

Mass Transfer Modeling of Nitrate in an Ion Exchange Selective Resin

A. A. Hekmatzadeh, A. Karimi-Jashani, and N. Talebbeydokhti

Abstract—The rate of nitrate adsorption by a nitrate selective ion exchange resin was investigated in a well-stirred batch experiments. The kinetic experimental data were simulated with diffusion models including external mass transfer, particle diffusion and chemical adsorption. Particle pore volume diffusion and particle surface diffusion were taken into consideration separately and simultaneously in the modeling. The model equations were solved numerically using the Crank-Nicholson scheme. An optimization technique was employed to optimize the model parameters. All nitrate concentration decay data were well described with the all diffusion models. The results indicated that the kinetic process is initially controlled by external mass transfer and then by particle diffusion. The external mass transfer coefficient and the coefficients of pore volume diffusion and surface diffusion in all experiments were close to each other with the average value of 8.3×10^{-3} cm/S for external mass transfer coefficient. In addition, the models are more sensitive to the mass transfer coefficient in comparison with particle diffusion. Moreover, it seems that surface diffusion is the dominant particle diffusion in comparison with pore volume diffusion.

Keywords—External mass transfer, pore volume diffusion, surface diffusion, mass action law isotherm.

I. INTRODUCTION

NITRATE is a common pollutant of groundwater in many regions around the world. Chemical fertilizer used in crop production and municipal or industrial wastewaters are characterized as the extensive source of nitrate in water sources [1]-[3]. The high concentration of nitrate in drinking water is a serious hazard to human health such as cancerous diseases in digestion system and blue baby syndrome in infants under six month. Moreover, nitrate can cause several environmental problems such as eutrophication in water supplies [4]-[6]. Ion exchange is considered as an attractive and feasible method for nitrate removal from aqueous solution due to its high efficiency, simple operation, and its regeneration offering long lifetime. It usually independent of the solution pH and can be achieved quantitatively [3], [5]-[7].

Several empirical, simplified kinetic models and more theoretical kinetic models have been developed to describe ion exchange mechanism. Pseudo first order and Pseudo second order models are the example of the empirical models. Several

researchers have used the empirical and simplified methods to illustrate the kinetics of ion exchange process [6]-[10].

However, they do not consider the rate limiting steps and they do not give any information about real kinetic mechanism consist of mass transfer through the particle and the film surrounding them. Determining the diffusion coefficients using the appropriate kinetic models enable ones to use these information in designing purpose and predicting the nitrate breakthrough curve of fixed bed columns in a real water treatment processes [11]-[13]. Although considerable researches have been performed on nitrate adsorption to several ion exchange resins, little attention has been given to the rate of nitrate adsorption and determining which kinetic mechanism is the rate controlling.

In this work, the overall rate of nitrate adsorption from aqueous solutions using a nitrate selective ion exchange resin was studied. Several batch kinetic tests were arranged including different initial nitrate concentration and different adsorbent dosage. A full rate kinetic model including external mass transfer, particle pore diffusion, and particle surface diffusion were developed and solved numerically using the Crank-Nicholson scheme in MATLAB software. Particle pore volume diffusion and particle surface diffusion were taken into consideration separately and simultaneously in the modeling. Also, an optimization technique was employed to optimize the model parameters.

II. EXPERIMENTAL

The ion exchange resin used in this study is a macro porous strongly basic nitrate selective anion exchange resin called, IND NSSR. The effective sizes of the resin particles range from 0.4 to 0.5 mm containing exchangeable chloride ion. The stock solution of nitrate used in these experiments was prepared by dissolving a specific amount of NaNO_3 in distilled water. a temperature-controlled rotating shaker was used to carry out several well-stirred batch kinetic and batch equilibrium tests. To perform the kinetic tests, a fixed accurately quantity of dry resin (0.05, 0.15, 0.3 and 0.5 g) was added to several glass bottles, containing 200 ml of nitrate solution with initial nitrate concentrations of 58.9, 87.25, and 119.4 mg/L. The bottles were sealed and placed in the shaker and were withdrawn from the shaker at selected intervals of time to measure the nitrate concentration.

