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REDUCING THE LEACHABILITY OF HEXAVALENT CHROMIUM BY USING VARIOUS REAGENTS

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Abstract:

Hexavalent Chromium is one of the major environmental pollutant. It is very difficult to stabilize the chromium due to its leach ability characteristic. The present study majorly focusing on stabilization of Hexavalent chromium by using various chemical reagents including waste ferrous sulphate, sodium thiosulphate, and sodium metabilsulphate used as stabilizing agents for the Hexavalent chromium. A comparison of leachability & stability of chromium was carried by using reagents the contaminated sample was characterized before and after stabilization & effectiveness of reagents was evaluated using leachability tests. Results showed that sodium thiosulphate is more effectively reduced the leachability & chromium content in the contamination soil, the acid buffering capacity & stability of hexavalent chromium content of sodium thiosulphate is better than other specific reagent. The study reveals that sodium thiosulphate had a better effect than other reagents on the chromium stabilization in contaminated sample. The sodium thiosulphate effectively enhanced the stabilization & immobilization of chromium and reduced the toxicity & leachability.

Key words: Hexavalent chromium, Sulphuric acid, Cement, Fly ash, contaminated sample & Sodium thiosulphate.

Introduction:

Chromium in hexavalent form one of the most important heavy metal in soil due to its high toxicity, carcinogenicity and leachability characteristics contamination of soil chromium is a serious problem in various parts of India. The chromium is released into the soil by different types of industries like tannery, electroplating etc., generally chromium in soil occurs in Cr (III) or Cr (VI) states. Whereas Cr (III) is a very useful nutrient for plant growth coming to Cr (VI) is dangerous species & carcinogenic to humans chemical reduction removes chromium (VI) very effectively based on the use of reducing agents such as ferrous sulphate, sodium thiosulphate and sodium metabisulphate. Among which sodium thiosulphate and ferrous sulphate are the effective reagents in chromium reduction, the reduction of Cr (VI) with the sodium thiosulphate, ferrous sulphate can be written as follows

Many researchers have focused & studies on how to established the chromium waste however many of them are focused on leachability & content of Cr (VI) among various known technologies Solidification/Stabilization is the best technology for the treatment of chromium & also pretreatment of waste before landfilling. The technology is cost effective safe & reliable where the metals are converted into highly insoluble form which the metals are converted into highly insoluble form which further cannot leach into surrounding environment. Under alkaline conditions digestion of chromium is almost completely reduced, when the Na & chromium ratio is in between 30-80 mg/ltr the chromium concentrations in the sample after WLT range between 0.15 to 0.4 mg/Ltr which that Sodium thiosulphate founds best reagent for the in-situ remediation chromium contaminated soil.

MATERIALS & METHODOLOGY:

Materials

The samples was collected in a structure way as area and depth of the waste (picture-1 & 2). The samples have brought to lab and made it as homogeneous with proper crushing and mixing (Picture-3).

Sampling Site

The study was carried out at Talcheru town which is found in Odisha State. The required waste samples were collected from the different areas and depths.

Sample Collection and Preparation

Waste Sampling

The waste samples were collected from six different places and various depths as top, middle & bottom (Figure 1). Sampling was done based on the waste pile height and total area. Two kg of waste samples was collected in a clean polyethylene bags and brought to the laboratory by an ice bag. All soil samples were mixed together and homogenized to form one composite sample. Then the composite sample was air dried for three days and sieved through a 2–mm sieve to remove large debris, stones, and gravels.

