Kinetics of TransMembrane ChemiSorption for wastewater with high ammonia contents

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ABSTRACT

The use of membrane contactor solutions (TransMembrane ChemiSorption) is a widely researched area for removing or recovering many kinds of gases from various fluids. In an earlier paper, we examined the removal of ammonia from industrial wastewater and provided a detailed description of the necessary equipment and the technology, as well as modeling the executed process. The aim of this work is to improve the model developed in our earlier study. The models found in literature usually interpret the whole process as a simple diffusion process through a flat sheet membrane. By applying the Bodenstein principle, the model introduced also considers the effect of chemisorption on the whole process. Furthermore, it also focuses on the transfer of the results obtained by the model to the membrane contactor, making its practical implementation possible. The proof of the model’s validity in industrial settings was provided by membrane contactor experiments. The results obtained during the measurements are in accordance with the model and results found in the literature; at the same time, they also reveal further development possibilities.

Keywords: Ammonia removal; Chemisorption; Mass transport; Model; Membrane contactors; Water treatment; Temperature dependence

1. Introduction

The recovery of ammonia from various wastewaters is particularly important since ammonia, as a nitrogen source, decreases the dissolved oxygen level of water, and, due to its fertilizing effect, it promotes eutrophication [1]. It is also toxic for aquatic organisms, such as fish. The use of transmembrane chemisorption also referred to as membrane contactor technology, is a widely researched area for removing or recovering many kinds of gases from various fluids [2,3] and has been demonstrated by a notable number of recently published reports to be efficient for extracting ammonia too [4–8].

In an earlier study, membrane contactor ammonia removal was chosen from the available methods [1], and described in detail the technology and equipment used. Two factors were essentially analyzed to describe the process, the mass transport through the membrane and the stripping (chemical reaction) thereafter [1]. During this latter process, the solvent liquid neutralizes the passing contaminant [9,10].

The mass transport through the membrane was considered a simple diffusion process based on Fick’s first law [10–13], while the stripping effect for the whole process was dismissed since the chemical reaction can be regarded as complete [1,10,11,14]. The model was developed for a flat sheet membrane, and the results were transferred to the membrane contactor with the empirical correlation known from the literature [1,10,13].

In this study, this model has been further developed. By applying the Bodenstein principle for the consecutive processes [15] the effect of the stripping parameters on the whole mass transfer process and the conditions to dismiss it...
is interpreted. Instead of the empirical correlation for membrane contactors, a straight mathematical calculation is provided for the connection between the properties of the mass transfer processes of the flat sheet membrane and the membrane contactor. The latter is very important because the flat sheet membrane is relatively easy to model, while the measurements and practical application take place in the membrane contactor.

2. Theory

2.1. Ammonia

In an aqueous solution, ammonia is present as free ammonia (gaseous ammonia, NH₃) and ammonium hydroxide (NH₄OH, NH₄⁺). The free ammonia concentration is determined by the equilibrium transformation of ammonia and ammonium hydroxide NH₃ + H₂O ↔ NH₄OH, and its ratio (FA) within the total ammonia concentration, [NH₃–N] = [NH₃] + [NH₄⁺] depends on temperature T and the pH of the solution [16].

\[
FA = \frac{[\text{NH}_3]}{[\text{NH}_3-\text{N}]} = e^{-8.467 + 10^{9T}}
\]  

(1)

Free ammonia (NH₃) is able to pass through the membrane, while the entire ammonia concentration [NH₃–N] can be determined by measurement. Going forward, let FA = 1. In this case, ammonia is present in the solution in its gaseous form, which is [NH₃–N] = [NH₃]. If FA < 1, this is considered a correction factor [16] or as alkalinity ([OH⁻] concentration) [10,17].

