Experimental Study on Chromium Containment by Admixed Soil Liner

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Abstract: Chrome tanneries generate large quantities of chromium-laden sludge that require proper disposal in engineered landfills to prevent contamination of subsurface soils and groundwater and reduce the risk to public health and the environment. This study investigates the feasibility of using a fine-grained soil as a suitable landfill liner material for the effective containment of chromium in the sludge leachate. Several series of laboratory permeability, adsorption, and column tests were conducted using soil without and with selected additives (rice husk, bentonite, and fly ash) to determine permeability and adsorption and transport of chromium in the soil. Permeability tests showed that the field soil amended with 17% rice husk and 2% bentonite provides the desired hydraulic conductivity of $10^{-7}$ cm/s (or less) to minimize the leachate migration into the surrounding subsurface environment. The rice husk and bentonite admixtures significantly reduced the hydraulic conductivity of the soil from $3 \times 10^{-7}$ to $2.8 \times 10^{-9}$ cm/s, and this admixture was further tested for its effect on the adsorption and transport of chromium in the soil. The batch kinetics and column tests results showed that the soil possesses relatively high chromium adsorption capacity under natural or slightly alkaline condition. The batch tests showed that the amendment marginally improved the chromium adsorptive capacity of the soil. The column tests showed a slight increase in breakthrough time due to the presence of the amendment. The inclined base column tests showed that a mildly inclined liner configuration has a marginal effect on the chromium attenuation in the soil. Overall, this study showed that soil amended with 17% rice husk and 2% bentonite significantly decreased the hydraulic conductivity of the soil and slightly increased the adsorption of chromium, and therefore, has the potential for usage as a landfill liner in a landfill system to contain chromium contamination. DOI: 10.1061/(ASCE)EE.1943-7870.0000563. © 2012 American Society of Civil Engineers.

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Introduction

Chromium is considered to be a toxic heavy metal that emanates from various industries such as metallurgy, refractory, chemical pigmenting, electroplating and tanning, along with liquid or solid waste. The chrome tanning industry is one of the large contributors of chromium pollution in land and water environment (Sarkar 1981; Apte et al. 2005; Leghouchi et al. 2009). One of the major environmental problems of the tanning industry is the generation of chromium-laden chemical sludge as a by product of the tannery process. Because scientific solid waste disposal practices are seldom followed in India, large amounts of chromium-contaminated sludge is usually dumped improperly as an uncontrolled topping method. The fate of chromium in such disposal sites is a cause of concern due to the leaching effect under favorable conditions. To contain such uncontrolled release and migration of hazardous contaminants into the environment, engineered waste landfills with liner systems consisting of low permeable materials (less than $10^{-7}$ cm/s) need to be implemented (Benson et al. 1994; Sharma and Reddy 2004). A major constraint to the development of engineered landfills in West Bengal, India is the high cost of synthetic liners and its scarcity in the local markets, thus, there is a need for other readily available local source materials for landfill liners, preferably soils of clayey origin.

Chromium in sludge potentially exists in the trivalent ($\text{Cr}^{3+}$) or hexavalent ($\text{Cr}^{6+}$) states under natural conditions. $\text{Cr}^{6+}$ is a highly toxic human mutagenic, but $\text{Cr}^{3+}$ is much less toxic than $\text{Cr}^{6+}$. The published literature entails that clay can be used as a liner material for the containment of heavy metals generated in leachates. The migration of heavy metals through soil liners, especially clay liners, is significantly affected by the hydraulic conductivity, cation exchange, and adsorption capacity of the soil (Sharma and Reddy 2004; Rajasekaran et al. 2005; Vaishya et al. 2008). Moreover, $\text{Cr}^{6+}$ reduction in soils can take place owing to surface chemical reactions. $\text{Cr}^{6+}$ adsorption also occurs on the surfaces of aluminum oxides and amorphous iron oxides present in soils. Soil composition (electron donor availability, soil texture, competing ions, and adsorption capabilities) and conditions in the soil (pH, moisture content, temperature, and the presence of vegetation) are the various factors affecting adsorption, leachability, and mobility of chromium in soils (Zachara et al. 1989; Hanson et al. 1993; James 1994; Chen and Hao 1996). Few guidelines have...
been compiled for selecting appropriate soil properties and compaction methods resulting in low hydraulic conductivity (Gordon et al. 1984; Daniel et al. 1990). Some researchers have found that natural reductants such as Fe, and organic matter present in the soil, can transform $\text{Cr}^{6+}$ to the less toxic $\text{Cr}^{3+}$, thereby resulting in the natural attenuation capacity of clay (Blowes et al. 1997; Jardine et al. 1999; Kozuh et al. 2000). Furthermore, it is reported that considerable chromium reduction in soils can be achieved by the use of admixtures like rice husk, fly ash, and bentonite (Hu et al. 2004). In this context, it is important to understand the migration of heavy metals through soil liners by defining the physical and chemical properties of the leachate-soil system. Moreover, a good understanding of the migration of leachate through the soil will also facilitate the rational design of an effective amended soil liner system for landfills. However, very few studies have been conducted to assess the performance of clay liner for reduction of chromium pollution through fine-grained soil (Avudainayagam et al. 2003).

