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Olfat EL-Sebaie,

Manal Ahmed, Mohamed Ramadan

Environmental Health Dept., HIPH, Alex. Univ.

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ABSTRACT

The aim of this study is to stabilize and solidify two different treated industrial hazardous waste sludges, which were selected from factories situated close to Alexandria. They were selected to ensure their safe transportation and landfill disposal by reducing their potential leaching of hazardous elements, which represent significant threat to the environment, especially the quality of underground water. The selected waste sludges have been characterized. Ordinary Portland Cement (OPC), Cement Kiln Dust (CKD) from Alexandria Portland Cement Company, and Calcium Sulphate as a by-product from the dye industry were used as potential solidification additives to treat the selected treated waste sludges from tanning and dyes industry. Waste sludges as well as the solidified wastes have been leach-tested, using the General Acid Neutralization Capacity (GANC) procedure. Concentration of concerning metals in the leachates was determined to assess changes in the mobility of major contaminants. The treated tannery waste sludge has an acid neutralization capacity much higher than that of the treated dyes waste sludge. Experiment results demonstrated the industrial waste sludge solidification mix designs, and presented the reduction of contaminant leaching from two types of waste sludges. The main advantages of solidification are that it is simple and low cost processing which includes readily available low cost solidification additives that will convert industrial hazardous waste sludges into inert materials.

INTRODUCTION

Hazardous wastes that cannot be reduced or eliminated by in-plant modification or cannot be reused or recycled, must be treated to convert them into non-hazardous materials prior to disposal. The treatment methods include neutralization, oxidation, and fixation into solids followed by coating with a flexible inert jacket to render them non-leachable (Michael & Huisman, 1983). Leaching is the rate at which hazardous or other undesirable constituents are removed from the waste and passed into the environment via the leachate (Means et al., 1995). Hydrogen ion concentration (pH) is an important factor affecting the leachability of the treated waste especially for metals release (Means et al., 1995)).

One of the more widely used methods of pre-landfill treatment for inorganic waste is Stabilization/Solidification (S/S) (Ramachandran & Ashton, 1986). S/S processes physically sorb, encapsulate, or change the physico-chemical form of the pollutants in the waste, resulting in a less leachable product. The concentrations of contaminants in the treated waste are often lower than in the untreated waste, because of incidental dilution by the binder rather than by destruction or removal of the contaminants (Means et al., 1995). S/S processes convert the waste into an insoluble, rock-hard material and are generally used as pretreatment prior to landfill disposal. Clements et al. (1985) and Conner (1990) stated that the technique utilizes the cementitious properties of Ordinary Portland Cement (OPC) to stabilize and solidify the waste components. The conversion is achieved by blending the waste with various reactants to produce a cement-like product (Michael & Huismans, 1983). Conner(1950) reported that cement and cement by-products are the most flexible and effective reagent/binders used in stabilization technology. Cement Kiln Dust (CKD) is a waste product from the cement-making process. It contains cement fines and un-reacted fines from the cement raw materials. The total alkalinity and acid neutralization capacity values of CKD are lower than those of cement.

The selected two different sludge wastes in this study are tannery waste sludge produced by EL-Nasr Tanning Company at the west of Alexandria and dyes waste sludge produced by ISMA DYE factory at the southeast of Alexandria. These wastes seriously affect the local environment and particularly the quality of underground water resources. They are often disposed-off by dumping at dumpsites in a relatively uncontrolled manner. After disposal, acidic leachates generated during acidogenic and acetogenic phases of waste decomposition processes form particularly aggressive leachants.

The aim of this study is to stabilize and solidify the two selected industrial treated waste sludges to ensure their safe disposal by reducing their potential leaching which may threaten the quality of underground waters.

Material and methods

Waste sludges have been characterized. The characterization involves moisture content, volatile solids, pH, and total content of heavy metals. It has been done according to the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WPCF, 1992).

Three potential solidification additives are used to treat the selected sludge wastes. They are locally available ordinary Portland cement, cement kiln dust (CKD) from the Alexandria Portland cement company at EL-Max and calcium sulphate produced as a by-product from the dyes industry.