2.2. Flat sheet membrane model, diffusion process

Free ammonia passes through the membrane by mass transport, which, for ideal solutions ([NH₃] → 0), is based on Fick’s first equation [10–13,18]. According to this, the material flux passing through the membrane is proportional to the concentration gradient:

\[
J_D = -D \cdot \text{grad}[\text{NH}_3]
\]  

(2)

where \( D \) is the diffusion coefficient (m² s⁻¹), and \([\text{NH}_3]\) is the concentration of ammonia as a function of time.

Let us assume the system consists of two (feed and receiving or stripping) boxes separated by a flat sheet membrane and there is full concentration equalization both on the feed ([NH₃]) and on the stripping ([NH₃]) side (in the case of turbulent flow this is a correct approximation). In this case, the concentration gradient can be approximated as:

\[
\text{grad}[\text{NH}_3] = \frac{[\text{NH}_3]_{\text{f}} - [\text{NH}_3]_{\text{s}}}{d}
\]  

(3)

where \( d \) is the membrane thickness (Fig. 1).

By incorporating Eq. (3) into Eq. (2), the (total) molar ammonia flux is as follows, that is, it is proportional to the ammonia concentration difference between the feed and stripping side:

\[
J_K = K \cdot \frac{[\text{NH}_3]_{\text{f}} - [\text{NH}_3]_{\text{s}}}{d}
\]  

(4)

where the proportional factor is the mass transfer coefficient [11–13], namely:

\[
K = \frac{D}{d}
\]  

(5)

For the change in the (feed-side) ammonia concentration per unit of time, the following equation (mass balance) can be formulated:

\[
-V_f \frac{d[\text{NH}_3]_{\text{f}}}{dt} = J \cdot A
\]  

(6)

where \( A \) is the (useful) mass transfer surface of the membrane, which is proportional to the total membrane surface [12], and \( V_f \) is the feed (wastewater) volume (Fig. 1). By comparing Eqs. (4) and (6), the change in ammonia concentration of wastewater per time unit (the diffusion process rate) is:

\[
\frac{d[\text{NH}_3]_{\text{f}}}{dt} = K \cdot \frac{[\text{NH}_3]_{\text{f}} - [\text{NH}_3]_{\text{s}}}{V_f}
\]  

(7)

To solve differential equation Eq. (7) it is generally assumed that the receiving or stripping-side ammonia concentration \([\text{NH}_3]_{\text{s}}\) is 0, since the chemical reaction following the transport process, that is, the stripping – is considered complete [10,11,14]. Nevertheless, the reaction being complete does not necessarily mean that \([\text{NH}_3]_{\text{s}} = 0\), since if the stoichiometric proportion of the solvent fluid exceeds that of the ammonia, the reaction will be complete anyway. Below we examine what the actual conditions are for the receiving-side ammonia concentration to be negligible.

2.3. Stripping process

The mass transfer process is followed by a stripping (chemical) process, during which ammonia that has diffused through the membrane reacts with the sorbent fluid, in our case sulphuric acid, that is, \(2\text{NH}_3 + \text{H}_2\text{SO}_4 = (\text{NH}_4)\text{SO}_4\) and
the (end) product (ammonium sulfate) cannot diffuse back [9]. The reaction rate of ammonium sulfate is proportional to the stripping-side ammonia concentration:

\[
\frac{d([\text{NH}_4\text{SO}_4])}{dt} = k \cdot [\text{NH}_3],
\]  

where \( k \) is the rate constant of the (chemical) process.

2.4. Bodenstein principle, quasi-steady-state approximation

Now the full process consists of two consecutive processes, Eq. (7) mass transfer and Eq. (8) chemical process. The law of mass balance can be applied for the overall process, which in differential form is as follows:

\[
V_f \frac{d[\text{NH}_3]}{dt} + V_s \left( \frac{d[\text{NH}_3]}{dt} + 2 \frac{d([\text{NH}_4\text{SO}_4])}{dt} \right) = 0
\]  

where \( V_s \) is the stripping-side volume. Eq. (9) means that the mass volume which “disappeared” on the feed side per time unit equals the mass volume that “appeared” on the receiving side (ammonia and ammonia sulfide). However, Eqs. (7)–(9) type differential equations can be solved analytically [19], it is complicated and their interpretation is difficult.

