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# Assement of the migratory behaviour of contaminant originating from tannery waste water through amended clay liner using HYDRUS-3D solute transport model

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Wastewater generated from leather industries contains huge amount of toxic chemical compounds. The leaching of contaminants through sub-surface soil media leads to various geo-environmental issues including the lithospheric pollution. The leaching of contaminants through sub-surface soil media leads to various geo-environmental issues including the lithospheric pollution. In the present study, laboratory-scale batch adsorption study, 3D migration tests were conducted to examine the Cr(VI) contaminant attenuation efficacy of the locally available clay soil blended with *Azadiracta indica* (neem), to be applied as primary liner material in waste disposal structures. Linear, Freundlich and Langmuir adsorption isotherm models were plotted based on the batch experimental data. Langmuir isotherm model shows the best fit ($R^2$ = 0.987, RMSE = 1.39) of the adsorbate-adsorbent interactive behavior. The HYDRUS-3D model was also implemented to assess the migration of the contaminant in amended clay soil of 1 m thick for the purpose of using the same as bottom liner material in waste containment structure.

Keywords: Leachate, Cr(VI) contaminant, waste containment structure, amended clay liner, HYDRUS-3D modeling.

## Introduction

Industrial waste water in developing countries like India is disposed directly on unlined canals or nearby land areas near cities. The naivety of life on Earth is connected intricately to the overall naivety of the environment. The difficulties associated with contaminated surroundings are now assumed to be increasing rapidly in many countries throughout the world. Presently at the cost of environmental degradation the standard of living have surely improved. In this present study the impacts and hazards caused by Cr(VI) pollution due to discharge of toxic wastes from leather industry is studied. Leather is considered as one of the oldest commodities globally.

## Materials and methods

*Study area:*

The study area is located in the Leather Industrial Zone, located in the southeastern part of Kolkata, West Bengal, India, near the Tangra region. For over 60 years, many small-scale leather industries have been situated adjacent to that area. The study area lies between 22°34′18″ to 22°33′59″ North latitudes 88°22′46″ to 88°22′58″ East longitudes.

*Azadirachta indica (AI):*

*Azadirachta indica* (AI), which belongs to the mahogany family Meliaceae and is mainly found on the Indian subcontinent, is commonly known as neem or Indian Lilac. In the present study in powdered form of the additive was used.

## Methods

*Preparation of the natural adsorbent:*

*Azadirachta indica* (AI) seed shells are collected and cleaned and grinded into pieces with an wooden mallet , it is then cleaned by distilled water and air dried and later it is grinded to required sizes. Such grinded materials were oven-dried at a temperature of up to 105±5°C for 24 h. The AI


**Fig. 1.** Study area at Tangra region of South Kolkata, West Bengal, India (Source: Google Earth).

seed shells were mixed with the clay soil by the weight of the soil in different percentages. Approximately 200 g of locally available oven-dried (60°C for 3 days) clay soil of was taken, maintaining the temperature is very essential otherwise it would kill biomass and may maximize the volatilization of few analytes (US EPA 2002, Puget Sound). Using a wooden mallet, the oven-dried soil samples were then pulverised and sieved by using a 425-micron sieve to form a homogenised sample, hence grain size is very significant in determining elemental soil concentrations. Al is combined with soil by the weight of the clay soil taken in (10%, 15% and 20%).

*Batch adsorption:*

A pre-defined amount of adsorbent is added to the batch adsorption test with a synthetically prepared aqueous Cr(VI) solution of various concentrations in a 120 ml polyethylene bottle. The solution was stirred for a predetermined time in a speed of 120 rpm on a rotary shaker. Using 0.1 ml/L HCl or 0.1 ml/L NaOH, the solution pH was maintained to the desired value. Using a vacuum filter, the supernatants of the agitated samples were subsequently filtered through the 0.45 µm filter paper. As estimated by the pHzpc test of clay soil, the solution pH was retained at 65 (Fig. 3). The residual chromium(VI) concentration was determined at a wavelength of 540 nm using a UV-Vis spectrometer. The percentage of removal of chromium(VI) ($R$ percent) and the solvent adsorption capacity ($q_e$) of both the clay soil and the modified soil was estimated on the basis of eq. (1) as well as eq. (2), respectively, respectively.

