



## Chromium and nickel migration study through fine grained soil

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### ABSTRACT

A comprehensive laboratory-scale investigation was carried out to explore the toxic metal attenuation capacity of a field clay sample collected from adjoining areas of an ash pond site of a Super Thermal Power Plant in West Bengal, India. The existence of two major elements viz., Cr<sup>6+</sup> and Ni<sup>2+</sup> in excess to permissible limit was observed in soil and water samples collected from the site. Batch kinetic performance results exhibited reasonable Cr<sup>6+</sup> and Ni<sup>2+</sup> uptake capacity of soil in equilibrium condition. The experimental data also fitted well in Freundlich isotherm model. The adsorption behaviour of above pollutants in both vertical and horizontal directions through soil was explored. The results showed that more than 80% of Ni and 72% of Cr were found to be sorbed by the soil. Breakthrough adsorption study also showed a good metal adsorption capacity of soil.

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### 1. Introduction

Uncontrolled and improper disposal of solid wastes poses a grave geo-environmental problem along with sub-surface and ground water pollution. In order to protect soil and ground water from leachable toxic waste emanating from such confined source for protecting lithospheric environment, soil–metal adsorption and interactive phenomenon should be unveiled in details. In ash slurry disposal pond of thermal power plants, Ni and Cr are found as leachable constituents along with others that attribute ground water pollution during course of its movement through soil and sub-surface strata. The mobility of leachable Ni<sup>2+</sup> and Cr<sup>3+</sup> ions depend on transport mechanism and adsorption–diffusion phenomena for soil–solute interaction. Hence, it is important to evaluate the migration mechanism of these heavy metals in soil and ground water and also to explore the adsorptive uptake potential of such soil.

A few literatures are available where metal adsorption behaviour of different kinds of soil is described. An investigation was carried out to study the different aspects of arsenic sorption on soil surfaces [1]. Batch adsorption tests were performed to study arsenic retention by soil. Two different soils namely clayey and silty in nature collected from Northern India were studied. The sorption experiments were conducted by varying arsenic concentrations and time intervals for both the soils. In all the experiments, it was observed that arsenic concentrations decreased rapidly up to 2 h, followed

by a minor reduction up to 8 h and thereafter equilibrium condition was obtained in all the cases. The total adsorption was found to be increased with an increase in initial concentration of arsenic for a particular soil.

In this context, sorption tests were conducted on three kinds of soils for Cd, Ni and Pb having different physicochemical properties [6]. The heavy metal adsorption by these soils was studied by isotherms and distribution co-efficient obtained for each metal. The sorption capacity of these soils was found to be decreased with the order like Pb  $\gg$  Ni > Cd. The distribution co-efficient ( $K_d$ ) values were small and higher percentage of metals was extracted in the exchangeable fraction corresponding to that soil–metal system.  $K_d$  value was higher for Pb for neutral and alkaline soils. The predominance of metals was associated with the exchangeable fraction. The low  $K_d$  values indicated higher mobility of metals entrained in the acidic soil compared with the others. Therefore, concentration of Cd and Ni in the soil was found in their relatively less mobile form while Pb distribution varied with the soil type.

The objective of the present study was to assess Ni and Cr attenuation capacity of soil collected around an ash pond site through laboratory studies. An understanding of contaminant (Ni and Cr)–soil interaction phenomena for unraveling the transport mechanism was also observed through soil and ground water with an attempt to validate two-dimensional mathematical modeling using the experimental results.

### 2. Materials and methods

The ash pond area of Kolaghat Thermal Power Plant, located on the bank of Rupnarayan River near Mecheda Railway Station in the

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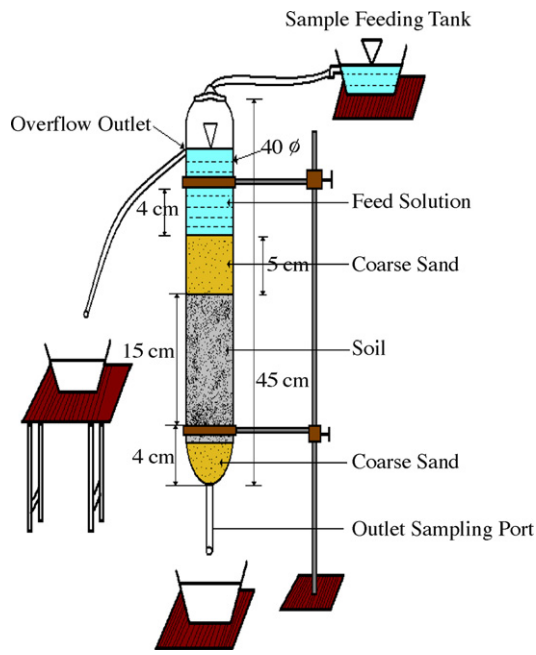


Fig. 1. Experimental set-up for vertical column test.

district of Purba Medinipur, West Bengal, India was chosen as an investigating site.

