© 2017 IJSRST | Volume 3 | Issue 4 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology

Catalytic Effect of Tropical Clay Minerals on the Organic Reduction of Hexavalent Chromium

Madu A. N., Ijiwade E. O.
Industrial Chemistry Department Crawford University Faith City Igbesa, Ogun State Nigeria

ABSTRACT

The organic reduction of hexavalent chromium in the presence of clay minerals found in some areas of the Eastern part of Nigeria has been studied. Remediation of chromium contaminated environment like soil, land, fills, sewage and plant bodies, can be effected by reducing hexavalent chromium to the trivalent analogue, which makes it unstable and less harmful to the environment since it cannot act on its own, but can be combined with other compounds which are insoluble such as calcium, magnesium which it can than been extracted from them. Results show that the overall reduction rate increased with increase in the mass of the clay mineral 1.0 – 5.0 g. However, the rate was higher in bentonite 0.043 – 0.014 g/dm3 and lower in kaolin 0.049 – 0.022 g/dm3 for corresponding mass of clay. The rate was also higher in bentonite with increasing concentration of the reductant – oxalic acid 0.043 – 0.012 g/dm3 and lower in kaolin 0.049 – 0.015 g/dm3 for corresponding reductant concentration. From experiment, it can be deduced that from the values obtained, the catalytic effect of bentonite is greatest (fastest) and that of kaolinite is slow, that is to say that the rate of catalysis of bentonite > kaolinite. These result suggest that Cr(VI) reduction rate in subsurface environments rich in organic compound may be elevated through catalysis of surface-bound metals and/or soluble species from the clay minerals, and as a result, higher than those expected from aqueous phase reaction alone.

Keywords : Kaolinite, Bentonite, Catalysis, Reductant, Chromium, Hexavalent

I. INTRODUCTION

Clay is a general term including many combinations of one or more clay minerals with traces of metal oxides and organic matter (Kalbus, Petrucci and Forman, 1991). Geologic clay deposits are mostly composed of phyllosilicate minerals containing variable amounts of water trapped in the mineral structure. Clay minerals are typically formed over long periods of time by the gradual chemical weathering of rocks, usually silicate-bearing, by low concentrations of carbonic acid and other diluted solvents. Knowledge of the nature of clay became better understood in the 1930s with advancements in x-ray diffraction technology necessary to analyse the molecular nature of clay particles. Standardization in terminology arose during this period as well with special attention given to similar words that resulted in confusion such as sheet and plate (Bates and Baqi, 1936). Clays exhibit plasticity when mixed with water in certain proportions. When dry, clay becomes firm and when fired in a kiln, permanent physical and chemical changes occur. These reactions, among other changes, cause the clay to be converted into a ceramic material. Because of these properties, clay is used for making pottery items, both utilitarian and decorative. Different types of clay, when used with different minerals and firing conditions, are used to produce earthenware, stoneware, and porcelain. Prehistoric humans discovered the useful properties of clay, and one of the earliest artefacts ever uncovered is a drinking vessel made of sun-dried clay (Bates et al.1936). Depending on the content of the soil, clay can appear in various colours, from a dull grey to a deep orange-red. The Kaolin group includes the minerals kaolinite, dickite, halloysite, and nacrite ; polymorphs of $Al_2Si_2O_5(OH)_4$ (Kalbus et al, 1991). Some sources include the kaolinite-serpentine group due to structural similarities (Bailey, Tunick, Friedman and Rest, 1984). Smectite group which includes di-octahedral smectites such as montmorillonite and nontronite and trioctahedral smectites for example saponite. Illite group includes the clay-micas-Illite is the only common mineral. Chlorite group includes a wide variety of similar minerals with considerable chemical variation (Kalbus et al.1991).

