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INFLUENCE OF HEXAVALENT CHROMIUM INITIAL CONCENTRATION ON RETARDATION FACTOR AND CONTAMINANT VELOCITY IN A SOIL MEDIA

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Abstract

Sources of soil and ground water contamination are many and include many folds of accidental spills and leaks of toxic and hazardous chemicals. Preparation of ground water contamination model needs good understanding of the behavior of contaminant transport through soil media for predicting the level of contamination of ground water in the near future at the intended site conditions. Sorption is a natural process; due to its presence, the contaminant can move slowly as compared to the ground water and hence the effects of sorption must be taken into consideration while predicting the travel time of the contaminant to reach the ground water sources. This paper discusses the results of column test studies carried out in the laboratory under controlled conditions about the spreading of contaminant (Hexavalent chromium, Cr (VI)) through the clay mixed red soil at two different initial concentrations (800 mg/L and 4200 mg/L). The variations of the contaminant flow velocity and retardation factor for two different initial concentrations of contaminant were brought out and discussed. The contaminant flow velocity drastically coming down for a relative concentration of 0 to 0.2 and beyond this range, the contaminant flow velocity value is decreasing in a slow rate for both the lower and higher initial contaminant concentrations tested. At the lower relative concentration, the higher retardation factor was observed and it may be due to slowly filling the available sorption sites in the soil column.

Keywords: Contaminant transport, Sorption, Column test, Retardation factor, Contaminant flow velocity.

Nomenclatures

C	Final concentration of the contaminant, mg/L
C_o	Initial concentration of the contaminant, mg/L
C/C_o	Relative concentration of the contaminant
e	Void ratio
k	Permeability of soil, mm/s
k^*	Permeability of soil for adjusted flow, mm/s
n	Porosity
R	Retardation factor
T	Normalized time
V	Velocity of flow, cm/s
V_c	Contaminant flow velocity, cm/s
Greek Symbols	
γ_b	Bulk unit weight of soil, kN/m^3
γ_d	Dry unit weight of soil, kN/m^3

1. Introduction

Environmental protection became a practice of protecting the natural environment for the benefit of natural environment and human health point of view. Due to the huge population, many facilities are developed to meet the demand and in this process the society is utilising all the natural resources with high end technology and causing many levels of polution to the environment. One of the present day environmental issues is ground water contamination mainly due to the development of industries, which produce heavy metals and these metals carried along with the water through porous media causes contamination. Soil contamination is caused by the presence of xenobiotic chemicals and also due to alteration in the natural soil environment [1]. Also contamination typically arises from the failure caused by corrosion of underground storage tanks, including piping used to transmit the contents, application of pesticides, percolation of contaminated surface water to subsurface strata, oil and fuel dumping, disposal of coal ash, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals which are abundantly discharged out from the industries are petroleum hydrocarbons, lead, polynuclear aromatic hydrocarbons, solvents, pesticides and other heavy metals [2].

In all these industrial wastes, hexavalent chromium (Cr (VI)) is one of the most toxic one. There are many conventional processes for the removal of Cr (VI) and the heavy metals from industrial waste streams, such as precipitation, coagulation, and ion exchange etc., these processes have disadvantages such as incomplete removal, high energy, reagents costs and disposal of toxic sludge. Cr (VI) is recognized as a human carcinogen via inhalation. Workers in many different occupations are exposed to hexavalent chromium. Problematic exposure is known to occur among workers who handle chromate - containing products as well as those who perform welding, grinding, or brazing on stainless steel [3]. In some parts of world, the Cr (VI) in electronic equipment is largely prohibited. Chromium exists in food, air, water and soil, mostly in the Cr (III) form. It is only as a result of human activities that substantial amounts of Cr (VI) become present.

Cr (III) is comparatively insoluble while Cr (VI) is quite soluble and is readily leached from soil to groundwater or surface water [4].

Chromium is a naturally occurring element found in rocks, animals, soil, and in volcanic dust and gases. It is present in the environment in several different forms, the most common being trivalent chromium Cr (III) and hexavalent chromium Cr (VI). Chromium is in steel-grey, lustrous, hard and is used on a large scale in the metallurgical and chemical industries.

The metallurgical industry commonly uses chromium for the production of stainless steel alloys, cast iron and nonferrous alloys as well it is used in plating steel. In the chemical industry, chromium is used primarily in pigments Cr (VI) and Cr (III), metal finishing and electroplating as well as in the wood preservatives (Cr (VI) only) and leather tanning (Cr (III) only) industries. Also in the good olden days chromium is used in cooling towers as a rust and corrosion inhibitor and also as a fungicide [5]. Inhaling high levels of Cr (VI) can cause irritation to the nose, such as runny nose, nose bleeding, ulcers and holes in the nasal septum. Ingesting large amounts of Cr (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain Cr (VI) compounds can cause skin ulcers. Some people are extremely sensitive to Cr (VI) or Cr (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted. In plants, chromium interferes with uptake translocation and accumulation by plant tops of calcium, potassium, magnesium, phosphorus, boron, copper and aggravates iron deficiency chlorosis by interfering with iron metabolism.

