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Utilization of industrial waste for cadmium removal from water and immobilization in cement

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ABSTRACT

The present study investigates the adsorption potential of metal sludge (a waste product of the electroplating industry) for the removal of cadmium from water. The adsorption capacity of the waste sludge for cadmium was ca. 40 mg g^{-1} at 25 °C. The adsorption was studied as a function of contact time, concentration and temperature by batch experiments. The adsorption has been found to be endothermic and data conform to the Langmuir model. The analysis of kinetic data indicates that the present adsorption system followed pseudo-first-order kinetics. After the adsorption studies, the metal-laden sludge adsorbent was immobilized in cement for its ultimate disposal. Physical properties such as initial and final setting time and the compressive strength of cement-stabilized wastes were tested to investigate the effect of the metal-laden sludge. The results of the present study clearly reveal that waste metal sludge can be used beneficially in treating industrial effluents containing cadmium and safely disposed of by immobilizing into cement. The proposed technology provides a two-fold advantage of wastewater treatment and solid waste management.

1. Introduction

The presence of heavy metals in the environment has been recognized as deleterious to the aquatic ecosystem and human health. There are numerous sources besides the mining and metal-related industries that discharge heavy metal-laden effluents, such as the tanning, battery, glassware, ceramics, electroplating, paints and photographic industries, to name a few. It is important to emphasize here that many metals are essential for human life in trace quantities, but become toxic if their concentration increases above a certain minimum level. Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn, may enter into the human food chain and result in health problems [1]. It may be added that most wastewaters contain heavy metals in concentrations greater than permissible limits, and therefore need to be removed. Treatment processes for metal contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and co-precipitation/adsorption [2].

Among these, the adsorption process has been found to be one of the most promising technologies in water pollution control [3]. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world [4] and has been successfully utilized for the removal of diverse types of pollutants including metal ions. However, the high capital and regeneration cost of activated carbon limits its large-scale applications for the removal of metals and other aquatic pollutants, which has encouraged researchers to look for low cost alternative adsorbents utilizing naturally occurring materials [5–8] and agro-industrial wastes [9–13]. Utilization of industrial waste materials has been a vital concern [14–16] over the past few years because these wastes represent unused resources and in many cases cause serious disposal problems. A number of industrial wastes [17–26] have been investigated as adsorbents for the removal of diverse types of pollutants from water and wastewaters. However, these have not been found to be as promising as activated carbon in water pollution control. Therefore, the search for efficient low-cost adsorbents is ongoing. Additionally, most adsorption studies do not suggest environmentally safe disposal methods for the metal-laden adsorbent generated as a result of the adsorption process.

The present study was undertaken with two main objectives: (i) to utilize industrial waste (electroplating waste metal sludge) as an adsorbent after proper treatment for the removal of cadmium from water and (ii) to dispose of this metal-laden sludge

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in cement by solidification/stabilization (S/S) technology, which is a widely accepted technology to control the release of hazardous waste directly into the environment.

Cadmium was selected as the adsorbate in the present study because it is a toxic heavy metal and has widespread industrial applications in electroplating, the manufacturing of nickel–cadmium batteries, smelting, alloy manufacturing, pigments, plastic, mining and refining processes [27–29]. Cadmium and its compounds are, compared to other heavy metals, relatively more water soluble. They are therefore more mobile in soil, generally more bioavailable and tend to bioaccumulate. Chronic cadmium exposure produces a wide variety of acute and chronic effects in humans. Cadmium accumulates in the human body and especially in the kidneys. Other effects of cadmium exposure are disturbances of calcium metabolism, hypercalciuria and the formation of stones in the kidney. High exposure can lead to lung cancer and prostate cancer. The permissible limit of cadmium discharge in wastewater is 0.1 mg/L in India [30].

Electroplating waste metal sludge was selected as the adsorbent since this waste has no application and poses a serious disposal problem. The treatment and use of this waste for cadmium adsorption would be desirable to the current waste disposal outcome and is the aim of this study. Equilibrium and kinetic studies were performed to describe the adsorption process. The study was extended to immobilize the metal-laden adsorbent into cement for environmentally safe disposal.