Other 2:1 clay types exist such as sepiolite or attapulgite, clays with long water channels internal to their structure. Mixed layer clay variations exist for most of the above groups. Ordering is described as random or regular ordering, and is further described by the term reichweite, which is German for range or reach. Literature articles will refer to a R1 ordered illite-smectite, for example. This type would be ordered in an ISISIS fashion. R0 on the other hand describes random ordering, and other advanced ordering types are also found (R3, etc). Mixed layer clay minerals which are perfect R1 types often get their own names. R1 ordered chlorite-smectite is known as corrensite, R1 illite-smectite is rectorite (Lepora, 2006). Like all phyllosilicates, clay minerals are characterized by two dimensional sheets of corner sharing SiO_4 tetrahedra and/or AlO_4 octahedral. The sheet units have the chemical composition $(Al,Si)_3O_4$. Each silica tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedra forming a hexagonal array in two-dimensions. The fourth vertex is not shared with another tetrahedron and all of the tetrahedral "point" in the same direction; i.e. all of the unshared vertices are on the same side of the sheet. In clays the tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as aluminium or magnesium, coordinated by six oxygen atoms. The unshared vertex from the tetrahedral sheet also form part of one side of the octahedral sheet but an additional oxygen atom is located above the gap in the tetrahedral sheet at the centre of the six tetrahedra. This oxygen atom is bonded to a hydrogen atom forming an OH group in the clay structure. Clays can be categorized depending on the way that tetrahedral and octahedral sheets are packaged into *layers*. If there is only one tetrahedral and one octahedral group in each layer the clay is known as 1:1 clay. The alternative, known as 2:1 clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing towards each other and forming each side of the octahedral sheet.

For the production of ferrochromium, the chromite ore ($FeCr_2O_4$) is reduced in large scale in electric arc furnace or in smaller smelters with either aluminium or silicon in an aluminothermic reaction (Papp, John and Lipin, 2006). For the production of pure chromium, the iron has to be separated from the chromium in a two steps roasting and leaching process. The chromite ore is heated with a mixture of calcium carbonate and sodium carbonate in the presence of air. The chromium is oxidized to the hexavalent form, while the iron forms the stable Fe2O3. The subsequent leaching at elevated temperatures dissolves the chromates and leaves the insoluble iron oxide. The chromate is converted by sulphuric acid into the dichromate (Papp et al. 2006).

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The dichromate is converted to the chromium (III) oxide by reduction with carbon and then reduced in an alumina-thermic reaction to chromium (Papp et al, 2006).

$$Na_2Cr_2O_7 + 2C \rightarrow Cr_2O_3 + Na_2CO_3 + CO$$
$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$

Chromium is remarkable for its magnetic properties: it is the only elemental solid which shows antiferromagnetic ordering at room temperature (and below). Above 38 °C, it transforms into a paramagnetic state (Fawcett, 1988). Chromium is a blue grey metal that can be polished to achieve a high shine. It is extremely lustrous. While it is relatively hard, it is also brittle. Chromium is a fairly active metal. While it does not react with water, it will react with most acids and reacts with oxygen at room temperature to for chromium (III) oxide. One of chromium's most important properties is its self-passivation. While stable in air, chromium will oxidize to form a thin layer that acts as a protective coating to prevent further corrosion. Chulsung, Yeqing and BaolinS (2007) reported the result on kinetic study of hexavalent Cr(VI) reduction by hydrogen sulphide through goethite surface catalytic reaction Hexavalent chromium reduction by sulphide in the presence of goethite was studied through several batch experiments. Under the specific experimental conditions including 20 μM of hexavalent chromium, 560–1117 μM of sulfide and 10.61–37.13 m^2/L of goethite at pH of 8.45 controlled by 0.1 M borate buffer, the obtained hexavalent chromium disappearance rate was –

d[Cr(VI)]/dt = k[surface area of goethite][Cr(VI)][S(-II)]T1.5 and the determined overall rate constant (k) was

{ 31.9 } 4.2 $(min)^{-1}(m^2/L)^{-1}(mol/L)^{-1.5}$.

