

Experimental Study of the Transport of Pollutants in Groundwater

Mohammad Asif

*Department of Chemical Engineering, K.S.U., PO Box 800, Riyadh 11421, FAX: (01) 467-8770
E-mail: masif@ksu.edu.sa*

Abstract

A quantitative understanding of the transport of pollutants in groundwater is of great importance from the environmental perspective. Some environmental pollution scenarios involving groundwater contamination are very real. For example, one may encounter a situation where an underground storage tank is leaking hydrocarbons into an aquifer at a constant rate. Similarly, an overturned oil tanker spilling fuel that might flow through the sandy soil and find its way to the groundwater aquifer leading to its contamination. Especially in the Kingdom where fossil-water resources are not very abundant and, therefore, their contamination is something which scientists and engineers of the Kingdom can least afford not being ready to handle. The first step in this direction is to understand the flow and transport mechanisms of pollutants in groundwater to quantify their effects before any effective *in situ* remediation or extraction strategies could be suggested.

Experimental study in a laboratory is carried out in order to gain a quantitative understanding of the main transport mechanisms of pollutants in groundwater. In this connection, residence time distribution (RTD) studies were carried out in a saturated but homogeneous porous medium with superimposed ambient water flow to simulate the groundwater flow. The porous medium was constructed using a non-porous and inert plastic resin in order to eliminate the internal and external mass transport resistances, thereby simplifying the mathematical model and the subsequent processing of the data. To this end, experiments were carried out using a non-reactive salt tracer instead of a pollutant to avoid the disposal and safety problems associated with their handling. The main focus of the present experimental study was to investigate the effect of the molecular diffusivity of the tracer on the dispersive transport or the spread of the pollutant. This was achieved using two different salt tracers of significantly different diffusivities. Pulse injections of tracers were made and their concentrations were monitored *in situ* downstream with the help of specially designed conductivity probes. The data thus obtained were processed in conjunction with the one-dimensional dispersion model to obtain the degree of dispersive transport as function of water flow for both cases of salt tracers of different molecular diffusivities.

Introduction

Large-scale problems of soil and groundwater contamination are the direct result of the development of the modern industrial society. The production of organic chemicals has increased immensely. More important are the changes in the types of compounds produced and the uses of these chemicals. In the past, chemicals used in agriculture were derived principally from animal wastes, plant residues, and minerals. Today a wide assortment of petroleum-derived compounds is used as pesticides and herbicides. Many compounds, in some cases after extensive worldwide use, have been found to be toxic to wildlife and fish (e.g., DDT), highly toxic to mammals (e.g., phosphate-based pesticides such as Parathion), or carcinogenic (e.g., halogenated compounds such as polychlorinated biphenyls and dibromochloro- propane).

The most common sources of groundwater pollution are perhaps leaking under-ground storage tanks, landfills, and waste-disposal ponds. Serious soil and groundwater contamination problems also result from spills and improper disposal of toxic materials. For example, accidents during transport of chemicals may result in spillage of large quantities of pure products on small areas of ground. Left untreated, the chemicals can percolate into the soil and eventually may contaminate the local groundwater. Many sites throughout the industrial world exist where chemicals accidentally or intentionally leaked, deposited, or were disposed of in soils have contaminated groundwater aquifers or rendered large tracts of land unusable and dangerous to humans and other forms of life. In order to gauge the magnitude of environmental damage caused by even small amounts of pollutant finding its way to groundwater. Even a liter of trichloroethylene (TCE), which has a density of 1.46 kg/L at 20 degree C and a maximum concentration limit of 0.005 mg/L, will lead to a contamination of 77 million gallons of drinking water (Eweis et al. [1]).