Waste sludges have also been tested for leaching using General Acid Neutralization Capacity (GANC) test as mentioned by Isenburg & Moore (1992). This is done as follows: the solid phase was dried to constant weight at 105°C, ground and sieved to <150um. One gram sub-samples of the dry ground waste are exposed to increasingly concentrated acetic acid leachants ranging from 0 to 20 equivalents per gm of waste. The composition of the added leachant systematically contains increasing additions of acetic acid. Leachate pH data gives information on acid neutralization capacity of the tested material. Compositional analysis and GANC testing have also been completed on the solidification additives.

Tested samples were hand-mixed with different ratios of additives, casted into cylindrical plastic containers, sealed and cured for 28 days. Solidified wastes have been leach-tested. Concentrations of concerning metals in the leachate were determined.

RESULTS AND DISCUSSIONS

1. Waste and solidification additives composition and leaching

The treated tannery and dye sludges from both companies have been characterized and their characteristics are presented in table (1).

It is evident from the results of the treated tannery sludge that pH was high (9.6) which could be attributed to the lime used in the plant. The presence of high calcium concentration (20,287mg/l) is due to the use of lime in both de-haring process and in treatment of final effluent on-site the industry. Volatile solids which represent the portion of organic content is small (4.3%). Moisture content is recorded in a percentage of 24.8%. The results showed that the sludge contains a high chromium content (5,993 mg/kg). This is due to the use of chromium sulphate in the tanning of the hide. The analysis also shows the presence of Sr, Al, and Fe in high concentration levels of 1,354; 3,692; and 13,062 mg/kg, respectively.

It is evident from the table that the treated dye waste sludge has a high moisture content (61%). Sludge contains high organic content that retains the moisture content within its pore size. Its pH is 7.5. This is due to that the generated waste is acidic and the lime is added to neutralize the produced waste in addition to precipitate the suspended solids. The level of volatile solids recorded is 35.6% as the main activity of the company is dyes preparation with the probability of raw organic materials or even small portion of the products escaping into the wastewater. The results also show the presence of high concentrations of the following metals: Al, Cr, Mn, Fe, and Cu with concentrations of 12,048; 1,271; 1,145; 12,038; and 3,759 mg/kg, respectively. This is attributed to the use of heavy metal salts as basic constituents for dyes preparation. These metals are the main cause of the color formation.

The characterization of the Ordinary Portland Cement (OPC) and Cement Kiln Dust (CKD) is presented in table (2). Cement Kiln Dust, produced as a waste product of the cement production process, is characterized by a silicate content less than that of the ordinary cement.

Fig. (1) shows GANC leachate pH data for the wastes sludges and additives. It is clear that the treated tannery waste sludge had Acid Neutralization Capacity (ANC) much higher than that of the treated dyes waste sludge. The treated tannery sludge waste consumed approximately 4meq acid per gm of sludge to reach pH 6.2 while the dye waste consumed almost 2meq acid per gm of sludge to reach the same pH. Cement has a high ANC and this is a major reason why cement-based materials produce high and very stable internal pH conditions, which are very effective at retaining heavy metals during leaching. CKD was less effective than cement but its ANC behavior may be sufficient for solidification. Cement consumed about 22meq acid per gm to reach pH 6 and 8meq acid per gm to reach pH 11, while CKD consume 12meq acid per gm to reach pH 6. These results of ANC of cement are almost in agreement with Conner (1950) who stated that the ANC of 8meq/gm of dry cement produced solution with pH in the range of 12 to 13 in a pure cement-water system. So, cementitious reaction requires pH>10. He also stated that the form of calcium in the CKD was different from calcium silicate in the cement and cement was a better-stabilized agent than CKD because of its ability to incorporate metals into the cured cement matrix.

Fig (2-[a&b]) shows metal leaching data from the treated tannery waste sludge against leachate pH. The leachate presented systematic increase in leaching and released metals levels were relatively low until the leachate pH was reduced below 7, where high concentrations of Cr, Zn, Fe, Al, and Mn were leached at pH 5. As pH falls from 7.2 to 4.5, a significant concentration of Cr was leached from 0.085 to 20 mg/l and Zn was leached from 0.009 to 1.2 mg/l, Fe was leached from 0.01 to 40 mg/l. Also, Al and Mn were leached from 0.01 to 40 and from 0.25 to 4 mg/l, respectively. This is in agreement with results obtained by Means et al. (1995) who stated that the ability of a material to maintain a high pH is an important factor in reducing leaching, as most of the heavy metals show rapid increase in solubility and leaching as the leachate pH becomes acidic.

