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Adsorption characteristics on sand and brick beds

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ABSTRACT

Adsorption can be used to treat wastewater containing low levels of pollutants efficiently. In this work adsorption isotherms are first obtained for phosphates, nitrates, chlorides and detergents from batch experiments. The motivation for the choice of these solutes stems from the fact that they are present in grey water i.e., domestic wastewater. The sorbents used are sand, brick and a 1:1 mixture (by weight) of sand and brick. Langmuir isotherm was found to best fit the equilibrium data. Experiments were also carried out in fixed beds using the above material as adsorbent for the different solutes. The Langmuir isotherm obtained from batch experiments was confirmed using the continuous experiments.

For each salt, four different feed concentrations were used for continuous experiments. Breakthrough curves were obtained by measurement of concentrations continuously at the exit using an on-line conductivity meter. A theoretical one-dimensional dynamic model (convection-dispersion equation) is used to understand the adsorption behavior in the fixed bed. The dispersion coefficient was obtained by minimizing the error between the experimental values and the predictions of the model using the method of least squares. This error was treated as an objective function and minimized for a set of operating conditions. The same dispersion coefficient was able to predict the breakthrough curves accurately for different operating conditions i.e., inlet concentrations.

1. Introduction

Grey water is defined as wastewater produced in bathtubs, showers, wash basins, laundry machines and kitchen sinks. The concentration of pollutant levels is low in grey water. The primary contaminants present in grey water are surfactants, nitrates, chlorides, phosphates, and sulphates. Grey water can hence be viewed as a valuable resource of nutrients and it can be used for horticultural and agricultural applications. Usually the water is passed through sand filters or packed beds with sorbent material where the various soluble contaminants are adsorbed. To facilitate recharge of ground water plants are grown on a soil bed resting on a highly permeable sand/brick bed, which facilitates the treated water to percolate down. During monsoons, the chemicals adsorbed on sand beds can be leached out and may eventually pollute the ground water [1]. Information on the adsorption characteristics of the pollutants in the different layers of soil is necessary to design such treatment systems. In particular, the adsorption beds for grey water need to be designed based on the flow rate of water so that we allow sufficient residence time for plant roots to adsorb solutes [2]. For a wide range of velocities and column lengths, contaminant transport in sand beds has been studied extensively [3]. Adsorption of various salts on soil beds has been extensively investigated. Iodate adsorption by 20 different types of soil from China was analyzed experimentally. This study revealed that iodate adsorption was strongly correlated with soil organic matter (free iron oxide contents) negatively (positively) [4].

The adsorption characteristic of a particular solute in a porous media is affected by presence of other solutes. For example, it was found that the adsorption of atrazine onto soils can be increased by the addition of detergents [5]. Laboratory batch experiments were carried out to study the adsorption of arsenate on 16 Chinese soils with different physiochemical properties [6]. Adsorption isotherms of the dyes calculated from breakthrough curves showed good agreement with those of batch studies [7]. The Langmuir and Freundlich adsorption isotherm equations were used to model caesium sorption in the soils [8]. Statistical analysis, accounting for differences in the number of fitting parameters, demonstrates that the dual Langmuir equation is in general superior or preferable to other isotherm equations [9]. Adsorption/desorption behavior of selenium was investigated in laboratory studies for surface soil samples varying in physico-chemical characteristics and mineralogical composition [10]. Adsorption was found to increase with the fineness and organic carbon content of soil [11]. Adsorption of iron, manganese and chromium onto a soil sample was studied as a function of reaction time, pH and metal concentration [12].

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Nomenclature

b	Langmuir isotherm coefficient (L/g)
C	concentration of the solute in the liquid phase (g/L)
D	diffusivity of the particle (m^2/s)
L	length of the bed (m)
q	concentration of the solute in the solid phase (mg/g)
q_s	maximum sorption capacity (mg/g)
t	time (s)
u	superficial velocity (m/s)
v_0	volumetric flow rate through the bed (m^3/s)
V	volume of the bed (m^3)
z	axial distance (m)
Greek letters	
ε	void fraction of the bed (m^3/m^3)
τ	space time (s)

Hamdaouri [13] has recently studied the adsorption characteristics of methylene blue using cedar saw dust and crushed brick, to determine if they are cost effective replacements for activated charcoal. Adsorption kinetics and isotherms were determined and cedar saw dust was shown to have better adsorption capacity than brick. In a later study [14] experiments were conducted in a fixed bed of cedar saw dust and crushed brick. The experimental data were compared with predictions of several models. Brick powder has also been used as an adsorbent in batch mode in defluoridation studies. A two-step mechanism for adsorption has been proposed [15] to explain the adsorption of the fluoride ion on brick. The performance of this was compared with activated charcoal. The study of photo catalytic degradation of propoxur on titanium dioxide coated supports such as brick using photo catalytic reaction has been recently investigated [16]. Experimental investigations using brick kiln ash adsorbents show that their adsorption capacities are comparable to that of the commercial activated carbon [17]. The performance of fired clay chips was compared with brick as an alternative for removing fluorine from water [18]. Brick powder was found to have a better performance. Recently adsorption characteristics of nitrates, chlorides and surfactants on sand beds at different flow rates were studied [19]. The adsorption isotherms were obtained from batch experiments. The convective dispersion equation was used to determine the dispersion coefficient from the break through curves. There has been recent work on using inexpensive material, possibly waste material from industries as adsorbents in wastewater treatment. The removal of lead and chromium metal ions from wastewater using bagasse fly ash from sugar industries as an adsorbent has been studied recently [20]. The bottom ash from thermal power plants was utilized as a potential adsorbent for the toxic textile dye “Malachite green” [21].

In this paper, we investigate laboratory scale experiments performed under controlled conditions to determine the adsorption characteristics of detergent solutions and inorganic salts in sand and brick beds. Sand beds are used in this study since they have higher permeability, and this facilitates the flow of water. Brick is chosen as the other material since it is made of oxides and hydroxides of aluminum, iron, calcium, manganese, silica and consequently has a higher adsorption capacity. A mixture of sand and brick consequently can be used to obtain an optimum mixture of good permeability and good adsorption. Also we want to confirm and determine whether brick has good adsorption characteristics for a wide variety of inorganic salts.