For consecutive processes, if the rate constant of the first process is significantly lower than that of the second, a good approximation can be achieved by applying the so-called Bodenstein principle [15], which is known in the literature as quasi-steady-state approximation [20], that is, in the largest part of the process the concentration change of the intermediate product (in this case \([\text{NH}_3]_s\)) can be considered zero:

\[
\frac{d[\text{NH}_3]}{dt} \approx 0
\]  

By applying Eq. (10) Bodenstein principle for equation Eq. (9), and by substituting Eqs. (7)–(8) for that, the receiving-side ammonia concentration is proportional to the feed-side ammonia concentration:

\[
[\text{NH}_3]_s = \frac{KA}{KA + 2kV_f} [\text{NH}_3]_f
\]  

2.5. Simple diffusion approximation

Since the rate constant of the Eq. (8) chemical process \( k \) is several magnitudes greater than that of Eq. (7) transport process \( AK/V_f \), and an hour respectively), and given that \( V_s = V_f \), Eq. (11) can be simplified as:

\[
[\text{NH}_3]_s \approx 0
\]  

According to Eq. (12) the differential Eq. (7) can be simplified as:

\[
- \frac{d[\text{NH}_3]}{dt} = \frac{A}{V_f} k [\text{NH}_3]_f
\]  

The solution of Eq. (13) with the initial condition of \([\text{NH}_3]_f(0) = [\text{NH}_3]_{0f}\) is well known means the process kinetics, which gives an exponential time dependence confirming the conditions generally used [13]:

\[
[\text{NH}_3]_f(t) = [\text{NH}_3]_{0f} e^{-\frac{A}{V_f} k t}
\]  

2.6. Membrane contactor

Ammonia removal by the membrane is usually carried out with a membrane contactor. The schematics of the equipment can be seen in Fig. 2. Wastewater in the feed reservoir is circulated on the feed side of the membrane at a \( Q_f \) rate, while the solvent liquid (2% sulphuric acid) in the stripping reservoir is circulated on the stripping side, and the chemical reaction takes place between the ammonia and the sulphuric acid.

The circulation operation mode made it possible to examine the process kinetics, that is, the dependence of the ammonia concentration of the feed reservoir relevant for the \( Q_f \) volume flow rate on the treatment time \( t \); without this, only the final state could be examined. This also helped stabilize the pH. We provided a detailed description of the equipment in another study [1].

The membrane contactor (Fig. 2) as a recirculation system is compatible with the system in Fig. 1 in case of homogeneous ammonia concentration in the contactor. This would mean that the ammonia concentration entering the contactor is equal to the concentration leaving, which would happen if \( Q_f \rightarrow \infty \). Nevertheless, at a finite rate, there is a concentration difference between the entering and leaving the end of the feed side in the membrane contactor [11].
Let us continue to use the flat sheet membrane approach described in 2.4 supplemented with the Bodenstein principle. According to this, let us assume the ammonia concentration of the wastewater entering the membrane contactor at time \( t \) is \([\text{NH}_3]_f\); the pass-through time is \( \Delta t \), the exit concentration is \([\text{NH}_3]_e\) (Fig. 3), and the feed-side volume of the membrane is \( V_f \). Applying Eq. (14) for these concentrations, the following equation can be given:

\[
[\text{NH}_3]_f = \frac{A e}{V} \left( e^{\frac{A e}{V t}} - 1 \right)
\]

Furthermore, the flow (volume) rate on the feed side is:

\[
\frac{V_f}{\Delta t} = Q_f
\]

Comparing Eqs. (15) and (16) and rearranging the resulting equation, the ammonia concentration out of the membrane contactor can be determined as follows:

\[
[\text{NH}_3]_e = [\text{NH}_3]_f \cdot e^{-\frac{A e}{V t}}
\]

which is in agreement with the results obtained from other models (film theory) [21].

