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Ammonia removal from wastewater streams through membrane contactors: Experimental and theoretical analysis of operation parameters and configuration

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ABSTRACT

Ammonia removal from water was studied through hydrophobic hollow fiber and flat sheet membrane contactors. These hydrophobic membrane contactors were used to separate the water stream to be treated and a receiving solution. A diluted solution of sulfuric acid was used as a receiving solution to accelerate the removal of ammonia by means of a reaction converting the ammonia into ammonium sulfate ($(NH_4)_2SO_4$), which could be recovered as a by-product [1–3].

Experimental work using commercial hollow fibers under different operation configurations, temperature and hydrodynamic conditions allowed obtaining significantly high extraction percentages of ammonia up to 99.83%. A theoretical model has been developed based on a resistance-in-series model that satisfies with the data those obtained from the experiments. The mass transfer of ammonia has been described by means of both Knudsen and molecular diffusion. However, it has not found a significant difference between the results obtained from the two mechanisms indicating both transport regimes could be possible for the studied system.

The circulation configuration of the solutions was found to have a strong effect on the efficiency of the process. Thus, the best circulation configuration of the solutions for the hollow fiber contactors entailed the flow of feed solution in the shellside while the receiving solution in the lumenside of the membranes.

1. Introduction

Ammonia is one of the major pollutants introduced into receiving natural waters by industrial, domestic and agricultural wastewater discharges. Usually, a complete removal or a very low ammonia concentration is desirable in final effluents for two reasons: (1) it is extremely toxic to most fish species and (2) it will be bio-oxidized by nitrifying microorganisms to nitrite and nitrates which are undesirable to humans [4,5]. High concentrations of ammonia are commonly present in industrial wastewaters such as coke-plant, tannery, textile, landfill leachate and fertilizer wastewater [6].

Removal of ammonia from industrial effluent is an important and dynamic area of research as well as being an important challenge, because environmental laws and regulations governing safe discharge levels are becoming increasingly stringent. Traditional methods for the removal of ammonia include biological treatments, chemical precipitation, advanced oxidation processes, air stripping, ion exchange, adsorption, membrane processes and so on [7–10]. Among these technologies, membrane contactors are good candidates for ammonia removal since they offer a large surface area that facilitates fast separation of the ammonia from the wastewater even at low energy input per mole ammonia removed. In the literature, although there are a number of studies on the use of gas–liquid membrane contactors for gas absorption and stripping [11–17], there are only few studies reported on the use of a liquid–gas–liquid membrane contactor through a reaction for the ammonia removal from wastewaters [1–3].

In this work, hydrophobic polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes were used in order to contact the aqueous solutions of ammonia and the receiving solution. Diluted solutions of sulfuric acid were used as the receiving solution. The principle of the removal of the ammonia from the feed to the receiving solution is illustrated in Fig. 1. The hydrophobic hollow fiber separates two circulating phases; the feed that is an aqueous phase containing ammonia on the shellside and the receiving solution; a diluted solution of sulfuric acid on the lumenside. An air gap fills the pore of the hydrophobic membrane, which is not wetted by the aqueous solutions. First, ammonia (NH_3) diffuses from the bulk of the feed to the feed–membrane interface. NH_3 volatilizes through the feed–membrane interface, diffuses across the air-filled pore of the membrane, and finally it reacts immediately with sulfuric acid

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Nomenclature

c_A	ammonia concentration (mol m^{-3})
c_A^b	ammonia concentration of the bulk solution (mol m^{-3})
c_A^i	ammonia concentration on the interface of the membrane (mol m^{-3})
$c_{A,g}^i$	ammonia concentration in gas phase in equilibrium with that in solution (mol m^{-3})
$D_{A,g}$	molecular self-diffusion coefficient of the ammonia in air (m^2 s^{-1})
$D_{A,W}$	diffusion coefficient of ammonia in water (m^2 s^{-1})
d_e	external diameter of the fiber (m)
D_h	dynamic diameter (m)
d_i	internal diameter of the fiber (m)
$D_{i,j}$	diffusion coefficient of component *i* in component *j* (m^2 s^{-1})
$D_{in,s}$	internal diameter of the shell (m)
D_{kn}	Knudsen diffusion coefficient of ammonia (m^2 s^{-1})
d_p	pore diameter of the membrane (cm)
H	Henry's constant (atm m^3 mol^{-1})
J	flux (mol m^{-2} s^{-1})
$J_{A,memb}$	flux of ammonia through the membrane (mol m^{-2} s^{-1})
$J_{A,shell}$	flux of ammonia through the boundary layer in the shell side (mol m^{-2} s^{-1})
K_s	mass transfer coefficient in the shell side (m s^{-1})
K_l	mass transfer coefficient in the lumenside (m s^{-1})
K_m	mass transfer coefficient in the membrane pores (m s^{-1})
K_{ov}	overall mass transfer coefficient (m s^{-1})
L	length of the fiber (m)
M	molecular weight of the compound (g mol^{-1})
M_A, M_g	molecular weight of ammonia and gas (air) (g mol^{-1})
N_F	number of fibers
P	pressure (Pa)
p_A	partial pressure of ammonia (Pa)
R	universal gas constant (J mol^{-1} K^{-1})
Q	flow rate of the solution (mL min^{-1})
u	velocity of the solution (m s^{-1})
T	temperature in Kelvin (K)
V_A, V_g	molecular volumes of ammonia and gas (air), respectively (g cm^{-3})