Among the potential major reducing agents in our comprehensive heterogeneous system such as aqueous phase sulphide, surface-associated sulphide, dissolved ferrous iron, ferrous iron on the goethite surface, as well as fresh ferrous sulphide in the solution, it was considered that the surface ferrous irons which could be produced following sulphide adsorption, played a leading role for Cr(VI) reduction as primary electron donors. In addition, no proof of the preliminary dissolution of ferrous iron from goethite to aqueous phase was observed in the experiments. Elemental sulphur was detected as the final stabilized product of sulphide and it took in charge for the promoted Cr(VI) disappearance for the successive addition of Cr(VI) at later stage. Elsayed and Saba (2009) reported the Electrochemical treatment of toxic hexavalent chromium from industrial effluents using rotating cylinder electrode cell This paper investigates a method to electro reduce toxic hexavalent chromium to trivalent state using rotating disc electrode (RDE) and rotating cylinder electrode (RCE) cell. Electrolysis of acidic hexavalent chromium solution using a rotating lead cathode reduces the hexavalent chromium Cr^{6+} to trivalent chromium. The effect of chromium, sulphuric acid concentration, current density, time and speed of cathode rotation on current efficiency has been investigated under galvanostatic and linears weep voltammetric techniques. The effect of these parameters on cell voltage and energy consumption has been also studied. It was found that the efficiency of the reduction method is directly proportional to the hexavalent chromium and sulphuric acid concentration. Trivalent chromium is successfully obtained from acidic industrial wastewater containing 1.5 g l-1 Cr^6+. High current efficiency is attained at current density 225 mA cm-2for 80 minutes. Débora, Leonard, Da Silva and Jardim (2009) reported the Chemical Reduction of Hexavalent Chromium and Its Immobilisation Under Batch Conditions Using a Slurry Reactor, Chemical reduction of the hexavalent chromium, Cr(VI), present in contaminated soil and groundwater was carried out in a slurry reactor under dynamic conditions (120 rpm and 25°C) using different reductants [ferrous sulphate (Fe(II))], sodium bisulphite, sucrose, ascorbic acid and zerovalent iron (ZVI)] in order to evaluate the influence of the reductant on the redox process. Chemical analysis of the contaminated soil revealed a Cr(VI) concentration of 528 ± 31 mg kg^{-1}. Batch studies under dynamic conditions (slurry reactor) using different [Cr(VI)]/[reductant] molar ratios revealed that only Fe(II) and ZVI species can promote both reduction of Cr(VI) and immobilisation of Cr(III). It was verified that 1.0 g of ZVI is capable of converting 104 ± 5 mg of Cr(VI) in Cr(III). A kinetic redox study was carried out using ZVI in different conditions. In all cases, it was verified that Cr(VI) reduction follows a pseudo-first-order kinetic behaviour. The dependence of the pseudo-first-order kinetic rate constant, k_{obs}, on [ZVI] indicates that the redox process taking place in the slurry reactor is rather complex. A phenomenological kinetic equation for the redox process taking place in the slurry reactor was presented in order to describe the behaviour of k_{obs} under non-ideal conditions. Mario and William (2009) reported the influence of various organic molecules on the reduction of hexavalent chromium mediated by zerovalent iron. Hexavalent chromium is a priority pollutant in many countries. Reduction of Cr(VI) to Cr(III) is desirable as the latter specie is an essential nutrient for maintaining normal physiological function and also has a low mobility and bioavailability. A variety of