Figure (3) shows metal leaching data for the treated dye waste sludge. It is clear that the only heavy metal, which leached at significant concentration, was Mn where its concentration increasing from 7 to 30 mg/l as the leachate pH falls from 7.3 to 6.3.

2. Characterization of solidified wastes

The mix design ratios used to solidify wastes sludge are presented in table (3), where treated tannery waste sludge was mixed with OPC and CKD additives, while, treated dye waste sludge was mixed with OPC and $CaSO_4$ additives. The ratio of water to solid content used was 0.4. Conner (1990) stated that as the water-cement (w/c) ratio increased, the percentage of larger pores increased substantially increasing the permeability of the waste form. He also said that in a pure water-cement system, the permeability was essentially zero at w/c ratio of 0.32, but increased exponentially as the w/c ratio reached 0.6 to 0.7. Very high w/c ratio will bleed water.

At the end of the 28-day curing period, a series of treated stabilized waste sludge products were obtained and their leachability was evaluated.

With respect to dyes waste sludge, figure (4) shows how leachate pH varies with acetic acid addition in the GANC test to the different mixes. It is noticed that replacement of cement by $CaSO_4$ progressively reduces the ANC of the mix. By adding of 1ml acid to the different mixes, the pH of the mix with 80% waste:20% OPC decreased from 12.5 to 10.3, while in the pH of the mix of 80% waste:10%$CaSO_4$:10%OPC decreased from 12 to 7.5.

Leachability of Mn and Cr from stabilized mix is shown in figures (5&6). Figure (5) shows that addition of 20% cement greatly reduces Mn leaching which reaches zero concentration at 1ml of acid in comparison to 33mg/l Mn leach from the sludge at the same ml of acid.

Replacement of 20% cement by 20% Ca-Sulphate progressively increases leaching of Mn to 26mg/l at 1ml of acid towards the levels found for the raw dyes sludge. Figure (6) shows that Cr did not leach at significant concentrations from the original sludge. Addition of 20% cement increased its leachability (0.01 in the sludge to 1.5 mg/l at 1ml of acid), while Ca-Sulphate-containing mixes (20%) shows significant increase of leaching of higher concentration of Cr (5.8mg/l). The low levels of Cr leaching from the sludge was due to the presence of $Ca(OH)_2$ which gave the sludge ANC ability, and addition of $CaSO_4$ may change the form of the Cr. Also, the high organic contaminants in the sludge and $CaSO_4$ enhance the release of Cr due to organic complexation effects. This conclusion was reached also by Montgomery et al.(1991 a,b) Gibbons et al. (1988), and Sheriff et al. (1989) who found that sludges containing organic compounds could not be satisfactorily treated by this method, as there was generally an interaction between organic compounds and the inorganic cement matrix. They also stated that many organic compounds had retarding effects on cement hydration and adverse effect on the microstructural and engineering properties of the final product. They recommended using additives as clay, fly ash, or quaternary ammonium sulphate to adsorb the organic fraction of industrial sludge prior to cement-based solidification as it had been shown to be highly effective.

With respect to the treated tannery waste sludge, the mix design ratio was not sufficient to provide a solidified form. This was due to the presence of long fibrous materials resulting from shaving and splitting of the tanned hide that may hinder the cementitious reaction.

CONCLUSION AND RECOMMENDATIONS

Treated tannery waste sludge shows high pH and low volatile solids. It contains high Cr, Sr, Al, and Fe concentrations. The treated dyes waste sludge has a high moisture content, neutral medium, and high level of volatile solids; Al; Cr; Mn; Fe; and Cu. CKD is characterized by a lower silicate content than that of the OPC.

The treated tannery waste sludge has ANC much better than that of the treated dyes waste sludge. Cement has a high ANC which makes it very effective at retaining heavy metals during leaching. For the treated tannery waste, the leachate present systematic increase in leaching and released methods are relatively low until the leachate pH is reduced to below 7.