Our analysis will enable us to (i) estimate the time taken for the bed to get saturated (ii) design the bed for a particular loading rate of pollutants [22]. From batch experiments we estimate the adsorption isotherm. The isotherm parameters are confirmed from continuous experiments. The convective dispersive equation is used to describe the distribution of solute concentration in the bed as a function of space and time. From the experimental data on breakthrough curves, the dispersion coefficient is estimated by minimizing the error between experimental data and model predictions. The results of the work here can be used for scale up of solute adsorption from the laboratory scale to the field scale.

2. Materials and methods

2.1. Sand and brick

Sand and brick used for construction activity in the Indian Institute of Technology Madras was taken without any chemical treatment. The bricks were broken down to increase the surface area. The sand and brick particles were sieved with mechanical sieves and the fraction containing particle size less than 710 μm was used for experiments. The desired fraction 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 solid particles were ready for use as the adsorbent.

Analysis of the physical characteristics of sand included specific surface area, pore specific volume and pore size distribution. These characteristics were determined by the nitrogen adsorption isotherm (BET analysis) using Sorptomatic 1990 Carlo Erba at 77 K. The specific area was found to be 2.315 m^2/g and pore specific volume was determined as 2.9×10^{-8} m^3/g. The average pore diameter was found to be 30 Å. The particle size distribution of sand was carried out using sieve analysis and it was found that about 61.2% of the particles are in the range of 600–710 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.

Analysis of the physical characteristics of brick was also carried out similarly. The specific area was found to be 9.84147 m^2/g and pore specific volume was determined as 1.849×10^{-6} m^3/g. The average pore diameter was found to be 18 Å. It was found that about 51.8% of the particles are in the range of 600–710 μm, 38.2% of the particles were in the range of 425–600 μm, 5.1% of the particles were in the range of 355–425 μm and the rest of the particles were below 355 μm.

Photomicrography of the sand and brick surface was obtained by SEM (FEI, The Netherlands). The distribution of elemental compositions of the solid sample was analyzed using SEM/EDAX (EDAX Inc., New Jersey, 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 for sand (Fig. 1a) .The analysis for brick showed the presence of silicon, oxygen and a small percentage of aluminum and other metals (Fig. 1b) Thus, while sand is mainly made of quartz, brick is made up of oxides of other metals as well. The presence of these oxides and hydroxides in brick results in its having a different (higher) adsorption capacity than sand as we will see later.

2.2. Batch experiments

Adsorption isotherms relate the adsorbate or solute concentration in the bulk liquid to the concentration of the adsorbent on the solid phase at equilibrium. These isotherms are used in the design of adsorption beds and in determining the transport of solutes through them. These isotherms were first obtained from experiments carried out in batch mode.

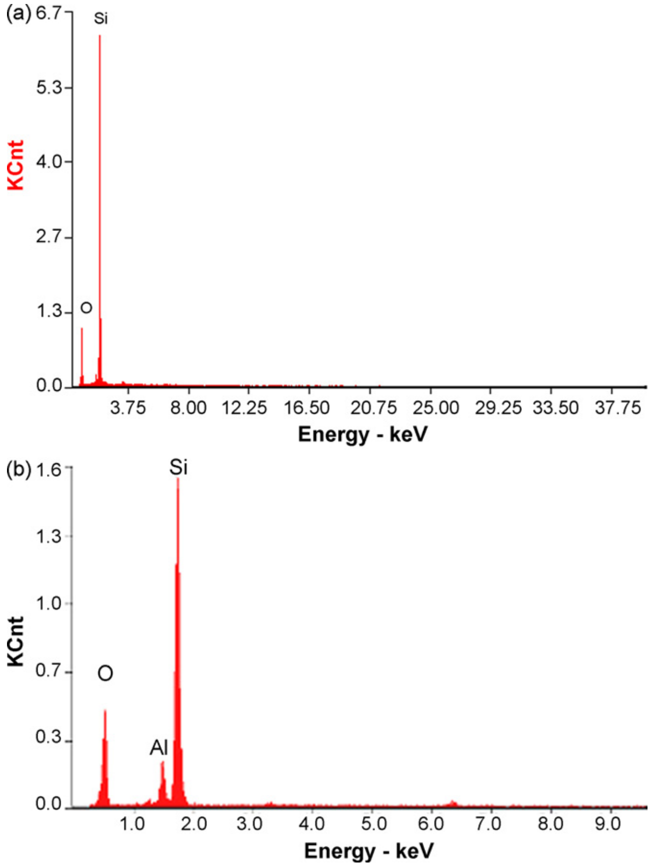

Fig. 1. (a) EDAX spectrum for sand and (b) EDAX spectrum for brick.

Preliminary adsorption 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 the initial concentration of the salt solution and that of the solution at equilibrium after shaking the mixture of solute and adsorbent using a mechanical shaker. The solute concentration in the solution was measured using a conductivity meter. Since experiments were performed with only one solute, this gave us directly the concentration of the solute.

Batch adsorption experiments were carried out at room temperature using different initial concentrations of salt solution. Conical flasks sealed with Teflon-lined caps are used for the experiments. Nitrate solutions (anhydrous potassium nitrate – Central Drug House, Mumbai) with initial concentrations of 100, 200, 500, 1000, 2000, 3000 and 4000 mg/L of solution was prepared. 100 mL of solution of a particular concentration was taken in each conical flask. About 30 g of sorbent 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 analyzed using the conductivity meter. The amount of salt in the liquid after equilibrium was measured and 'q' the nitrate concentration in the adsorbent (mg/g) was obtained by the following relation,

$$q = \frac{(C_i V_i - C_f V_f)}{m} \tag{1}$$

Here, 'm' is the mass of sand adsorbent (g), C_i and C_f are the initial and final concentration of the nitrate solution (mg/L), V_i and V_f are the liquid volume present in the flask at initial and final times, respectively. The final concentration C_f is the equilibrium value of the liquid phase concentration occurring in the isotherm.