### 2.1. Leachate characteristics

Fly ash sample was collected from the ash pond and mixed with distilled water in a leaching column and the water emerging from the bottom was collected and analyzed for chemical parameters. The test results showed Ni and Cr concentration of 4.68 mg/L and

0.325 mg/L, respectively which are well above the permissible limit of 0.2 mg/L and 0.05 mg/L, respectively. However, physicochemical tests of tube-water samples from the above locations showed that the concentration of other heavy metals is within the permissible limit. Soil samples were also collected from the site at 4 m depth for determining soil moisture content, bulk density, particle size distribution, atterberg limits, optimum moisture content and permeability (falling head).

### 2.2. Analytical methods

Nickel and Cr were measured analytically by atomic adsorption spectrophotometer (Perkin-Elmer, USA make) using respective cathode lamps following the procedure as delineated in 'Standard Methods' [2].

### 2.3. Batch adsorption studies

Batch adsorption tests were carried out in a thermostatically controlled horizontal shaker fitted with water bath to maintain constant temperature. Several high-grade PVC bottles (100 ml capacity) were taken for carrying out the batch test. In this test, a 100 ml water sample containing 1 mg/L of Ni and 10 g field soil was placed in each of seven polythene bottles of 200 ml capacity and kept in a thermostatically controlled shaker. After every 30 min, one bottle was taken from a shaker and the supernatant was analyzed for residual Ni concentration. The same procedure was followed with Cr of concentrations 0.4 mg/L and 0.76 mg/L with field soils of 5 g and 10 g, respectively. The test was repeated with similar time intervals with different Ni and Cr concentrations and different amounts of soil.

### 2.4. Vertical column test

The vertical column test was performed in a laboratory-scale experimental set-up comprising of a cylindrical column made of

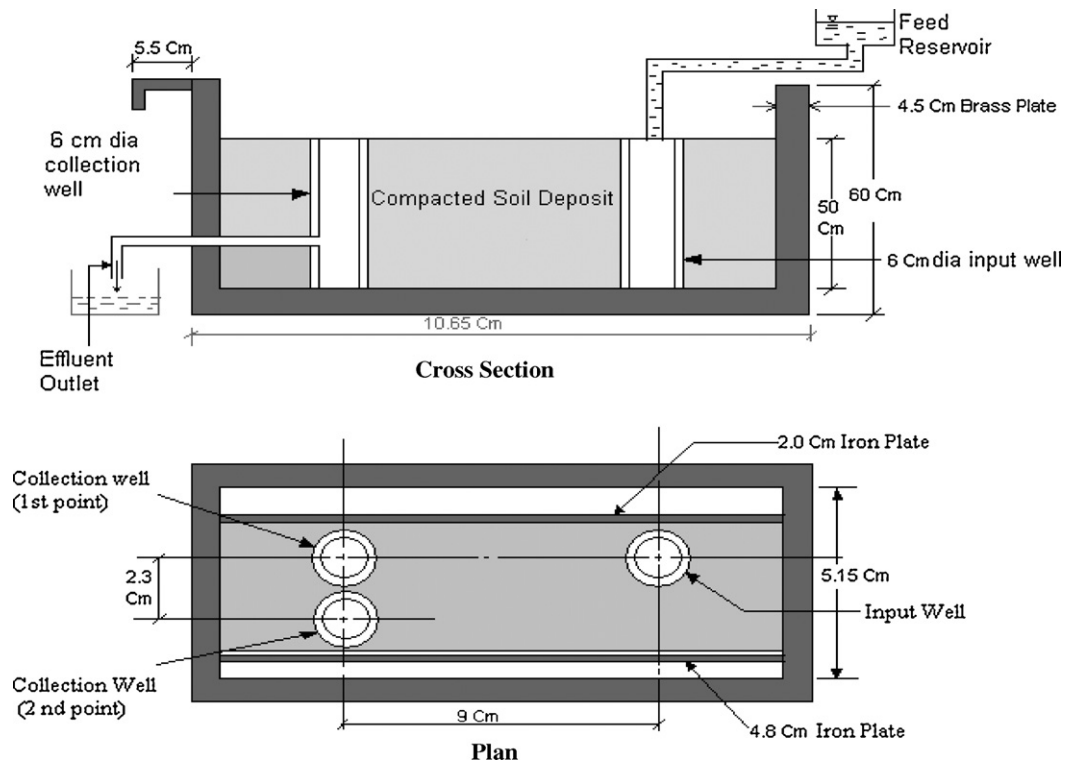
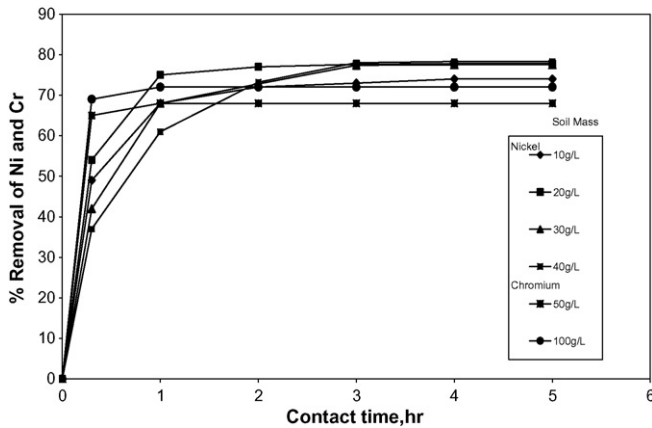