For the treated dyes waste sludge, the only heavy metal, which leaches at significant concentration, is Mn. With respect to solidified dyes waste sludge for a curing period of 28 days, replacement of cement by $CaSO_4$ progressively reduces the ANC of the mix. Addition of 20% cement greatly reduces Mn leaching. On the other hand, Cr does not leach at significant concentrations from the original waste sludge. Addition of 20% cement increased its leachability, while Ca-Sulphate-containing mixes (20%) shows significant increase of leaching of higher concentration of Cr. The high organic contaminants in the waste sludge and $CaSO_4$ enhance the release of Cr due to organic complexation effects. So, it is recommended to use some additives to adsorb the organic fraction prior to cement-based solidification of dye waste sludge. On the other hand, tannery waste sludge does not give a solidified form with the tested mix design ratio of additive. Therefore, it is recommended to have an in-plant control system to separate fibrous materials as much as possible and then more trials must be carried out to use different additives mix ratios.

Finally, there are major difficulties and questions, which have to be addressed before a waste solidification scheme could be introduced to treat industrial hazardous waste sludges. These include:

- Availability and variability in the solidification additives
- Suitability of the waste for treatment by solidification
- Behavior of solidified forms after disposal
- Availability of mono-landfill site for solidified waste
- Long-term durability and leaching characteristics of solidified wastes

Some of these questions are under trial as a continuation of this study to optimize the mix for the two selected wastes sludges including trials for new inert wastes (as fly ash). Also, long-term durability tests and leaching characterization of the solidified wastes are going on.

ACKNOWLEDGEMENT

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Table 1: Characterisation of wastes sludge collected from tannery and dyes preparation industry

Metal (mg/kg)	Treated tannery waste sludge	Preparing dyes industry waste
Na	3,671	2,133
K	351	1,025
Mg	7,643	8,573
Ca	20,287	121,213
Sr	1,354	163
Ba	188	379
Al	3,692	12,048
Cr	5,993	1,271
Mn	168	1,145
Fe	13,062	12,038
Co	0.5	7
Ni	11	28
Cu	66	3,759
Zn	81	228
Cd	N.D.	N.D.
Pb	40	673
P	1,261	1,246
Physical Analysis:		
Moisture%	24.8	61
V.S.%	4.3	35.6
PH (units)	9.6	7.5

Table 2: Cement and CKD additives characterization

Ordinary Portland Cement (OPC) Characteristics		Cement Kiln Dust (CKD) Characteristics	
Tri-Calcium Silicate	50%	SiO_2	8-12%
Di-Calcium Silicate	25%	Fe_2O_3	2-4%
Tri-Calcium Aluminate	10%	Al_2O_3	3-5%
Calcium Alumino Ferrite	10%	CaO	40-48%
		MgO	0.8-1.2%
		SO_3	0.2-0.3%
		Na_2O	0.1-0.3%
		K_2O	0.7-0.9%

Table 3: Mix designs used to solidify tannery and prepared dyes wastes

Waste	Waste%	OPC%	CKD%	$CaSO_4$%	Water/Solid
Treated tannery waste sludge	80	20	0	0	0.4
Treated tannery waste sludge	80	10	10	0	0.4
Treated tannery waste sludge	80	5	15	0	0.4
Treated tannery waste sludge	80	0	20	0	0.4
Preparing dyes industry waste	80	20	0	0	0.4
Preparing dyes industry waste	80	10	0	10	0.4
Preparing dyes industry waste	80	5	0	15	0.4
Preparing dyes industry waste	80	0	0	20	0.4