A commonly used adsorption isotherm is the Langmuir isotherm. Here, for a single component solute the equilibrium relationship between concentration of solute in solid phase (q) and fluid phase (C) is given by

$$\frac{q}{q_s} = \frac{bC}{1 + bC} \tag{2}$$

Here 'C' is the equilibrium adsorbate concentration (mg/L), q is the mass of adsorbate per unit mass of adsorbent at equilibrium (mg/g), q_s is the maximum amount which can be adsorbed at saturation conditions per unit mass of adsorbent (mg/g), 'b' is the empirical constant which has the unit of inverse of concentration (L/g). The experimental data i.e., the various values of q and their corresponding C_f's is then used to find the parameters (b, q_s) occurring in the Langmuir adsorption isotherm. In Fig. 2(a–c), we depict a plot of the experimentally obtained $1/q$ versus $1/c$ (where $c = C_f$) for nitrate adsorption on sand, brick and sand–brick beds. We find that the dependency is almost linear confirming that the equilibrium relation can be modeled as a Langmuir isotherm. The isotherm parameters are found from the slope ($1/bq_s$) and intercept ($1/q_s$) of the line. For various combinations of salts (sodium chloride – Merck, Mumbai), potassium dihydrogen phosphate – Merck, Mumbai) and sorbent the Langmuir parameters were determined from batch studies using the above approach and these are depicted in Table 1. The detergent used in our study is Ariel from Hindustan Lever Limited. The molecular weight of the detergent is 288.

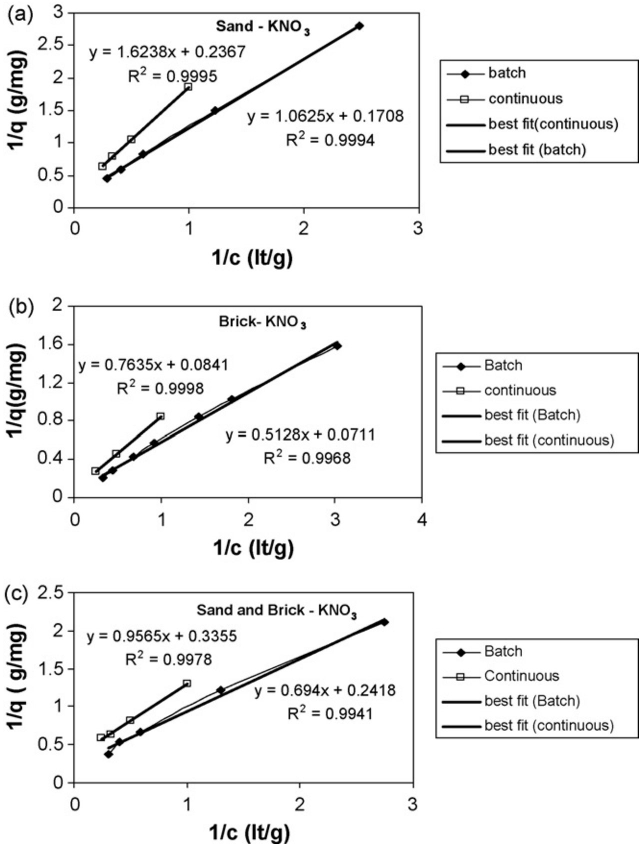

Fig. 2. Langmuir isotherm for nitrate solution experiment and best fit curve. (a) sand; (b) brick; and (c) sand–brick.

Table 1
Best fit parameters of Langmuir isotherm for different combinations of solute and adsorbent

Salt	Adsorbent	Langmuir isotherm-batch			Langmuir isotherm-continuous			Dispersion coefficient (m^2/s)
		q_s (mg/g)	b (L/g)	R^2	q_s (mg/g)	B (L/g)	R^2	
Nitrate	Sand	5.8548	0.1607	0.9994	4.2247	0.1457	0.9995	2.1472E−05
Nitrate	Brick	14.0646	0.1386	0.9968	11.8906	0.1101	0.9998	1.3961E−05
Nitrate	Sand and brick	4.1356	0.3484	0.9941	2.9806	0.3507	0.9978	6.6170E−05
Chloride	Sand	2.1910	0.7594	0.9968	1.5458	0.7479	0.9935	2.3358E−05
Chloride	Brick	12.9870	0.1460	0.9994	5.1387	0.3018	0.9997	6.2811E−05
Chloride	Sand and brick	3.0497	0.3867	0.9799	2.9325	0.2603	0.9818	4.6387E−05
Phosphate	Sand	3.3277	0.2904	0.9967	3.4013	0.1651	0.9982	3.7445E−05
Phosphate	Brick	18.2481	0.0964	0.9956	13.4083	0.07575	0.9955	2.0842E−05
Phosphate	Sand and brick	4.7709	0.2104	0.9959	7.5018	0.07437	0.9944	2.9640E−05
Surfactant	Sand	2.1565	0.9588	0.9552	3.2299	0.4356	0.9863	3.2456E−05
Surfactant	Sand and brick	2.5601	0.5278	0.9943	2.4545	0.3447	0.9993	4.0217E−05

Optimal dispersion coefficient values of continuous experiments are also included.

2.3. Continuous experiments

We have also performed continuous experiments in packed beds to determine the breakthrough curves. The bed in the experimental set-up (Fig. 3) for continuous experiments consists of two sections (i) a test section and (ii) a distributor section. The test section consists of a plexiglass tube of length 30.48 cm and inner diameter 9.54 cm. The thickness of the wall is 0.6 cm. The distributor section is 15 cm long and has a diameter of 9.54 cm. The cross sectional area and volume of the bed are 0.00710 m^2 and 0.0022 m^3, respectively. The distributor section precedes the test section. A perforated plate is placed at the junction of the test section and the distributor section. This supports the sand or brick bed and allows the water to flow through. The diameter of the perforated plate equals that of the plexiglass tube. The perforations are holes of 2 mm diameter drilled at regular intervals and arranged along a square grid. The distance between two adjacent holes is 0.5 cm.

Liquid is pumped through the distributor section vertically upwards. This arrangement ensures that the distribution of the flow is uniform across the cross-sectional area of the packed bed. Consequently the velocity can be viewed as being uniform across the cross-section in the test section. The up flow configuration is preferred since it ensures that the bed is completely saturated [23]. The inlet to the distributor section is through a 1.2 cm diameter hole at the center of the bottom plate of the distributor section. Similarly the outlet is through a 1.2 cm diameter hole at the middle of the top plate of the test section. A plexiglass tube of inner diameter 1.2 cm is used as an inlet port and a flexible pipe is used to connect it to the feed tank.

