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Assessment of efficacy of clayey soil as liner material in retarding sub-surface leaching of chromium

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Cr^{VI} is considered as one of the priority pollutant emanated mainly from the wastewater discharge of the tannery industries. In the present research work, batch and column adsorption studies were performed to evaluate the Cr^{VI} adsorptive potential of the clayey soil. The batch adsorption test results indicate the optimum Cr^{VI} removal efficiency at a soil dose of 200 g/L with an initial solute concentration of 5 mg/L at an equilibrium reaction time of 12 h and optimum pH level of 7.0. The maximum chromium removal efficiency was achieved at 76%. The hydrodynamic parameters estimated through tracer studies and CXTFIT modeling were used as input parameters in numerical modeling of Cr^{VI} migration through clay soil using HYDRUS-1D solute transport software to assess the efficacy of the soil as primary liner material in chromium laden waste containment structures.

Keywords: Chromium(vi) pollution, clayey soil liner, adsorption study, hydrodynamic parameters, CXTFIT modeling, HYDRUS-1D solute transport software.

Introduction

Now-a-days, environmental pollution due to indiscriminate release of heavy metal pollutants generated mainly from various industries viz. tanneries, coke ovens, fertilizers, etc. raises a global concern, as these heavy metals have toxic impacts on living organisms, causing different health disorders such as skin problem, kidney disease, cancer, anemia, etc. in human beings when the concentration levels of these candidates exceed the permissible limits¹⁰. These industries discharge high concentrations of heavy metals i.e. Cr^{VI}, Cd, Ni, Zn, etc. Chromium is considered one of the priority pollutant when exists in its hexavalent state⁷. The maximum permissible limit as par WHO (World Health Organization) for trivalent chromium and hexavalent chromium in wastewater are 5 mg/L and 0.05 mg/L respectively.

Various technological solutions applied so far in eliminating chromium ions from industrial wastewaters such as reverse osmosis, chemical precipitation, electrolytic methods, solvent extraction, freeze separation and ion exchange¹³. However, these techniques were seen limited applications in wastewater treatment mainly because of high establishment and operational expenditures. On the other hand, ad-

sorption is an effective method in reducing Cr^{VI} concentrations from wastewater and furthermore, it resolves the difficulty of sludge disposal and also make the system more economically viable, particularly if low-cost adsorbents are used.

The present study was undertaken to explore the potentiality of the chromium attenuating capacity of the locally available clayey soil so that the later can be used as a primary liner material for safe containment of waste generated from the industry. The solute transport softwares viz. CXTFIT and HYDRUS-1D were applied in the present study to assess the hydrodynamic parameters and chromium migratory behavior through clay soil.

Materials and methods:

Experimental procedure:

Study of soil samples:

In the present study, natural clayey soil was collected from the lowermost deposit of a nearby pool on the NIT campus, Durgapur, West Bengal, India. The samples were brought to the Geotechnical Engineering Laboratory, NIT Durgapur for determining physical properties following the guidelines as depicted in the Bureau of Indian Standards (BIS 2720-1983).

Batch adsorption tests:

The batch test procedure was followed according to USEPA (1992) method, to determine the adsorption of hexavalent chromium on the studied soil. In the present investigation, initial chromium concentrations were varied in between 2–10 mg/L, soil dosage: 4–20 g/100 ml and pH: 4–10.

The synthetic chromium solutions were prepared by using analar grade potassium dichromate ($K_2Cr_2O_7$, ACS certified). The concentration of metal ion in the supernatant was determined using UV-Vis spectrophotometer (USEPA 1986) at 540 nm wavelength and the percent removal of chromium from aqueous solutions was calculated using the following eq. (1):

$$R = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where R is the percentage of chromium removal by the adsorbent, C_i and C_f are the initial and solution concentration at the end of the sorption process (mg/L) respectively.

Column studies:

Laboratory scale fixed-bed column experiments were performed for different heights of soil bed (5, 10, 15 cm) to study the migration of chromium under constant flow. The tracer test using NaCl solutions was performed prior to chromium migration study to estimate the hydrodynamic parameters in the clay soil. A steel column (Fig. 1) of internal diameter 6.0 cm and 21 cm high was used to undertake the vertical column experiment. The clayey soil after passing through 600 μ m sieves were taken to prepare compacted column bed. 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. Chromium solutions having an initial concentration of 5 mg/L were applied to the upper surface of the column at a specific flow rate and the effluent samples were obtained at predefined time intervals from the bottom out let.

