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Mathematical model: Retention of beryllium on flow-through fixed bed reactor of Amb-IR-120

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ABSTRACT

A mathematical model was proposed to simulate the beryllium uptake within a fixed porous flow-through reactor. The effects of various structural, kinetic and hydraulic parameters on the behavior of the flow reactor were studied. These include linear velocity of the fluid, packing density, void fraction and adsorption coefficient. The proposed mathematical model is solved analytically and its predictions were compared with experimental results. A reasonable agreement between model predictions and experimental data was obtained. The model is approved to simulate the behavior of beryllium uptake along the fixed bed reactor of Amb-IR-120 and can be easily applied to similar systems.

1. Introduction

Beryllium is a strategic and critical material for many industries. It is widely used despite its relatively high cost, because it performs better than alternative in certain critical applications. The beryllium industry produces three primary forms of beryllium. Copper beryllium alloy is the largest, followed by pure beryllium metal and beryllium oxide ceramics. Specifically, beryllium is used in nuclear reactors as a neutron reflector or moderator and in the aerospace industry in inertial guidance systems.

Different approaches in this respect were reported to separate beryllium from aluminum and the other impurities. One of them is the separation of beryllium from its solutions using ion exchange technique where beryllium can strongly be adsorbed on cation exchange resin. The process consists of leach, continuous counter current decantation, resin-in-column ion exchange, evaporative crystallization of beryllium salt, followed by its decomposition. The most important aspect of such process is a resin system which is highly selective for beryllium and which rejects substantially all impurities except for minor amounts.

Sorption of beryllium was studied on the carbonate form of AB-16, AB-17 and AN-2F as anion exchangers and AB-17 was found to give the highest efficiency [1]. Separation of beryllium from Ni, Cu, Al, and Fe was achieved by using AV-17 anion exchanger in carbonate form at pH 2.5; beryllium was eluted with ammonium carbonate or sodium hydroxide [2]. The mentioned study was pursued by using the carbonate form of AV-16, AV-17, EDE-IOP and AN-2F on sorption of beryllium in various dynamic conditions and it was proved that AV-17 in carbonate form was the most effective one. Na_2CO_3, $(NH_4)_2CO_3$, NaOH, NH_4OH solutions were used as eluents for adsorption of beryllium from AV-17 in carbonate form [3]. Such exchanger in the carbonate form was also used for the quantitative separation of beryllium from W and Mo [4].

Another important and applicable exchange resin for separation of beryllium from its solutions is Amb-IR-120 where beryllium can strongly be adsorbed to be later eluted with hydrochloric acid [5,6].

Metal extraction reactions in ion-exchange resins are treated and explained like other heterogeneous reactions between solids and fluids. It is accepted that the resin ion-exchange processes normally are diffusion controlled and not reaction controlled [7]. The rate-controlling mechanism can be diffusion across the liquid film surrounding the resin particle (film diffusion) or diffusion inside the particle (particle diffusion). Concerning the kinetics of sorption, some simple criteria can be directly adopted from ion exchange kinetics (Helfferich [7], Swami and Dreisinger [8]). On the other hand, Gonzalez and Streat [9] studied uranium sorption in phosphoric acid solutions using Levextrel resins containing DEHPA and TOPO based on the homogeneous diffusion model (HDM) and shrinking-core model (SCM). They indicated that particle diffusion is rate-controlled. Cortina and Miralles [10] recently used HDM and SCM to analyze kinetic data of metal sorption on XAD-2 loaded with organic phosphorus extractant. They found that the process is controlled by film diffusion at low metal concentrations and by particle diffusion at high concentrations. In addition, the inner structure of

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Nomenclature

List of symbols

C_o	initial concentration of sorbing species, mg l^{-1}
C_e	equilibrium concentration of sorbing species, mg l^{-1}
k	pseudo-first order rate constant, s^{-1}
k_a	the adsorption coefficient, kg m^{-3}
k_r	pseudo-first order rate constant at the rapid step, min^{-1}
k_s	pseudo-first order rate constant at the slow step, min^{-1}
m	the mass of the resin, g
q_{max}	amount of solute sorbed at equilibrium, mol kg^{-1}
$q(t)$	amount of solute sorbed at time t, mol kg^{-1}
Q	accumulated Beryllium over all the column, mol
r	average particle radius, m
t	time, min
u	Linear velocity of fluid, m s^{-1}
U	uptake percent
V	volume of solution, ml
z	the bed thickness, m
z_m	the height of the column, m
z_b	the height of the absorption band, m

List of Greek symbols

β	The solid–liquid partition coefficient, kg m^{-3}
ε	the void fraction
ρ	The packing density, kg m^{-3}
Ψ	Reactor parameters, m^{-1}

polymeric supports has a significant but complex effect on the rate phenomena. Juang and Lin [11,12] analyzed the rate data for sorption of Cu(II) and Zn(II) from aqueous solutions with XAD-2 and XAD-4 containing DEHPA using a modified shrinking core model (SCM), and further they confirmed the used mass transfer equations based on Fick's law.

In such studies several of experiments have been performed to study the process of adsorption to determine different parameters necessary for describing the process of adsorption. Each parameter must be appropriately chosen to accurately simulate the overall performance. However, the design of an industrial resin column of Amb-IR-120 requires many parameters, which can be obtained by doing a series of laboratory experiments. Such practices are time consuming and costly so that accurate modeling and simulation are frequently used as an alternative for predicting the dynamic behavior of fixed bed systems to optimize column design and operation parameters.