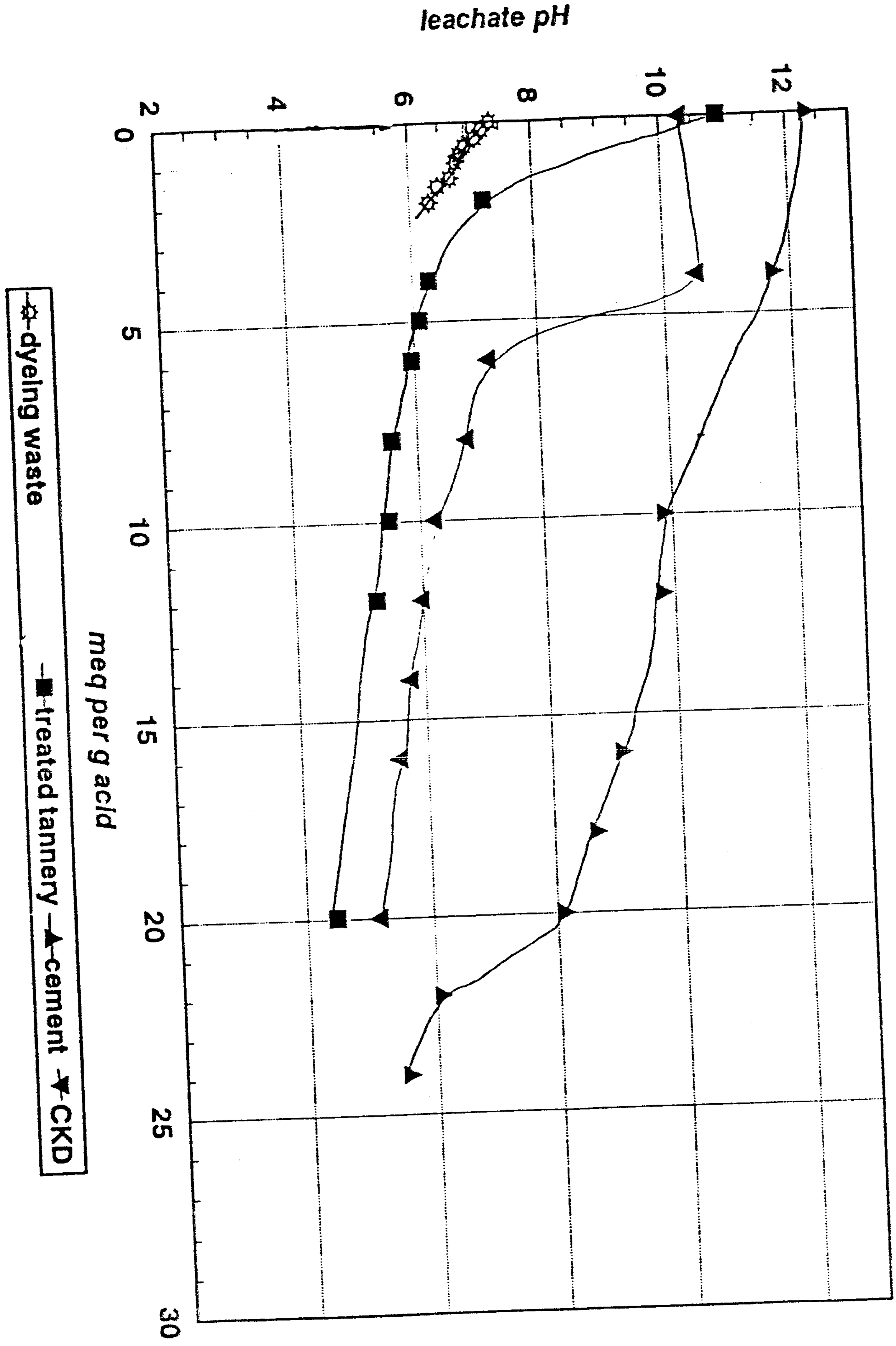

Fig. 1: Acid neutralization data for waste sludge and additives

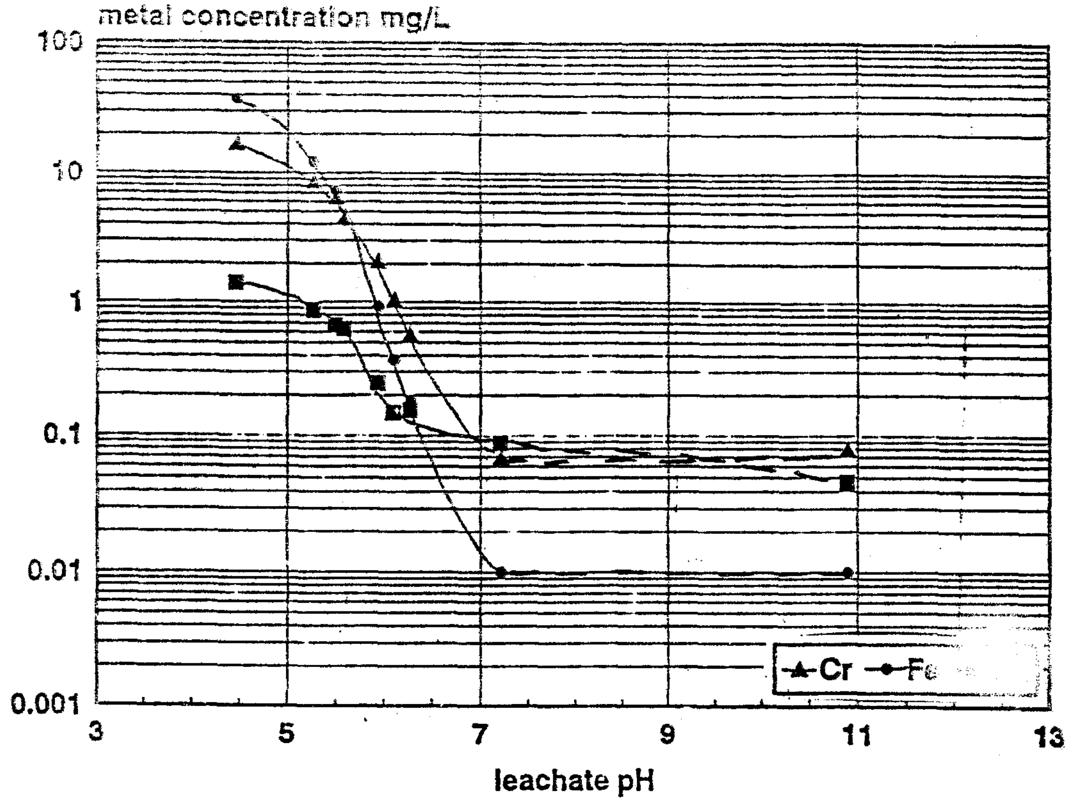

Figure (2-a): Metal Leaching