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Mathematical modeling and numerical simulation of ammonia removal from wastewaters using membrane contactors

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ABSTRACT

This study investigates simulation of ammonia transport through membrane contactors. The system studied involves feed solution of NH_3, a dilute solution of sulfuric acid as solvent and a membrane contactor. The model considers coupling between equations of motion and convection-diffusion. Finite element method was applied for numerical calculations. The effect of different parameters on the removal of ammonia was investigated. The simulation results revealed that increasing feed velocity decreases ammonia removal in the contactor. The modeling findings also showed that the developed model is capable to evaluate the effective parameters which involve in the ammonia removal by means of contactors.

1. Introduction

Nowadays, wastewater treatment is of vital importance for providing drinking water and protecting environment. Finding and developing new methods and processes for wastewater treatment has been a subject of great interest. Researchers are trying to find new solutions to remove all contaminants from water and wastewaters. Among the water contaminants, ammonia (NH_3) is a major contaminant which can cause adverse effects. Ammonia can be found in either municipal or industrial wastewaters. Dissolved ammonia in solutions is generated from industrial wastewaters such as coking, chemical fertilizer, coal gasification, petroleum refining, pharmaceutical and catalyst factories [1–7]. From environmental perspective, a complete removal of ammonia from wastewaters is desirable. The concentration of ammonia in industrial wastewaters varies from 5 to 1000 mg/L [8]. The removal of dissolved ammonia from wastewaters is thus mandatory to protect the environment and human health.

Currently, conventional separation processes are applied to remove ammonia from water and wastewaters including selective ion exchange, air stripping, break-point chlorination, denitrification, and biological nitrification [1,9–11]. Recently, hollow-fiber membrane contactors (HFMCs) have attracted large attentions as an effective device for separation processes. A major part of the interest toward HFMCs is due to their capability in providing a dispersion free contact between two phases. In addition, the velocities of both phases can vary independently, while neither flooding nor unloading problems may happen [12]. Membrane contactors can be considered as a promising technology for separation of ammonia from wastewaters.

The mechanism of separation in membrane contactors is based on the mass transfer between the two phases. For removal of ammonia in membrane contactors, ammonia containing solution flows in the tube or shell side of the membrane contactor. The ammonia evaporates from the aqueous solution, diffuses through the membrane pores, and reacts with the stripping solution (solvent). This process could be carried out in one-through or recycling mode. Recycling mode provides high separation factor, but is difficult to simulate. One-through mode is easy to design and model.

New modeling approach for ammonia removal in membrane contactors is based on solving conservation equations for ammonia in the aqueous feed and membrane phases. In this method, conservation equations including equations of motion and mass are derived and solved simultaneously by appropriate numerical methods. The computational fluid dynamics (CFD) are usually carried out to solve the governing equations.

The main objective of the present study is to develop and solve a mathematical model for the simulation of ammonia removal in a membrane contactor. The type of membrane contactor is assumed to be hollow-fiber. The equations of the model are solved by numerical method based on finite element method (FEM). An

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Nomenclature

C	concentration (mol/m^3)
C_{outlet}	outlet concentration of ammonia in the tube side (mol/m^3)
C_{inlet}	inlet concentration of ammonia in the tube side (mol/m^3)
$C_{i\text{-tube}}$	concentration of solute in the tube side (mol/m^3)
$C_{i\text{-membrane}}$	concentration of solute in the membrane (mol/m^3)
D	diffusion coefficient (m^2/s)
$D_{i\text{-tube}}$	diffusion coefficient of solute in the tube (m^2/s)
$D_{i\text{-membrane}}$	diffusion coefficient of solute in the membrane (m^2/s)
H	Henry's law constant (mol/(m^3 kPa))
J_i	diffusive flux of species i (mol/(m^2 s))
L	length of the fiber (m)
M	molecular weight (kg/mol)
n	number of fibers
p	pressure (Pa)
r	radial coordinate (m)
r_{in}	inner radius of fibers (m)
r_{out}	outer radius of fibers (m)
t	time (s)
T	temperature (K)
u	average velocity (m/s)
V	velocity in the module (m/s)
$V_{z\text{-tube}}$	z-velocity in the tube (m/s)
z	axial coordinate (m)
Greek symbols	
ε	membrane porosity
η	dynamic viscosity (kg/(m s))
ρ	density (kg/m^3)
Abbreviations	
FEM	finite element method
HFMC	hollow-fiber membrane contactor
2D	two-dimensional
CFD	computational fluid dynamics

algorithm is developed for the numerical simulation. Mass transfer and Navier–Stokes equations are solved simultaneously for the ammonia in the membrane contactor to obtain the concentration distribution.