In the present work, the process of beryllium retention within a fixed bed reactor of Amb-IR-120 from its synthetic solution has been experimentally and theoretically studied. The present framework can help in better understanding of the process and optimization of structural, kinetic and hydrodynamic parameters.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade reagent and were used as received. Amb-IR-120 (Aldrich product) its matrix component is styrene–divinyl benzene (gel type) and the matrix active group is sulfonic acid. The beryllium sulfate was obtained from Fluka.

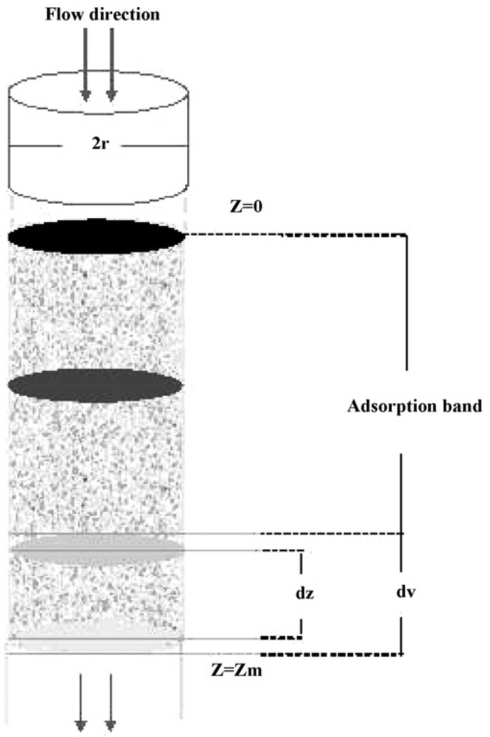

Fig. 1. Arrangement of the flow direction and column simulation.

2.2. Procedure

Fixed-bed column sorption studies of beryllium were performed by passing 1.25 L of 360 ppm Beryllium sulfate $BeSO_4{\cdot}4H_2O$ solution of a pH 3.5 continuously upon 8.0 g dry Amb-IR-120 resin particles in the sodium form at a residence time of 3 min at temperature of 30 °C. Aliquot samples were taken from the column at appropriate time intervals as necessary. Batch sorption studies of beryllium and the concentrations of beryllium were analyzed as previously reported [13]. All experiments were performed at pH of 3.5 in duplicate and the averaged values were taken.

3. Physical picture and assumptions

A column packed with Amb-IR-120 which is used to retain beryllium ion could be considered as a fixed-bed reactor. It is assumed that once the adsorption zone has been reached a transient sorption band is formed. The sorption band is the zone of the reactor which retains the beryllium ions and start from the top of the reactor. Fig. 1 is a schematic arrangement of the flow direction and column simulation. Where r (m) is the column radius, dz is the differential unit length of the beryllium band in the direction of the solution flow and dv is the differential unit volume which equals to πr^2 dz.

The following assumptions were suggested to simplify the model:

(A1) The adsorption band is subdivided into an infinite number of small layers.

(A2) At any time, the concentration of beryllium in the first layer ($z = 0$) is maximum and beyond which a concentration gradient is obtained, i.e. the concentration within the fixed bed resin decreases gradual from the top of the column to the end of the band.

(A3) Beryllium retention upon the working resin follows a pseudo-first order kinetics [13].

(A4) The pseudo-first order constant gives the general rate of adsorption and the diffusion effects are included in the rate constant as assumed by the pseudo-first order equation.

(A5) The concentration at the first layer can be calculated from batch experiment if the concentration of the feeding solution was assumed to be equal to the concentration in the solution phase of the batch experiment and the change in it was assumed to be negligible, i.e. the concentration in the batch experiment in the solution phase is very high or the amount of adsorbent is very low.

(A6) The gradual decrease in concentration (q) from layer to layer is directly proportional to the decrease in the solution concentration (C) along the height of the reactor (z) (i.e. $\mathrm{d}C/\mathrm{d}z = \beta\,\mathrm{d}q/\mathrm{d}z$) while the rate of change in the adsorbed ions concentration is opposite to the rate of change in the ions concentration in the solution phase (i.e. $\mathrm{d}C/\mathrm{d}t = -k_a\,\mathrm{d}q/\mathrm{d}t$). Where k_a is the adsorption coefficient and β is the solid–liquid partition coefficient.

(A7) The band length increases with the time due to more beryllium retention only.

(A8) At the end of the experiment, i.e. after saturation of the resin column there is one layer (its concentration equals $q_{\max}$) by which the column could be described.

(A9) The band formed at certain time interval is retained (fixed) during the flow of the mobile phase (the working solution).

(A10) At any time, the mobile phase flows uniformly throughout the reactor, i.e. the flow rate of the mobile phase is constant throughout the reactor during the experiment.

(A11) The solution velocity appears in the over all material balance and the process controlled by an external mass-transfer for the reactor as a whole.

(A12) The flow of the mobile phase does not affect the chemistry of the ion exchange resin.

4. Model equations and solution

According to assumption (3), a simple kinetic equation that describes the process for the sorption of solid–liquid systems given by Lageren [13] can be applied.

$$\frac{\partial q(t)}{\partial t} = k(q_{\max} - q) \tag{1}$$

where k (s^{-1}) is the rate constant of the adsorption for pseudo-first order reaction and $q_{\max}$ ($\mathrm{mol\,kg}^{-1}$) is the equilibrium concentration. The integration for the last equation with the initial condition $q = 0$ at $t = 0$ can be used to follow the adsorption in batch experiment and can be given by:

$$q(t) = q_{\max}(1 - e^{-kt}) \tag{2}$$

This equation can be applied to describe the adsorption in the first layer of the column, i.e. at $z = 0$ (assumptions 1, 2, 3 and 4) if the reaction take place under pseudo-first order condition.

