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**СТРАНИЧКА МОЛОДОГО УЧЕНОГО**

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## Removal and Stabilization of Chromium Ions from Industrial Effluents

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### Abstract

Laboratory experiments were designed to investigate the removal of chromium ions from industrial effluent by stabilizing in silica sand, acting as adsorbents, to prevent leaching. Removal of chromium (III) ions from industrial effluents using silica sand (originated from the river of Ravi) was studied to optimize the physicochemical conditions for maximal removal. The range of pH and temperature was adjusted to achieve maximal removal of metal ions. The initial and final concentration of chromium was measured by atomic absorption spectroscopy. The residual concentration of chromium in waste water after treatment was less than 1.0 mg/l which is the value recommended by National Environment Quality Standards (NEQS). Maximal removal (94–96 %) of chromium is achieved with pH 10 and at a temperature of 28 °C.

Under optimized conditions within temperature range of 301–315 K the values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G_{301\text{ K}}$  for 100 ppm solution are  $(-94.41 \pm 0.48)$  kJ/mol,  $(-287.02 \pm 1.56)$  J/mol and  $(-7.93 \pm 0.60)$  kJ/mol, respectively, and for 150 ppm solution thermodynamic entities are  $\Delta H = (-74.57 \pm 0.20)$  kJ/mol,  $\Delta S = (-287.39 \pm 0.66)$  J/mol and  $\Delta G_{301\text{ K}} = (-6.88 \pm 0.40)$  kJ/mol. The removal of chromium metal ions using silica sand is followed by its stabilization to minimize the desertion of sorbed metal ions under changed physicochemical conditions during final disposal. The stabilization was obtained by converting the silica sand along with the sorbed chromium ions into the glass matrix. Due to the large amount of glass network former in sand, it is cheap and proved as a promising basic material for glass. The characteristics of the matrix show no leachability of chromium ions.

### INTRODUCTION

The elements, which have been identified from different effluents, are heavy metals. Heavy metals are metallic elements, which have their atomic density greater than 6 g/cm<sup>3</sup>. Heavy metals including chromium, copper, lead, nickel and zinc are either toxic themselves to biological organism or induce deficiency in other metals. Considerable proportions of most heavy metal ions are toxic or carcinogenic and hence present a threat to human health and the environment when they are discharged into

various water bodies. Chromium being heavy metal is not biodegradable like other toxic pollutants and once in the environment, their potential toxicity is controlled by their physicochemical form [1]. When introduced into soil, these elements are either dissolved in soil solution or leached down with excess water or part of it is fixed temporarily or permanently on to soil colloidal/ complex. These elements which move downward through the soil contaminate ground water which is often used for drinking; they can cause toxic effect in human beings/animals [2, 3].

Chromium is a metallic element which exists primarily in the minerals, chromites. Chromium is generally present in its metallic or trivalent form, both of which are stable throughout the lifetime of the product. Chromium enters the air, water and soil as chromium (III) and chromium (VI) through natural processes and human activities. The main human activities that increase the concentrations of chromium (III) include dyes, electro painting, paint pigments, textile manufacturing and salts for leather tanning [4].

These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils. Most of the chromium in air will eventually settle and end up in waters or soils. Soluble trivalent chromium substances can be irritating to the eyes and skin. Some people can be chromium sensitive in which case trivalent chromium compounds can cause skin rashes. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma). Ingestion may affect kidney and liver functions. Skin contact may result in systemic poisoning, damage or even severe burns, interference with the healing of cuts or scrapes may lead to ulceration and severe chronic allergic contact dermatitis.

Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III) that may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur. High concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals, chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumour formation.

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for chromium (III) compounds of  $0.5 \text{ mg/m}^3$  as a value allowed for up to a 10 h workday and a 40 h workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chromium (III) compounds a threshold limit value (TLV) of  $0.5 \text{ mg/m}^3$  as a

value allowed for a normal 8 h workday and a 40 h workweek [5, 6].

For removal of heavy metals, different naturally occurring adsorbents like activated carbon [7–10], tea waste [11], egg shells [12], mineral mixtures [13] and rice husks [14] are being used as adsorbents for industrial waste management.

The removal is maximized under certain physicochemical conditions, therefore there are chances of the desorption of the adsorbed metal ions under changed physicochemical conditions in final disposal. Therefore, there is need to stabilize these adsorbed metals ion after sorption. Solidification/stabilization (S/S) reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means. Unlike other remedial technologies, S/S seeks to trap or immobilize contaminants within their “host” medium, *i. e.*, sand, that sorbed them).

