

Physical and numerical modeling for assessing chromium migration and retention dynamics in clayey soil

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The disposal of chromium laden sludge from tannery industries is a real challenge to the geo-environmental professional due to sub-surface migration of toxic leachate may cause serious depletion of the soil and groundwater quality. Therefore, scientific disposal of sludge is very much encouraged instead of the poor practice of uncontrolled tripping in an unlined containment structure or any open dumping yard. In the present research work, the migration behavior of chromium(VI) through clayey soil has been examined through column test for assessing the contaminant buffering potential of the considered soil so that the same can be utilized as a landfill liner material in waste containment structures. The breakthrough curve (BTC) generated from column test data showed soil bed of 10 cm height became exhausted (reached more than 90% saturation with solute) after a period of 45 days. The slope of the BTC was also flat in nature. These indicate that the good Cr^{VI} retention capacity of the clayey soil. Numerical modeling of Cr^{VI} transport through the soil column was also performed using HYDRUS 1D solute transport software package. The model predicted results were found closely matching with the experimental BTC ($R^2 = 0.7212$, RMSE = 0.4418). Thus, the HYDRUS 1D model can be considered as a worthy tool in optimizing the clayey soil liner thickness in chromium laden waste containment structures to arrest toxic leachate migration through sub-surface soil media and also to protect the precious groundwater from contamination.

Keywords: Chromium(VI) pollution, landfill, clayey soil liner, adsorption study, numerical modelling.

Introduction

Most of the industries in developing countries like India discharge their untreated or partially treated wastewater directly on depression land or containment structures outside their boundary premises and subsequently channelling them to nearby surface water bodies viz. pond, lake, river, sea, etc. This industrial wastewater most of the cases contain very high concentrations of toxic heavy metals such as Cr, Cd, Co, Cu, Zn, Ni, Ag¹⁻³. The potential for migration of these contaminants through soil media in depression land or waste containment structures causing serious lithospheric (soil and ground water) pollution⁴⁻⁷. Hence, proper attention is to be made to restrict the transportation of these pollutants from the source points either providing suitable barrier material of designed thickness or *in situ* treating the contaminants through effluent treatment plant (ETP), bio-remediation tech-

nology or advanced available technologies to limit their concentrations within the permissible levels as already depicted in the standards in different countries.

Among of these heavy metals, chromium is considered one of the priority pollutant (119th out of 126 priority pollutants) in USEPA (United States Environmental Protection Agency) list and highly toxic when exists in its hexavalent state. Chronic inhalation and consumption of chromium either from the air or groundwater may cause severe health hazard like lung, nasal and skin cancer, kidney damage, infertility, etc. Cr^{VI} has been utilized on a large scale in several industries like electroplating, metallurgy, tanning, Cr chemical production, wood preservation and paper production⁸. These industries discharge huge quantities of Cr compounds in different form like solid, liquid and gaseous wastes into the surroundings and causes major adverse biological and

ecological effects. The maximum permissible limit as per WHO (World Health Organization) for trivalent chromium and hexavalent chromium in wastewater are 5 mg/L and 0.05 mg/L respectively.

Various procedures used for eliminating chromium ions from industrial wastewater followed by reverse osmosis, chemical precipitation, electrolytic methods, solvent extraction, freeze separation and ion exchange⁹⁻¹¹. These procedures have seen limited applications because above said procedures often comprise high capital and operational expenses. Adsorption is an active and useful method to eliminate Cr^{VI} which resolves the difficulty of sludge disposal and reduces the system more economically workable, particularly if low-cost adsorbents are used.

However, selection of landfill liner material in waste containment structures is mainly based on adsorption technology. The suitability of liner material is judged by its chemical susceptibility, compatibility with contaminants, pollutants attenuative potential and also some engineering properties viz. permeability and shear strength to bear the waste overburden pressures¹²⁻¹⁴. In the present investigation, the efficacy of locally available clayey soil has been explored for using as primary landfill liner material in chromium laden waste containment structure. This investigation was performed in the laboratory scale by column experiment to assess the solute adsorption affinity of the considered soil and ability to chromium migration buffering potential.

