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Vanadium removal from water by waste metal sludge and cement immobilization

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Abstract

The present study was first carried out to investigate the adsorption potential of metal sludge (a waste product of electroplating industry) in removing vanadium from water. The adsorption capacity of metal sludge for vanadium was found 24.8 mg/g at 25 °C. The adsorption was studied as a function of contact time (0.5–10 h), concentration ($1.5 \times 10^{-4} - 9.5 \times 10^{-4}$ M) and temperature (25 and 45 °C) by batch method. The adsorption has been found to be endothermic and data conform to Langmuir model. The analysis of kinetic data indicates that present adsorption system is a pseudo-first-order process and intraparticle diffusion controlled. After adsorption studies, the metal-laden sludge adsorbent was immobilized into the cement for its ultimate disposal. Physical properties such as initial and final setting time, compressive strength of cement stabilized wastes were tested to see the effect of metal-laden sludge in cement. The results of present study clearly reveal that metal sludge can be fruitfully employed in treating industrial effluents containing vanadium and further safely dispose of by immobilizing it into cement. The proposed technology provides a two-fold advantage of wastewater treatment and solid waste management.

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1. Introduction

Millions of people worldwide are suffering with the shortage of fresh and clean drinking water, which is a basic need for all human beings. Freshwater resources are continuously degrading mainly due to the rapid pace of unplanned urbanization, industrialization, population growth, over exploitation and, poor management. The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and

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toxic industrial wastes, dumping of industrial effluent, and runoff from agricultural fields. It is well known that 70-80% of all illnesses in developing countries are related to water contamination, particularly susceptible for women and children [1]. Metal ions are one of the important categories of water pollutants, which are toxic for humans through the food-chain pyramid. Various toxic heavy metal ions discharged into the environment through different industrial activities, constituting one of the major causes of environmental pollution. Treatment processes for metals contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and co-precipitation/adsorption [2].

Among these, adsorption process has been found as one of the most promising technology in water pollution control [3]. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications

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throughout the world [4] and has been successfully utilized for the removal of metal ions, dyes, phenols, detergents, pesticides, humic substances, chlorinated hydrocarbons and many other chemicals and organisms. However, prolific use of activated carbon is sometimes restricted due to its higher cost if compared to other physical and chemical treatment processes. Attempts have therefore, been made to develop low-cost alternative adsorbents utilizing naturally occurring materials [5–8] and agro-industrial wastes [9–13]. Utilization of industrial waste materials is of vital concern [14–16] over the past few years because these wastes represent unused resources and, in many cases, cause serious disposal problems. The aim behind using waste materials as adsorbents is that it will provide a two-fold advantage to environmental pollution. Firstly, the volume of solid waste materials could be partly reduced and secondly, prepared adsorbent can treat toxic industrial effluents at a reasonably cost. Thus, a number of industrial wastes [17–26] have been investigated so far as adsorbents for the removal of diverse types of pollutants from water and wastewaters. However, these have not been found as promising as activated carbon in water pollution control. Therefore, the search for efficient low-cost adsorbents is still going on. Further, most of the adsorption studies did not suggest any environmentally safe disposal method of metal-laden adsorbent generated after 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 vanadium from water and (ii) to dispose of this metal-laden electroplating sludge in cement by solidification/stabilization (S/S) technology, which is widely accepted technology to control the release of hazardous waste directly into the environment.Vanadium was selected as adsorbate in present study because it is toxic metal and has widespread industrial applications. The major industries that contribute to water pollution by vanadium are ceramic, glass, textile, photography, metallurgy, rubber and plants producing industrial inorganic chemicals and pigments [27].

The average concentration of vanadium in the earth's crust is 150 μ g/g [28,29]; concentrations in soil vary in the range 3–310 μ g/g [28,30] and may reach high values (up to 400 μ g/g) in areas polluted by fly ash [28,31]. The concentration of vanadium in water is largely dependent on geographical location and ranges from 0.2 to more than 100 μ g/L in freshwater [28,29], and from 0.2 to 29 μ g/L in seawater [28,30].

Vanadium may exist in oxidation states +3, +4, and +5 in the environment. V^{3+} and V^{4+} act as cations, but V^{5+} , the most common form in the aquatic environment, reacts both as a cation and anion [32]. Speciation of vanadium in solution is complex and highly dependent on vanadium concentration. Under most common environmental conditions of pH and redox potential, and at the low concentrations reported for vanadium in natural waters, the vanadate is largely monomeric. At higher concentrations, such as those used in toxicity testing, dimeric and trimeric forms may predominate, and this can have an effect on how the vanadium compounds interact with biological systems [32,33]. Within tissues in organisms, V^{3+} and V^{4+} predominate because of largely reducing conditions; in plasma, however, which is high in oxygen, V^{5+} is formed [32,33].