Greek symbols

δ	wall thickness of the membrane (m)
ε	porosity
τ	tortuosity
ϕ	packing density
λ	molecular mean free path length (m)
$\Delta c_{A,m}$	concentration gradient of ammonia through the membrane in the gas phase
μ	viscosity (kg m^{-1} s^{-1})
ρ	density (kg m^{-3})

on the interface to form nonvolatile compound, ammonium sulfate ($(NH_4)_2SO_4$). Thus, the concentration of ammonia in the receiving solution is essentially zero. Total ammonia removal could be theoretically possible under this configuration, since the driving force for this liquid–gas–liquid membrane contactor operation is the difference in ammonia partial pressure between the feed and the receiving solution.

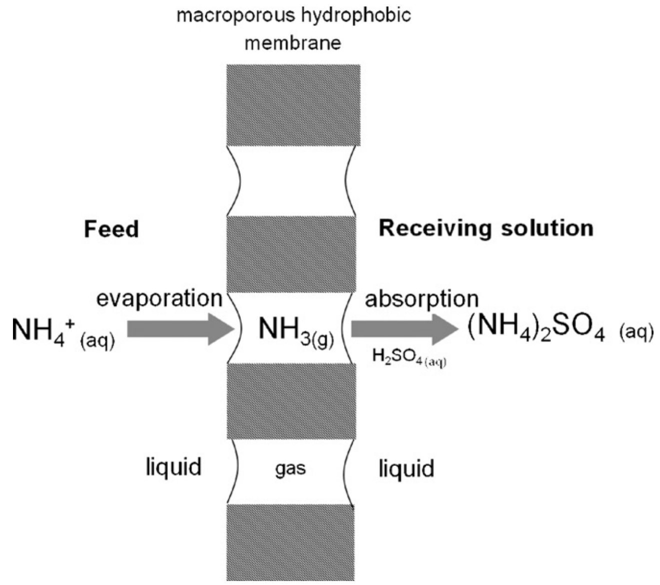

Fig. 1. Principle of the extraction process.

There are few studies in the literature on this principle for ammonia removal from wastewaters, where membrane separates an aqueous feed and the acidic receiving solution while a reaction was carried out on the interface of the membrane [1–3]. Zhu et al. reported a study in order to investigate the effect of the pH and the viscosity of the wastewater containing ammonia on the mass transfer in hydrophobic hollow fiber membrane contactors [1]. They carried out the experiments at 20 °C at different feed pH values ranged between 9 and 13 with the ammonia concentrations varying from 50 to 10,000 mg L^{-1} interval. It has been reported that higher efficiencies of ammonia removal could be reached only at relatively higher pH values of feed for a given time. In the reported work, the removal efficiency of ammonia was over 98% in 40 min when the initial pH values of the feed solution were over 11, while it only reached about 60 and 26% in the same period of time when the initial pH values of the feed solution were 10 and 9, respectively. Tan et al. reported a work for ammonia removal from water through polyvinylidene fluoride hollow fiber membranes [2]. It has been indicated that increased pH values allowed higher efficiencies of ammonia removal, and remarkable efficiencies have been reached when the pH value was higher than 11 after a time period of 120 min. Another study about effect of the pH value and the temperature on the efficiency of ammonia removal was reported by Norddahl et al. [3]. It has been found that the relative effect of temperature on ammonia mass transfer rates was noticeably higher at pH values exceeding 10, while the noticeable efficiencies were performed about 100 min. In our work, over 98% of efficiencies were reached in 30 min at a feed pH around 7.0 without using a buffer solution. Unbuffered feed solutions were used to estimate the behavior of the untreated wastewater streams containing ammonia. Furthermore, the effect of the process parameters such as temperature, circulation rate, concentration of receiving solution, and circulation configuration of the solutions on the efficiency of ammonia removal have been investigated in order to estimate optimal conditions. It has been noted that all the previous reported works were performed circulating the ammonia feed in the lumenside of the hollow fiber membrane. In this work, it was experimentally shown that the flow of the ammonia feed in the shellside of the membrane allows higher yields of ammonia removal.

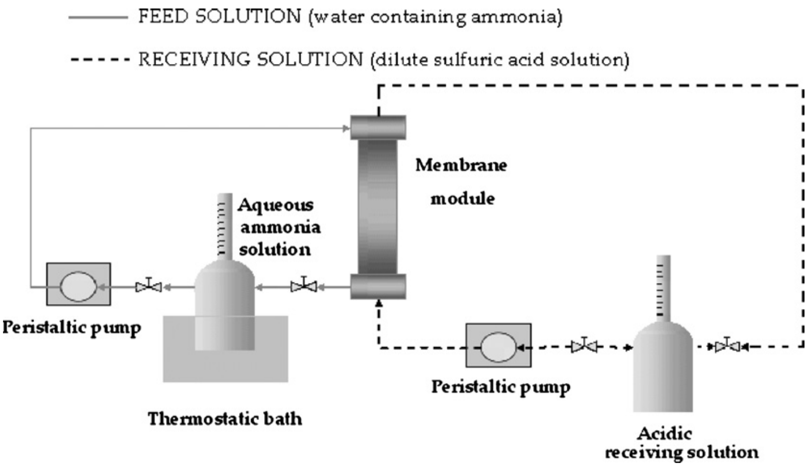

Fig. 2. Outline of the experimental setup used in this work.