The present study assesses the potential use of a local fine-grained clayey soil obtained from a site in West Bengal, India, as a landfill liner to prevent sludge leachate containing chromium from contaminating the subsurface environment. Physical and chemical tests were performed to characterize the soil. The field soil was amended with admixtures to improve its properties. Batch adsorption and breakthrough column tests were also conducted to evaluate the adsorption affinity and attenuation capacity of the field and amended soils for chromium.

Materials and Methods

Leachate Characteristics

Sludge samples collected from a leather tannery plant in the Kolkata district of West Bengal, India, were used to assess leachate quality in this study. The total concentrations of the heavy metals in the sludge were extracted by performing acid digestion in accordance with the United States Environmental Protection Agency (USEPA) 3050 procedure (1986). The mixture was stirred for 15 min. After the sample was cooled, 5 mL of concentrated HNO$_3$ were added and it was refluxed again for 30 min. The conical beaker was then covered with a watch glass and heated to 95°C, and then it was refluxed for 15 min. After the sample was cooled, 5 mL of concentrated HNO$_3$ were added and it was refluxed for 30 min. The sample was allowed to evaporate to 5 mL. The sample was cooled, and 2 mL of deionized water and 3 mL of 30% hydrogen peroxide (H$_2$O$_2$) were added. The mixture was warmed to observe the peroxide reaction and heated until the effervescence subsided. The sample was then cooled and the addition of 1 mL H$_2$O$_2$ continued until the effervescence was minimal. The maximum amount of H$_2$O$_2$ added was less than 10 mL. The sample was cooled, and 5 mL of concentrated HNO$_3$ and 10 mL of deionized water were added and the mixture was refluxed for 15 min. The sample was diluted to 100 mL and centrifuged to separate the supernatant. Then, the concentrations of the heavy metals in the supernatant were determined using an atomic absorption spectrophotometer (AAS) with a detection limit of 0.01 mg/L. Table 1 shows the heavy metals concentrations found in the tested sludge. The concentration of chromium was found to much higher than the other heavy metals, exceeding the permissible limit. Thus, in the present study, chromium was selected as the contaminant of major concern.

| Table 1. Heavy Metals Found in the Sludge from Tannery |
|--------------------------------------------------------|
| Metal | Concentration (gm/kg) |
|-------|-----------------------|
| Cr    | 14                    |
| Fe    | 0.70                  |
| Mn    | 0.58                  |
| Mg    | 1.83                  |
| Zn    | 0.24                  |
| Ni    | 0.27                  |
| Pb    | 0.06                  |
| Cd    | Not detected          |
| Cu    | Not detected          |

Soil Characterization

A clayey soil obtained from a site close to the leather tannery plant site in the Kolkata district of West Bengal, India was used in this study. The soil was collected from 2 m below the ground surface. The soil was characterized by performing variety of physical and chemical tests. ASTM standard procedures were used to determine the physical properties of the soil, including density (ASTM 2010a), particle size distribution (ASTM 2007), Atterberg limits (ASTM 2010b), hydraulic conductivity (ASTM 2010c), and maximum dry density and optimum moisture content (ASTM 2012b). The cation exchange capacity (CEC) of the soil was determined using the Ag-Tu method (Pleysier and Juo 1980). The electric constant of the soil was estimated at 1 MHz frequency (Carrier and Soga 1999). The dielectric constant of soil is an indication property by which the extent of ions in soil can be approximated. As the ionic strength of the pore fluid increases, the dielectric constant of the soil decreases (i.e., the dielectric constant of pure water is 80).