Materials and methods:

Soil sample collection and determination of physico-chemical properties:

The material used in the studies is natural clayey soil collected from near Kamalpur, Durgapur, West Bengal, India. The soils are subjected to different physical tests. The physical properties of the studied soils, as well as the Atterberg limits (Liquid Limit and Plastic Limit), grain size distribution, specific gravity, direct shear test and hydraulic conductivity (k) were determined as per Bureau of Indian Standards (BIS 2720)¹⁵. The optimum moisture content (OMC) and the maximum dry density (MDD) of the soil were determined using the standard Proctor compaction method as described in BIS 2720. Soil passing 600 μ m sieve had used for determination of physico-chemical properties.

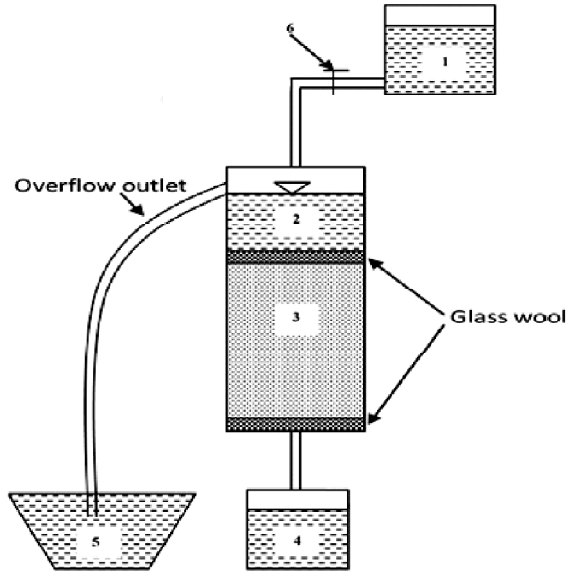
Preparation of synthetic Cr^{VI} solution:

Potassium dichromate ($K_2Cr_2O_7$) was dissolved in 1.0 L of de-ionized water to prepare Cr^{VI} stock solution (50 mg/L). De-ionized water was added to the prepared stock solution to get the required concentration of the solutions. UV-Vis spectrophotometer (Agilent 8453) was utilised to determine the concentration of the test solution, at a wavelength of 540 nm which corresponds to the maximum adsorbance for Cr^{VI} (APHA, 1995). pH of the solutions was adapted using 0.1 mmol NaOH or HCl (1 N) with the help of a pH meter.

Fixed-bed column studies:

Continuous adsorption test in a fixed-bed column was performed in a steel column with 6.2 cm internal diameter and 23 cm height as shown in Fig. 1. The clayey soil after passing through 600 μ m sieves and retained on 300 μ m sieves, were taken to prepare compacted column bed by adding de-ionised water to attain water content of 2% wetter than the optimum moisture content (OMC) and compacted in layers with 90% relative compaction of Proctor's density up to a depth of 10 cm to obtain the hydraulic conductivity (k) of studied soil samples. Glass wools and glass beads were placed at the bottom and top of the column respectively to maintain the uniform flow of solution to the soil surface and also to protect the same from the impact of water pressure. A freshly prepared double distilled water (pH 3) was applied to the column under down flow mode at a flow rate of 6 ml/h for about 24 h to saturate the soil prior to start of the solute transport process¹⁶. As the bed soil got saturated, chromium solutions having an initial concentration of 5 mg/L were applied to the top of the soil bed at a specific flow rate and the effluent samples were obtained at pre-defined time intervals from the bottom outlet of the column to analyze the effluent concentration of chromium by using UV-Vis spectrophotometer at a wavelength of 540 nm. The performance of the column is assessed from the breakthrough curve. The solute breakthrough curve of chromium migration in the soil column was obtained by plotting the dimensionless concentrations (C_f/C_i) ratio versus the number of days elapsed where, C_f and C_i are effluent and influent concentration of solutes in mg/L. Blank test (soil having distilled water in the absence of any chromium content) was also performed in the confirm to

examine the pre-existence of chromium in the studied soil as described by Hanna *et al.*¹⁷.



(1) Synthetic chromium(VI) solution tank; (2) Head of chromium(VI) solution above soil bed; (3) Compacted clayey soil; (4) Effluent chromium(VI) solution; (5) Overflow chromium(VI) solution; (6) Adjustable flux valve

Fig. 1. Experimental setup used for column study.

Analysis of the column study:

The following eqs. (1), (2), (3) and (4) have been used for analysis of dynamic flow sorption data^{14,18}.