2. Experimental

2.1. Experimental setup

Experiments were carried out using two different modules of membrane contactors: hollow fiber and flat sheet membrane modules. The experimental setup implemented in this study using hollow fiber module is described in outline showed in Fig. 2. The feed ammonia solution was circulated through the shellside of the hollow fiber contactor by means of a peristaltic pump, while the receiving solution containing sulfuric acid was circulated into the lumenside in a countercurrent flow by another peristaltic pump. Both solutions were recycled to their respective reservoirs. The volumes of the feed and the receiving solutions were 1500 and 750 mL, respectively. The temperature of the feed reservoir was maintained by a thermostatic bath. Ammonium hydroxide (24.8%) and sulfuric acid were purchased from Bio Pack and J.T. Baker, respectively. During the experiment runs, the concentration of ammonia in the feed solution reservoir was monitored using an ion-selective electrode for ammonia.

2.2. Operation conditions

The operating conditions have been summarized in Table 1. The experiments were carried out both in hollow fiber and flat sheet membrane modules. Structural parameters of the hollow fiber and the flat sheet membranes were given in Tables 2 and 3, respectively.

3. Mass transfer model

3.1. Mass transfer equations

The transfer of ammonia through the membrane can be explained by means of a resistances-in-series model, which considers the transport phenomena at the proximities of the membrane. The overall mass transfer coefficient, K_{ov}, can be expressed as follows for a hollow fiber module:

$$\frac{1}{K_{ov}} = \frac{1}{K_s} + \frac{1}{K_m} + \frac{1}{K_l} \tag{1}$$

where K_{ov}, K_s, K_m and K_l are the overall, shellside, membrane and lumenside mass transfer coefficients, respectively. For the flat sheet membrane module shellside and the lumenside mass transfer coefficients refer to mass transfer coefficients of aqueous feed side and the receiving solution side, respectively. Thus, the transfer of ammonia can be described by following sequence of steps: transfer from the bulk of the feed solution through the boundary layer to the feed–membrane interface, diffusion through the membrane pores filled with gas to the receiving solution interface, reaction on the interface, and diffusion of the ammonium salt into the extraction solution. The liquid mass transfer coefficient for the species *i* in the shellside, under laminar flow condition, can be calculated from the Sherwood correlation proposed by Prasad and Sirkar for the hollow

Table 1
Operation conditions used in experiments.

Parameter	Interval of values	Units
Temperature	35–50	°C
Ammonia concentration in feed	250–500	ppm
Sulfuric acid concentration in receiving solution	0.1–0.3	$\mathrm{mol\,L^{-1}}$
Flow rate of the solutions	782–2000	$\mathrm{mL\,min^{-1}}$

Table 2
Membrane properties of flat sheet membranes and its structural parameters.

Parameter, unit	Interval of values
Module geometry	Flat (Sartorius®)
Membrane material	PTFE
Surface contact area (m^2)	0.014
Membrane thickness (μm)	65
Mean pore diameter (μm)	0.2
Porosity	0.6
Length (m)	0.1685
Width (m)	0.079
Height of feed side (m)	0.003
Height of acid side (m)	0.0015

Table 3
Membrane properties of hollow fiber membranes and its structural parameters.

Parameter, unit	Interval of values
Module geometry	Hollow fiber (Celgard Liquicel®)
Membrane material	PP
Number of fibers	7400
Surface contact area (m^2)	0.58
Fiber O.D. (μm)	300
Fiber I.D. (μm)	220
Porosity	0.4
Mean pore diameter (μm)	0.2
Length (m)	0.12
Shell I.D. (m)	0.043

fiber modules [18]:

$$Sh = 5.8\left[\frac{D_h(1-\phi)}{L}\right].Re^{0.6}.Sc^{0.33} = \frac{K_s.D_h}{D_{A,W}} \tag{2}$$

where $D_{h,}$ ϕ, L, Re, Sc, $D_{A,W}$ are the dynamic diameter, packing density, length of the fibers, Reynolds number ($Re = D_h u\rho/\mu$), Schmidt number ($Sc = \mu/\rho D_{A,W}$) and the diffusion coefficient of ammonia in water, respectively. The packing density can be calculated by means of Eq. (3):

$$\phi = N_F\left(\frac{d_e}{D_{in,s}}\right)^2 \tag{3}$$

N_F represents the number of fibers, d_e is external diameter of the fibers and $D_{in,s}$ is the internal diameter of the shell. Diffusion coefficient of ammonia in water can be calculated from Wilke–Chang equation [19].