NaCl tracer test:

The soil hydrodynamic properties are the essential input parameters to run the HYDRUS-1D model³. These hydrodynamic parameters were assessed from the experimental NaCl tracer breakthrough curve (BTCs) and also by using the non-linear least square parameter optimization code CXTFIT¹³

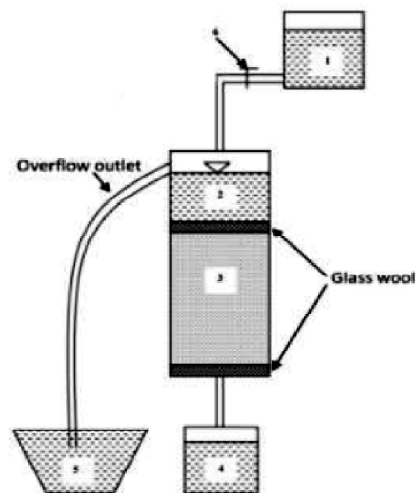


Fig. 1. Experimental setup used for vertical column test: 1 – tracer/chromium solution; 2 – head of tracer/chromium-solution above soil bed; 3 – compacted clayey soil; 4 – effluent tracer/chromium solution; 5 – overflow tracer/chromium solution; 6 – adjustable flux valve.

considering convection dispersion equilibrium (CDE) model.

Results and discussion

Soil characteristics:

The physical properties of the clay soil are shown in the Table 1. The soil possessed higher percentage of silt and clay content (67%). The soil was acidic in nature (pH 4.88)

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

Soil type		MI
Grain size distribution	Sand (%)	33
	Silt (%)	46
	Clay (%)	21
	NMC ^a (%)	33.29
	LL (%)	40.24
	PL (%)	26.04
	MDD ^b (g/cc)	1.78
	OMC ^c (%)	18.52
	G ^d	2.43
	OCC ^e	4.37
	K _s (cm/s)	6.37 × 10 ⁻⁸
	pH	4.88
	pHzpc ^f	7.3

^aNatural moisture content. ^bMaximum dry density. ^cOptimum moisture content. ^dSpecific gravity. ^eOrganic carbon content. ^fpH point of zero charge.

and the saturated hydraulic conductivity of the soil was $K_s = 6.37 \times 10^{-8}$ cm/s which is very low. Hence, the studied soil can be considered as a promising candidate for using as liner material in the waste containment structures⁶.

Batch adsorption test results:

The batch adsorption experiments were performed using laboratory prepared synthetic chromium solutions with initial concentrations of 2.0, 3.0, 5.0, 7 and 10 mg/L in a series of 100 mL capacity conical flasks along with soil adsorbent dosages of 40, 80, 120, 150 and 200 g/L at a solution pH of 7. The test results indicated that chromium removal percentage increased with the increment of adsorption dosage as shown in Fig. 2. A similar behavior of chromium adsorption was stated before by Amin *et al.*². With increase in adsorbent dosage in solution, surface area of the adsorbent also increase and as a result higher amount adsorbate (chromium) gets adsorbed on the surface of the adsorbent. After certain period of time the system reaching in equilibrium condition, an overlapping of active places prevailed and the surface area of the adsorbent decreased, resulting in the conglomeration of exchanger elements^{8,9}. The maximum chromium uptake capacity of the studied soil was found to be 19.04 mg/kg at an optimum adsorbent dose of 200 g/L, initial chromium concentration of 5 mg/L at solution pH of 7 for a reaction time of 12 h.

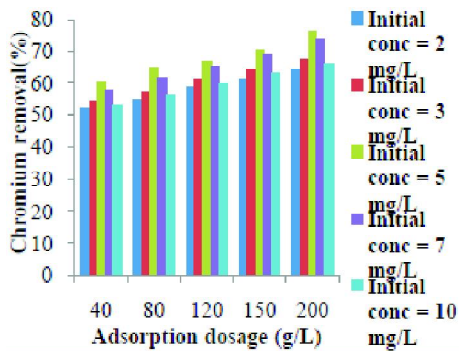


Fig. 2. Percentage chromium removal as a function of adsorption dosage at different initial concentrations (2–10 mg/L); solution pH 7.0 and contact time = 12 h.