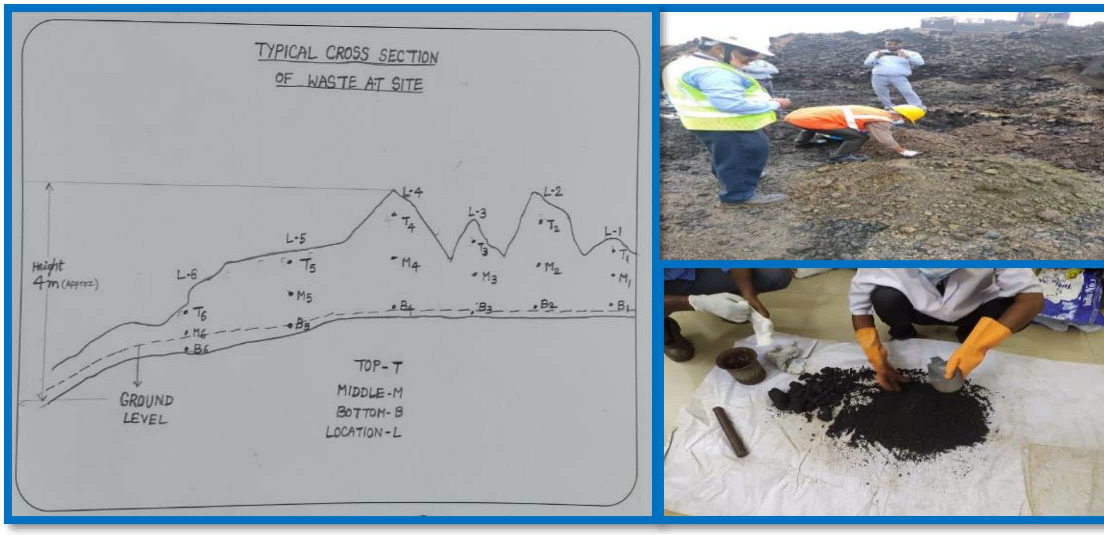


Figure-1 Sample collection diagram, sampling and preparing homogeneous samples

Validation of the Method

The metal concentration and speciation were determined at optimum conditions of ratio of acids mixtures, time of digestion, and temperature by varying each condition and keeping others constant. Then, the determination of the concentration of total Cr & Cr (VI) was done using the optimized parameters using AAS & Colorimetric method. The spiking experiments were analyzed by using standard reference materials. The validations of the method were done by adding 1 mL of reference standard material to waste samples. The digestion was carried out side by side with the sample digestion. For the case of Cr (VI) on the above spiked samples prepared diphenyl carbazide solution was added and a red violet color was developed immediately. From the absorbance reading the amount of Cr (VI) was obtained using calibration curve. Cr (VI) was measured using calorimetric method.

Water Leaching Test

Leachability tests are conducted by preparing a suspension of waste and water i.e taking 100 gm. of waste and filling up to 1 liter with distilled water, stirring or shaking for 24 hrs. at 30 rpm by rotating shaker, filtering the solids and analyzing the filtrate.

Sample Preparation

The above filtered samples was transferred into 100 ml volumetric flask. Add 0.25 mL H_3PO_4. Use 0.2N H_2SO_4 and a pH meter to adjust solution to pH 2.0 ± 0.5. Transfer solution to a 100-mL volumetric flask, dilute to 100 mL, and mix. Add 2.0 mL diphenylcarbazide solution, mix, and let stand 5 to 10 min for full color development. Then measure the absorbance at 530 or 540 nm, using reagent water as reference. Correct absorbance reading of sample by subtracting absorbance of a blank carried through the method (APHA). Measure the concentration of Cr (VI) using standard graph as reference.

Analysis of Waste Samples for Total Cr and Cr (VI) Levels

The instruments were calibrated using five series of working standards for AAS (Analytical Jena 800, Germany) and five for UV/Vis spectrophotometer (Lab India, India). The working standard solutions of Cr were prepared freshly from 1000 ppm stock solution (Merck, 99.99%) by diluting the intermediated standard solution (25 mg/L). The instrument was calibrated using five series of working standards for UV/Vis spectrophotometer. A solution of 1 mL of diphenyl carbazide was added to each sample and working standard solution. Similarly, the pH of the spiked sample solution was adjusted to the desired value (pH = 1) at which the recovery of Cr (VI) is the highest. Then the equilibrium concentration of Cr (VI) in the organic phase was determined spectrophotometric ally by measuring the absorbance of Cr (VI)-DPC (diphenyl carbazide) complex at 540 nm.