2. Materials and methods

2.1. Reagents and materials

A stock solution of cadmium was prepared from $Cd(NO_3)_2{\cdot}4H_2O$ by dissolving it in double distilled water. The stock solution was diluted further to obtain the standard and simulated sample solutions. Commercial Ordinary Portland cement 43 grade was used to immobilize metal-laden sludge. All reagents used were of analytical reagent grade.

2.2. Preparation of adsorbent using waste metal sludge

The waste metal sludge was first washed with double distilled water several times to remove adhering impurities and dried in an oven at 110 °C for 24 h. Thermal activation of this material was done at 500 ± 10 °C in muffle furnace for one hour in the presence of air, and then cooled at room temperature. After cooling, it was again washed with distilled water to remove the ash. Finally it was dried in an oven at 110 °C for 24 h. The resulting product was kept in a desiccator until further use. The particle size of British Standard Sieve (BSS) 150–200 mesh fraction was used in the present study. Some important characteristics of sludge adsorbent used are: surface area = 19.6 $m^2\,g^{-1}$; carbon content = ca. 21.6%; methylene blue number = 4; iodine number = 10.

2.3. Apparatus

An atomic absorption spectrophotometer (AAS) from Hitachi, model no. Z-7000, was used to determine the concentration of cadmium in aqueous solutions. A Vicat apparatus (CE360, Vicat apparatus, Geotest Instrument Corporation, USA) was used to determine the initial and final setting time (IST and FST) of mortar samples. A hazardous waste filtration system from Millipore model no. YT-30142 HW was used for the toxicity characteristic leaching procedure as recommended by the United States Environmental Protection Agency (USEPA) [31]. A compressive strength-testing machine from Central Scientific Instruments Company was used to determine the compressive strength of mortar samples.

2.4. Adsorption studies

The adsorption of cadmium on metal sludge was studied by batch method. A known volume (10 mL) of cadmium solutions of varying initial concentrations (1.0×10^{-4}–10.0×10^{-4} M), taken in 50-mL stoppered tubes, was shaken with a fixed dose of adsorbent (0.10 g) for a specified contact time in a thermostated shaking assembly. After equilibrium, samples were filtered using 0.45 μm filters (Whatman) and the concentration of cadmium was analyzed by AAS. Reproducibility of the measurements was determined in triplicate and the average values are reported. Relative standard deviations were found to be within ±3.0%. The amount of cadmium adsorbed (q_e in $mg\,g^{-1}$) was determined as follows:

$$q_e = \frac{(C_0 - C_f)V}{m} \tag{1}$$

where C_0 and C_f are the initial and final concentrations of cadmium in solution ($mol\,L^{-1}$), V is the volume of solution (L) and m is the mass of the adsorbent (g). The pH of all solutions in contact with the adsorbent was found to be in the range 6.5–7.5.

2.5. Preparation and curing of cement pastes and mortars

A separate batch adsorption experiment similar to that described previously (under similar conditions) but with a larger volume (1 L) of adsorbate solution with a larger quantity of sludge adsorbent (10 g) was conducted to produce the metal-laden adsorbent for preparation of the solidified specimens. After the equilibration time, the solid was separated from the liquid. The metal-laden adsorbent was then dried in an oven at 110 °C for 24 h. After drying, the metal-laden adsorbent was added in different proportions to cement and sand to produce a cementitious system. Well-mixed mortar pastes were cast in 2.78 in. cubic iron molds. The cubes were demolded after 24 h and dipped in water for curing. These cubes were tested for compressive strength on 3, 7, 28, 60 and 90 days of curing. Three replicates were tested for each time and the average value was compared with the values obtained for the blank sample (without the addition of metal-laden sludge). All the cement pastes and mortars were prepared by the methods described in the IS: 4031-1968 guidelines [32].