On the other hand, the liquid mass transfer coefficient for the species *i* in the feed, under the laminar conditions for the flat sheet membrane module can be calculated from the Sherwood correlation as in Eq. (4) [20]:

$$Sh = 0.023.Re^{0.83}.Sc^{1/3} \tag{4}$$

The flux of the ammonia from the aqueous bulk feed solution to the feed–membrane interface can be estimated by Eq. (5) where the superscripts i and b indicate interface and bulk, respectively:

$$J_{A,\ shell} = K_s(c_A^b - c_A^i) \tag{5}$$

Ammonia is considered in thermodynamic equilibrium with its vapor at the liquid–membrane interfaces. In this way, Henry's law may be applied at the interfaces. In this work, the partial pressures of the ammonia that are in equilibrium with the liquid at the interfaces of the membrane were estimated from the correlation for Henry constant given below where the temperature, *T*, is in Kelvin and the Henry constant, *H*, in atm m^3 mol^{-1} [21]:

$$\ln H = -\frac{4200}{T} + 3.133 \tag{6}$$

It is worth noting that the Henry's law constant can be defined as follows:

$$H = \frac{p_A}{c_A} \tag{7}$$

where p_A is the partial pressure of the ammonia in the air phase in equilibrium with the concentration c_A [mol m^{-3}] of this compound in the aqueous solution.

The membrane mass transfer coefficient, K_m, can be estimated from the following equation [14,18]:

$$K_m = \frac{\varepsilon D_{i,j}}{\tau\delta} \tag{8}$$

where $D_{i,j}$ is the diffusion coefficient of ammonia in the air gap within the pores, ε, τ and the δ are the porosity, the tortuosity and the wall thickness of the hollow fiber, respectively. $D_{i,j}$ can be considered as either a molecular self-diffusion or the Knudsen diffusion due to the value of Knudsen number ($Kn = \lambda/d_p$) [18] where λ is the molecular mean free path length and the d_p is the pore diameter. In this work, the Knudsen number of the hollow fiber was calculated as 0.38. Since the Knudsen number is close 1.0, the diffusion mechanism of ammonia inside the pores can be considered as a transition regime where various mechanisms could coexist and thus, ammonia diffusion through the pores could be described either by a molecular or a Knudsen like diffusion mechanism. Hence, both Knudsen and the molecular self-diffusion coefficients were calculated and compared in order to evaluate the mass transfer of ammonia in this study. The Knudsen transfer coefficient could be written as follows:

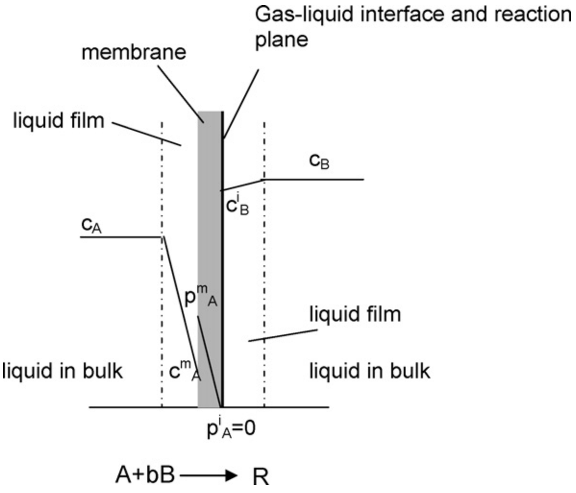

Fig. 3. Mass transfer with an instantaneous reaction with high c_B.

$$D_{kn} = \frac{d_p}{3}\left(\frac{8RT}{\pi M}\right)^{0.5} \tag{9}$$

where d_p is the pore diameter (cm), *T* the temperature in Kelvin (K), *R* is the universal gas constant (J mol^{-1} K^{-1}) and *M* is the molecular weight of the compound (g mol^{-1}). The self-diffusion coefficient of the ammonia in free space (in this case in air) $D_{A,g}$ (m^2 s^{-1}), can be calculated using the correlation given by Fuller and co-workers [20]:

$$D_{A,g} = \frac{1\times10^{-7}T^{1.75}((1/M_A)+(1/M_g))^{1/2}}{P\left[\left(\sum V_A\right)^{1/3}+\left(\sum V_g\right)^{1/3}\right]^2} \tag{10}$$

The permeation flux of ammonia through the membrane, $J_{A,memb}$ can be expressed by the following equation considering $\Delta c_{A,m}$ is the concentration gradient of ammonia in the gas phase through the membrane:

$$J_{A,\ Memb} = K_m\Delta c_{A,m} \tag{11}$$

In this study, the reaction between ammonia and sulfuric acid has been considered to be instantaneous. The acid concentration is in excess comparing to ammonia concentration. Under this condition, the reaction takes place on the interface of the membrane and consequently the concentration of ammonia on the interface is essentially zero. Described transportation is illustrated in Fig. 3.

The boundary layer resistance on the receiving solution could be considered negligible because the protonation reaction of ammonia is supposed to be instantaneous. Therefore, only the feed solution boundary layer and the membrane resistance have to be taken into account in the model. Since NH_3 reacts immediately with sulfuric acid at the interface to form a nonvolatile compound, the concentration of ammonia in the stripping solution is zero. Consequently, the molar flow of ammonia, *N* (mol s^{-1}), across the membrane may be written as the following expression, which has been obtained from Eqs. (5) and (11):

$$N = K_sA_s(c_A^b - c_A^i) = K_mA_m\frac{RT}{H}c_{A,g}^i \tag{12}$$

in which $c_{A,g}^i$ is the ammonia concentration in gas phase in equilibrium with that in solution, A_s is the membrane area of shellside, and A_m is the logarithmic mean of the membrane area. In the case of the flat sheet membrane module, the area of the membrane on the feed side is equal to that of on the receiving solution side.

