



Sorption and transport modeling of hexavalent chromium on soil media

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ABSTRACT

Chromium–soil adsorption system exhibited both Langmuir and Freundlich isotherm models fit to the sorption data in the studied range of concentration. However the model fit was much better for Freundlich isotherm, this was primarily due to low adsorptive capacity of the soil, $1/n$ is equal to about 1.08 which is quite close to 1.0, indicating low adsorptive capacity of the soil for chromium(VI) system and the Q_{\max} was observed very low in range of 0.196–0.220 mg Cr(VI)/g of soil. The initial concentration of Cr(VI) in the solution remarkably influenced the equilibrium Cr(VI) uptake on soil sorption process. The model simulated results for the natural redemption of the soil show the periodic movement of the chromium concentration front ultimately reaching quite low concentration at the end of the cycles. In the case of inorganic chemicals, the absence of chemical decay makes the adsorption phenomena as the major contaminant removal mechanism where as for biodegradation the chemical depletion becomes a major factor in the transport of pollutant. Consequently, the concentration of contaminants reaching the ground water table becomes quite low.

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1. Introduction

Industrial disposal of liquid and solid wastes resulted soil and water pollution at many part of the industrial zones with various hazardous chemicals and metals. However, due to regulations, this has been controlled to a little extent nowadays. Recently, general people have started paying attention to disposal of liquid and solid wastes into soil. Remediation of soil or ground water is become an important issues in most part of the disposed sites. Remedial measures to be applied appropriately and efficiently as per the nature of contaminant, transport and its adsorption and desorption characteristics [1]. The random disposal of wastes on land and subsequent leaching of toxic pollutants results in soil contamination, which has the potential to affect the sub-surface water in the aquifer. There are several instances of such uncontrolled disposal causing severe problem for sub-surface water quality and became polluted, which resulted restricted use of underground water in many places. The distillery waste disposal on land and toxic organic and inorganic chemicals from dye, metal finishing and other manufacturing industries are some of the most visible example of such contamination [2,3]. In most cases after the initial dumping even though the further disposals are stopped the rainfall causes their movement through the system relentlessly. It causes extensive damage on soil and subsurface water present at various aquifers and it has been seen in several areas. The transport of leachate from dumping

sites to soils is subjected to various physical, chemical and biological processes that affect the eventual concentration of pollutants in soil and groundwater [4–7].

The common methods of soil remediation are viz. soil vapor extraction, land farming, soil flushing, solidification/stabilization, biopiles, phytoremediation, etc. [8–10]. In situ biological remediation in addition to solvent washing is one of the more preferred remediation techniques wherever feasible.

Rainwater infiltration through soil, landfills and other waste sites containing chromium results in the continuous release of chromium leachate into the underground environment. Due to the highly mobile and high solubility nature of hexavalent chromium, it poses direct threat to the quality of groundwater and consequently to the human health using ground water resources. Chromium migrates through the soil through physical and biological processes viz. advection, dispersion, sorption and decay [11–13]. Due to continuous adsorption/desorption of chromium, soils are adsorbed and desorbed (cleaned) progressively by the movement of rainwater and the solute contaminant concentration diminishes with time once the dumping of chromium waste is stopped. It is important to be able to predict the time period for such cleaning as well as that required for the ground water contamination to be developed.

Adsorption and desorption characteristic integrated with mathematical models may serve as important tools to evaluate the effects of infiltrating leachate and design remedial options. In the present study, the adsorption of Cr(VI) from aqueous solution by soil was investigated in both batch and continuous mode of operations. An attempt has been made to model the transport of Cr(VI) through soil and estimate the time required for the contaminant

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Nomenclature

Greek symbols

ε	porosity (%)
ε_g	air filled porosity (%)
μ	viscosity (kg/m s)
μ_m	maximum utilization rate
ρ	Density (kg/m ³)
ρ_b	bulk density of porous media (gm/cm ³)
$\Delta x, \Delta t$	small increment in distance (x) and time (t)
ΔP	pressure difference (bar)
A	area (m ²)
b	Langmuir constant (l mg ⁻¹)
C	concentration (mg/l)
C_0	initial sorbate concentration (mg/l)
C_b	bulk feed concentration (mg/l)
C_e	equilibrium chromium concentration in solution (mg/l)
c_i	sorbed phase conc. of species i (mol/g)
C_i	Aq. phase conc. of species i (mol/l)
C_t	chromium concentration in solution at time t (mg/l)
D	diffusion coefficient (m ² /s)
D'	diffusion coefficient of oxygen in soil
D_0	diffusivity coefficient through air
D_d	diffusion coefficient (m ² /s)
D_e	effective diffusion coefficient (cm ² /s)
D_L	axial dispersion coefficient (m ² /s)
D_p	fick pore diffusivity (m ² /s)
D_x	dispersion coefficient in the flow direction (m ² /s)
dx	differential element in the x -direction
D_y	transverse dispersion coefficient (m ² /s)
dy	differential element in the y -direction
f_x	one-dimensional mass flux (mg/m ² s)
h	depth of soil (m)
h	height of column (cm)
i, j	dimensional matrix indices corresponding to distance (x) and time (t)
K	hydraulic conductivity (m/s)
k	decay coefficient (1/s)
K_0	equilibrium constant
k_a	coefficient in mass transfer correlation
K_d	distribution coefficient
K_p	intraparticle diffusion coefficient (mg kg ⁻¹ h ^{-1/2})
K_s	half saturated constant
L	length of column/soil bed (cm)
M	mass of the adsorbent per unit volume of particle free adsorbate solution (kg)
m	mass of the adsorbent (kg)
n	Freundlich constant
N_0	adsorption capacity as in BDST model (mg solute/kg)
P	pressure (Pa)
Pe	Peclet number
q	weight of Cr(VI) adsorbed per unit wt. of soil (mg/gm)
Q	flow rate (m ³ /s)
q_e	amount of solute uptake per unit mass of adsorbent at equilibrium (mg/kg)
q_t	uptake capacity at any time t (mg/kg)
r	radius (m)
R	retardation coefficient
R_L	separation factor
S	mass of chemical constituent adsorbed per unit mass of the solid aquifer

S_{Ci}	source-sink for the species i due to aq. phase
S_r	degree of saturation of soil
T	temperature (°C)
t	time (h)
U	pore velocity (m/s)
v	Darcy velocity (m/s)
v'	seepage velocity (m/s)
v_x	average seepage velocity in x -direction (m/s)
x	distance (m)
Q_s	a sink or source of contaminant

to reach various layers of the aquifers. The approach considers the advective and dispersive transport of solutes dissolved in water, which may undergo linear sorption and consequent retardation and simple first-order decay due to chemical/biochemical reaction taking into account spatial variations of the contaminants.

2. Materials and methods

2.1. Method of analysis

Concentration of Cr(VI) in the sample was determined by using UV–vis spectrophotometer (Varian, Carry 50 Conc.) at 540 nm wave length by using 1,5-diphenylcarbazide as a color complexing agent. The adjustment of pH was made by using NaOH and HCl. The chemicals which were used in these studies (K₂Cr₂O₇, NaOH, HCl and 1,5-diphenylcarbazide) were of A.R. grade from Merck. The chromium solutions were prepared using distilled water.

A 10 kg quantity of virgin soil sample was collected and physical characterization of soil sample was conducted, same soil was used for all the experiments in this investigation. Samples of the soil were separated by means of quartering technique. The soil samples were first used to determine its physical characteristics in terms of in situ bulk density, natural moisture content, permeability and grain size distribution. The property of the soil and size distribution is shown in Table 1.

2.2. Experimentation

The experiments were carried out using synthetically prepared chromium solution with a known concentration of the solute. It was prepared by dissolving required quantity of potassium dichromate in distilled water to make stock solution of 1000 mg/l conc. This

Table 1
Properties of the soil and size distribution.

