

Study on Removal and Immobilization of Cadmium Ions

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Abstract

A technique was developed to remove and immobilize the cadmium ions from simulated industrial effluents. The cadmium ions were removed from industrial effluents by applying most economical method of sorption under certain physicochemical conditions. Removal of cadmium ions from industrial effluents using silica sand (originated from Ravi River) was studied to optimize the physicochemical conditions for maximum removal. The range of pH and temperature was optimized to get maximum removal of metal ions. Maximum removal (94–98 %) of cadmium was achieved with pH 10 and at temperature 25 °C. Under optimized conditions with temperature range of 298–318 K, ΔH , ΔS and ΔG_{298} for 200 mg/L solution were -71.10 ± 3.8 kJ/mol, -220.2 ± 11.5 J/(mol · K) and -6.70 ± 0.4 kJ/mol, respectively, and for 250 mg/L solution thermodynamic entities were $\Delta H = -108.7 \pm 5.7$ kJ/mol, $\Delta S = -335.7 \pm 17.5$ J/(mol · K) and $\Delta G_{298} = -9.64 \pm 0.4$ kJ/mol. This removal required certain physicochemical conditions; therefore, there were chances of desorption of the adsorbed metal ions under changed physicochemical conditions in final disposal. It was necessary to stabilize/immobilize sorbed metals ions by converting this “secondary waste” in a stable vitreous material having high resistance to leachability. Such stabilization/immobilization of sorbed metal ions was obtained by converting the silica sand along with the sorbed cadmium ions into the glass matrix to prevent leaching/mobilization in final disposal under natural conditions. Stability of sorbed metals ions in final matrix was tested by desorption attempts in acidic and basic media and in ground water as well.

Key words: cadmium removal, sorption, kinetics, physicochemical conditions, stabilization, glass matrix, leachability

INTRODUCTION

Cadmium is introduced into bodies of water from smelting, electroplating industries, cadmium-nickel batteries, fertilizers, pesticides, dyes, mining, pigments, stabilizers, alloy industries and sewage sludge. All these sources contribute in making the water toxic above 0.01 mg/L. The harmful effects of cadmium include a number of acute and chronic disorders, such as itai-itai disease, renal damage, emphysema, hypertension, and testicular atrophy-nausea, vomiting, diarrhea, muscular cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure [1, 2].

Various procedures have been reported for the removal of cadmium from aqueous media such as reductive precipitation [3, 4], solvent

extraction [5, 6], ion exchangers [7, 8] and adsorption. Adsorption is most economical method for the removal of cadmium from wastewater. Much work has been done on the removal of cadmium by clays [9–12], minerals such as goethite [13], hydroxyapatite [14] and calcite [15–18], calcareous soils [19, 20], some industrial by-product and waste materials such as slags, sludges [21], modified asphaltite ashes [22], bark, fly ash [23], chitosan, dead biomass, modified wool, moss, peat, seaweed, zeolite, humic acid [24], sesquioxides (iron, aluminium or manganese oxides) [25] and others.

The removal is optimized under certain physicochemical conditions therefore there are chances of desorption of the adsorbed metal ions under changed physicochemical conditions in final disposal. This possibility emphasized the

need to immobilize these adsorbed metal ions 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 encapsulate or immobilize contaminants within their "host" medium *i. e.*, sand, that sorbed them.

Due to network forming behaviour of sand, it is economical and a promising basic material for glass. Because of its good chemical durability and inexpensiveness, SiO₂ is the most widely used glass forming oxide and therefore the major ingredient of glass. Many glass forms of different waste streams have been developed [26, 27]. The chemical resistance of glass can allow it to remain in a corrosive environment for thousands or millions of years. Other strong reason is that glass has an ability to incorporate the waste contaminates in its microstructures [28]. The silica sand contains 80.361 % SiO₂; it was chosen for adsorption providing a basis from which glass formulation was developed. The cadmium 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 further additives with reasonable melting temperature is an achievement of the present work. Leachability testing is typically performed to measure the immobilization of sorbed metal ions.

EXPERIMENTAL

Silica sand (Origin: Ravi River) was washed twice with distilled water after washing with dilute HCl and dried in air. The composition of silica sand was analyzed by using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer Optima 3100 RL), as given in Table 1.