There is an immense need to understand the mechanism by which the contaminant is sorbed to soil and the sediment. Some of the researchers carried out studies relevant to the contaminant transport into the porous media. The decrease in particle size up to nano scale may increases the surface area and hence there may be possibility of increase in the number of adsorption sites. The vacant sites in the structure are mainly responsible for the adsorption of heavier ions [6]. Chromium contaminated wastewaters can originate from dyes and pigment manufacturing, wood preserving, electroplating and leather tanning. Chromium exists in +3 and +6 oxidation states as all other oxidation states are not stable in aqueous solutions.

In a water environment the MAIC acts as a strong reducing agent. A series of Cr (VI) model solutions with initial pH ranging between 1 and 5 were treated in the original semi-flow system (SFS), which simulated flow conditions well and the results demonstrate a high MAIC efficacy, considering that at the end of the treatment, concentrations of Cr (VI) were below the maximal allowed concentrations for drinking water in all model solutions [7]. The MAIC mechanism of action is based mainly on processes of reduction and co-precipitation by Al $(OH)_3$, because Cr (VI) is removed from the water phase as metal chromium and insoluble Cr $(OH)_3$. Behaviour of the composite in water is under significant influence of pH, which affects its efficacy and mechanism of action. Finally the ratio of [metal chromium] / [Cr $(OH)_3$] in precipitate, at the end of the treatment, decreases with increasing initial pH of the model solution.

The industrial sources of Cr (VI) include leather tanning, cooling tower blow down, plating, electroplating, anodizing baths, rinse waters, etc., were used. Overviews of the sorption capacities of commercial developed carbons and other low cost sorbents for chromium remediation were discussed [8]. Adsorption of Cr (VI) ions on wheat bran has been studied thoroughly using batch adsorption techniques [9]. The findings revealed that adsorption of chromium by wheat bran reached to equilibrium after 60 min and after that a little change of chromium removal efficiency was observed. Higher chromium adsorption was observed at lower pH, and maximum chromium removal (87.8 %) obtained at pH of 2. The adsorption of chromium by wheat bran decreased at the higher initial chromium concentration and lower adsorbent doses. The obtained results showed that the adsorption of Cr (VI) by wheat bran follows Langmuir isotherm equation with a correlation coefficient equal to 0.997. In addition, the kinetics of the adsorption process follows the pseudo second-order kinetics model with a rate constant value of 0.131 g/mg.min. The results indicate that wheat bran can be employed as a low cost alternative to commercial adsorbents in the removal of Cr (VI) from water and wastewater.

At a given concentration of hexavalent chromium and to achieve 50% removal, the removal half time (t-50) of Jatropha was about twice shorter than pterocarpus [10]. Effect of concentration of fifty (EC-50) of hexavalent chromium for plant dry matter (PDM) Jatropha was higher than for PDM pterocarpus. No significant effect was found for aerial plant parts of Jatropha. Compost amendment was preferable when Jatropha was planted in hexavalent chromium polluted soil because Jatropha could remediate higher concentration than pterocarpus. The findings revealed that the Jatropha was more effective than pterocarpus to remediate hexavalent chromium polluted soil. The potential to remove Cr (VI) from aqueous solutions through biosorption using coffee husk was investigated [11]. The data obeyed Langmuir and Freundlich adsorption isotherms. The Langmuir adsorption capacity was found to be 44.95 mg/g. The Freundlich constants K_f and n were 1.027 [mg/g (l/mg) *n*] and 1.493, respectively. Desorption studies indicated that the removal of the hexavalent chromium is around 60%.

Activated carbon prepared from cashew nut shells using potassium hydroxide activation at 850°C in N_2 and CO_2 atmosphere was used as an adsorbent for the removal of chromium ions from aqueous solutions [12]. The Freundlich and Langmuir isotherm fitted well to data of Cr (III) adsorption. Cr (III) uptake capacity was 13.93 mg/g which was calculated from the Langmuir isotherm. Reduction of Cr (VI) to Cr (III) in artificial, contaminated soil using ferrous sulfate heptahydrate and sodium thiosulfate [13]. Due to widespread use in industrial applications, chromium compounds are often considered one of the most serious heavy metal pollutants found at environmental sites. However, the possibility of chromium release after such treatment has also been called into question. The effect of organic and inorganic amendments on sorption of Cr (VI) and Cr (III) in soil [14]. Clay minerals represented by the SiO – H appear to play an important role in the sorption of Cr (VI) and Cr (III). Soil and amended soil treated with solutions containing Cr (III) adsorbed 1.3 to 9 times more Cr than those treated with Cr (VI). The adsorption of the Cr (VI) and Cr (III) in the soils with organic amendments was in the order: oak > pine > olive oil mill residues > reed > soil. While the adsorption of the Cr (VI) and Cr (III) in the soils with inorganic amendments was in the order: coal > clay > oil shale > soil > zeolite, when the equilibrium concentration of chromate was 85 mg/L.