naturally-occurring organic molecules (containing α-hydroxyl carbonyl, α-hydroxyl carboxylate, α-carbonyl carboxylate, phenolate, carboxylates and/or thiol groups, siderophore, ascorbic acid); chelating agents (ethylenediaminetetraacetic acid derivatives, acetyl acetone) and others were examined their reducing activity towards a surfactant preparation (Tween 20) containing Cr(VI) and Fe(0) under a variety of reaction conditions. An appreciable enhancement (up to 50-fold) of the pseudo-first-order rate constant was achieved at acidic and neutral pH values for those compounds capable of reducing Cr(VI) (α-hydroxyl carboxylate, ascorbic acid, cysteine). Comparable enhancements were obtained for certain chelating agents (ethylenediaminetetraacetic (EDTA) acid derivatives and siderophores) which is attributed to the formation of complexes with reaction products, such as Cr(III) and Fe(III), which impede the precipitation of Cr(III) and Fe(III) hydroxides and $Cr_xFe_{1-x}(OH)_3$ and thus reduce passivation of the Fe(0) surface. The results suggest that these molecules might be used in effective remediation mediated by Fe(0) of Cr(VI)-contaminated soils or groundwater in a wide range of pH, thus increasing reaction rates and long-term performance of permeable reductive barriers. Xiang-Rong X, Hua-Bin, Xiao-Yan and Ji-Dong (2004) reported the Reduction of hexavalent chromium by ascorbic acid in aqueous solutions. Hexavalent chromium is a priority pollutant in the USA and many other countries. Reduction of Cr(VI) to Cr(III) is environmentally favorable as the latter species is not toxic to most living organisms and also has a low mobility and bioavailability. Reduction of Cr(VI) by ascorbic acid (vitamin C) as a reductant was studied using potassium dichromate solution as the model pollutant. Effects of concentration of vitamin C, pH, temperature, irradiation and reaction time on the reduction of Cr(VI) were examined. Cr(VI) might be reduced by vitamin C not only in acidic conditions but also in weakly alkaline solutions. The reduction of Cr(VI) by vitamin C might occur not only under irradiation but also in the dark. Vitamin C is an important biological reductant in humans and animals, and not toxic. It is water-soluble and can easily permeate through various types of soils. The results indicate that vitamin C could be used in effective remediation of Cr(VI)-contaminated soils and groundwater in a wide range of pH, with or without sunlight. Donghee Park, Yeoung-Sang Yun, Jong Moon Park (2005) reported the enhanced abiotic reduction of Cr(VI) in a soil slurry system by natural biomaterial addition among various plant-based natural biomaterials, pine bark was chosen as an efficient biomaterial capable of removing toxic Cr(VI) from aqueous solution. XPS spectra indicated that Cr(VI) was abiotically reduced to Cr(III) in both liquid and solid phases. The Cr(VI)-reducing capacity of pine bark was determined as 545 (±1.3) mg-Cr(VI) g−1 of it, which was 8.7 times higher than that of a common chemical Cr(VI)-reductant, FeSO4·7H_2O. Because pine bark could completely reduce toxic Cr(VI) to less toxic or nontoxic Cr(III) even at neutral pH, it was used as an organic reductant to remediate Cr(VI)-contaminated soil in this study. Soil slurry system using a bottle roller was applied to ex situ slurry-phase remediation experiments. In the soil slurry system, pine bark completely reduced Cr(VI) to Cr(III) and adsorbed the reduced-Cr(III) on its surface. Abiotic remediation rate of Cr(VI)-contaminated soil increased with the increase of pine bark dosage and with the decreases of Cr(VI) and water contents. In conclusion, pine bark can be used to remediate Cr(VI)-contaminated soil efficiently and environmentally friendly.