Samples of effluents from the various chemical industries situated in the industrial area of Lahore (Punjab), expecting to release cadmium compounds in their waste water, were collected and analyzed. The plastic sampling bottles were dipped in dilute nitric acid solution for 24 h and then washed with double distilled water and dried, prior to use. It was observed

TABLE 1

Chemical composition of silica sand (oxide basis)

Oxides	Mass %
SiO ₂	80.361
Al ₂ O ₃	5.301
CaO	4.369
Fe ₂ O ₃	2.988
MgO	1.456
Na ₂ O	1.232
K ₂ O	1.101
MnO	0.053
ZnO	0.004

that average concentration of cadmium in these effluents was between 200 to 250 mg/L. Therefore samples (A) 200 mg/L and (B) 250 mg/L were prepared for cadmium to cover the observed concentration of cadmium present in actual industrial waste. Standard solution of 1000 mg/L was prepared using extra pure cadmium nitrate tetrahydrate. From 1000 mg/L standard solution, different concentrations of cadmium nitrate tetrahydrate solutions were prepared by dilution. An assembly of glass columns was used for the adsorption treatment with dimensions of, inner diameter 2.35 cm, bed height 15.69 cm, and volume 68 cm³. The mass of the silica sand filled in column was 18.64 g. For adsorption treatment the effluents were allowed to pass through the column and removal efficiency of adsorbent was maximized by varying pH and temperature of samples.

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 cadmium. The change in the concentration of cadmium after treatment was calculated by taking difference between two concentrations. The concentration of cadmium ions in solutions was measured by atomic absorption spectrophotometer (Hitachi Z-2000) equipped with hollow cathode lamp of cadmium.

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

$$\text{Sorption (\%)} = [(C_i - C_t) / C_i] \cdot 100 \quad (1)$$

where C_i is the initial concentration of cadmium in solution, mg/L; C_t is concentration of solution after treatment, mg/L; V is volume of adsorbate, cm^3 ; m is amount of adsorbent, g.

The Sorption (%) and the distribution coefficient can be correlated as

$$(\% \text{ Sorption}) = 100K_d m/V \quad (2)$$

RESULTS AND DISCUSSION

Table 2 explains the effect of temperature on adsorption. Each sample solution with different temperature *i. e.* 25, 28, 32, 40 and 45 °C was passed through the adsorbent. Removal (%) was substantially affected by change in temperature and increased with decrease in temperature, as reported by [19, 20], but contrary to those of ceric oxide [29] and zirconium oxide [30]. Sorption was at maximum at 25 °C, in this order (%): 25 > 28 > 32 > 40 > 45.

The values ΔH and ΔS 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 in Kelvin; F represents the fraction sorbed at equilibrium, straight lines with correlation factor of 0.94 to 0.97 were obtained (Figs. 1, 2).

The values of ΔH and ΔS were computed using the relation

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

The free energy of adsorption ΔG was calculated using equation

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

TABLE 2

Effect of temperature on removal of cadmium (pH 10)

Adsorbing material (packed in 2.3 cm \varnothing \times 15.7 cm column)	Concentration of Cd, mg/L	Removal (%) at temperature, °C:				
		25	28	32	40	45
Silica sand	200	95	90	86	76	70
	250	98	95	89	80	72

TABLE 3

Thermodynamic quantities for adsorption of cadmium (pH 10)

Adsorbing material (packed in 2.3 cm \varnothing \times 15.7 cm column)	Concentration of Cd, mg/L	Thermodynamic quantities		
		ΔH , kJ/mol	ΔS , J/(mol \cdot K)	ΔG_{298} , kJ/mol
Silica sand	200	-71.10 \pm 3.8	-220.2 \pm 11.5	-6.70 \pm 0.4
	250	-108.7 \pm 5.7	-335.7 \pm 17.5	-9.64 \pm 0.4

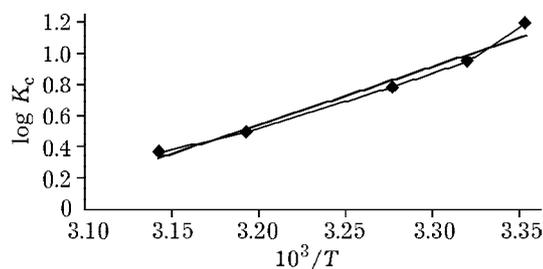


Fig. 1. Removal of Cd (200 ppm) on silica sand (pH 10).