Due to the large amount of glass network former in sand, it is cheap and a promising basic material for glass. Because of its good chemical durability and inexpensiveness,  $\text{SiO}_2$  is the most widely used glass forming oxide and therefore the major ingredient of glass. The glass is used for the immobilization of metals due to its excellent chemical durability or resistance to corrosion. Many glass forms of different waste streams have been developed [15, 16]. The chemical resistance of glass can allow it to remain in a corrosive environment for several thousand or million years. Another strong reason is that glass has an ability to incorporate the waste contaminants in its microstructures [17]. The silica sand chosen for adsorption provided a basis from which glass formulation was developed. The silica sand contains  $\text{SiO}_2$  about 80.361%. The chromium metal was sorbed onto the silica sand and then developed into glass frit with required characteristics regarding to its stability. The development of suitable glass without considerable addition of other additives with reasonable melting temperature is an achievement of the present work. Leachability testing is typically performed to measure the immobilization of contaminants.

## EXPERIMENTAL

Silica sand (origin: the river of Ravi) was washed with dilute HCl, then washed twice with distilled water and air dried. The composition of silica sand (oxide basis) was analyzed by using inductively coupled plasma spectrometry (ICP) as given below:

Oxide	Mass %
SiO <sub>2</sub>	80.361
Al <sub>2</sub> O <sub>3</sub>	5.301
CaO	4.369
Fe <sub>2</sub> O <sub>3</sub>	2.988
MgO	1.456
Na <sub>2</sub> O	1.232
K <sub>2</sub> O	1.101
MnO	0.053
ZnO	0.004

Samples of effluents from the various chemical industries situated in the industrial area of Lahore (Punjab), expecting to release chromium compounds in their waste water, were collected and analyzed. It is observed that average concentration of chromium in these effluents is between 100 to 150 ppm. Therefore, the samples containing 100 and 150 ppm were prepared for chromium to cover the observed concentration of chromium present in actual industrial waste. Standard solution of 1000 ppm was prepared using extra pure chromium (III) chloride hexahydrate (CrCl<sub>3</sub>·6H<sub>2</sub>O). From 1000 ppm standard solution, different concentrations of chromium sulphate solutions were prepared by dilution. An assembly of glass columns was used for the adsorption treatment. The dimensions of columns for samples is taken are: inner diameter, 2.35 cm; bed height, 15.69 cm; volume, 68 cm<sup>3</sup>. The mass of the silica sand filled in column was 18.64 g. The removal efficiency of adsorbent was maximized by varying pH of samples and temperature. For adsorption treatment the effluents were allowed to pass through the glass columns packed with silica sand.

Silica sand was carefully introduced from the top, continuous tapping ensured the uniform packing up to desired level. The known volume of particular sample was then introduced at the top. The effluent was collected from the bottom in plastic bottles and again analyzed for

the concentration of chromium. The change in the concentration of chromium after treatment was calculated by taking difference between two concentrations. The concentration of chromium ions in solutions was measured by atomic absorption using Varian (A.A 1275) atomic absorption spectrophotometer equipped with hollow cathode lamps of chromium.

The percentage sorption and distribution coefficient ( $K_d$ ) was calculated using the following relationship:

$$\text{Sorption} = [(C_i - C_t)/C_i] \cdot 100 \%,$$

$$K_d = [(C_i - C_t)/C_i] \cdot V/m$$

where  $C_i$  is the initial concentration of chromium in solution and  $C_t$  is its concentration in solution after treatment;  $V$  is volume of adsorbate, cm<sup>3</sup>; and  $m$  is amount of adsorbent, g. The % sorption and the distribution coefficient can be correlated as: Sorption = 100  $K_d m/V$ .

## RESULTS AND DISCUSSION

Table 1 explains the effect of temperature on adsorption. Each sample solution with different temperature, *i. e.* 28, 32 and 42 °C was passed through the adsorbents. It was observed that the adsorption of chromium increases with the decrease in temperature, as reported by [19, 20]. Low temperature gave maximum adsorption and the adsorption increases with order as 28 °C > 32 °C > 40 °C.