Parameter	Value
Percentage gravel	09%
Percentage sand	23%
Percentage silt	58%
Percentage clay	10%
Particle size distribution	
Diameter at 10% finer	4.57 μm
Diameter at 50% finer	39.18 μm
Diameter at 90% finer	91.16 μm
Mean diameter	44.14 μm
Porosity	0.45
Specific gravity	2.6
Bulk density (g/ml)	2.21 g/cm ³
Moisture content	4.56%
Soil pH	7.90
Hydraulic conductivity	6 × 10 ⁻⁴ cm/s
Organic content	0.92%
Infiltration rate	25.40 mm/l

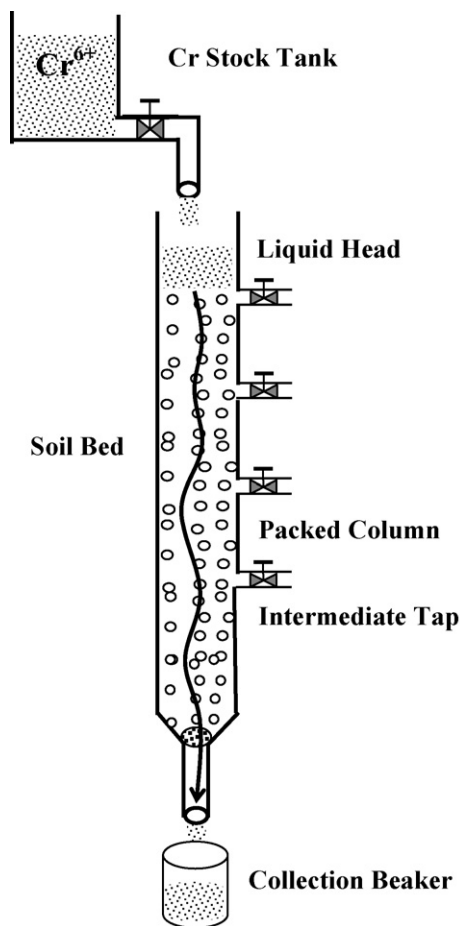


Fig. 1. Schematic of packed soil adsorption study column.

was subsequently diluted to make the contaminated stream with desired chromium concentration. The experiments were carried out in two distinct phases. One was to determine the adsorption characteristics of the soil (batch study) and the second one was column study to establish the model parameters for transfer of solute and was carried out in a glass column of packed bed with soil shown in Fig. 1. The conditions of batch and column study are given in Tables 2 and 3 respectively.

To study the adsorption characteristics experiments were carried out using a shaker-flask unit with flasks filled with dried soil sample and aqueous solution of $K_2Cr_2O_7$ for various initial concentrations ranging from 10 to 100 mg/l. The flasks were shaken at a constant speed of 120 rpm for a period of 8 h. The liquid to solid ratio taken in most of the experiments was 100 ml:5 mg of soil, i.e. ($L/S=20$). Total volume of the dichromate solution was kept constant at 100 ml for all the studies. Variation in L/S ratio was obtained by changing the quantity of solids. Samples were withdrawn at regular time intervals. These samples were centrifuged to separate the solids from the liquid. The filtrates were analyzed for residual chromium concentration by UV spectrophotometer. The concentration of chromium in the soil adsorbent was calculated from the mass balance.

In the case of column study synthetic chromium ($Cr(VI)$) solution was allowed to flow through the soil filled column at the desired flow rate of chromium solution by controlling the stock chromium tank valve shown in Fig. 1. The samples were collected at regular time intervals. All the samples collected from the experimental run were analyzed for chromium content by UV spectrometric technique. Then pure distilled water was allowed

Table 2

The operating condition for the batch study (synthetic chromium).

Parameters	Values
Temperature	Room temperature ($\sim 29^\circ C$)
pH	4 (Cr^{6+})
L/S ratio (liquid to solid ratio)	10, 15, 20, 50

to flow through the column to study the desorption behavior of the chromium contaminated soil. Chromium solution was passed in the soil packed column to saturate with chromium solution; the column saturation was monitored by analyzing the chromium inlet and outlet concentration in the column. In the case of saturated column the inlet and outlet concentration would be equal. Different flow rates of 0.8, 1.0 and 1.2 ml/min of chromium solution were studied. In all the cases the bed was allowed to get saturated before starting the remediation/desorption process.

3. Results and discussion

3.1. Adsorption isotherm of soil and $Cr(VI)$ system

Results of batch equilibrium studies provide information about the retention capacity and the mechanism by which the chromium ions are held onto the soil. The amount of chromium retained on the soil depends on the nature of bondage between the chromium–soil as well as on the number of layer of adsorbate on the pore structures of the soil. The most commonly used isotherms viz. Langmuir and Freundlich isotherms were used for the determination of the applicability of the specific isotherm for chromium–soil adsorption system in the present investigation.

3.1.1. Freundlich adsorption isotherm

Freundlich isotherm states that the adsorption process may be multilayered due to the heterogeneity of the surface charges. The Freundlich equation is based on the adsorption on a heterogeneous surface and is expressed as

$$q_e = K_d C_e^{1/n} \quad (1)$$

The above equation was linearised in the following form:

$$\log\left(\frac{x}{m}\right) = \log(K_d) + \left(\frac{1}{n}\right) \log(C_e) \quad (2)$$

where x is the amount of solute adsorbed (mg), m is the mass of adsorbent used (g), C_e is the equilibrium solute concentration in solution (mg/l) and K_d and n are constants representing the adsorption capacity (mg/g) and intensity of the adsorbent respectively. Studied experimental Freundlich parameters are reported in Table 4 along with the correlation coefficient (R^2). The high R^2 values (>0.99) obtained for adsorption of $Cr(VI)$ –soil system indicates that equilibrium data fitted well to Freundlich isotherm. Higher values of $1/n$ means the adsorption bonds are weak because the value of x/m experiences a large change for small changes in C_e . As

Table 3

The operating condition for the adsorption/desorption column study.

Parameters	Values	
	Adsorption condition	Desorption condition
Temperature	Room temperature ($\sim 29^\circ C$)	Room temperature
Solute and solvent	Cr^{6+} synthetic solution	Water
Soil bed height	20 cm	20 cm
Feed flow rate	0.8, 1.0, 1.2 ml/min	0.8, 1.0, 1.2 ml/min
Concentration Cr^{6+}	25, 50, 100, 200 mg/l	25, 50, 100, 200 mg/l

Note: L/S = volume of chromium solution (ml)/soil (gm)

Table 4
Isotherm parameters for Cr(VI) sorption on soil.

L/S ratio	Langmuir constant			Freundlich constant		
	Q_{max} (mg/g)	b (l/mg)	R^2	K_d	n	R^2
10	0.196	0.00098	0.9918	0.0115	0.915	0.982
15	0.202	0.00080	0.9721	0.0087	1.018	0.993
20	0.220	0.00078	0.9818	0.0063	1.062	0.986

n becomes very small ($n < 1$), the isotherm plot approaches horizontal and isotherm is termed as irreversible. In the present case the values of n obtained is 0.92 which is less than unity. Usually, $1/n$ (adsorption intensity) less than unity indicates a favorable isotherm for solute on the soil [14]. In the present case $1/n$ is equal to about 1.08 which is quite close to 1.0, indicating low adsorptive capacity of the soil for chromium(VI). The distribution coefficient (K_d) has been calculated from Freundlich isotherm, shown in Table 4. This K_d value has been used in all aspects of the study including the advection–dispersion model for the investigation of washing of contaminant from soil and calculation of retardation factor (R) which has the effect of retarding the adsorbed species relative to the advection velocity of ground water.

The value of retardation coefficient has been found equal to 9 from following:

$$R = \left(1 + \frac{\rho_b K_d}{\varepsilon} \right) \quad (3)$$

where ρ_b is bulk density of soil (g/cm^3), ε is porosity of soil.

Analyzing the values of K_d and n from Table 4, it can be concluded that adsorption of Cr(VI) is significantly low. Higher values of n for Cr(VI) indicate that adsorption bond is quite weak [15].