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e\ (\text{mg g}^{-1}) = \frac{(C_0 - C_e)\nu}{M} \tag{2}$$

where, $C_0$ and $C_e$ are the initial and equilibrium concentrations of the solute, respectively.

Every experiment was repeated three times and the average values were considered. Adsorption isotherm studies were carried out with varying initial Cr(VI) concentrations ranging from 0.5 to 5 mg/L, the adsorbent dose was maintained as 10 g/L.

The numerical modelling study on the assessment of Cr(VI) migratory behaviour by soil media was carried out using HYDRUS-3D solution transport software based on finite elements. In an open end rectangular tank (L= 30 cm; B = 20 cm; H = 40 cm) made of perspex sheet, as shown in Fig. 7, the physical modelling of Cr(VI) migration was performed (a). The tank was fitted with three perforated cylindrical columns (internal diameter = 3 cm) made of perspex sheet. The first column is considered to be an injection well or source, and the observation wells are two later. The effluent was collected from the bottom outlets of each of the two observation wells at predetermined time intervals.

In the solute transport numerical modelling, the physico-chemical properties of the modified clay soil were considered as input parameters. In HYDRUS-3D modelling, water flow as well as standard single porosity solute transport modules were considered. To obtain accurate outcomes, the mesh size was kept fine.

## Result and discussion

Descriptive statistics for the concentrations of background pollutants (heavy metals) in groundwater samples collected at the leather industrial zone at Kolkata, West Bengal, India are presented in Table 2, which indicate a wide variation of pH, TDS, COD, BOD and Cr(VI) (0.04–2.6 mg/L) in the studied water. The results indicate that the amount of heavy metals and other chemical and physical parameters are existing in higher concentration with respect to their threshold values according to BIS 10500 standard.

In the study area, the high concentration of Cr in groundwater was due to prolonged disposal of chromium laden waste generated from the small scale leather industry located nearby. The detail characterization of the sludge collected from the nearby tanneries are illustrated in Table 1. By analyzing the data from Table 1, it can be said that, the leaching of the chromium from the unlined canals is responsible for the rise of Cr(VI) level in the nearby groundwater.

In the present study, an attempt was made to use naturally available clayey soil as the primary liner material in the engineered landfill structure to prevent contaminants from the waste disposal site from sub-surface migration. Table 3 shows the physico-chemical characteristics of the clay soil to be used as the liner material. Laboratory scale batch adsorption studies (Fig. 2) were also performed as a test contaminant with synthetically prepared Cr(VI) solution and as an adsorbent on clay soil. The time of contact (*t*) was retained as 2, 6, 12, and 24 h. The initial chromium(VI) concentration ($C_0$) was maintained at 0.5, 1, 2, 4 and 5 ppm, and the adsorbent dose was considered to be 1 g/100 ml solution. The study reveals that the clay soil achieved lower removal efficacy (74%) of Cr(VI), as shown in Fig. 2. Although the hydraulic conductivity of the clay soil is very low ($6.5\times10^{-7}$ cm/s), the poor adsorption capacity of the same contaminant ($Cr^{6+}$) does not make it suitable for use as a liner material in waste containment structures.

**Table 1.** Characterization of sludge collected from tannery effluents

| Parameters | Concentrations |
|---|---|
| pH | 5.6 |
| Temperature (°C) | 42 |
| Organic matter (%) | 9.24 |
| Ca (mg/L) | 234.68 |
| Mg (mg/L) | 67.1 |
| TN (mg/L) | 22 |
| Cd (mg/L) | 0.92 |
| Cu (mg/L) | 48.1 |
| Pb (mg/L) | 4.7 |
| Cr (mg/L) | 8154 |
| Zn (mg/L) | 20.02 |
| As (mg/L) | 3.5 |
| BOD5 (mg/L) | 950 |
| COD (mg/L) | 3980 |

Further attempts were made in this present study to blend AI seed shells with the clay soil to improve the adsorption capacity of its contaminants. Considering synthetically prepared Cr(VI) solution as adsorbate and AI modified clayey soil as adsorbent, the pH of the solution was maintained at 6.5 because pHzpc of clay soil was found to be 6.75, as shown in Fig. 3. The batch adsorption studies were carried out. The impact of the contact time and varying percentage of adsorbent dosage on the removal of Cr(VI) from aqueous solution is shown in Fig. 4. It is very clear from the plot that maximum removal was achieved at 12 h contact time, and when 20% (by weight) AI was mixed with the clay soil, the Cr(VI) removal percentage was found above 90%. It was observed from Fig. 4 that during the first 2 h of agitation, the removal rate of chromium(VI) was rapidly increased to 44% with 10% by weight of AI mixed with clay soil. The removal percentage was then gradually reduced to 30% with an increase in reaction time of up to 24 h. When 15% and 20% by weight of AI were mixed with clay soil, this trend of Cr(VI) removal was not observed. As shown in Fig. 4, the percentage removal of $Cr^{6+}$ increases with further addition of AI to the clay soil.