The values  $\Delta H$ ,  $\Delta S$  were calculated from the slope and intercept of the linear van't Hoff plot of  $\log K_c$  vs.  $1/T$ , where  $K_c = F/(1 - F)$ ;  $T$  is absolute temperature, K; and  $F$  represents the fraction sorbed at equilibrium, straight line with the correlation factor of 0.96 to 0.99 was obtained (Fig. 1, *a*, *b*). The values of  $\Delta H$  and  $\Delta S$  were computed using the relations:

$$\log K_c = -\Delta H/(2.303RT) + \Delta S/(2.303R)$$

TABLE 1

Effect of temperature on the removal of Cr(III) ions, %

Adsorbing material (packed in 2.3 cm Ø × 15.7 cm column)	Concentration of Cr, ppm	Temperature, °C		
		28	32	42
Silica sand	100	96	94	82
	150	94	90	80

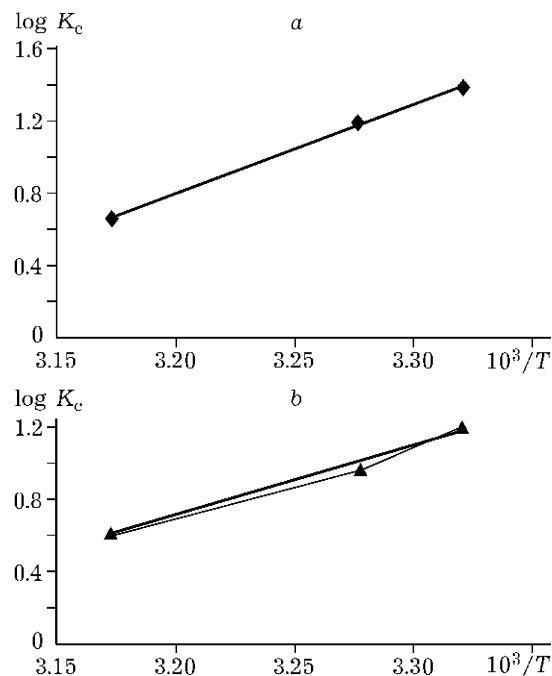


Fig. 1. Effect of temperature on sorption of 100 (a) and 150 ppm (b) solutions of Cr(III) ions.

The free energy of adsorption  $\Delta G$  was calculated using equation

$$\Delta G = -RT \ln K_c$$

The slope and intercept of Fig. 1, a and b gave thermodynamic entities for 100 and 150 ppm solution. The values of thermodynamic entities are given in Table 2.

TABLE 2

Thermodynamics quantities for adsorption of Cr(III) ions

Adsorbing material (packed in 2.3 cm $\varnothing$ $\times$ 15.7 cm column)	Concentration of Cr, ppm	$\Delta H$ , kJ/mol	$\Delta S$ , J/(mol K)	$\Delta G$ , kJ/mol
Silica sand	100	$-94.41 \pm 0.48$	$-287.02 \pm 1.56$	$-7.93 \pm 0.6$
	150	$-74.57 \pm 0.20$	$-287.39 \pm 0.66$	$-6.88 \pm 0.4$

TABLE 3

Effect of pH on the removal of Cr(III) ions, %

Adsorbing material (packed in 2.3 cm $\varnothing$ $\times$ 15.7 cm column)	Concentration of Cr, ppm	pH				
		2	4	7	10	12
Silica sand	100	65	74.5	86.7	94	88
	150	58	63	80.5	90	82.5

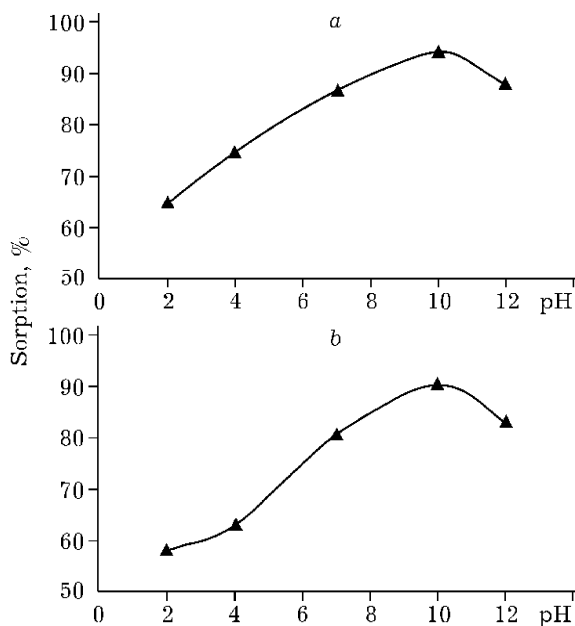


Fig. 2. Sorption of 100 (a) and 150 ppm (b) solutions of Cr(III) ions.

The negative enthalpy and negative free energy reflect the exothermic and spontaneous nature of sorption, respectively.

