Chemical Engineering Journal 352 (2018) 737–744

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Experiment and modeling for flux and permeate concentration of heavy metal ion in adsorptive membrane filtration using a metal-organic framework incorporated nanofibrous membrane

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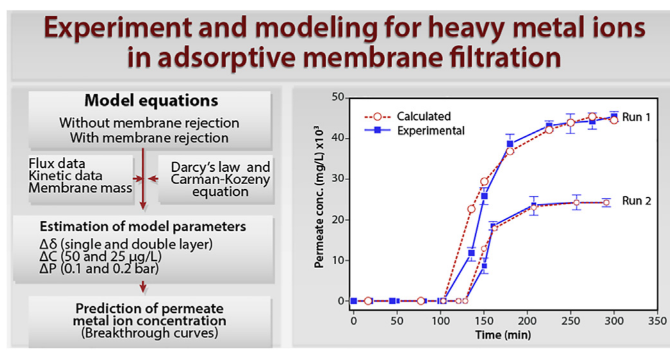
HIGHLIGHTS

- A simple mathematical model was presented for membrane adsorption by nanofibrous membrane.
- A model based on the combined Carmen-Kozeny equation and Darcy's law.
- A model based on mass balance reproduction of the breakthrough curve of heavy metal ions.
- Model parameters were correlated to membrane properties and operating conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Membrane adsorption
Modeling
Flux prediction
Prediction of permeate concentration
Transmembrane pressure difference

ABSTRACT

The environmental consequences of lead ion accumulation have been linked to detrimental health impacts in humans. Hence, removal of heavy metal (lead, Pb) ions by membrane adsorption/filtration was studied in this work using nanofibrous membranes in which the adsorbent metal-organic framework, MOF-808, was embedded. S-shaped breakthrough curves were obtained experimentally when the heavy metal concentration in the permeate was plotted vs the filtration period. Simple model equations that enable the reproduction of the S-shaped breakthrough curve were derived. It was found that the model equations could simulate the experimental data reasonably well. Attempts were further made to correlate the parameters involved in the model equations to the properties of mixed matrix nanofibrous membranes, including the pore size and pore size distribution, membrane thickness, fiber diameter, the adsorption rate constant, the Langmuir adsorption constant and the maximum adsorption capacity. The model equation parameters were also correlated to the operating conditions including the heavy metal concentration in the feed and the transmembrane pressure difference. It is believed that the model equations, despite this simplicity, can provide deeper insight into the membrane adsorption/filtration phenomena. These equations also contribute to the process design for successful removal of heavy metal ions from the environment to improve health factors for humans.

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https://doi.org/10.1016/j.cej.2018.07.077
Received 18 May 2018; Received in revised form 7 July 2018; Accepted 10 July 2018

Nomenclature

J	water flux [$m^3/m^2\,s$]
A	effective membrane area [m^2]
w	amount of MOF [g]
q_{max}	maximum adsorption capacity [mol/g]
q_t	time adsorption capacity [mol/g]
c_f	feed concentration [mol/m^3]
c_p	permeate concentration [mol/m^3]
k_1	first order kinetic constant [s^{-1}]
t	time [s]
R	rejection [%]
V	volume of feed [m^3]
K_{CK}	Carman-Kozeny constant [-]
K	permeability coefficient [m/s]
d_f	average fiber diameter

Greek letters

δ	membrane thickness [m]
ε	porosity [-]
μ	dynamic viscosity [Kg/m s]

1. Introduction

With the continual increase in water pollution and emergence of new pollutants, the growing need for efficient and effective removal systems has surged in the last decade, resulting in processes like chemical precipitation combined with other methods [1]. These adsorbents are expected to pose fast kinetic rates for fast adsorption of pollutants and also to be regenerated easily [2]. Several materials have been engineered for this purpose, these materials ranging from naturally occurring substances [3–6] abundant in nature, with ease of availability and the requirement for very little pre-treatment, to highly complex 3D metal-organic frameworks [5,7–11] that have phenomenal surface area, pore geometry and a simple electrostatic interaction mechanism associated with these frameworks and the adsorbent. In most of these materials, the rate of removal of heavy metal ions ranges from very slow to extremely fast, thus broadening the scope of choice for application depending on the process and the contaminant to be removed. Specific materials like partially fluorinated Cu and Zn MOFs were used for removal of radioactive material from aqueous solution with significant results [12]. Adsorbents for adsorption of multi-ions were also tested for removal of more than five ions simultaneously, with significant reusability and high adsorption capacity [13–16]. These intrinsic properties of the adsorbent serve to enhance the economic viability of the existing process.