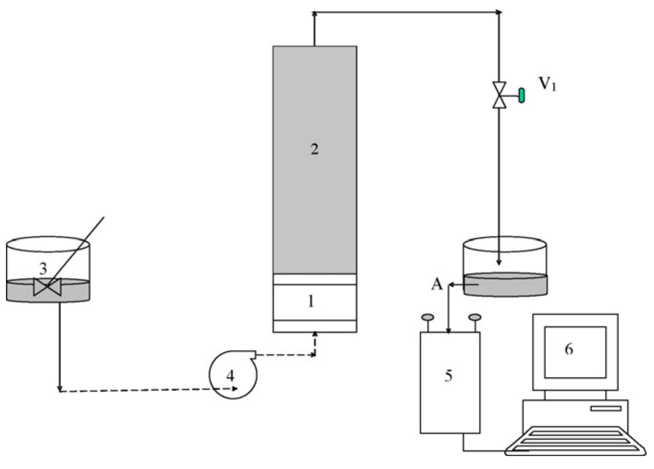

Fig. 3. Experimental setup for continuous adsorption: (1) distributor section; (2) test section; (3) feed tank; (4) peristaltic pump; (5) conductivity meter; (6) computer. (A) is sampling port for measuring TDS.

The test section of the column is filled with a fixed quantity of sand, brick and sand–brick mixture which are used as adsorbents. The weights of sorbents are 3.05, 3.21 and 3.21 kg on a dry basis for sand, brick and mixture of sand and brick beds, respectively. The effective porosity of the bed is measured as 0.39, 0.47 and 0.42 by the volume displacement method for these three beds, respectively. The adsorption process is analyzed using a detergent solution and various inorganic solutions as the feed. The speed of peristaltic pump (Model: VSP-400, Miclins India) was set to ensure a flow rate of 5.0333×10^{-6}, 4.9167×10^{-6} and 3.9667×10^{-6} m^3/s for sand, brick and mixture of sand and brick beds, respectively. The actual velocities corresponding to these flow rates are 1.8×10^{-3}, 1.2×10^{-3} and 1.6×10^{-3} m/s. Twelve to 14 L of feed solution of a given concentration was prepared for carrying out the experiments.

The adsorbent is initially washed and saturated with distilled water before the experiments are started. A feed solution of known concentration is prepared by adding a known amount of solute in a fixed volume of distilled water and this is kept in a well-mixed feed tank. The feed concentrations used were 1000, 2000, 3000 and 4000 ppm for the continuous experiments. This feed solution is pumped at a constant flow rate using the peristaltic pump from the feed tank to the distributor section. The flow is uniformly distributed through out the test section and moves vertically upward against gravity inside the bed. The contaminants are adsorbed in the test section. The effluent concentration is continuously measured by the conductivity meter in the sampling port A (see Fig. 3) on the outlet stream of the test section. The conductivity of the solution is continuously recorded in the computer. After some time the effluent concentration reaches a constant value and equals the feed concentration. This indicates that the bed has become saturated with the solute and that no further adsorption can take place. Experiments were carried out to study the adsorption process in the set up. Here, the feed solution of a fixed concentration was pumped from a feed tank through the adsorbent bed. Sand particles and brick particles making the bed are such that their size is less than 710 μm. The effluent stream from the bed was collected in another vessel. The concentration of the effluent stream was measured continuously using an on-line data acquisition system.

The total dissolved solid (TDS) is the solute concentration. In the feed solution this is measured using a conductivity meter (Model: EE-9042, Elixir Electronics, and Chennai, India). The conductivity meter is connected to a personal computer for continuous acquisition of data. The conductivity meter has a digital indicator which indicates conductivity of the solution. In addition to this it has two ports. The first port leads to the probe. The second port is connected to the A to D card of a computer. The current output from the meter which lies in the range of 4–20 mA, is converted to a voltage in the range of 2.02–10.10 V. The output voltage is measured at intervals of 1 s in the data acquisition system. This is determined by the conductivity of the system, which varies with concentration of solute or TDS.

To find the relationship between the conductivity and concentration the conductivity meter is calibrated for different concentrations of feed solution by measuring the resultant output voltage and determining their conductivity. This is used to relate the output voltage to the concentration of the feed solution. The concentration measured is indicative of the total dissolved solids. However, since in all our controlled experiments we use only one solute at a time the TDS directly gives the concentration of the solute.

The saturated bed is flushed with 10–15 pore volumes of distilled water before the next set of experiments. This ensured that the bed was free of solute at the beginning of every experiment. A feed solution with a new concentration was prepared for the next set of experiments. This is pumped from the feed tank and the same procedure is repeated for the other concentrations of feed solution.

2.4. Modeling and simulation

The one-dimensional solute transport model which governs the adsorption of a solute in a packed bed is described by the following convection-dispersion equation (CDE) [24]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}\frac{\partial q}{\partial t} \tag{3a}$$

Here, C is the dimensionless effluent solute concentration; D is an effective dispersion coefficient m^2/s; u is the superficial velocity of the solution through the bed; t is time; ε is the porosity of the bed; and q is the solute concentration in the solid phase. This equation describes the variation of the concentration with space and time in saturated beds, where the inter particle space is completely occupied by the solvent.

Eq. (1) is used as the mathematical model to describe our continuous system. The model is based on the following assumptions:

1. Flow is one-dimensional in the vertical direction and uniform across the cross-sectional area.
2. The equilibrium adsorption relation is represented by the Langmuir isotherm.
3. The bed is fully saturated. (i.e. all interparticle voids are filled with liquid)
4. There is no mass transfer resistance on the liquid side.

Eq. (3a) is a non-linear parabolic partial differential equation and describes how the liquid phase concentration C varies with z and time. It contains two dependent variables, C and q. Hence, one more relationship is needed to formally solve the problem. This relationship between C and q is given by the equilibrium isotherm. The relationship is assumed as the classical Langmuir isotherm (2) in this work. This is characterized by two parameters b, q_s. These parameters depend on the choice of the solute as well as the particles used as an adsorbent. These parameters are obtained from batch experiments as described before when detergents and some inorganic salts are solutes and sand or brick particles are the adsorbent. The solute transport Eq. (3a) and the equilibrium isotherm (2) can be combined to obtain the following equation for $C\,(t, z)$,

$$\frac{\partial C}{\partial t} = \frac{D\partial^2 C/\partial z^2 - u(\partial C/\partial z)}{[1 + ((1-\varepsilon)q_s b/(\varepsilon)(1+bC)^2)]} \tag{3b}$$

This equation is solved subject to the following initial and boundary conditions.