2. Theory of ammonia removal

When ammonia is dissolved in aqueous solutions, it exists in two forms. One form is ammonia (NH_3) and the other form is ammonium ions (NH_4^+). The composition of these species depends on the pH and temperature of the solution. The compositions can be calculated from the following reaction:

$$NH_3 + H_2O \underset{K_a}{\overset{K_b}{\rightleftarrows}} NH_4^+ + OH^- \quad (1)$$

where K_a and K_b values are equal to 5.6×10^{-10} and 1.8×10^{-8}, respectively [13]. The total concentration of ammonia in the solution is the summation of equilibrium concentrations of ammonium ($[NH_4^+]$) and ammonia ($[NH_3]$):

$$C_{total} = [NH_4^+] + [NH_3] \quad (2)$$

2.1. Mechanism of ammonia transport through membrane contactors

In ammonia removal process, an aqueous solution of ammonia as feed is flown inside the tube side. The stripping solution is passed in the shell side of the membrane contactor either in co-current or counter-current mode. The most effective stripping solution is sulfuric acid solution because reaction rate between ammonia and sulfuric acid is high. By contacting feed and stripping phases in the membrane contactor, ammonia is transferred from the bulk toward the feed–membrane interface due to concentration gradient. At the feed–membrane interface, ammonia is volatilized into the membrane pores which are filled by gas. The membrane is microporous and provides the contact between two phases. Ammonia then diffuses across the gas-filled pores of the membrane, and is transferred into the stripping solution. At the shell–membrane interface, ammonia immediately reacts with the stripping solution. Therefore, the ammonia concentration in the stripping solution is assumed to be zero. On the other hand, water cannot diffuse through the membrane pores due to hydrophobic nature of the fibers. The principle of ammonia removal through membrane contactors is schematically shown in Fig. 1.

3. Mass transfer model

A mathematical model was proposed to describe the transport of ammonia through membrane contactors. The model was based on the "non-wetted" mode. In this mode, it is assumed that the gas phase fills the membrane pores. The aqueous feed solution containing ammonia is fed to the tube side of the membrane contactor and the stripping solution flows in the shell side. Velocity distribution in the tube side is determined using Navier–Stokes equations. The ammonia concentration is determined using continuity equation. Axial and radial diffusions inside the tube side are considered in the mass transfer equations. Furthermore, chemical reaction between ammonia and sulfuric acid, which occurs in the shell side, is assumed to be instantaneous. Fig. 2 shows model domain for numerical simulation.

3.1. Equations of the model

The feed solution containing dissolved ammonia (NH_3) flows with a laminar velocity inside the hollow fibers. Since the diameters of hollow fibers are very low, flow regime is assumed to be laminar in the calculations. The feed solution is flown to the tube side (at $z = 0$), while the stripping solution is passed through the shell side. Ammonia is removed from the feed phase by subsequent diffusion through the bulk of liquid and membrane, and becomes absorbed into the solvent. The model is built considering the following assumptions:

- Steady state and isothermal conditions.
- Laminar flow in the membrane contactor.
- Henry's law is applied for feed–membrane interface.
- Non-wetted mode for the membrane is assumed; in which the feed aqueous solution do not fills the membrane pores.
- There is no reaction zone (the reaction of ammonia with the sulfuric acid is fast (instantaneous) and always occurs in excess).
- Velocity of both ammonia solution and sulfuric acid are constant.

The last assumption is justified by low mass transfer flux of ammonia from feed phase to solvent phase.