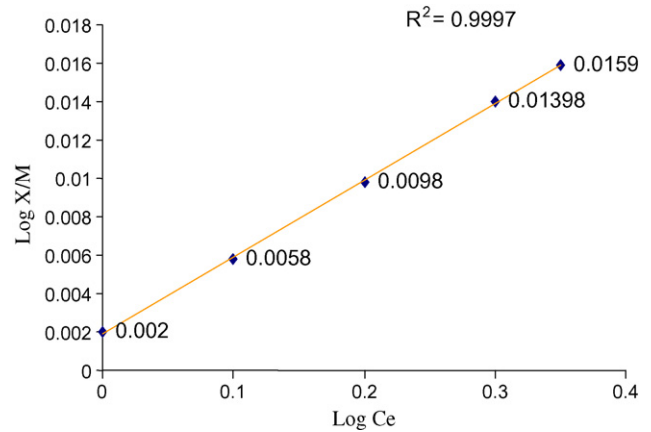
Fig. 2. Experimental set-up for horizontal migration test.

**Table 1**  
Physical properties of soil.

Bulk density (g/cm <sup>3</sup> )	Optimum moisture content (%)	Maximum dry density (g/cm <sup>3</sup> )	Water content (%)	Liquid limit (%)	Plastic limit (%)	Co-efficient of permeability (cm/s)	Grain size distribution		
							Sand (%)	Silt (%)	Clay (%)
1.88	18.79	1.50	26	47	20	1.40 × 10 <sup>-8</sup>	2	61	37



**Fig. 3.** Per cent removal of Ni and Cr with time (batch study).



**Fig. 5.** Linearized Langmuir isotherm from batch kinetics for Cr.

steel of height 45 cm and diameter 4 cm as shown in Fig. 1. Field soil brought from the site was placed inside the column and compacted in layers up to a height of 15 cm with relative compaction of 85% with respect to field density and subsequently saturated with water. A sand layer of 5 cm height was placed on the top and bottom of the sample. Nickel sulfate (NiSO<sub>4</sub>) solution was used as test sample and allowed to pass through soil with a steady flow (vertical) with an initial concentration of 4 mg/L. The samples were collected at different time intervals at the outlet point of soil column and analyzed for residual concentration of Ni. Similar procedure was adopted with spiked solution of potassium di-chromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) having Cr<sup>6+</sup> concentration of 0.4 mg/L as influent solution.