Hexavalent chromium removal from aqueous solutions by adsorption onto synthetic nano sizes zero valent iron (nZVI) [15]. Synthesis of nano size zerovalent iron (nZVI) and hexavalent chromium Cr (VI)) removal as a highly toxic pollutant by using these nanoparticles. nZVI was synthesized by reduction of ferric chloride using sodium borohydrid. SEM and XRD examinations applied for determination of particle size and characterization of produced nanoparticles. The removal efficiency decreased with Cr (VI) concentration and pH of solution and increased with adsorbent dosage and contact time. The Langmuir and Freundlich isotherm models were used for the adsorption equilibrium data and the Langmuir isotherm model was well fitted nZVI presented an outstanding ability to remove Cr (VI) due to high surface area, low particle size and high inherent activity.

From the aforementioned review of previous studies, it is understand that there are few studies available to explain the mechanisms of transport of Cr (VI) contaminant into the soil media. An experimental study is planned in the laboratory under controlled conditions to study the effect of variation of the contaminant flow velocity (V_c), and retardation factor (R) with the relative concentration (C/C_o) and normalized time (T) by using leaching soil column tests. The experimental set - up, procedures and materials used are discussed in the following sections.

2. Experimental Set Up and Properties of Materials Used

In this study, a series of column tests were conducted to study the effect of contaminant Cr (VI) transport through the soil media. In order to conduct the tests, an experimental apparatus was planned and developed.

2.1. Schematic view of test set- up

The typical column test set up is shown in Fig. 1 and also various accessories of set up are indicated in the order. Test set up typically consists of the following accessories: contaminant storage tank, flexible tube, flow adjusting clamp, air removing valve and permeability mould (soil column).

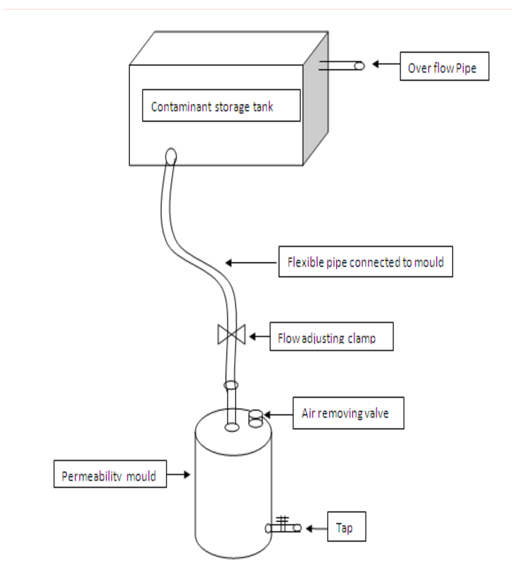

Fig. 1. Test setup of column test.

2.1.1. Contaminant storage tank

The tank was made up of iron sheet with inside dimensions of 300×300×550 mm of 50 litres capacity was used to contain the contaminant (Fig. 1). At the bottom of the test tank a small outlet is provided connecting permeability mould through a flexible tube of diameter 10 mm. The tank is placed at a height of 1860 mm from the centre of the outlet of the permeability mould.

2.1.2. Flexible tube, flow adjusting clamp, air removing valve and mould

A flexible tube is used to pass through the contaminant from contaminant storage tank to permeability mould (soil column). The contaminant was introduced vertically downward through a thin circular pipe (called inlet tube) with an internal diameter of 51 mm. To this a clamp was used to adjust the required velocity of flow, by which the permeability can be adjusted. The adjusted velocity of flow can be obtained from the measured permeability value. It is provided mainly to remove or avoid the entrapped air in the soil column without causing disturbance to the soil sample in the column. A permeability mould with 100 mm diameter and height 127 mm was used and in which soil column was prepared at a dry density of 14.3 kN/m^3 by means of static compaction under controlled means.

2.2. Properties of Materials Used

In the present study the soil and hexavalent chromium Cr (VI) were used to study the transport mechanisms of the contaminant through soil media.

2.2.1. Soil

The soil used in the study was collected from the Patancheruvu, Hyderabad in India. The soil is red in color and has the percentage fines (size < 0.075 mm) of 54 with liquid and plastic limits are 46% and 22% respectively. The specific gravity of the soil is 2.68. The soil is intermediate compressible clay and it can be classified as *CI*. The physical properties of the soil are tabulated in Table 1.

Table 1. Properties of soil used in the column Tests 1 & 2 (T1 & T2).