In order to obtain the equilibrium data, different accurately weighted amounts of resin (0.025 to 0.8 g) were added to the bottles containing nitrate solutions of various concentration (60, 90, and 120 mg/l). The bottles were placed in the shaker for 24 hours to reach equilibrium. In these experiments, the temperature and pH were kept constant at 20°C and 7, respectively.

A. A. Hekmatzadeh is with the department of civil and environmental engineering, Islamic Azad University, branch of Eghlid, Eghlid, Iran, (phone: +98-752-4252600; fax: +98-752-4253318); e-mail: hekmatzadeh@yahoo.com, hekmatz@shirazu.ac.ir).

A. Karimi-Jashani, is with the department of civil and environmental engineering, Shiraz University, Shiraz, Po. Box 7134851156, Iran. (e-mail: akarimi@shirazu.ac.ir).

N. Talebbeydokhti is with the department of civil and environmental engineering, Shiraz University, Shiraz, Po. Box 7134851156, Iran. (e-mail: taleb@shirazu.ac.ir).

III. MATHEMATICAL MODELING

The adsorption process of ion exchange resin consists of three general mechanisms: (i) external mass transfer through the liquid film surrounding the ion exchange particles associated to film diffusion, (ii) mass transfer in the exchanger phase associated to particle diffusion, and (iii) chemical interaction between counterions and fixed group. The particle diffusion may be caused by mass transfer through pore volume (pore diffusion) or mass transfer on the solid surface (surface diffusion) or a combination of both [14]-[16].

In order to interpret the adsorption rate of nitrate to resin particles, the mathematical model (Equation 1) was developed by applying a mass balance in a differential element of an adsorbent particle including all diffusion mechanisms [16]-[18]. This model was derived by assuming instantaneous chemical interaction between adsorbate and adsorbent surface. Hence, local equilibrium exists between liquid phase and solid phase in the pore space and therefore an equilibrium isotherm model should be considered. Moreover, spherical resin particles were supposed.

$$\varepsilon_p \frac{\partial C}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_p r^2 \frac{\partial C}{\partial r} \right] + \frac{\rho_p}{r^2} \frac{\partial}{\partial r} \left[D_s r^2 \frac{\partial q}{\partial r} \right] \quad (1)$$

The initial and boundary conditions of the above equation are as follow:

$$C = 0, 0 \leq r \leq a_p, t = 0 \quad (2)$$

$$\frac{\partial C}{\partial r} = 0, r = 0, t \geq 0 \quad (3)$$

$$D_p \frac{\partial C}{\partial r} + \rho_p D_s \frac{\partial q}{\partial r} = K_f (C_b - C), r = a_p, t \geq 0 \quad (4)$$

Equation 1 and its boundary condition (equation 4) contain three unknown variable: C , C_b , and q and therefore two more relationships are needed to solve the respective equations. The mass balance for the batch system is represented by the following equations [13], [18]

$$\frac{d\bar{q}}{dt} = \frac{M}{V} \frac{dC_b}{dt} \quad (5)$$

$$\bar{q} = \frac{3}{a_p^3} \int_0^{a_p} q r^2 dr \quad (6)$$

Because of assuming local equilibrium in particle pore space, the mass action law isotherm model was used to explain the relationship between C and q [19], [20].

$$q = \frac{k q_T C}{C_0 + (k-1)C} \quad (7)$$

Equation 1 is a general diffusion model, which contains both pore volume diffusion and surface diffusion with external

mass transfer. This model was entitled as pore volume surface diffusion model, PVSDM [16], [21]. If the surface diffusion is neglected, equation 1 change to a simpler form, nominated as pore volume diffusion model, PVDM. In the other hand, if the surface diffusion is the only particle diffusion mechanism, the model called surface diffusion model, SDM [16], [21]. A computer code was developed and run in the MATLAB software using finite difference techniques to simultaneously solve Equation 1 to 7. The Crank-Nicolson approximation, centered in space was employed to state the time and length derivatives in the equations.

The model parameters can be obtained by minimizing an objective function. This function can be stated as sum of the square errors (SSE) between experimental data and the model estimations.

$$SSE = \sum_{i=1}^n (C_{\exp,i} - C_{\text{model},i})^2 \quad (8)$$

Where C_{\exp} and C_{model} are the experimental and model predictions of nitrate concentration obtained in the solution. The 'lsqnonlin' function in the optimization toolbox of MATLAB software was used to optimize the values of the aforementioned parameters. This function uses non-linear least square techniques to minimize the objective function.

