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Heavy Metal Stabilisation

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Abstract: Heavy metal chemical stabilization with synthesized heavy metal chelating agents was assessed for the solid waste from chrome plating process. In the central railway workshop at Trichy, Tamilnadu, India chrome plating is done for rail engines. The solid waste (chrome sludge) finally obtained consists of heavy metals chromium, lead, zinc, cadmium, etc. which can leach. A new kind of heavy metal chelating agent showed more attractive competition than inorganic chemicals in stabilizing chrome sludge. The synthesizing method and treatment efficiency of heavy metal chelating agent in treating chrome sludge are experimentally studied and compared with the results of inorganic chemical agent sodium sulfide and organic chemical agent EDTA. The stabilized product using the synthetic chelating agent and EDTA can meet the land fill disposal controlling standards for heavy metal waste. The pH dependent leaching experiment showed the stabilized chrome solids by treatment with heavy metal chelating agents could ensure long term stabilization with a broad range of pH value. Thus the risk of secondary pollution for the stabilized products was reduced dramatically when the environmental condition changes during its disposal period

Introduction

Heavy metal contamination may be found at battery acid recycling sites, electroplating facilities, military installations, firing ranges and associated mining activities. Due to the broad range of vital applications, it is obvious that the waste produced from the industry would also be high. The sludge is termed hazardous due to its containment of the heavy metals chromium, lead, zinc and cadmium. There is much concern over the emissions of heavy metals to the environment due to their associated health hazards, especially heavy metals can exert a range of toxic health effects including carcinogenic, neurological, hepatic, renal and hematological. With regard to toxicity, the chrome sludge is most harmful because of its high content of leachable heavy metals. Chemical stabilization[1,2] is one method of reducing the leachablity of heavy metals in the solid waste and will not increase the volume of the stabilized products. The principal aim of chemical stabilization is to form new less soluble mineral phases that are more geo -chemically stable in leaching environments. In this paper, the chrome sludge obtained from the central railway workshop at Trichy, Tamilnadu, India was stabilized using chelating agents.

Materials and Methods

The chrome sludge samples were taken from the central railway work shop, Trichy, India. The particle size of the chrome sludge is between 1 and 1000 μm and 50% of the particle size is less than 100 μm. The samples of 0.5 g weighed are digested in 5:1 ratio of hydrochloric acid and nitric acid and evaporated to near dryness. Further nitric acid was added and digested for 8 hrs. The solution was then filtered and diluted prior to introduction to atomic absorption spectroscopy system. The chelator EDTA is used for metal stabilization. The heavy metal chelating agents can be synthesized experimentally[3] through the reaction by different types of polyamines and carbon disulfide in alkaline conditions. Heavy metal chelating agents were synthesized in an autoclave reactor. The sludge material used should be processed to provide size fraction less than 1 mm. chrome sludge. The chrome sludge, chelating agent and water are mixed in a mixer and stabilized product has been collected. The toxicity of the chrome sludge should be determined using TCLP[4] (Toxic characteristics leaching procedure).

Extraction procedure

The extraction fluid 1 has been prepared from glacial acetic acid, water and 1N sodium hydroxide and diluted to 1litre of pH = 4.93. The extraction fluid 2 has been prepared with glacial acetic acid and water to a volume of 1 litre of pH = 2.88. The sample of 50 g and extraction fluid are taken in a extractor bottle and secure in a rotatory agitator at 32 rpm for 20 hrs. After extraction, the material in the extractor has been separated by filtration. The filtered liquid extract is TCLP extract and analysed for pH. This extract has been subjected to atomic absorption spectrometer. The pH dependent leaching procedure[5] has been followed.

Results and Discussion

Table 1 Primary composition and leachablity toxicity of chrome solid waste

Metal	Dry sludge mg/l	TCLP mg/l
Chromium	105.63	120.45
Cadmium	0.01	0.02
Lead	0.09	2.20
Zinc	36.40	24.50

Table 2 Composition of chrome and lead in a sample of solid waste

Sample	Chromium	Lead
Chrome sludge 1	104.83	2.27
Chrome sludge 2	105.97	2.19
Chrome sludge 3	104.98	2.13
Average	105.26	2.20

