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Extended adsorption transport models for permeation of copper ions through nanocomposite chitosan/polyvinyl alcohol thin affinity membranes

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ABSTRACT

Transport of copper ions through nanocomposite chitosan/polyvinyl alcohol thin adsorptive membranes has been mathematically investigated in the current study. Unsteady-state diffusive transport model was coupled with the Freundlich isotherm to predict the concentration of the ions in dialysis permeation operation. Pristine model was not successful in predicting the experimental data based upon its low coefficients of determination ($0.1 < R^2 < 0.65$). Well-behaved polynomial and exponential functions were used to describe time-dependency of the inlet-concentration in the first extension of the model with a little improvement in the model adjustment ($0.4 < R^2 < 0.69$). Similar time-dependent functions were employed for tracking the ion diffusivity and then applied in combination with the optimized functions of inlet-concentration in the second extension of the model. A sensible enhancement was obtained in the adjustment of the second extended models as a result of this combination ($0.73 < R^2 < 0.93$). APRE, AAPRE, RSME, RMSE, STD and R-square statistical analyses were performed to verify the agreement of the models with the experimental results. Concentration distribution versus time and location (inside the membrane) was obtained as 3D plots with the help of the optimized models. Modeling results emphasized on the transiency of diffusivity and feed-side concentration in dialysis permeation through chitosan membranes.

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1. Introduction

In recent years, membrane technology has attracted increased attention among researchers due to conspicuous advantages such as low energy consumption, high separation efficiency, small footprint, ease of scale up and comfortable monitoring and control [1–2]. Membrane adsorption i.e., integration of membrane and adsorption concepts, has also emerged as an effective technique for the removal of a wide range of pollutants such as dyes, macromolecules, humic substances and heavy metals from aqueous environments [3–8]. Chitosan (a natural polysaccharide biopolymer) and its blends with other hydrophilic polymers like polyvinyl alcohol and cellulose acetate are potential materials for fabricating membrane adsorbents [9–13]. Thermodynamic and kinetic study of membrane adsorption processes is also of great importance, especially for detailed characterization of adsorbents, better process design, optimization and scale up [14–16]. Moreover, thermodynamic studies reveal a good deal of information on heat sensitivity, favorability and isothermal nature of adsorption. Kinetic models however, provide useful insight of mechanisms incorporated

in adsorption as well as the time required for completion of adsorption capacity [7,17].

Mathematical modeling is regarded as an important part of process development studies especially in progressive separation fields like membrane adsorption. Mathematical modeling of membrane adsorption as an immature separation technology has recently attracted specialist researchers' attention [18–23]. Rapid prototyping and presenting efficient scale-up strategies (from lab to full scale) are some major benefits of modeling projects. Comprehensive knowledge of the adsorption/transport mechanisms is also another possible outcome. Mathematical modeling is rather a state of the art approach for efficient analysis of dialysis permeation using affinity membranes. In other words, lack of accurate and straightforward transport models for the simulation, optimization and data prediction is obvious in dialysis process using membrane adsorbents.

In few works, adsorptive transport through affinity membranes has been mathematically investigated [20,21]. These types of models take advantages of convection, diffusion and adsorption mechanisms in combination. Some drawbacks are mainly resulted from rough assumptions of the proposed models that are commonly employed for simplicity and ease of application. Model extensions generally do revise rough hypotheses/assumptions accompanied by the pristine models. This may

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result in development of the models and also improvement of their agreement with the experimental results. In some extended models, effects of systems non-idealities such as dead regions, delay times, porosity variation and simultaneous transport of several solutes have been taken into account [21–24].