IV. RESULT AND DISCUSSION

The adsorption isotherms of nitrate ions by the resin particles for the different batch equilibrium tests are shown in Fig. 1. The equilibrium data were approximated by the mass action law isotherm (Equation 7). Non linear regression analysis was employed to determine the isotherm constants, k and q_T . The estimated isotherm parameters are $q_T=2.55$ meq/l and $k=5.7$ and the correlation coefficient is 0.96, which indicates a satisfactory description of each set of the equilibrium data by the isotherm model.

The contribution of both external mass transfer coefficient and particle diffusion (pore volume and surface diffusions) was investigated through PVDM, SDM, and PVSDM. Fig. 2(a) and Fig. 2(b) show the experimental decay time profiles of nitrate adsorption onto resin particles at different initial solute concentration and different mass of resin, and the model predictions with PVDM using optimized model parameters. In the PVDM model, the surface diffusion has been neglected. As shown, the mentioned model well describes the experimental data. The correlation coefficients for all experiments were computed and reported in Table I. All correlation coefficients are in excess of 0.95, indicating satisfactory fitted of model prediction and experimental data. The model constants (k_f and D_p) was estimated by minimizing the sum of residual squares (SRS) between measured and calculated nitrate concentration in the solution. The estimated values of k_f and D_p are in the range of 6.35×10^{-3} to 11.3×10^{-3} cm/S, and 4.58×10^{-5} to 1.11×10^{-4} cm²/S, respectively and they are reported in the Table I. The calculated values of external mass transfer coefficient (k_f) are close to each other with the average value of 8.3×10^{-3} cm/S.

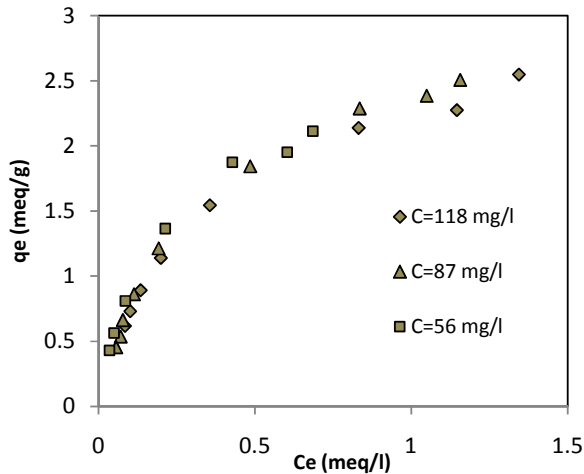


Fig. 1 Meseasured experimental isotherm data for three set of batch equilibrium tests with different initial nitrate concentration

In order to quantify the effect of k_f and D_p on the model prediction, sensitivity analysis was performed on the result of kinetic test with an initial nitrate influent concentration of 119.4 mg/l and the resin mass of 0.5 g. The value of D_p varied between 100 times lower and 100 times higher than the optimized value (i.e., $1.05 \times 10^{-4} \text{ m}^2/\text{s}$) and the value of k_f ranged in 10 times lower and 10 times higher than the estimated value (i.e., $7.25 \times 10^{-3} \text{ m/s}$). According to the result of sensitivity analysis given in Fig. 3, the model predictions are influenced by both parameters. The larger the external mass transfer coefficient, the smaller mass transfer resistance in the film around the particles, consequently the steeper decay concentration curve especially in the initial part of the decay concentration profile. Similarly, the larger the pore volume diffusivity, the smaller the mass transfer resistance in the particles, as a result a sharper concentration decay profile. However, the initial part of the concentration decay curve less affected by changing in the D_p . this results indicate that the kinetic process is initially controlled by external mass transfer and then by intraparticle diffusion. In addition, a decrease in k_f and D_p has much greater impact on the sensitivity of the model than does a rise in the values of these variable.