Speciation of vanadium has been discussed by few workers [34,35] suggesting that 12 vanadium species can coexist in solution, which can be categorized as cationic $[VO_2^+]$, neutral $[VO(OH)_3]$ and anionic species $V_{10}O_{26}(OH)_2^{4-}$, $V_{10}O_{27}(OH)^{5-}$, $V_{10}O_{28}^{6-}$ and other mono or polyvanadate species $VO_2(OH)^{2-}$, $VO_3(OH)^{2-}$, VO_4^{3-} , $V_2O_6(OH)^{3-}$, $V_2O_7^{4-}$, $V_3O_9^{3-}$ and $V_4O_{12}^{4-}$ [34,35]. Speciation diagrams for vanadium can be found elsewhere [34,36] which imply that below pH 3, vanadium exists in cationic forms and anionic form dominates in the pH range of 4–11.

The electroplating waste metal sludge was selected as adsorbent and its adsorption efficiency was examined for vanadium removal from water. Electroplating metal sludge is one of the main industrial wastes, which is produced in enormous quantities every year. A total volume of 125,000 tons of electroplating waste was generated in USA in 2001 [37]. This waste finds no proper application anywhere and poses a serious disposal problem. It was thought desirable to treat this waste and use as an adsorbent for vanadium removal from aqueous solutions. Little attention has been focused on vanadium removal however, adsorption studies of vanadium are important as vanadium compounds show harmful health effects to human beings [38].

The aim of this study was to investigate the efficiency of electroplating waste metal sludge as adsorbent for the removal of vanadium from aqueous solutions. Equilibrium and kinetic studies were performed to describe the adsorption process. Different models were tested to determine the rates and mechanisms of the adsorption process. The study was further extended to immobilize the metal-laden adsorbent into cement for environmentally safe disposal.

2. Experimental

2.1. Reagents and materials

Standard solutions of vanadium were prepared from ammonium vanadate by dissolving it in double distilled water. Commercial Ordinary Portland cement 43 grade was used to immobilize metal-laden sludge. The chemical composition and physical properties of cement are shown in Tables 1 and 2, respectively. All reagents used were of analytical reagent grade.

Table 1
Chemical composition of the cement

Constituents	% (w/w)
Si	20.80
Al	4.40
Fe	3.79
Ca	66.10
Mg	3.30
Na	0.20
К	0.70

Table 2Physical properties of the cement

Parameters	Results
Loss on ignition (%)	0.7
Consistency (%)	31.6
Soundness [*] (mm)	1.0
Initial setting time (min)	175
Final setting time (min)	300

*"Soundness" refers to the ability of a hardened cement paste to retain its volume after setting without delayed destructive expansion Ref. [52].

2.2. Preparation of adsorbent using waste metal sludge

Electroplating waste metal sludge was collected from Metal Industries, Mohkampur, Phase I, Meerut, U.P., India. The waste metal sludge was chemically analyzed and results are shown in Table 3. It was first washed with double distilled water several times and dried in an oven at $120 \,^{\circ}$ C overnight. Thermal activation of this material was done at $550 \,^{\circ}$ C in muffle furnace for 1 h in the presence of air. Then the product was allowed to cool at room temperature. After cooling, it was again washed with distilled water to remove the ash content. Finally, it was dried in an oven at $120 \,^{\circ}$ C overnight. The final product obtained after a series of treatment processes mentioned earlier was kept in desiccator for further use as an adsorbent. The particle size of British Standard Sieve (BSS) 150–200 mesh fraction was used in the present study. The BET surface area of metal sludge adsorbent was found $19.6 \, \text{m}^2/\text{g}$.

2.3. Apparatus

An Atomic Absorption Spectrophotometer (AAS) from Hitachi model No. Z-7000 was used to determine the concentration of vanadium in aqueous solutions. Vicat apparatus (CE360, Vicat apparatus, Geotest Instrument Corporation, USA) was used to determine the initial and final setting time (IST and FST). Hazardous waste filtration system from Millipore model no. YT-30142 HW was used to carry out toxicity characteristic leaching procedure as recommended by United States Environ-

Table 3				
Chemical	composition	of the	waste	sludge

	% (w/w)
Loss on ignition	22.87
Al	1.25
Ba	0.03
Ca	24.02
Cr	1.21
Cu	3.05
Fe	20.02
К	0.22
Mg	0.15
Mn	0.17
Na	1.07
Ni	0.03
Pb	0.02
Si	2.54
Zn	21.38

mental Protection Agency (USEPA) [39]. Compressive strength testing machine from Central Scientific Instruments Company was used to determine the compressive strength of mortar samples.

