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Acid Free Cr(VI) Reduction in Contaminated Ground Water Collected from Chromite Ore Processing Residue Dump Site

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ABSTRACT

Present study explore the possibility of reducing toxic Cr(VI) to Cr(III) without adding acid externally to the level of regulatory norms. Trial experiments were carried out with standard solution having Cr(VI) concentration of 1976 mg/L to reveal the suitability of $SnCl_2$ for the reduction of Cr(VI) in the absence of mineral acid. Under the same conditions contaminated ground water from COPR dump site was examined. Complete reduction of Cr(VI) and level of total Cr to discharge limit were observed within fifteen min. for both simulated and contaminated water. This green chemistry approach and lower time duration for reduction is not reported earlier. The efficacy of the process is ascertained by analysing the other important heavy metals like Ni, Cu, Pb and Zn using AASP. Level of chloride, sulphate, BOD, TDS and pH of the treated water were also recorded. Results imply that SnCl2 effectively reduces Cr(VI) to Cr(III) in the absence of acid.

Keywords: Contaminated groundwater, Hexavalent Chromium, Tin Chloride, Reduction and Precipitation.

INTRODUCTION

Industrial pollution is one of the evils that challenge the earth, air, water and land. Thus there is a striving need for efforts to manage its natural resources, eco system and bio-diversity from the dumping of hazardous waste on land. Many of the countries in the world are prone to land and ground water pollution that endures from Industrial activity. COPR contaminated sites have been identified in USA, UK, China, Russia, Kazakhstan, India and Pakistan[1]. Improper dumping of Chromite Ore Processing Residue (COPR) significantly contaminate the soil and ground water by leaching of Cr(VI) and cause environmental impact to the aquifers and surface water and health problems to the surrounding inhabitants[2-3]. Much studies have already been done to remediate Cr(VI)contaminant in ground water by physical remediation[4], Chemical[5], electrochemical[6] and biological transformation[7]. Adsorbents synthesized from groundwater treatment residuals, eucalyptus bark, palm shell activated carbon with polyethyleneimine, agricultural waste biomass, distillery sludge, have been used for the removal of Cr(VI)[8-9]. Removal of Cr(VI) has also been carried out by Phytoremediation[10], constructed wetland[11] and electrochemical methods[12].

The most commonly used technology is the precipitation of metal ions as hydroxides, under appropriate pH conditions[13]. For the reduction of toxic Cr(VI) into nontoxic form of Cr(III), a number of reducing agents like ferrous sulphate heptahydrate and monohydrate, Sodium meta bisulphite, Sodium sulphite, Sodium dithionite, amine based compounds (hydrazine, hydroxylamine) and Ferrous sulphate have been used[14-15]. Addition of 1.0% of tin chloride reduces 25mg/L Cr(VI), present in the hydrated cement[16].

Tin(II) chloride is an important industrial reducing agent, used in the preparation of glass and plastic for metallizing, metallized glazing, and electronic components on a plastic base, as a soldering flux, as a mordant in dyeing, and in the manufacture of tin chemicals, colour pigments, and sensitized paper[17-18]. Tin(II) chloride is added to lyophilized kits to prepare 99mTc-labelled tracers (which account for about 80% of radiopharmaceuticals). It is important in nuclear medicine as an essential component in diagnostic agents used to visualize blood, heart, lung, kidney, and bone[19-21]. Tin(II) chloride is also used in certain countries as a food additive (as a preservative and colour retention agent)[22].

The main objective of the present work is to investigate the performance and effectiveness of $SnCl_2$ for reduction of Cr(VI) to zero level in the contaminated groundwater at TCCL study area located at Ranipet, Vellore, Tamilnadu, India. Present work explore a green chemistry approach for the complete removal of Cr(VI) using Tin Chloride.

METHODS AND MATERIALS

Laboratory studies

The analytical grade $SnCl_2$, HCl and NaOH procured from E-Merck India Ltd., were used as such. High purity distilled water was used for analysis. Analytical grade HCl and NaOH were used for pH adjustment using pH meter 240 (Elico L1614). By measuring the absorbance at 540 nm using UV-Visible Spectro-photometer (UV- 3200, Lab India), the concentration of Cr(VI) was measured photometrically with diphenylcarbazide and heavy metals were determined on an Atomic Absorption Spectrometer (Shimadzu 6800).