Heavy metal concentration of the samples were determined by composition analysis method. The primary composition and leachablity toxicity of chrome solid waste are shown in Table- 1. The concentration of the heavy metals chromium and lead alone were tested for some of the three samples to arrive at an average concentration. The composition was determined by the acid digestion method using nitric acid. The composition of chrome and lead in a sample of solid waste are shown in Table -2. The experiment dosage of different chemicals in each group has been taken as 2, 4 and 6 and another set as 20, 40 and 60% by weight respectively. The % reduction rate in heavy metal lead and chromium concentrations at 2, 4, 6, 20, 40 and 60 % dosage of the stabilizing agent has been shown in Table -3 and Figure 1. The Leached concentration of lead and chromium at various pH values under 40, 60% dosage of EDTA, synthetic chelating agent and sodium sulphide has been shown in Table 4 and 5 respectively.

Table 3 The % reduction rate in heavy metal lead and chromium concentration at 2, 4, 6, 20, 40 and 60 % dosage of the stabilizing agent

% dosage of the stabilizing agent		Sodium sulphide		EDTA%		Synthetic chelating agent %	
Lead	**chromium**	**Lead**	**chromium**	**Lead**	**chromium**	**Lead**	**chromium**
2	2	0.18	1.54	5.77	4.26	6.45	3.11
4	4	7.50	4.18	9.78	7.48	10.36	6.29
6	6	9.68	8.50	14.80	12.10	15.62	11.02
20	20	32.91	59.39	65.56	72.95	74.31	65.53
40	40	93.73	85.72	95.44	91.76	95.64	88.94
60	60	95.38	90.15	96.53	98.67	98.85	93.98

Table 4 Leached concentration of lead at various pH values under 40, 60% dosage of EDTA, synthetic chelating agent and sodium sulphide

pH	Leached concentration of lead under 40% Dosage mg /litre			Leached concentration of lead under 60% Dosage mg /litre		
	EDTA	Synthetic chelating agent	Sodium sulfide	EDTA	Synthetic chelating agent	Sodium sulfide
2	41.36	40.51	43.78	23.30	25.76	27.83
4	25.63	21.94	35.26	14.32	13.97	18.57
6	5.89	3.82	10.74	6.29	5.88	8.82
8	2.13	1.27	35.52	3.87	1.92	2.96
10	1.87	1.35	1.66	1.31	1.27	1.54
12	1.87	1.28	1.18	1.22	1.03	1.32

Table 5 Leached concentration of chromium at various pH values under 40, 60% dosage of EDTA, synthetic chelating agent and sodium sulphide

pH	Leached concentration of chromium under 40% Dosage mg /litre			Leached concentration of chromium under 60% Dosage mg /litre		
	EDTA	Synthetic chelating agent	Sodium sulfide	EDTA	Synthetic chelating agent	Sodium sulfide
2	1701.83	1753.20	1931.66	925.41	953.58	1257.80
4	985.67	1168.56	1454.64	489.33	502.86	889.60
6	88.12	125.42	366.28	72.91	83.67	213.83
8	11.75	23.89	100.68	3.86	5.32	28.97
10	1.02	1.05	2.30	0.50	0.50	0.51
12	1.00	1.05	1.52	0.50	0.48	0.50

From the graphical result obtained in Figure 1, observe that the percentage composition of the stabilizing agents is very low that the amount of lead leached is more than the regulated composition. Hence the reduction rate of lead being leached is very low which implies that the amount of stabilizing agents to be added is to be increased. In figure 2, the heavy metal lead is stabilized to a greater extent rather than the previous composition. Also from the result we could observe that synthetic chelating agent has more effect of stabilizing lead than EDTA and sodium sulfide. In figure 3, it could be seen that the percentage composition 2,4 and 6% of the stabilizing agents are not considerably enough to stabilize the heavy metal chromium and obtain poor reduction rate in the amount of chromium being leached. Hence an increase in the amount of stabilizing agents is essential for the chromium to be effectively stabilized. In figure 4, the heavy metal chromium is stabilized to a greater extent.