The mass balance of metal in differential height (dz) for differential period (dt) for the whole column is expressed by:

$$u\frac{\partial C}{\partial z} + \rho\frac{\partial q}{\partial t} + \varepsilon\frac{\partial C}{\partial t} = 0 \tag{3}$$

where u is the linear velocity of solution (mobile phase) ($\mathrm{m\,s}^{-1}$), ρ is the packing density and ε is the void fraction.

By considering assumptions (1, 2, 3, 4, and 5) and Eq. (1) we will have:

$$\frac{\partial q}{\partial t} = -\frac{1}{k_a}\frac{\partial C}{\partial t} = k(q_{\max} - q) \tag{4}$$

$$\frac{\partial C}{\partial z} = \beta\frac{\partial q}{\partial z} \tag{5}$$

Table 1
Values of the column parameter that used in calculation of Figs. 2–7.

Adsorption parameters	
Pseudo-first order rate constant, k (s^{-1})	6.38×10^{-4}
The adsorption coefficient, k_a ($\mathrm{kg\,m}^{-3}$)	8.05
Amount of solute sorbed at equilibrium, $q_{\max}$ ($\mathrm{mol\,kg}^{-1}$)	1.16
The height of the column, Z_m (m)	0.1
The packing density, ρ ($\mathrm{kg\,m}^{-3}$)	7.13×10^{2}
The void fraction ε	0.434
Linear velocity of fluid, μ ($\mathrm{m\,s}^{-1}$)	4.156×10^{-4}
The solid–liquid partition coefficient, β ($\mathrm{kg\,m}^{-3}$)	49.61

Substitution by (4) and (5) in (3) gives:

$$u\beta\left(\frac{\mathrm{d}q}{\partial z}\right) + \rho k(q_{\max} - q) - \varepsilon.kk_a(q_{\max} - q) = 0 \tag{6}$$

From (8) and let $\Psi = \rho k - \varepsilon\, kk_a/u\beta$.

We will have:

$$\frac{\mathrm{d}q}{\partial z} = -\Psi(q_{\max} - q) \tag{7}$$

By applying steady state approximation given that $q = q(t)$ at $z = 0$ (assumption (3)), the integrated form of Eq. (7) will be:

$$q(t, z) = q_{\max} - ((q_{\max} - q(t)))\exp(\Psi z) \tag{8}$$

Substitution by (2) in (8) gives:

$$q(t, z) = q_{\max}(1 - \exp(\Psi z - kt)) \tag{9}$$

The last equation will be applied for $z \le z_b$ where $z_b = kt/\Psi$ and t is the selected time interval. The concentration considered to be zero for $z > z_b$ and z_b can be considered as the band length after period of time t.

5. Results and discussion

Eq. (9) can be used to follow the beryllium concentration onto the solid phase at any point inside the reactor after any time interval. According to the assumed model, the parameters which affect the conversion are the pseudo-first order rate constant (k), the adsorption coefficient (k_a) between the mobile phase (beryllium solution) and the stationary phase (Amb-IR-120), the void fraction (ε), the packing density of the column (ρ) ($\varepsilon = 1 - (\rho$/actual density)), the linear velocity of the mobile phase (u), the column radius (r), the column height (z_m), and the solid–liquid partition coefficient (β). The study of the effects of such parameters in the behavior of the fixed bed reactor using the provided model can help in design optimization of the operation conditions. Hence Eq. (9) can be normalized to give:

$$\overline{q(t, z)} = 1 - e^{(\Psi Z - kt)} \tag{10}$$

where $\overline{q(t, z)} = q(t, z)/q_{\max}$

The model can simulate the gained value of the normalized concentration $\bar{q}$ ($\mathrm{mol\,kg}^{-1}$) at any layer as a function of (z) at various reactors parameters. Fig. 2 shows simulated concentration profile using Eq. (10) at selected time intervals ($t_1 = 1$ h, $t_2 = 3$ h and $t_3 = 5$ h). Table 1 lists the column parameters used in simulation and calculation of Figs. 2–7.

From this simulation, the time at which the reactor starts to level off can be predicted under these conditions. As shown in Fig. 2 the normalized layer concentration of a given band decreases exponentially with the reactor height at the given selected time interval.

5.1. Theoretical validation

While it is difficult to experimentally study the effects of specific parameters on the behavior of the flow reactor, theoretical simulation can give us an insight into the flow reactor. Such simulation

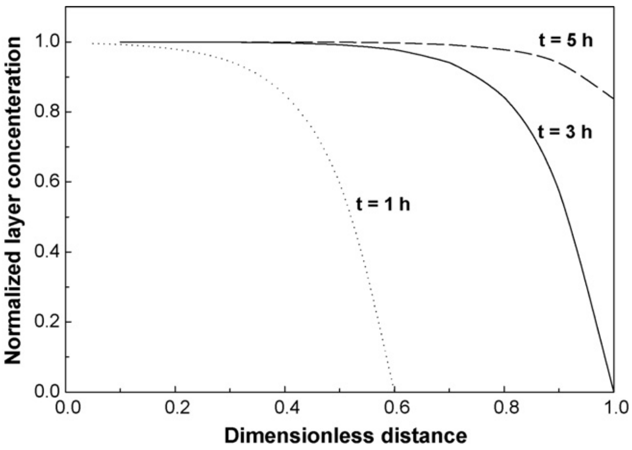

Fig. 2. Simulation profile for Eq. (10) for the rapid and slow steps.

indicates the effects of each parameter on the reactor efficiency. The reactor efficiency decrease in case of:

a) Flow of the species out of the reactor before attaining the maximum possible full capacity.
b) Decreasing in the full capacity without decreasing in the concentration of active sites on the resin bed.
c) Increasing in the time of leveling off without increasing in the reactor capacity. Eq. (10) will be used to study the effect of each parameter in the layer concentration profile along the height of the band theoretically. The leveling time is an effective factor in this simulation. It is an indication of column capacity if the flow, feed concentration and packing density are kept constant.