Results and Discussion

Recovery of the Method

As shown in Tables 1 and 2, the results of percentage recoveries of total Cr and Cr (VI) for samples were within the acceptable range (figure-2). The average percent recoveries were 95±3.5 for waste samples using FAAS and UV Vis spectrophotometer. Therefore, this verifies that the optimized digestion procedure was valid for sample analysis.

Figure-2 Standard and samples analysis for Cr^{6+} in UV Vis- Spectrophotometer

Calibration graph for Cr^{6+}

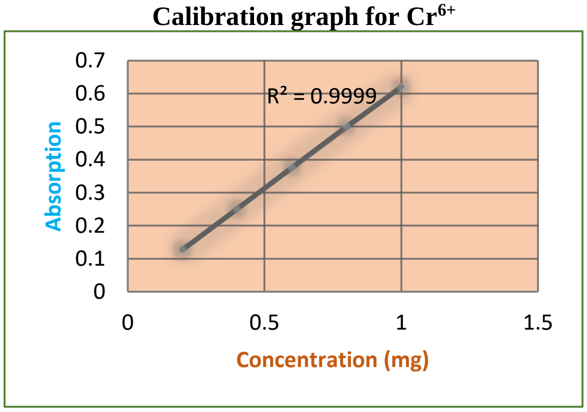


Table-1 Standard linearity for Cr^{6+}

Standard Concentration (mg/l)	Absorbance
Blank	0000
0.2	0.1260
0.4	0.2501
0.6	0.3764
0.8	0.5000
1.0	0.6184

Table-2 sample analysis before stabilization

S. No.	Sample ID	pH	LOD (%)	Total Chromium (WLT), mg/L	Hexavalent Chromium (WLT), mg/L
1	TOP-1	10.81	15.26	99.2	88.8
2	MID-2	10.91	16.33	86.2	70.7
3	BOT-3	10.82	15.87	139	96.9
4	COMP-4	10.75	14.31	82.2	68.1
5	COMP-5	10.52	13.96	63.2	50.9
6	COMP-6	10.99	15.73	81.9	68.6
Maximum		**10.99**	**16.33**	**139**	**96.9**
Minimum		**10.52**	**13.96**	**63.2**	**50.9**
Average		**10.80**	**15.24**	**91.9**	**74.0**

Table-3 Stabilization with Ferrous sulfate

Material	Trail-1	Trail-2	Trail-3
Waste (gm)	20	20	20
1:1 HCl (%)	15	15	15
Ferrous Sulphate (%)	20	20	20
Lime (%)	5	10	5
Cement (%)	10	10	10
Fly ash (%)	20	20	0
LD Slag (%)	0	0	50
WLT Cr^{6+}) (mg/L)	**20**	**18**	**8**
Status	**Fail**	**Fail**	**Fail**

Table-4 Stabilization with sodium metabisulfite

Material	Trail-1	Trail-2	Trail-3
Waste (gm)	20	20	20
H2So4 (%)	1.5	1.5	1.5
Sodium Metabisulfite (%)	0.5	1	1.5
Cement (%)	10	10	10
Fly ash (%)	20	20	20
WLT Cr^{6+} (mg/L)	**22**	**17**	**11**
Status	**Fail**	**Fail**	**Fail**

Stabilization chemical equation

Ferrous Sulfate - $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$.

Sodium metabisulfite - $Cr_2O_7 + 2Na_2S_2O_5 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 2Na_2SO_4 + H_2O$

Stabilization with Sodium thiosulfate (Effect of Sodium thiosulphate)

The Cr waste samples has been treated with sodium thiosulfate in different concentration and the stabilization process start with acidify the sample (<1 pH) followed by adding sodium thiosulfate, fixing the Cr^{3+} with cement and fly ash (Table-5).
Stabilization Trails were carried as per the standard procedures with great safety precaution.