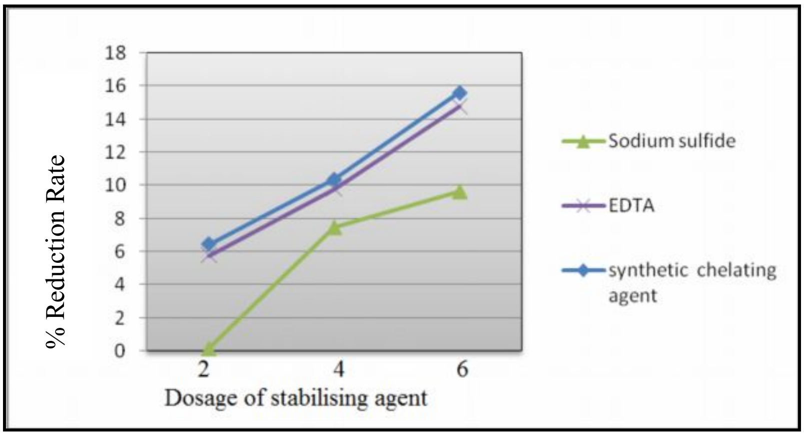

FIG 1. % Reduction rate in heavy metal lead concentration at 2,4,6% dosage of the stabilizing agent

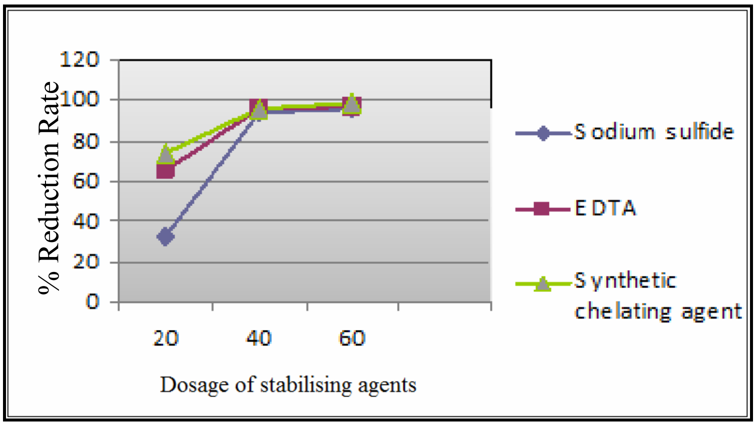

FIG 2. % Reduction rate in heavy metal lead concentration at 20, 40, 60% dosage of the stabilizing agents

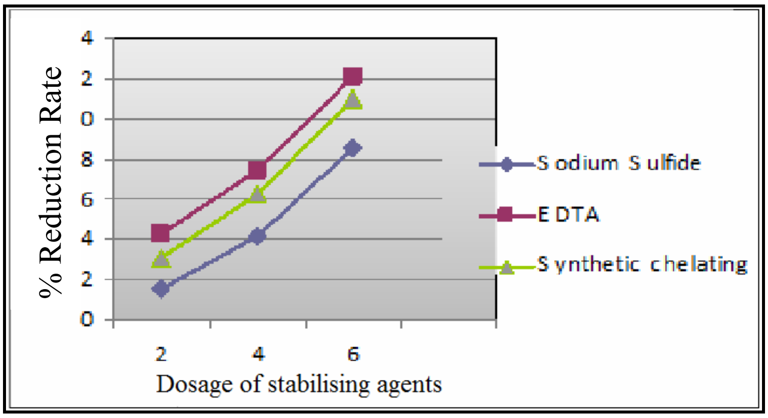

FIG 3 % Reduction rate in heavy metal chromium concentration at 2, 4, 6% dosage of the stabilizing agents

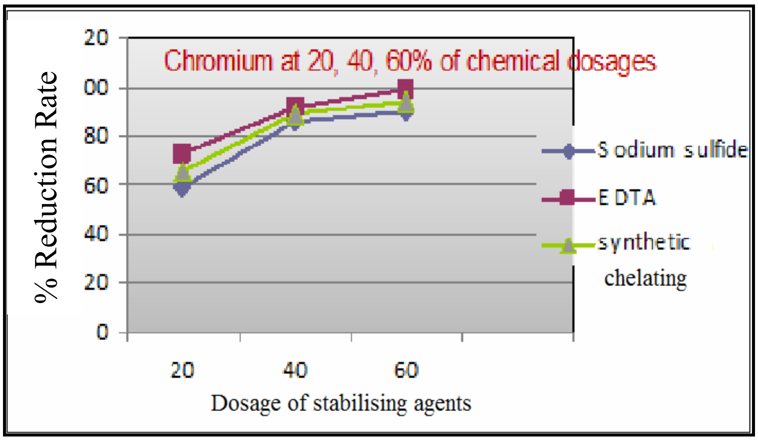

FIG 4 % Reduction rate in heavy metal chromium concentration at 20, 40, 60% dosage of the stabilizing agents