*Adsorption isotherms:*

Due to the increasing percentage of adsorbents, the presence of more surface functional groups and surface area is directly proportional to Cr(VI) adsorption, which results in greater removal of Cr(VI). On the other hand, at a lower ad-

**Table 2.** Descriptive statistical analysis of the groundwater samples collected near the leather industrial zone, Kolkata, West Bengal, India

| | pH | COD (mg/L) | BOD (mg/L) | TDS (mg/L) | $Cl^-$ (mg/L) | $NO^{3-}$ (mg/L) | Cd (mg/L) | $Cr^{+6}$ (mg/L) | $Pb^{2+}$ (mg/L) | Fe (mg/L) | $Zn^{2+}$ (mg/L) | $SO^{4-}$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 6.79 | 1285 | 6.1 | 101.02 | 328.6 | 9.331 | 0.003 | 4.40 | 0.0265 | 0.925 | 2.4575 | 37.638 |
| SD | 2.15 | 585.50 | 2.34 | 57.33 | 201.53 | 7.492 | 1.81E–18 | 0.009 | 1.81E–18 | 0.079 | 0.0089 | 33.195 |
| Max | 8.69 | 2100 | 25.2 | 210 | 801.3 | 19.26 | 0.005 | 2.6 | 0.05 | 1.8 | 4.8 | 98.71 |
| Min | 2.35 | 400 | 0.9 | 32.1 | 107.7 | 0.796 | 0.001 | 0.04 | 0.003 | 0.05 | 0.115 | 2.24 |
| Permissible limit | 6.5–8.5 | 250 | Nil | 500–2000 | 250–1000 | 45 | 0.003 | 0.05 | 0.01 | 0.3 | 5–15 | 200–400 |

**Table 3.** Physico-chemical properties of the clay soil

| Properties | Test results |
|---|---|
| Specific gravity | 2.6 |
| Maximum dry density | 15.5 kN/m$^3$ |
| Optimum moisture content | 23.4% |
| Grain size distribution | Clay – 56%, Silt – 32%, Sand – 12% |
| Liquid limit (%) | 47 |
| Plastic limit (%) | 19.33 |
| Plasticity index | 14.7 |
| pH | 7.70 |
| $Cr^{6+}$ (mg/L) | Nil |
| Permeability (cm/s) | 6.5×10$^{-7}$ |

when the adsorption surface is completely saturated and yields less removal efficiency, desorption of contaminants may take place. The comparable trend of removal of $Cr^{6+}$ occurred when the percentage of Al (10%) in clay soil is lower.

It expresses the relationship at the specified temperature between the quantities of adsorbate (mg) sorbed from the solution by the adsorbent (g). In the current Cr(VI) batch adsorption study using Al blended clay soil as adsorbent, the Langmuir isotherm model provided the best fit ($R^2$ = 0.98) compared to the Freundlich isotherm ($R^2$ = 0.92) model. As shown in Figs. 5 and 6, Al blended soil showed a higher