Table 3 and Fig. 2, a, b show the effect of pH of sample on adsorption, three different samples were prepared with different pH values which are 2, 4, 7, 10 and 12 using buffer solutions. The removal of chromium by adsorbents is highly dependent on the pH of the solution which affects the surface charge

TABLE 4  
Composition of glass frits

Glass frit name	Melting temperature, °C	Composition, mass %			
		SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>
AG 301	1150	65	20	10	5
AG 312	1200	70	15	10	5
AG 319	1200	75	20	10	3
AG 327	1250	80	10	5	5
AG 328	1300	85	5	5	5
SG	1250	80	10	5	5

of the adsorbents, degree of ionization and speciation of the adsorbates. Samples with different pH were passed through columns filled with silica sand. Change in adsorption efficiency with change in pH of samples is found to be significant. The maximum sorption was obtained at pH 10 [22]. The difference in removal efficiency due to the solution pH is attributed to the precipitation of chromium hydroxide Cr(OH)<sub>3</sub> at a higher pH. Increasing the pH implied a promotional increase in OH ion concentrations in solution disturbing equilibrium which could be achieved again through formations of greater amount of hydroxide out of the solution.

The results of studies of chromium concentration dependence on adsorbents were also subjected to analysis in terms of Langmuir and Freundlich adsorption isotherms. The data do not fit Langmuir equation. However, Freundlich adsorption isotherm was capable of describing the data over the concentration range studied. The Freundlich isotherm was tested in the following linearized form:  $\log C_{\text{ads}} = \log A + (1/n)\log C_e$ , where  $C_{\text{ads}}$  is amount of chromium ion adsorbed at equilibrium, mol/g;  $C_e$  is equilibrium concentration of chromium in the solution, mol/l; and  $A$  and  $1/n$  are Freundlich constants.

Almost all these adsorptive separation processes depend on physical adsorption rather than chemisorption and this is therefore the focus of the present review. The heat of adsorption provides a direct measure of the strength of bonding between the sorbate and the surface. Physical adsorption from the liquid

phase is invariably exothermic, although there are very small heat changes, as may be shown by a simple thermodynamic argument. Since the adsorbed molecule has at most two degrees of translational freedom on the surface and since the rotational freedom of the adsorbed species must always be less than that of the liquid phase molecule, the entropy change on adsorption  $\Delta S = S_{\text{ads}} - S_{\text{gas}}$  is necessarily negative. In order for significant adsorption to occur, the free energy change on adsorption  $\Delta G$  must also be negative and since  $\Delta G = \Delta H - T\Delta S$ , this requires  $\Delta H$  negative, or exothermal adsorption. Therefore, maximal sorption at low temperature (28 °C) is exactly according to this theory.

Once chromium is removed from the industrial effluent through sorption, then, the next step is its stabilization which can be achieved by converting the sorbent into the stable and leach resistant glass material.

There has been much research focused on the composition durability relationship of glass. The glass formers are the major constituents of all waste glasses. If the inorganic oxides present in the silica sand are insufficient glass formers to fall within the accepted formulation range, additional glass formers must be added through the process. The silica sand selected for sorption has very suitable composition required to develop glass frits. An attempt was made to develop different glass formulations by varying composition of modifiers and fluxes based on the calculations (Table 4). The developed glass frits were characterized mainly focusing on their density and leachability (Table 5).

TABLE 5  
Characteristics of developed glass frits

Glass frit name	Density, g/ml	ML*, g/m <sup>2</sup>	Leachate pH	Elements in leachate, µg/ml				
				Si	Na	Al	Ca	Cr
AG 301	2.15	2.10	8.7	0.4	5.3	0	0.2	–
AG 312	2.35	2.00	8.2	0.6	3.8	0.1	0.1	–
AG 319	2.49	1.98	7.9	0.6	3.2	0	0.3	–
AG 327	2.59	1.58	7.7	0.8	2.3	0.2	0	–
AG 328	3.01	1.23	7.4	1.2	2.1	0	0	–
SG	2.60	1.62	7.6	0.5	2.4	0.1	0	0

\*ML is the total mass loss of glass.

Density was measured on the basis of volume displacement method using simple relation of  $D = m/v$ , where  $m$  is mass of glass, and  $v$  is the volume displaced by sample when dipped in a known volume of water.

In order to rapidly determine the chemical durability of the glass, a leaching test method was derived from the standard PCX leach test method named M-PCT. The glass sample was grinded to the particle size of 1.0–1.2 mm. The sample was washed with acetone to remove the fine particles before testing. The surface area of the sample was calculated by the following equation [23, 24]:  $SA = 6M/(\rho\phi) \cdot 0.89$ , where  $SA$  is the surface area, cm<sup>2</sup>;  $M$  is the mass of the glass sample, g;  $\rho$  is density of glass sample, g/cm<sup>3</sup>;  $\phi$  is a average diameter, cm; and 0.89 is factor to convert the results from spherical particles to glass.