A large number of the adsorption-transport models are supported by the results of the thermodynamic and/or kinetic analyses of batch adsorption. For example, Langmuir–Freundlich isotherm has been used to describe adsorption equilibrium in a convection/diffusion/adsorption combined model developed for predicting Ni(II) ion transport through an ion-imprinted affinity membrane [23]. Thermokinetic analysis of papain adsorption on ligand-immobilized chitosan-coated nylon membranes revealed an endothermic and spontaneous adsorption [25]. In addition, rapid protein uptake was recognized on the basis of superior adjustment of the pseudo-second-order kinetic model to the experimental data. Freundlich isotherm could appropriately represent the equilibrium adsorption of the enzyme on the chitosan-coated membranes. Thin (12–15 μm thick) membrane adsorbents have been fabricated from chitosan/poly(vinyl) alcohol blend containing different values of aminated multi-walled carbon nanotubes and investigated for adsorption of Cu(II) by the current authors [5,16]. To our knowledge, transport aspects of thin membrane adsorbents have not been adequately tackled in literature. In addition, effects of time-dependency of model components like diffusivity coefficient have not been addressed elsewhere.

This study is oriented to provide a mathematical model and computer-aided framework for the simulation of Cu(II) diffusive transport through thin membrane adsorbents applied in dialysis permeation. As a novel approach, effects of feed-side concentration and diffusivity variation during dialysis transport are investigated in the model extensions. Different polynomial and exponential functions are employed and validated using the model solver program to attain appropriate representation of time-dependency of the inlet-concentration and diffusivity. The most important advantage of the current study is to disclose the transient nature of diffusivity and inlet concentration during dialysis transport through the membranes.

2. Experimental

Chitosan/polyvinyl alcohol nanocomposite membrane adsorbents, prepared via the solvent evaporation technique, have been fully studied in our previous publications [5,16]. Some important properties of the synthesized membranes are listed in Table 1. Batch adsorption experiments and isothermal, thermodynamics and kinetics have been also investigated and discussed in the above-mentioned works from the current authors. We utilized thermokinetic study results obtained in our prior projects for the purpose of model development in the current study.

Permeability of Cu(II) ions through the membranes was monitored using a long-time batch permeation dialysis setup at room temperature and pH = 5.5. The experimental procedure has been explained with full details elsewhere [26]. Briefly, a two-section dialysis setup was applied for this purpose. Membrane samples were placed and sealed (using proper O-rings) between the two half-cells of the setup. Feed-side and receive-side half-cells were filled with 100 ml of 20 $\text{mg} \cdot \text{L}^{-1}$ copper

nitrate solution and double-distilled water, respectively. Three hours once, 3 ml samples were taken from the receive solution and then, immediately compensated with the same amount of distilled water. Copper concentration in the samples was analyzed by a flame atomic absorption spectrophotometer (AA-6300 Shimadzu).

3. Mathematical Framework

Adsorption-transport model, in unsteady state mode, has been applied to describe the transport behavior of copper ions through the membrane adsorbents. This model has been frequently applied and validated in transport modeling of affinity membranes in literature [20,21,24]. Some hypotheses and assumptions have been employed to adapt the adsorption-transport model for the dialysis permeation system:

- 1- Ion transfer through the membrane adsorbent is assumed to be one dimensional (perpendicular to the membrane surface), with negligible dispersion in the direction of the ions transport.
- 2- Mechanism of transport through the membrane is controlled by adsorption and diffusion simultaneously. It is assumed that the convective transport mechanism plays no significant role in this stationary system from hydrodynamic viewpoint.
- 3- Freundlich isotherm is the best-fitted model for describing equilibrium adsorption of Cu(II) ions on the membrane surface and pore walls according to the results obtained in our prior works [5,16,26]. Beside adsorption, physical attachment phenomena such as sieving, pore filling and inertia (drag) retardation can act as retarding mechanisms. These mechanisms are essential components of unsteady-state term in the governing equation (final PDE) obtained through the modeling.

3.1. Pristine model

Concentration variation *versus* time and distance (measured from the membrane inlet) can be obtained based on basic mass balance concepts. The resultant governing equation is obtained as follows:

$$\varepsilon \frac{\partial C}{\partial t} + (1-\varepsilon)\rho_s \frac{\partial Q}{\partial t} = \varepsilon D_i \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where ε is the membrane bulk porosity, ρ_s is the density of the copper ions ($\sim 8.96 \text{ g} \cdot \text{cm}^{-3}$), C is equilibrium concentration in the aqueous phase equilibrated with the adsorbed phase, Q is the equilibrium adsorbed phase concentration, D_i is the diffusion coefficient of copper ions ($D_0 = 2.5 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ in pristine model) and x represents the transport direction perpendicular to the membrane surface.