Contaminants or pollutants released into the environment rarely remain at the point of discharge. Transport through mechanisms of advection, dispersion, and inter-phase transfer normally takes place. In most cases, contaminant mixtures are involved and individual species may be transported at significantly different rates. Successful hazardous-waste management and site remediation therefore requires an understanding of contaminant fate and transport. Different aspects of contaminant transport have been an active area of research [2-6]. A good deal of literature is also available suggesting effective remediation strategies for different types of contaminations. For example, factors affecting the chemical remediation of oil contaminated water-wetted solid has been recently reported [7]. However, the present work is mainly concerned with the transport of contaminant in a saturated porous medium with a superimposed groundwater flow. In particular, the issue of the molecular diffusivity on the dispersive transport of the contaminant is examined.

In this connection, the approach used in the present experimental investigation consisted of using a non-porous and non-adsorbing plastic resin for the construction of

porous media in a tall cylindrical column. A continuous flow of the tap water at ambient conditions was superimposed in the saturated porous media to simulate the actual groundwater flow conditions. As a first step, two different salt tracers of different molecular diffusivities were chosen instead of actual pollutant to avoid problems associated with their handling and disposal. The residence time distribution (RTD) studies were then carried out by injecting a pulse of the salt tracer. The conductivity of the flowing water was monitored *in situ* downstream. The transient data, thus obtained, were recorded and stored using a data acquisition system connected to a PC. The experimental data were then processed in conjunction with the well-known dispersion model to obtain parameters governing the dispersive transport of the tracer in the saturated porous media.

Experimental Method

The flow setup consisted of a 140-mm internal diameter and 1.5-m long transparent plexiglass column containing the porous medium. Details of the experimental set-up and the particles used for the construction of the porous medium can be seen elsewhere [8]. Details of the tracer injection and its *in situ* monitoring system are however discussed in the following.

Tracer Injection and *In Situ* Monitoring System

Proper design of the tracer injection and *in situ* monitoring system is always a crucial component of the overall experimental design for the reliability of the data obtained in such studies. In order to avoid problems associated with the handling and disposal of the actual pollutants or contaminants, 1-M salt solutions were used as tracers instead of pollutants. Two different salt tracers of different molecular diffusion coefficient were used. One was potassium chloride (KCl). Its molecular diffusivity is $1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ in the aqueous solution [9]. Magnesium sulfate (MgSO_4) with a molecular diffusion coefficient of $0.45 \times 10^{-5} \text{ cm}^2/\text{s}$ in the aqueous solution [10] was the other salt solution used as a tracer in present experiments. Consequently, the comparison between these two cases would reveal the information about the influence of tracer diffusivity, if any, on the dispersive transport. In order to minimize the uncertainty and have reliable data, a minimum of three replicate runs were made for each individual experiment.

A uniform planar source of tracer injection was achieved with the help of a 4-mm OD brass tubing, along the axis of which 4 equally spaced 1.5-mm holes were drilled. It was situated along the diameter of the column cross-section such that the tracer ejecting under pressure through the holes of the tube provided a plane source of tracer injection. The tracer was air-pressurized (200 - 320 kPa) in a 3-liter tank. The time and duration of the pulse of the tracer injection was controlled with a switch-to-

open solenoid valve connected to a Strawberry data acquisition and control system interfaced with a PC. The choice of a pulse tracer input instead of a any other form of input is clearly important in the context of contaminant transport study as lesser amount of inventory is needed, and subsequently used should there arise any need of using actual contaminant.

The concentration of the salt tracer was recorded in terms of conductivity of the solution using a YSI (Yellow Spring Instrument Co., Inc.) conductivity meter. A conductivity probe was specifically designed for the on-line measurement of the specific conductivity of the solution. The electrodes of the probe were made of two platinum wires of 0.55-mm diameter and 5-mm length separated by a distance of 2-mm. The probe was situated across the diameter of the column in such a way that the electrodes were at the center of the column. The response of the conductivity meter using the designed probe was linear in the range of specific conductivity considered here [8].