Total amount of chromium adsorbed in the compacted soil column

$$(q_{ad}, \text{mg}) = T \int_{t=0}^{t=T_e} C_{ad} dt \quad (1)$$

The total amount of chromium migrates through the compacted soil column

$$(q_{total}, \text{mg}) = C_o T T_e \quad (2)$$

Total percentage removal of chromium (%)

$$= \frac{q_{ad}}{q_{total}} \times 100 \quad (3)$$

$$\text{Length of mass-transfer zone } (H_m, \text{cm}) = H \left(1 - \frac{T_b}{T_e} \right) \quad (4)$$

where, C_{ad} is the adsorbed chromium concentration = influent chromium concentration (C_i) – effluent chromium concentration (C_f), T is the volumetric flow rate (ml/h), T_b and T_e are breakthrough and bed exhaustion time in hour respectively, H is the soil bed height (cm).

Application of HYDRUS-1D software:

The HYDRUS-1D model was used for migration studies of chromium solution in soil media. HYDRUS-1D simulates one-dimensional solute transport in incompressible, porous, variably saturated media, in a steady or transient regime for a known metric system and at various time steps¹⁹. HYDRUS-1D model numerically solves the following forms of advection-dispersion equation for a reactive solute transport in saturated homogeneous and isotropic porous media under steady-state conditions using Freundlich isotherm model constant as described by Lee *et al.*²⁰.

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x} \left[\theta D_x(\theta, q) \frac{\partial C}{\partial x} \right] - \frac{\partial(qC)}{\partial x} - \frac{\rho_d}{\theta} \frac{\partial(K_F \theta C^n)}{\partial t} \quad (5)$$

The following boundary conditions are considered for solving the above partial differential equation,

$$C(0, t) = C_0; t \geq 0 \quad (6)$$

$$C(x, 0) = 0; x \geq 0 \quad (7)$$

$$\partial C / \partial x = 0; x = \infty \quad (8)$$

where C is the solution phase solute concentration (mg/L), θ is the saturated water content (cm^3/cm^3), q is the water flux (cm/day), $D(\theta, q)$ is the dispersion co-efficient (cm^2/day), t is the time in days, C_0 is the inlet concentration of solute the aqueous phase (mg/L), ρ_d is the dry density of soil, x is the distance in the direction of flow (cm), and K_F and n are the Freundlich isotherm parameters.

Results and discussion

Soil characteristics:

The physic-chemical properties of clayey soils are shown in Table 1. The result of grain size analysis of the soil showed that the soil was cohesive in nature with high finer particles (70%). The soil was reddish in color and acidic in nature (pH 5.14). The Atterberg limits of the soil were found as liquid limit (LL) – 42.16%, plastic limit (PL) – 27.28% and plasticity index (PI) – 14.88%. The soil may be classified as MI (sandy

Table 1. The physical and chemical characteristics of the test soils

Soil type	Grain size distribution			NMC ^a (%)	LL (%)	PL (%)	G^b	f_{oc}^c	K_s (cm/s)	pH
	Sand (%)	Silt (%)	Clay (%)							
MI	30	48	22	31.25	42.16	27.28	2.57	4.45	4.58×10^{-8}	5.14

^aNatural moisture content; ^bSpecific gravity; ^cOrganic carbon content.

silt of medium plastic) type as per the Indian Standard Classification System (BIS 1498). Falling head permeability test result showed that the saturated hydraulic conductivity ($K_s = 4.58 \times 10^{-8}$ cm/s) of the soil was very low. Therefore, the soil can be used as primary liner material as reported by Daniel¹². The adsorptive behavior of soils for chromium removal was reported in the literature^{21,22}. Banks *et al.*²¹ examined the leaching behavior and reductive property of chromium in soil in the presence of organics. The soil used in their study was primarily silty loam in nature, containing clay and silt (23 and 58% respectively) and organic matter was also high (23 g/kg).

Physical and numerical modelling results:

Hexavalent chromium breakthrough curve (BTC) plot of the column experiment has shown in Fig. 2 which is expressed as the ratio of effluent and influent concentrations (i.e. C_f/C_i) versus time in days for 10 cm bed height. Clayey soil was used as liner material in the column. Fixed bed column experiments were executed with influent chromium concentration of 5 mg/L and solution pH of 6.0 under downward flow mode. Amount of chromium adsorbed in the column (q_{ad}) was 18.76 mg, the total amount of chromium migrates through the column (q_{total}) was 32.40 mg, initial breakthrough time