Chitosan polymer interacts with the cations through its amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) functional groups as reactive sites. The Freundlich isotherm model offers the best interpretation of the adsorption equilibrium based on the isothermal investigations performed in our previous work [16]. The isotherm equation is as follows:

$$Q = k \cdot C^m \quad (2)$$

k and m are Freundlich isotherm constants which have been obtained elsewhere [5]. One can combine Eqs. (1) and (2) by using simple

Table 1
Characteristics of nanocomposite membrane adsorbents [5]

Membrane (abbreviation)	Made of	MWCNT content /%	Water absorption /%	Bulk porosity /%	Thickness / μm	Maximum adsorption capacity / $\text{mg} \cdot \text{g}^{-1}$
M0	Chitosan/polyvinyl alcohol	nil	134 $\pm$ 5	8 $\pm$ 2	12–15	11.1
M0.5	Chitosan/polyvinyl alcohol /MWCNTs	0.5	172 $\pm$ 5	20 $\pm$ 5	12–15	15.0
M1	Chitosan/polyvinyl alcohol /MWCNTs	1	195 $\pm$ 5	17 $\pm$ 5	12–15	18.3
M2	Chitosan/polyvinyl alcohol /MWCNTs	2	222 $\pm$ 5	12 $\pm$ 2	12–15	20.1

chain role differentiation technique and obtain the following governing equation:

$$(\varepsilon + \rho_s(1-\varepsilon) \cdot k \cdot m \cdot C^{m-1}) \frac{\partial C}{\partial t} = \varepsilon D_i \frac{\partial^2 C}{\partial x^2}. \quad (3)$$

Eq. (3) is the pristine model structure in which constant diffusivity coefficient ($D_i = D_o$) and inlet concentration ($C_i = C_o$) are applied. In next section, we try to modify some uncertain hypotheses of this model. The model includes one dependent variable (C) and couple of independent variables (t and x) and thus, requires two boundary conditions and one initial condition as follows:

$$C = C_i \quad x = 0, t > 0 \quad (4)$$

$$\frac{\partial C}{\partial x} = 0 \quad x = \delta, t > 0 \quad (5)$$

$$C = 0 \quad x > 0, t = 0. \quad (6)$$

At feed inlet ($x = 0$), the inlet (feed-side) concentration is C_i . Concentration of the ions in the vicinity of the membrane surface in the feed part of the dialysis setup is called inlet-concentration from now on. Eqs. (5) and (6) are frequently used for indicating the minimum concentration of the ions at the membrane outlet and the absence of solute in the receive solution at the permeation commencement, correspondingly [18,19,21,23].

3.2. Model extensions

Inlet concentration (C_i) can be increased with time as a result of the concentration polarization in the feed side compartment at the vicinity of the membrane surface. Initial concentration was assumed to be constant during permeation time in the pristine model. In the C_o -extended model, we examine several well-behaved time-dependent functions including polynomials (from 1° to 3°) and combined polynomials/exponentials for representing inlet-concentration variation during permeation process. All the functions satisfy the initial condition at the start of the permeation process. The most important reason for selecting these types of functions is simplicity and well-behaved nature of these math functions. In addition, polynomial and exponential functionalities widely appear in formulating molecular phenomena in engineering science. Concentration polarization near membrane surface, concentration distribution inside boundary layer and diffusivity in porous media are obvious examples of the phenomena which are mathematically correlated by the exponential and/or polynomial functions. Table 2 indicates the applied functions.