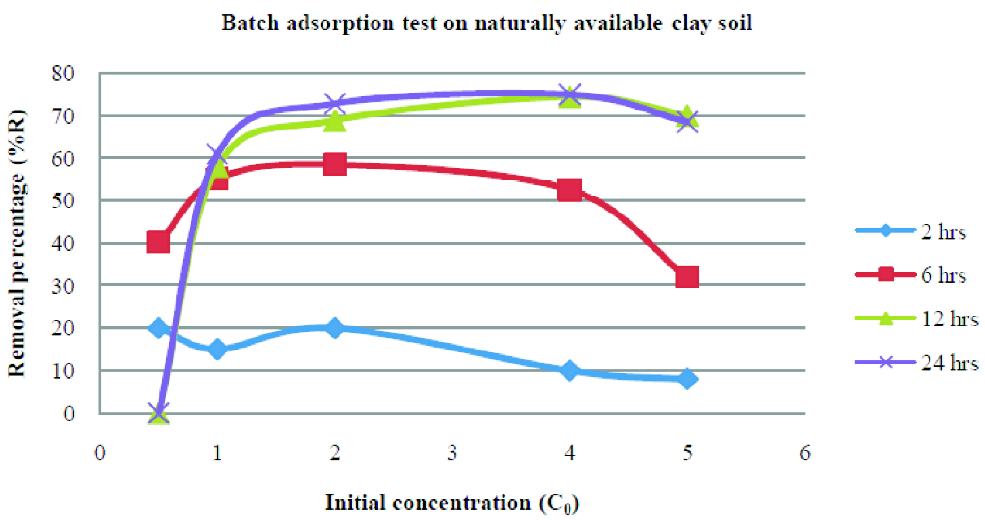



**Fig. 2.** Graphical representation of batch adsorption test using Cr(VI) solution as adsorbate and clay soil as adsorbent.

sorbent dosage, the specific surface area is reduced, resulting in lower adsorption of contaminants due to faster saturation of the adsorbent surface with contaminants. In addition,

potential to adsorb Cr(VI) ($Q_{max}$ = 65,789 mg/g) from aqueous solution. The low hydraulic conductivity, high adsorption capacity of the contaminant ($Cr^{6+}$) and good chemical compatibility of the Al seed dust blended clay soil indicate that the latter can be considered as a good candidate in chromium laden waste containment structures as the primary liner material.

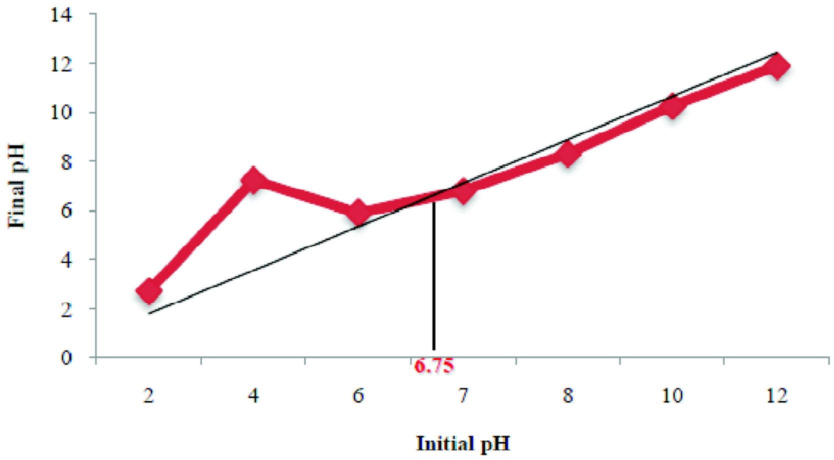



**Fig. 3.** Graphical representation of pH Zero Potential Charge test of the amended clay soil.

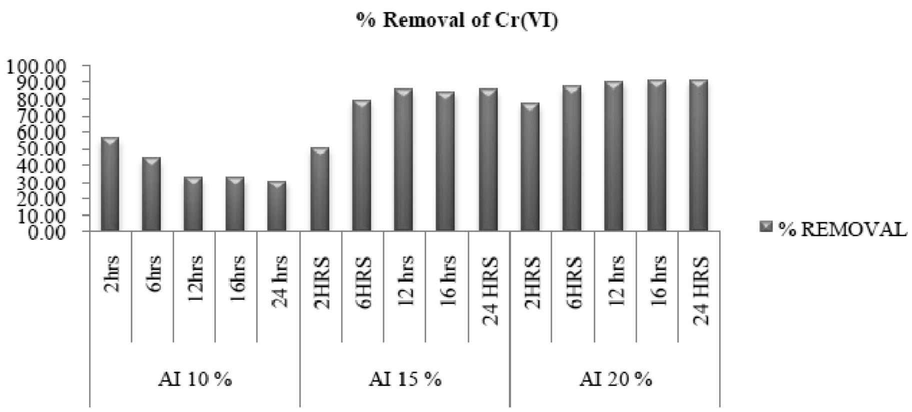



Fig. 4. Plot of batch adsorption test result of Al amended clay soil as adsorbent and $Cr^{6+}$ solution as adsorbate.