**2.5. Horizontal migration test**

The horizontal migration test was conducted in laboratory to validate the existing two-dimensional mathematical model and to trace the hydraulic migration behaviour of Ni and Cr. In this test, a tank of 107 cm length, 60 cm height and 52 cm width (Fig. 2) was filled with field soil up to 50 cm depth with relative compaction of 85% with respect to field density. There were three perforated wells at three different locations as shown in Fig. 2. The compacted soil was saturated with distilled water for 24 h. After complete satu-

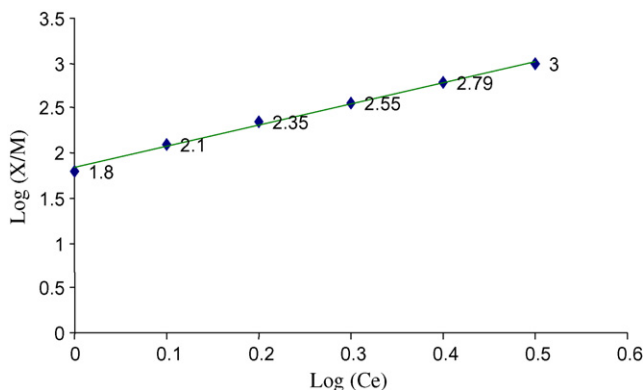
ration of soil, the test was carried out in three phases. In the first phase, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution of an initial concentration of 0.74 mg/L was applied to the injection well with steady flow at different time intervals. The samples were collected at different time intervals from observation wells for measuring residual concentrations of Ni. In second phase, the study was repeated using NiSO<sub>4</sub> solution of concentration 1.366 mg/L after reconditioning of soil in the tank. In third phase, the same procedure was followed for combined concentrations of Ni and Cr as 1.340 mg/L and 0.74 mg/L, respectively. The bulk density of soil was also checked before and after the test.

**2.6. Modeling aspects**

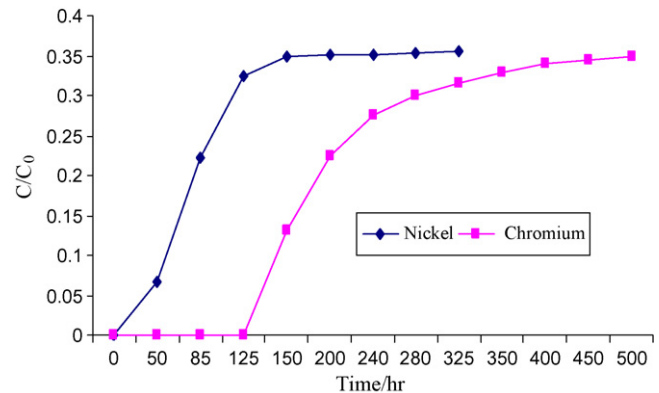
In a homogeneous medium with a uniform velocity field for a two-dimensional direction of flow parallel to the abscissa (*x*-axis), the governing advection–dispersion equation is suggested by Rowe and Booker [4] as provided in literature [5]:

$$D_L \frac{\delta^2 C}{\delta x^2} + D_T \frac{\delta^2 C}{\delta y^2} - v \frac{\delta C}{\delta x} = \frac{\delta C}{\delta t} \tag{1}$$

where *C*: concentration of contaminant in the liquid phase (mg/L); *v*: average pore fluid flow velocity (m/sec); *t*: time (seconds);



**Fig. 4.** Freundlich isotherm from batch kinetics for Ni.



**Fig. 6.** Breakthrough curve from vertical column.

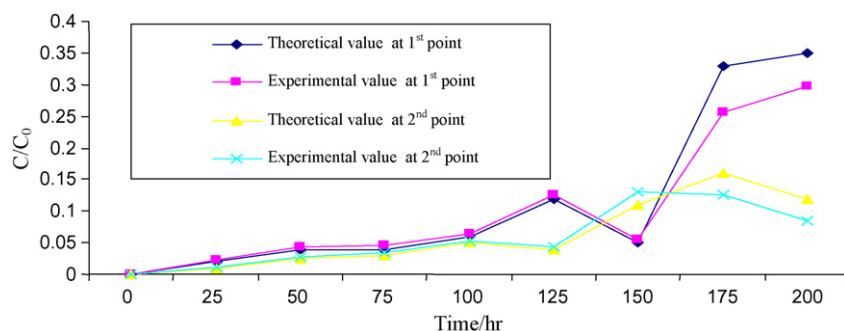


Fig. 7. Breakthrough curve from horizontal migration test for influent. Concentration of Cr 0.76 mg/L.