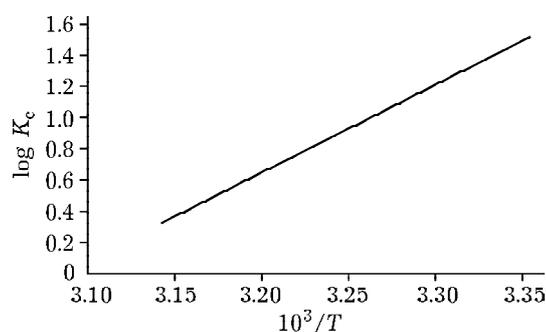


Fig. 2. Removal of Cd (250 ppm) on silica sand (pH 10).

The slope and intercept of Figs. 1 and 2 gave thermodynamic entities for 200 and 250 mg/L solutions, respectively. The values of thermodynamic entities were given in Table 3.

The negative enthalpy and negative free energy suggested an exothermic and spontaneous nature of sorption, respectively. This temperature dependent phenomenon led us to assume that almost all these adsorptive separation processes depended on physical adsorption rather than chemisorptions and therefore

TABLE 4
Effect of pH on the removal of cadmium at 25 °C

Adsorbing material (packed in 2.3 cm Ø × 15.7 cm column)	Concentration of Cd, mg/L	Removal (%) at pH:				
		2	4	7	10	12
Silica sand	200	60	68	85.5	94	82
	250	58	66	87	98	82.5

this is the focus of the present review. The heat of adsorption provided a direct measure of the strength of bonding between sorbate and surface. Physical adsorption from the liquid phase was invariably exothermic, although there were very small heat changes, as may be shown by thermodynamic data. 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 $\Delta S = S_{\text{ads}} - S_{\text{liq}}$ was necessarily to be negative. In order for significant adsorption to occur, the free energy change on adsorption ΔG must also be negative and since $\Delta G = \Delta H - T\Delta S$, this requires ΔH negative, or exothermic adsorption. Therefore maximum sorption at low temperature (25 °C) was exactly according to this theory.

Table 4 showed the effect of pH of sample on adsorption. The pH values of samples were adjusted by using buffer solutions as 2, 4, 7, 10 and 12. Samples with different pH were passed through column. The change in adsorption efficiency with change in pH of samples was found to be significant. The maximum sorption was obtained at pH 10 [22]. The effect of pH on sorption was justified by the fact that pH of the solution significantly affected the surface charge of the sorbents, de-

gree of ionization and speciation of the sorbates. Furthermore the difference in removal efficiency due to the solution pH was attributed to the precipitation of cadmium hydroxide ($\text{Cd}(\text{OH})_2$) at a higher pH. Increasing the pH implied a promotional increase of OH ions concentrations in solution disturbing equilibrium which could be achieved again through formations of greater amount of hydroxide out of the solution.

Once cadmium was removed from the industrial effluent through sorption, the next step was its stabilization which was obtained by converting the sorbent and sorbate into a stable and leach resistant glass matrix.

There is much research focused on the composition durability relationship of glass. If the inorganic oxides present in the silica sand have 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 was found to have suitable composition required to develop glass frits. The attempt was made to develop different glass formulations by varying composition of modifiers and fluxes based on the calculations (Table 5). The developed glass frits were characterized mainly focusing on their density and leachability.

Density was measured on the basis of volume displacement method using simple relation

TABLE 5
Composition of glass frits

Glass frit name	Melting point, °C	Composition, mass %			
		SiO ₂	Na ₂ O	CaO	Al ₂ O ₃
AG-301	1150	65	20	10	05
AG-312	1200	70	15	10	05
AG-319	1200	75	20	10	03
AG-327	1250	80	10	05	05
AG-328	1300	85	05	05	05
SG	1250	80	10	05	05

$D = m/v$, where m is mass of glass, v is the volume displaced by sample when dipped in known volume of water.