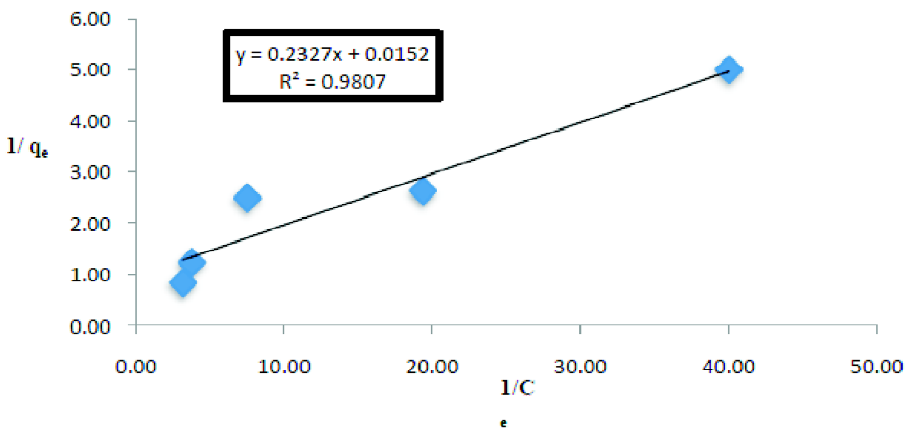



**Fig. 5.** Plot of Langmuir isotherm model for the adsorption of $Cr^{6+}$ by Al blended clay soil.

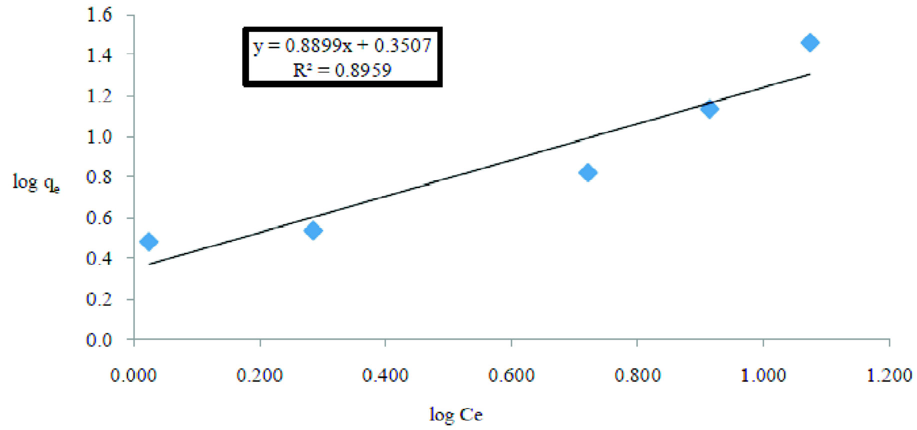



**Fig. 6.** Plot of Freundlich isotherm model for the adsorption of $Cr^{6+}$ by Al blended clay soil.

*Modelling of $Cr^{6+}$ migration through amended clay soil:*

The physical modelling studies were carried out to evaluate the three-dimensional migratory extent of $cr^{6+}$ from a source point in the modified clay soil in a laboratory scale tank made of perspex sheet. The dimensions of the tank were considered to be 40, 15, 30 cm (length, width, height) and filled up to a height of 25 cm with a modified clay soil, as shown in Fig. 7. The soil sample was first saturated inside the tank by flooding for 7 days with deionized water at the top. Synthetically prepared Cr(VI) solutions with an initial Cr(VI) concentration of 5 mg/L were then injected into the injection well and effluent concentrations from two observation columns were measured at a predetermined time interval, as shown in Fig. 7.