Separated by a distance of 1.05-m, both the tracer injection and the detection points were located away from the boundaries of the bed. This configuration was chosen in order to prevent the flow irregularities at the boundaries influencing the experimental data. Moreover, the boundary conditions (open-open) of the dispersion equation for these experiments gave a rather simpler form of the solution. The concentration read by the conductivity meter was recorded at regular time interval using the data acquisition system (DAQ). The time interval was suitably selected to ensure enough data points were recorded for each pulse injection of the tracer.

Mathematical Model and Parameter Estimation

The one-dimensional unsteady-state concentration distribution in a saturated porous medium containing inert, non-porous and non-adsorbing packing can be represented using the dispersion model as follows:

$$\frac{\partial C}{\partial t} = D_a \left(\frac{\partial^2 C}{\partial z^2} \right) - U_i \left(\frac{\partial C}{\partial z} \right) \quad 1)$$

where, D_a is the dispersion coefficient in the axial direction, and U_i is the interstitial liquid velocity. Main assumptions involved in this equation are following:

- ✚ Uniform interstitial velocity, U_i , across the column cross-section
- ✚ Constant dispersion coefficient, D_a
- ✚ Uniform tracer injection across the bed cross-section to justify the 1-d assumption

The solution of eqn (1) depends upon the boundary conditions chosen to describe the system. In the present experimental setup, both tracer injection as well as tracer detection points are located away from the boundaries of the bed. This configuration allows the flow-domain to be considered as an infinite medium for the

solution of the dispersion model represented by eqn (1). For a pulse of tracer injection, its solution is given by:

$$C(t) = \frac{U_i}{\sqrt{4\pi D_a t}} \exp\left(-\frac{(L-U_i t)^2}{4D_a t}\right) \quad 2)$$

where, L is the distance between the tracer injection and the detection point points. From the experimental measurement of tracer concentration, C(t), the residence time distribution function, E(t), and the mean residence time, t_m , can be found as

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} \quad 3)$$

$$t_m = \int_0^{\infty} t E(t) dt \quad 4)$$

For evaluating the value of the dispersion coefficient using the real-time domain curve-fitting, the following objective function was minimized:

$$S(D_a, U_i) = \frac{1}{N} \sum_{k=1}^N (E(t_k) - C_p(t_k, D_a, U_i))^2 \quad 5)$$

where S is the average of the sum of squares of deviations per data point, N is the number of data points, C_p is the model prediction using eqn (2) and E(t) is the normalized concentration for each run at the time t. It should be noted here that besides the dispersion coefficient, the liquid interstitial velocity was also varied here. An IMSL subroutine called UMINF was used for the minimization of the objective function over D_a and U_i simultaneously by solving the normal equations

$$\left(\frac{\partial S}{\partial D_a}\right) = 0 \quad \text{and} \quad \left(\frac{\partial S}{\partial U_i}\right) = 0 \quad 6)$$

A computer program to carry out computations of the concentration normalization of the raw data as well as for the parameter estimation is discussed somewhere else [8].

It is worthwhile to point out at this stage that although moment's method for evaluating the parameters of the model appears to be much simpler than the real-time domain curve-fitting used here limitations of the former has been discussed in detail by Asif [11].

Results and discussion

Figure 1a shows the data obtained with three runs carried out for the superficial velocity U_o , of 0.25-cm/s using KCl. Note that the liquid interstitial velocity is related to the superficial velocity as $U_i = U_o / \varepsilon$. It can be seen in the figure that all the three curves show a good agreement. As expected, the meter reading of conductivity is initially constant as the ambient water passes through the tracer detection point. When the solenoid valve opens for about 500-millisecond to make a pulse injection of the salt solution at time = 0, the DAQ starts to simultaneously record the time as well the conductivity of the flowing water at the detection point. It is only after a lapse of over 120-s that the salt tracer first appears at the detection point which is reflected in the change of the conductivity of the flowing water. As the pulse of salt tracer passes through the detection point, the conductivity of the water shows corresponding change. The voltage signal ultimately decays as the salt tracer injected in the flow system is gradually washed away.