S. No	Soil property	Test 1 & 2 (T1 & T2)
1	**Soil Type**	Clay mixed with red soil
2	**Sample height (mm)**	82
3	**Porosity, n**	0.46
4	**Void ratio, e**	0.85
5	**Bulk density, γ_b (kN/m^3)**	15.5
6	**Dry density, γ_d (kN/m^3)**	14.3
7	**Permeability, k (mm/s)**	3.9×10^{-3}
8	**Permeability for adjusted flow, k* (mm/s)**	4.02×10^{-3}
9	**Velocity of flow, V (mm/s)**	8.91×10^{-2}
10	**Contaminant flow velocity, V_c (cm/s)**	1.43×10^{-3}

2.2.2. Hexavalent chromium Cr (VI)

Hexavalent chromium was collected from the chemical research laboratory in Hyderabad, India in the form of powder and stored in an air tight bottle without destroying its initial form. It was dissolved in water and prepared at two different initial concentrations 800 mg/l and 4200 mg/l to study the effect of initial concentration of the contaminant on the transport mechanism. These initial concentrations were selected because to ascertain low and high levels of concentrations. The initial concentrations of the contaminant are further presented in Table 2.

Table 2. Contaminant initial concentration used in Tests 1 & 2 (T1 & T2).

S. No	Tests	Contaminant Initial Concentrations (mg/L)
1	**Test 1 (T1)**	800
2	**Test 2 (T2)**	4200

2.3. Test Procedure

Soil column was prepared at a dry density of 14.3 kN/m^3 in the permeability mould and sample was allowed for saturation and upon ensuring the saturation, the contaminant was allowed to pass through the soil column. The contaminant concentrations were measured by using the Atomic Absorption Spectrophotometer (AAS) shown in Fig. 2.

Fig. 2. Atomic absorption spectrophotometer (AAS).

2.3.1. Preparation of soil sample

An air dried soil sample was collected and weighed around 1000 gm. In a permeability mould with dimensions of size 100 mm and height 127 mm, soil was accommodated by pressing static means.

2.3.2. Saturation of the soil specimen

The soil column was saturated with the help of arrangement made for flow to takes place in the test set up. The saturation was ensured such that there was observed constant volume of water flow from the outlet. The arrangement was made to remove the entrapped air in the soil column.

2.3.3. Measurement of permeability

A constant outflow was maintained at regular intervals of time, to determine the hydraulic conductivity of the soil specimen by constant head method. The water was collected at bottom of the soil column through outlet; the quantity of water collected in a specified time interval was noted. Initially the tap was opened fully to evaluate the permeability of the soil.

2.3.4. Preparation of contaminant solution and test procedure

Contaminant solution was prepared at two initial concentrations 800 mg/l and 4200 mg/l by using hexavalent chromium in order to bring out the influence of low and high concentration on contaminant flow transport through porous media. The contaminant prepared corresponding to a particular concentration was placed in a storage reservoir of capacity of 50 litres and allowed to pass through the soil column with the necessary arrangement made in the form tube connections. During the testing, a constant head was maintained and accordingly the samples were collected with the varied time intervals and analyzed for contaminant concentrations, and velocity of flow of the contaminant was determined. This process was continued until the relative concentration, C/C_o = 0.9 was achieved.

The constant head, that is the vertical elevation between upstream to downstream levels was maintained at 2.5 m throughout the observation period. In the test set up, before introducing the contaminant into the soil column, the tap at the base of the column was closed, and the connecting pipe from the overhead tank to the column was disconnected to drain out water from the tank. The water column above the surface of the soil column was also removed. The prepared contaminant with an initial concentration, C_o, is poured in the overhead tank which is connected to the permeability mould. Simultaneously the tap was opened at the base to allow free flow of contaminant through the soil column. The tap was put in open throughout the observation period of testing. The contaminant's samples at regular intervals were collect by opening the tap provided above the base of the mould. The tap was opened simultaneously to facilitate collection of 5-10 ml of the contaminant every time of observation. The chemical concentrations of the samples are obtained from time to time, till the concentration of the contaminant sample collected from the base tap is almost equal to, or a minimum of 0.9 times the initial concentration (C_o), i.e., C/C_o = 0.9. The concentrations of contaminant samples collected from regular time intervals were measured using Atomic Absorption Spectrophotometer (AAS) (Fig. 2).

Different relative concentrations (C/C_o) followed in the study are presented in Table 3 and also in the same table, the time taken for contaminant for each relative concentration which is obtained from break through curve [16] is presented. The test results are discussed in the following section.

Table 3. Relative concentrations and respective time used in the column Tests 1 & 2 (T1 & T2).

Relative concentrations of contaminant (C/C_o)		Time (minutes)	
Test 1 (T1)	**Test 2 (T2)**	**Test 1 (T1)**	**Test 2 (T2)**
0.16	0.16	$t_{0.16}$ = 36	$t_{0.16}$ = 61
0.50	0.50	$t_{0.50}$ = 95	$t_{0.50}$ = 97
0.84	0.84	$t_{0.84}$ = 270	$t_{0.84}$ = 139

3. Results and Discussions

3.1. Variation of contaminant flow velocity (Vc)

In the present study a laboratory testing was conducted on a soil sample which is being prepared at 14.3 kN/m^3 dry density in a soil column, mainly to understand contaminant flow behavior at two different initial concentrations. The initial concentrations of contaminant Cr (VI) considered were 800 mg/l & 4200 mg/l. The test results are presented with respect to relative concentration (C/C_o), normalized time (T). The main parameters discussed here are contaminant flow velocity (V_c) and retardation factor (R). The variation of V_c for lower initial concentration (800 mg/l) and higher initial concentrations (4200 mg/l) are presented in Figs. 3 to 4 and Figs. 5 to 6 respectively with the relative concentration (C/C_o) and normalized time (T).