Numerical modelling of $Cr^{6+}$ migration through soil were carried out using HYDRUS-3D solute transport software. The

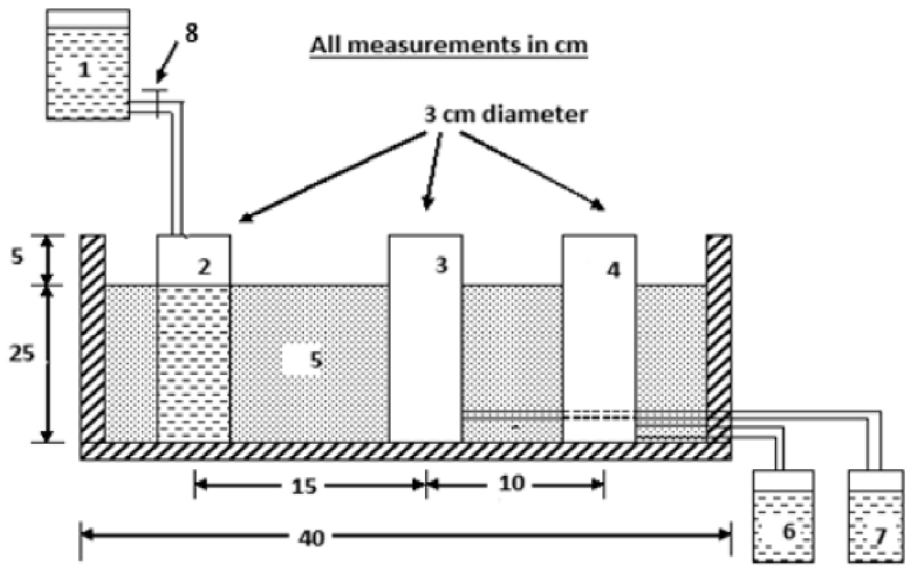
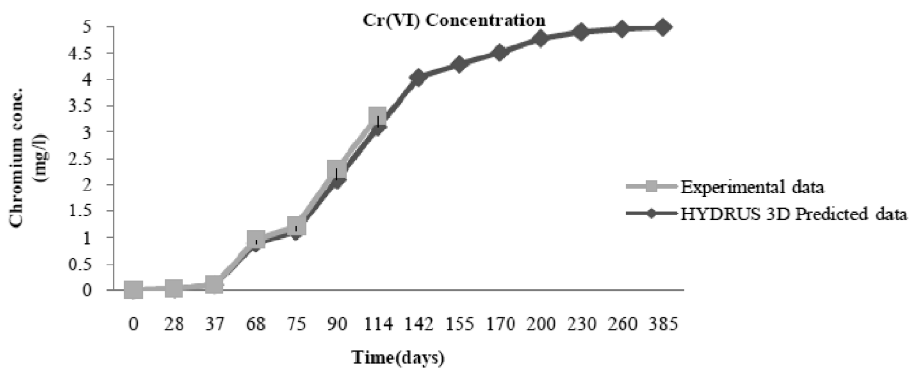


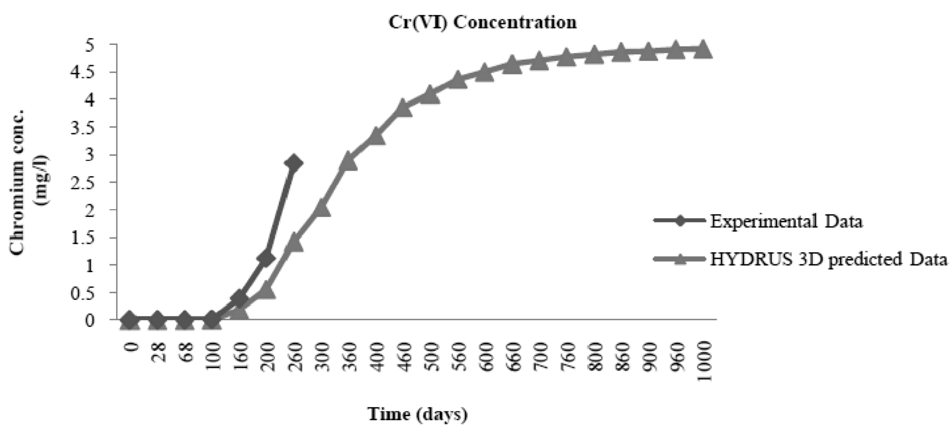

**Fig. 7.** Laboratory experimental setup used for the Cr(VI) migration test. 1 - Synthetic Cr(VI) solution; 2 - Solution injection well; 3 - Observation well no. 1; 4 - Observation well no. 2; 5 - Compacted amended clay soil; 6 - Effluent of the Cr(VI) solution from Observation well no. 2; 7 - effluent of the $Cr^{6+}$ solution from Observation well no. 1; 8 - Adjustable valve.

nonlinear Langmuir isotherm coefficients were used as input parameters in the HYDRUS-3D model to estimate the $Cr^{6+}$ breakthrough curves (BTCs) considering assumed soil tortuosity value as 0.5.