2.6. Leaching studies

An appropriate way to examine the effectiveness of the fixation of contaminants after solidification process is to perform leaching tests. These tests are commonly used to determine leachability under the selected test conditions. Standard method no. 1311 [31] as recommended by the United States Environmental Protection Agency (USEPA) was used for the leaching tests. The sample was mixed with acetic extractant of a pH value of 2.88. The solid-to-liquid ratio was 1:20, following an agitation extraction with a speed of 30 rpm for 18 h. The leachate was filtered through a 0.45 μm filter to remove suspended solids. The concentration of cadmium was analyzed by AAS. Each extraction was done in triplicate, and the average value is reported to ensure the reproducibility of the data.

3. Results and discussion

3.1. Effect of contact time

In order to establish the equilibration time for maximum uptake and to know the kinetics of the adsorption process, cadmium adsorption on sludge was investigated as a function of contact time

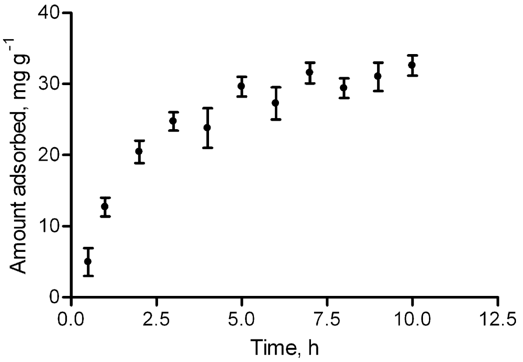

Fig. 1. Effect of contact time on the adsorption of cadmium on metal sludge adsorbent ($C_o = 5.5 \times 10^{-4}$ M, temperature = 25 °C, adsorbent dosage = 10 g L^{-1}).

and the results are shown in Fig. 1. The figure shows that the uptake rate was initially rapid, with 50% of the adsorption was complete within 2 h. Equilibrium was achieved within 7 h (Fig. 1), so an equilibration period of 10 h was selected for all further experiments.

The effect of concentration on the equilibration time was also investigated as a function of initial concentration of cadmium (results are not shown here). It was found that equilibrium time as well as the time required to achieve a definite fraction of equilibrium adsorption was independent of initial concentration. These results indicate that the present adsorption study follows pseudo-first-order kinetics, which is confirmed by Lagergren's plots discussed under kinetic modeling (Section 3.2).

3.2. Kinetic modeling

Kinetics of adsorption is an important characteristics in defining the efficiency of adsorption. Various kinetic models have been proposed by different researchers, where the adsorption has been treated as first order [17,33], pseudo-first-order [34,35], and pseudo-second-order process [36]. Different systems conform to different models. The Lagergren's rate equation [37] is the one most widely used [17,33,38] for the sorption of a solute from a liquid solution. The linear form of pseudo-first-order equation is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \qquad (2)$$

where q_e and q_t (mg g^{-1}) are the amount of cadmium adsorbed at equilibrium and at time t (h), respectively, and k_f (h^{-1}) is the pseudo-first-order rate constant. The values of $\log(q_e - q_t)$ were calculated from the kinetic data from Fig. 1 and plotted against time (t) in Fig. 2(A). The plots were found to be linear with good correlation coefficients ($R^2 = 0.9993$) indicating that Lagergren's model is applicable to the cadmium adsorption on sludge and that the process is pseudo-first-order. The theoretical $q_{e(cal)}$ values were also found in accordance with the experimental uptake values $q_{e(exp)}$ (Table 1). This suggests that the adsorption system follows pseudo-first-order kinetics.

The kinetics were also described as pseudo-second-order process [36,39,40]

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where q_e and q_t are the amount of cadmium adsorbed (mg g^{-1}) at equilibrium and at time t (h), respectively, and k_s (g mg^{-1} h^{-1}) is the rate constant of pseudo-second-order kinetics. The plots between t/q_t versus t were drawn and are shown in Fig. 2(B). The correlation coefficient (R^2) for the pseudo-second-order kinetic model was 0.9746 (less than 0.99), and the theoretical $q_{e(cal)}$ values calculated for the pseudo-second-order model did not give reasonable values with regard to the experimental uptake values, $q_{e(exp)}$ (Table 1). This suggests that the present adsorption system cannot be fully described by pseudo-second-order process.