In addition, amended soil was prepared by mixing the field soil with selected admixtures. The admixtures were added to the soil to lower the hydraulic conductivity to an acceptable level (i.e., $\lambda \leq 10^{-7}$ cm/s) (Benson et al. 1994). Three admixtures were used in this study: rice husk, bentonite, and fly ash. The rice husk was obtained from a rice mill near Kolkata, India. The husk was thoroughly washed with water to remove all dirt and then oven dried at 105°C temperature for 24 h. To optimize the admixture fractions in the field soil (i.e., to obtain hydraulic conductivity less than $10^{-7}$ cm/s), three permeability tests were performed on the soil mixed with each of the selected admixtures. The permeability tests for the amended soils were performed in a rigid-wall permeameter according to the falling head testing method (ASTM 2010c).

Batch Adsorption Tests

Two batch adsorption tests series were performed to determine the adsorption behavior of the tested soils for chromium. In the first series, the soil was used without admixtures. In the second series, the same soil was mixed with rice husk and bentonite. These admixtures were found to be effective in reducing the hydraulic conductivity of the soil used. The fractions by dry weight of rice husk and bentonite in the soil in the second test series were 17 and 2%, respectively. In each test series, the USEPA batch-type test procedure was followed to determine the adsorption behavior of the tested soil for chromium (USEPA 1992). The batch adsorption experiments for the soil were conducted for five different soil to solution ratios [3:10, 4:10, 5:10, 6:10, and 7:10 (mass/volume)] with a constant solution volume (100 mL) and two different initial concentrations of chromium (2 and 3 mg/L). The source of the
hexavalent chromium used in the batch tests was potassium dichromate (K$_2$Cr$_2$O$_7$, ACS certified). All adsorption tests were performed for six different contact times: 30, 60, 90, 120, 150, and 180 min. In each test, samples were shaken at room temperature (22°C), then centrifuged at 3,500 rpm for 20 min and filtered using Whatman filter paper. The chromium concentration in the supernatant was determined using a AAS with a detection limit of 0.01 mg/L. Then, the percentages of chromium removed by the soil in all tests were calculated. The minimum time after which there was no increase in the adsorption rate of chromium was assumed to be the equilibrium time, and the concentration of chromium remaining at that time in the supernatant is called the equilibrium concentration. The amount of chromium adsorbed per unit mass of dry soil was then determined by:

$$\frac{x}{m} = \frac{C_0 - C_{eq}}{m} V$$

(1)

where $x/m$ = amount of chromium adsorbed per unit mass of dry soil; $C_0$ = initial chromium concentration before exposure to soil; $C_{eq}$ = chromium concentration after exposure to soil at equilibrium; and $V$ = volume of metal solution added to the reaction container.

To ensure the accuracy and repeatability of the test results, the following precautions were taken: (1) clean glassware was used for each adsorption batch experiment, (2) the glassware components were soaked in a dilute acid solution for 24 h and then rinsed with tap water followed by deionized water to avoid cross-contamination between the experiments, (3) chemical analyses were performed in triplicate and the results were within 5% error from the mean, (4) the interference with other elements in the atomic absorption spectrophotometer was avoided by using nitrous oxide and an acetylene flame for chromium analysis, and (5) the atomic absorption calibration was checked after testing every five samples.

**Column Breakthrough Experiments**

Two column experiments were conducted to determine the breakthrough chromium concentrations of the tested soil when permeated with chromium. In the first experiment, the soil was used without admixtures. In the second experiment, the soil was mixed with 17% rice husk and 2% bentonite. In each experiment, a burette column made of glass was used (Fig. 1). The column had an inside diameter of 115 mm and a total length of 750 mm. To mimic the field density (i.e., 90% relative compaction), the tested soil was placed in the column and compacted in layers. The soil water contents at compaction were 26 and 35% for the soil with and without amendments, respectively. After compaction, the compacted soil was 550 mm thick. Below the compacted soil layers, three consecutive layers of filter paper, glass wool, and glass bead were placed as supporting medium. The compacted soil column was permeated initially with distilled water to achieve the first exposure effect (Gleason et al. 1997). Then, K$_2$Cr$_2$O$_7$ solution was used to simulate the chromium in sludge leachate with a concentration of 7.5 mg/L. The solution was allowed to vertically pass through the soil at a steady rate of 0.27 mL/min. Effluent was periodically collected. The concentration of chromium in the effluent solution was determined using AAS (Model No: Varian 50 Bio).

