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Adsorption characteristics of inorganic salts and detergents on sand beds

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Abstract

Experiments were carried out to study the adsorption of two inorganic salts and a commercial detergent on sand. Adsorption isotherms were obtained from batch experiments by measuring the bulk concentration of the feed and that of the liquid after the equilibration period. Langmuir isotherm was found to predict the experimental observations accurately. Column experiments were performed to obtain the breakthrough curves for these inorganic salts and detergents. Two different modes of operation are discussed: (1) straight through mode and (2) recycle mode. The latter can be used for studying features of expensive chemicals in a cost effective manner. The experimental setup was designed so that by switching the valves, the same column can be utilized to study both modes. A convective-dispersion equation is used to describe the continuous operation and the effective dispersivity, D is estimated from the experimental breakthrough curves using an optimization technique. The optimized dispersivity, D is calculated so that the theoretical predictions match the experimental breakthrough curves. In our studies, we find that the behavior of the recycle mode is sensitive to the parameter, D. Hence, the dispersion coefficient is obtained using the recycle mode data. The results of the adsorption study described here can be used in scale up to the field level.

Keywords: Adsorption; Isotherms; Non-linear optimization; Dispersivity; Porous media

1. Introduction

Fertilizers and pesticides used in agriculture are a major source of groundwater contamination [1,2]. Most often they are applied in excess of the plant requirements. The excess amount is adsorbed in the soil and is leached to the groundwater. An understanding of the adsorption and the transport of these solutes through the porous soil matrix is hence essential to investigate the extent of groundwater contamination [3]. Similarly, domestic waste-water containing soaps and detergents can also lead to groundwater contamination if added to the soil matrix without any treatment [4]. Cost-effective remediation tools are needed to mitigate the effect on the environment of these chemicals, and identify areas which are potentially vulnerable to this source of pollution [5]. Although these studies of adsorption on a soil matrix are important for establishing the range of treatment efficiencies, there is very little information about the mechanisms involved in the remediation processes involving adsorption. An understanding of these mechanisms is necessary to design adsorption beds for removing these pollutants and predicting the long-term sustainability under different environments of water and hazardous material loadings.

Recently the use of grey water (wastewater from washing machines and bathrooms) coming out of domestic houses for artificial recharge of groundwater has been investigated [6]. This grey water primarily containing soap, detergents, nitrates and phosphates can be used for gardening. This is very alkaline (pH around 10). Usually, sand beds are used as filters to remove suspended solids. These can also adsorb the dissolved contaminants like nitrates and phosphates, which are soluble in water. Pits filled with porous sand can also be used to facilitate recharge of ground water. Plants growing on soil layers above these sand beds can adsorb these chemicals. During monsoons, adsorbed chemicals on sand can be leached out of the bed and this may pollute the ground water [7].

Information on the adsorption characteristics of the pollutants on the different types of soil is necessary to determine (i) how quickly and (ii) how much the water quality will deteriorate for a particular loading. In particular, water treatment systems based on adsorption need to be designed based on the flow rate and the residence time. These parameters determine the adsorption of solutes in the soil [8]. For a wide range of velocities and column lengths, contaminant transport has been studied extensively [9]. The adsorption characteristics also play a vital role in solute

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Nomenclature

b	Langmuir isotherm coefficient
C	concentration of the solute in the liquid phase (mol/m^3)
D	dispersion coefficient (m^2/s)
E	mean free energy of sorption (kJ/mol)
k	Freundlich adsorption coefficient
L	length of the bed (m)
m	mass of the adsorbent (g)
n	Freundlich adsorption exponent
q	concentration of the solute in the solid phase (mg/g)
$q_{\max}$	maximum sorption capacity (mg/g)
R	universal gas constant (kJ/(mol K))
t	time (s)
u	interstitial velocity (m/s)
v_0	volumetric flow rate (m^3/s)
V	volume (m^3)
z	axial distance (m)

Greek symbols

β	constant related to sorption energy (mol^2/kJ^2)
ε	Polanyi potential (kJ^2/mol^2)
ϕ	void fraction of the bed (m^3/m^3)
τ	space time (s)

transport in heterogeneous porous media. The increase in the adsorption of atrazine onto soils by the addition of detergents has been studied in [10]. They found that higher concentration of surfactants (which is present in detergents) could significantly increase the adsorption of atrazine on soils. Their results suggest that using a low concentration of non-ionic surfactant does not have any effect on the sorption of atrazine.

The transport of contaminants (dissolved solids) in porous media consists of four different processes [11]. They are advection, dispersion, adsorption and degradation. Advection refers to the transport primarily in the direction of the flow by convection. Molecular diffusion is the chief cause of spreading the pollutants in a direction orthogonal to the flow direction. In a porous medium the changes of bed porosity result in a large scale heterogeneity leading to flow non-homogeneities. The spread of contaminants due to molecular diffusion and these non-homogeneities is represented in terms of an effective dispersion coefficient [12]. Adsorption on sorbent results in the decrease in the concentration of a solute as it flows through a packed bed and degradation refers to the chemical transformation, which results in a change in the chemical nature of the pollutant.

In this paper we investigate laboratory scale experiments performed under controlled conditions to determine the adsorption characteristics of inorganic salts (chlorides and nitrates) and detergents in sand beds. Adsorption equilibrium isotherms are obtained from batch experiments. Three theoretical isotherms, viz., Langmuir, Freundlich and *D–R* isotherms are tested as possible candidates [13]. These are based on three different mechanisms. The predictions of the three models are compared with experimental data and a mechanism of adsorption is proposed. The continuous experiments are carried out in two modes: (i) the straight through mode as well as (ii) a recycle mode. The latter is a novel method proposed for studying the adsorption characteristics of expensive and toxic chemicals in a cost effective manner. The convective dispersive equation is used to determine the distribution of solute concentration in the bed as a function of space and time. Through the column experiments, the dispersivity is estimated by the optimization method. The dispersion parameter thus determined is used to predict the bed performance under various conditions. This can be used for scale up of solute adsorption from the laboratory scale to the field scale. This fundamental study will allow us to estimate (i) the time taken for the bed to get saturated and (ii) to design the bed for a particular loading rate (amount of contaminated water added per day) [14].