Let us assume the (average) concentration in the feed reservoir at time \( t \) is \([\text{NH}_3]_0\) and at \( t + \Delta t \) is \([\text{NH}_3]_0 + \Delta [\text{NH}_3]_0\). In this case, the following correlation can be established for the mass volume passing through the membrane contactor per time unit from the mass balance:

\[
\frac{V}{\Delta t} \Delta [\text{NH}_3] = V_f \left( [\text{NH}_3]_f - [\text{NH}_3]_e \right)
\]

where now \( V \) is the volume of the feed reservoir.

Combining Eq. (17) into Eq. (18) we obtain the following differential equation for the feed-side concentration:

\[
\frac{\Delta [\text{NH}_3]}{\Delta t} = \frac{Q_f}{V} [\text{NH}_3]_f \cdot e^{-\frac{A e}{V t}} - 1
\]

Furthermore, is proportional to \( t_{cyc} \), the cycle time.

\[
\Delta t = \frac{V_f}{V} t_{cyc}
\]

Let us assume \( V \gg V_f \) so according to Eq. (20) \( \Delta t \rightarrow 0 \). In this case \([\text{NH}_3]_e \approx [\text{NH}_3]_f\) and \( \frac{\Delta [\text{NH}_3]}{\Delta t} \approx \frac{\Delta [\text{NH}_3]}{\Delta t} \). Considering these, the differential Eq. (19) for the case of the membrane contactor, instead of Eq. (13), becomes the following differential equation:

\[
\frac{d[\text{NH}_3]}{dt} = \frac{Q_f}{V} \left( e^{-\frac{A e}{V t}} - 1 \right) [\text{NH}_3]_0
\]

Integrating this between \([\text{NH}_3]_0 - [\text{NH}_3]_0\) and \( 0-t \), the following correlation can be obtained:

\[
\ln \left( \frac{[\text{NH}_3]_0}{[\text{NH}_3]_0} \right) = \frac{Q_f}{V} \left( 1 - e^{-\frac{A e}{V t}} \right) t
\]

where the mass transfer coefficient \( K \) conforms to the \( K_{exp} \) used earlier by ourselves [1] and in the other works [10,13] deduced empirically.

### 2.7. Virtual mass transfer coefficient

By calculating the feed reservoir ammonia concentration from Eq. (22) as the function of treatment time for the membrane contactor will be:

\[
[\text{NH}_3]_0 = [\text{NH}_3]_0 e^{-\frac{A e}{V t}}
\]

This function is analogous to Eq. (14) for the flat sheet membrane:

\[
K_{cont} = \frac{Q_f}{A} \left( 1 - e^{-\frac{A e}{V t}} \right)
\]

where the equivalent (virtual) mass transfer coefficient for the flat sheet membrane solution. In Eq. (24) the \( K_{cont} \) the virtual mass transfer coefficient, is measurable and can be determined from the measurements, while the \( K \) calculated from Eq. (24) is the following:

\[
K = \frac{Q_f}{A} \ln \left( 1 - e^{-\frac{A e}{V K_{cont}}} \right)
\]

In the case of \( Q_f \rightarrow \infty \), \( K_{cont} \) is transferred to \( K \), and, according to this, Eq. (23) to Eq. (14).