Figs. 8(a) and 2 shows the experimental and HYDRUS-3D predicted breakthrough curves for observation points 1 and 2(b). It is observed from the figures that the experimental breakthrough of almost 50% was achieved within the experimental time. However, in the laboratory scale experiment, prolonged time is needed to reach the exhaustion breakthrough. It is evident from the fact that the Al modified clay soil has a high buffering capacity to attenuate Cr(VI) migration through the subsurface soil media and thus prevent the subsequent contamination of groundwater. Up to 50% of the experimental BTCs were found to be closely similar to the HYDRUS-3D projected BTCs. However, the numerical model predicted that after a period of 400 and 1000 days for observation points 1 and 2, respectively, BTCs reached exhaustion. In order to use the same as the bottom liner material in the waste containment structure, the HYDRUS-3D model was further extended to predict the migration of the contaminant in modified clay soil 1 m thick. The breakthrough curve predicted by the HYDRUS-3D model showed that, as shown in Fig. 9, liner bed exhaustion occurs after a period of 38 years. The results of the present study clearly indicate that the Al modified clay soil has a high potential to restrict the spread of contaminants emanating from chromium laden waste to open land or water bodies from the subsurface.




(a)




(b)

**Fig. 8.** Cr(VI) breakthrough curves generated from experimental and HYDRUS-3D predicted data: (a) first observation point of tank test and (b) second observation point of tank test.

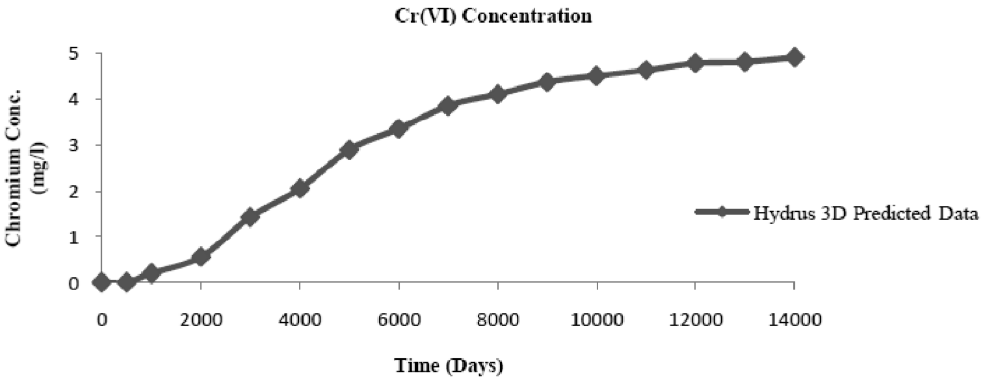



**Fig. 9.** Breakthrough curve drawn from the HYDRUS-3D predicted data for 1 m thick amended clay liner.

## Conclusion

The current study shows that at the solid waste disposal site in Durgapur, West Bengal, India, there is an alarming level of chromium pollution in the subsurface soil. The analysis of soil quality in the study area revealed that, as shown in the CCME (1991) guidelines, the concentration of chromium (12.5 mg/kg) in soil exceeded the prescribed limit (1.4 mg/kg). Cr(VI) pollutant was also found to be highly contaminated by surface water bodies near the leather industrial zone at Kolkata, West Bengal, India. Due to the high levels of chromium concentrations in the surrounding groundwater as well as the surface water that is directly consumed by the people in the slum areas close to the industries, people living near the aforementioned waste disposal points also suffer from various chronic diseases. Therefore, immediate precautionary measures are to be taken to limit chromium pollution migration from these sites.

In the present study, keeping this in mind, an attempt was made to evaluate the efficacy of Al blended clay soil as liner material in structures of chromium laden waste containment. Al blended clay soil has been shown to provide low saturated hydraulic conductivity, good chemical compatibility, and reasonably good capacity for chromium uptake, thus conforming to the criteria for use as liner material in waste containment structures.

Numerical modelling using HYDRUS-3D solution transport software demonstrates its effectiveness in using liner material as a predictive tool for assessing the migratory behaviour of contaminants through liner material to help geoenviron-mental consultants and contractors select the liner material and provide optimum thickness of the same in the structure of waste containment.

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