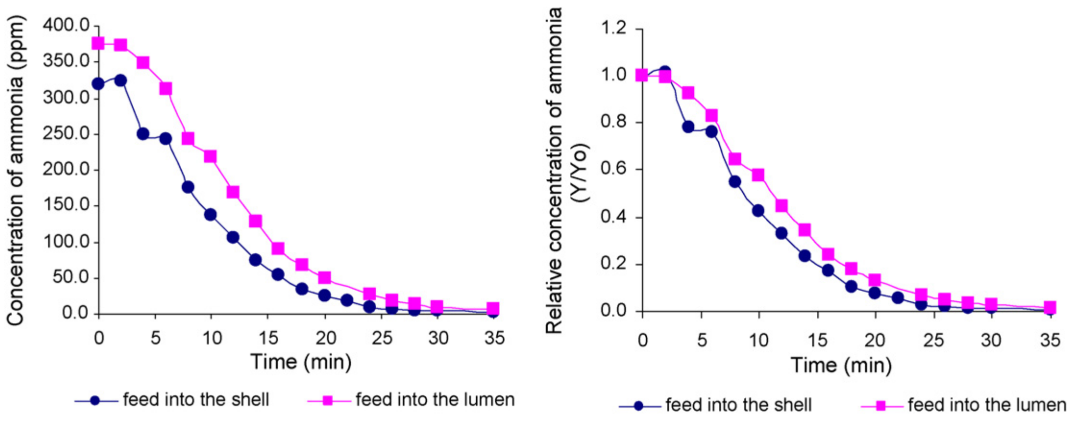

Fig. 4. Concentration of ammonia in the feed solution as a function of time using different circulation configurations into a hollow fiber contactor ($Q = 2000\,\text{mL min}^{-1}$, $T = 40\,^{\circ}\text{C}$, $[H_2SO_4] = 0.3\,\text{mol L}^{-1}$).

Finally, considering a negligible mass transfer resistance in the receiving solution side, the overall mass transfer coefficient in Eq. (1) can be written as in Eq. (13):

$$\frac{1}{K_{\text{ov}}} = \frac{1}{K_{\text{s}}} + \frac{1}{K_{\text{m}}} \tag{13}$$

3.2. Numerical solution

The model described in the previous section involves the local mass transfer resistances of each step by means of Eqs. (5), (11) and (12). Resistances-in-series model was solved estimating the interfacial concentration when corresponding molar flow equations represent the same flow values under instantaneous steady-state conditions. The Regula Falsi algorithm [22,23] was applied to reduce the number of iterative calculations, which have been achieved by means of a program developed in Matlab®. After these iterative calculations, the concentration of ammonia in the bulk of the feed solution was recalculated by mass balance. Interfacial concentrations were estimated for each time interval by modifying the initial feed concentrations of each corresponding step.