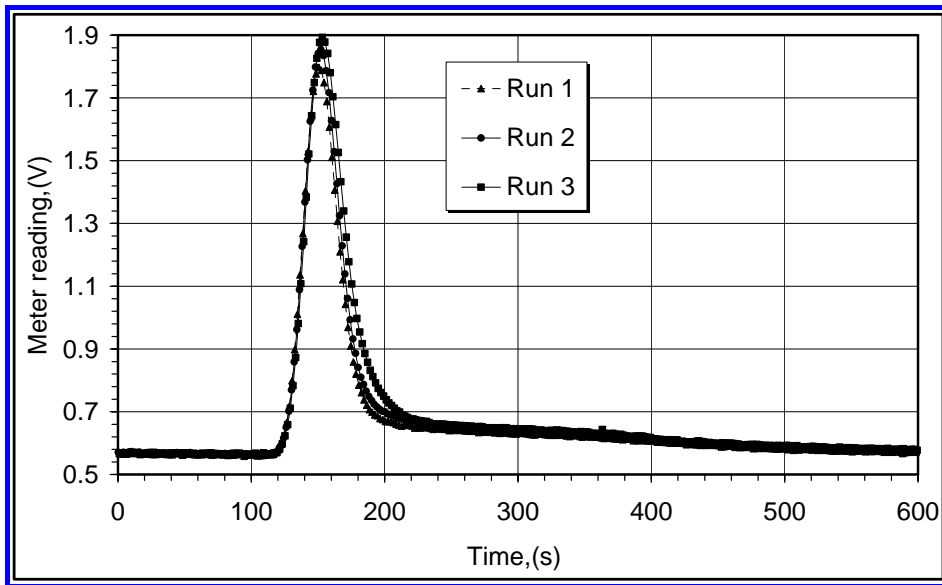


Figure 1a: Response to pulse injection for $U_o = 0.25$ -cm/s using KCl

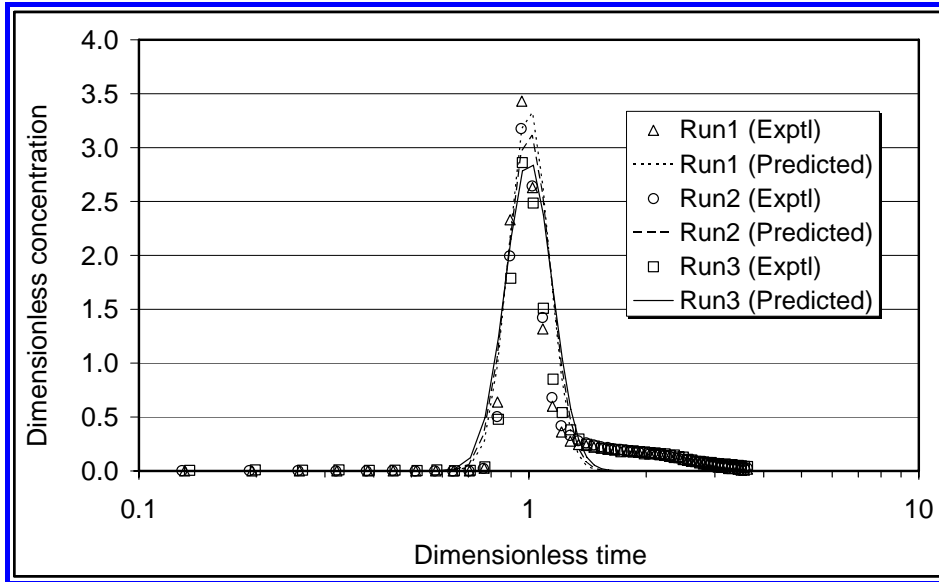


Figure 1b: Comparison of experimental data of Figure 1a with model predictions $U_o=0.25\text{-cm/s}$