The percentage removal of hexavalent chromium was calculated as

$$\% \text{ Removal (Cr VI)} = [(C_i - C_f)/C_i] \times 100$$

Where Ci is the initial Cr(VI) concentration (mg/l) in wastewater sample, Cf is the final Cr(VI) concentration after treatment.

Chromium Contaminated Ground water

The samples of chromium contaminated groundwater (CGW) was collected from the bore wells located at the TCCL site, Ranipet, Vellore, Tamil Nadu, India. The samples were collected in polypropylene containers. The concentration of Cr(VI) was 1976 mg/L. The other parameters measured were turbidity - 25.4NTU, total dissolved solid - 9960 mg/L , electrical conductivity - 15,659 µs/cm, Sodium - 125-140 mg/L, Ammonium -1.5 - 4 mg/L, Sulphate - 2500-2860 mg/L, Calcium Hardness 310-350 mg/L, Magnesium Hardness - 1820-1910 mg/L, Chloride - 595 mg/L and Nitrate - 210 mg/L.

RESULTS AND DISCUSSION

Treatment of synthetic Cr(VI) contaminated water. The concentration of Cr(VI) in the sample was brought to 1976 mg/L by dissolving 5.588 g of $K_2Cr_2O_7$ in 1000 ml of distilled water[23]. The pH and reducing agents[24] are the two important variables in removing Cr(VI) by reduction and precipitation method. When the two variables are combined together, the net result shows the synergy effect of the reducing agent and pH in the reduction of Cr(VI). In order to ascertain the individual efficiency of reducing agent and the effect of pH in the removal of Cr(VI), the studies were carried out by varying the concentration of reducing agent with and without adjusting the pH externally. The results obtained are presented in Table 1.

Results implied, incremental effect of reducing agent on reduction of Cr(VI). Additional increase in dosage after 1400 mg/L, displayed no significant change in the percentage reduction.

Allowing the treated sample for long duration did not show any appreciable change in the reduction of Cr(VI).

Earlier report[25] recommended pH 2 as the convenient pH for the reduction of Cr(VI) to Cr(III).

Based on this, an approach was made at pH 2 by adding HCl along with $SnCl_2$. The results presented in Table 2 reveals that the presence of acid did not alter appreciably the reducing power of stannous chloride. This is in agreement with the earlier report by Marks Neidle *et al.,*[26].

Table 1: Reduction of Cr(VI) without adjusting pH in SCW

Dosage of $SnCl_2$ (mg/L)	pH after addition of $SnCl_2$	Concentration of Cr(VI) after 15 min. (mg/L)	% reduction after 15 min.
200	4.6	1429	27.68
400	3.4	1070	45.85
600	2.88	676.8	65.74
800	2.75	507.5	74.31
1000	2.70	308.76	83.87
1200	2.66	148.55	92.48
1400	2.68	0	100

Table 2: Reduction of Cr(VI) at pH-2 in SCW

Dosage of $SnCl_2$(mg/L)	Concentration of Cr(VI) after 15 min. (mg/L)	% reduction after 15 min.
200	1287.5	34.84
400	1046.5	47.03
600	614.0	68.92
800	410.0	79.25
1000	220.8	88.82
1200	90.8	95.40
1400	0	100

Comparison of the results presented in Table 1, Table 2 and Fig. 1 reveals that the present observation took forward the precipitation studies towards green chemistry approach.