The object of this work is to determine to what extent the organic acid-induced reduction of hexavalent chromium can be carried out in the presence of clay minerals as surface catalysts. Kaolin and Bentonite were chosen as tropical clay minerals available in most soils in Nigeria.

II. MATERIALS AND METHODS

1.0 – 5.0g of dry bentonite and kaolin obtained locally from Isiagu in Ebonyi State Nigeria were measured into 5 clean and dry 250ml conical flasks labelled $\mathbf{x_1}$ to $\mathbf{x_5}$ for bentonite and $\mathbf{y_1}$ to $\mathbf{y_5}$ for kaolin. A blank was also prepared to serve as a control. A 0.1g/dm^3 $K_2Cr_2O_7$ solution was prepared and made up to 100cm^3 of solution. 5ml was measured and placed in each of the containers and shaken. Also, 2.0ml of freshly prepare 0.1g/dm3 of oxalic acid was introduced in the conical flasks followed immediately by 1.0ml of calcium oxalate to serve as a buffer. The containers are quickly closed with their stoppers, away from the influence of ultraviolet light since the reaction is also light catalysed. The containers are kept away from light sources for 10 days and the filtrate was recovered by double filtration using filter paper. The concentration of hexavalent chromium was determined on each sample using Atomic Absorption Spectrophotometry; THERMOSCIENTIFIC iCE ™ 3000 SERIES with dedicated flame and furnace at 540nm. The same was repeated with varying concentration of the reductant oxalic acid but same mass of each clay sample.

III. RESULTS AND DISCUSSION

The result obtained from the spectroscopic determination of the hexavalent chromium remaining after 10 days of reduction was as follows:

Mass of clay(g)	Conc. of Cr^{6+} (g/dm^3) for Kaolin	Conc. of Cr^{6+} (g/dm^3) for Bentonite	% of Cr^{6+} reduced by Kaolin	% of Cr^{6+} unreduced by Kaolin	% of Cr^{6+} reduced by Bentonite	% of Cr^{6+} unreduced by Bentonite
1.0	0.049	0.043	51.0	49.0	57.0	43.0
2.0	0.044	0.035	56.0	44.0	65.0	35.0
3.0	0.038	0.029	62.0	38.0	71.0	29.0

4.0	0.031	0.022	69.0	31.0	78.0	22.0
5.0	0.022	0.014	78.0	22.0	86.0	14.0
Blank	0.100	0.100				

Table 1. Concentration of reduced hexavalent chromium in both clay minerals at different masses of the clay

Conc. oxalic acid (mol/dm^3)	Conc. of Cr^{6+} (g/dm^3) for Kaolin	Conc. of Cr^{6+} (g/dm^3) for Bentonite	% of Cr^{6+} reduced Kaolin	% of Cr^{6+} unreduced Kaolin	% of Cr^{6+} reduced Bentonite	% of Cr6+ unreduced Bentonite
0.10	0.049	0.043	51.0	49.0	57.0	43.0
0.20	0.035	0.032	65.0	35.0	68.0	32.0
0.30	0.026	0.023	74.0	26.0	77.0	23.0
0.40	0.021	0.018	79.0	21.0	82.0	18.0
0.50	0.015	0.012	85.0	15.0	88.0	12.0
Blank	0.100	0.100	0.100	0.100	0.100	0.100

Table 2. Concentration of reduced Chromium in 1.0 g clay sample at different concentrations of the reductant