Effect of contact time on adsorption:

The effect of contact time of chromium removal by studying soil at optimized initial chromium concentrations of 5 mg/L for different adsorbent dosage are plotted in Fig. 3. The result showed that the chromium removal efficiency gradu-

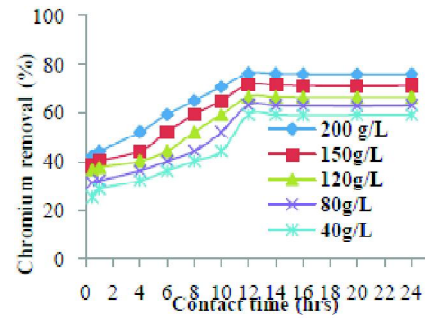


Fig. 3. Kinetics for Cr^{VI} removal; initial chromium concentration = 5 mg/L with varying adsorbent dosage (40–200 g/L).

ally increased with increasing contact time up to 12 h and after that tiny effect on the amount of chromium adsorbed. Thus the reaction between adsorbent-adsorbate reaches equilibrium at a contact time of 12 h.

Effect of pH on chromium removal:

In the present investigation pH of the solution varied in between 4 and 10 to study the effect of pH on chromium removal by clayey soil as shown in Fig. 4. It was found that the chromium removal efficiency gradually increased with increasing of pH from 4 to 7 and then further increase of pH removal efficiency decreased. So, optimum pH level in the present study considered at pH 7. The sudden fall in chromate adsorption at higher pH values due to the existence of various forms of Cr^{VI} anions in the aqueous phase. At lower pH values the soil surfaces become positively charged due to strong protonation. The Cr^{VI} adsorption increased due to electrostatic forces between the positively charged of the soil surface and the negatively charged Cr₂O₇²⁻ and HCrO₄⁻ ions in the interlayer region. Therefore, at lower pH higher amount of Cr^{VI} was adsorbed by the clayey soil. The surface charge of the soil as well as the ionization of organic contaminants

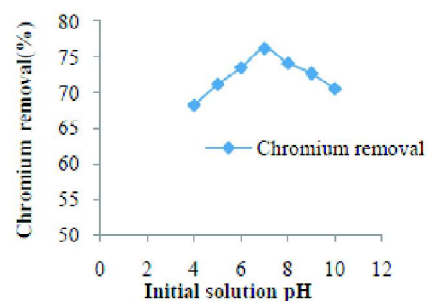


Fig. 4. Effect of pH for chromium removal; adsorbent dose = 200 g/L, initial chromium concentration = 5 mg/L, contact time = 12 h.

was influenced by the solution pH. At higher pH values (pH > pH_{Zpc}), the soil surfaces become negatively charged due to deprotonation of the functional group⁴. The chromium removal efficiency of the soil decreased due to electrostatic repulsion between chromate ions and negatively charged soil surfaces. A similar observation was reported by Ahmaruzzaman and Sharma¹ and Plaska *et al.*¹¹.

Scanning Electron Microscopy (SEM):

Fig. 5 and Fig. 6 exhibit the scanning electron microscope (SEM) images of unused clayey soil and chromium adsorbed clayey soil under optimum conditions. The plate (Fig. 5) shows that tiny pores are present on the surface of the clayey soil. A smoothing effect was also observed in Fig. 6 which was absent earlier in Fig. 5. The apparent smoothness of the soil as observed, perhaps due to the binding of chromium elements on the surface of the soil.

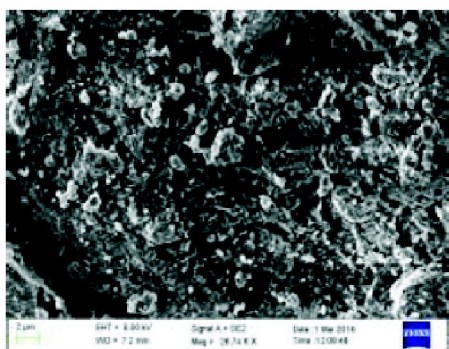


Fig. 5. Scanning electron micrograph of clayey soil before adsorption.

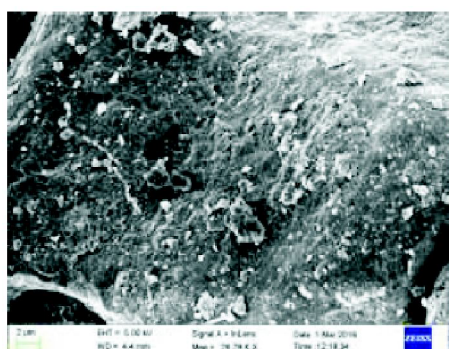


Fig. 6. Scanning electron micrograph of clayey soil after chromium adsorption.