As a first step in processing the data, the conductivity of the ambient water was subtracted throughout to obtain the change in the conductivity due to the variation of the concentration of the salt tracer. The concentration data is then normalized as represented by eqn (3). The normalized concentration data, thus obtained, is used for the purpose of parameter fittings as described by eqn (6). The abscissa of Figure 1b is dimensionless time. The real time here was made dimensionless by taking its ratio with (L/U_i) . For the data presented in Figure 1a, the comparison is presented in Figure 1b. It can be seen here that the comparison is satisfactory in view of the simplicity of the model presented here. The peaks are represented very well by the model notwithstanding the rather slower decay of the

Table 1: Relevant parameters for data presented in Figure 1				
Run	Liquid Interstitial velocity (cm/s)		Dispersion Coefficient (cm ² /s)	Residence Time (s)
	Actual	Predicted		
1	0.67	0.69	0.38	248.6
2	0.67	0.68	0.38	248.2
3	0.67	0.67	0.41	249.3

actual signal. Table 1 presents some relevant parameters for data presented in Figure 1. One can see that there is not much difference between the actual and the predicted interstitial velocities. Moreover, the estimated parameters for all the three runs are very consistent. The dispersion coefficient that characterizes the degree of dispersive transport in the saturated porous medium is approximately found to be in the range of 0.38 to 0.40 cm²/s. The table also presents the residence time (using eqn 4) for each of these runs.

The values of dispersion coefficients obtained for four different cases of liquid velocities considered here are presented in Figure 2. Potassium chloride is used as a tracer in these experiments. It is abundantly clear from the figure that the dispersion coefficient increases as the liquid velocity increases. This means that the dispersive transport shows a corresponding increase with the convective transport. Although the standard deviation in the estimated value of D_a also shows an increase, yet the overall trend clearly points to a significant rise in the dispersive transport in a saturated porous medium with the increase in the liquid velocity.

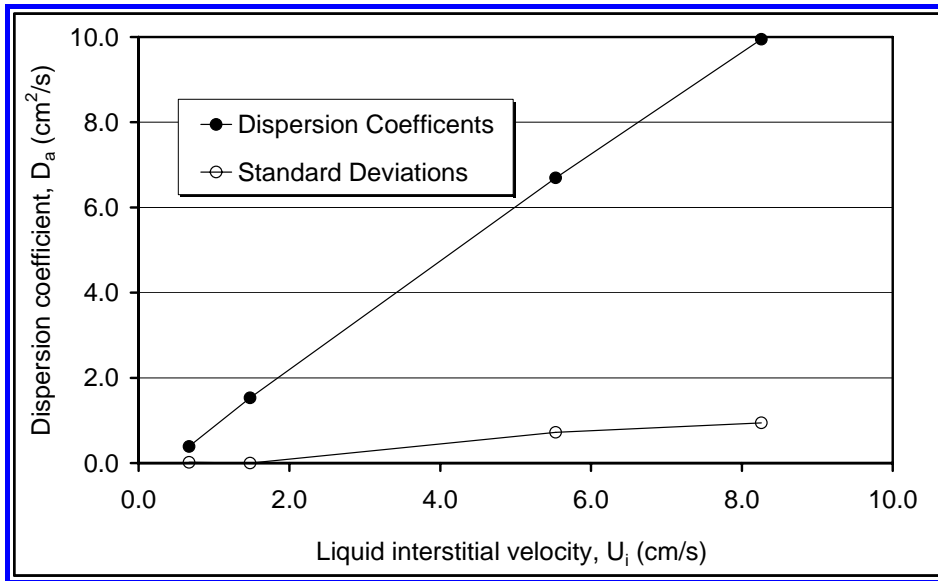


Figure 2: Estimated Dispersion coefficients and their standard deviations for KCl