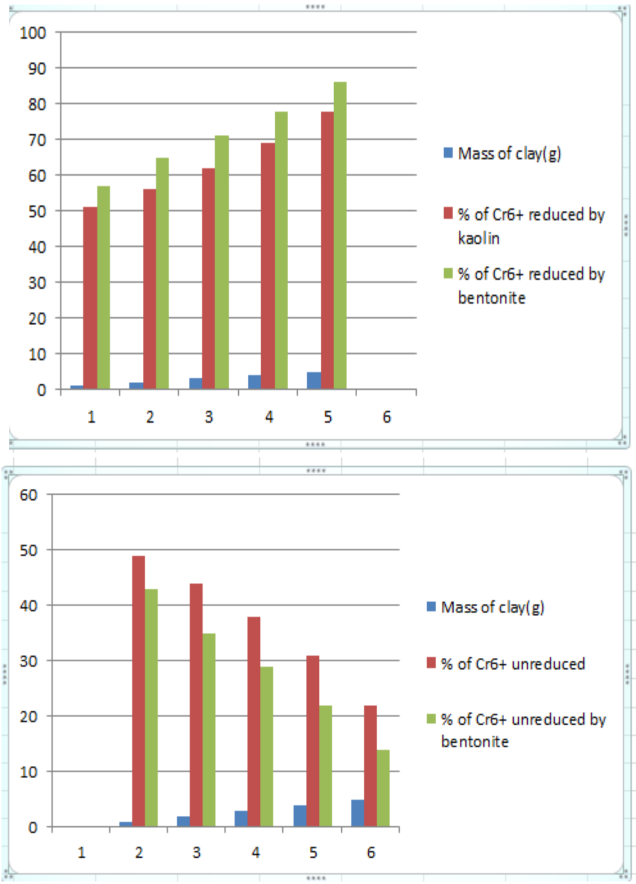

Figure 1. Concentration of reduced hexavalent chromium in both clay minerals at different masses of the clay

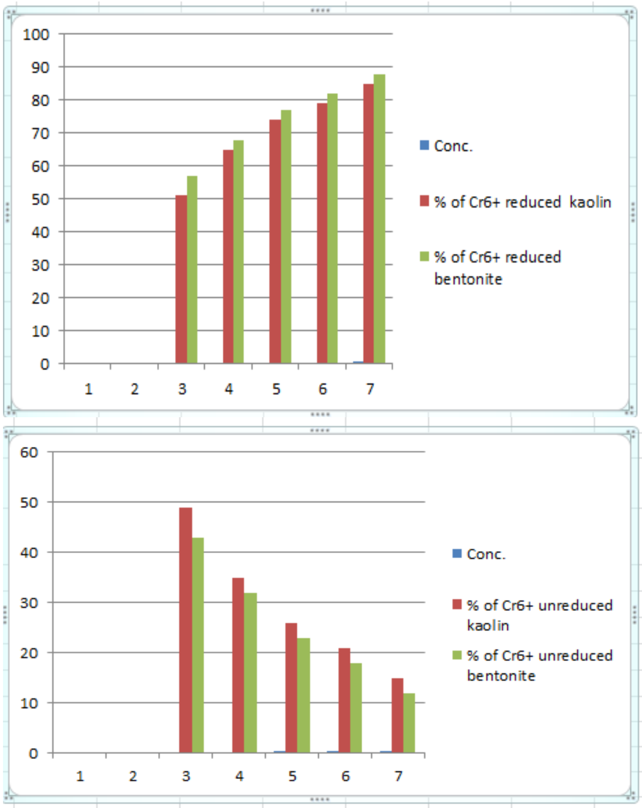

Figure 2. Concentration of reduced Chromium in 1.0 g clay sample at different concentrations of the reductant

Deduction

Results obtained shows increased reduction rate of chromium for bentonite at increasing mass of the clay mineral. This direct proportionality of the reduction rate with mass of clay relates to the obvious increase in surface area with attendant increase in the extent of interaction between the reductant molecules and the chromium molecules. The same was observed when the reduction was carried out using varying concentrations of the reductant. Quantitatively, results show the overall reduction rate of chromium to increase with increase in the mass of the clay mineral 1.0 – 5.0g. However, the rate was found to be higher in bentonite 0.043 – 0.014g/dm^3 and lower in kaolin 0.049 – 0.022g/dm^3 for corresponding mass of clay used. The rate was also found to be higher in bentonite with increasing concentration of the reductant – oxalic acid to the extent of 0.043 – 0.012g/dm^3 and lower in kaolin 0.049 – 0.015g/dm^3 for corresponding reductant concentration used. From experiment, it can be deduced that from the values obtained, the catalytic effect of bentonite is greatest (fastest) and that of kaolinite is slow, that is to say that the rate of catalysis of bentonite > kaolinite. These result suggest that Cr(VI) reduction rate in subsurface environments rich in organic compound may be elevated through catalysis of surface-bound metals and/or soluble species from the clay minerals, and as a result, higher than those expected from aqueous phase reaction alone.