For pH varying from 2, 4, 6 8, 10, 12 the leachate test[5] was performed for the chrome solids. In figure 5, it is observed that at 40% dosage of EDTA, the heavy metal lead is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact[6], which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH hence the metal lead is leached more during lower pH. In figure 6, the metal lead is leached more during lower pH. It could also be understand that lead would exhibit long term stabilization at alkaline pH conditions. In figure 7, the heavy metal lead is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact, which the heavy metals show higher solubility under acidic condition and tend to show attractiveness to lower pH. In figure 8, at 60% dosage of EDTA, the heavy metal lead is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact, which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. From fig 9 it is observed that, at 60% dosage of synthetic chelating agent, the heavy metal lead is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact, which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. Hence the metal lead is leached more during lower pH. From the fig 10 it is observed that, at 60% dosage of sodium sulfide, the heavy metal lead is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact[7], which the heavy metals show higher soluble under acidic condition and tend to show attractiveness to lower pH. Hence the metal lead is leached more during lower pH. Hence the metal lead is leached more during lower pH. At 40% dosage of EDTA, the heavy metal chromium is being leached at a higher rate at acidic pH than at alkaline condition as observed from the fig 11. This is due to the fact, which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. Hence the metal chromium is leached more during lower pH. From fig 12 it is observed that at 40% dosage of synthetic chelating agent, the heavy metal chromium is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact, which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. There is considerably very less amount of chromium being leached from pH 10 onwards, which implies that the heavy metal is stabilized strongly only at alkaline pH levels. From fig 13, it is observed that at 40% dosage of sodium sulfide, the heavy metal chromium is being leached at a higher rate at acidic pH than at acidic pH than at alkaline condition. This is due to the fact[8], which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. There is logarithmic decrease in the amount of chromium leached as the pH level is increased. Hence it is understood that the heavy metal chromium is in stable condition without any movement, bound to the chemical agent, only at alkaline pH levels. From fig 14, it is observed that at 60% dosage of EDTA, the heavy metal chromium is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact, which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. Hence the metal chromium is leached more during lower pH. The amount of chromium leached has considerably decreased to a greater extent than for 40% composition. So it implies long-term stabilization of the immobilized heavy metal. From fig 15, it is observed that at 60% dosage of synthetic chelating agent, the heavy metal chromium is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact, which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. Hence the metal chromium is leached more during lower pH. The amount of chromium leached has considerably decreased to a greater extent than for 40% composition. So it implies long-term stabilization of the immobilized heavy metal. From fig 16, it is observed that at 60% dosage of sodium sulfide, the heavy metal chromium is being leached at a higher rate at acidic pH than at alkaline condition. This is due to the fact, which the heavy metals are highly soluble under acidic condition and tend to show attractiveness to lower pH. Hence the metal chromium is leached more during lower pH. The amount of chromium leached has considerably decreased to a greater extent than for 40% composition. Hence at acidic pH conditions the amount of chromium leached is very high that imposes severe hazardous problem. Therefore the pH of the disposal site should be moderate and high to ensure stabilization of the heavy metal.

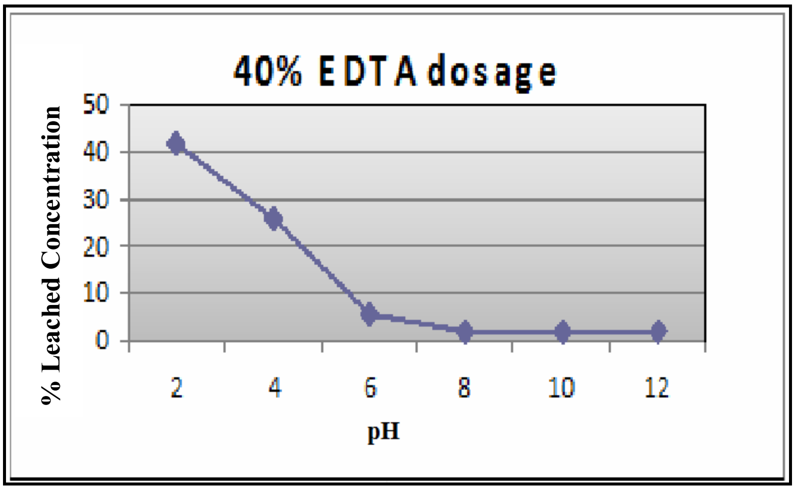

FIG 5 % Leached concentration of lead at various pH value under 40% dosage of EDTA.