3.1.2. Langmuir adsorption isotherm

According to Langmuir theory the adsorbate forms a monolayer over the adsorbate surface. In the present case adsorption takes place due to physical forces only and no chemical energy is involved as in the case of Freundlich isotherm. The main assumption of the Langmuir model is that adsorption occurs uniformly on the active sites of the adsorbent surface, and when a molecule is adsorbed on a site, the latter does not have any effect upon other incident molecule.

Mathematically Langmuir equation is expressed as

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (4)$$

where q_m is the maximum amount of sorbate adsorbed per unit weight of the adsorbent to form a complete monolayer on the surface. C_e and q_e are equilibrium solute concentration (mg/l) and equilibrium adsorption capacity (mg/g) respectively, b is a constant related to the affinity of the binding sites (bond energy). Eq. (4) indicates that q_e approaches q_m asymptotically as C_e approaches infinity. Eq. (4) may be rewritten as

$$\frac{1}{q_e} = \left(\frac{1}{b q_m C_e} \right) + \frac{1}{q_m} \quad (5)$$

Thus a graph of $1/q_e$ vs. $1/C_e$ will give a straight line plot. The values of q_m and b were calculated from the slope and intercept of the linear plot of $1/q_e$ vs. $1/C_e$. The Langmuir isotherm parameters are reported in Table 5.

The adsorption of Cr(VI) onto soil follows Langmuir isotherm and an adsorption capacity of the soil is very low in range of 0.196–0.220 mg/g. The value of b , which is a measure of heat of adsorption ranges from 0.00078 to 0.00098. In order to predict the adsorption efficiency of the process at different initial solute concentration values, the dimensionless separation factor (R_L) was

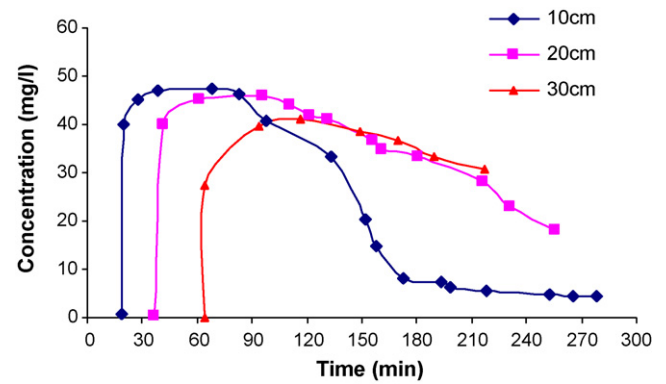


Fig. 2. Effect of contaminant flow on different depths of soil column.

determined by the following equation:

$$R_L = \left(\frac{1}{1 + b C_0} \right) \quad (6)$$

where C_0 is the initial Cr(VI) concentration (mg/l) and b is the Langmuir isotherm constant. The value of $R_L < 1$ represents the favorable adsorption and value greater than 1 represents unfavorable adsorption [16]. The value of R_L for Cr(VI)–soil adsorption system was found to vary in the range of 0.91–0.93. The parameter values less than one indicate that in the range of temperature and concentrations studied for adsorption of Cr(VI) onto the soil, the adsorption is favorable, although the adsorption capacity is quite low as mentioned earlier.

The results show that the experimental results match with Freundlich isotherm better compared to that of Langmuir, although both the experimental results conform to both the isotherm models to a certain extent. This is quite expected since the adsorption capacity is quite low and the solute concentration is quite low. At low concentration both the isotherm equations are transformed to the following equation:

$$q_e \approx K_d C_e \quad (7)$$

Since $n \approx 1.0$.

Thus in the following studies Freundlich isotherm has been used in the form of Eq. (7).

3.2. Continuous flow column study

Studies with different flow rates of chromium solution were conducted to find the effect of contaminant flux on the solute transport through the soil column. Three flow rates considered for the study were 0.8, 1.0 and 1.2 ml/min, while initial concentration of Cr(VI) was kept constant at 25 mg/l and pH at 2. The soil bed height for these studies was kept constant at 20 cm.

The estimated dispersion parameter changes $1.6\text{--}5.3 \times 10^{-3}$ for the flow rate of 0.8–1.2 ml/min. However, the difference is not very significant indicating the general applicability of the model equations.

It is thus desirable that a higher flow rate of solvent water is maintained through the bed of contaminated soil to achieve the best overall results in terms of high efficiency within shortest period of operation with lower amount of total solvent flow required. This reduces the treatment requirement for the recycled and/or disposal of contaminated solvent for proper disposal. Comparative chart has been made with different solvent flow rates for bed redemption in terms of extent of recovery, time period needed and the various dispersion parameters involved. The data for the same is presented in Table 5.

Table 5
Effect of flow rate on recovery and dispersion coefficient on soil column.

Flow rate (ml/min)	Recovery (%)	K (cm ² /s)	v_x (cm/s)	D_x (cm ² /s)	Time of operation (min)
1.2	99.30	6.00E-04	1.46E-03	4.75E-03	120
1.0	94.23	6.00E-04	1.46E-03	7.32E-03	170
0.8	90.47	6.00E-04	1.46E-03	7.68E-03	250

Since the soil is a heterogeneous mixture of several components, diffusion and surface adsorption may contribute simultaneously towards metal immobilization and/or sorption. The behavior of Cr(VI) transport through soil was studied at various inlet initial Cr(VI) concentrations. The other parameters, i.e. flow rate, soil bed height and solution pH were kept constant. Three levels of Cr(VI) concentration were studied. These are 25, 100 and 200 mg/l. After saturating the soil bed with Cr(VI) solution, the desorption of Cr(VI) from the soil was also carried out by solvent extraction with distilled water. The water was passed through soil bed after draining out all the liquid solution over a period of 2 h. A change in inlet Cr(VI) concentration affected the operating characteristics of the soil column during adsorption and desorption operation. Effect of concentration on recovery and dispersion coefficient on soil column is presented in Table 6.

The results indicate that percent recovery of Cr(VI) is maximum, i.e. 99% at 25 mg/l Cr(VI) in soil in comparison to very less recovery of Cr(VI), i.e. 90% at higher Cr(VI) concentration, i.e. 200 mg/l. The reason behind in this phenomenon is that at higher concentration more Cr(VI) ions are presented in the soil and some of them would require longer time to desorb. Therefore, within the time period the extent of recovery is less at lower concentration compared to that at higher concentration.

Experiments were carried out to find the effect of the contaminant movement with discontinuous discharge of contaminant flow in a packed soil column. Intermittent flow of solvent was considered to study the contaminant movement within the bed. These experiments were carried out to study the three different conditions of flow viz. continuous flow of contaminant for specific duration, nonflow of solution (idle condition) and continuous flow of solvent (water) for the specific time span. Normally the contaminant movement is governed by advection, dispersion and sorption, which also in turn reflect soil-contaminant washing process. These experimental results show the effect of seasonal changes and contaminated flow on soil.

Effect of contaminant flow was investigated with three different time periods viz. 30, 60 and 90 min of flow condition. The column used was designed with a provision of collecting samples at three different depths. Experiments were conducted with different periods of sequence of contaminant flow, idle phase and solvent flow through the bed. One such sequence consisted of the following flow conditions.

Chromium was allowed to pass through the packed soil column for 30 min and kept on idle situation for 30 min and water was applied on the packed soil column for the rest of the period to wash the chromium present in contaminant soil column. The result of contaminant concentration at different depths and time is shown in Fig. 2. Fig. 2 shows that the contaminant transport behavior for single contamination followed with continuous idle and washing period simultaneously for 30 min up to 300 min of total operation.

Table 6
Effect of concentration on recovery and dispersion coefficient on soil column.