3. Methods

3.1. Adsorption studies

The adsorption of vanadium on metal sludge was studied at room temperature $(25 \pm 2 \,^{\circ}\text{C}$, humidity 37%) by batch method. A known volume (10 mL) of vanadium solutions of varying initial concentrations $(1.5 \times 10^{-4} - 9.5 \times 10^{-4} \text{ M})$, taken in 50-mL stoppered glass 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 nylon filters (Whatman) and the concentration of the adsorbate (vanadium) in the residual solution was analyzed by AAS. The amount of vanadium adsorbed on the adsorbent was determined from difference between the initial and equilibrium concentrations. Reproducibility of the measurements was determined in triplicates and the average values are reported. Relative standard deviations were found to be within $\pm 3.0\%$. The pH of the solutions was measured before and after the equilibration. The pH of blank vanadium solutions was observed 5.2, and after adding the adsorbent, it was 7.6 in the batch reactor.

3.2. Column studies

In the present study, a glass column ($50 \text{ cm} \times 1.05 \text{ cm}$) was fully loaded with adsorbent on a glass wool support. Double distilled water was used to rinse the adsorbent and to remove any bubbles present. Vanadium solution was poured over the column and the column effluent was allowed at a flow rate of 2.5 mL/min. A definite amount of the column effluent (10 mL) was taken and the concentration of vanadium determined from time to time by AAS. This process has continued until the concentration in the column effluent started increasing and finally becomes constant. The plots of concentration of the adsorbate in the column effluent and volume of the effluent provide breakthrough curves.

3.3. Preparation and curing of cement pastes and mortars

A separate batch adsorption experiment similar to that described above (under identical conditions) but with a larger volume (1 L) of adsorbate solution with a larger quantity of metal 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 by decantation. The metal-laden adsorbent was then dried in an oven at 110 °C overnight. 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" cubic iron molds. The cubes were demolded after 24 h and were kept 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 every 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 IS: 4031-1968 guidelines [40].

3.4. Leaching studies

An appropriate way to examine the effectiveness of the immobilization of contaminants after solidification process is to perform the leaching test. These tests are commonly used to determine the leachability under the selected leach testing conditions. This study has been carried out by following the standard method no. 1311 [39] as recommended by United States Environmental Protection Agency (USEPA). 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- μ m membrane filter to remove suspended solids. The vanadium concentrations were analyzed by using AAS. Each extraction was done in triplicate, and the average value is reported to ensure the reproducibility of the data.

4. Results and discussion

4.1. Effect of contact time

In order to establish the equilibration time for maximum uptake and to know the kinetics of adsorption process, the adsorption of vanadium on metal sludge was studied as a function of contact time and results are shown in Fig. 1. It is seen from figure that the uptake rate is rapid in the beginning, and 50% adsorption is complete within 2 h. The equilibrium adsorption of vanadium on metal sludge was achieved within 7 h (Fig. 1), and therefore, the 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 vanadium. It was found that time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption was independent of initial concentration (results are not shown here). These results indicate that the



Fig. 1. Effect of contact time on the uptake of vanadium on metal sludge adsorbent (temperature $25 \,^{\circ}$ C).



Fig. 2. Adsorption isotherms of vanadium on metal sludge adsorbent (\blacktriangle) 25 °C and (\odot) 45 °C.

adsorption process is a pseudo-first-order, which is confirmed by Lagergren's plots discussed later under dynamic modeling.

4.2. Adsorption isotherms

In order to determine the adsorption potential of metal sludge, the equilibrium adsorption studies were carried out at room temperature (25 °C) and the adsorption isotherms are shown in Fig. 2. It is clear from Fig. 2 that initially isotherm rises sharply indicating that plenty of readily accessible sites are available in the beginning for adsorption. However, after achieving equilibration, when adsorbent becomes saturated, a plateau is reached indicating that no more sites are available for further adsorption. An adsorption capacity of 24.8 mg/g was observed for vanadium on metal sludge at 25 °C. Since the metal sludge mainly contains calcium and iron (produced during the treatment with lime and ferrous sulfate), which make surface of metal sludge more positively charged (unpublished data). This positively charged surface of metal sludge gives rise more adsorption of negatively charged species on the surface of adsorbent due to electrical attraction between anionic species and positively charged surface of the adsorbent. Similar results have been reported by other workers while studying dyes adsorption on metal sludge [41].