Figures 3 and 5 present the variation of contaminant flow velocity (V_c) with the relative concentration (C/C_o). From this figure, it can be clearly seen that as the relative concentration increases from 0 to 0.1, the contaminant flow velocity drastically coming down for a relative concentration range of 0 to 0.2 and from the relative concentration 0.2 to 0.6 the V_c value is decreasing in a slow rate with a linear pattern. From the relative concentration of 0.6 onwards the V_c is almost reached a constant value of about 0.02 mm/s and with this value it is moving parallel even further increase in the relative concentration. This behavior of contaminant flow indicates that the sorption sites available in the porous media are getting sorbed by the contaminant and because of it, though there is increased concentration the contaminant flow velocity becoming constant. The variation of contaminant flow velocity with the relative concentration shows a definite trend of power law variation. The equation was fitted for the V_c versus C/C_o for initial concentration of contaminant (C_o= 800 mg/l) and the equation is given below

$$V_c = 0.005\left(\frac{C}{C_o}\right)^{-1.08} \quad (1)$$

The regression coefficient of the above equation is 0.98. Figure 4 presents the variation of contaminant flow velocity (V_c) with the normalized time (T) for lower initial concentration, C_o = 800 mg/l. From this figure, it can be clearly observed that as the normalized time, T increases from 0 to 3 at the interval of 0.5, the contaminant flow velocity drastically coming down up to a normalized time, T = 0.3 and T = 0.3 onwards and up to T = 1, the trend is curvilinear. Beyond T = 1, the decrease in contaminant flow observed is slow rate and this decrease is in the linear pattern and finally the contaminant flow velocity, V_c is reaching a constant value of 0.005 mm/s. The trend line is fitted between V_c and normalized time, T and the equation is presented below (Eq. (2)).

$$V_c = 0.014\,(T)^{-1} \tag{2}$$

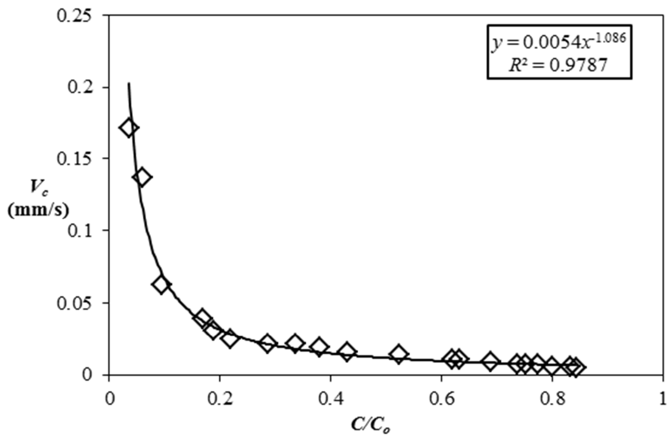

Fig. 3. Variation of contaminant flow velocity (V_c) vs. relative concentration (C/C_o) for test 1(T1).

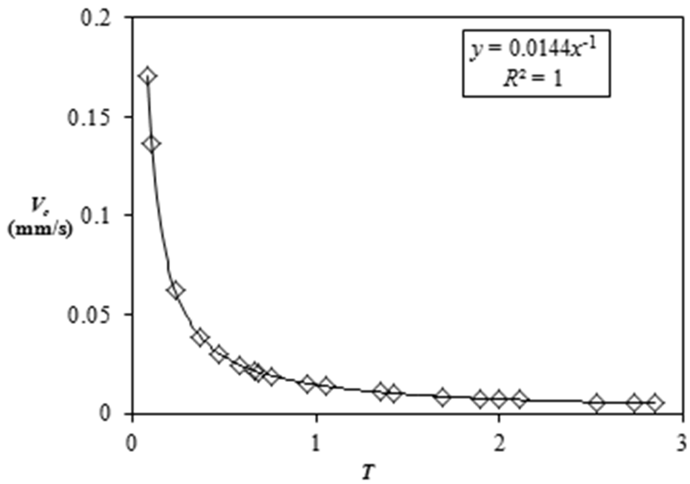

Fig. 4. Variation of contaminant flow velocity (V_c) vs. normalized time (T) for Test 1 (T1).