The initial condition is

$$C(t=0) = 0; \quad \text{for } 0 < z < L \tag{4a}$$

since the bed is assumed to have no solute at the start of the experiment.

The boundary conditions are,

$$\text{At } z = 0\text{(entry)},\ uC_{\text{in}} = -D\frac{\partial C}{\partial Z} + uC \tag{4b}$$

This is called the closed Danckwerts boundary condition [25]. Here, we neglect the dispersion in the distributor section just upstream of the test section. Here, C_{in} is the concentration of the solution entering the bed. In our case this is a constant equal to C_{feed}.

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

$$uC(L^+) = uC(L^-) - D\frac{\partial C(L^-)}{\partial z} \tag{4c}$$

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

$$D\frac{\partial C(L^-)}{\partial z} = 0 \tag{4d}$$

The parabolic partial differential Eq. (3b) is solved using the method of lines. The concentration in the bed is discretized in the spatial direction. The bed is divided into '$n-1$' grids. The grid points are numbered from 1 to n as we vary z from 0 (entrance) to L (exit). The evolution of the concentration with time in each node is modeled through ordinary differential equations.

Eq. (3) is thus converted into a set of ODE's by finite differencing in space. The resulting set of equations is integrated by the Runge-Kutta method. For the ith grid point, Eq. (3) becomes,

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \frac{D\partial^2 C_i/\partial z^2 - u(\partial C_i/\partial z)}{g(C_i)} \tag{5}$$

where

$$1 + \frac{(1-\varepsilon)q_s b}{(\varepsilon)(1+bC_i)^2}$$

On using the second order finite difference scheme for the derivatives, we obtain

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \frac{D(C_{i+1} - 2C_i + C_{i-1})/\Delta z^2 - u((C_{i+1} - C_{i-1})/2\Delta z)}{g(C_i)} \tag{6}$$

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \frac{(1/\Delta z^2)[D(C_{i+1} - 2C_i + C_{i-1}) - (u\Delta z(C_{i+1} - C_{i-1})/2)]}{g(C_i)} \tag{7}$$

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \left(\frac{D/\Delta z^2}{g(C_i)}\right)\left[\left(1 - \frac{Pe}{2}\right)C_{i+1} - 2C_i + \left(1 + \frac{Pe}{2}\right)C_{i-1}\right] \tag{8}$$

where Pe is Peclet number defined as $u\Delta z/D$. This equation is valid for grid points $i = 2$ to $n-1$. The boundary condition at the inlet ($z = 0$), (4b) is written as

$$C_0 = C_2 - \frac{2u\Delta z}{D}(C_1 - C_{\text{in}}) \tag{9}$$

Here, we assume C_0 is the hypothetical concentration upstream of the inlet at a distance Δz when the upstream section also has a dispersion coefficient D prevailing in the bed. This approach is used to ensure that the discretization of all differential equations and boundary conditions are done to the same order of accuracy. Using the central difference approximation for the first derivative, we obtain for the evolution of C_1,

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = \frac{D(C_2 - 2C_1 + C_0)/\Delta z^2 - u((C_2 - C_0)/2\Delta z)}{g(C_i)} \tag{10}$$

We use the expression for C_0 from (9) in this equation.

Using the BC (4d) at the outlet, we have at node (n), $C_{n+1} = C_{n-1}$. Here 'C_{n+1}' is the fictitious grid point used just outside the bed and plays a role similar to C_0 at the entry. For C_n we have

$$\frac{dC_n}{dt} = \frac{D(C_{n+1} - 2C_n + C_{n-1})/\Delta z^2 - u((C_{n+1} - C_{n-1})/2\Delta z)}{g(C_n)} \qquad (11)$$

$$\frac{dC_{n+1}}{dt} = \frac{(2D/\Delta z)(C_{n-1} - C_n)}{g(C_n)} \qquad (12)$$

These equations are subject to the initial condition, $C_i = 0$ for all $i = 1, \ldots, n$ at time $t = 0$. This specifies that the concentration at all grid points in the bed is equal to zero at $t = 0$.

For the numerical simulation the bed is divided into 20 grids. 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 no of grids was increased beyond 40.

2.5. Optimization

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 q_s – maximum adsorption capacity; b – Langmuir constant; 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.

To ensure that our approach has a firm physical basis we estimate the isotherm parameters and the dispersion coefficient independently. The former have been determined by batch experiments as explained earlier.

They were also confirmed from the breakthrough curves. For this the amount of solute adsorbed on the solid phase in the bed when the experiment is run for a sufficiently long time T (so that the bed is saturated) is determined as

$$v_0 \int_0^T (C_{in} - C(t))dt - V\varepsilon C_{in}$$

Here, v_0 is the volumetric flow rate through the bed and $C(t)$ is the instantaneous concentration leaving the bed measured by the conductivity meter.

The term under the integral sign represents net mass influx to the bed. The second term represents the solute in the liquid phase after the bed is saturated. If the amount of solid in the bed is M, we obtain

$$q = \frac{v_0 \int_0^T (C_{in} - C(t))dt - V\varepsilon C_{in}}{M} \qquad (13)$$

We can use this to independently obtain the isotherm parameters from continuous experiments. This can be compared with the adsorption parameters for the Langmuir adsorption isotherm obtained from batch experiments. The isotherm parameters so obtained are shown in Table 1. We discuss these results in detail in the next section

The dispersion coefficient parameter is obtained by minimizing the error between the experimental data and the theoretical prediction of the model. The experimental data used was from the 4000 ppm solution of different salts in continuous mode .The unconstrained optimization routine in MATLAB 'lsqnonlin' is used to optimize the parameters (D) involved in this problem. The objective function which was minimized is, sum of squares of error between experimental values and model predictions

$$J = \int_0^{t_f} (C^{\text{experiment}} - C^{\text{model}})^2 dt \qquad (14)$$

3. Results and discussion

We now discuss the results of experiments we have carried out in the batch as well as the continuous modes for various solutes. The initial and final liquid phase concentrations C_i, C_f (at the beginning and end of the experiment) was determined experimentally. We estimate the solid phase concentration 'q' for the batch experiment using equation (1). A plot of $1/q$ vs $1/C$ is made from the batch experimental results. For the case of adsorption of potassium nitrate on sand, brick and mixture of sand–brick the experimental points are depicted as filled boxes in Fig. 2(a–c). The best fit line was found and from this the slope and intercept were estimated. The isotherm parameters (q_s and b) were found and these are reported in Table 1. From the break through curves (continuous experiments) we have estimated the solid phase concentration in equilibrium with the liquid phase concentration using Eq. (13). These are plotted in Fig. 2(a–c) again as open boxes for the same solute adsorbate combination. It can be seen that the points lie on a straight line. The isotherm parameters of these best fit lines from continuous experiments are also reported in Table 1.