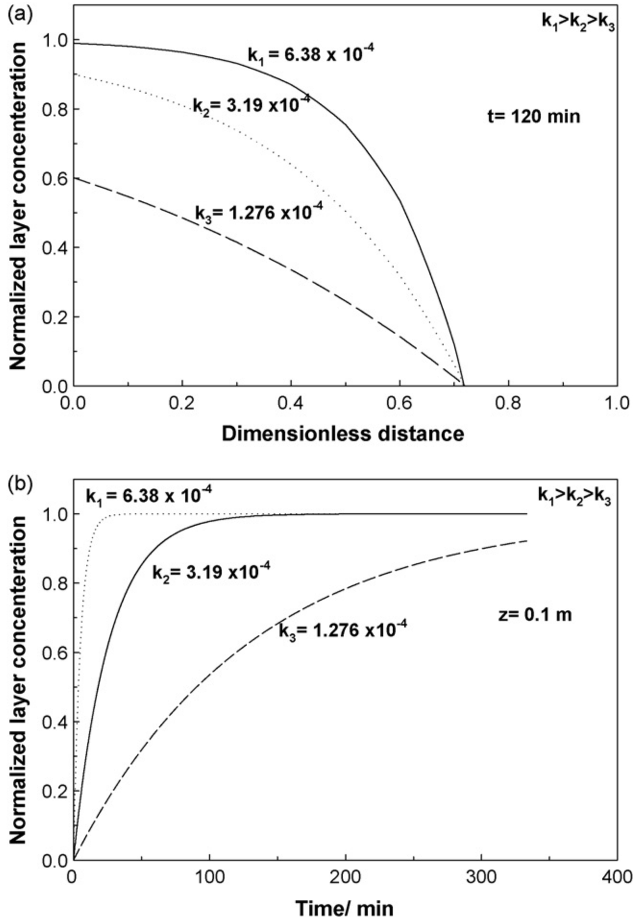

Fig. 3. (a) Profiles of layer concentration at different rate constants and (b) layer concentration–time relation at different rate constants at specific band width.

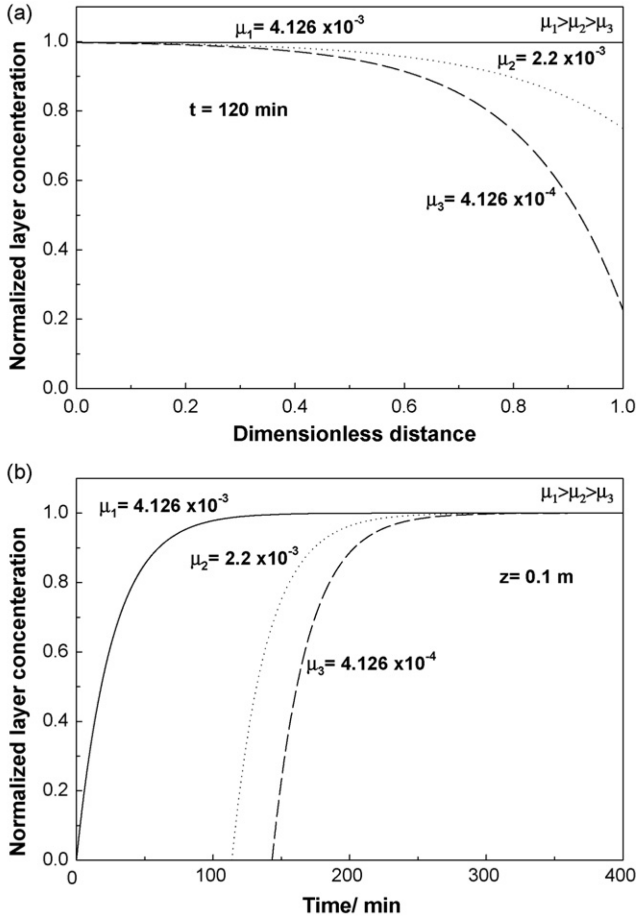

Fig. 4. (a) Profiles of layer concentration at different linear velocity of the fluid and (b) layer concentration–time relation at different linear velocity of the fluid at specific band width.

5.1.1. *Effect of the rate constant of adsorption*

Simulation of the reactor behavior using Eq. (10) at different values of the rate constant k is shown in Fig. 3a and b at time interval of ($t = 2$ h) and (band width $z = 0.1$ m). In Fig. 3a the concentration at a selected layer increases as the rate constant increases and the effect of the rate constant becomes more pronounced at the front than at the back of the bed.

Note that the increase in the rate constant k can be obtained with increase in temperature, increases the number of active sites. As shown in Fig. 3 as the rate constant an increases the time at which the sorption starts and the concentration at the selected point decreases. Also the time of leveling off decreases, i.e. the time required for saturation at this layer decrease. Hence the column efficiency increases.