2. Materials preparation

Sand used for construction activities in the Indian Institute of Technology, Madras was taken without any chemical treatment. The sand particles were sieved with mechanical sieves and the fraction containing particle size less than 700 μm was used for experiments. The sieved sand was then washed with water and then decanted. After settling, the water was poured out and the sand was taken for drying. After drying at 85 °C, the sand was ready for use as the adsorbent.

The physical characteristics of sand were quantified using specific surface area, pore specific volume and pore size distribution and particle size distribution. These characteristics were determined by the nitrogen adsorption isotherm (BET analysis) using Sorptomatic 1990 Carlo Erba at 77 K. The specific surface area was found to be 2.315 m^2/g and the average pore diameter to be 30 Å. The pore size distribution is found to be between 7 and 50 Å. The pore specific volume is found to be 0.029 cm^3/g. The particle size distribution was carried out using sieve analysis and it was found that about 61.2% of the particles were in the range of 600–700 μm, 32.3% of the particles were in the range of 425–600 μm, 3.4% of the particles in the range of 355–425 μm and the rest of the particles were in the range of 212–355 μm.

Photomicrography of the sand surface was obtained by SEM (FEI, The Netherlands). Besides the distribution of elemental compositions for the solid sample was analysed using SEM/EDAX (EDAX Inc., USA). Samples for EDAX analysis were coated with thin carbon film in order to avoid the influence of charge effect during the SEM operation. EDAX spectrum showed the presence of silicon and oxygen only (Fig. 1). This rules out the possibility of any coatings on the sand particles.

3. Reagents

3.1. Preparation of solutions

Feed solution of nitrate is prepared by dissolving 1.645 g of anhydrous potassium nitrate (Central Drug House, Mumbai) in 1 l of distilled water. This corresponds to a concentration of

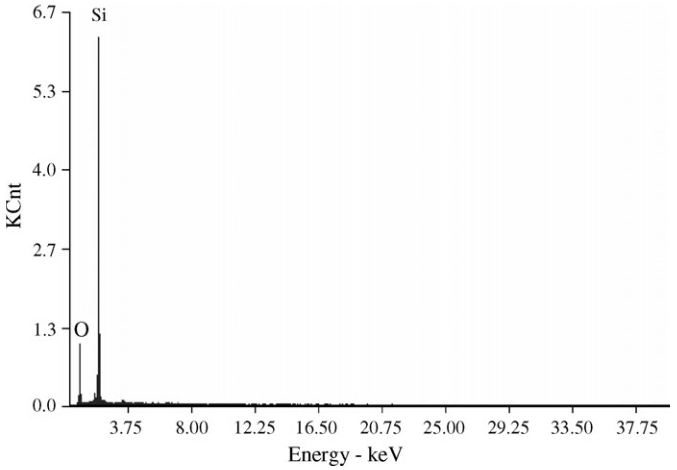

Fig. 1. EDAX spectrum for sand.

1000 mg/l of nitrate solution. The concentration of nitrate in the samples was measured using a UV–vis spectrophotometer (Jasco V-530) at 220 nm. The instrument was calibrated for the range of 0–4000 mg/l of nitrate solution. Similarly, the chloride solution is prepared in the concentration range of 0–4000 mg/l using sodium chloride (Merck, Mumbai). The concentration of this solution is measured using a conductivity meter (Model: EE-9042, Elixir Electronics). The detergent used in our study is Ariel from Hindustan Lever Limited. The molecular weight of the detergent is 288. This has a composition of 30% sodium salt of benzene sulphonic acid, 30% of sodium carbonate and 20% sodium carbonate peroxide. The rest being citric acid and alcohol ethoxylates. The amount of anionic surfactant present in the detergent is obtained after eliminating the interference effect using a UV–vis spectrophotometer at 652 nm. The detergent forms a blue coloured salt when methylene blue (Merck, Mumbai) reacts with the anionic surfactant. The intensity of the blue colour obtained from the interference measurement is proportional to the concentration of the surfactant. The detergent concentration is prepared in the range of 0–4000 mg/l. The range of concentrations studied in this work is typical of that present in wastewater. Wastewater streams in general contain a mixture of compounds at these concentration levels. Here, we consider the pollution to arise from a single compound and carry out the study.

3.2. Batch experiments

Adsorption isotherms relate the adsorbate or solute concentration in the bulk liquid and the solid adsorbent on the solid surface at equilibrium. These isotherms are used in design of the adsorption bed and in determining the transport of solute through a packed bed. These isotherms were obtained from experiments carried out in batch mode.

Preliminary sorption experiments were performed at room temperature (28 ± 2 °C) to determine the contact time in batch mode required to attain equilibrium. About 75 min was found to be sufficient to achieve equilibrium. The equilibrium isotherms were obtained by measuring concentration of the nitrate solution in the feed and that of the solution at equilibrium after shaking using a mechanical shaker. The nitrate concentration in the adsorbent is measured using a conductivity meter as well as a UV–vis spectrophotometer. A similar procedure was adopted for the chloride and detergent adsorption experiments.