We similarly determined the isotherm parameters using batch as well as continuous experiments for all the other solute adsorbent combinations. The figures for these are not depicted. However, we report the isotherm parameter values and the corresponding R^2 values in Table 1 for all these cases. The isotherm parameters determined by both experimental methods match very well. The differences between the batch and continuous experiments can be attributed to the non-uniform flow through the bed due to nonhomogeneity in packing and the fact that the assumed equilibrium between the two phases may not be attained. We now discuss the behavior of the breakthrough curves for the various salts. For each salt we discuss the performance for different adsorbents and compare the model predictions with experimental results.

3.1. Potassium nitrate solution

Experiments were carried out in the continuous mode operation using KNO_3 solution of different concentrations. When a 4000 ppm of KNO_3 solution is used as the feed the time taken for the sand bed to get saturated was 1230 s (Fig. 4a). It took 4080 s when brick alone is used as adsorbent (Fig. 4b) and 1770 s when a mixture of sand and brick is used as adsorbent (Fig. 4c). This difference in the times occurs since we have used different volumetric flow rates for each bed. The volumetric flow rate is highest for the sand bed, and the lowest for the brick bed. This is to be expected since the sand bed has higher permeability than the brick bed and so the effective permeability for each bed is different. From experimental results it is observed that the adsorption capacity was increased when brick was used as an adsorbent. This can be attributed to the presence of oxides and hydroxides of Al and other metals in brick.

The optimized parameter D was obtained using a nonlinear least squares technique as outlined above when the feed concentration was 4000 ppm. The estimated parameter was 2.1472×10^{-5} m^2/s for a sand bed and is depicted in Table 1. This optimized parameter was used to predict the performance of the continuous experiments for different feed concentrations. Fig. 4a shows the comparison of simulation predictions for sand bed using this optimized parameter with the experimental data at four different concentrations of 1000, 2000, 3000 and 4000 ppm. For nitrate with sand as adsorbent the Peclet number found to be

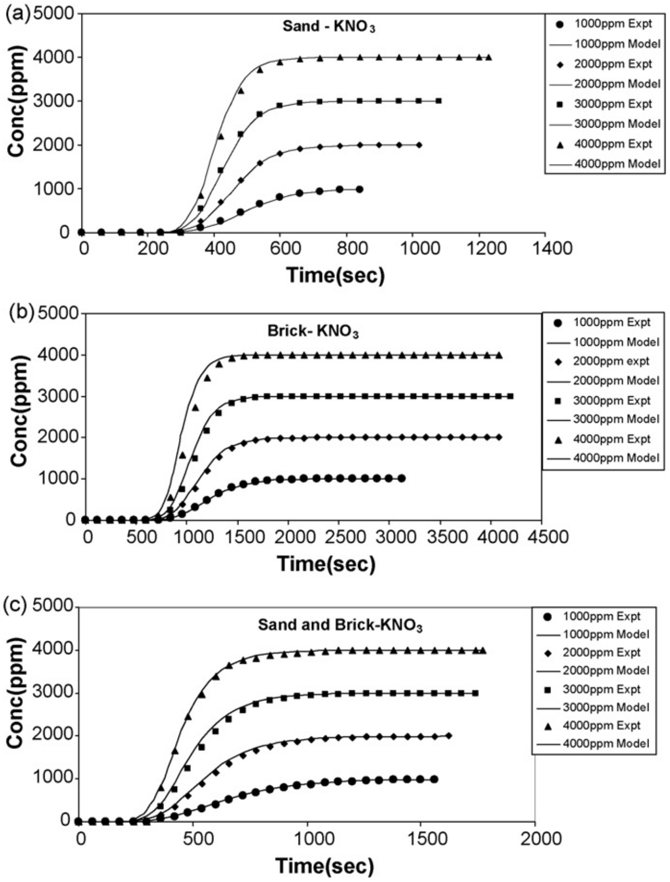

Fig. 4. Comparison of break through curves: model prediction and experimental data for potassium nitrate solution. (a) sand; (b) brick; and (c) sand–brick.

uL/D is 25.558. This number is a measure of the ratio of convective transport to the dispersive transport. In Fig. 4(b–c) we depict the breakthrough curves for various adsorbents and show how the model predictions compare with the experimental values. The dispersion coefficient depends on the packing used and the optimized values used for the predictions are shown in Table 1. As expected sand containing mainly silicon and oxygen and has a very poor adsorption capacity. The removal efficiency in batch mode is around 20%. Brick on the other hand, has higher removal efficiency and this can be attributed to the presence metals such as aluminum and their oxides. Based on the results obtained from the batch experiments approximately 26% nitrate removal was achieved with a mixture of sand and brick. The removal efficiency by brick alone was determined to be much higher—approximately 33% for nitrate at the concentrations ranging between 500 and 4000 mg/L.

3.2. Sodium chloride solution

When an initial concentration of 4000 ppm of sodium chloride solution was used the sand bed got saturated after 1140 s of operation as shown in Fig. 5a. The concentration of the liquid stream at the exit of test section is plotted against time in that figure. It takes around 4020 s for the bed to get saturated when only brick is used as adsorbent. It takes around 1770 s for the bed to get saturated when a mixture of sand and brick is used as adsorbent (Fig. 5c). The optimization procedure described above is applied to the experimental data obtained for various adsorbents when the feed concentration was 4000 ppm.This determines the best dispersion coefficient for each adsorbent for which the model prediction matches the experimental data. In the case of sodium chloride the dispersion coefficient is found to be 2.3358×10^{-5} m^2/s when sand is used as adsorbent and 4.6387×10^{-5} m^2/s when a mixture of sand and brick was used as an adsorbent (see Table 1). The variation of dispersion coefficient from one adsorbent to the other can be attributed to heterogeneities and different porosity in the bed. Fig. 5b compares the prediction of the model for the optimal set of parameters with the experimental data when brick is used as an adsorbent for various feed concentrations. The excellent predictions for the different concentrations justify the assumptions on which the model is based.