In addition, two series of large scale column tests were performed to obtain the breakthrough curves of chromium through the soil by evaluating time concentration parameters. In each test, an aluminum tank of 600 mm in diameter and 900 mm in height was used [Fig. 2(a)]. In each test series, three experiments were...
performed using three different soil layer thicknesses of 100, 200, and 300 mm, respectively. In the first series of tests, the soil used was without admixtures, and the soil was mixed with 17% rice husk and 2% bentonite in the tests of the second series. As per the EPA minimum technology guidance for hazardous waste, slopes in landfill liners should be provided. Knerr et al. (1981) showed that slopes up to 2% improve landfill performance with respect to better drainage into leachate collection and removal system. Therefore, to investigate the effect of soil liner inclination on chromium attenuation in the soil, two additional large-scale column tests were performed in this study using the soil without admixtures for two different configurations. In the first test, the soil was placed without a slope at the bottom of column in a thickness of 100 mm. In the second test, the soil was placed in a slope of 1% using a prefabricated perforated template, as shown in Fig. 2(b). The relative compaction of the soil in all tests was 90% with respect to standard proctor density. The soil was saturated with distilled water for 24 h before conducting the test. In all large-scale tests, potassium dichromate solution was used as the source of Cr at an initial concentration of 7.5 mg/L. The solution was allowed to pass vertically through the soil at a steady flow of 2.7 mL/min. Effluent leachate samples were periodically collected at the bottom of the soil column. The concentration of chromium in the effluent solution was determined using AAS.

Results and Discussions

Soil Properties

The physico-chemical properties of the tested clayey soil are shown in Table 2. The grain size distribution and Atterberg limits results show that the soil is classified as medium plasticity clay (CL) according to the Unified Soil Classification System, indicating the potential of the soil for use as a liner to minimize the migration of leachate into the subsurface environment (Benson et al. 1999). Moreover, the soil exhibited a low cation exchange capacity of 1.9 meq/100 g. The low cation exchange capacity of the soil may limit the replacement of the adsorbed metals by other ions exist in the pore water. Thus, adsorption phenomenon becomes predominant for the attenuation mechanism of hexavalent chromium.

Using the falling head test, the soil hydraulic conductivity was found to be relatively low ($2.7 \times 10^{-7}$ cm/s). The soil hydraulic conductivity can be further reduced by using proper compaction or admixtures to achieve the desired hydraulic conductivity for landfill liners, as suggested by Benson et al. (1994) (i.e., $k \leq 10^{-7}$ cm/s). Benson et al. (1999) developed a correlation between the geometric mean hydraulic conductivity and the soil compaction condition through the average wetness and scattering value relative to the line of optimum of the compaction curve ($P_o$). Benson et al. (1999) defines $P_o$ as the ratio of number of ($w, \gamma_d$) points above line of optimum to the total number of ($w, \gamma_d$) point measurements, where $w$ is the water content after compaction and $\gamma_d$ is the compacted soil dry unit weight. Soils with high $P_o$ percentages have the potential to achieve the desired hydraulic conductivity for landfill liners. In this study, compaction tests were performed and the maximum dry density and optimum moisture content were determined using the standard Proctor (ASTM 2012b), modified Proctor (ASTM 2012a), and reduced standard Proctor compaction methods. The reduced Proctor method involved using 15 blows of the hammer per layer instead of 25 blows normally used in the standard Proctor test. The $P_o$ percentages for the tested soil were approximately 70 and 67% for the modified and standard Proctor compaction methods, respectively. Therefore, the soil possesses the potential to achieve the desired hydraulic conductivity for landfill liners ($\leq 1 \times 10^{-7}$ cm/s) and is adequate strength under compaction. Moreover, the maximum dry unit weights of the soil under the standard and modified Proctor compaction efforts were 16.8 and 17.2 kN/m$^3$, respectively, indicating that the soil possesses high strength and resistance to damage (Blotz et al. 1998).