data for Treated Tannery Waste Sludge (GANC TEST DATA)

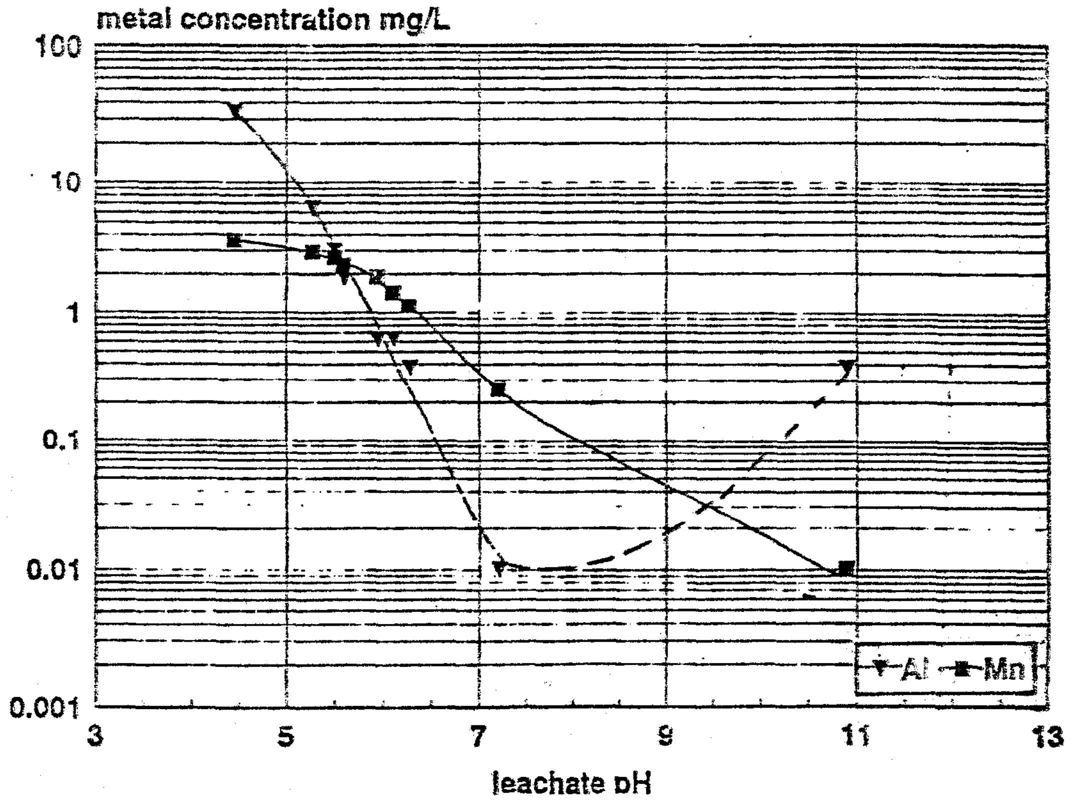

Figure (2-b): Metal Leaching data for Treated Tannery Waste Sludge (GANC TEST DATA)