Column test results:

The hydrodynamic dispersion coefficients (D) in the ver-

tical direction of the soil were estimated through the tracer test and CDE model in the CXTFIT code are shown in Table 2. The experimental and CXTFIT estimated pore water velocities were found to be closely resembled to each other and sum of squared errors were also very less for different soil bed heights which clearly justified the CDE model selection in the study for evaluating the hydrodynamic parameters. The breakthrough curves (Fig. 7) are identical in nature which also confirms the equilibrium transport of tracer in the clay soil. The dispersivity (α) values were estimated approximately 1% of the soil bed height. A similar finding was reported earlier by researchers elsewhere⁵. The dispersivity and pore water velocity are two dominant hydrodynamic properties of soil which are required as input parameters in the solute transport models to predict the sub-surface migratory behaviour of pollutants and also design of liner thickness in waste containment structures. HYDRUS-1D model was used in the

Table 2. Measured and CXTFIT estimated parameters for NaCl BTCs

L ^a (cm)	Measured values vp ^b (cm/day)	Estimated values by using equilibrium convection dispersion model in CXTFIT code			
		vp ^b (cm/day)	A ^c (cm)	SSE ^d	D ^e (cm ² /day)
5	0.611	0.624	0.667	0.015	0.42
10	0.659	0.648	1.381	0.011	0.89
15	0.647	0.624	2.290	0.004	1.43

^aSoil bed height. ^bPore water velocity. ^cDispersivity. ^dSum of square errors. ^eDispersion co-efficients.

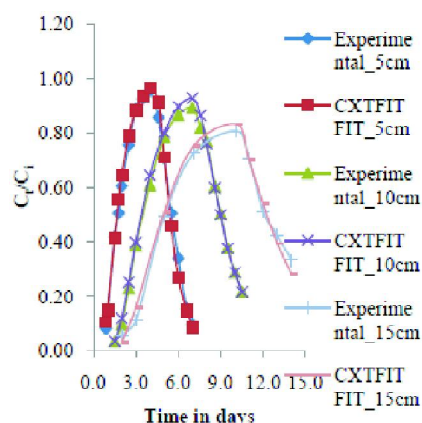


Fig. 7. Experimental and CXTFIT simulated NaCl BTCs in the vertical column test.

present study to predict the vertical transportation of chromium for a soil bed height of 1 m (considered as liner thickness) using Langmuir isotherm co-efficients (evaluated from batch adsorption studies) and estimated hydrodynamic parameters as input in the model. The BTC as shown in Fig. 8, indicates prolong time (25 years) required to exhaust the bed of clayey soil used as a liner material in waste containment structure in real life scenario. Hence, the studied soil are found to be excellent candidate for using as liner material in chromium laden waste containment structures.

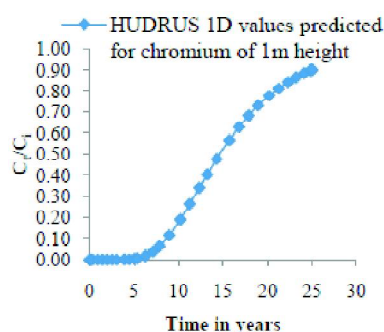


Fig. 8. HYDRUS-1D predicted BTC of chromium in 1 m high soil column.

Conclusions

In the present study, locally available clayey soil with fine contents of 67%, saturated hydraulic conductivity of 10^{-7} cm/s, 4.37% of organic carbon are found in conforming to the criteria for using as liner material in waste containment structures. Batch adsorption test results also showed reasonably good (76.18%) chromium removal by the soil at adsorbent dose of 200 g/L with an initial chromium concentration of 5 mg/L at an equilibrium time of 12 h and optimum pH level of 7.0. The estimated dispersivity values are indicating the scale dependent dispersion (1% of soil bed height) of the solute in the soil media. The low pore water velocities also indicate the suitability of soil as contaminants barrier material. The HYDRUS-1D predicted chromium BTC for 1 m

soil bed height shows that the soil bed can be considered as excellent liner material for a design life of approximately 25 years for chromium laden waste containment structures.

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