5.1.2. *Effect of flow rate*

The increase in solution flow rate leads to decrease in the residence time of the solution within the bed and the beryllium diffusion as well. According to the assumed model, the increase in the linear velocity of solution may lead to an increase in the adsorption band length. Simulation of the reactor performance at different values of linear velocity of solution is shown in Fig. 4a and b at constant selected time interval ($t = 2$ h). The effect of the linear velocity of fluid becomes more pronounced at end of the column,

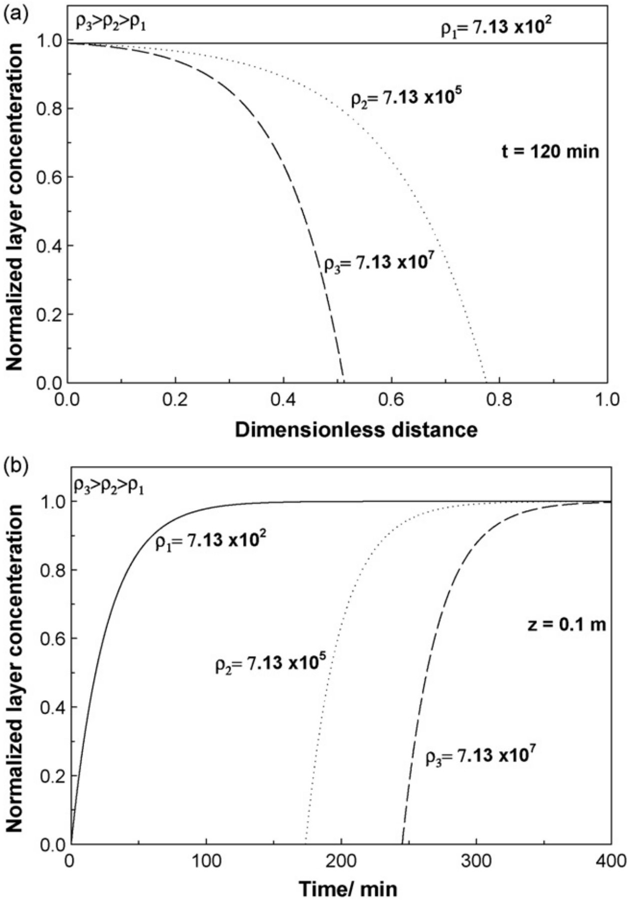

Fig. 5. (a) Profiles of layer concentration at different packing density and (b) layer concentration–time relation at different packing density at specific band width.

i.e. the band length increases as *u* increases. The linear velocity of solution has adverse effects on the elapsed time. For instant as the elapsed (residence) time increases the column efficiency increase. The decrease in column efficiency means an increase of the band length which may lead to flowing the examined species out of the column before attaining its full capacity. As shown in Fig. 4a and b, as the linear velocity of solution decreases, the time at which the sorption starts to at a selected point increases and the time of leveling off increases. In other words the time required for saturation at this layer increases which leads to an increase in the elapsed time required for saturation for the entire of column. This leads to decrease in the column efficiency. The reactor efficiency is sensitive to the change in the velocity of fluid. Optimization between the rate of sorption and the flow rate should be implied to attain better reactor efficiency.

5.1.3. Effect of packing density and void fraction

The void fraction ε can be defined as $\varepsilon = 1\text{-}(\rho/\rho_{real})$ where ρ is the packing density and ρ real is the real density of the packing solid (resin). From the definition, ε decreases as ρ increases. The suitable packing density should be optimized to give best performance. Formation of voids inside the column leads to formation of sites with no resin, which may accumulates air bubbles. The accumulation of air bubbles decreases the column efficiency.

The change in the packing density can be attained by two ways, changing the particle size or the volume of the bed. In the first way the specific surface area $(\text{cm}^2\,\text{g}^{-1})$ is changed too but in the second way the volume can be changed practically by adding an inert bed (particle) with the active bed (resin particle) so the volume is changed but the amount is not. The second way will be used in the following discussion to simulate the effects of packing density. By this way, the effect of the amount of active material in the column capacity can be compensated and in the same time the effect of packing in the reactor efficiency can be studied. Simulation of the column behavior using equation (10) at different values of (ρ) at constant selected time interval ($t = 2$ h) and at constant band width ($z = 0.1$ m) are shown in Fig. 5. As the packing density decreases the larger concentration increases as shown in Fig. 5a. As the packing density increase the column efficiency decreases if we keep the amount of active sites constant. As the packing density increases the time at which the sorption starts at a selected layer increases and the time of leveling off in turn increase, i.e. the required time for saturation increases. This can be attributed to the decrease in the void fraction, i.e. decreasing of the surface area of the active material. One important note should be explained here, the decrease in surface area due to the increasing of packing density is not enough to block the active sites in the reactor bed but it can lead to decrease in the availability of the active sites for sorption. The reactor capacity was not affected by the packing density if the amount of active material was constant. The effect of packing density becomes more pronounced in the leveling off stage than the initial stage.