In cases where the particles cannot be used as standalone materials, they are immobilized onto a substrate [17–21] which also contributes to improve the dispersion and, at times, adsorption increases due to improved surface coverage. Substrate materials have mostly been either flat sheet membranes or nanofibers made from water stable polymers like polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyethersulfone (PES), polytetrafluoroethylene (PTFE) [5,22–32], among others. These polymers have shown significant chemical and thermal stabilities suitable for aqueous applications. Non-polymeric materials like ceramics have also been developed and used as substrate [11].

For applicability purposes, these composite membranes can either function as membranes for adsorption or filtration, or a combination of the two mechanisms, as presented in adsorptive-filtration membrane processes [32,33]. These have been more prevalent in environmental research, and range from health-protection textile [34] and environment-friendly non-woven matrix for in- and out-door volatile organic compounds removal [35] to removal of heavy metal ions [36,37] and other environmental pollutants [38–42]. Depending on the pore size distribution and the size of the pollutant to be treated, the composite membrane will adopt membrane adsorption when the size of pollutant is smaller than the membrane pore; Hence, size exclusion is insignificant. Here, the adsorbent particles immobilized on the substrate play the dominant role which in most cases depends on the extent of exposure and contact between the pollutants and the adsorbent. If the particles are completely embedded or enmeshed into the polymer matrix or nanofiber, then exposure and contact could be reduced, leading to low adsorption capacity and vice versa. The performance of these particles outside of the substrate, and when immobilized, has been debated by some researchers saying that the performances are comparable in the immobilized and free-standing state. However, it should be noted that this particular report is more prevalent for nanofiber membranes than flat sheet membranes [25]. The composite membranes are usually used as filters to remove heavy metal ions and their performances are evaluated in terms of the membrane flux and the heavy metal concentration in the permeate. Obviously, the performance is affected by many parameters which include the properties of the composite membranes such as the pore size, pore size distribution, porosity, thickness, fiber diameter (in the case of nanofibrous membranes), amount of the adsorbent embedded and its adsorption capacity. Other parameters are the process parameters such as the heavy metal ion concentration and the transmembrane pressure difference. Therefore, some mathematical models are required to describe the effects of the parameters on the membrane performance quantitatively, especially for process design purposes. Most of the models developed in membrane processes, however, focus on prediction of flux and fouling [43–48] with little attention on permeate quality. The transport models developed for the nonporous membranes are not applicable for the highly porous nanofibrous membranes. Specifically, no model has been developed for the adsorbent embedded nanofibrous membranes, although the applicability of such composite membranes for membrane adsorption was shown by our previous work [49,50].

The objective of this work is to, as accurately as possible, present a model to describe the breakthrough curve (time dependent permeate concentration) obtained from the membrane adsorption/filtration experiments. Although the model is very simple, it includes all the above-mentioned parameters that can potentially affect the membrane adsorption performance. It should also be emphasized that those parameters were determined quantitatively in our previous work, in which no detailed filtration experiments were conducted. Thus, we believe that the analysis of the experimental data by the proposed model will not only provide in-depth understanding of the phenomena but also contribute to the process design of membrane adsorption. We should submit, however, that further refinement of the model is required.

2. Modeling approach

The model consists of two parts as presented in Scheme 1. In the first, the Carman-Kozeny equation is employed to estimate the flux of the nanofibrous membrane. The Carman-Kozeny equation has been used in several mathematical models in predicting the flux of porous membranes [44,51] with high compatibility between the model and the experimental data. The model calculation is made under the condition that the heavy metal concentration is in the ppb range so that the permeate flux is nearly equal to that of pure water. In the second part, an attempt is made to reproduce the breakthrough curve of the permeate concentration based on the mass balance, including the rate of heavy metal in- and out-flux, and the heavy metal adsorption rate. This is easy to implement but the reliable mass balance approach has shown its presence in modeling designs from reverse osmosis (RO) to ultra-filtration (UF) [52–54].