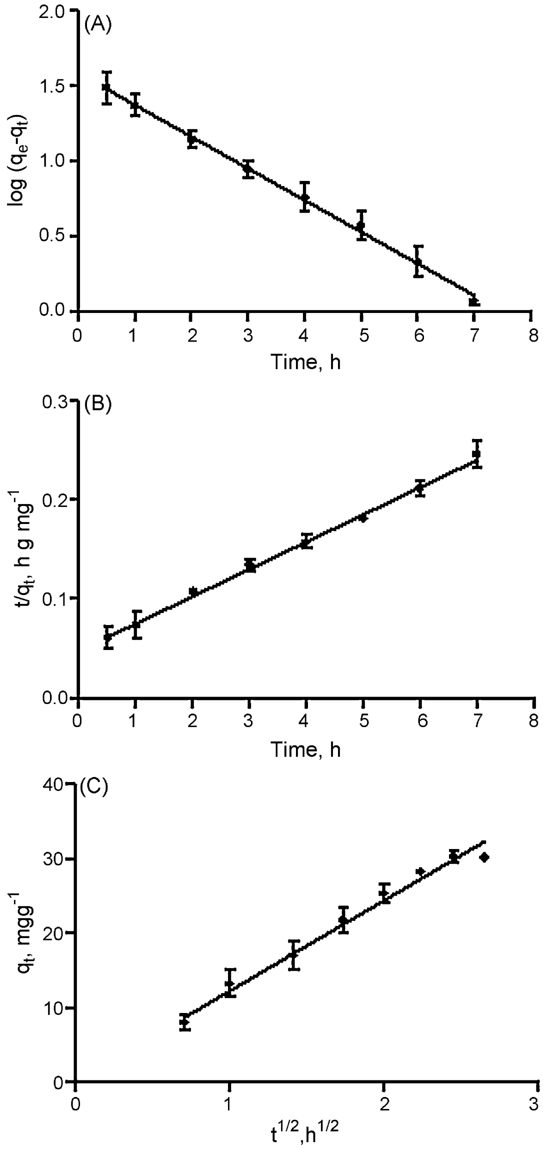

Fig. 2. Kinetic modeling of cadmium adsorption on metal sludge adsorbent (A) pseudo-first-order kinetic plot, (B) pseudo-second-order kinetic plot, and (C) Weber and Morris intraparticle diffusion plot.

There are essentially three consecutive mass transport steps associated with the adsorption of solute from the solution by an adsorbent. These are (i) film diffusion, (ii) intraparticle or pore diffusion, and (iii) sorption into interior sites. The third step is very rapid and hence film and pore transports are the major steps controlling the rate of adsorption. In order to understand the diffusion mechanism, kinetic data was further analyzed using the intraparticle diffusion model based on the theory proposed by Weber and Morris [41]. The amount of cadmium adsorbed (q_t) at time (t), was plotted against the square root of t ($t^{1/2}$), according to Eq. (4) proposed by Weber and Morris and the resulting plot is shown in Fig. 2(C).

$$q_t = k_{id} t^{1/2} + C \qquad (4)$$

where k_{id} (mg g^{-1} $h^{-0.5}$) is the intraparticle diffusion rate constant. According to Eq. (4), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C when the adsorption mechanism follows the intraparticle diffusion process [42]. As can be seen

Table 1
Comparison of pseudo-first-order and pseudo-second-order model parameters, and calculated amount adsorbed, $q_{e(cal)}$ and experimental amount adsorbed, $q_{e(exp)}$ values for initial cadmium concentration.

C_0 (M)	$q_{e(exp)}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		k_f (h^{-1})	$q_{e(cal)}$ (mg g^{-1})	R^2	k_s (g mg^{-1} h^{-1})	$q_{e(cal)}$ (mg g^{-1})	R^2
3.0×10^{-4}	31.2	4.81×10^{-1}	31.9	0.9993	9.84×10^{-3}	41.5	0.9746