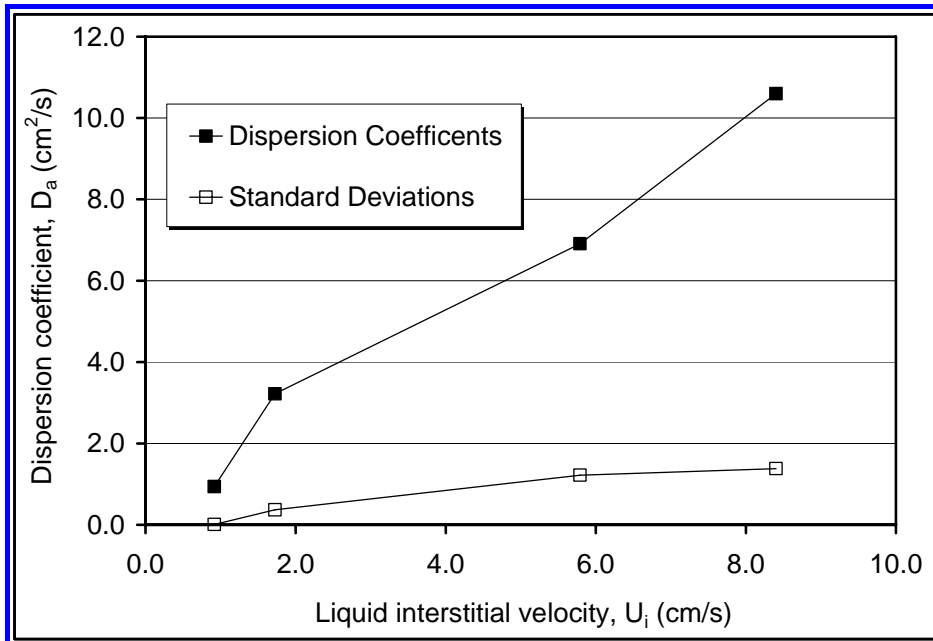


Figure 3: Estimated Dispersion coefficients and their standard deviations for MgSO_4

Figure 3 presents the case when magnesium sulfate, with a molecular diffusivity which is almost one third that of the potassium chloride, is used as the salt tracer. Results obtained in this case is similar to what was obtained using KCl in that the dispersive transport shows a corresponding increase with the convective transport of the tracer. The standard deviations obtained here also show similar trend.

The comparison of the two salts tracers are presented together in Figure 4. There appears to be some difference in two cases; marked by a little higher value of dispersion coefficient for the case of MgSO_4 at lower liquid velocities where the standard deviation is almost negligible. The difference is clearly lost at higher liquid velocities. This could be explained in terms of the two main contributions to the overall dispersive transport of the tracer. One is understandably molecular in nature, and is therefore smaller in magnitude. The second is mechanical dispersion arising due to the local non-homogeneity of the porous medium. The contribution of the mechanical dispersion to the overall dispersive transport increases with the increase in the local liquid velocity. At higher liquid velocities where the molecular contribution is insignificant as compared to the mechanical contribution, the use of salt tracer of different diffusivities does not make any difference.