Afterward, the experimental kinetic data were simulated with SDM and the comparison between experimental concentration decay curve and the model predictions with optimal estimations are shown in Fig. 4. As shown, the model predictions and the experimental data are fitted very satisfactory. The high correlation coefficients given in Table I represent the satisfactory of model predictions. The optimal external mass transfer (k_f) and the surface diffusion (D_s) coefficients were obtained by minimizing of equation 8 as described before, and the estimation are presented in Table I. The estimated values of k_f with this model were nearly the same with those obtained with PVDM, ranging from 6.1×10^{-3} to $10.7 \times 10^{-3} \text{ cm/S}$, while the estimation of D_s are between 1.2×10^{-8} to $5.5 \times 10^{-8} \text{ cm}^2/\text{S}$. Furthermore, sensitivity analysis on this model lead to similar results obtained by PVDM, which for the sake of brevity they were not presented here.

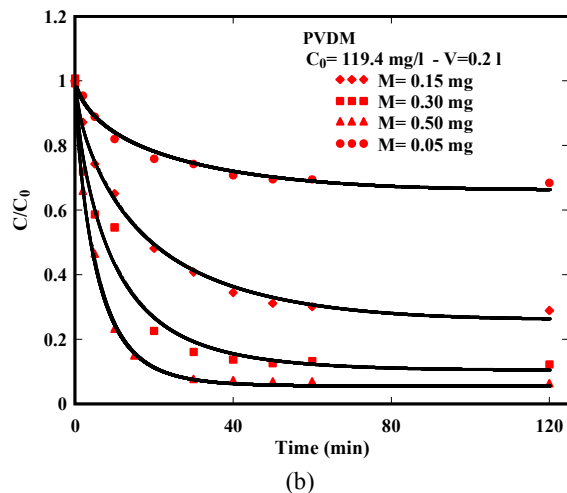
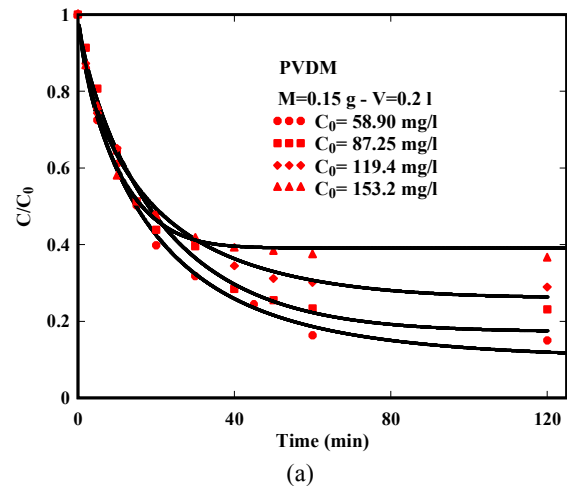


Fig. 2 Experimental and calculated decay time profiles with PVDM of nitrate adsorption onto resin particles (a) at different initial solute concentration (b) different mass of resin

The contribution of both pore volume and surface diffusion with external mass transfer were considered in PVSDM. The estimated values of k_f , D_p , and D_s obtained from PVDM and SDM as described previously were used in PVSDM to predict the experimental kinetic curves (Fig. 5). According to Fig. 5, although the predictions with PVSDM using model parameters of PVDM and SDM less estimated the decay concentration curve, the predictions were close to the experimental data and the model precisions were satisfactory. Afterward, PVSDM was solved for different values of D_p and D_s and then the resulting kinetic profiles were compared to experimental decay profiles to find the best fitting values of D_p and D_s . Different values of D_p and D_s contributed to give the same model prediction with PVDM. Table II shows these values for a kinetic test with an initial nitrate concentration of 119.4 mg/l and a resin mass of 0.5 g.