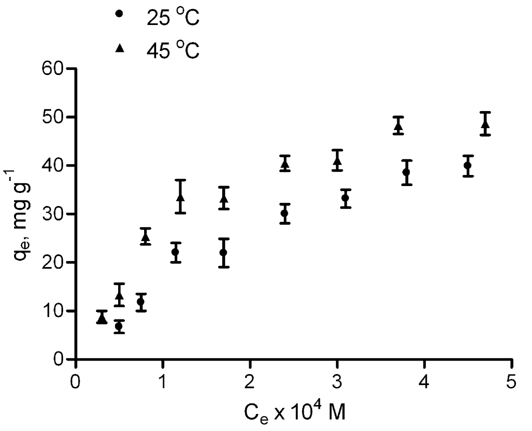

Fig. 3. Adsorption isotherms of cadmium on metal sludge adsorbent at different temperatures (adsorbent dosage = 10 g L^{-1}).

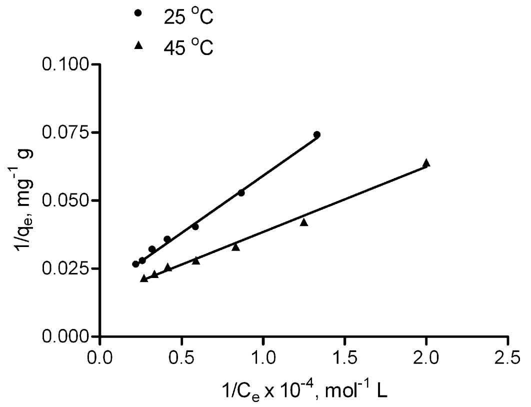

Fig. 4. Langmuir isotherms of cadmium adsorption on metal sludge adsorbent at different temperatures.

from Fig. 2 (C), the intercept of the line does not pass through the origin and the correlation coefficients (R^2) are less than 0.99 indicating that the mechanism of cadmium adsorption onto the prepared adsorbent does not follow Weber and Morris model.

3.3. Adsorption isotherms

In order to determine the adsorption efficacy of sludge for cadmium adsorption, the equilibrium adsorption studies were carried out at room temperature (25 °C) and the adsorption isotherms are shown in Fig. 3. It is clear from Fig. 3 that the isotherm initially rises sharply, indicating that plenty of readily accessible sites are available in the beginning for adsorption. However, after equilibration when the adsorbent becomes saturated, a plateau is reached indicating that no more sites are available for further adsorption. An adsorption capacity of 37.8 mg g^{-1} was observed for cadmium on sludge adsorbent at 25 °C. Adsorption capacities from the present study were compared with other adsorbents from previous studies [43–50] and are shown in Table 2. It is evident that the prepared adsorbent in this study has efficient adsorption capacity for cadmium removal from water.

To understand the effect of temperature on the adsorption of cadmium to the sludge, experiments were conducted at 45 °C and results are compiled in Fig. 3. A comparison of adsorption isotherms at 25 and 45 °C shows that adsorption increases (37.8–48.3 mg g^{-1}) with temperature.

Table 2
Adsorption capacities of cadmium on different adsorbents.

Serial number	Adsorbents	Amount adsorbed (mg g^{-1})	References
1.	Rice husk	21.3	[43]
2.	Sodium hydroxide treated rice husk	20.2	[44]
3.	Sugar beet pulp	17.2	[45]
4.	Corncobs	8.9	[45]
5.	Sulfuric acid treated rice husk	34–41	[46]
6.	Chitosan	5.9	[47]
7.	Eutrophic peat	20.2	[48]
8.	Waste sludge	15.7	[49]
9.	Red mud	10.6	[50]
10.	Waste metal sludge	37.8	Present study

Table 3
Langmuir constants for the adsorption of cadmium on metal sludge adsorbent at different temperatures.

Temperature (°C)	q_m (mg g^{-1})	b (L mol^{-1})	R^2
25	58.48	4.27×10^3	0.9958
45	68.96	7.25×10^3	0.9910

The adsorption data was further analyzed and found to conform best to following Langmuir model (Eq. (5)):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \tag{5}$$

where q_e (mg g^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mol L^{-1}), q_m (mg g^{-1}) is the Langmuir constant representing the maximum monolayer adsorption capacity and b (L mol^{-1}) is the Langmuir constant related to energy of adsorption. The plots of $1/q_e$ as a function of $1/C_e$ for the adsorption of cadmium are shown in Fig. 4. The plots are linear with good correlation coefficients. The values of the monolayer capacity (q_m) and equilibrium constant (b) have been evaluated from the intercept and slope of these plots and given in Table 3. It is seen from Table 3 that monolayer capacity (q_m) of the adsorbent for the cadmium is comparable to the maximum adsorption obtained from the adsorption isotherms (Fig. 3).