### Table 2. Physico-Chemical Properties of the Tested Soil

| Property                     | Value       |
|------------------------------|-------------|
| Bulk density (kN/m$^3$)       | 18.3        |
| Optimum moisture content (%)  | 17.20       |
| Maximum dry density (kN/m$^3$)| 16.80       |
| In-situ water content (%)     | 23          |
| Liquid limit (%)              | 44          |
| Plastic limit (%)             | 19          |
| Grain size distribution       |             |
| Sand (%)                      | 6           |
| Silt (%)                      | 62          |
| Clay (%)                      | 32          |
| Classification (USCS)         | CL          |
| Coefficient of permeability (cm/s) | $2.7 \times 10^{-7}$ |
| Cation exchange capacity (meq/100 gm) | 1.9     |
| pH                           | 7.64        |
| Dielectric constant           | 16.46       |
| pHZPC                         | 7.3         |

Fig. 3. Soil permeability mixed with admixtures: (a) bentonite; (b) rice husk; (c) fly ash.
The falling head permeability tests (ASTM 2010c) results for the field soil mixed with rice husk, bentonite, and fly ash are depicted in Fig. 3, which shows that the soil hydraulic conductivity decreases considerably as the admixture fraction (by dry weight) of rice husk and bentonite increases. The optimum admixture weight fractions mixed with the soil were 17 and 2% for rice husk and bentonite, respectively. These optimum fractions of admixtures considerably lowered the soil hydraulic conductivity from $10^{-7}$ to $10^{-9}$ cm/s. When mixed with soil, bentonite reduces the soil hydraulic conductivity because of its high plasticity index (LL = 30%, PL = 30%), small particles, and thick double layer (Mesri and Olson 1971). On the other hand, rice husk contains 15–20% silica ($\text{SiO}_2$), which contributes to its hard and abrasive protective casing, covering the rice grain and soil, and subsequently filling the soil voids and leading to reduced hydraulic conductivity values. The hydraulic conductivity results suggest that an amended soil made from the local site soil mixed with 17% rice husk and 2% bentonite would have the potential for use as a landfill liner to reduce leachate transmission to groundwater.

**Batch Adsorption Results**

Fig. 4 shows the batch kinetics profiles of chromium adsorption by both tested soils (i.e., with and without admixtures) for different soil to solution ratios. As the soil to solution ratio in the suspension increases, the amount of the chromium adsorbed to the soil increases. This could be attributed to the increase in the available adsorption sites. The kinetic profiles also show that approximately 40–80% of chromium adsorption occurred within a contact time of 90 min; thereafter, the rate of chromium adsorption by the soil was noticeably decreased. This could be attributed to the significant reduction in the available adsorption sites of the soil. Fig. 4 also suggests that the presence of admixtures in soil increased the adsorption of chromium to the soil. When the soil contained no admixtures, the percent removal of chromium after 90 min of contact time was between 70–80%, which increased to 90–92% when the soil was mixed with 17% rice husk and 2% bentonite. The addition of bentonite to the soil increases its clay content, increasing the available adsorption sites for chromium. Furthermore, as shown in Fig. 5, the pH and electrical conductivity of the suspension decreases as the clay content in the solution increases (i.e., $\text{H}^+$ ions released into the solution). The adsorption affinity of anions (hexavalent chromium) to the soil surfaces increases in an acidic environment (pH < 7) (Al-Hamdan and Reddy 2005). However, the use of bentonite and rice husk with soil marginally improved the sorption capacity of soil because of the relatively high initial pH condition of the soil (pH = 7.64) limiting the effect of admixtures on the uptake adsorption capacity of soil. These results also confirm...
the findings of Guo et al. (2003). Moreover, the adsorbed chromium in the presence of rice husk is in organic form that is represented by \( \text{Cr}_3(\text{OH})_2(\text{OOCCH}_3)_7 \). This chromium is considered to link with the rice husk through \(-\text{COO}\) and \(-\text{O}^-\) groups via weak ionic exchange with a proton (Hu et al. 2004). The scanning electron microscope (SEM) morphology of the soil before and after chromium sorption with and without rice husk is shown in Fig. 6. The SEM images suggest that the surface structure of soil has disintegrated after \( \text{Cr}^{6+} \) adsorption. This may be attributed to the considerable oxidation capability of \( \text{Cr}^{6+} \) toward soil. Due to such disintegration, more pore spaces may be available for adsorption of \( \text{Cr}^{6+} \). When rice husk is added to the soil [Fig. 6(c)], further coalescences of soil particles appear to take place. Rice husk reinforces the soil structure, preventing further disintegration. Therefore, soil particles did not loosen due to the addition of rice husk, enhancing the resulting adsorption of \( \text{Cr}^{6+} \) for this amendment.