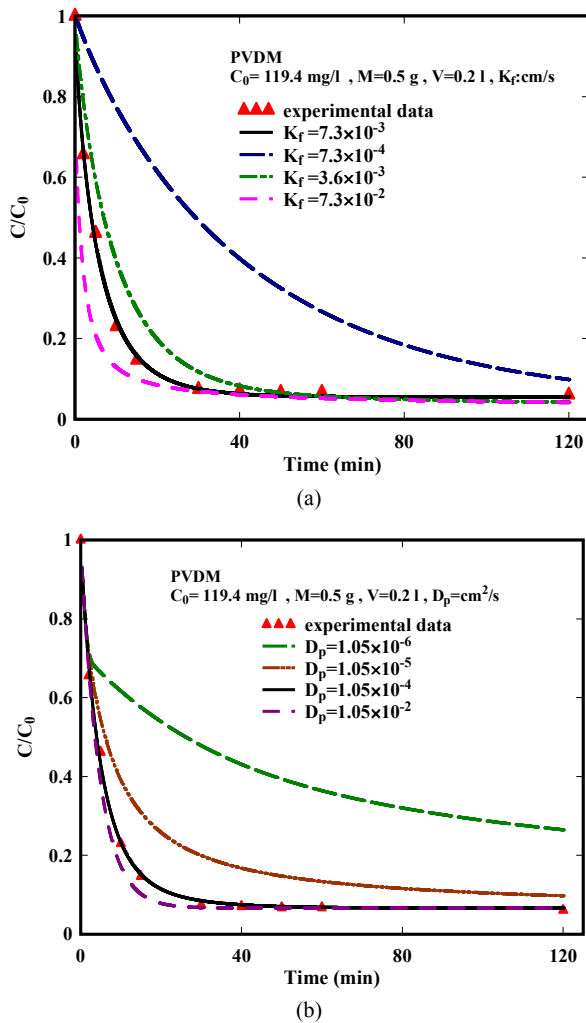


Fig. 3 Effect of variation in model parameters values on concentration decay profile: (a) external mass transfer coefficient, k_f (b) pore volume diffusion coefficient, D_p

The effective pore volume diffusion coefficient can be predicted by the following equation:

$$D_p = \frac{\varepsilon_p D_m}{\tau} \quad (9)$$

Where D_m is the molecular diffusion of nitrate in infinite solution, ε_p is the particle porosity (0.341) and τ is the Tortuosity. The diffusion coefficient of nitrate in water in literature was obtained to be between 0.5×10^{-5} to 2×10^{-5} cm²/s [22]-[23]. The tortuosity of this resin is not known, a tortuosity of three was assumed based on works with the other types of macroporous resins [24]. Assuming the higher value for molecular diffusion, the pore volume diffusion coefficient based on equation 9 is computed to be 2.09×10^{-6} cm²/s, which is much smaller than those obtained by PVDM. Afterward, the new values of surface diffusion coefficients for all experiments calculated using PVSDM by considering D_p equal to 2.09×10^{-6} cm²/s and the computation was close to the

values of D_s obtained by SDM (Table I). Consequently, the surface diffusion is the dominant particle diffusion in this resin.

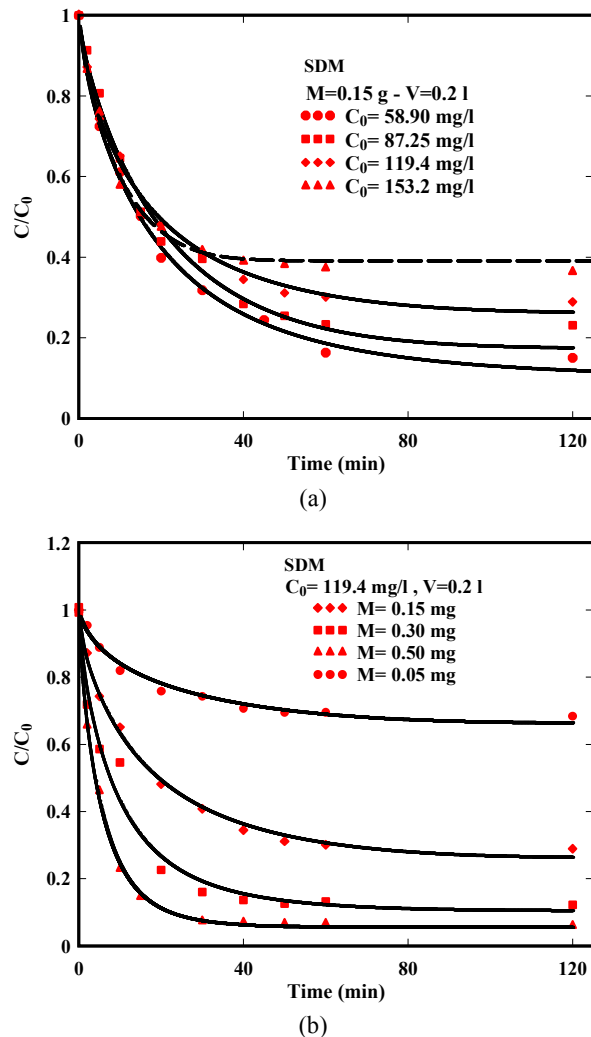


Fig. 4 Experimental and calculated decay time profiles with SDM of nitrate adsorption onto resin particles (a) at different initial solute concentration (b) different mass of resin