Diffusivity of solutes through the membranes is affected by many factors such as porosity, concentration gradient, surface and internal morphology and retardation mechanisms including chemical and physical attachment phenomena [21,23]. Predominance of retardation mechanisms may gradually change during permeation period. As a

result, diffusivity may be a function of time. Finally, C_o - D extended model was proposed as the final generation of the model extension. Both inlet concentration and diffusivity coefficient were correlated using similar types of transient functions as indicated in Table 2. An advanced MATLAB® (R2009a, License no.: 161051) code was prepared to solve the governing equation with different transient function alternatives. The best transient functions for the inlet concentration and diffusivity were obtained according to the highest agreement between the experimental results and model predictions. The agreement accuracy of the models was also analyzed by exact statistical functions.

3.3. Statistical error functions

The presented models were carefully validated with the experimental dialysis data according to the statistical error analyses including APRE, AAPRE, STD, R-square and RMSE [27–29]. Brief definitions of these functions are as follows:

A. Average percent relative error (APRE,%):

$$APRE = \frac{100}{N} \sum_i \frac{(\text{calc.}(i) - \text{exp.}(i))}{\text{exp.}(i)} \quad (7)$$

B. Average absolute percent relative error (AAPRE,%):

$$AAPRE = \frac{100}{N} \sum_i \left| \frac{(\text{calc.}(i) - \text{exp.}(i))}{\text{exp.}(i)} \right| \quad (8)$$

C. Root mean square error (RMSE):

$$RMSE = \sqrt{\frac{\sum_i (\text{calc.}(i) - \text{exp.}(i))^2}{N}} \quad (9)$$

D. Standard deviation error (STD):

$$STD = \frac{1}{N} \sum_i \sqrt{(\text{calc.}(i) - \text{average}(\text{calc.}(i)))^2} \quad (10)$$

E. Coefficient of determination (R^2):

$$R^2 = 1 - \frac{\sum_i (\text{calc.}(i) - \text{exp.}(i))^2}{\sum_i (\text{calc.}(i) - \text{average}(\text{exp.}(i)))^2} \quad (11)$$

4. Results and Discussion

By solving the governing equations, the permeate concentration of the ions at the membrane outlet (receive phase) was obtained. A software analyzer code was developed to measure the fitting adjustment of the modeling results with the experimental data on the basis of the nonlinear regression (NLR) method [28,29].

4.1. Pristine model

Pristine model is not successful in predicting permeate concentration as it is obvious from Figs. 1 to 4. Statistical parameters (Table 3) also indicate similar results. This outcome motivated us to modify the model by revising some doubtful assumptions of the model. Accumulation of the ions near the surface of the membrane (so-called ‘concentration polarization’) causes the feed-side concentration to vary during permeation. This phenomenon

Table 2
Applied functions for transient inlet-concentration and diffusivity

Inlet-concentration functions ^①	Diffusivity functions
$C_i = C_o \times (1 + a \times t)$	$D_i = D_o \times (1 + a \times t)$
$C_i = C_o \times (1 + a \times t + b \times t^2)$	$D_i = D_o \times (1 + a \times t + b \times t^2)$
$C_i = C_o \times (1 + a \times t + b \times t^2 + c \times t^3)$	$D_i = D_o \times (1 + a \times t + b \times t^2 + c \times t^3)$
$C_i = C_o \times \exp(a \times t)$	$D_i = D_o \times \exp(a \times t)$
$C_i = C_o \times \exp(a \times t + b \times t^2)$	$D_i = D_o \times \exp(a \times t + b \times t^2)$
$C_i = C_o \times \exp(a \times t + b \times t^2 + c \times t^3)$	$D_i = D_o \times \exp(a \times t + b \times t^2 + c \times t^3)$

^① a , b and c are constants. C_o and D_o are initial inlet-concentration and diffusivity, respectively.