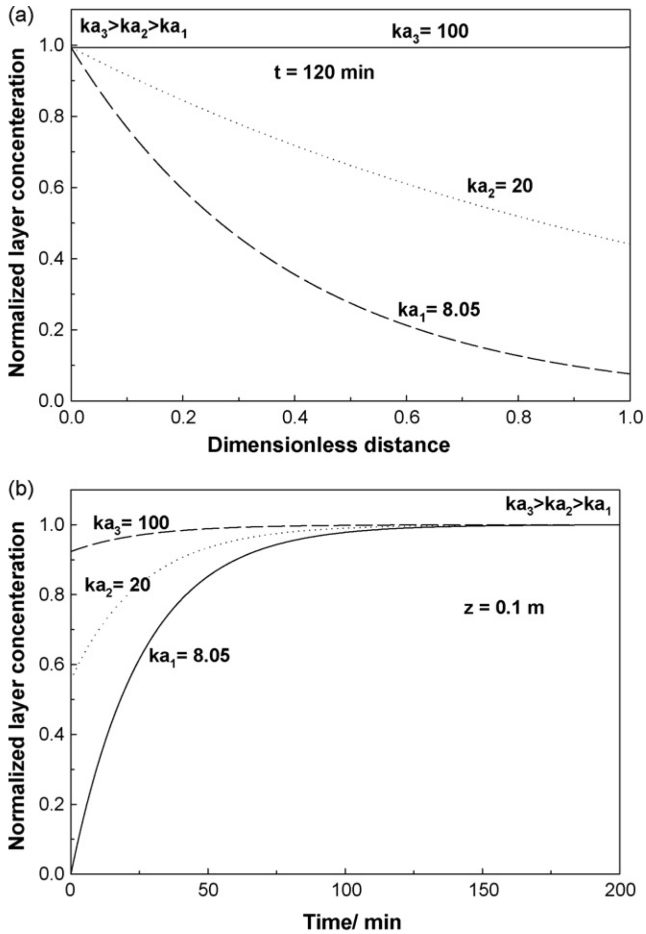

Fig. 6. (a) Profiles of layer concentration at different adsorption coefficient and (b) layer concentration–time relation at different adsorption coefficient at specific band width.

5.1.4. Effect of adsorption coefficient

According to the model assumptions, adsorption coefficient is the absolute ratio between the rate of change in the adsorbed ions concentration in the resin phase and the rate of change in the ions concentration in the solution phase. Simulation of Eq.

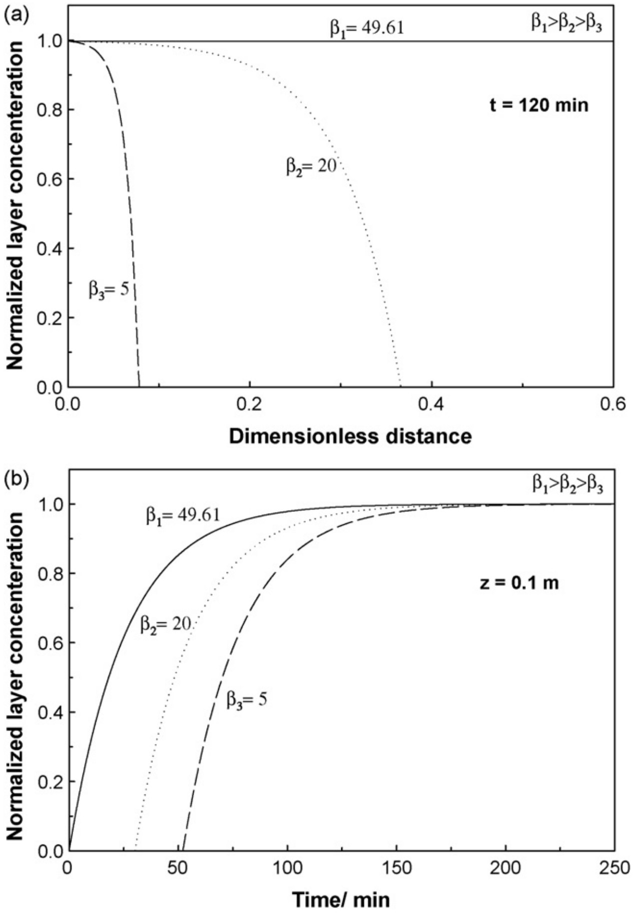

Fig. 7. (a) Profiles of layer concentration at different solid–liquid partition coefficient and (b) layer concentration–time relation at different solid–liquid partition coefficient at specific band width.

(10) at different value of the adsorption coefficient is shown in Fig. 6 at constant selected time interval ($t = 2$ h) and at constant band width ($z = 0.1$ m) taking $k_{a1} = 8.05\,\mathrm{kg\,m^{-3}}$, $k_{a2} = 20\,\mathrm{kg\,m^{-3}}$ and $k_{a3} = 100\,\mathrm{kg\,m^{-3}}$, respectively.

The rate of saturation of the selected layer and hence the efficiency of the column increases as the adsorption coefficient increases as shown in the simulated reactors (Fig. 6a and b).

5.1.5. *Effect of solid–liquid partition coefficient*

An important controlling parameter on the sorption process is the affinity of the resin to absorb the active ion from the mobile phase. The partition coefficient between two liquid phases is the concentration ratio of solute between the two phases at equilibrium. The ratio between the concentration of solute in the resin phase and that had not been extracted at equilibrium can be called solid–liquid partition coefficient β. It is an indication of the capability of the resin to adsorb the examined species from the mobile phase. After any selected time interval, the solid–liquid partition coefficient in the column is the ratio between the concentration of solute in the resin phase and in the mobile phase along the height of the column. It is clear from this definition, as the solid–liquid partition coefficient increases the adsorption extent increases. Consequently, the effect of increase in the solid–liquid partition coefficient, and hence, the decrease in leveling off time leads to an increase in the column efficiency. Simulation of the behavior of the flow reactor using Eq. (10) at different values of (β) is shown in Fig. 7a and b at a constant selected time interval ($t = 2$ h) and at constant band width ($z = 0.1$ m). As β increases the penetration inside the bed increases and the time required for specific attainment decreases. The increase in (β) leads to increase in the amount adsorbed along the heighet of the column.