Concentration (mg/l)	Recovery (%)	K (cm ² /s)	v_x (cm/s)	D_x (cm ² /s)
25	99.26	6.00E-04	1.46E-03	4.75E-03
100	93.18	6.00E-04	1.46E-03	6.59E-03
200	90.38	6.00E-04	1.46E-03	5.43E-02

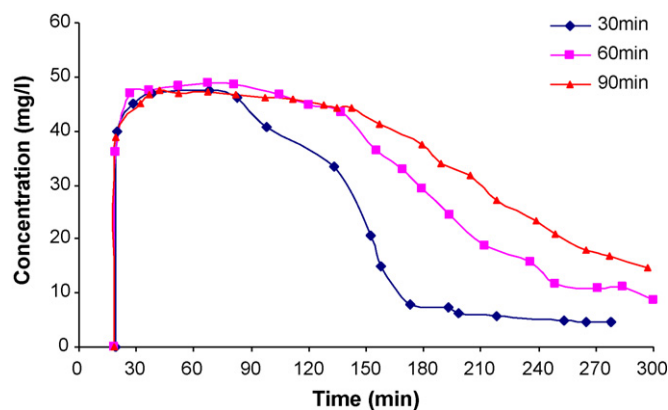


Fig. 3. Effect of contaminant flow duration on contaminant transport.

The figure shows that the contamination flows from top of the soil column to the final depth (30 cm). It can be observed that the contaminant appears the first depth (10 cm) at about 15 min. The inlet chromium concentration in the liquid was 50 mg/l and constant flow rate of 1.2 ml/min was maintained throughout the experiment.

It can be observed from Fig. 2 that the concentration reached initial level in relatively short period and indicates the effect of dispersion. Further the peak concentration level was lower than the feed concentration. This is due to the sorption of the solute within the bed. The concentration starts going down due to the effect of flow of solvent water. At a depth of 20 and 30 cm also similar results were observed. However, at 30 cm (end of the column) the peak concentration is much lower than the feed concentration, showing the effect of adsorption. Other than the adsorption phenomena on the soil surface, the chromium ions are also retained within the porous space of the soil bed. Similar results are shown for the case of longer period of contaminant discharge. The concentration of chromium solution collected at 10 cm depth is plotted for three time spans (30, 60 and 90 min), as shown in Fig. 3. Larger period of contaminant flow showing a much prolonged high concentration discharges from the column.

Similar experiments were carried out for different idle periods to find the effect of chromium adsorption and its migration. Fig. 4

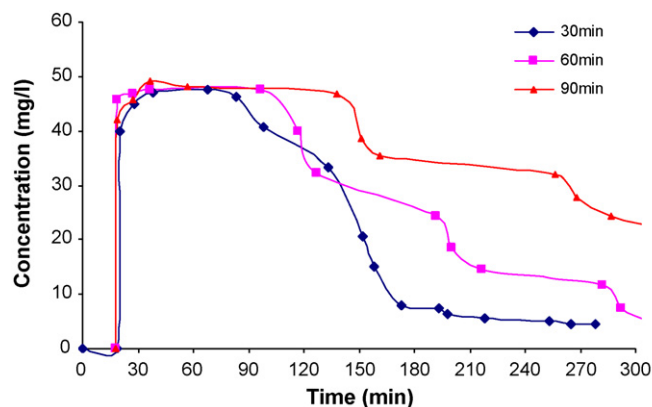


Fig. 4. Effect of idle (no flow) period on contaminant transport.

shows the effect of idle period on chromium transport through the packed soil column for the 10 cm depth. Three different idle periods were taken in this study viz. 30, 60 and 90 min. In idle conditions the flow of chromium solution and water was stopped and the columns were only kept idle for the contaminant and solvent migration. The migration of contaminant solution was observed for some duration, even in idle condition. This is due to the seepage of solution present in the column voids and pores of the soil particles. In this case it was observed that the seepage rate from the void space controls the contaminant migration during idle condition.

A major feature of the plot is that the prolonged idle condition of more than 60 min showed its effect as no flow condition and the concentration level was same when the solvent flow started. However, at lower idle flow condition the liquid retained within the porous space flowed continuously, with the rapid dilution by solvent flow. This is quite important from the practical remediation situation. It appears that idle period has a stabilization effect of consolidation of the chromium solute on the soil surface, which makes it more difficult to wash out.

The contaminant sources and its release to environment may be described by two extreme cases: continuous release and instantaneous release. Continuous release implies a continuous influx of the contaminant as in the case of a landfill for relatively long periods of time, whereas instantaneous release implies a pulse or sudden influx of contaminant for a very short period of time. In most cases, further disposals are stopped after the initial dumping. But at contaminated field areas the periodic rainfall causes further movement of the contaminant through the system. The rainwater washes the contaminant from the first few layers of soil to subsequent layers. As a result, there is a cyclic movement of contaminant, whereby the concentration of contaminant decreases in the top layers but gradually increases as we move down the soil column.

The mathematical analysis cyclic washing of soil column simulated with rainfall was done with the help of same advection–dispersion–sorption model. In the case of inorganic chemicals, the absence of chemical decay makes adsorption as the major contaminant removal mechanism. But gradual washout due to rainfall ultimately carries the contaminant to the underground water table. In the case of organic contaminants, biodegradation plays a major role in the transport. The concentration of contaminant reaching the ground water table becomes quite low and this can be further reduced when cycles were repeated for many years. The rainwater washes the contaminant from the first few layers of soil to subsequent depths. As a result, there is a cyclic movement of contaminant whereby the concentration of contaminant decreases in the top layers but gradually increases in bottom layers.

3.3. Theoretical modeling

The contaminant transport is mostly dependent on advection, diffusion, dispersion, sorption and decay of solution during the flow of contaminant and that of washing medium for the case of remediation [17,18]. Thus it is essential to study the adsorption and desorption characteristics of solute on the soil material. In the present investigation modeling and simulation of organic and inorganic contaminant has been considered and its movement through the soil together with adsorption and desorption characteristics as well as chemical degradation has been studied through modeling.

An effort has been made to model the contaminant transport at a uniform rate presuming the availability of sources to be continuous. Further it has also been considered to model this transport due to periodic rainfall in the case where further disposals are stopped after the initial dumping. The rainwater washes the contaminant from the first few layers of soil to subsequent depths. As a result, there is a cyclic movement of contaminant whereby the concentration of contaminant decreases in the top layers but gradually

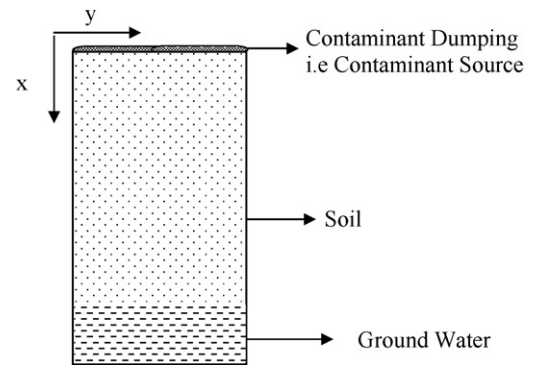


Fig. 5. Schematic of the soil column.

increases as one move down the soil column. Theoretical modeling has been done to predict the contaminant transport during washing by rainwater, which has the potential to enhance the remediation process. Appropriate differential equations have also been developed to model the flow of contaminants through the soil matrix and predict their transport behavior in a variety of situations. These have been solved numerically by the finite difference method using computer simulations in MATLAB software.

3.3.1. Advection–dispersion equation for solute transport through porous media

This kind of transport has been considered for two extreme cases: continuous release and instantaneous release. Continuous release implies a continuous influx of the contaminant as in the case of a landfill for relatively long periods of time, whereas instantaneous release implies a pulse or sudden influx of contaminant for a very short period of time as in the case of accidental spills. The governing set of equations describing the transport of water through soil is a statement of the law of conservation of mass. It is assumed that the porous medium is homogeneous, isotropic, and saturated in nature. It is further assumed that the flow is steady-state and the Darcy's law applies. The flow is described by the average linear velocity or seepage velocity which transports the dissolved substance by advection [19].

In a homogeneous medium in which the velocity is steady and uniform (i.e., it does not vary through time or space), and dispersion coefficients D_x , D_y , and D_z do not vary through space, (but $D_x \neq D_y \neq D_z$, in general) a material balance equation may be formulated to mathematically define the process. A schematic representation of the soil system with contaminant source at top and ground water table at a certain depth, to which the transport equation is applied, is shown in Fig. 5.