In order to understand the effect of temperature on the adsorption of vanadium on metal sludge adsorbent, experiments were also conducted at 45 °C and results are compiled in Fig. 2. A comparison of adsorption isotherms at 25 and 45 °C shows that adsorption slightly increases (24.8–27 mg/g) by increasing temperature, indicating that the process is endothermic in nature.

The adsorption data was further analyzed and found to conform best to following Langmuir model (Eq. (1))

$$\frac{1}{q_{\rm e}} = \frac{1}{q_{\rm m}} + \frac{1}{q_{\rm m}bC_{\rm e}}\tag{1}$$

where ' q_e ' (mg/g) is the amount adsorbed at equilibrium concentration ' C_e ' (mol/L), ' q_m ' (mg/g) is the Langmuir constant representing the maximum monolayer adsorption capacity and 'b' (L/mol) 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 vanadium are shown in Fig. 3. The plots were found to be linear with good correlation coefficients $R^2 = 0.9992$ and 0.9989, at 25 and 45 °C, respectively.



Fig. 3. Langmuir isotherms of vanadium adsorption on metal sludge adsorbent at different temperatures (\blacktriangle) 25 °C and (\bigcirc) 45 °C.

4.3. Kinetic modeling

Kinetics of adsorption is one of the 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 [17,42], pseudo-first-order [43,44], and pseudo-second-order process [45]. Different systems conform to different models. The Lagergren's rate equation [46] is the one most widely used [17,42,47] for the sorption of a solute from a liquid solution. Thus this pseudo-first-order equation

$$\log(q_{\rm e} - q_{\rm t}) = \log q_{\rm e} - \frac{k_{\rm ads}}{2.303}t$$
(2)

where ' q_e ' and ' q_t ' (mg/g) are amount of vanadium adsorbed at equilibrium and at time *t*, respectively, and k_{ads} is the pseudo first order rate constant, was applied to the present study of adsorption. The values of $\log(q_e - q_t)$ were calculated from the kinetic data of Fig. 1 and was plotted against time (*t*) in Fig. 4. The plots were found to be linear with good correlation coefficients ($R^2 = 0.9997$) indicating that Lagergren's model is applicable to the vanadium adsorption on metal sludge and the adsorption process is a pseudo-first-order process.

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



Fig. 4. Lagergren's plot for vanadium adsorption on metal sludge adsorbent.



Fig. 5. Weber and Morris intraparticle diffusion plot for vanadium adsorption on metal sludge adsorbent.

the diffusion mechanism, kinetic data was further analyzed in the light of intraparticle diffusion model based on the theory proposed by Weber and Morris [48]. The amount of vanadium adsorbed (q_t) at time (t), was plotted against the square root of t, ($t^{1/2}$) according to the following equation proposed by Weber and Morris and resulting plot is shown in Fig. 5.

$$q_{\rm t} = k_{\rm id} t^{1/2} + C \tag{3}$$

where k_{id} is the intraparticle diffusion rate constant. According to Eq. (3), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept *C* when adsorption mechanism follows the intraparticle diffusion process [49]. Fig. 5 shows a plot of the linearized form of the intraparticle diffusion model. The plot yields a perfect linear curve ($R^2 = 0.9996$) indicating that present adsorption system followed intraparticle diffusion model.

4.4. Column operations

The column operations were carried out by passing vanadium solution with a flow rate of 2.5 mL/min on column (crosssectional area: 0.9 cm²; height: 3.1 cm; mass: 0.5 g of metal sludge adsorbent). Particle size of 50-200 mesh was used for column operations. The column did not get clogged due to mixing of particles of larger size with smaller ones and influent flowed freely over a period of 6-8 h involving a total outflow of 600 mL of vanadium solution. Column operation was continued till concentration of vanadium in the aliquot of effluent collected reached nearly 90% of the influent concentration, i.e. $C/C_0 \sim$ 0.9. In a traditional S-shape breakthrough curve, the concentration ratio (C/C_0) of a given species in the effluent was plotted against the effluent volume of the target solution. The breakthrough curve was obtained (Fig. 6) by plotting C/C_0 against volume of the effluent. Those points on the breakthrough curve have been considered as breakpoints at which C/C_0 attains a value of 0.02. The breakthrough capacity, exhaustion capacity and degree of column utilization have been evaluated from Fig. 6 and are given in Table 4. It was observed that breakthrough capacity is $\sim 9-10\%$ less than the batch capacity. This may be due to (i) lesser contact time/equilibration time of the solute with adsorbent and (ii) larger size of particles (50-200 mesh), which require longer time for equilibration and thus, inhibit-