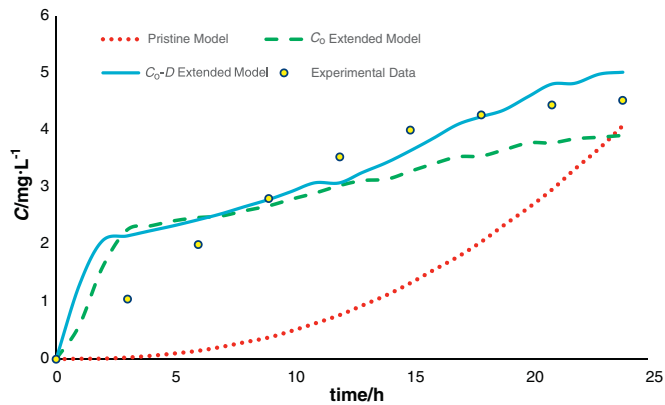


Fig. 1. Models versus experimental data for dialysis permeation of copper ions through the plain membrane (M0).

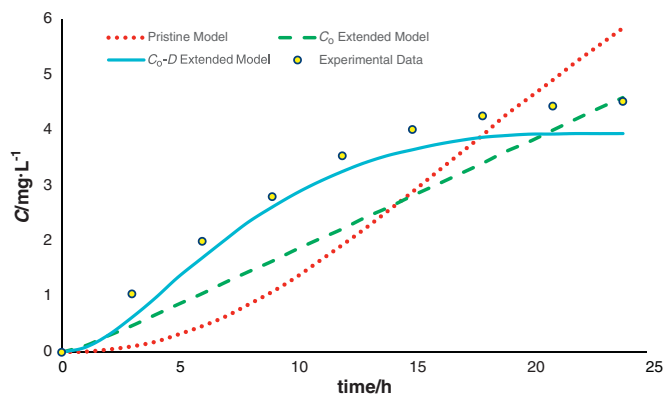


Fig. 2. Models versus experimental data for dialysis permeation of copper ions through 0.5 wt% MWCNT contained membrane (M0.5).

has been ignored in the pristine model. Furthermore, diffusivity of the ions through the membranes may be affected by various retardation mechanisms such as adsorption, pore-clogging and sieving. Domination (strength and weakness) of the retardation mechanisms against ion transfer may vary with time. Accordingly, diffusivity can be also defined as a function of time as obtained by other researchers [30–32]. Transiency of diffusion coefficient is not considered in the pristine model.

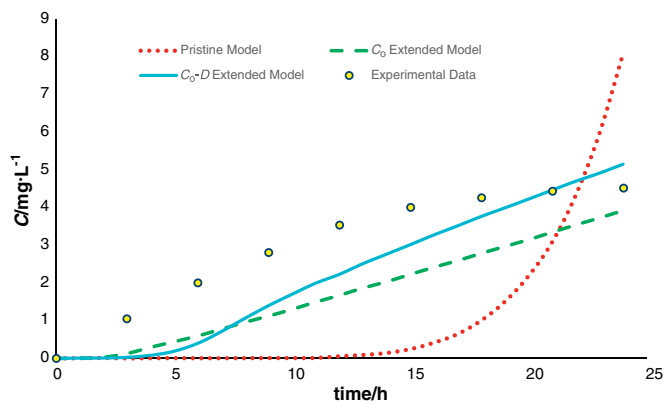


Fig. 3. Models versus experimental data for dialysis permeation of copper ions through 1 wt% MWCNT contained membrane (M1).

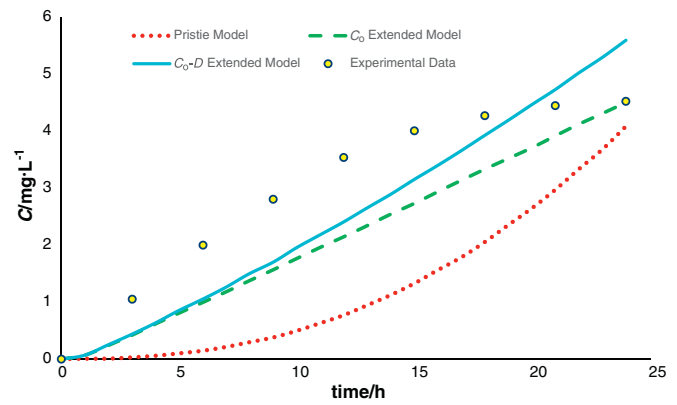


Fig. 4. Models versus experimental data for dialysis permeation of copper ions through 2 wt% MWCNT contained membrane (M2).