Thermodynamic parameters were calculated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. Thermodynamic parameters were calculated using Eqs. (6)–(8):

$$\Delta G^\circ = -RT \ln K \tag{6}$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\ \Delta S^\circ \tag{8}$$

Table 4
Thermodynamic parameters for adsorption of cadmium on metal sludge adsorbent at different temperatures.

Temperature (°C)	K	ΔG° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})
25	2.36×10^5	−20.7	69.58	20.82
45	4.02×10^5	−23.5	73.97	

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in Kelvin and K is the equilibrium constant, related to the Langmuir constant b via Eq. (9), where the value 55.5 corresponds to the molar concentration of the solvent (in this case water) with units of mol L^{-1} [51–53].

$$K = b \times 55.5 \tag{9}$$

The values of the above stated parameters are summarized in Table 4. The positive value for ΔH° indicates that the process is endothermic and a negative ΔG° value indicates a spontaneous process. A positive ΔS° value indicates the affinity of the adsorbent for cadmium.

3.4. *Treatment of effluent of a local battery industry*

The adsorption study of cadmium on prepared adsorbent revealed that the adsorbent adsorbs cadmium to an appreciable extent, and therefore, can be fruitfully used for the removal of metal ions from wastewaters. The applicability of this adsorbent was further assessed by column operations by treating battery wastewater obtained from a local battery industry for the removal of diverse types of trace and heavy metal ions and other pollutants.

The treatment of battery industry wastewater was carried out by passing it through a column (cross-sectional area: 0.9 cm^2; height: 3.1 cm; mass: 1.0 g) of prepared adsorbent, of particles of size 50–200 mesh, at a flow rate of 2.5 mL min^{-1}. 10 mL aliquot was collected and analyzed. The breakthrough curve obtained after passing the wastewater through prepared adsorbent column is shown in Fig. 5. From the breakpoint of this curve, it can be seen that a column of 1 g of prepared adsorbent, as used by us can treat 150 mL of battery industry wastewater. Thus, the results show that 1 kg of prepared adsorbent can treat 150 L of the battery industry effluent obtained from local factory. It is therefore, reasonable to infer that the prepared adsorbent can be fruitfully used as an alternative adsorbent for treating metal-containing wastewater.

3.5. *Initial and final setting time*

One of the most important properties of cement is its setting time, as this will regulate how much time the contractor will have to get the concrete placed and finished. Setting tests are used to characterize how a particular cement paste sets and can give some indication of whether or not cement is undergoing normal hydration. Normally, two setting times are defined [54]: (i) *initial setting* occurs when the paste begins to stiffen considerably and (ii) *final setting* occurs when the cement has hardened to the point at which it can sustain some load. A Vicat apparatus defines initial and final setting time based on the time at which a needle of a particular size and weight either penetrates or fails to penetrate a cement paste sample to a given depth.

Initial and final setting time (IST and FST) were determined following the method described in Indian standard method IS: 8112-1989 [55], according to which initial setting time of 43 grade Ordinary Portland cement is at least 30 min, while the final setting time is less than 600 min. Both of these parameters were determined for the blank samples as well as after the addition of 1–20% metal-laden sludge in cement. All the experiments were carried out in triplicate to assure accuracy and reproducibility. The results of these studies are compiled in Fig. 6. It is seen from the results that there was a delay in the initial and final setting time of cement as the metal-laden sludge content was increased.