Table 4	
Comparison of batch and column capacities and degree of column utilization	

Batch capacity (mg/g) (from adsorption isotherms)	Breakthrough capacity (mg/g)	Exhaustion capacity (mg/g)	Degree of column utilization (%)
24.8	22.6	42.7	70.6



Fig. 6. Breakthrough curve of vanadium on metal sludge adsorbent (C_0 5.5 × 10⁻³ M).

ing the utilization of column capacity. Similar results were also obtained by other workers [43] for the removal of chlorophenols by bituminous shale. It is further seen from Table 4, that the exhaustion capacity of column is relatively higher than the batch capacity. This appears due to establishment of continuously larger concentration gradient at the interface zone as the influent passes through the column. The concentration gradient generally remains maintained because of fresh inflow of influent, whereas, in case of batch experiments, the concentration gradient continuously decreases with time resulting in smaller adsorption capacity. Further, Table 4 shows that the degree of column utilization is 70.6%. Thus, these results have shown that the columns of metal sludge adsorbent can be used to remove vanadium from wastewaters.

4.5. 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. Setting times can give some indication of whether or not cement is undergoing normal hydration. Normally, two setting times are defined [50]: (i) *initial setting* occurs when the paste begins to stiffen considerably, (ii) *final setting* occurs when the cement has hardened to the point at which it can sustain some load. Vicat apparatus define initial setting and final setting time based on the time at which a needle of particular size and weight either penetrates a cement paste sample to a given depth or fails to penetrate a cement paste sample.

Initial and final setting time (IST and FST) were determined following the method described in Indian standard IS: 8112-1989 [51], 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 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 Table 5. It is seen from the results that there was a delay in initial and final setting time of cement as the metal-laden sludge content was increased in the cement. Addition of 1% metal-laden sludge in cement showed delay of 7 min in IST and 11 min in FST of cement, which was further delayed to 52 min in IST and 57 min in FST by adding 20% metal-laden sludge in cement.

4.6. 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 variability associated with batch preparation steps to avoid any substantial variability within a specific batch. It is clear from figure that increasing the ratio of metal-laden sludge in cement, the compressive strength was reduced slightly.

5. Cost factor

Commercial activated carbon of cheapest variety (generally used for effluent treatment) cost \approx US\$ 2000/tons in India. The industrial waste material used in the present study is generally available at a very cheap rate (US\$ 4–5/tons). The finished prod-

Table 5	Tal	ble	5
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Effect of fixation of metal-laden sludge on initial and final setting time of cement

Sample no.	Metal-laden adsorbent added in cement (%, w/w)	IST (S.D.)	FST (S.D.)
1	Blank	175.0 (5.0)	300.0 (5.0)
2	1	182.0 (4.5)	311.0 (5.0)
3	5	195.0 (5.0)	323.0 (3.5)
4	10	210.0 (5.0)	333.0 (5.1)
5	20	227.0 (3.5)	357.0 (4.8)

IST, initial setting time (in min); FST, final setting time (in min); S.D., standard deviation.



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

ucts would cost approximately US\$ 100–200/tons by adding all expenses (transportation, chemicals, electrical energy, etc.). Since the cost of final adsorbent prepared from industrial wastes is ca. 10 times less than the cost of activated carbons of cheapest variety, it is reasonable to conclude that waste metal sludge after proper treatment can be fruitfully used as low-cost adsorbent for the removal of vanadium from wastewaters. Further, the cost for metal-laden sludge disposal in a secure landfill is ca. US\$ 100/tons.

6. Conclusions

Results of the present study clearly show that waste metal sludge from electroplating industry can be fruitfully utilized for the removal of vanadium from water and wastewater. The adsorption of vanadium on metal sludge was found 24.8 mg/g at 25 °C. The adsorption has been found to be endothermic and data conform to Langmuir model. The analysis of kinetic data indicates that present adsorption process is pseudo-first-order and intraparticle diffusion controlled. The metal-laden adsorbent was then immobilized into 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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