$D_L$ : longitudinal hydrodynamic dispersion (m); and  $D_T$ : transverse hydrodynamic dispersion (m).

If a tracer with concentration  $C_0$  is injected to a two-dimensional flow field over an area  $A$ , at a point  $(x_0, y_0)$ , the concentration at a point  $(x, y)$  at time  $t$  after the injection is given by the Eq. (2):

$$C(x, y, t) = \frac{C_0 A}{4\pi \sqrt{D_L D_T}} \left[ \exp \left[ \frac{(x - x_0 - vt)^2}{4D_L t} - \frac{(y - y_0)^2}{4D_T t} \right] \right] \quad (2)$$

### 3. Results and discussion

The test results of some relevant physical parameters of soil are presented in Table 1. The data revealed that the soil was predominantly cohesive with high silt content and low permeability. Hence, soil in and around the ash pond apparently possesses good resistance against transmission of leachate to surrounding ground water.

#### 3.1. Batch adsorption studies

Fig. 3 exhibits the batch kinetics results during the time course study against different initial concentrations of Ni and Cr in solution. The figure demonstrated a set of identical removal patterns for which approximately 70% of the total adsorption occurred within the first 2 h; thereafter the rate of removal was found to be decreased noticeably. The equilibrium time for  $Ni^{2+}$  and  $Cr^{6+}$  adsorption were considered as 4 h and 1 h, respectively. Similar results for Cr were noticed depicting that about 70% of the total adsorption occurred within first 20 min and after 1 h the curve is asymptotic. Therefore, 4 h contact time was considered as the equilibrium time for Ni.

The experimental data showed that initially, all the available sites of the soil media were active, for which, high solute concentration gradient prevailed and high affinity between the solute and the soil mass exists as adsorbent. The predominant phenomenon of

the adsorption of ions is perhaps due to the result of film diffusion adsorption.

#### 3.2. Isotherm studies

The experimental data were plotted in both Freundlich and Langmuir isotherm models. However, the Freundlich model ( $r^2 = 0.98$ ) fitted well for predicting the adsorption equation for Ni, whereas for Cr, Langmuir model ( $r^2 = 0.98$ ) was found to be more accurate, as evident from Figs. 4 and 5. The low value of  $n$  (slope of the line) in both the cases revealed that the soil has a high rate of Ni and Cr adsorption capacity. Because of low value of  $n$  (0.14) due to flat slope, the retardation co-efficient  $R$  would also be less which corroborated high Ni attenuation capacity of test soil. In case of Cr 'n' value is 0.42 due to comparatively steep slope, which indicated relatively lesser attenuation capacity of the test soil.

The general equation is  $y = mx + c$

$$\frac{x}{m} = \frac{1}{n} C_e + c$$

where  $x$  is amount of sorbate adsorbed;  $m$  is unit weight of sorbent;  $C_e$  is equilibrium concentration.

#### 3.3. Breakthrough study results from vertical column test

Fig. 6 showed the variation of concentration ratio (i.e.,  $C/C_0$ ) with time for effluents collected from outlet point for a 5 mg/L of initial Ni concentration with a continuous flow rate of 0.3 ml/min and the breakthrough time of 60 h for Ni was found, when approximately 0.5 mg/L Ni was observed in the effluent point.

The equilibrium concentration was attained at 150 h, though approximately 32% of the initial concentration was traced in the effluent solution in the domain of experimental time constraints. The breakthrough time for Cr was observed as 400 h when approximately 0.008 mg/L of Cr was found. The results

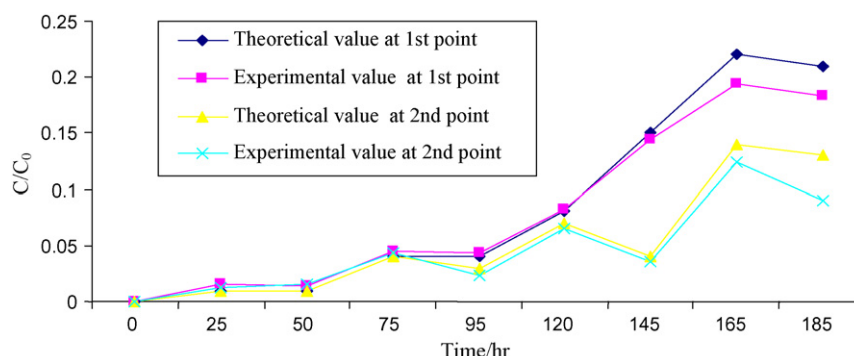


Fig. 8. Breakthrough curve from horizontal migration test for influent. Concentration of Ni 1.366 mg/L.