4.2. Influence of transient feed-side concentration

Some simple and straightforward mathematical functions (see Table 2) have been applied to represent the transiency of feed-side concentration in the adsorption/diffusion model. The code solver can optimize the parameters of the transient functions for the best agreement of the model with the experimental results. Figs. 1 to 4 show the results for different membranes. Statistical analysis results are also reported in Table 3. It is clear from both the figures and the statistical analyses results that the predictions of the extended model are in better agreement with the experimental data. This indicates the impact of time-dependency of inlet-concentration in transport of ions through the membranes. Models for M0 and M2 show higher agreement elevation compared to M0.5 and M1. Structure of M0 and M2 is rather denser than M0.5 and M1. Accordingly, the impact of concentration polarization in altering the inlet-concentration may be more significant for the dense membranes. This may be connected to the difficulties in ion transport through dense structures compared to porous ones. This idea also motivated us to examine the time-dependency of the diffusivity coefficient for permeation through the membranes. The optimized functions for inlet-concentration are depicted in Table 4.

Table 3

Statistical parameters for optimized models fitted to the experimental data for different membranes

Membrane	Pristine model	C_0 extended model	C_0 -D extended model
M0	APRE = 66.1% AAPRE = 66.372% RMSE = 1.89 STD = 1.07 R^2 = 0.173	APRE = 9.193% AAPRE = 27.996% RMSE = 0.619 STD = 0.72 R^2 = 0.6	APRE = 28.237% AAPRE = 33.45% RMSE = 0.5215 STD = 0.989 R^2 = 0.821
M0.5	APRE = 37.9% AAPRE = 47.33% RMSE = 1.203 STD = 1.7037 R^2 = 0.655	APRE = 32.978% AAPRE = 33.11% RMSE = 0.891 STD = 1.217 R^2 = 0.693	APRE = 16.646% AAPRE = 16.646% RMSE = 0.3518 STD = 1.178 R^2 = 0.9366
M1	APRE = 70.0435% AAPRE = 85.084% RMSE = 2.56 STD = 1.481 R^2 = 0.1059	APRE = 52.742% AAPRE = 52.472% RMSE = 1.417 STD = 1.098 R^2 = 0.399	APRE = 40.27% AAPRE = 42.47% RMSE = 0.995 STD = 1.548 R^2 = 0.728
M2	APRE = 65.92% AAPRE = 66.33% RMSE = 1.88 STD = 1.07 R^2 = 0.173	APRE = 36.2% AAPRE = 36.2% RMSE = 0.958 STD = 1.205 R^2 = 0.655	APRE = 26.9% AAPRE = 31.732% RMSE = 0.796 STD = 1.49 R^2 = 0.801

Table 4

Optimized functions for diffusivity and inlet-concentration in dialysis permeation through nanocomposite membranes

Membrane	Inlet-concentration	Diffusivity
M0	$C_o = 0.2 \times 10^{-4} \exp(t + 0.0001 \times t^2 + 0.00001 \times t^3)$	$D = 0.2 \times 10^{-6} (1 + 0.01 \times t + 0.0001 \times t^2)$
M0.5	$C_o = 0.2 \times 10^{-4} (1 + 10000 \times t)$	$D = 0.9 \times 10^{-6} \exp(0.1 \times t + 0.001 \times t^2)$
M1	$C_o = 0.2 \times 10^{-4} (1 + 100 \times t)$	$D = 0.425 \times 10^{-6} (1 + t + 0.01 \times t^2)$
M2	$C_o = 0.2 \times 10^{-4} (1 + 10000 \times t + 100 \times t^2)$	$D = 0.3 \times 10^{-6} (1 + 0.1 \times t + t^2)$