The sample was first leached for 19 h in an ammonium hydroxide buffer of pH 9, followed by a second leach of 19 h in an acetate buffer of pH 3.9, both solutions at ambient temperature. After exposure to the buffered solutions, the glass is leached for 24 h at 99 °C in deionized water. The leachate of every phase was analyzed using ICP for the concentrations of Si, Na, Al and particularly Cr. The total mass loss of glass (ML) and the normalized elemental loss (NL) were obtained. The ML and NL were used to monitor the chemical durability of glass forms during glass formulation development.

The ML value was calculated as  $ML = (m_0 - m_1)/SA$ , where ML is total mass loss, g;  $m_0$  is the mass of unleached specimen, g;  $m_1$  is the mass of specimen after leaching, g; and SA is the sample surface area, m<sup>2</sup>.

Regarding to elemental analysis in leachate, the normalized element mass loss NL was calculated using formula  $NL = C_i \cdot V/SA \cdot f_i$ , where NL is element mass lost, g/m<sup>2</sup>;  $C_i$  is the concentration of element in the leachate, g/m<sup>3</sup>;  $V$  is the volume of leachant, m<sup>3</sup>;  $f_i$  is the mass fraction of element in unleached glass sample.

Amongst the studied formulations, the formulation AG 327 was found excellent in terms of its low leachability and greater chemical stability. The composition of the used silica sand was very similar to the composition AG 327. The only difference was there was percentage of Na<sub>2</sub>O. The formulation AG 327 contains 10 % Na<sub>2</sub>O whereas the percentage of Na<sub>2</sub>O in studied silica sand was only 1.2 %. The percentage of Na<sub>2</sub>O from 1.2 to 10 % was achieved by adding 15.04 g Na<sub>2</sub>CO<sub>3</sub> as source material calculated by the given formula as  $W_{sm} = W_{pm} \cdot 100/C_{pm}$ , where the  $W_{sm}$  is mass of the source material, g;  $W_{pm}$  is the required mass of particular metal oxide, g; and  $C_{pm}$  is the content of particular metal oxide in the used source material. Mostly Na<sub>2</sub>CO<sub>3</sub> is used as the source of its alkali metal oxide (Na<sub>2</sub>CO<sub>3</sub> gives 58.5 % Na<sub>2</sub>O on thermal decomposition).

The sorbent along with the sorbed metal ions was converted into glass product by adding 15.04 g extra sodium carbonate. This composition was melted at 1250 °C. The end product has an excellent glass appearance without bubbles and any cracks.

## CONCLUSION

Silica sand, a cheaper and abundantly available material, was proved to be an

excellent adsorbent for adsorption of chromium from aqueous solutions under certain physico-chemical parameters. The maximum adsorption can be obtained at 28 °C in basic media (pH 10).

The negative value of  $\Delta H$  and negative value of  $\Delta G$  show the exothermal and spontaneous nature of sorption, respectively. The maximum sorption at 28 °C also supports the exothermal nature of sorption. The lower sorption at higher acid concentration and lower pH values may be due to the competition between the positively charged  $Pb^{++}$  and  $H^+$ . The lower sorption at higher pH might be due to the surface complexation phenomenon, which is facilitated by the dissociation of surface functional groups.

The used silica sand was the best glass forming material as it contains almost all basic components required to develop a good quality glass. The composition of the used sand was adjusted to suitable composition by adding small amount of  $Na_2O$ . This formulated composition was heated at elevated temperature and the best quality glass was formed immobilizing the adsorbed metal ions. The leachability test was performed both in highly acidic and basic media. The leachability of the adsorbed metal ions in both acidic and basic media was negligible. Comparative experimental data obtained in this study reveal that silica sand may be employed for the removal of chromium from aqueous industrial effluents before discharging them into water bodies. The sorbent may be converted into the leach resistant glass. The silica sand taken as sorbent contains a large amount of  $SiO_2$  and  $Al_2O_3$  which would be desirable network former. Because the glasses developed from the silica sand contain very small amount of  $Na_2O$ , the pH value of leachate was very low. In order to decrease the melting temperature,  $Na_2O$  in the form of sodium carbonate was added to silica sand in very small quantity and this composition was converted into a stable leach resistant glass form. The leachate of the developed glass in both acidic and basic media gave very ignorable quantity of sorbed chromium ion. The experimental data of its leachability proved it a stable product regarding to chemical durability, since one of the major objectives of the work is to effectively prevent

the release of sorbed metal ions into the environment. As the silica sand itself is a good sorbent for other heavy metals, this technique may be applied for removal and stabilization of other heavy metals as well.

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