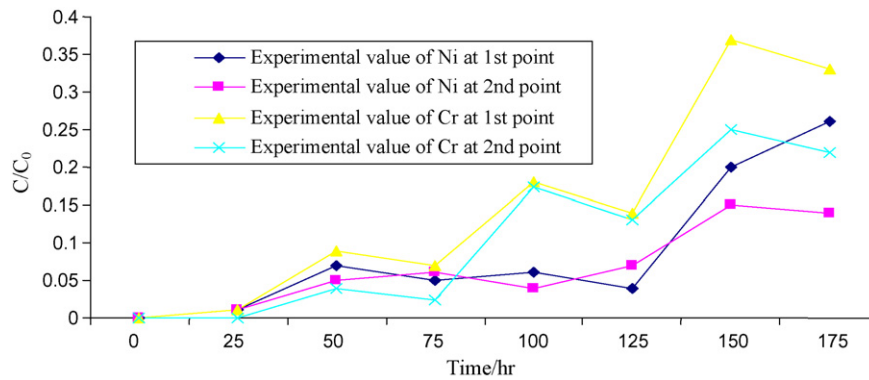


Fig. 9. Breakthrough curve from horizontal migration test for combined influent. Concentration of nickel 1.340 mg/L and chromium 0.738 mg/L.

also indicated high adsorption capacity of soil for Ni and Cr.

#### 3.4. Breakthrough curve from horizontal migration test

Figs. 7 and 8 represent results in 'Horizontal Migration Study' for input concentrations of 0.76 mg/L and 1.366 mg/L for Cr and Ni, respectively.

It is evident from figures that though complete halfway breakthrough did not attain, but a trend of imminence for getting the same at deferred time lag was noted. However, it was found that both theoretical and experimental results are in agreement to a significant extent.

The results also indicated high retention and adsorption capacity of soil with respect to Cr and Ni ions. Fig. 9 showed variable trend of attainment of residual concentrations of respective metal solution (Ni and Cr) at different time intervals, when bisolute metallic solution (both Ni and Cr) were fed continuously in the system.

The breakthrough curve from horizontal migration test indicated that up to 50 h, an insignificant amount of both Ni and Cr ions are available in both the outlets after which a sudden appearance of residual metals (both Ni and Cr) as traceable concentration in the effluent solution is observed. From the instance of 50 h, there has been an increasing trend of Ni and Cr ions in the outlet solution (Fig. 7). It is evident that even though complete halfway breakthrough did not occur within the time frame of the experiment due to high adsorption capacity of soil, though there was a probability of attaining a higher degree of residual of the said ion concentrations in the effluent if the experimental time would have been prolonged. There was a possibility of channelization and also a variable nature of tortuosity of flow. It was also revealed that for selectivity sequence of the above metallic ions that were competing for the same adsorptive clayey surface, Ni ions were preferred to be sorbed more than Cr ions due to higher potential concentration of influent Ni solution and was thermodynamically more reactive by the soil.

#### 4. Conclusions

The following conclusions are drawn from the present study on the basis of the test results:

- Nickel and Cr were found to be a traceable toxic metal, which were satisfactorily attenuated by soil samples taken from the field around the ash pond area;
- Physical and high adsorptive properties of the soil revealed that the pollutants from the ash pond cannot be transported to an appreciable distance;
- The value of  $r^2$  from adsorption isotherm model was found as 0.98 followed by low value of 'n' (slope of the line) which indicates good adsorption property of soil;
- Breakthrough curves from vertical column tests indicated that the equilibrium time for Ni and Cr were achieved after 120 h;
- Test results were also compared with theoretical values based on a two-dimensional model, as suggested by Rowe and Booker [4] and Fetter [3]. Some agreement of predictive and theoretical values were noticed but due to non-availability of simulated test set-up with the field condition, a very close agreement of these two values did not achieve;
- The breakthrough curves are fluctuating in nature due to tortuous movement of pollutants through soil indicating that further time is necessary to get 50% breakthrough values. Nickel ions are preferred to be sorbed more than Cr ions due to high potential concentration of influent Ni solutions.

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