Adsorption experiments were carried out at room temperature at different initial concentrations of nitrate solution. Conical flasks sealed with Teflon lined caps are used for the experiments. Solutions of different initial concentrations, 500, 1000, 1500, 2000, 2500, 3000 and 3500 mg/l of solution were prepared. One hundred milliliter of this solution was taken in each conical flask. The pH for nitrate solution was about 7.2. About 5 g of sand (adsorbent) was added in each flask. All the flasks were shaken using a mechanical shaker and the system was allowed to equilibrate for about 75 min. After equilibration, the samples were filtered using a 2 μm filter paper. The filtrates were then analysed using the UV–vis spectrophotometer. The amount of salt in the liquid after equilibrium was measured and ‘q’, the nitrate concentration in the adsorbent (mmol/g) was obtained by the following relation:

$$q = \frac{C_\mathrm{i} V_\mathrm{i} - C_\mathrm{f} V_\mathrm{f}}{m} \tag{1}$$

where ‘m’ is the mass of sand adsorbent (g), C_i and C_f the initial and final concentration of the nitrate solution (mmol/l), V_i (ml) and V_f (ml) are the liquid volume present in the flask at initial and final times, respectively. The experimental data is then used to obtain insight into the mechanism of adsorption. We depict in Table 1 the pH, initial and final concentration obtained for various salts from our batch experiments. We now discuss the basic mechanism of three classical forms of isotherms used in adsorption studies. Each form corresponds to a unique adsorption mechanism.

Table 1
Summary of data obtained by batch experiments

Compound and sample number	pH	Initial concentration (mmol/l)	Final concentration (mmol/l)
Nitrate			
1	7.0	8.06	7.45
2	7.1	16.12	14.81
3	7.2	24.19	22.61
4	7.3	32.25	29.81
5	7.4	40.32	37.4
6	7.4	48.38	44.91
7	7.4	56.45	52.20
Chloride			
1	6.7	42.25	9.87
2	6.8	56.33	14.76
3	6.9	70.42	21.59
4	6.9	84.50	23.28
5	7.0	98.59	26.56
Detergent			
1	10.4	6.94	3.77
2	10.4	8.68	5.06
3	10.5	10.42	5.97
4	10.5	12.15	6.91

3.3. Langmuir isotherm

Langmuir isotherm can be used to characterize solute adsorption as a monolayer. This model assumes that adsorption occurs at specific homogeneous sites within the adsorbent and intermolecular forces decrease rapidly with distance from the adsorption surface. It is further based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent. This adsorption isotherm assumes limited sorption sites. The Langmuir equation is represented by:

$$\frac{q}{q_{\max}} = \frac{bC}{1+bC} \tag{2a}$$

where 'C' is the equilibrium adsorbate concentration (mmol/l), q the mass of adsorbate per unit mass of adsorbent at equilibrium (mmol/g), $q_{\max}$ the maximum amount adsorbed at saturation conditions per unit mass of adsorbent (mmol/g), and 'b' is the empirical constant which has the unit of inverse of concentration (l/mmol). The Langmuir equation can also be rewritten as:

$$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{bq_{\max}C} \tag{2b}$$

A plot of $1/q$ versus $1/C$ for a system following the Langmuir isotherm should yield a straight line and the values of '$q_{\max}$' and b can be calculated from the intercept and slope of the plots, respectively. Fig. 2 shows the relation $1/q$ versus $1/C$ obtained using different initial concentrations, C_{f} of nitrate solution. It can be seen that a straight line passes through the points with a good fit ($R^2 = 0.9928$).

3.4. Freundlich isotherm

Freundlich equation is used to represent multilayer adsorption and is applicable for adsorption on heterogeneous surfaces. The Freundlich model is formulated as:

$$q^* = kC^{1/n} \tag{3a}$$

where q^* is the equilibrium solute concentration on adsorbent (mg/g), and C is the equilibrium concentration of the solute (mmol/l). Here, k is the Freundlich constant (mmol/g) which indicates the adsorption capacity of the adsorbent while 'n' represents the heterogeneity factor. A linear form of the Freundlich equation can be obtained by taking logarithm of the Eq. (3a):

$$\log q^* = \log k + \frac{1}{n}\log C \tag{3b}$$

Here, a plot $\log q^*$ versus $\log C$ yields a straight line with a slope of $1/n$ and intercept of $\log k$.

3.5. *D–R* isotherm

Information on sorption mechanism can also be obtained by using a *D–R* isotherm [15]. This describes adsorption on a single type of uniform pores. The *D–R* isotherm is similar to the Langmuir model but it does not assume a homogeneous surface or constant energy potential. The *D–R* isotherm is represented as:

$$q = q_{\max}\exp(-\beta\varepsilon^2) \tag{4a}$$

where q is the amount of solute adsorbed per unit weight of adsorbent (mmol/g), $q_{\max}$ the maximum adsorption capacity (mmol/g), β the constant related to sorption energy (mol^2/kJ^2), and ε is the Polanyi potential given by $RT\ln(1+1/C)$ where R is the universal gas constant (kJ/(mol K)), T the temperature (K), and C is the equilibrium concentration in bulk solution (mol/l).

Eq. (4a) can be written in the linear form by taking logarithm on both sides yielding the form as:

$$\ln q = \ln q_{\max} - \beta\varepsilon^2 \tag{4b}$$

Experimental data obtained from the studies of different initial concentrations of the adsorption of nitrates, chlorides and detergents on sand were evaluated using the above equation. Fig. 3 shows the best fit *D–R* isotherm predictions as well as experimental data for nitrate, chloride and detergent solutions. A plot of $\ln q$ versus ε^2 yields a straight line with a slope of "$-\beta$."