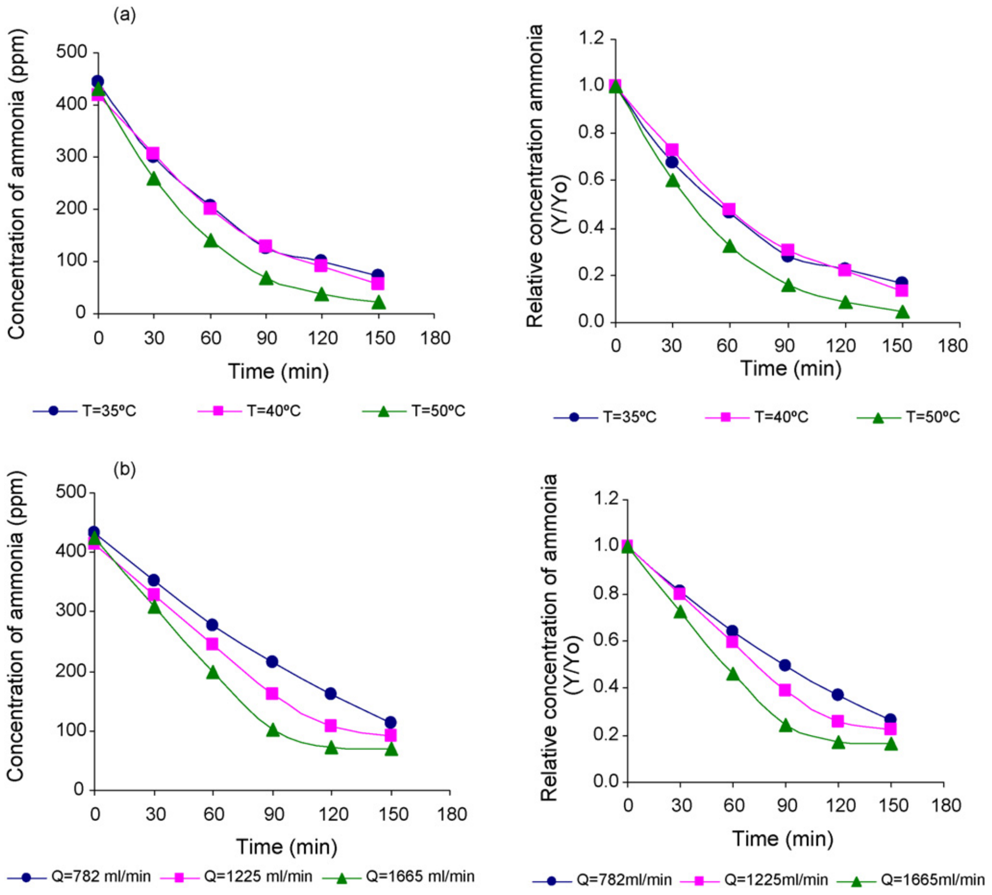

Fig. 5. Concentration of ammonia in the feed solution as a function of time at different: (a) feed temperatures using flat sheet membrane modules ($Q = 1225\,\text{mL min}^{-1}$, $[H_2SO_4] = 0.1\,\text{mol L}^{-1}$) and (b) flowrates of solutions using flat sheet membrane modules ($T = 35\,^{\circ}\text{C}$, $[H_2SO_4] = 0.3\,\text{mol L}^{-1}$).

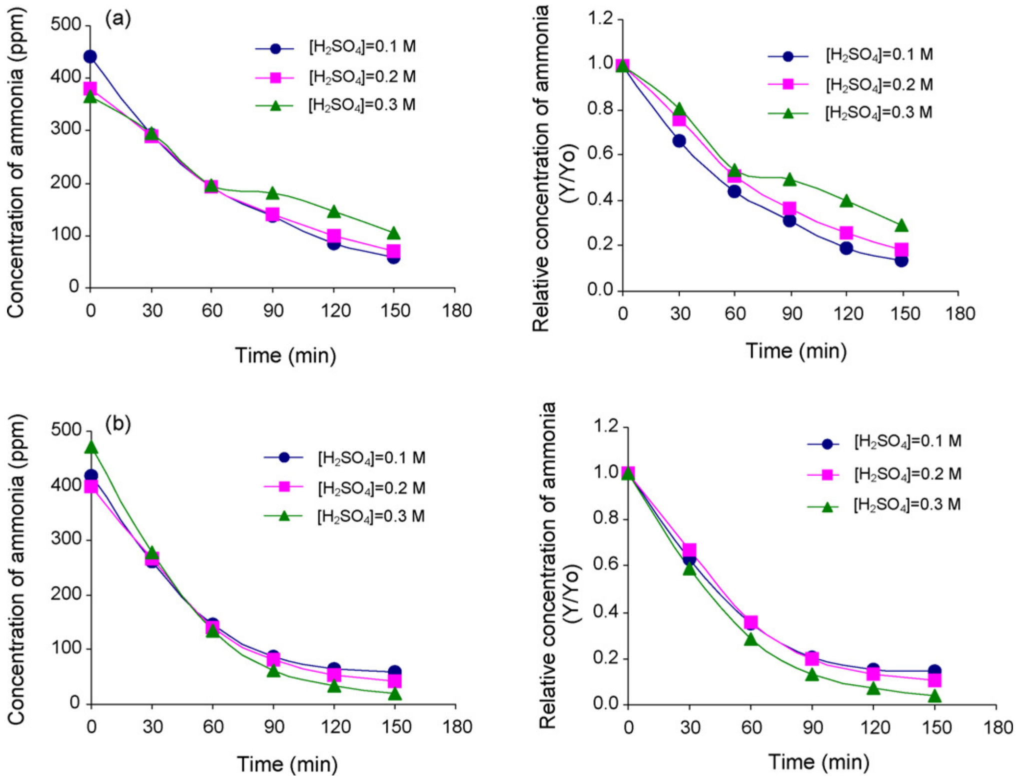

Fig. 6. Concentration of ammonia in the feed solution as a function of time with different concentrations of the receiving solution using flat sheet membrane modules: (a) (T = 50 °C, Q = 782 mL min^{-1}) and (b) (T = 50 °C, Q = 1665 mL min^{-1}).

4. Results and discussion

4.1. Evaluation of the transmembrane fluxes and extraction percentages

A range of experiments was performed to determine the effect of different process parameters on the mass transfer such as temperature, circulation rates of solutions, concentration of receiving solution and the circulation configuration of the solutions. In all experiments using hollow fiber modules, a minimum extraction percentage of 98% ammonia was achieved in 35 min processing a volume of 1500 mL feed solution. The best results were obtained with a diminution from an initial concentration of ammonia of 400 mg L^{-1} to a value of 2.5 mg L^{-1} ammonia that corresponds to 99.38% of ammonia removal. Using the flat sheet membranes, remarkable extraction percentages were reached in 150 min. The average flux value obtained with flat sheet membranes was 3.5×10^{-6} mol m^{-2} s^{-1} while it was approximately 3×10^{-5} mol m^{-2} s^{-1} using hollow fiber membranes. The experiments carried out with different circulation configurations of solutions using hollow fiber module in order to obtain the best conditions for solution circulation. Fig. 4 presents a comparison of the concentration change with time for two cases where the feed solution was in the lumenside and in the shellside. It can be seen that extraction percentages of ammonia are higher when the feed solution flows in the shellside and the acid solution in the lumenside of the membranes.