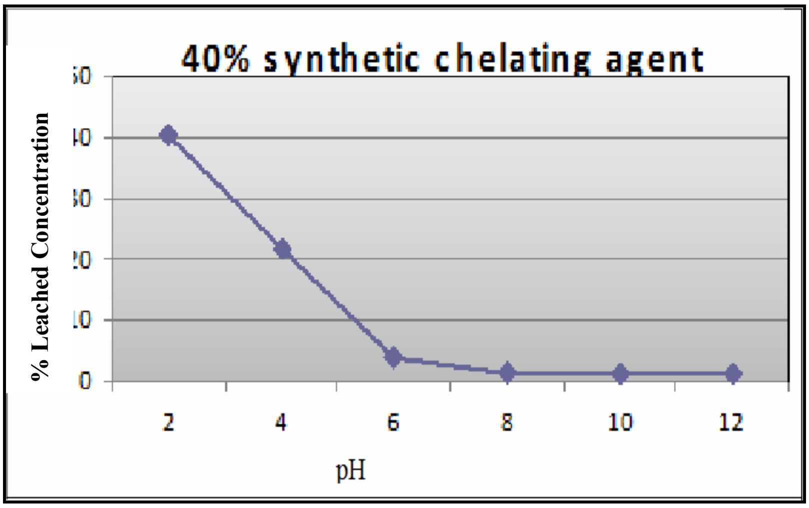

FIG 6 % Leached concentration of lead at various pH value under 40% dosage of synthetic chelating agent.

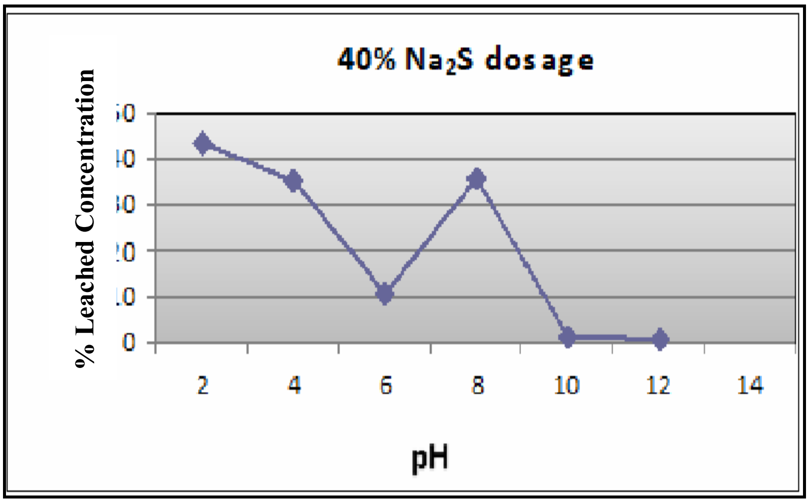

FIG 7 % Leached concentration of lead at various pH value under 40% dosage of sodium sulfide.

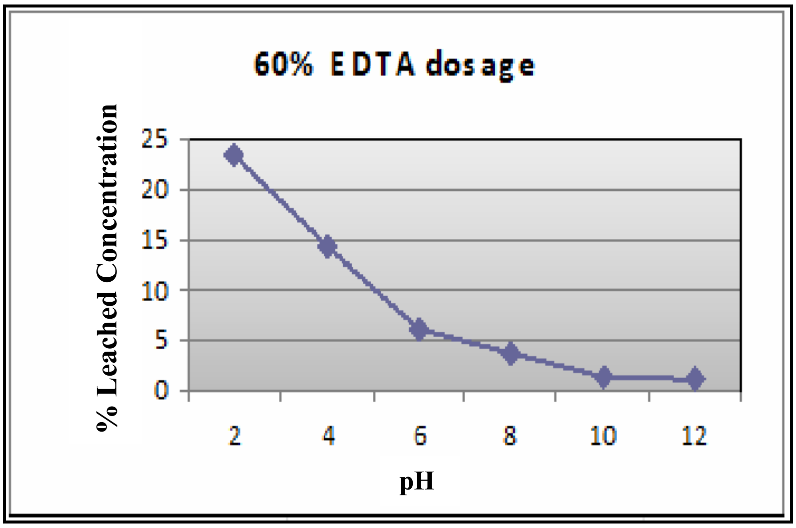

FIG 8 % Leached concentration of lead at various pH value under 60% dosage of EDTA.