The data from batch experiments were fitted to the three different isotherms proposed. The best fit parameters were found for each model and the corresponding R^2 is reported in Table 2. On comparing the R^2-values, it can be seen that the Langmuir

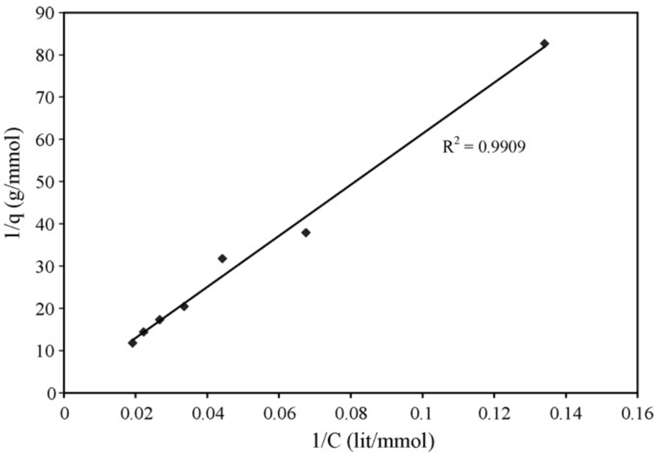

Fig. 2. Best fit Langmuir isotherm for nitrate solution and experimental data.

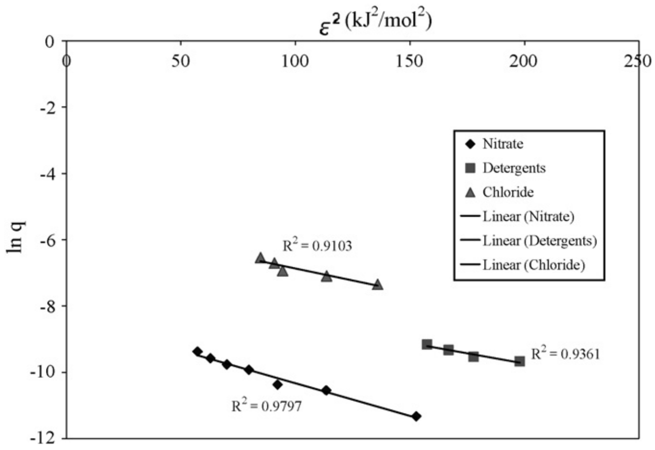

Fig. 3. Best fit *D–R* isotherm for three different salts.

Table 2
Best fit parameters obtained from fitting Langmuir, Freundlich and *D–R* isotherm to batch data

Ions	Langmuir isotherm			Freundlich isotherm			*D–R* isotherm			
	b (l/mmol)	$q_{\max}$ (mmol/g)	R^2	k (mmol/g)	n	R^2	$q_{\max}$ (mmol/g)	β (mol^2/kJ^2)	E (kJ/mol)	R^2
Nitrate	0.0015	1.109	0.99	0.0017	1.03	0.98	0.25	0.0198	5.02	0.98
Chloride	0.026	3.093	0.94	0.110	1.33	0.92	0.08	0.0144	5.79	0.91
Detergent	0.055	0.363	0.94	0.020	1.21	0.94	0.70	0.0124	6.35	0.94

isotherm predicts the experimental data very well for all the solutes. Table 2 also reports the parameters 'β' for different salts. The mean free energy of sorption (E) was calculated from β as:

$$E = (-2\beta)^{-0.5} \tag{4c}$$

This mean free energy for the three different salts is reported in Table 1. It can be seen that the values of E are lower than 8 kJ/mol, which indicates that the adsorption is primarily physical in nature.

In the rest of this work, the Langmuir isotherm is used to describe the relation between q and C as this predicts the behavior of batch experiments accurately. The value of b and $q_{\max}$ depicted in Table 2 for the various salts is used in simulating the behavior of the column experiments.

3.6. Column experiments

We now discuss the column experiments, which were performed to obtain the breakthrough curves and to estimate the dispersion coefficient in the soil bed.

3.7. Experimental design

The experimental bed has two sections: (1) an adsorption section where the sand is packed and (2) a distributor section upstream of adsorption section. The experimental setup is as shown in Fig. 4. The adsorption and distributor sections are made of a Plexiglass column. The length of the adsorption section is 30 cm. It has an inner diameter of 9 cm and a wall thickness of 0.6 cm. The distributor section has a length of 15 cm. The inner diameter and thickness of this are the same as that of the adsorption section. The adsorption section is placed above the distributor section. A perforated Plexiglass plate with 2 mm diameter holes drilled at regular intervals is placed at the junction of the adsorption section and the distributor section. The perforations are arranged along a square grid and the distance between two adjacent holes is 0.5 cm. The diameter of the perforated plate is the same as that of the Plexiglass tube. This arrangement could support the sand bed. A nylon cloth is pasted on either side of the perforated plate to prevent the ingress of soil.

The feed solution is pumped through the distributor section vertically upwards using a peristaltic pump (Model: VSP-400, Miclins India). The pump is calibrated for various speeds by measuring the volumetric flow rate of the feed solution. Uniform distribution of flow in the bed is ensured by pumping the fluid upwards. Moreover, the upflow configuration is preferred since it ensures that the bed is completely saturated with minimal bypassing and channeling [16]. The distributor section in the setup serves to reduce the pulsations of the peristaltic pump. The inlet to the distributor section is through a 1.2 cm diameter hole at the centre of the bottom plate of the distributor section. Similarly, the outlet is through a 1.2 cm diameter hole at the centre of the top plate of the adsorption section. A Plexiglass tube of 1.2 cm inner diameter and a length of about 2 cm is used as an inlet port and a flexible pipe is used to connect the pump to the feed tank. A similar arrangement is used to withdraw the fluid from the bed through the top. There is a drastic decrease in the cross-section across the exit port. Convective transport dominates diffusive transport in the exit tubes and we can hence neglect dispersion effects in the downstream of the bed.