### 3. Experiments

#### 3.1. Mathematical method

The values of \( K_{cont} \) of Eq. (23) are calculated by linear regression (Excel) taking the logarithm of Eq. (23) (Fig. 4).
The logarithm of ammonia concentration rate as a function of treatment time. The symbols are measured values, the line is that calculated from Eq. (23).

\[ y = ax + b \]  \hspace{1cm} (26)

The graphic of the function is a linear with \(a\) and \(b\) parameters. The estimated values (point estimation) from the sample are in Eq. (23): \( y = \ln[\text{NH}_3]_\text{r} \)

\[ a = -\frac{K_{\text{trans}}}{V}, \quad x = t \]  \hspace{1cm} (27)

where \(n\) is the number of elements (measured data). The 0-hypothesis is accepted at a 95% probability level, if \( t_{n-2} \geq t_{0.05} \) where \( t_{0.05} \) is the value with a 95% (one side) probability level and \( f = n-2 \) variability (table of the student's test).

The standard errors of parameters are as follows \([23]\):

\[ s_a = \sqrt{\frac{\text{Res}}{n(n-2)\sum(x_i-\bar{x})^2}} \quad \text{and} \quad s_b = \sqrt{\frac{\text{Res} \cdot \sum x_i^2}{n(n-2)\sum(x_i-\bar{x})^2}} \]  \hspace{1cm} (28)

where

\[ \text{Res} = \sum (y_i - y)^2 \]  \hspace{1cm} (29)

is the residual (remaining), the sum of the average differences between measured \( y_i \) and estimated \( y \) values, and \( \bar{x} \) is the average value of \( x_i \).

The confidence interval (both sides) of 95% for \(a\) will be \([\hat{a} - t_{0.025} s_a; \hat{a} + t_{0.975} s_a]\) and similar for \(b\) (interval estimation). \( P = 1-0.95 = 0.05 \) is the significance level \([1]\) – and means the probability that \(a\) is outside the confidence interval in the case of a 0-hypothesis.

3.2. Materials

For the examination presented in the paper, wastewater was used with a high ammonia concentration (5,900–6,150 mg L\(^{-1}\)). These values considerably exceeded the concentrations used in other works to check models (by an order of magnitude) \([9,10,14,16,17]\). The volume of the feed reservoir was \(V = 1\ m^3\), the useful surface of the membrane \(A = 260\ m^2\), and the feed-side wastewater flow rate \(Q_f = 5\ m^3h^{-1}\) respectively. Alkalization was applied to ensure that ammonia is present on the feed side in the form of free ammonia (\(FA = 1\)).

Three parallel measurements with a 0.2 mol L\(^{-1}\) (2%) sulphuric acid concentration on the receiving side at 25°C, 32°C, and 40°C initial temperatures, inside ±2°C–3°C by cooling the receiving circuit were performed (Fig. 4). These values were considered the (nominal) process temperatures. A detailed description of the measurements and the measuring equipment can be found \([1]\).

4. Results

The measurement values are presented in Fig. 4. The \(K_{\text{trans}}\) virtual mass transfer coefficient for the membrane contactor calculated with Eq. (23), and the \(K\) actual mass transfer coefficient, determined from Eq. (25). The number of elements is \(n = 6\) with an \(f = 4\) variability \(t_{4,0.975} = 2.78\) (two-side probability), \(t_{4,0.95} = 2.13\) (one-side probability). The estimated and regression characteristics are contained in the table.

The mass transfer coefficient \(K\) depends on the temperature \(T\). In Fig. 5 the estimated values of the transfer coefficient with a confidence interval of 95% as a function of the temperature can be seen from the data of the table.

5. Discussion

Model Eq. (23) gives a fairly good approximation for the TransMembrane Chemisorption kinetics \((R^2 = 0.9776–0.9853, \ t_{4,0.975} > 2.13)\) with the probability level of 95% generally used (however, the 0-hypotheses can be accepted at a higher level, for example, 99.9%, yet in this case, the confidence interval will be higher as well). The value calculated from the measurements at a 95% probability level for the mass transfer coefficient is \(K = 0.0097–0.0113\) \(\text{m}\ h^{-1}\) at 25°C, which is nevertheless somewhat higher than the value calculated by Semmens under laboratory conditions (albeit for concentrations one magnitude smaller), 0.0095 \(\text{m}\ h^{-1}\) \([10]\), as discussed in the above-mentioned paper \([1]\) with differences between the shell and tube side, and flow directions.