(t_b) was 336 h, exhaustion time (t_e) was 1080 h, percentage of chromium removal and the length of the mass transfer zone (H_m) for 10 cm bed height (H) were 58.55%, 6.88 cm respectively as depicted in Table 2. Similar chromium adsorption efficiency (74%) by laterite soil was observed by Mitra *et al.*²³. Otero *et al.*²⁴ observed chromium adsorption on three different types of soils viz. forest soil (between 22.1 and 86%), mussel shell (between 20.9 and 31.2%) and the

Table 2. Column parameters for 10 cm soil bed height with initial chromium concentration of 5 mg/L

Parameters	H (cm)	t_b (h)	t_e (h)	q_{ad} (mg)	q_{total} (mg)	Removal (%)	H_m (cm)
Values	10	336	1080	18.76	32.40	58.55	6.88

granitic material (between 19.5 and 31.2%). The slope of the experimental BTC was found flat in nature which indicates reasonably good Cr^{VI} adsorption potential of the studied soil. The moderate percentage of Cr^{VI} removal and high length of mass transfer zone also corroborate with the finding that the studied soil can be a good candidate as liner material in Cr laden waste containment structures. The BTC predicted (shown in Fig. 2) by the HYDRUS-1D solute transport numerical model closely resembles with the experimental BTC

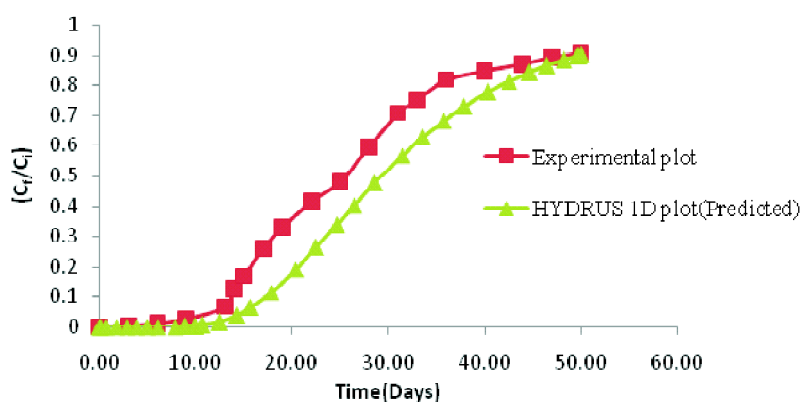


Fig. 2. Experimental and HYDRUS-1D predicted chromium BTCs in column test.

($R^2 = 0.7212$, RMSE = 0.4418). The model was also used to predict the Cr^{VI} migration through 1 m high clayey soil column. The BTC as shown in Fig. 3 indicates prolong time (25 years) is required to exhaust the bed of clayey soil used as a liner material in waste containment structure in real life scenario.

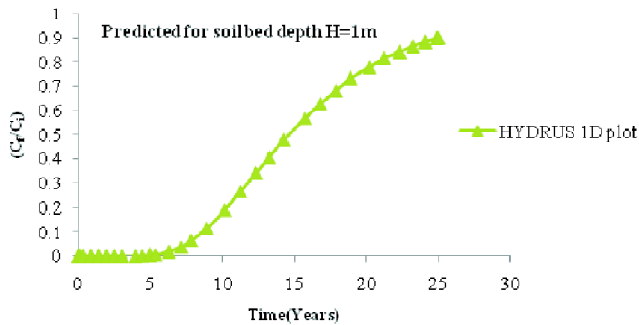


Fig. 3. HYDRUS-1D predicted chromium BTCs in the 1 m soil column.

Conclusions

Locally available clayey soil was used in the present investigation for the removal of hexavalent chromium. The physico-chemical properties of clayey soils showed that the soil was cohesive in nature with high finer particle (70%) with low saturated hydraulic conductivity ($K_s = 4.58 \times 10^{-8}$ cm/s). The engineering properties of the studied soil match with the criteria ($k \leq 1 \times 10^{-7}$ cm/s, LL $\geq 20\%$, PI $\geq 7\%$ and fine particle content $\geq 30\%$) for using as a liner material for waste containment structures as described by Ghosh *et al.*¹³. The breakthrough curve predicted by the HYDRUS-1D solute transport numerical model closely resembles with the experimental breakthrough curve obtained from the vertical column experiment. The maximum chromium removal efficiency for the studied soil was observed 58.55%. The slope of the experimental BTC was found flat in nature which indicates reasonably good Cr^{VI} adsorption potential of the studied soil and have ability for chromium removal from leachate and thus the soil may be considered as a candidate for utilizing as a liner material in chromium laden waste containment structures to prevent the migration of the solute to the lithosphere.

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