Two different modes of operation were studied using the same column. They are: (1) straight through mode and (2) recycle mode. In the straight through mode, the feed solution is pumped from the feed tank to the adsorption section and the effluent from the top of the adsorption section is collected in another vessel. In the recycle mode, the effluent from the bed is recycled back to the feed tank. Valves V_1 and V_2 shown in Fig. 4 are used to operate the bed either in the straight through or in the recycle mode. When the bed is operated in the straight through mode, valve V_2 is closed and V_1 is open while in the recycle mode V_2 is opened and V_1 is closed. In the straight through mode, the conductivity of the effluent stream is measured online at a point A (Fig. 4), on the effluent line. In the case of recycle mode, the concentration of the treated solution is measured in the feed tank by directly immersing the conductivity probe in it. The concentration of the total dissolved solids is measured using a conductivity meter. The conductivity meter is connected to the computer for continuous data acquisition and the output voltage is measured. The conductivity meter is calibrated for different concentrations of the various salt solutions (nitrate, detergent and sodium chloride solutions) by measuring their respective output voltages.

3.8. Experimental procedure

The adsorption section is filled with sand as adsorbent. The porosity of the bed is obtained as 0.39 by volume displacement method. The sand is filled by wet-filling process to prevent any formation of channels in the porous media. Experiments were carried out for the two different modes discussed above. The effluent concentrations are measured online using the conductivity meter. Each experiment was repeated twice for reproducibility.

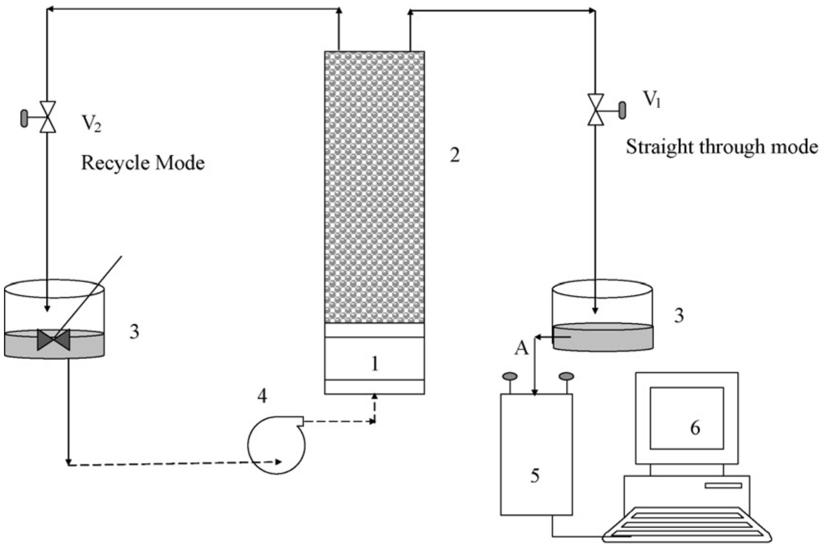

Fig. 4. Experimental setup of straight through and recycle mode-continuous operation. (1) Distributor section, (2) test section, (3) feed tank, (4) peristaltic pump, (5) conductivity meter and (6) computer. Valves V_1 and V_2 are used for controlling the mode of operation. A is sampling port for straight through mode.

3.9. Straight through mode

The sand bed is initially filled and saturated with distilled water before the experiments were started. The feed solution is pumped from the well-mixed feed tank to the distributor section at a constant flow rate by using the peristaltic pump. The flow is uniformly distributed throughout the adsorption section and moves vertically upwards against gravity inside the bed. The contaminants get adsorbed in the bed and the effluent concentration is measured by the conductivity meter in the sampling port A (see Fig. 4) on the outlet stream of the adsorption section. After the bed gets saturated, breakthrough occurs in the bed when the effluent concentration reaches a constant value equal to the feed concentration. The saturated bed is cleaned using five pore volumes of distilled water for the next set of experiments. Preliminary experiments were performed and it was found that five pore volumes were sufficient to completely remove all adsorbed solute. This ensured that the bed is free of solute at the beginning of every experiment.

3.10. Recycle mode

In this mode, the feed solution is pumped from the feed tank at a constant flow rate using the peristaltic pump through the distributor section. The contaminants are adsorbed in the column and the effluent stream from the top of the column is recycled to the feed tank. The feed tank is well mixed tank with constant stirring. The concentration in the feed tank is measured using the conductivity meter. The conductivity of the solution in the tank drops due to the recycle of the effluent concentration. Subsequently, the bed becomes saturated leading to a constant concentration in the feed tank. Fig. 5 shows the variation of concentration in the feed tank with respect to time for the nitrate solution in the recycle mode. It can be seen that the concentration in the feed tank decreases and reaches a plateau once the bed gets saturated. The saturated bed is cleaned using five pore volumes of distilled water before the next set of experiments was conducted.

3.11. Modeling and simulation

The transport of non-reactive solutes during unsteady one-dimensional saturated flow can be written as [17]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} - \rho\frac{1-\phi}{\phi}\frac{\partial q}{\partial t} \tag{5}$$

where C is the effluent solute concentration (mol/m^3), D the dispersion coefficient (m^2/s), u the interstitial velocity (m/s), q the amount of solute per unit weight of adsorbent (mol/g), z the spatial distance (m), t the time (s), ρ the bulk density of the adsorbent (g/m^3), and ϕ is the porosity of the bed. This equation describes the variation of the concentration with space and time in saturated beds, where the interparticle space is completely occupied by the solvent.