The regression coefficient of the above equation is 1. Similarly to understand the effect of higher initial concentration of contaminant on the contaminant flow velocity, the results are presented in Figs. 5 and 6. The variation of V_c corresponding to higher initial concentration is presented in Fig. 5, with respect to the relative concentration (C/C_o). From this figure, some interesting findings are observed. As the relative concentration increases, the contaminant flow velocity is coming down drastically from higher velocity levels (0.7 mm/s) to lower levels (0.04 mm/s). At a relative concentration of about 0.2, the contaminant flow velocity reaching a constant flow velocity level around 0.04 mm/s and it is continuing in a slow rate and in a linear pattern even further increase in the relative concentration and attaining a constant velocity of about 0.02 mm/s. Figures 3 and 6 are plotted for contaminant flow velocity for different initial concentrations. In case of lower initial concentration the contaminant flow velocity at the beginning of the test is 0.175 mm/s (Fig. 3), whereas for the higher initial concentration, the contaminant flow velocity at the test beginning is 0.7 mm/s (Fig. 5). Though, there is a difference in the velocity at the beginning of the test for the lower and higher initial contaminant concentrations, the final attained velocity with the increased relative concentrations are almost same and it is about 0.02 mm/s. The equation was fitted for the V_c versus C/C_o for initial concentration of contaminant (C_o= 4200 mg/l) and the equation is given below (Eq. (3))

$$V_c = 0.006 \left(\frac{C}{C_o}\right)^{-0.1} \tag{3}$$

The regression coefficient for the above expression noticed is 0.876. Figure 6 presents the variation of contaminant flow velocity (V_c) with the normalized time (T) for higher initial concentration, C_o = 4200 mg/l. From this figure it can be clearly observed that as the normalized time, T increases from 0 to 2 at the interval of 0.5, the contaminant flow velocity drastically coming down from 0.7 mm/s to 0.08 mm/s up to a normalized time, T = 0.2 and from T = 0.2 to 0.5, the variation is curvilinear and from T = 0.5 onwards, the decrease in contaminant flow velocity observed is slow rate and this decrease is in the linear pattern. The contaminant flow velocity is almost attaining a constant value of 0.007 mm/s. The trend line is fitted between V_c and normalized time, T and the equation is presented below (Eq. (4)).

$$V_c = 0.014\,(T)^{-1} \tag{4}$$

The regression coefficient of the above equation is 1. Irrespective of the initial concentration, the trend of the contaminant flow velocity (V_c) with the normalized time, T showing the similar curve fitting.

3.2. Variation of Retardation Factor (*R*)

3.2.1. Variation of retardation factor (*R*) with relative concentration (C/Co)

Contaminant may be some time sorbed to the soil depending upon the available sorption sites in soil. Retardation factor is defined as the ratio between velocities of water (V) to the contaminant flow velocity (V_c). This factor is mainly used to understand the amount of concentration remained in the soil after subjecting the soil to contaminant transport. To understand the soil – sorption behavior, in this study the results are plotted with respect to the retardation factor relating to the initial concentration 800 mg/l and 4200 mg/l. Figures 7 to 10, present the variation of retardation factor with the C/C_o and T for lower and higher initial concentrations.

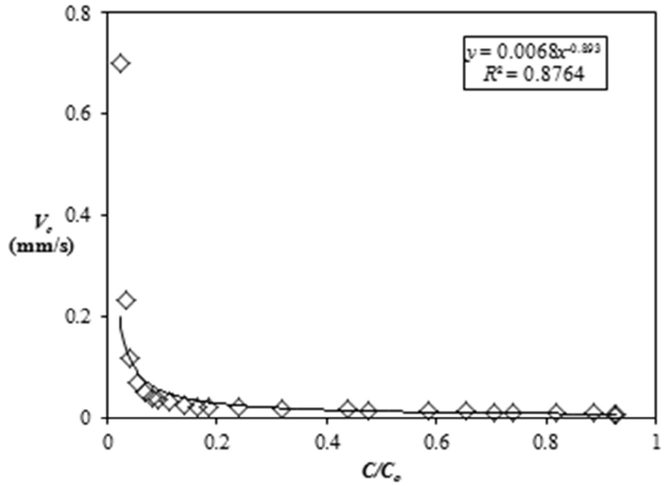

Fig. 5. Variation of contaminant flow velocity (V_c) vs. relative concentration (C/C_o) for Test 2 (T2).

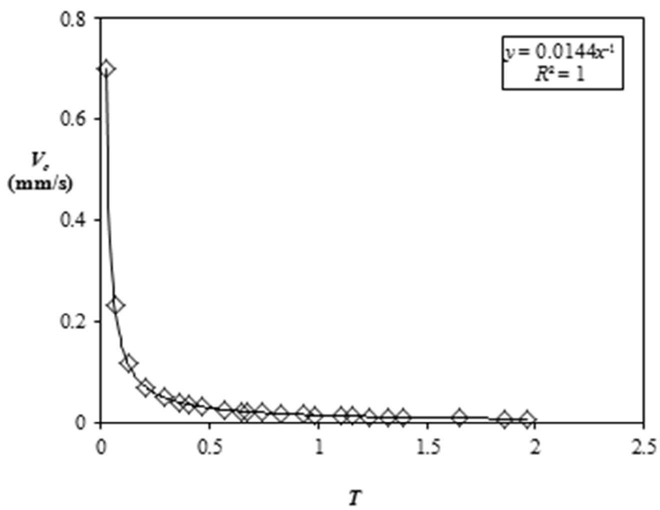

Fig. 6. Contaminant flow velocity (V_c) variation vs. normalized time (T) for Test 2 (T2).