Table-5 Stabilization with Sodium thiosulfate

Material	Trail-1	Trail-2	Trail-3	Trail-4
Waste (gm)	20	20	20	20
H2So4 (%)	1.5	1.5	1.5	1.5
Sodium Thio Sulphate (%)	4	4.5	5	6
Cement (%)	10	10	10	10
Fly ash (%)	20	20	20	20
WLT Cr^{6+} (mg/L)	**1.3**	**0.8**	**0.38**	**0.23**
Status	**Fail**	**Fail**	**Pass**	**Pass**

Stabilization chemical equation

$$Cr_2O_7 + Na_2S_2O_3 + 2H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Na_2SO_4 + 2H_2O$$

Conclusions

This study compared the leachability and stability of $FeSO_4$, $Na_2S_2O_5$ and $Na_2S_2O_3$ 5 -stabilized Cr (VI)- Contaminated waste. A series of Water leachability Test (WLT), sequential extraction, and Colorimetric tests were performed on Cr (VI)-contaminated waste. The influence of stabilizing agent dosage on the leachability and stability was assessed. The following conclusions are made

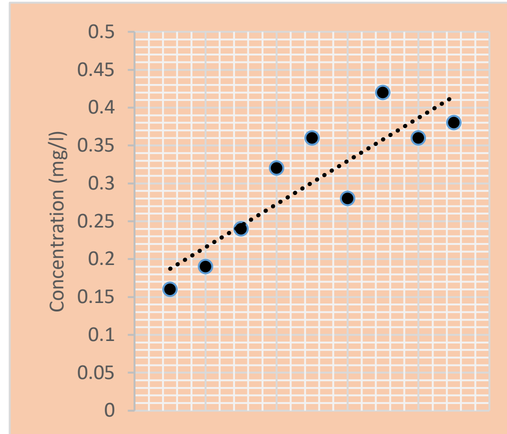
1. The pH and redox potential of the $Na_2S_2O_3$ stabilized were better than those of the $FeSO_4$ stabilized waste regardless of $Na_2S_2O_3$.The concentrations of Cr(VI) and Cr leached from the stabilized waste with $FeSO_4$ were larger than those of $Na_2S_2O_3$ at the same amount or less. The Cr (VI) content in the stabilized waste was decreased with the increase in $FeSO_4$ and $Na_2S_2O_3$ % and that in the $Na_2S_2O_3$ stabilized waste decreased more noticeably compared with that in the $FeSO_4$ stabilized waste at the same amount. This finding reflected that $Na_2S_2O_3$ presented a better effect than $FeSO_4$ in the stabilization of Cr (VI) and Cr.
2. The leached Cr (VI)/Cr from the TCLP was considerably larger than that from WLT leaching due to the difference in the stabilization mechanism and the pH of the leaching solutions. The bio accessibility risk of Cr in the FeSO4-stabilized soils was higher than that in the $Na_2S_2O_3$ stabilized soils due to the difference in stabilization mechanisms of Cr (VI) between $FeSO_4$ and $Na_2S_2O_3$.

3. The differences in the leachability, bio accessibility, and toxicity of Cr(VI) and Cr in the $FeSO_4$ and $Na_2S_2O_3$-stabilized soils were attributed to the changes in mineral composition. For the FeSO4-stabilized soil, the Cr (VI) was mainly converted to Cr (OH) 3. For the $Na_2S_2O_3$ stabilized waste, the Cr (VI) was reduced to Cr (III).

Table-6 confirmation trails in different concentration

S. No.	Sample No.	Cr^{6+} in WLT (mg/L)	Recipe	After Stabilization Cr^{6+} in WLT (mg/L)	Status (<0.5mg/l)
1	5	51	**Waste + 1.5% H_2SO_4 + 5% $Na_2S_2O_3$ + 10% Cement + 20% Fly Ash.**	0.16	Pass
2	5	51		0.19	Pass
3	5	51		0.24	Pass
4	2	71		0.32	Pass
5	2	71		0.36	Pass
6	2	71		0.28	Pass
7	3	97		0.42	Pass
8	3	97		0.36	Pass
9	3	97		0.38	Pass

Cr^{6+} (Stabilized waste) concentration



This technical process is very good and long term stable with chromium and there is no impact & very low leachable with water and also low cost treatment. It is used for avoid toxic leachate generation and contamination of environment while and after stabilization/solidification process concern.

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