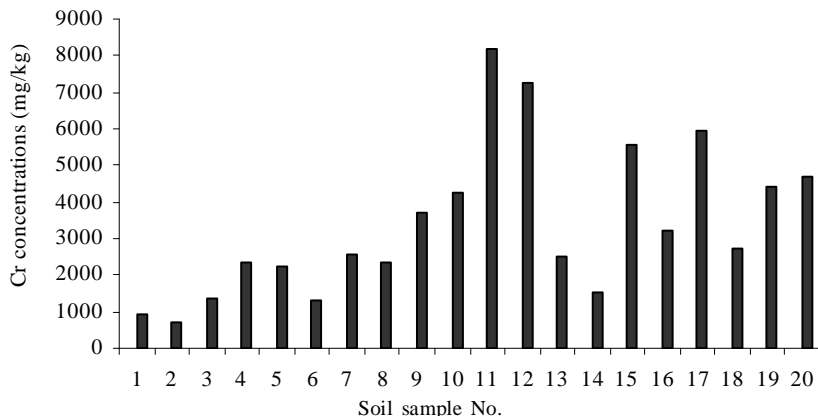


Fig. 1: Chromium (III) concentrations on the soils (g/kg)

chromium between approximately 2 to 4 g/kg. Results of statistical analysis from a multiple linear regression analysis that related soil properties to Cr (III) sorption, are presented in Table 2.

Table 2: Parameter estimates, standard errors (SE), and statistics obtained from a multiple linear regression analysis that related soil properties to Cr (III) sorption

Parameter	Value	SE	P value
Intercept	12666.3	1794.5	0.001
Clay (%)	113.8	30.4	0.001
pH	1916.7	250.7	0.001
CEC, cmol/kg	364.6	155.7	0.026
TIC (%)	1743.2	850.1	0.049
R ²	0.794	-	0.001

DISCUSSION

The large difference in Cr (III) sorption by the various soils (Fig. 1) can be explained by the differences in soil properties. Multiple linear regression showed that 4 soil properties were important in determining the amount of Cr adsorbed by the soils: pH, TIC, clay content, and CEC. The relationship describing Cr adsorption was:

$$\text{Cr(III) (mg/kg on soil)} = -12666.3 + (113.8 * (\% \text{ clay})) + (364.6 * \text{CEC}) + (1743.2 * (\% \text{ TIC})) + (1916.7 * \text{soil pH}) \quad R^2 = 0.794 \quad (1)$$

Chromium sorption by the soils was strongly correlated with these soil properties (R²= 0.794),

suggesting that nearly %80 variability in Cr (III) sorption could be described by soil pH, TIC, clay, and CEC (Table 2). Incorporating the other measured soil properties from Table 2 (such as TOC) did not improve the model fitness. In fact, TIC could have been removed from the model if necessary, since the other 3 independent soil variables could describe approximately %77 of the variability in soil Cr (III) sorption. The four parameters model (Eq. 1) was statistically rigorous at the %95 of confidence level since P values for the independent variable, were all <0.05 (Table 2). The pH of the soil affects the solubility and form of Cr and therefore affects sorption. As the soil pH increases, the amount of Cr on the soil increases. At low pH, Cr (III) is adsorbed or complexed on soil negative charges; at higher soil pH values, (>5.5), Cr precipitates as hydroxides covering the surface of the soil (Bartlett, 1976). As with pH, TIC or carbonate content in soils enhanced Cr (III) sorption.

The mechanism of increased sequestration is most likely a localized pH effect at the carbonate surface, which promotes the formation of Cr (OH)₃ species. The model also showed a positive correlation between the amount of Cr adsorbed and the soil clay content and CEC. This was expected since clay minerals tend to be dominated by negatively

charged sites on the surface due to isomorphic substitution (Klein and Hurlbut, 1993). These negatively charged sites attract the cation Cr and a weak, electrostatic bond is formed. The more negatively charged sites that are available (i.e. larger CEC), the greater propensity for Cr sorption. This study showed that site assessment of soil metal availability based solely on soil metal concentrations may not accurately reflect the risk posed by the soils (i.e. groundwater pollution and phytotoxicity). The sequestering properties of soil significantly lower the percent of soil solution Chromium (III) can be immobilized as strongly bound species on clay and organic matter and Cr hydroxides precipitates on soil mineral surfaces. It has been shown this is strongly correlated with Cr sorption. The ability to rapidly assess metal sorption in soils will facilitate decision making strategies regarding the need for more detailed and expensive site specific bioavailability (animal feeding) studies, which are designed to assess actual clean-up needs at contaminated sites to level safe for human use.

REFERENCES

- Bartlett, R. J., (1976). Behavior of Cr in soils. I: Trivalent forms. *J. Env. Qual.*, **8** (2): 31-35.
- Bartlett, R., James, B., (1979). Behavior of Cr in soils: III. Oxidation. *J. Environ. Qual.*, **8** (3): 31-35.
- Chung, J., (1998). Kinetics of Cr (III) oxidation by various Mn oxides. *Korean J. Agric. Chem. Biotechnol.* **37** (4): 414-420.
- Endorf, S. E., Sparks, D. L., (1992). Inhibitory mechanisms of Cr (III) oxidation by MnO₂. *J. Colloid Inter. Sci.*, **153** (2): 37-54.
- Endorf, S. E., Zasoski, R. J., (1992). Cr (III) oxidation by MnO₂. I. Characterization. *Env. Sci. Technol.*, **26** (1): 79-85.
- Klein, C., Hurlbut, C., (1993). *Manual of mineralogy*. 21st Ed. John Wiley and Sons, N. Y. USA.
- Klute, A., Nielson, D. R., Jackson, R. D., (1965). *Methods of soil analysis, Part 1*. 2Ed, Agronomy Monog. 9, ASA, Madison, WI USA.
- Levis, A. G., (1982). Mutagenic and cytogenic effects of Cr compounds. P. 171-208. In S. Langid (Ed). *Biological and environmental aspects of Cr*. Elsevier Biomedical Press, N. Y. USA.
- Nriagu, J. O., Nieboer, E., (1988). *Cr in the natural and human environments*. John Wiley and Sons, N. Y. USA.
- Page, A. L., Miller, R. M., Keeney, D. B., (1965). *Methods of soil analysis, Part 2*. 2ed, Agronomy Monog. 9, ASA, Madison, WI USA.
- Proctor, D. M., (1997). Health based soil action levels for trivalent and hexavalent Cr. *J. Soil. Contam.*, **6** (3): 595-648.