The chromium adsorption isotherm of the soil was obtained from the batch adsorption experimental results, expressed in the relationship between the amount of chromium adsorbed per unit mass of dry soil and the equilibrium concentration of chromium. The literature includes various isotherm equations ranging from almost fully empirical to largely theoretical (Cheng et al. 2004). Among them, the simplest isotherm is the Langmuir model, which applies to uniform surfaces. The Freundlich isotherm is probably the most commonly used isotherm when the surface is not energetically uniform (Cheng et al. 2004). The Freundlich isotherm is given by

\[
\frac{x}{m} = K_F C_{eq}^{1/n} \tag{2}
\]

where \( x/m = \) amount of chromium adsorbed per unit mass of dry soil; \( x = \) amount of solute adsorbed by the soil in gm; \( m = \) amount of soil in the reactor in gm; \( K_F = \) Freundlich adsorption constant; \( 1/n = \) Freundlich exponent constant; and

\[
20\mu m
\]

\[
3\mu m
\]

\[
20\mu m
\]

**Fig. 5.** pH and electrical conductivity versus clay (bentonite) content

**Fig. 6.** SEM morphology of the soil: (a) clean; (b) spiked with \( \text{Cr}^{6+} \); (c) mixed with rice husk admixture and spiked with \( \text{Cr}^{6+} \)
$C_{eq}$ = chromium concentration in solution at equilibrium (mg/L). The Langmuir isotherm is given by

$$\frac{x}{m} = \frac{\alpha \beta C_{eq}}{1 + \alpha C_{eq}}$$

(3)

where $\alpha$ = adsorption constant related to the binding energy (L/mg); $\beta$ = maximum amount of solute that can be adsorbed by the soil (mg/kg); and $C_{eq}$ = chromium concentration in solution at equilibrium (mg/L).

In this study, Freundlich and Langmuir adsorption models were fitted to the test results, as shown in Fig. 7. The relevant isotherm parameters of Freundlich model are ($K_F = 4.80$ L/g, $1/n = 0.269$) and ($K_F = 4.04$ L/g, $1/n = 0.472$) for the soil without and with admixtures, respectively. The Freundlich constant $1/n$ corresponds to adsorption intensity. The low value of $1/n$ in Freundlich model implicates that the retardation factor ($R$) is relatively low and the soil has relatively low chromium attenuation capacity (Agarwal et al. 2002). However, the presence of rice husk and bentonite in the soil slightly improved the chromium adsorption intensity. In addition, the Langmuir model parameters are ($\alpha = 185$ L/mg, $\beta = 5.33$ mg/kg) and ($\alpha = 69.7$ L/mg, $\beta = 6.15$ mg/kg) for the soil without and with admixtures, respectively. Hence, the maximum amount of chromium can be adsorbed by the soil without and with admixtures are 5.33 and 6.15 mg/kg, respectively, indicating that the soil with and without amendment has relatively low chromium adsorption capacity at natural pH condition (i.e., pH = 7.8 > pH$_{PZC}$ = 7.3). In addition, the presence of rice husk and bentonite in the soil slightly improved its adsorption capacity. However, at natural and slightly alkaline conditions, the low adsorption capacity of the soil for the anion hexavalent chromium is not significant.
chromium may be considered significant because the pH of the system is greater than the soil pH$_{PZC}$. Hence, the adsorption and attenuation capacity of the test soil for the chromium increases as the system pH decreases to levels lower than the soil pH$_{PZC}$.