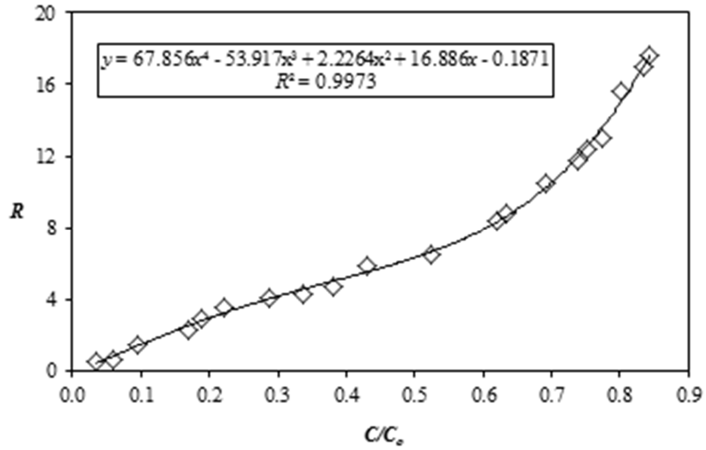

Fig. 7. Variation of retardation factor (*R*) vs. relative concentration (C/C_o) for Test 1 (T1).

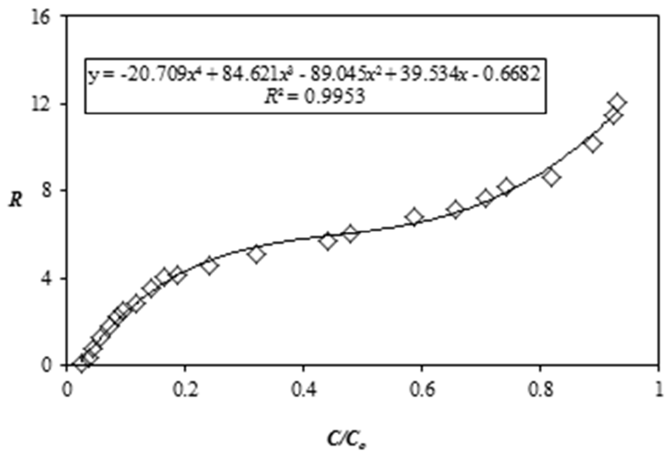

Fig. 8. Variation of retardation factor (*R*) vs. relative concentration (C/C_o) for Test 2 (T2).

Figures 7 and 8 present the variation of retardation factor with respect to the relative concentration. The solution prepared corresponding to a contaminant initial concentration of 800 mg/l and 4200 mg/l are allowed to pass through the soil column and the contaminant discharge was collected at different time intervals.

Almost similar trend is noticed in the retardation factor variation for both the initial concentrations tested. For the initial concentration 800 mg/l (Fig. 7), the retardation factor is 1.5 corresponding to a relative concentration, C/C_o = 0.1 and at about 0.8 relative concentration, the retardation factor is around 16. From this it can be attributed that the retardation factor is increasing as the relative concentration increases for a given initial concentration. For the initial concentration 4200 mg/l (Fig. 8), the retardation factor is 3 corresponding to a relative concentration, C/C_o = 0.1 and at about 0.8 relative concentration, the retardation factor is around 8. From this it can be attributed that the retardation factor is increasing as the relative concentration increases for a given initial concentration. From this it can be noticed that at the higher initial concentration, the retardation factor, *R* corresponding to a relative concentration C/C_o = 0.1, is 3 where as for lower initial concentration, the *R* value is 1.5 and similarly corresponding to a relative concentration C/C_o = 0.8, the retardation factor for lower initial concentration (C_o = 800 mg/l) is 2 times than that of retardation factor of the higher initial concentration (C_o = 4200 mg/l). At lower relative concentrations, the *R* is double the higher initial concentration as compared to the lower initial concentration. But, at higher relative concentration C/C_o = 0.8, the trend is reverse, i.e., the *R* values are double the lower initial concentration as compared to the higher initial concentration. This can be attributed that at the contaminant prepared with lower initial concentrations is slowly filling the available sorption sites in the soil column and hence there is an increased retardation factor at the lower relative concentrations. Corresponding to a contaminant higher initial concentration, the lower retardation factor is noticed at higher relative concentration, C/C_o = 0.8 because the available sorption sites are getting completely filled with the available contaminant and there may not be further sorption of the contaminant in the soil column.