The governing equation of transport of water through the soil bed can be written (considering advection and hydrodynamic dispersion factors controlling the mode of transport) as

$$\frac{\partial C}{\partial t} = \left[D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right] - \left[v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} + v_z \frac{\partial C}{\partial z} \right] + Q_s(t) \quad (8)$$

One-dimensional form of Eq. (8), with the following assumptions: (i) transport is one-dimensional and water moves in x -direction only, i.e. along the depth of the packed column, (ii) the porous medium is homogenous and isotropic so that transport in any one direction describes in the other two directions as well, is considered for this case. Hence, ρ_b , K_d , D_x and η are constants and $D_x = D_y = D_z$, (iii) the density and viscosity of the liquid stream remain constant and (iv) saturated flow is considered with constant seepage velocity v_x .

Eq. (2) can be expressed as

$$\frac{\partial C}{\partial t} = \left[D_x \frac{\partial^2 C}{\partial x^2} \right] - \left[v_x \frac{\partial C}{\partial x} \right] + Q_s(t) \quad (9)$$

Using finite difference approximations to further solve in MATLAB software, Eq. (9) may be reduced to the following set of simultaneous ordinary differential equations.

$$C_{i,j+1} = \left(\frac{D_x \Delta t}{\Delta x^2} - \frac{v_x \Delta t}{\Delta x} \right) C_{i+1,j} + \left(\frac{D_x \Delta t}{\Delta x^2} \right) C_{i-1,j} + \left(\frac{1}{\Delta t} - 2 \frac{D_x}{\Delta x^2} + \frac{v_x}{\Delta x} \right) C_{i,j} + Q_s(t) \quad (10)$$

where i, j are two-dimensional matrix indices corresponding to distance (x) and time (t). Δx and Δt are small increments in distance (x) and time (t).

3.3.2. Advection–dispersion–sorption equation for solute transport through porous media

While there exist many process conditions that can alter contaminant concentration, adsorption into the soil matrix appears to be one of the most dominant mechanisms. Solutes that sorb strongly onto soil materials are retarded in their movement. Adsorption into the soil matrix is thus the most important process for physical removal of many contaminants, either inorganic or organic. The adsorption of the solute retards its movement and slows down its transport to aquifer. The mass balance equation (1) in this case would incorporate the mass of solute adsorbed on the soil bed.

Advection, dispersion and sorption phenomena can be written as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} + \left(\frac{\rho_b}{\varepsilon} \right) \frac{\partial S}{\partial t} + Q_s(t) \quad (11)$$

The concept of isotherm is used to relate the amount of contaminant adsorbed by the solids S to the concentration in solution. Using Freundlich's isotherm

$$S = K_d C_e^{1/n} \quad (12)$$

If $1/n = 1$, the isotherm is linear and the following transformation can be made to incorporate this isotherm into the mass balance equation:

$$S = K_d C_e \quad (13)$$

Partial derivative of Eq. (13) we get

$$\partial S = K_d \partial C \Rightarrow \frac{\partial S}{\partial C} = K_d \quad (14)$$

Also

$$\frac{\partial S}{\partial t} = \frac{\partial S}{\partial C} \frac{\partial C}{\partial t} = \frac{\partial S}{\partial C} \frac{\partial C}{\partial t} = K_d \frac{\partial C}{\partial t} \quad (15)$$

And hence Eq. (11) will become

$$\left(1 - \frac{\rho_b}{\varepsilon} K_d \right) \frac{\partial C}{\partial t} = Q_s(t) + D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \quad (16)$$

or

$$\frac{\partial C}{\partial t} = \frac{Q_s(t)}{R} - \frac{D_x \partial^2 C}{R \partial x^2} - \frac{v_x \partial C}{R \partial x} \quad (17)$$

where

$$R = 1 + \frac{\rho_b}{\varepsilon} K_d \quad (18)$$

R is known as retardation factor, which has the effect of retarding the adsorbed species relative to the advective velocity of ground water and is a useful tool in the case of linear isotherms with fast, reversible adsorption [20,21].

The finite difference form of Eq. (10) may be written as

$$\frac{C_{i,j+1} - C_{i,j}}{\Delta t} = \frac{D_x}{R} \left(\frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{\Delta x^2} \right) - \frac{v_x}{R} \left(\frac{C_{i+1,j} - C_{i,j}}{\Delta x} \right) + \frac{Q_s(t)}{R} \quad (19)$$

3.3.3. Advection–dispersion–sorption–decay equation for solute transport through porous media

There are several contaminants where significant changes occur due to the decay by chemical reaction (hydrolysis, oxidation/reduction) with soil matrix or among the different contaminants or more importantly get biologically degraded due to the presence of microorganisms. The latter is especially valid for organic contaminants which may happen by simple decomposition or by biological oxidation process with the oxygen diffusing into the soil or produced locally by a secondary reaction. In the case of chemical decay, the rate expression may follow simple zero-order or first-order kinetics whereas in the case of biodegradation the rate may be described by Monod kinetics.

For the case of first-order decay, in addition to adsorption, dispersion and sorption, the final mass balance equation becomes

$$\frac{\partial C}{\partial t} = \frac{Q_s(t)}{R} - \frac{D_x \partial^2 C}{R \partial x^2} - \frac{v_x \partial C}{R \partial x} - \frac{k}{R} C \quad (20)$$

The finite difference form of the equation is given below

$$\frac{C_{i,j+1} - C_{i,j}}{\Delta t} = \frac{D_x}{R} \left(\frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{\Delta x^2} \right) - \frac{v_x}{R} \left(\frac{C_{i+1,j} - C_{i,j}}{\Delta x} \right) - \frac{k}{R} C_{i,j} - \frac{Q_s(t)}{R} \quad (21)$$

or

$$C_{i,j+1} = \left(\frac{D_x \Delta t}{\Delta x^2} - \frac{v_x \Delta t}{\Delta x} \right) \frac{C_{i+1,j}}{R} + \left(\frac{D_x \Delta t}{\Delta x^2} \right) \frac{C_{i-1,j}}{R} + \left(\frac{1}{\Delta t} - \frac{2D_x}{\Delta x^2} + \frac{v_x}{\Delta x} - k \right) \frac{\Delta t C_{i,j}}{R} + \frac{Q_s(t)}{R} \quad (22)$$

For Monod kinetics, the rate equation is given by

$$r = \frac{\mu_m C X}{K_s + C} \quad (23)$$

where μ_m = maximum utilization rate, K_s = half saturation constant.

As a result, the mass balance equation takes the form:

$$\frac{Q_s(t)}{R} - \frac{D_x \partial^2 C}{R \partial x^2} - \frac{v_x \partial C}{R \partial x} - \frac{\mu_m C X}{K_s + C} = \frac{\partial C}{\partial t} \quad (24)$$

The boundary conditions were used to predict the plume behavior in soil column by a continuous release of contaminant on the soil bed, e.g. continuous input of hazardous waste from a landfill (leachate), at $x=0$, the concentration is set to $C(0, t) = C_0$ for $t > 0$. The concentration at other boundary, $x = \infty$ is set to zero, $C(\infty, t) = 0$ for $t = 0$. In this case the feed contaminant concentration was taken as 20 mg/l for different background concentrations in the soil bed. Plot 1 shown in Fig. 6 shows the outlet concentration profile for advection–dispersion transport with $D_x = 1.15 \times 10^{-7} \text{ m}^2/\text{s}$, $v = 3.19 \times 10^{-5} \text{ m/s}$ and background concentration zero. It is a typical S-shaped breakthrough curve.

If the background concentration, i.e. concentration of contaminant initially present in the soil column is assumed to be uniform and equal to 10 mg/l, one gets Plot 2 as the result. However if the background concentration is greater than the source concentration, as in the case of Plot 3, relative washouts occur removing contaminant and giving a desorption type breakthrough curve.