6. Experimental validation

It is accepted that the resin ion-exchange processes normally are diffusion controlled and not reaction controlled [13]. The rate-controlling step can be diffusion across the liquid film surrounding the resin particle (film diffusion) or diffusion inside the particle (particle diffusion). In our previous studies [13] on the kinetics adsorption of Be(II) with Amberlite-IR-120 resins, we have indicated that:

- At the early stage of the process, the adsorption is rapid and the rate-determining step of the metal extraction is the liquid-film diffusion.
- At the final stage of the process, the adsorption is slow and the rate-determining step of the metal extraction is the matrix (resin)-phase diffusion.
- The two-stage concept allows the estimation of the mean or average diffusion coefficient which provides an insight into the diffusion mechanism and a parameter for subsequent design calculations.

The determined integration of equation (9) with respect to $\rho\,\mathrm{d}V$ from $V = 0$ to V_b ($\mathrm{m^3}$) will give the accumulated beryllium Q (mol) over all the reactor of a volume V (m^3) at a selected time interval t (s) if the process is explained by the previous suggested model, where V_b is the formed band volume at the given time interval t (s) and ρ ($\mathrm{kg\,m^{-3}}$) is backing density.

The integration of Eq. (9) will be given as follow:

$$Q(t,z) = \int_0^{v_b} q_{\max}(1 - \exp(\Psi z - kt))\rho\,\mathrm{d}v \qquad (11)$$

Given that $V_b = \pi r^2 Z_b$, $\mathrm{d}v = \pi r^2\,\mathrm{d}z$, z_b (m) is the band length and r is the column radius the integration will be in the form:

$$Q(t,z_b) = \left(\frac{\pi r^2 \rho q_{\max}}{\Psi}\right)[z_b\Psi - (\exp(\Psi z - kt)) + (\exp(-kt))] \qquad (12)$$

The two stages of adsorption mechanism represent a good general approach to the kinetics of metal extraction reactions on polymeric macroporous ion exchange resin. This makes us to apply this concept (two stage of adsorption) when we use Eq. (12). As the initial stage of adsorption involves a rapid metal uptake involving liquid-film diffusion, the determination of the reactors parameters k_r and Ψ_r (the subscript r indicates for the rapid step of adsorption) is possible. At the rapid step of the process z_b equals $k_r t/\Psi_r$ which allow the rewriting of Eq. (12) as function of (t) as follows:

$$Q(t,z_b) = \left(\frac{\pi r^2 \rho q_{\max}}{\Psi_r}\right)(k_r t + \exp(-kt) - 1) \qquad (13)$$

The experimental results allow the determination of k_r and Ψ_r using computer-based program knowing that $\rho = 7.13 \times 10^2\,\mathrm{kg\,m^{-3}}$ and $r = 6 \times 10^{-3}$ m using the above equation. The experimental linear fit of the last equation pass through the origin as it was expected with a correlation coefficient of 0.997 given that $k_r = 5.09 \times 10^{-4}\,\mathrm{s^{-1}}$ and $\Psi_r = 17.65\,\mathrm{m^{-1}}$. Nevertheless, the determination of k_r and Ψ_r is not sufficient to describe and interpret the influence of both phenomena (the slow and rapid steps). It is well known that the over all reactor kinetic is controlled by the slow step. At the leveling off stage (the slow step), z_b equals z_m, k equals k_s and Ψ equals Ψ_s where z_b is the band length, z_m is the reactor height and k_s and Ψ_s are reactor parameters for the slow step (the subscript s indi-

Table 2
A comparison between the first order rate constants which determined by column experiment with that determined by batch experiment of beryllium adsorption on Amberlite-IR-120 after the slow step and the rapid step is treated separately at 30 °C.

Batch experiment		Column experiment	
Rapid step		Rapid step	
k_r, s^{-1}	5.41×10^{-4}	k_r	5.09×10^{-4}
Corr.	0.984	Corr.	0.997
Slow step		Slow step	
k_s, s^{-1}	2.09×10^{-3}	k_s	1.1×10^{-3}
Corr.	0.918	Corr.	0.995

cates for the slow step of adsorption). So the linearization of Eq. (14) equation at the leveling off stage will give:

$$\ln\left(1-\frac{Q(t)}{\pi r^2 \rho z_m q_{max}}\right) = -k_s t + \ln\left(\frac{\exp(\Psi_s z_m)-1}{\Psi_s z_m}\right) \qquad (14)$$

The slope of the resulting experimental linear fit of the last equation is -1.1×10^{-3} and the intercept is 11.621 with a correlation coefficient of 0.995. By knowing the reactor height (z_m = 0.1 m), the reactor parameters k_s and Ψ_s were determined to be 1.1×10^{-3} s^{-1} and 38.14 m^{-1}, respectively. As shown from this result, k_r is not much greater than k_s which indicates the high affinity of Amb-IR-120 towards beryllium. Table 2 shows a comparison between the rate constants which determined by column experiment with that determined by batch experiment using pseudo-first order rate equation as a basic equation for derivation of the model equations. The comparability between k_r and k_s which measured experimentally in batch experiment with that measured using column experiment confirms the predicted mechanism, the validity of the predicted model and the suitability of Eq. (14) to simulate the over all process.

According to the developed model the ratio Ψ_r/k_r and Ψ_s/k_s for the rapid and slow steps, respectively, from a selected experiment should equal a constant value which is $(\rho - \varepsilon k_a/u\beta)$ if the model is valid. It is found to be 34.676×10^3 s m^{-1} for the rapid step while it is found to be 34.673×10^3 s m^{-1} for the slow step. This is another experimental validation for the predicted model.