Fig. 5c compares the predictions of model using the dispersion coefficient calculated with experimental data when the initial concentration in the feed tank is 4000 ppm for a bed with a 1:1 sand–brick mixture. It can be seen that the optimal parameter D obtained for this adsorbent mixture predicts the performance of the bed very accurately even when the feed concentrations are varied. Our main focus is to study the adsorption capacity of inexpensive materials in their natural state, without any coating. The use of sand and brick for removal of arsenic has been studied in the literature [15]. Following this we have used brick in our experiments and found that the adsorption capacity increases as compared to the case when sand alone is used. This is due to the presence of several other metals their oxides and hydroxides in brick, which are absent in sand. The combination of sand and brick helps us optimize pressure drop across the bed and the adsorption capacity of the bed. Based on the results obtained from batch approximately 27% chloride removal was achieved experiments when sand and brick is used as an adsorbent. The removal efficiency by brick was

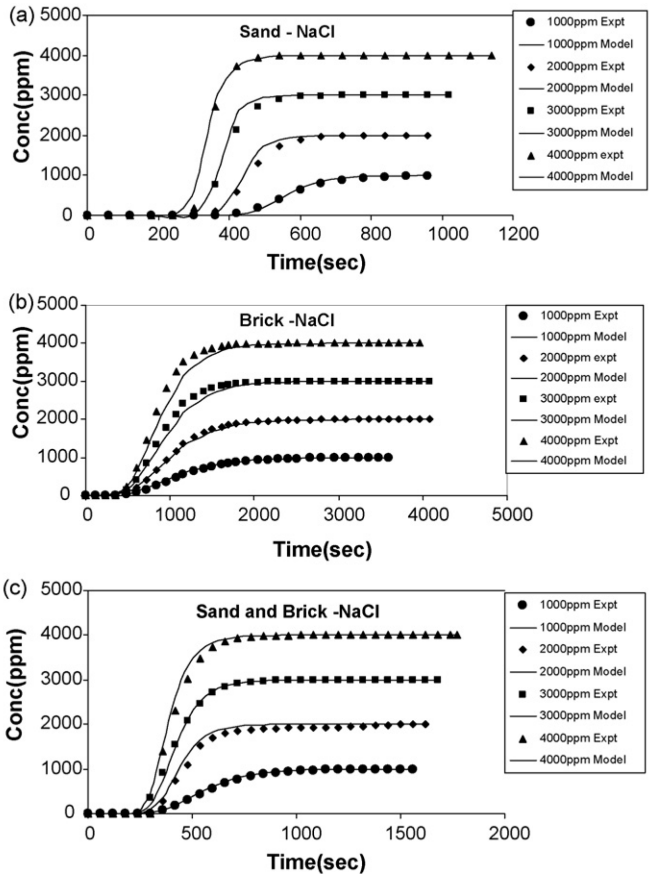

Fig. 5. Comparison of break through curves: model prediction and experimental data for sodium chloride solution. (a) sand; (b) brick; and (c) sand–brick.

determined to be much higher—approximately 32% for chloride at the concentrations ranging between 500 and 4000 mg/L. In contrast to this only 22% removal of chloride was achieved for sand.

3.3. Potassium dihydrogen phosphate solution

A similar approach was used to determine the dispersion coefficient parameters when using KH_2PO_4 as the solute. When sand is used as an adsorbent (Fig. 6a) the bed gets saturated in 1230 s for an initial concentration 4000 ppm. It gets saturated in 1770 s when a mixture of sand–brick is used as an adsorbent (Fig. 6b) and when brick alone is used as adsorbent (Fig. 6c) the bed gets saturated in 4080 s. From the experimental data it is observed that adsorption capacity is relatively higher when a mixture of sand and brick is used as adsorbent than when sand alone used. The improved performance with the addition of brick can be attributed to the acid sites present in brick which have higher affinity for phosphate than sand. For KH_2PO_4 solution of 4000 ppm in continuous mode of operation, the optimized parameter D was determined by minimizing the error between experimental data and the model prediction. This was found to be $3.7445 \times 10^{-5}\ \mathrm{m^2/s}$ for the sand bed (Table 1). Fig. 6a shows the comparison of the model prediction and the experimental data for this optimal set of parameters. The parameter was used for predicting the performance for feed concentrations 1000, 2000, 3000 and 4000 ppm. In Fig. 6(b and c) we show that the simulation results agree well with the experimental values. Here, again the optimized diffusion coefficient D was obtained from experimental data using the feed concentration of 4000 ppm for each bed. Based on the results obtained from the batch experiments we have approximately 19% phosphate removal when sand and brick are used. The removal efficiency by brick was determined to be much higher—approximately 32% for phosphate at the concentrations ranging between 500 and 4000 mg/L. When sand alone used, only a 16% removal was achieved.

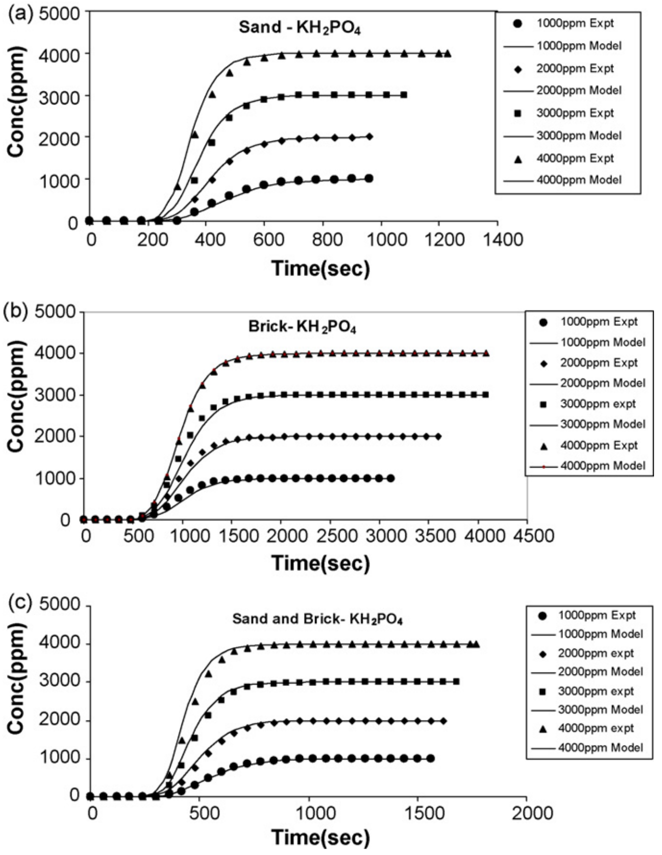

Fig. 6. Comparison of break through curves: model prediction and experimental data for potassium dihydrogen Phosphate (KH_2PO_4) solution. (a) sand; (b) brick; and (c) sand–brick.