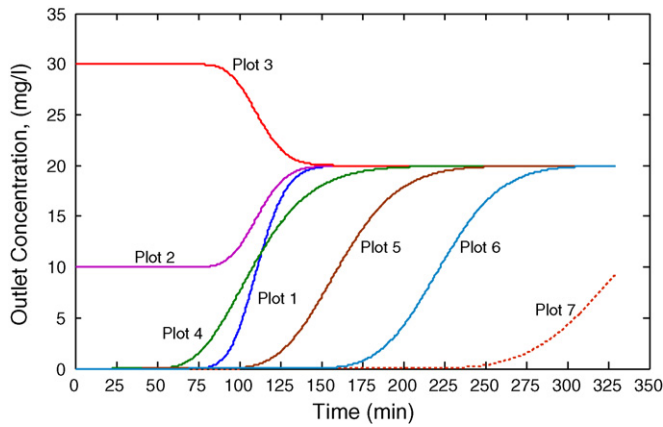


Fig. 6. Concentration profile for advection–dispersion transport for continuous input.

In Plot 4, the dispersion coefficient D_x has been increased with the same velocity. Here due to increase in D_x , there is more spreading of the contaminant and as a result the contaminant starts to appear at the outlet earlier. For the same reason, it takes more time for the contaminant to attain saturation value. Initial boundary conditions are similar to Plot 1 as is the case for all the other plots (Plots 5–7) mentioned below.

In Plot 5, the seepage velocity v has been decreased, keeping D_x the same. The contaminant front appears later and advection mechanism is seen to be less dominating than before.

The effects of adsorption can be seen in curves 6 and 7, where solution of Eq. (18) has been plotted for the two values of retardation factors of 2 and 3. Curve 6 shows the results of concentration profile where the retardation factor R is taken to be as 2. The retardation factor reduces the effect of both D_x and v by a factor R . Due to this, the contaminant starts to appear after a very long time as compared to Plot 1. This implies that the species has been retarded by the corresponding time period. This also indicates that the contaminant was retained by the soil, slowing down its transport. This has significant importance in terms of the contamination following the discharge of contaminant laden waste water, whereby the time required for the contamination of the soil is increased to a great extent. This also has strong implication for the remediation of the contaminated soil, by requiring much longer period and larger amount of solvent flow for the cleanup of the soil. Retardation is intensified as R increases to 3 in Plot 7.

3.3.4. Discontinuous contaminant discharge

This kind of transport is seen more commonly. Even though further disposals are stopped after the initial dumping, rainwater carries the contaminant into further depths in the soil from the top layers. The transport differs from the earlier ones, depending on the nature of contaminant—whether it is inorganic or organic, as the fate processes vary. In the case of inorganics, adsorption is the most important contaminant removing mechanism. However, in the case of organics, biodegradation also affects the transport, sometime even preventing the contaminant from reaching sub-soil water.

The results of simulation of advection–dispersion–sorption cyclic transport are shown in Fig. 7 in terms of concentration profile with time at different depths of the soil for different durations of idle period and rainfall events. The results show a continuous rise in the concentration of contaminant at top level of the bed, for a long time after the contaminants flow stopped and then a very sharp drop in concentration followed by a static level during idle and rainfall events.

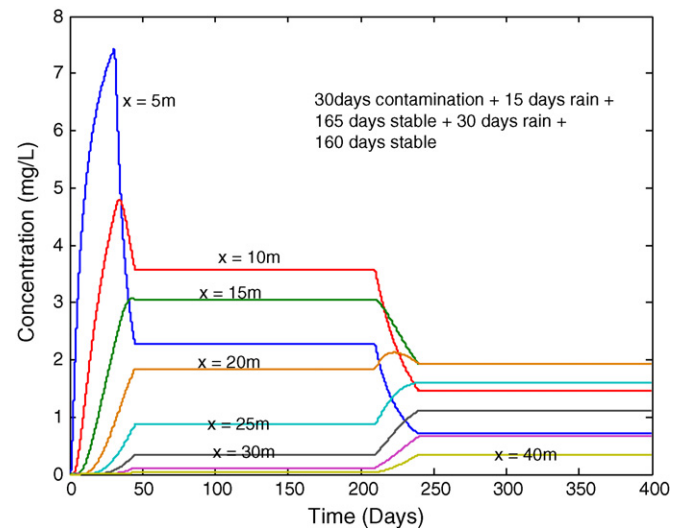


Fig. 7. Advection–dispersion–sorption cycle transport of inorganic in soil for discontinuous source.

The results show that, at the end of each cycle there is a significant drop in concentration of contaminants for the top layers. In this case soil bed up to 15 m shows a continuous drop at the end of 1-year cycle. However the similar results at depth 20 m and below show further increase during each cycle resulting in increase in concentration even at a depth of 30 and 40 m. It is of utmost importance, since the buildup of this contaminant over the years is indicative of the potential for the development of potential danger in the underground water system.

3.3.5. Effect of model parameters on contaminant transport mechanism in soil bed

The effect of various parameters affecting contaminant transport has been analyzed with respect to variation in one parameter and keeping others transport parameters constant through advection–dispersion–sorption–decay model under different boundary conditions. Contaminant concentration of 20 mg/l is added once and on a landmass for a period of 1 month followed by a rainfall period of 15 days. This is followed by 5.5 months of stable period when there is no rainfall or any contaminant discharge. This is followed by another rainfall for a period of 1 month and then again a stable period of 4.5 months for a complete 1-year cycle. This resembles a situation in northern India, where the rainfall is mostly concentrated in two period's viz. in winter for January to February for a short spell and in July to August for a large period. The results are presented for 15 m depth of soil layer for different time profiles, concentration of contaminant in Figs. 8–11. The effect of each parameter is presented in the following paragraphs.

3.3.6. Effect of seepage velocity (v_x) on contaminant transport

It is important to realize that seepage velocity variation provides an estimate of contaminant arrival time at groundwater table. From Fig. 8 it can be understood that as the seepage velocity is increased, the contaminant front will appear faster and advection process will be the dominating mechanism. The contaminant will reach the bottom of the bed sooner and would need lesser number of cycles of washing in comparison to that would have required for the case with lower velocity.

The figure shows that with the increase in the velocity the top layers of the soil bed get washed much faster. Highest advective velocity shows that the top layer reaches a very low concentration, even in the first washing cycle itself. However, the concentration buildup in the intermediate layers is much higher compared to

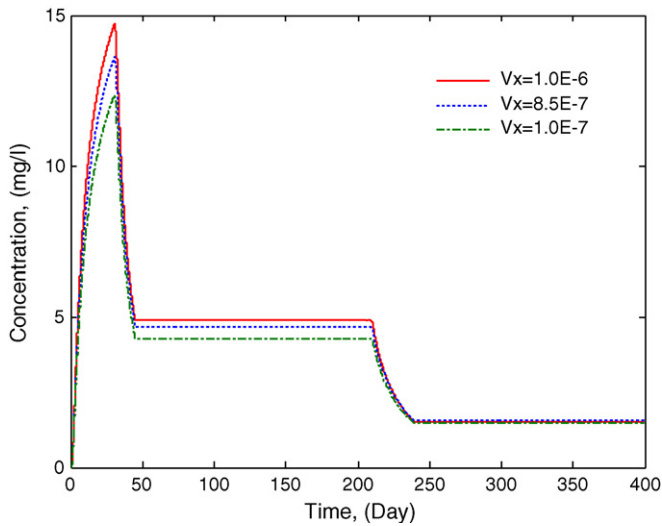


Fig. 8. Effect of seepage velocity (v_x) on contaminant transport.