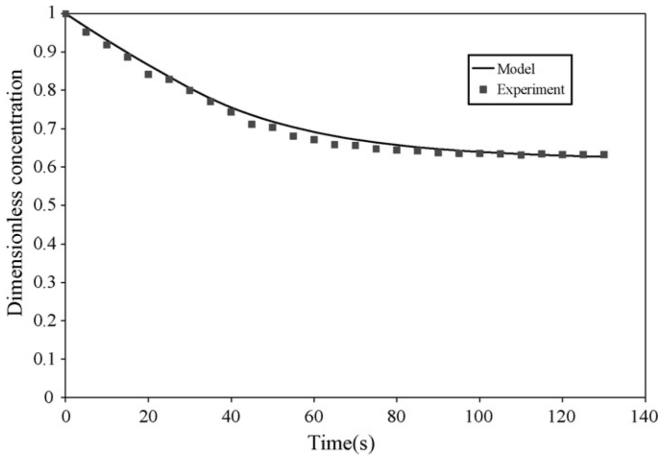

Fig. 5. Comparison of optimal model prediction and experimental data for recycle mode for 2000 mg/l nitrate solution.

The initial and boundary conditions for the two different modes are:

- Initial conditions:

  $$C = 0 \quad \text{at } t = 0 \text{ for all } z$$

  The bed is assumed to be free of solute since the bed is washed with five pore volumes of distilled water at the beginning of every experiment.
- Boundary conditions:
  - Straight through mode:

    At the bottom or inlet, $z = 0$, we use:

    $$uC_{\text{feed}} = -D\frac{\partial C}{\partial z} + uC \tag{6}$$

    This is called the closed Danckwerts boundary condition [18]. Here, we neglect the dispersion in the distributor section just upstream of the test section. Here C_{feed} is the concentration of the solution entering the bed and for the straight through operation, this is a constant equal to the concentration in the feed tank. The transport inside the bed is due to dispersion as well as convection and this reflects on the right side of the equation.

    At $z = L$ (top), the closed Danckwerts boundary condition is used again where we neglect dispersion in the exit pipe. This yields:

    $$uC(L^+) = uC(L^-) - D\frac{\partial C(L^-)}{\partial z} \tag{7a}$$

    where L^+ indicates a position outside the column after the exit while L^- indicates the point inside the column.

    Imposing continuity of concentration at the exit of the bed, we obtain:

    $$D\frac{\partial C(L^-)}{\partial z} = 0 \tag{7b}$$

  - Recycle mode:

    At the bottom, $z = 0$, we have:

    $$uC_{\text{tank}} = -D\frac{\partial C}{\partial z} + uC \tag{8}$$

    For the recycle process, C_{tank} is the concentration in the mixing tank, which changes with time. In this mode the feed to the bed comes from the feed tank where the concentration varies with time due to recycle of effluent. The concentration in the feed tank is denoted as C_{tank}.

    The concentration in the feed tank, which is assumed to be well mixed is described by:

    $$V\frac{dC_{\text{tank}}}{dt} = v_0[C(L) - C_{\text{tank}}] \tag{9}$$

    where v_0 is the volumetric flow rate as set by the pump.

At the top, the boundary condition used is same as that given in the straight through mode (7b).

The partial differential equation is solved using the method of lines. The concentration in the bed is discretized in the spatial direction and the evolution of the concentration with time in each node is modeled through ordinary differential equations.

Eq. (5) can be used to obtain the concentration profiles in time and space for a given value of dispersion coefficient. We can estimate the dispersion coefficient, D by comparing the model predictions with the experimental data.

Eq. (5) has two dependent variables, C and q. Hence, one more relationship is required to formally solve the problem. The relation between C and q given by the adsorption equilibrium isotherm is used. The isotherm data obtained from the batch experiments was used to describe the last term in Eq. (5). The parameters occurring in the governing equations can be classified into two groups: (i) those which can be measured independently as velocity, porosity, feed concentration and (ii) those which have to be estimated like D, dispersion coefficient. The former are used as fixed parameters in simulations. The latter are specific to the system being investigated and are estimated by comparing the predictions of the model with the experimental data.

The system of equations is solved using the boundary and initial conditions discussed earlier. The concentration evolution with time was obtained using a variable step-size Runge–Kutta algorithm in MATLAB. A grid independence study was performed by increasing the number of grids. It was found that the numerical results did not vary significantly when the number of grids was increased beyond 101. The dispersion parameter is obtained by minimizing the error between the experimental data and the theoretical prediction of the model. The non-linear least squares optimization routine in MATLAB 'lsqnonlin' is used to determine the optimum value of the parameter in this problem. The objective function which was minimized is:

$$J = \int_0^{t_f} (C^{\text{experiment}} - C^{\text{model}})^2 \, dt \tag{10}$$

where $C^{\text{experiment}}$ is the concentration obtained from experiments while C^{model} is the concentration obtained from the convective-dispersive model for a given dispersion coefficient. Clearly, J depends on the choice of D and we find D, which minimizes J using a non-linear least squares regression.