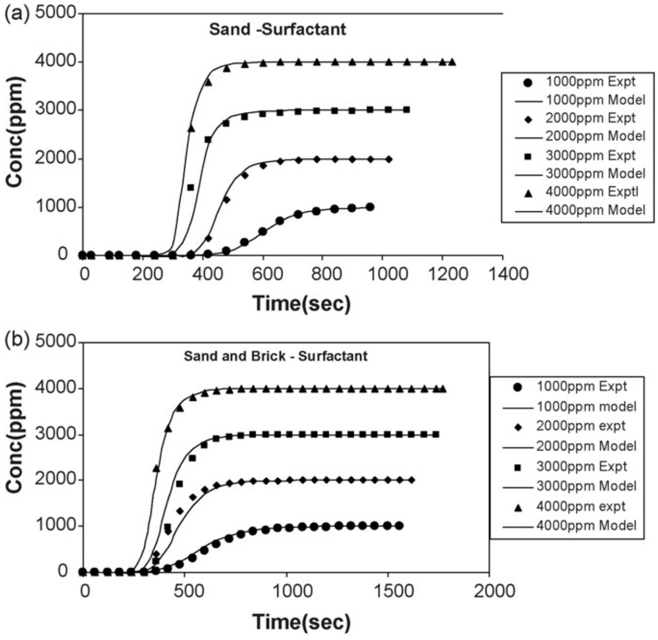

Fig. 7. Comparison of break through curves: model prediction and experimental data for surfactant solution. (a) sand and (b) sand–brick.

3.4. Ariel powder solution

While so far we have concentrated on individual inorganic salts we now focus on adsorption of a commercial detergent Ariel. This consists of a mixture of surfactants LAS (linear alkyl benzene sulfonate), alkyl sulfate (an anionic surfactant) and other compounds which are added like phosphates, builders, etc. Experiments were carried out using Ariel powder solution of different concentrations. When surfactant solution of 4000 ppm is used as the feed concentration the time taken for the bed to get saturated was 1230 s when sand alone is used as adsorbent (Fig. 7a). It was 1770 s when a mixture of sand and brick is used as adsorbent (Fig. 7b). The optimized parameter D was obtained for each bed as outlined above for a feed concentration of 4000 ppm. Fig. 7a shows the comparison of simulation predictions and experimental data for the continuous mode at four different concentrations of 1000, 2000, 3000 and 4000 ppm for a sand bed. Similar behavior is observed for a bed containing a mixture of sand and brick (Fig. 7b). We were unable to conduct the experiments for surfactant adsorption with brick alone, since the surfactant foam carried the brick particles and clogged the exit port. Based on the results obtained from the batch experiments approximately 24% removal was achieved when sand alone is used as adsorbent. The removal efficiency of a sand–brick bed was determined approximately to be 31% at the concentrations ranging between 500 and 4000 mg/L.

4. Conclusions

The maximum adsorption capacity for brick beds was always found to be higher than that of sand beds. The reason for the increase in adsorption capacity is the higher specific surface area and the increase in wettability of brick when compared to sand.

Adsorption experiments were performed in batch as well as in continuous mode using sand/brick as sorbents. This choice was motivated primarily from economic consideration and their abundance. Sand has good permeability and so the pressure drop across the bed is very low. A brick bed has higher adsorption capability and hence a mixture of sand and brick allows us to combine good hydrodynamics with good adsorption.

The isotherm parameters for various solutes in the sand, brick and sand–brick beds were obtained. These were found to be valid when the solute concentrations were in the range of 1000–4000 ppm. The experimental observations agree closely with the theoretical predictions in this range. The isotherm parameters found from batch and continuous experiments agree reasonably well. It has been found that the adsorption capacity of the bed increases with the addition of brick particles for all the solutes under investigation. An important result this study confirms is that brick has a better adsorption capacity than sand for a wide range of solutes. We believe that this is true for all solutes in general.

The work here focuses mainly on single solute adsorption. The difference in the values of isotherm parameters found from batch and continuous experiments can be attributed to (i) the extreme sensitivity to the experimental data (so that small errors in the experimental data can result in significant changes in the parameters estimated); (ii) to the fact that equilibrium may not be established in the bed; and (iii) to spatial in homogeneities in the bed. The model used here can be used for scale up and design large scale beds. The isotherm parameters determined and the dispersion coefficient determined depend on hydrodynamic conditions of operation. Hence, these parameters can be used if the hydrodynamics in the field studies are the same as those in the experiments.

Normally chloride, phosphate and nitrate are the anions present in grey water. So a mixture of sand and brick can be used as an adsorbent in grey water treatment. Brick is a better adsorbent for nitrate than sand as can be seen from the higher q_s or saturation adsorption capacities for brick. Adsorption of potassium nitrate, sodium chloride and Ariel on a bed of mixture of sand and brick is higher than on sand alone. Hence, a mixture of sand and brick can be used as a good adsorbent for a wide range of solutes. The mixture of sand and brick enables us to obtain an optimum between good adsorption and low pressure drop in a packed bed. The mixture of composition (sand and brick) has not been optimized for performance. This can be done by studying adsorption features for various ratios by weight of sand and brick mixture. While the removal efficiency of a brick bed (approx. 35%) is better than that of a sand bed (approx. 20%) it is still inferior to that of a bed of activated charcoal (50%). The removal efficiencies obtained in this study are comparable to values reported in literature [15]. However, considering that brick is less expensive than activated charcoal it can be used as a suitable adsorbent for a wide variety of salts. To conclude sand by itself is not an effective adsorbent. However, when the pollutant levels are high we can mix it with brick powder to increase the efficiency. Higher weight percentage of brick however reduces permeability and increases pressure drop.

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