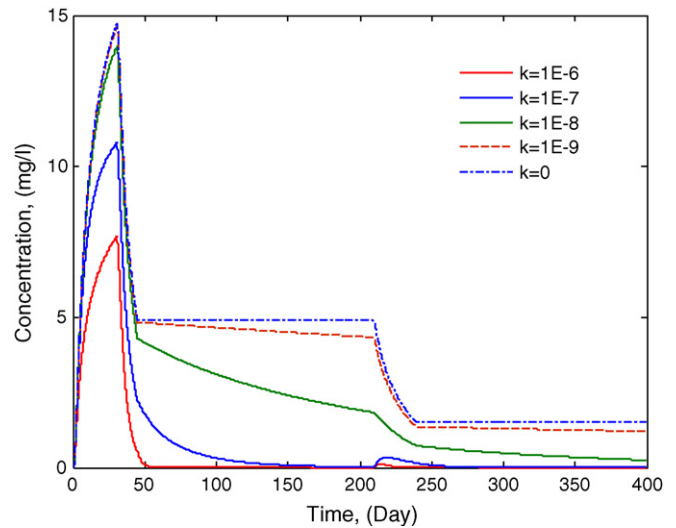


Fig. 11. Effect of decay coefficient (k) on contaminant transport.

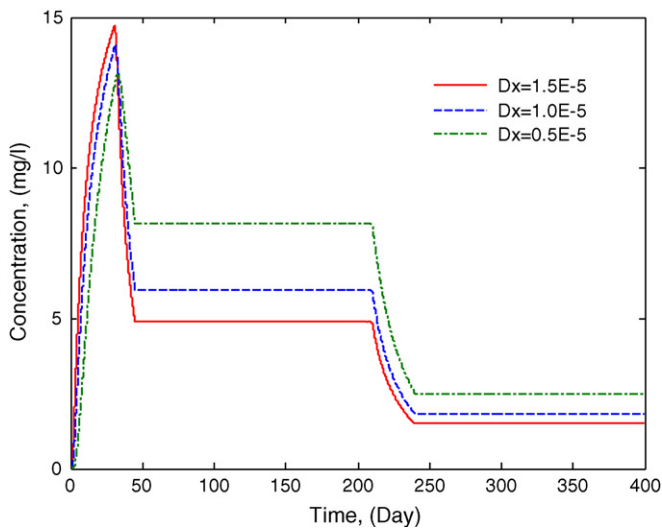


Fig. 9. Effect of dispersion coefficient (D_x) on contaminant transport.

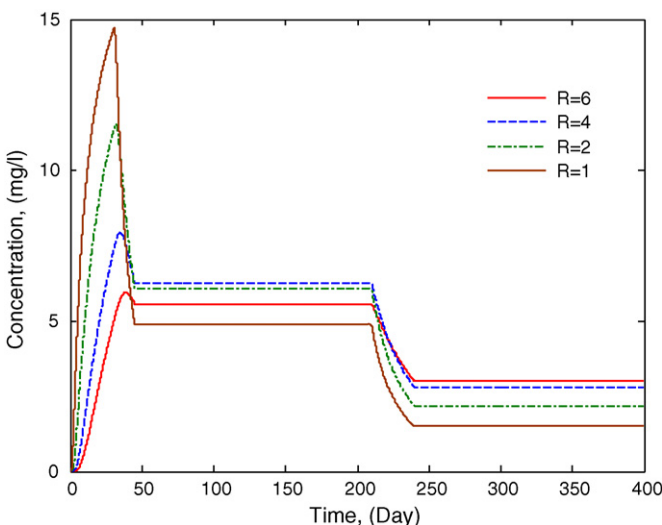


Fig. 10. Effect of retardation factor (R) on contaminant transport.

other case. Thus it is evident that with porous solid bed with permeation velocity, the contaminant would move much faster and accumulate near the bottom of the bed, washing the top layers free of the contaminants.

3.3.7. Effect of dispersion coefficient (D_x) on contaminant transport

Dispersion coefficient is a measure of spread of the concentration front and deviation from ideal condition. Its impact on the contaminant transport is quite important for one to be predict the concentration profile. This specially happens when the soil bed shows extensive heterogeneous characteristic. Model computations were carried out at different values of D_x . The typical results are shown in Fig. 9, where contaminant concentration at 15 m is shown for different D_x values. The results show that at lower D_x value the concentration profile moves further down, although the effect is relatively marginal even for 10-fold increase in the value of D_x .

3.3.8. Effect of retardation factor (R) on contaminant transport

The retardation coefficient depicts the extent of the influence of adsorption mechanism on concentration profile of the contaminant during its transport through the soil bed, while washing process for the contaminated bed. The results are shown in Fig. 10, where the concentration profiles for different retardation factors varying from 1 to 6 are shown. It may be mentioned here that the retardation factor is proportional to adsorption coefficient. Retardation factor has the effect of retarding the adsorbed species relative to the advective velocity of the groundwater. The retardation factor is equivalent to the ratio of velocity of the sorbing contaminant and groundwater.

The higher retardation factor also indicates higher amount of solute being retained within the bed. The concentration profile shows that concentration value at 15 m depth during the initial provided shows a much higher value for higher R value. Same is the case at the end of long period. However, during the intermediate stable period also transpired that the large value of R tends to slow the velocity of transport and reduces the effective value of D_x and v_x by factor $1/R$ and due to this the contaminant starts to appear after a long time as compared to that have been with out R . As a result more washing cycles would be required to clean the contaminated soil bed.

The results show that with the increase of retardation from 1 to 6 the concentration profile undergoes significant change. Retardation factor of 1 indicates no adsorption of solute within the soil bed.

Gradual increases of retardation factor shift the concentration profile for upper layers to northward, with higher component concentration being retained for longer period of time. However, the concentration at lower depth remains at low level for a longer period. Two significant observations can be made from these profiles. First the low retardation factor showed faster movement of the solute indicating rapid desorption of adsorbed component.

On the other hand at higher retardation factor the movement slows down, consequently the build up component concentration at the deeper layers of soil will be quite low. The relevance of this phenomenon is most evident for remediation of the soil layer. The remediation will be faster with lower retardation factor compared to that for higher retardation factor values, when longer remediation period will be needed.

The second observation is the amount of solutes retained by soil layer increases with the increase of retardation factor. This will delay the possible contamination of groundwater aquifer. The retained contaminant within the soil bed will need much greater efforts to clean the same. However, its retention within the top layers of the soil for a longer has the potential for larger damage to the atmosphere.

3.3.9. Effect of decay coefficient (k) on contaminant transport

The significant changes may occur due to decay by chemical reactions (hydrolysis, oxidation/reduction) with soil matrix or biodegradation due to the presence of microorganisms. This aspect has been taken into consideration to know the effect of decay on transport in case if the chromium undergoes decay by biological reduction/adsorption and stabilization or any of the other mechanisms and the results are presented in Fig. 11, where the decay coefficient has been varied from 0 to 1×10^{-6} . Due to the increase in decay coefficient long term concentration at 15 m depth of column will be lower and after washing final concentration will diminish gradually. The results show that the decay coefficient increases the concentration drops much faster. In fact with high decay coefficient concentration rapidly reduces to zero with a short period of time, making the remediation process that much easier.

All the above results show the cases when the decay constant is zero. This is indicative of the fact that there is no consumption or depletion of the contaminant by any mechanism other than adsorption. However, the reactive decay is an important feature of any transport system. This could be due to biodegradation for the organic components or chemical reaction and stabilization with soil materials as in the case of inorganic components. This decay process significantly changes the concentration profiles of the chemicals.

A significant feature of these plots is that the concentration level continuously decreases at all depths of the bed after the initial rise due to contaminant discharge, particularly at higher values of decay constant. Even at low values of the decay constant the rise in concentration is limited to a very marginal values for a short period, after that there is continuous drop in concentration. These results also show an important feature of such scenario, whereby there is high potential that all the components are consumed, before the contamination level reaches the bottom of the soil bed and disturbs the underground aquifer. This is particularly important for the organic component, which have good potential for biodegradation or chemical degradation.