TABLE I
MODEL PARAMETERS OF PVDM AND SDM FOR DIFFERENT BATCH KINETIC EXPERIMENTS

Solutions	PVDM				SDM				Initial concentrations and resin masses	
	K_f cm/s	D_p cm ² /s	RMSE meq/l	R^2	K_f cm/s	D_s cm ² /s	RMSE meq/l	R^2	NO_3^- mg/l	m g
Sol. 1	0.00796	5.92E-05	0.015	0.996	0.0081	1.18E-08	0.015	0.996	58.88	0.15
Sol. 2	0.00635	1.11E-04	0.027	0.995	0.0061	4.12E-08	0.026	0.995	87.25	0.15
Sol. 3	0.00855	5.70E-05	0.023	0.998	0.0079	3.83E-08	0.024	0.997	119.39	0.15
Sol. 4	0.00936	1.10E-04	0.044	0.993	0.0083	1.21E-07	0.044	0.993	153.17	0.15
Sol. 5	0.0143	4.58E-05	0.015	0.995	0.01076	5.51E-08	0.013	0.996	119.39	0.05
Sol. 6	0.00713	7.28E-05	0.096	0.972	0.0074	2.67E-08	0.096	0.972	119.39	0.3
Sol. 7	0.00725	1.05E-04	0.030	0.997	0.0073	3.14E-08	0.028	0.998	119.39	0.5

TABLE II
DIFFERENT VALUES OF D_p AND D_s CONTRIBUTE TO GIVE THE SAME MODEL PREDICTION WITH PVSDM

Model run	D_p cm ² /s	D_s cm ² /s
Run 1	9.49E-05	9.43E-09
Run 2	7.38E-05	1.57E-08
Run 3	5.27E-05	2.20E-08
Run 4	3.16E-05	2.83E-08

Kinetic test with an initial nitrate influent concentration of 119.4 mg/l and a resin mass of 0.5 g

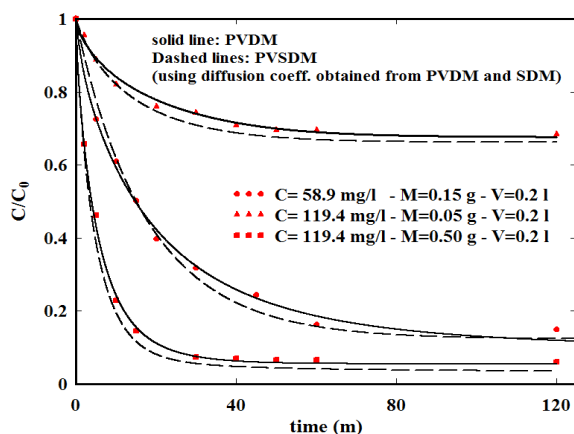


Fig. 5 Experimental and calculated decay time profiles with PVSDM using model parameters obtained from PVDM and SDM for three set of kinetic data

V. CONCLUSION

The adsorption kinetic of nitrate to a selective ion exchange resin was studied in several batch kinetic tests. The nitrate concentration decay curve data were modeled by different diffusion models based on external mass transfer and particle diffusion. Particle pore volume diffusion and particle surface diffusion were taken into consideration separately and simultaneously in the modeling. All diffusion models describe the experimental data very well.

It was found that the kinetic process is initially controlled by external mass transport and then by intraparticle diffusion. In addition, the models are more sensitive to mass transfer coefficient (k_f) in comparison with particle diffusion (D_p and D_s). The higher values of particle diffusion (more than estimated values) have little effect on the prediction of nitrate concentration decay curve in comparison with lower values. Moreover, the external mass transfer coefficient in all experiments are close to each other with the average value of 8.3×10^{-3} cm/s. furthermore, it seems that surface diffusion is the dominant particle diffusion in comparison with pore volume diffusion.

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