Treatment on contaminated Cr(VI) groundwater

The concentration of hazardous Cr(VI) in the ground water indicates not only the toxicity of the solution but also the oxidizing power of the

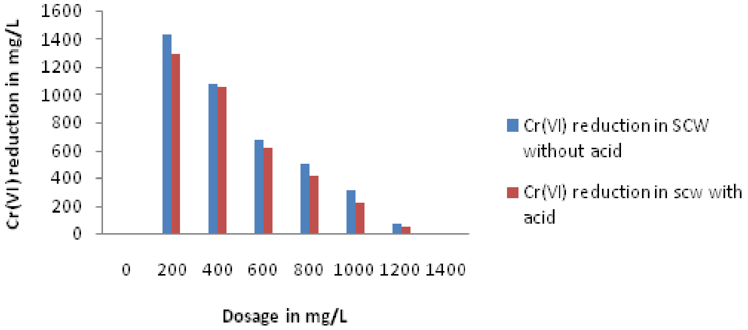

Fig. 1. Reduction of Cr(VI) with and without addition of acid in SCW

contaminated water. Based on the results obtained from synthetic Cr(VI) water, an experiment on real contaminated Cr(VI) ground water was executed at the optimized concentration of reducing agent.

Table 3: Reduction of Cr(VI) without external addition of acid in CGW containing 1976 mg/L of Cr(VI)

Dosage of $SnCl_2$ (mg/L)	pH	Concentration of Cr(VI)	%reduction of Cr(VI)
200	5.2	1504	23.88
400	4.2	1220	38.25
600	3.61	986	50.10
800	3.34	608	69.23
1000	3.102	383.5	80.59
1200	3.06	85	95.69
1400	2.769	0	100

Comparison of Table 3, Table 4 and Fig. 2 shows that the amount of stannous chloride reduces with reduction in concentration of Cr(VI) present in untreated water.

Table 4: Reduction of Cr(VI) without external addition of acid in CGW containing 1271 mg/L of Cr(VI)

Dosage of $SnCl_2$ (mg/L)	pH	Concentration of Cr(VI)	% reduction of Cr(VI)
200	6.2	730	42.56
400	4.6	429.8	66.18
600	3.4	193	84.81
800	2.9	52.7	95.85
1000	2.6	0	100

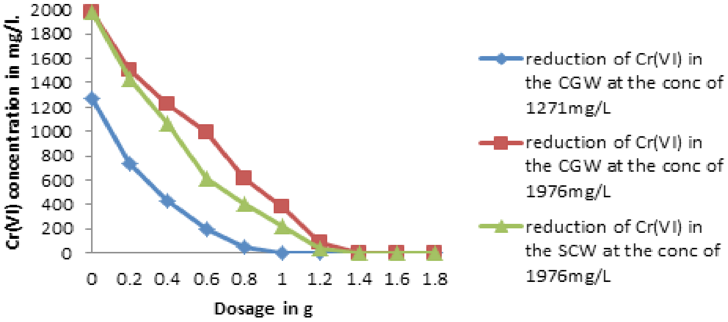

Fig. 2. Reduction of Cr(VI) without addition of acid in SCW and CGW

Table 5: Results of the various parameters before and after treatment for CGW at pH-9 precipitation

Parameters	CGW	Treated CGW	Disposal standard
pH	6.22	7.1	5.5-9.5
Cr(VI) (mg/L)	1976	0.00	0.05
Total Chromium (mg/L)	2399.9	0.0256	2.00
Chloride(mg/L)	135	5494	1000
Sulphate (mg/L)	2526	1139	1000
BOD (mg/L)	53	13	30
Cadmium (mg/L)	0.0549	0.0142	2.0
Nickel (mg/L)	0.2737	0	3.0
Copper (mg/L)	0.1200	0.0230	3.0
Lead (mg/L)	0.6236	0.052	0.1
Zinc (mg/L)	2.8893	0.042	1.0
Total Dissolved Solids (mg/L)	4200	10000	2100

The treated water was analysed for other important parameters and the results obtained are given in Table 5. The concentrations of Cr(VI) and total Cr in the treated water fall within the regulatory level.

CONCLUSION

The observations in the above results reveal that the reduction of Cr(VI) can be achieved without adding acid externally. This observation has not been reported elsewhere. Further, the level of Cr(VI), total Cr and pH of the discharge water are within the recommended level. Shortest time duration reported in this paper is the first observation reported so far. The high value of TDS can be reduced by Reverse Osmosis Process. To handle the sludge generated in this process, solidification[27] method is under investigation.

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