3.2.2. Variation of retardation factor (*R*) with normalized time (*T*)

The variation in retardation factor (*R*) is further discussed with the normalized time (*T*). The results are presented in the Figs. 9 and 10 for lower and higher contaminant initial concentrations. The trend of the R is verified along with the *T* in these results. For both the cases of lower and higher contaminant initial concentrations, the trend or variation of *R* with the *T* is almost similar and found to be linear throughout. As the normalized time *T* increase from 0 to up to about 2, there is increase in retardation factor from 0 to 12 irrespective of the contaminant initial concentration. The fitting observed is almost similar and are presented below in Eqs. (5) and (6) respectively for contaminant lower and higher initial concentrations.

$$R = 6.193T - 2 \times 10^{-14} \quad (5)$$

$$R = 6.173\,T \quad (6)$$

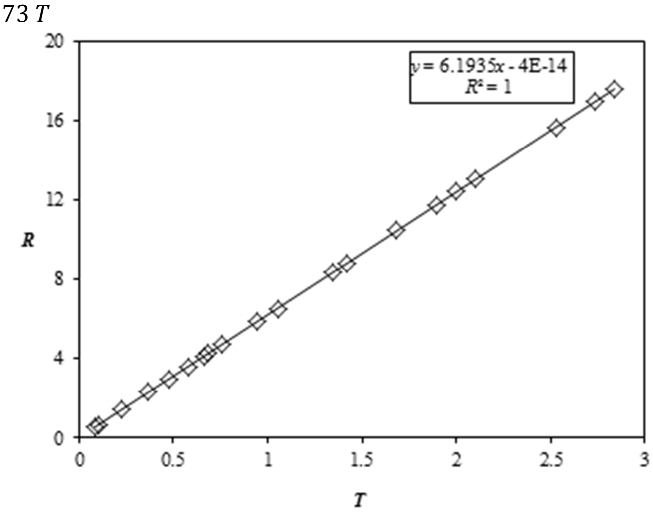

Fig. 9. Variation of retardation factor (*R*) vs. normalized time (*T*) for Test 1 (T1).

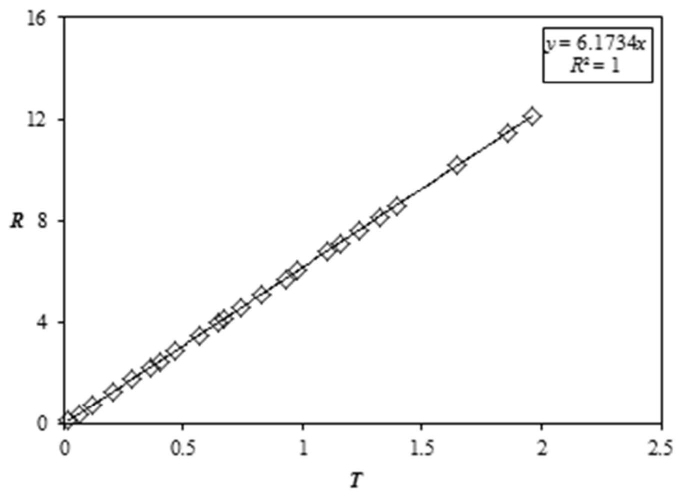

Fig. 10. Variation of retardation factor (R) vs. normalized time Test 2 (T2).

In both the cases, the regression coefficients observed are 1. Also, if the fraction value 2×10^{-14}, if it is removed from the Eq. (5), the equations both Eqs. (5) and (6), may become the same. Hence, for better understanding point of view a unique equation is proposed irrespective of the contaminant initial concentration in place of both the equations and is presented in Eq. (7).

$$R = 6.183\, T \tag{7}$$

4. Conclusions

From the results and discussion the following conclusions are drawn. The contaminant flow velocity (V_c) drastically coming down for a relative concentration range of 0 to 0.2 and from the relative concentration levels 0.2 to 0.6 the V_c value is decreasing in a slow rate with a linear pattern. The normalized time, T value beyond 1, the decrease in contaminant flow velocity is in slow rate. At a relative concentration of about 0.2, the contaminant flow velocity reaching a constant flow velocity level around 0.04 mm/s and it is continuing in a slow rate and in a linear pattern even further increase in the relative concentration and attaining a constant velocity of about 0.02 mm/s. Almost similar trend is noticed in the retardation factor variation for both the lower and higher initial concentrations tested. For the lower initial concentration 800 mg/l, the retardation factor is 1.5 corresponding to a relative concentration, C/C_o = 0.1 and at about 0.8 relative concentration, the retardation factor is around 16. For the higher initial concentration 4200 mg/l, the retardation factor is 3 corresponding to a relative concentration, C/C_o = 0.1 and at about 0.8 relative concentration, the retardation factor is around 8. This can be attributed that the contaminant prepared with a lower initial concentrations is slowly filling the available sorption sites in the soil column and hence there is an increased retardation factor at the lower relative concentrations. A unique equation is proposed irrespective of the contaminant initial concentration between the retardation factor and the normalized time, T i.e., R = 6.183T and it showed a regression coefficient 1. The retardation factor is varying linearly with normalized time (T). The contaminant flow velocity (V_c) varies with normalized time (T) through power law variation. The contaminant flow velocity (V_c) is related to relative concentration (C/C_o) through power law variation, and that of retardation factor with relative concentration (C/C_o) through polynomial variation.

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