Knowing $\rho = 7.13 \times 10^2$ kg m^{-3}, $\varepsilon = 0.434$ and $u = 4.126 \times 10^{-4}$ m s^{-1} from the column experiment and $k_a = 8.04$ kg m^{-3} from the batch experiment ($dC/dt = -k\, dq/dt$) allows the determination of β to be 49.61 kg m^{-3} from $(\Psi_r/k_r) = (\Psi_s/k_s) = (\rho - \varepsilon k_a/u\beta)$.

The previous model is a general model, which could be applied to describe the physical picture of the retention of any species by a fixed bed reactor. The suggested model is approved to simulate the system under investigation theoretically. Experimental validation for the model could be established by comparing the computed values for the accumulated beryllium Q (mol) over the entire reactor after a selected time intervals with those which obtained experimentally. Computing of $Q(t,z)$ requires knowing of the band length z at the selected time interval t. The band length will be calculated from the relationship which states that $z = kt/\Psi$ at the initial stage of retention while $z = z_m$ at the leveling off stage.

The model described above (Eqs. (12)–(14)) applied to the experimental data in flow system experiment at 31 °C. The shape of the curve representing metal uptake versus time (Fig. 8) suggests a two-step mechanism.

Fig. 9a and b shows a comparison between the measured Q–t relations for beryllium retention by a column backed with Amb-IR-120 with those predicted by the presented model after the application of the two stages concept. This figure indicated that the agreement between the measured and the predicted results by the suggested model is satisfactory in most of the flow stages as the greater part of accumulation takes place during the fast step the column capacity is controlled by the fast step.

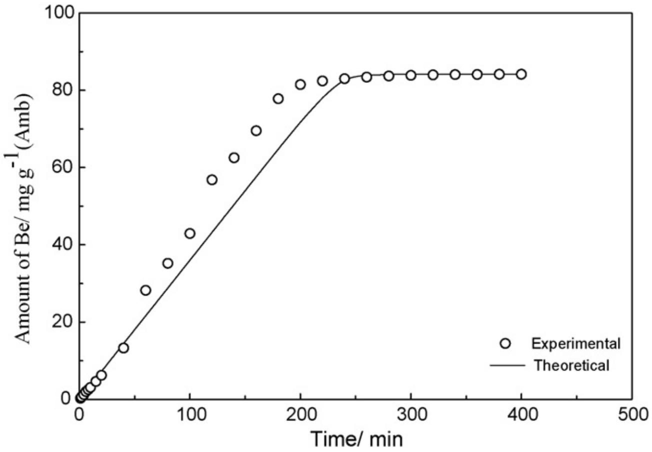

Fig. 8. Comparison between experimental and calculated data for flow system experiment at 31 °C.

This model is very useful for prediction of the reactor uptake, and the predicted value satisfactory agrees with the measured one. It is also useful to predict the time of complete saturation with beryllium. The effect of the working parameters (solution and column composition, reactor design, working condition, etc.) on the reactor performance can be studied directly or indirectly using the

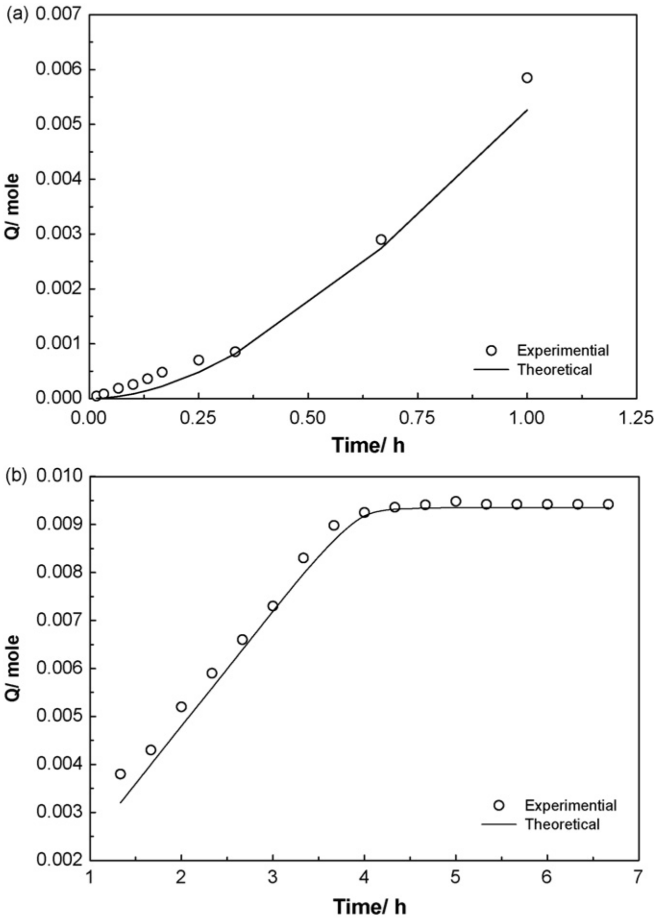

Fig. 9. (a and b) Comparison between the experimentally obtained data for the accumulated beryllium and that calculated for (a) the rapid step and (b) the slow step.

suggested model and this can be suggested to be the near future work. The obtained data will be used in the design of a column reactor for the beryllium uptake upon Amb-IR-120.

7. Summary and conclusions

A mathematical model has been developed to simulate beryllium retention within a fixed bed reactor of Amb-IR-120 exchange resin. For this purpose, several structural, kinetic and hydrodynamic parameters have been taken in consideration. The model predictions of the accumulated uptake, *Q* has been verified by comparing the experimental data with the calculated data. A satisfactory agreement between the model prediction and the experimental data was obtained. Theoretical results and the compared experimental data can be used for optimization of the operating parameters and design purpose.

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