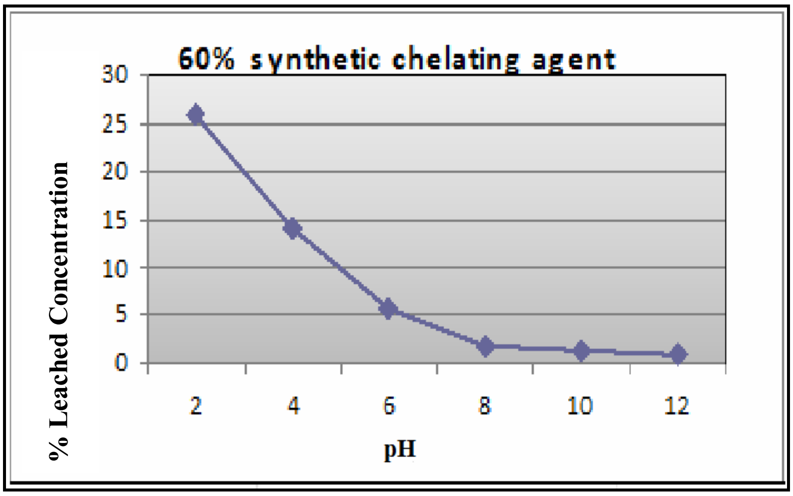

FIG 9 % Leached concentration of lead at various pH value under 60% dosage of synthetic chelating agent.

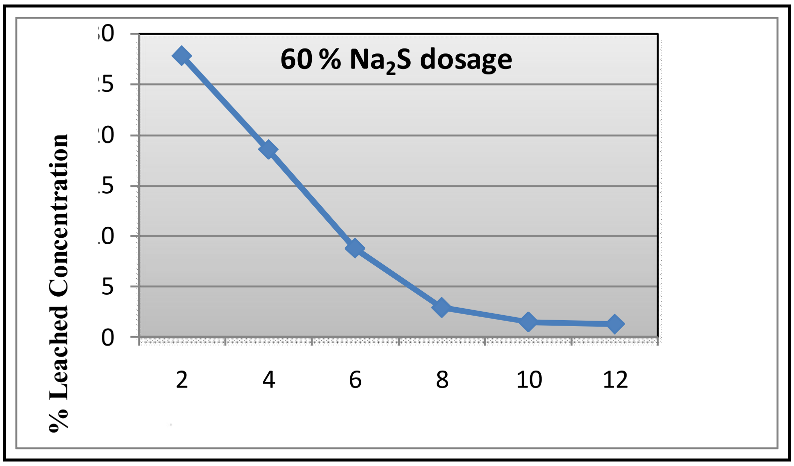

FIG 10 % Leached concentration of lead at various pH value under 60% Na_2S

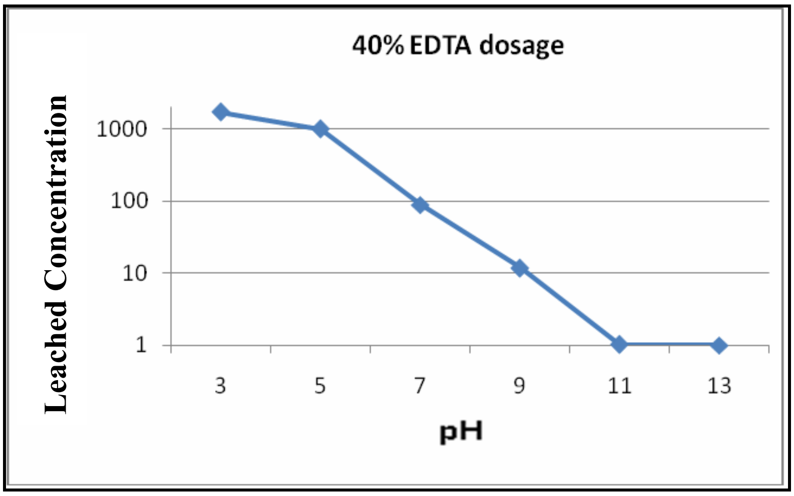

Fig 11 Leached concentration of chromium at various pH value under 40% of EDTA.