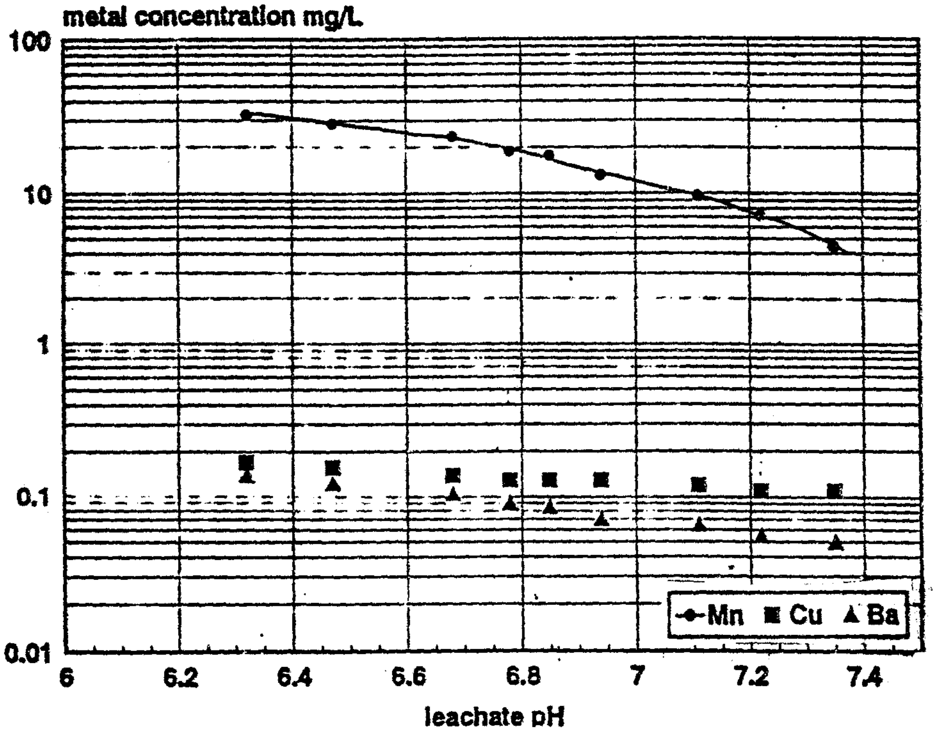

Fig. 3: Metal leaching data for treated dyes waste sludge (GANC test data)