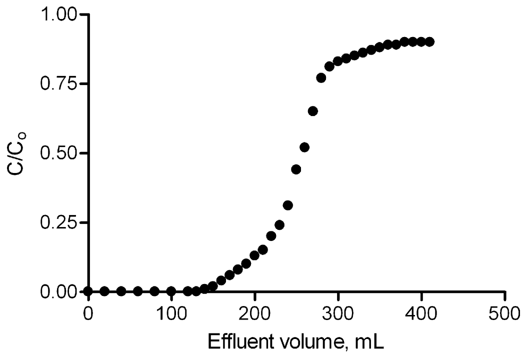

Fig. 5. Breakthrough curve of battery industry effluent on metal sludge adsorbent.

3.6. *Compressive strength of solidified blocks*

The effect on compressive strength of cement containing 1–20% metal-laden sludge is presented in Fig. 7. The results of compressive strength on 3, 7, 28, 60 and 90 days of curing are reported here. The addition of metal-laden sludge in cement exhibits considerable effect on the rate of strength attainment as well as on the compressive strength of the binding system. Great care was taken to reduce the variability associated with batch preparation steps. It is clear from Fig. 7 that increasing the ratio of metal-laden sludge causes a slight reduction in the compressive strength.

3.7. *Leaching studies*

Preliminary results of the leaching study show that cadmium did not significantly leach from mortar samples with 1–20% sludge composition. These results suggest that cadmium has the tendency to bind in cement-based systems. The important binding mechanisms of cadmium in cement may involve sorption of cadmium on calcium–silicate–hydrate (C–S–H) [56]. Based on these findings, it is reasonable to infer that solidification/stabilization technology offers safe disposal of metal-laden adsorbents.

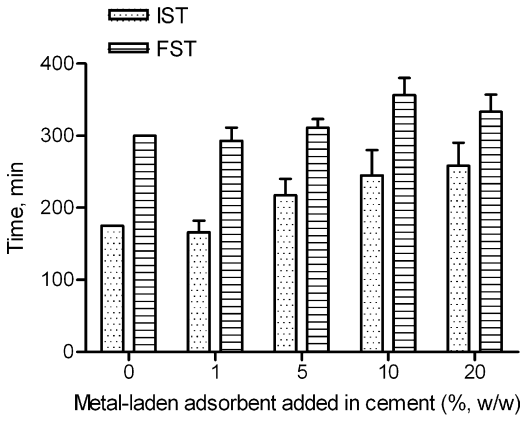

Fig. 6. Effect of addition of 1–20% metal-laden sludge adsorbent on the initial (IST) and final setting time (FST) of cement.

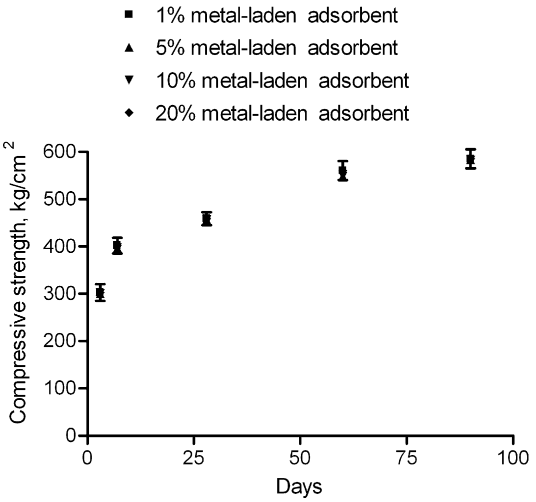

Fig. 7. Effect of fixation of metal-laden sludge adsorbent on the compressive strength of cement.

4. Conclusions

The results of the present study clearly suggest that waste metal sludge from the electroplating industry can be successfully utilized for the removal of cadmium from water and wastewater. The adsorption of cadmium on sludge was 37.8 mg g^{-1} at 25 °C. The adsorption was found to be endothermic and data conform to the Langmuir model. The analysis of kinetic data indicates that the adsorption process followed pseudo-first-order kinetics. The metal-laden adsorbent was then immobilized into the cement for ultimate disposal. The proposed technology (utilization of industrial wastes for effluent treatment and ultimate disposal of adsorbents laden with pollutants in cementitious materials by fixation) provides a twofold benefit of wastewater treatment and solid waste management.

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