4.3. Combined effect of transient diffusivity and initial concentration

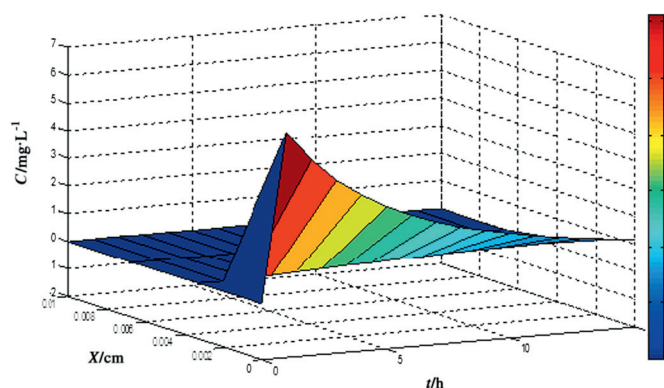
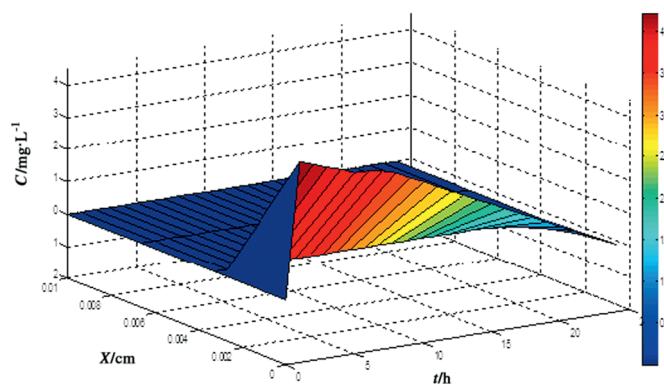
The transport model has been further modified by using similar mathematical relations for interpreting diffusivity (Table 2) in combination with the optimized inlet-concentration functions. Simultaneous effect of D_i and C_i variation has been taken into account in the final extension of the model. The optimized diffusivity functions are shown in Table 4.

Figs. 1 to 4 illustrate the agreement of the model with the experimental data. Statistical parameters (Table 3) confirm better agreement of the second extended model with the empirical data compared to the pristine one. In addition, the results indicate an elevation in the agreement accuracy of the model in comparison to the first extension.

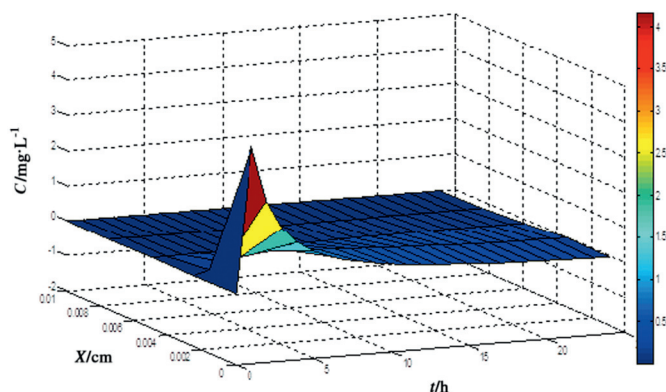
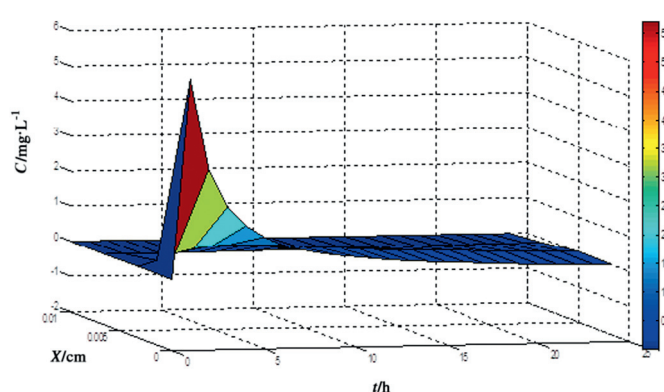
As inferred from Table 3, the agreement accuracy of the models is elevated step by step during our modeling strategy. Accommodation accuracy of the plain model is somewhat elevated in the first extension; however, it is not still satisfactory. The observed elevation is due to consideration of transiency of the inlet-concentration in the model. The second generation of the model however, offers more acceptable agreement with the experimental results. This model takes simultaneous advantages of time-dependent diffusivity and inlet-concentration. It is concluded from the modeling outcome that time-dependency of diffusivity and inlet-concentration is conspicuously important for simulating transport behavior of the membranes.