On the other hand, only one membrane contactor with polypropylene fibers and one flat sheet membrane were used to accomplish all the experimental runs during 4 months under intensive operation without any observable performance change.

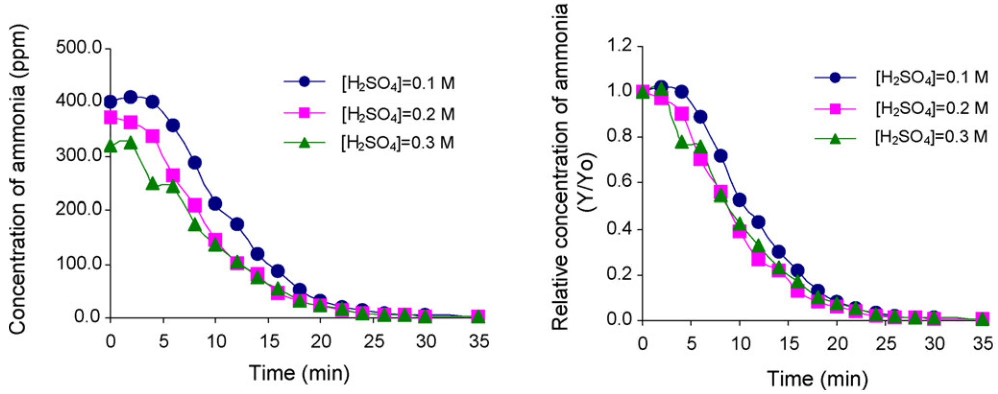

Fig. 7. Concentration change of ammonia in the feed solution as a function of time with different concentrations of the receiving solution using hollow fiber membrane modules (T = 40 °C, Q = 2000 mL min^{-1}).

4.2. Effect of the temperature of the feed solution

The experiments were carried out at 35, 40 and 50 °C using the flat sheet membranes. Fig. 5(a) shows a comparison of the concentrations of ammonia as a function of time at different temperatures.

As can be seen from Fig. 5(a), the mass transfer flow of ammonia increases with the increasing temperature. The curves of 35 and 40 °C are similar however, as the temperature is increased to 50 °C, the concentration change of ammonia is significant. Increasing the temperature is capable of promoting the extraction of ammonia however the increase of the temperature gives a noticeable effect after 40 °C in the studied system. The effect of the temperature on ammonia removal can be explained by the increase of the partial pressure of ammonia with increasing temperatures. As the partial pressure increases, the pressure gradient for the mass transfer increases yielding to a higher driving force and consequently, to higher percentages of extraction in a given time.

4.3. Effect of the circulation rates of solutions

In Fig. 5(b) concentration change of ammonia with different rates of the solutions are compared as a function of time. The velocity of both feed and acid solutions ranged from 782 to 1665 mL min^{-1}. It can be seen that, as the rate of the fluids increases, the extraction percentage of ammonia increases. This can be explained by the boundary layer effect, greater speeds of fluids reduce the resistance for mass transfer indicating that the resistance in the solvent boundary layer is not negligible in the studied range of flow rates.

4.4. Effect of the concentration of the receiving solution

The effect of the concentration of receiving solution was investigated for two different circulation rates of solutions using flat sheet membranes. The experiments were carried out using 0.1, 0.2 and 0.3 M H_2SO_4 solutions at 782 and 1665 mL min^{-1} circulation rates. Fig. 6(a) shows the concentration change of ammonia with time at 782 mL min^{-1} circulation rate using different concentrations of acid solutions. Although a change in the acid solution concentration does not effect the ammonia absorption significantly, a slight decrease can be noticed in the extraction percentages with increasing acid concentrations at 782 mL min^{-1} circulation rate. Fig. 6(b) presents the variation of the concentrations with time at 1665 mL min^{-1} circulation rate using different concentrations of acid solutions. Unlike the case represented in Fig. 6(a), it can be seen that there is a slight increase in extraction percentages with increasing concentration of acid solutions in Fig. 6(b). Nevertheless, an increase in the concentration of the acid solution does not essentially increase of the extraction rate, on the contrary, as can be seen in Fig. 6(a), it was observed an inverse behavior for lower circulation rates, which indicates an influence of the boundary layer of the acid solution when the speed of circulation is lower (782 mL min^{-1}). On the comparison of Fig. 6(a) and (b) it can be seen that the variation of concentration of acid in the receiving phase does not seem to modify the efficiency of the process significantly. This could be due to that the acid is in excess comparing to the ammonia content in the feed.

The effect of the concentration of the receiving solution was also investigated in hollow fiber membranes. Fig. 7 represents variation of ammonia concentration with time using different concentrations of acid solution at 2000 mL min^{-1} circulation rate by means of hollow fiber membranes.

As can be seen in Fig. 7, the effect of acid concentration on ammonia extraction is similar to the behavior observed in Fig. 6(b). Although the influence of acid concentration is not significant for the total extraction time, the extraction percentage of ammonia tends to increase slightly with increasing acid concentration for the first 15 min. However, after 15 min the ammonia concentration curves get closer until the end of the experiment period indicating that the acid concentration does not effect the total process considerably since the acid is excess comparing to ammonia content in the feed.