4. Results and discussion

In the recycle mode, the column experiment was started with 2000 mg/l of nitrate solution in the feed tank with a velocity of 0.0014 m/s corresponding to a flow rate of 2.33 l/h. The dimensionless concentration (defined as effluent concentration divided by the initial tank concentration) in the tank is plotted against time. Experimental data was obtained at regular intervals and is shown as filled squares in Fig. 5. It took 160 s to obtain saturation in the bed. The optimization procedure described above was applied to this experimental data. This determines the dispersivity for which the model prediction matches the experimental data. Excellent agreement between the experiment and model occurs for dispersion coefficient of 1.2×10^{-6} m^2/s. The best

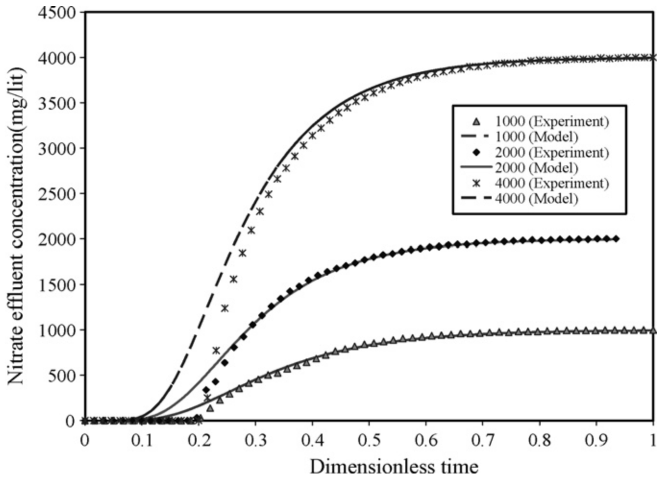

Fig. 6. Comparison of experimental data and simulation results predicted for the optimized dispersion coefficient, *D* for straight through mode for nitrate solution. The feed concentrations are in mg/l.

fit model prediction is depicted as a solid line in Fig. 5. The dispersion coefficient so obtained is of the same order of magnitude as that reported in the literature for adsorption of nitrates in sand [19,20]. For straight through mode, simulations were performed for an initial feed concentration of 2000 mg/l using the dispersion coefficient obtained from the recycle mode. Fig. 6 shows the model predictions (solid lines) on using the optimal dispersion coefficient obtained from the recycle mode for different feed concentrations. Here, we also depict the experimental data for different feed concentrations. In the straight through mode, the velocity is maintained the same as that in the recycle mode. It can be seen from Fig. 6 that there is a good agreement between the model predictions and experimental data. The optimal dispersion parameter predicts the performance of the bed very accurately even when the feed concentration is varied. It may be mentioned that there is an excellent agreement between the experimental data and model predictions for other feed concentrations, viz., 1000 and 4000 mg/l when we use the optimal dispersion coefficient calculated from the recycle mode for an initial tank concentration of 2000 mg/l.

4.1. Sodium chloride (NaCl) solution

The same approach as discussed earlier is used to estimate the dispersion coefficient for sodium chloride solution in the packed bed. When a 2000 mg/l NaCl solution is used as an initial concentration in the tank for the recycle mode experiments, the bed gets saturated in 100 s. The superficial velocity in this case is 0.0014 m/s and the corresponding flow rate is 2.33 l/h. The optimized dispersion coefficient parameter, *D* was evaluated to be 3.0×10^{-5} m^2/s by minimizing the results between the experimental data and the model predictions for NaCl solution of 2000 mg/l feed concentration in the recycle mode of operation. Fig. 7 shows the comparison of the experimental data points (filled squares) and model prediction for the optimized *D*. The experimental values and model predictions are very close to each other. Simulations were also done for 1000, 2000 and 4000 mg/l feed concentration in straight through mode using the optimized '*D*'. The experimental data and simulation prediction results agree well for the feed concentrations of 1000, 2000 and 4000 mg/l as depicted in Fig. 8.

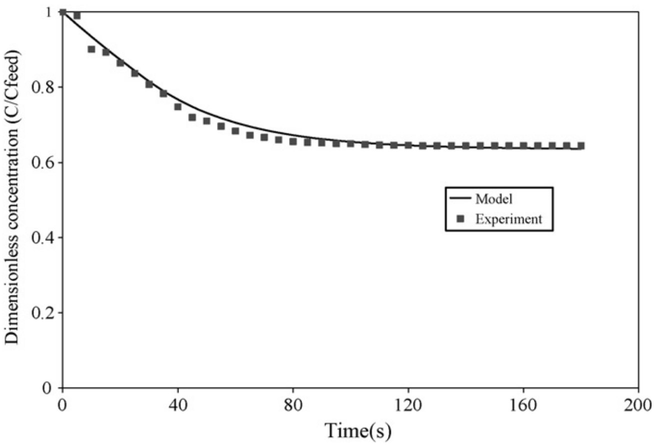

Fig. 7. Comparison of optimal model prediction and experimental data for recycle mode for 2000 mg/l chloride solution.

4.2. Detergent solution

Experiments were conducted in recycle mode with a 2000 mg/l of detergent solution in the feed tank. The superficial velocity during the recycle mode was 0.0009 m/s corresponding to a flow rate of 1.5 l/h. The corresponding experimental data is shown as filled squares in Fig. 9. It can be seen that when a concentration of 2000 mg/l of detergent solution is used as an initial concentration in the tank in the recycle mode, the bed gets saturated after 180 s of operation as shown in Fig. 9. Optimization is performed to determine the dispersion coefficient, *D* by comparing the experimental data with the model predictions. For a dispersion coefficient of 4.012×10^{-5}, the model predictions are in very close agreement with the experimental results. Simulations are performed using the optimized dispersion coefficient for straight through mode for various feed concentrations (2000

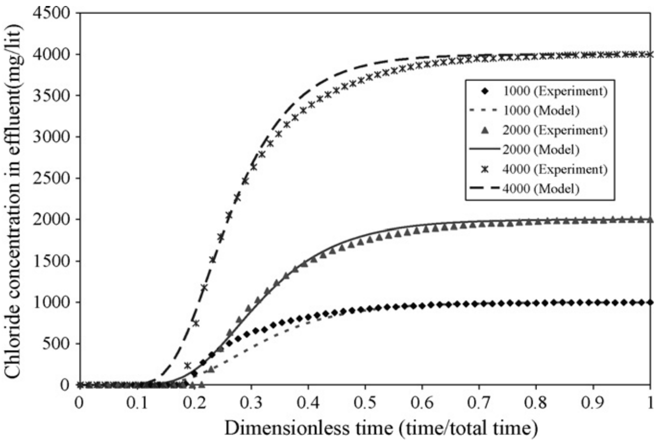

Fig. 8. Comparison of experimental data and simulation results predicted for the optimized dispersion coefficient, *D* for straight through mode for chloride solution. The feed concentrations are in mg/l.