4.4. Three dimensional plots

Figs. 5 to 8 are three-dimensional plots of permeate concentration versus time and location (distance from the membrane inlet). The graphs are obtained from the final extended (C_o - D extension) model with the optimized functions adjusted for diffusivity and inlet-concentration. It is inferred from 3D plots that the concentration gradient (versus time and distance) are almost fully developed at early permeation times and in the vicinity of the membrane surface. Concentration variation is not

**Fig. 6.** 3D plots of permeate concentration versus time and distance from the membrane inlet for 0.5 wt% MWCNT contained membrane (M0.5).**Fig. 7.** 3D plots of permeate concentration versus time and distance from the membrane inlet for 1 wt% MWCNT contained membrane (M1).

so significant for remaining times of permeation and at locations far from the membrane inlet. It is also obvious from the Figs. 5 to 8 that the concentration gradient is further developed (along with the transport direction through the membrane) for M0.5 and M1 membranes with larger porosity (Table 1), compared to the dense membranes (M0 and M2). This may be attributed to the lower hindrances acting against mass transport in porous rather than dense structures. In other words, concentration gradient can be further developed in porous structures because of facilitated transport of the ions [21,22]. On the other hand, porous membranes offer higher void-capacity and larger specific surface area for adsorption. The observed effects are in contrast with each other. Accordingly, the effect of porosity on transport mechanism is not still so clear. As future perspective, transport models would be further extended by application of time-dependent functions for describing

**Fig. 5.** 3D plots of permeate concentration versus time and distance from the membrane inlet for the plain membrane (M0).**Fig. 8.** 3D plots of permeate concentration versus time and distance from the membrane inlet 2 wt% MWCNT contained membrane (M2).

porosity variation to better investigate the effect of porosity in transport mechanism.

5. Conclusions

Application of pristine and extended adsorption/transport models could result in better insight into the dialysis permeation. Pristine model with constant diffusivity and feed-side concentration was not well fitted to the experimental results. Accuracy of predictions was improved from near 10% up to 60% considering time-dependency of feed-side concentration in the first extension of the model. Increased agreement (up to 90%) was also achieved considering time-functionality of feed-side concentration and diffusivity simultaneously in the final extension of the model. As inferred from the modeling results, membranes with larger porosity could support better concentration gradient development through the membrane due to reduced mass transfer hindrances against ion transport. Developed adsorption/diffusion models could not only be used to reduce the volume of the experimental efforts but also elevate our understanding about the mechanisms of ion transport through the chitosan-based composite membranes. In addition, this work revealed the importance of time-dependency of diffusivity as well as inlet concentration on the transport mechanism through the membranes.

Nomenclature

a, b, c	constants of time-dependent functions
C	equilibrium concentration, $\text{mg} \cdot \text{L}^{-1}$
C_i	feed-side (inlet) transient concentration, $\text{mg} \cdot \text{L}^{-1}$
C_o	feed side (inlet) concentration, $\text{mg} \cdot \text{L}^{-1}$
D_i	transient diffusivity of ion through the membrane, $\text{cm}^2 \cdot \text{h}^{-1}$
D_o	initial diffusivity of ion through the membrane, $\text{cm}^2 \cdot \text{h}^{-1}$
k, m	Freundlich isotherm constants
Q	equilibrium ion adsorbed amount, $\text{mg} \cdot \text{g}^{-1}$
t	time, h
x	distance from the membrane inlet, cm
δ	membrane thickness, μm
ε	membrane bulk porosity
ρ_s	ion density, $\text{g} \cdot \text{cm}^{-3}$

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