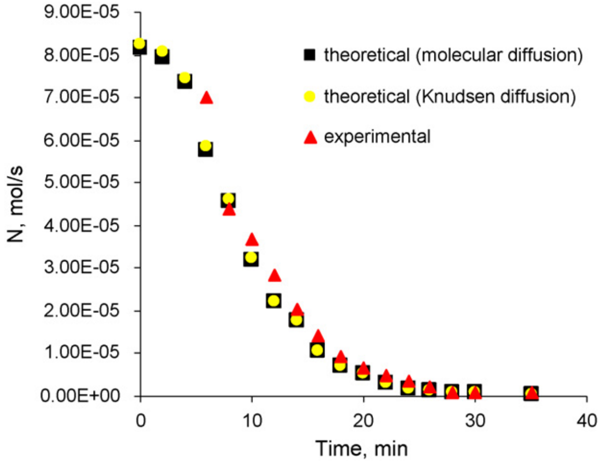

Fig. 8. Comparison of calculated and experimental molar flows as a function of time for hollow fiber membranes ([H_2SO_4] = 0.2 mol L^{-1}, Q = 2000 mL min^{-1}, T = 40 °C, initial ammonia concentration is 500 ppm).

4.5. Modeling and simulation of mass transfer

Theoretical molar flows for hollow fiber and flat sheet membranes were calculated as it was described in Section 3.2. Figs. 8 and 9 present the comparison of the calculated and experimental results for hollow fiber and flat sheet membranes, respectively.

As seen in Figs. 8 and 9 calculated results are in good agreement with experimental results. Theoretical results were calculated for both molecular and Knudsen diffusion in the pores. However, as can be seen from the figures, it has not found a significant difference between calculated results for two mechanisms indicating both mechanisms could be possible. Thus, a transient regime could explain the mass transfer through the membrane pores. These predictions are coherent with the value of the Knudsen number, which

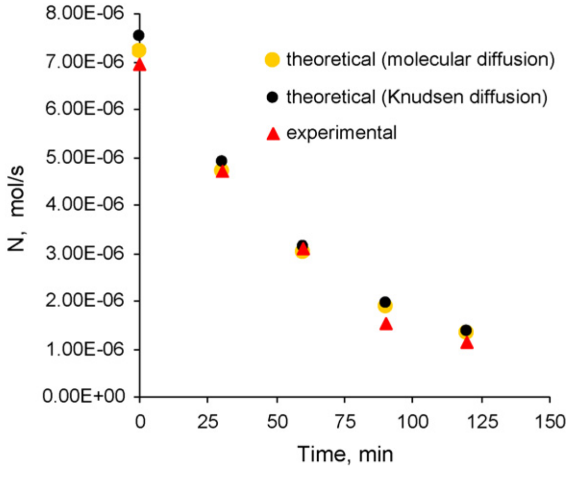

Fig. 9. Comparison of calculated and experimental molar flows as a function of time for flat sheet membranes ([H_2SO_4] = 0.2 mol L^{-1}, Q = 1665 mL min^{-1}, T = 40 °C, initial ammonia concentration is 500 ppm).

was calculated as 0.38 under the conditions considered in this study.

5. Conclusions

Optimal process parameters were investigated for ammonia removal using flat sheet and hollow fiber membrane contactors. The circulation configuration of the solutions was found to have a strong effect on the efficiency of the process. The best circulation configuration of the solutions for the hollow fiber contactors entailed the flow of the feed solution in the shellside while the receiving solution in the lumenside of the membranes. Temperature has also an important influence on the performances since it acts on both the kinetics of the reaction and of transportation through the membrane. For an efficient ammonia removal, ammonia has to be in its volatile form. Increasing the temperature ensures the presence of the free ammonia in the solution. Although sulfuric acid concentration of the receiving solution does not effect the process significantly, higher concentrations of acid solutions at lower circulation rates causes a diminution in the yield of this system, indicating formation of a boundary layer of acid solution, which increases the resistance. The extraction percentages of ammonia increased slightly with increasing flow rates of the solutions due to the decrease of the boundary layer effect. High extraction percentages of ammonia were achieved even at very low ammonia concentrations in the feed. This result may be very advantageous for some specific applications of wastewater treatments considering the ammonium concentrations of interest are quite specific to the source of the wastewater and some applications such as aquaculture requires ammonia removal at levels of 1 mg L^{-1}. Therefore, membrane contactors coupled with a reaction in the receiving phase converting ammonia to an ammonium salt are a good candidate for removal of ammonia from specific wastewater streams with very low concentrations.

A theoretical resistances-in-series model was developed that satisfies with the data obtained from the experiments. This model is based on phenomenological equations considering an instantaneous reaction, which takes place on the interface of the membrane. In order to identify the mass transfer mechanism in the pores, mass transfer equations were calculated for both diffusion mechanisms; molecular diffusion and the Knudsen diffusion. However, it was established that the transport could be described either molecular diffusion or Knudsen diffusion, since there was not a distinct difference between calculated results of each mechanism.

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