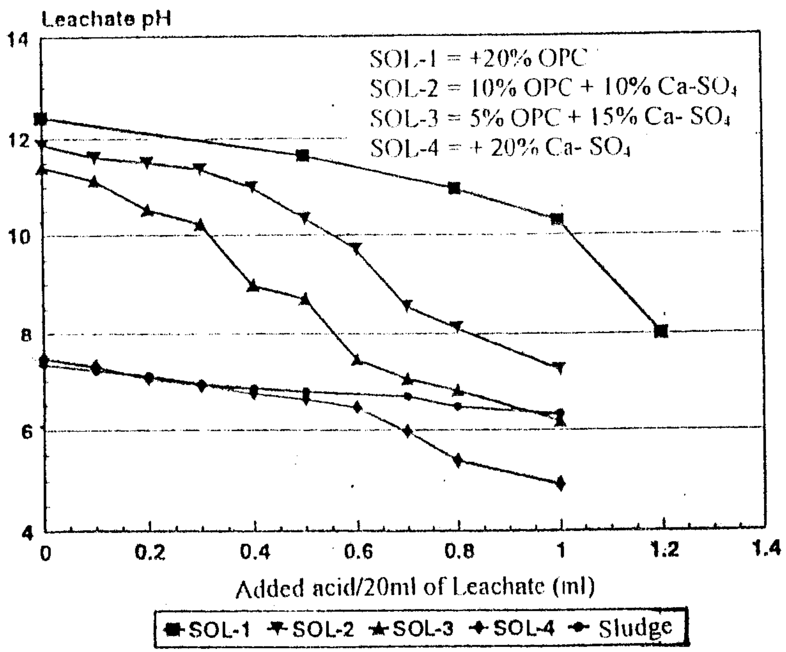

Figure (4): GANC Leachate pH data for Solidified Dye Waste Sludge

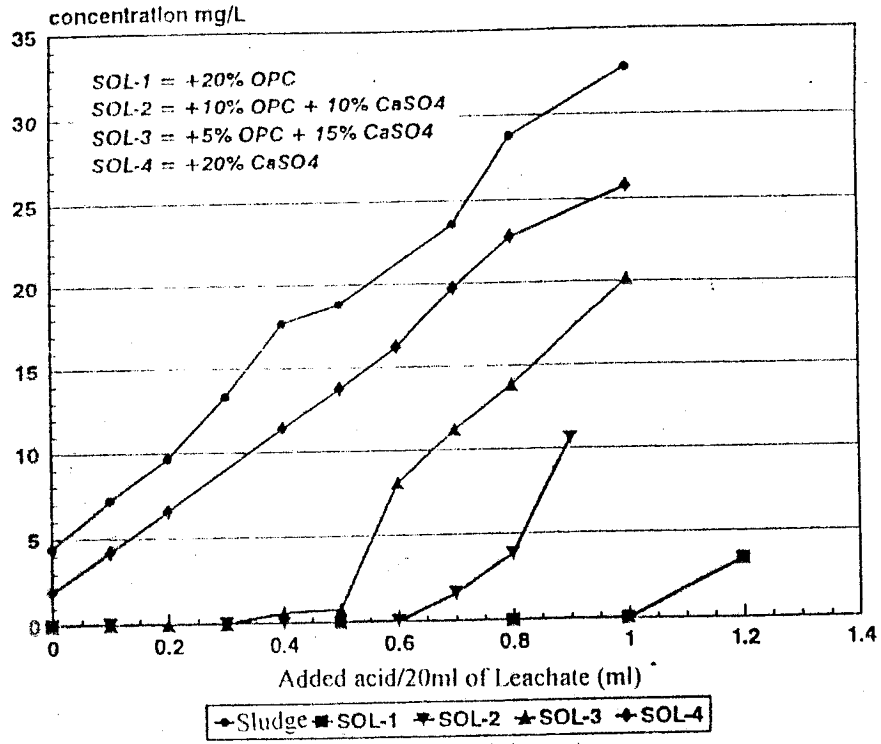

Figure (5): Mn Leaching data from Solidified Dyes Industry Waste Sludge

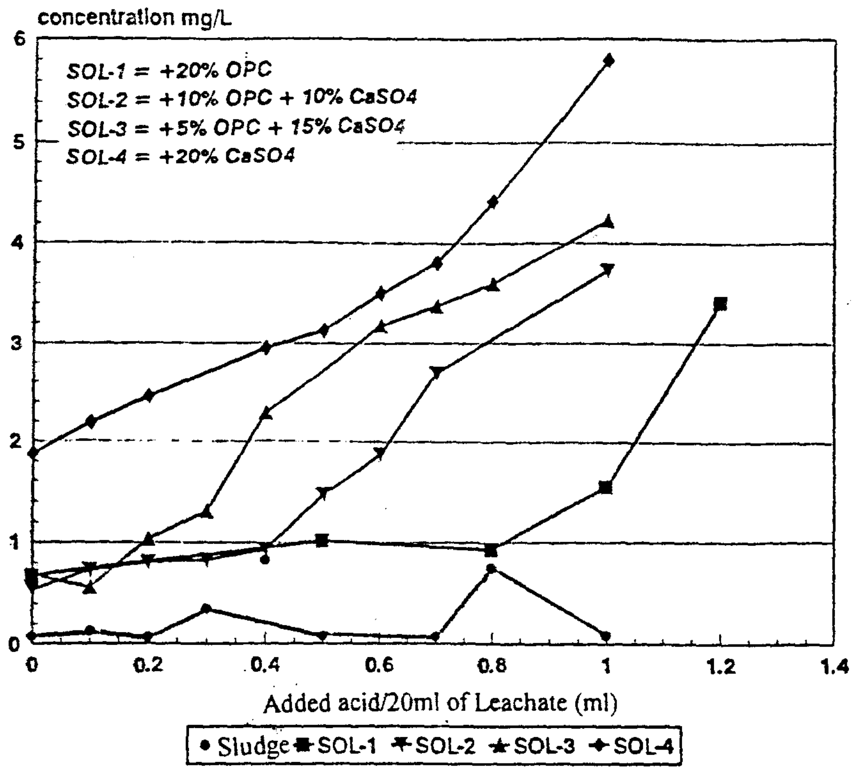

Fig. 6: Cr leaching data from solidified dyes industry waste sludge