3.3.10. Variation of periods of contaminant discharge, idle period and rainfall/washing cycle

The results of variation of the stable or idle period when there is no flow of contaminant or rainfall takes place is shown in Fig. 12. It shows the effect of number of cycles. The individual periods of cycles are similar in all the cases excepting in the stable period for the last part of cycle. The washings in the figure are due to rainfall over the area. The increase in the number of cycles show a gradual

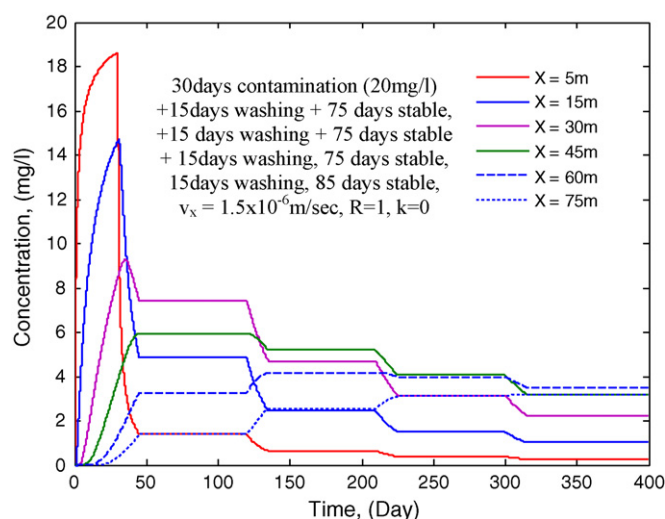


Fig. 12. Effect of contaminant transport for four times rainfall period.

decrease in the concentration of the contaminant at the top level of the soil bed up to 30 m.

However, the contaminant concentration in the soil layer beyond 30 m shows gradual increase over the 1-year cycle of operation. This is quite expected due to the fact that the rainfall washes the top layers and carries the solute towards the bottom of the bed, thus accumulating the same in that zone. In the absence of any removal technique other than the sorption, with the limitation of equilibrium concentration, the contaminant remains within the zone.

The top layer getting washed is quite important in that the concentration goes down to a very low value, similar to the background concentration. This is beneficial from the environmental point of view as it prevents any surface exposure of contaminant to human life and other living bodies. A major danger from this sequence of events is accumulation of the components at lowest levels, which may contaminate the groundwater aquifer. It also allows the removal of contaminants by proper design of removing the water and treating the same before disposal.

4. Conclusion

Detailed experimentation program was undertaken to determine the adsorption parameters as well as to simulate the flow condition through the soil bed. It was noted that for all the Cr-soil system both Langmuir and Freundlich isotherms models exhibited good fit to the sorption data of Cr(VI) in the studied range of concentration. However the model fit was much better for Freundlich isotherm, which was considered for further application. The value of n indicates a positive adsorption of hexavalent chromium in soil. Over all adsorption capacity was found to be quite low and indicate that Cr(VI) is mobile and less adsorbed in studied silt-sand soil.

The initial concentration of Cr(VI) in the solution remarkably influenced the equilibrium Cr(VI) uptake. It was noted that as the initial concentration increased the loading on soil mass increased. The increase of loading of soil with increase of Cr(VI) ion concentration is due to increased availability of Cr(VI) ions in the solution for the sorption.

The results of simulation for the natural redemption of the soil show the periodic movement of the inorganic contaminant concentration front ultimately reaching quite low concentration at the end of the cycles. In the case of inorganic solute (Cr(VI)) the absence of chemical decay makes the adsorption phenomena as the major contaminant removal mechanism. In the case of biodegradation,

the solute depletion becomes a major factor in the transport of pollutant. Consequently, the concentration of contaminants reaching the subsurface layers becomes quite low.

The application of the model under different operating conditions viz. change in seepage velocity, retardation factor, dispersion coefficient, decay coefficient and variation in rainfall and idle condition (no rain) provides unique results in terms of solute concentration profile along the depth of the soil bed. Particularly integrating results were obtained for periodic rainfall condition when the subsequent rainfall washes the top layers of soil and carries the pollutant downward, ultimately accumulating in the subsurface layers. However for organic pollutants with biodegradation, it was found that under some condition contaminant does not reach the higher depth of the subsurface layers or aquifer, but get degraded before that. This result will help in determining the possibility and extent of the discharge of solute containing effluent on land for irrigation, as is carried out under controlled condition.

References

- [1] P. Bedient, R. Hanadi, N. Charles, *Ground Water Contamination*, 2nd ed., Prentice Hall, PTR, New Jersey, 1999.
- [2] E. Bou-Zeid, M. El-Fadel, Parametric sensitivity analysis of leachate transport simulations at landfills, *Waste Manag.* 24 (2004) 681–689.
- [3] W.M. Edmunds, P. Shand, P. Hart, R.S. Ward, The natural (baseline) quality of groundwater: a UK pilot study, *Sci. Total Environ.* 310 (2003) 25–35.
- [4] H. Ole, Leachate from land disposal of coal fly ash, *Waste Manag. Res.* 8 (1990) 429–449.
- [5] A. Moghaddam, C. Mulligan, Leaching of heavy metals from chromated copper arsenate (CCA) treated wood after disposal, *Waste Manag.* 28 (2008) 628–637.
- [6] T. Christensen, H.P. Kjeldsen, P. Bjerg, D. Jensen, J. Christensen, B.A. Baun, H. Albrechtsen, G. Heron, Biogeochemistry of landfill leachate plumes, *Appl. Geochem.* 16 (7–8) (2001) 659–718.
- [7] J.A. Riyad, H.S. Edward, Heavy metal contaminants removal by soil washing, *J. Hazard. Mater.* 70 (1999) 71–86.
- [8] C. Mulligan, R. Yong, B. Gibbs, Remediation technologies for metal-contaminated soils and groundwater: an evaluation, *Eng. Geol.* 60 (2001) 193–207.
- [9] L. Palma, P. Ferrantelli, C. Merli, F. Biancifiori, Recovery of EDTA and metal precipitation from soil flushing solutions, *J. Hazard. Mater.* 103 (2003) 153–168.
- [10] I. Khan, T. Husain, R. Hejazi, An overview and analysis of site remediation technologies, *J. Environ. Manag.* 71 (2004), 95–12.
- [11] R. Mattuck, P. Nikolaos, Chromium mobility in freshwater wetlands, *J. Contam. Hydrol.* 23 (1996) 213–232.
- [12] B. Nivas, A. David, B. Shiao, H. Harwell, Surfactant enhanced remediation of subsurface chromium contamination, *Water Res.* 30 (3) (1996) 511–520.
- [13] M.P. Julita, A. Hursthouse, P.K. Hanna, The interaction of heavy metals with urban soils: sorption behaviour of Cd, Cu, Cr, Pb and Zn with a typical mixed brown field deposit, *Environ. Int.* 31 (2005) 513–521.
- [14] G. Subhashini, K. Pant, Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed, *Chem. Eng. J.* 98 (2003) 165–173.
- [15] D. Mall, C. Srivastava, K. Agarwal, Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash—kinetic study and equilibrium isotherm analyses, *Dye Pigment* 69 (3) (2006) 210–223.
- [16] G. Mckay, S. Blair, R. Gardner, Adsorption of dyes on chitin. I. Equilibrium studies, *Appl. Polym. Sci.* 27 (1982) 3043.
- [17] P. Viotti, M. Papini, N. Stracqualursi, C. Gamba, Contaminant transport in an unsaturated soil: laboratory tests and numerical simulation model as procedure for parameters evaluation, *Ecol. Model.* 182 (2) (2005) 131–148.
- [18] E. Worch, Modelling the solute transport under nonequilibrium conditions on the basis of mass transfer equations, *J. Contam. Hydrol.* 68 (1–2) (2004) 97–120.
- [19] J. Watts, *Hazardous Waste: Sources, Pathways, Receptors*, Wiley, New York, 1998.
- [20] M.Th. van Genuchten, P. Wierenga, Solute dispersion coefficients and retardation factors. In: A. Klute (Ed.), *Methods of Sol Analysis. Part 1. Physical and Mineralogical Methods, Agronomy* 9 (1) (1986) 1025–1054, 2nd ed., Am. Soc. Agron., Madison, WI.
- [21] T.H. Skaggs, F.J. Leij, Solute transport: theoretical background. In: J.H. Dane, G.C. Topps (Eds.), *Methods of Soil Analysis. Part 4. Physical Methods, Soil Sci. Soc. Am., Madison, WI* (2002) 1353–1380.