**Contaminant Breakthrough Curves**

Fig. 8 shows the chromium breakthrough curves in the column tests for both soils (with and without admixtures). In the soil without admixtures, the initial breakthrough was observed after 600 h. The equilibrium concentration reached after 900 h, at which approximately 93% of the initial concentration had been traced in the effluent solution, which indicated exhaustion of the soil column. Fig. 8(b) shows the breakthrough of chromium in the amended soil column. Fig. 8 demonstrates that the addition of admixtures in the soil changed the contaminant breakthrough from 600 to 750 h (C/C$_0$ = 0.95). The equilibrium concentration was reached after 950 h, at which approximately 99% of the initial concentration was traced in the effluent solution.

Fig. 9 shows the chromium breakthrough curves in the large tank tests for both soils (with and without admixtures). In the soil without admixtures and for the three soil thicknesses [Fig. 9(a)], the breakthrough for C/C$_0$ = 0.5 was observed at approximately 175 h. The equilibrium concentration reached after 900 h, at which approximately 90% of the initial concentration had been traced in the effluent solution, which indicated exhaustion of the soil column. Fig. 9(b) shows the breakthrough of chromium in the amended soil column, and demonstrates that the addition of admixtures in the soil retarded the contaminant breakthrough at a relative concentration of 50% (C/C$_0$ = 0.5) to approximately 360, 435, and 580 h for the tests with the soil thicknesses of 100, 200, and 300 mm, respectively. The addition of admixture was also found to retard the equilibrium concentration in all three cases to after 950 h.

Fig. 10 shows the chromium breakthrough curves for field soil without amendment, as obtained from the large scale tank tests for both cases (i.e., with and without slope at the bottom of the soil). Fig. 10 exhibits the variation of concentration ratio (i.e., C/C$_0$) with time for an input chromium concentration of 7.5 mg/L and a soil thickness of 100 mm. Without a slope at the bottom of soil layer, the initial breakthrough was observed after 175 h, when 50% of initial concentration was found in the effluent. The equilibrium concentration reached after 900 h, at which approximately 98% of the initial concentration was traced in the effluent solution. When a mild slope was provided at the bottom of the soil column, the breakthrough occurred earlier than when there was no slope at the bottom. The mild slope helped the leaching solution drain to the effluent point more quickly. Fig. 10a shows that the effect of slope on leachate behavior is marginal. This observation is similar to the results of a study done by Drury (1997).

**Conclusions**

The study investigated the potential usage of a fine-grained clayey soil with and without amendment (mixed with 17% rice husk and 2% bentonite) as a liner material to contain chrome tanning waste sludge in India. Physical-chemical characterization tests and batch and column experiments were conducted for the soil before and after amendment. Based on this study, the following conclusions can be drawn:

1. The field soil is a clayey soil, with the potential to meet the basic engineering properties for clay liners in terms of the

![Graph](image)

**Fig. 9.** Chromium breakthrough curve from large-scale tank tests with different soil layer thicknesses: (a) soil contains no admixtures; (b) soil mixed with admixtures (17% rice husk and 2% bentonite)
required hydraulic conductivity and adsorption capacity. The field soil possesses a low hydraulic conductivity that is slightly higher than the required value; however, the soil hydraulic conductivity can be further reduced by using admixtures. The soil hydraulic conductivity was substantially reduced from $3 \times 10^{-7}$ to $2.8 \times 10^{-9}$ cm/s when it was mixed with 17% rice husk and 2% bentonite.

2. The mechanism of chromium attenuation was primarily attributable to adsorption by the soil, as indicated by the adsorption studies. The batch kinetics tests results showed that the soil possesses relatively a good chromium adsorption capacity at natural or slightly alkaline condition. The presence of 17% rice husk and 2% bentonite in the soil marginally enhanced its adsorption capacity.

3. The addition of admixtures in the soil columns slightly increased the chromium attenuation. The initial chromium breakthrough in the soil column was changed from 600 h to 900 h for different soil thicknesses when 17% rice husk and 2% bentonite was mixed with the soil. The chromium breakthrough curves reached equilibrium concentration after 900 h for the field soil and 1,000 h when the soil was amended with the admixtures.

4. Placing the field soil liner in a mildly inclined configuration had a marginal effect on the chromium breakthrough.

Overall, this study showed that the amended soil has the potential for use as a low hydraulic conductivity landfill liner or as a component of a landfill barrier system to contain chromium leachate. The positive environmental implication of this study lies in the high prospect of utilization of local clayey soils as low-cost landfill liner materials.

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