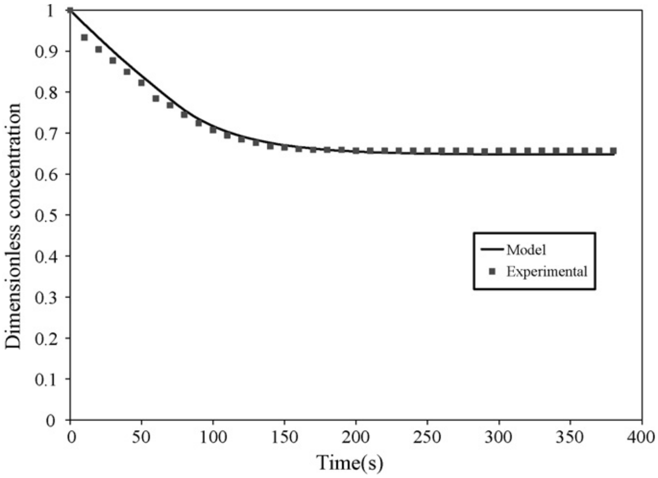

Fig. 9. Comparison of optimal model prediction and experimental data for recycle mode for 2000 mg/l detergent solution.

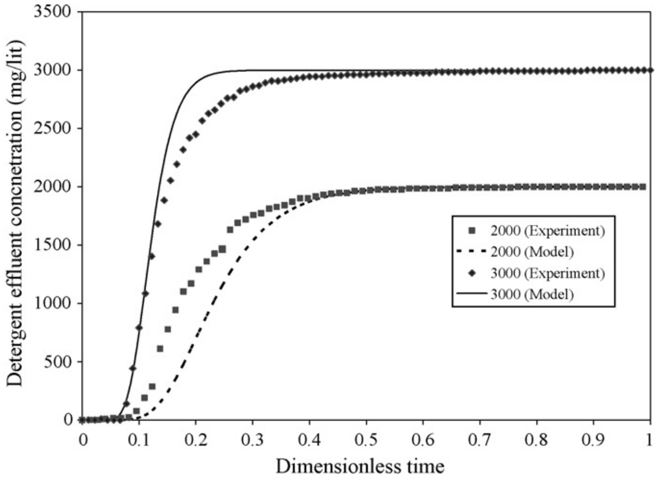

Fig. 10. Comparison of experimental data and simulation results predicted for the optimized dispersion coefficient, D for straight through mode for detergent solution. The feed concentrations are in mg/l.

and 3000 mg/l). Fig. 10 shows the simulation results for two different feed concentrations of detergent solutions in straight through mode. It can be seen that the simulations predict the experimental results closely when using the optimized dispersion coefficient, D.

5. Conclusions

In this work we have determined the adsorption isotherms for various solutes on sand and their dispersion coefficients in packed sand beds. The isotherm parameters were obtained from batch experiments and the dispersion coefficients from continuous experiments. This approach ensured that the parameters have a physical basis and the parameter estimation was not just a mathematical exercise in curve fitting.

Batch experiments were conducted to study the equilibrium parameters for three different solutes, viz., nitrate, chloride and detergent. Three different isotherms were used for predicting experimental data, i.e., Langmuir, Freundlich and *D–R*. Langmuir isotherm was found to predict experimental data accurately indicating monolayer coverage of salts on the sorbent. Physical sorption was found as the main mechanism for all the three inorganic salts. This was confirmed by using the *D–R* isotherm where the value of energy of adsorption, E obtained is less than 8 kJ/mol. Adsorption capacities on sand is highest for chloride among the three solutes studied.

Column experiments were conducted to characterize the breakthrough curves. The adsorption experiments were performed in two different modes, viz., straight through mode and recycle mode. The convection dispersion equation was used to determine the performance of the bed. The adsorption isotherms from batch experiments were used for this purpose. Using the optimization routines, the dispersion coefficient was obtained such that the behavior predicted by the model for various salt solutions was in close agreement with the experimental observations. From the dispersion coefficients estimated, it can be seen that the nitrate solution moves through the column as plug flow while chloride and detergent exhibit a more dispersive behavior. The Peclet number (Pe), a measure of the ratio of the convective to the dispersive transport was measured for nitrate, chloride and detergent as 900, 36 and 17, respectively. The Peclet number defined as (uL/D) represents how close the flow in the bed is to plug flow. A high value of D results in low Pe and here the effect of axial dispersion is significant. A low value of D results in a high Pe and here the effect of axial dispersion can be neglected as in the case of nitrate. Thus, the dispersion coefficient gives us insight into the mode of transport in the bed. The dispersion coefficient obtained from one set of experiments for a fixed feed concentration could predict the bed performance for other feed concentrations accurately.

The recycle mode adopted here can be used to study the adsorption characteristics of expensive and toxic chemicals. Here, the isotherms and breakthrough curves can be determined using smaller amounts of chemicals. The advantage of the recycle mode of operation also lies in the fact that the bed behavior in this mode is sensitive to the adsorption parameters as compared to the straight through mode. The recycle mode can hence be used for dispersion coefficient determination accurately. The parameters of the adsorption isotherm and dispersion coefficient determined in this study can be used for scale-up from the laboratory scale to field scale.

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