In order to rapidly determine the chemical durability of the glass, a **leaching test method** was derived from the standard PCT leach test method named as M-PCT [23, 24]. The glass sample was grinded and attained in 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 following equation: $SA = 6M/\rho\phi \cdot 0.89$, where SA is the surface area, cm^2 ; M is the mass, g; ρ is the density of glass sample, g/cm^3 ; ϕ is an average diameter, cm; 0.89 is factor to convert the results from sphere 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 was leached for 24 h at 99 °C in deionised water. The leachate of every phase was analyzed using Inductively Coupled Plasma Spectrometry (ICP) for the concentration of Si, Na, Al and particularly Cd. 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 formulations development.

The ML value was calculated as follows

$$ML = (m_0 - m_1)/SA$$

where ML is total mass lost, g/m^2 ; m_0 is mass of unleached specimen, g; m_1 is mass of specimen after leaching, g; SA is the sample surface area, m^2 .

Regarding to elemental analysis in leachate, the normalized element mass loss NL was calculated using formula

$$NL = C_i V/SAf_i$$

where NL is element mass lost, g/m^2 ; C_i is the concentration of element in the leachate, g/m^3 ; V is the volume of leachant, m^3 ; f_i is the mass fraction of element in unleached glass sample.

Amongst the studied formulations the composition AG-327 was found excellent in terms of its low leachability and higher chemical stability. The formulation AG-327 contained 10 % Na_2O whereas the percentage of Na_2O in studied silica sand was 1.2 %. This difference in percentage of Na_2O from 1.2 to 10 % was achieved by adding 15.04 g Na_2CO_3 as source material calculated by the given formula as

$$W_{s/m} = W_{p/m}100/C_{p/m}$$

where the $W_{s/m}$ is mass of the source material, g; $W_{p/m}$ is the required mass of particular metal oxide, g; $C_{p/m}$ is contents of particular metal oxide in used source material. The Na_2CO_3 was used as the source material for its alkali metal oxide. (Na_2CO_3 gives 58.5 % Na_2O on thermal decomposition.)

The silica sand along with the sorbed cadmium was converted into a composition (SG). The calculated amount of sodium carbonate was added in the silica sand (sorbing Cd) and was melted at 1250 °C. The end product was an excellent glass without bubbles and any crack. The leachability results of end glass product (SG) suggested no leachability/or mobility of sorbed cadmium ions (Table 6). The leachability results suggested encapsulation of sorbed Cd ions in the basic network of glass matrix, making its safe final disposal.

TABLE 6

Characteristics of developed glass frits

Glass frit name	Density, g/cm^3	ML*, g/m^2	Leachate pH	Concentration of elements in leachate, mg/L				
				Si	Na	Al	Ca	Cd
AG-301	2.2	2.10	8.8	0.5	6.3	0.2	0.2	–
AG-312	2.5	2.00	8.4	0.5	4.0	0.3	0.1	–
AG-319	2.4	1.98	7.8	0.7	3.8	0.4	0.3	–
AG-327	2.6	1.58	7.5	0.8	2.7	0.2	0	–
AG-329	3.2	1.23	7.0	1.6	2.5	0.2	0	–
SG	2.8	1.62	7.2	0.3	2.1	0.1	0	0

*ML is the total mass loss of glass.

CONCLUSIONS

The maximum sorption of cadmium was obtained at 25 °C in basic media (pH 10) by using the silica sand (cheaper and abundantly available material) under certain physicochemical parameters. The negative value of ΔH and maximum sorption at 25 °C supported the exothermic nature of sorption and negative value of ΔG suggested a spontaneous nature of the sorption. The lower sorption at higher acidic concentration and lower pH values was due to the competition between the positively charged cadmium and H^+ , and surface complexation phenomenon, which was facilitated by the dissociation of surface functional groups.

The silica sand retaining cadmium was converted into a stable and leachability resistant matrix by adding small amount of fluxes. This formulated composition was heated at elevated temperature and glass matrix was achieved. The leachability tests of the glass matrix were performed in both acidic and basic media where no leachability of cadmium was found. Comparative experimental data obtained in this study revealed that silica sand (a cheap and abundantly available sorbent) may be employed for the removal of cadmium from aqueous industrial effluents before discharging them into water bodies. Furthermore conversion of silica sand into stable vitreous matrix immobilized the sorbed metal ions in final disposal under existing natural physicochemical conditions.

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