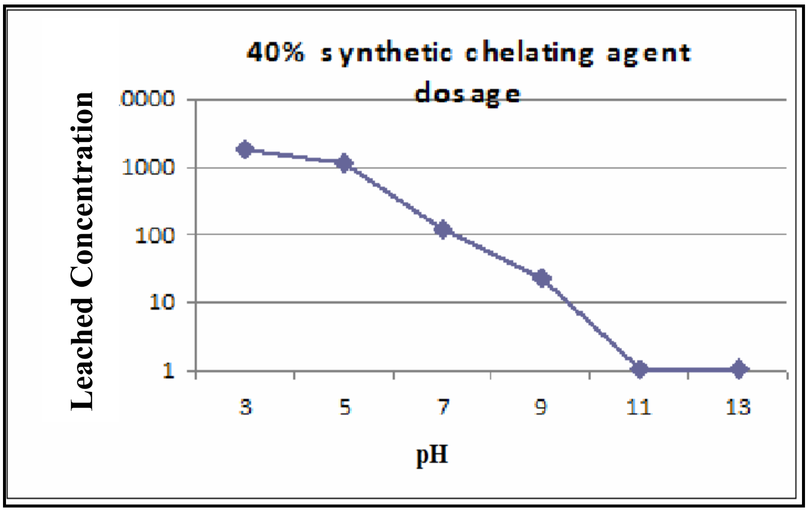

FIG 12 Leached concentration of chromium of various pH values under 40% dosage of synthetic chelating agent

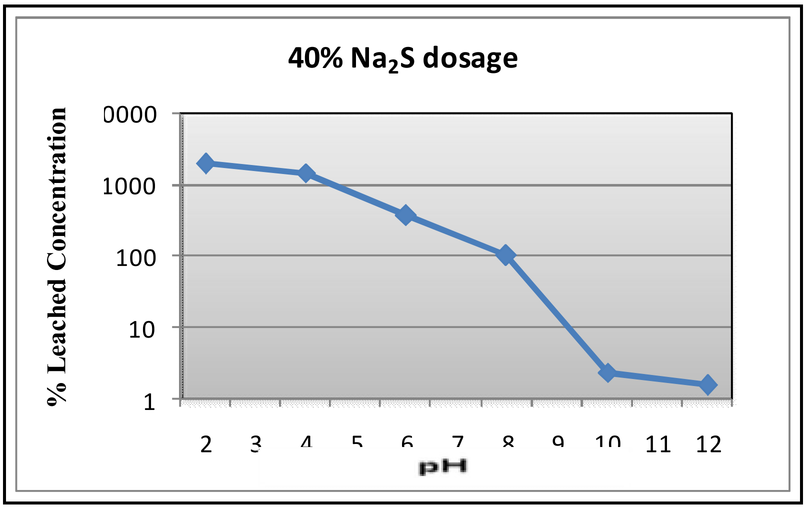

FIG 13 Leached concentration of chromium at various pH values under 40% Na_2S

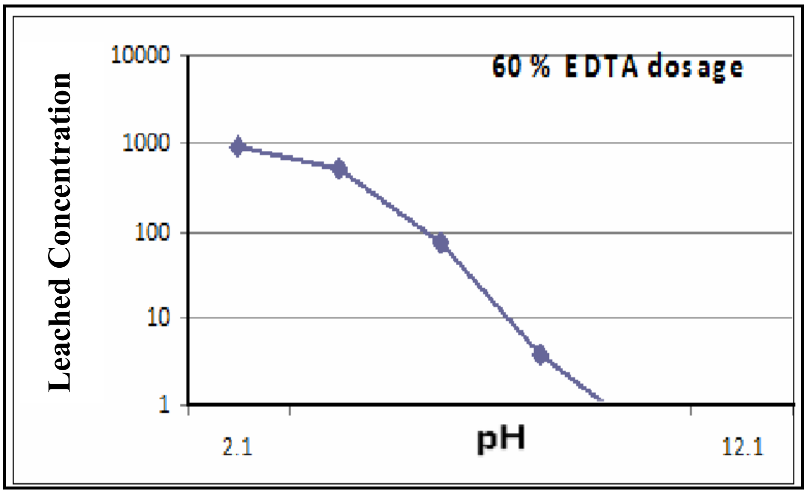

FIG 14 Leached concentration of chromium at various pH values under 60% of EDTA.