The mass transfer coefficient is dependent relatively strongly on temperature; at higher temperatures it also becomes greater (by approximately 60% from 25°C to 40°C). The temperature dependence can be described with an Arrhenius-type correlation \([24]\).
According to the model, the rate constant of stripping is determined by that of the chemical process. Since this is several magnitudes greater than for diffusion, in the event of full equalization the free ammonia concentration on the receiver side of the membrane is $[\text{NH}_3]_0$. That is, if certain conditions are met – neither does it depend on stripping (type and concentration of the stripping liquid), while the initial ammonia concentration only has a minor effect because of exponential kinetics.

### Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\hat{K}_{\text{cont}}$ (mh⁻¹)</th>
<th>$\hat{K}$ (mh⁻¹)</th>
<th>$R^2$</th>
<th>$t_{\alpha/2}$</th>
<th>$s_\alpha$ (mh⁻¹)</th>
<th>$K$ (95%) (mh⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.0081</td>
<td>0.0105</td>
<td>0.9776</td>
<td>13.2</td>
<td>0.003</td>
<td>0.0097-0.0113</td>
</tr>
<tr>
<td>32</td>
<td>0.0098</td>
<td>0.0135</td>
<td>0.9753</td>
<td>12.6</td>
<td>0.003</td>
<td>0.0127-0.0143</td>
</tr>
<tr>
<td>40</td>
<td>0.0114</td>
<td>0.0173</td>
<td>0.9853</td>
<td>16.4</td>
<td>0.002</td>
<td>0.0168-0.0178</td>
</tr>
</tbody>
</table>

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### 6. Conclusion

The most important conclusion based on the model is that it is a good approximation even for relatively large ammonia concentrations (a few thousand mg L⁻¹) to describe the mass transfer process. Based on the model and the measurements, the maximum emission level permitted (75 mg L⁻¹) at 25°C can be achieved in 2 h, which can be decreased by increasing the temperature (80 min at 40°C, and 60 min at 50°C). However, it must also be considered that there are limits for increasing the temperature, primarily concerning the useful life of the membrane. By measuring the temperature, the model can be used to optimize treatment time.

Treatment time can be proportionally decreased by increasing the membrane surface. The (total) time necessary to treat a given quantity of wastewater, according to the model, does not depend on the volume of the feed reservoir, and, due to the negligible receiver-side ammonia concentration – if certain conditions are met – neither does it depend on stripping (type and concentration of the stripping liquid), while the initial ammonia concentration only has a minor effect because of exponential kinetics.

### Symbols
- $A$ — Membrane area, m²
- $D$ — Diffusion constant, m² s⁻¹
- $E$ — Energy, kJ mol⁻¹
- $FA$ — Fraction of free ammonia, –
- $J$ — Flux, mole m⁻² s⁻¹
- $K$ — Mass transfer coefficient, mh⁻¹, mmin⁻¹
- $P$ — Probability, –
- $Q$ — Flow rate, m³ h⁻¹
- $R$ — Correlation coefficient, –
- $R_g$ — Gas constant, 8.314 J mol⁻¹ K⁻¹
- $T$ — Temperature, K
- $V$ — Volume, volume liquid/reservoir, m³
- $[X]$ — Solute concentration, molm⁻³, mgL⁻¹
- $a$ — Parameter, slope, unit
- $b$ — Parameter, axis section, unit
- $f$ — Variability, –
- $k$ — Rate constant, s⁻¹
- $d$ — Thickness, m
- $n$ — Number of measured values
- $s$ — Standard error, unit
- $t$ — Time, h, min
- $t_f$ — Random variable of student’s test

### Indexes
- $cont$ — Membrane contactor
- $cycl$ — Cycle
- $f$ — Feed side
- $s$ — Stripping side
- $T$ — Belonging to $t$ time

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