IV. CONCLUSION

The main human activities that increase the concentration of chromium are steel, leather, textile processing including electroplating. These activities will consequently increase chromium concentrations in both surface and ground water. Chromium also escape to the atmosphere through coal combustion and through waste disposal, chromium end up in soils and water. Chromium in soil strongly attaches to soil particles and as a result will not move freely towards ground water and when in ground water, it will adsorb on sediments to become immobile thereby dissolving only a little fraction. However crops contain systems that arrange the chromium up-take to be low enough not to cause any harm to the plant but when the amount in the soil rises to a particular level, it may lead to higher concentrations in plants and crops. Acidification of soils can also influence chromium up-take by crops but it is not known to bio-accumulate in fish. However it is known that high concentrations of chromium due to the disposal of metal products in surface waters can damage the gills of fish residing near the point of disposal. Increased chromium concentrations causes respiratory problems in animals, lower their ability to resist or fight diseases, birth defects, infertility and formation of tumours. The demonstrated accelerated reduction of high levels of chromium by addition of clay minerals indicates that the approach of using clay minerals as catalysts in such in situ remediation may be promising. However, similar studies on different soils and sediment types are required as well as the possibility of a reverse process when allowed over a time.

V. REFERENCES

[1]. Bailey D. G, Tunick M. H, Friedman A. A and Rest G. B (1984). Anaerobic treatment of Tannery waste proceedings of 38th Industrial Waste Conference. Pp 673 – 684 (Google Scholar).

[2]. Bates, L F and Baqi A (1936) *Proc. Phys. Soc.* 48 781 doi: 10.1088/0959-5309/48/5/311

[3]. Chulsung Kim, Yeqing Lan and Baolin Deng (2007). Kinetic study of hexavalent chromium (VI) reduction by hydrogen sulfide through goethite surface catalytic raction. Geochemical Journal vol. 41 pp 397 – 405.

[4]. Débora Vilea Franco, Leonard Morais Da Silva and Wilson F Jardim (2009). Chemical reduction of hexavalent chromium present in contaminated soil using a packed-bed column reactor. Journal of CLEAN – Soil Air Water. (37) 858 – 865.

[5]. Donghee Park, Yeoung-Sang Yun, Jong Moon Park (2005). Studies on hexavalent chromium biosorption by chemically treated biomass of Ecklonia spp. Chemosphere vol. 60 issue 10 pg. 1356 – 1364.

[6]. Elsayed E. M and Saba A. E. (2009). Electrochemical treatment of toxic hexavalent chromium from industrial effluents using rotating cylinder electrode cell. International Journal of Electrochemical Science (4) 627 – 639.

[7]. Fawcett, E (1988). Spin-density-wave antiferromagnetism in chromium. *Reviews of Modern Physics* **60**:209. Bibcode 1988RvMP...60..209F.

[8]. Kalbus, L. H.; Petrucci, R. H.; Forman, J. E. and Kalbus, G. E. (**1991)** Titration of chromate-dichromate mixtures. *J. Chem. Educ.* pg 1-20

[9]. Lepora, Nathan. (2006). Chromium. New York. Marshall Cavendish Benchmark.

[10]. Mario Rivero Huguel and William D. Marshal (2009). Reduction of hexavalent chromium mediated by micron – and nano – scale zero – valent metallic particles. Journal of Environment Monitoring. 11 1072 – 1079.

[11]. Papp, John F; Lipin and Bruce R. (2006). Chromite; *Industrial Minerals & Rocks: Commodities, Markets, and Uses* (7th ed.). SME. ISBN 9780873352338.

[12]. Xiang-Rong Xu, Hua-Bin Li, Xiao-Yan Li and Ji-Dong Gu (2004). Reduction of hexavalent chromium by ascorbic acid in aqueous solutions. Chemosphere 57 (7) 609 – 613.