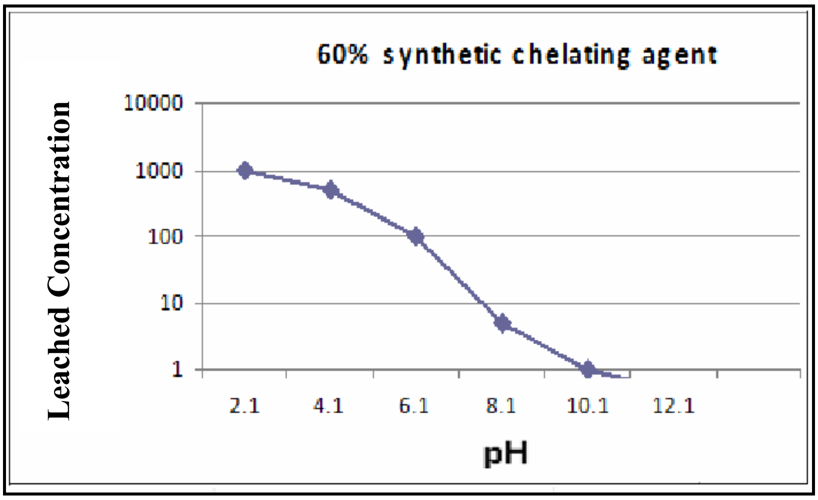

FIG 15 Leached concentration of chromium at various pH values under 60% dosage of synthetic chelating agent

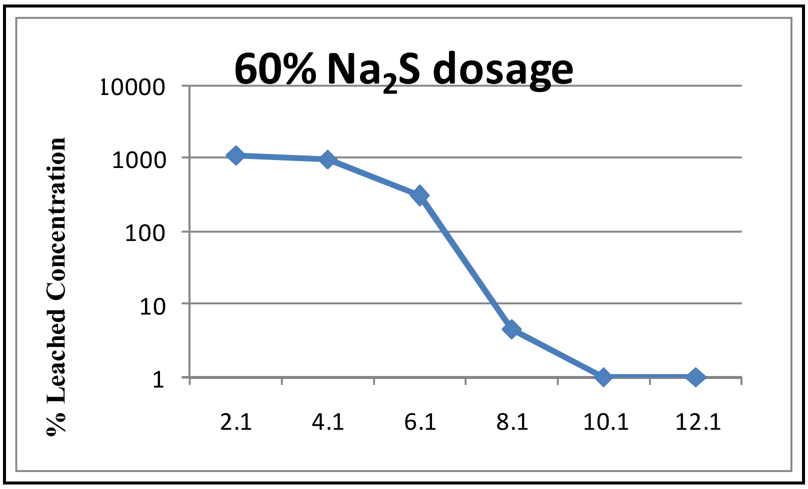

FIG 16 Leached concentration of chromium at various pH values under 60% dosage of sodium sulfide

Conclusion

The heavy metals chromium and lead in the chrome solid waste from the chrome plating industry can be stabilized by the chemical agents. In addition to the existing inorganic chemical sodium sulfide and the organic chelating agent EDTA, the synthesized chelating agent shows greater effectiveness in stabilizing the heavy metals in the solid waste. On comparing the three chemical stabilizing agents, EDTA and the synthesized chelating agent show better performance in immobilizing the heavy metals.The inorganic chemical sodium sulfide stabilizes both the heavy metals lead and chromium to an extent, which is lower than of EDTA and synthetic chelating agent.The stabilization efficiency with sodium sulfide is moderate. The Synthetic chelating agent works best for the heavy metal lead and EDTA has higher efficiency for stabilizing chromium.The pH dependent leaching experimental results demonstrates that the treated chrome solids using EDTA and synthetic chelating agent can ensure stabilization at a relatively wider range of pH value. Thus it enhances the long-term stabilization of the heavy metals in the treated chrome solids when the environment pH changes, so that the risk of secondary pollution can be minimized effectively. The treated chrome solids thus have the heavy metal composition as regulated by the pollution control board and instead of dumping in the bags in the site, it could be safely disposed of in the landfills.

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