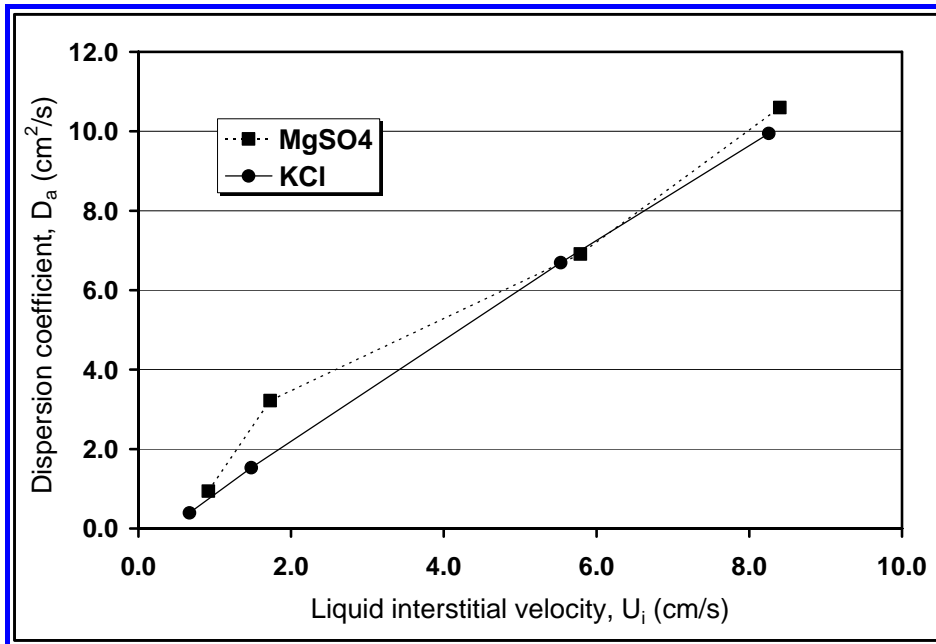


Figure 4: Comparison of dispersion coefficients for KCl and Mg SO₄

Conclusion

From results presented in the foregoing, one might be tempted to conclude that individual species in a mixture of contaminant would still transport at the same rate even if their molecular diffusivities are significantly different. It should however be kept in mind that using a non-porous packing material for the construction of the porous media in the present experimental study is gross approximation of the actual field situation. Its clear consequence is the elimination of both internal and external mass transport resistances. Both these mechanisms are clearly sensitive to the molecular diffusivity of the ant species present in the system. Therefore, the results obtained herein, which points to relatively insignificance of the molecular diffusivity should only be extended to porous packing material with caution.

Acknowledgement

The project was supported by Research Center, College of Engineering, King Saud University.

References

- Eweis, J.B., Ergas, S.J., Chang, D.P.Y. and Schroeder, E.D. 1998**, Bioremediation Principles, WCB/McGraw Hill, Singapore .
- Dosskey, M.G. and Bertsch, P.M., 1997**. “Transport of dissolved organic matter through a sandy forest soil”, *Soil Science Society of America J.* , **61**, pp. 920-927.
- Gerritse, R.G., 1996**. Dispersion of cadmium in column of saturated sandy soil”, *J. of Environmental Quality*, **25**, pp. 1344-1349.
- Vikas, S., 1997**. “Monte Carlo simulation to study contaminant transport in heterogeneous aquifer”, Proceedings of the 67th Annual Western Region Meeting June 25-June 27., Long Beach, CA, USA.
- Ishaq, A.M. and Ajward, M.H., 1995**. “Investigation of chloroform plumes in porous media”, Proceedings of the Symposium on Engineering Hydrology, San Francisco, CA, USA, Publ by ASCE, New York, NY, USA, pp. 970-976.
- Saiers, J.E. and Hornberger, G.M.; Harvey, C., 1994**, Colloidal silica transport through structured, heterogeneous porous media”, *J. of Hydrology*, **163**, pp 271-288.
- Amro, M. M., 2004**. Factors affecting chemical remediation of oil contaminated water-wetted soil”, *Chem. Eng. Technol.*, **27**.
- Asif, M. and Al-Sugair, K., 1999**. “Effect of tracer adsorption on the flow dynamics of packed bed reactors” Final Research Report No. K08/16/19, Research Center, College of Engineering, King Saud University, Riyadh, Saudi Arabia,.
- Bruins, H., 1928**. International Critical Tables, Vol. 5, McGraw Hill, New York, p.66.
- Bruins, H., 1928**. International Critical Tables, Vol. 5, McGraw Hill, New York, p.68.
- Asif, M., 2000**. Contaminant Dispersion in porous media: Method of data analysis. STCEX 1, 18 –22 November, Riyadh, Vol. 3, pp.31-37.