Ammonia Removal from Water by Liquid-Liquid Membrane Contactor under Closed Loop Regime.

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Introduction:

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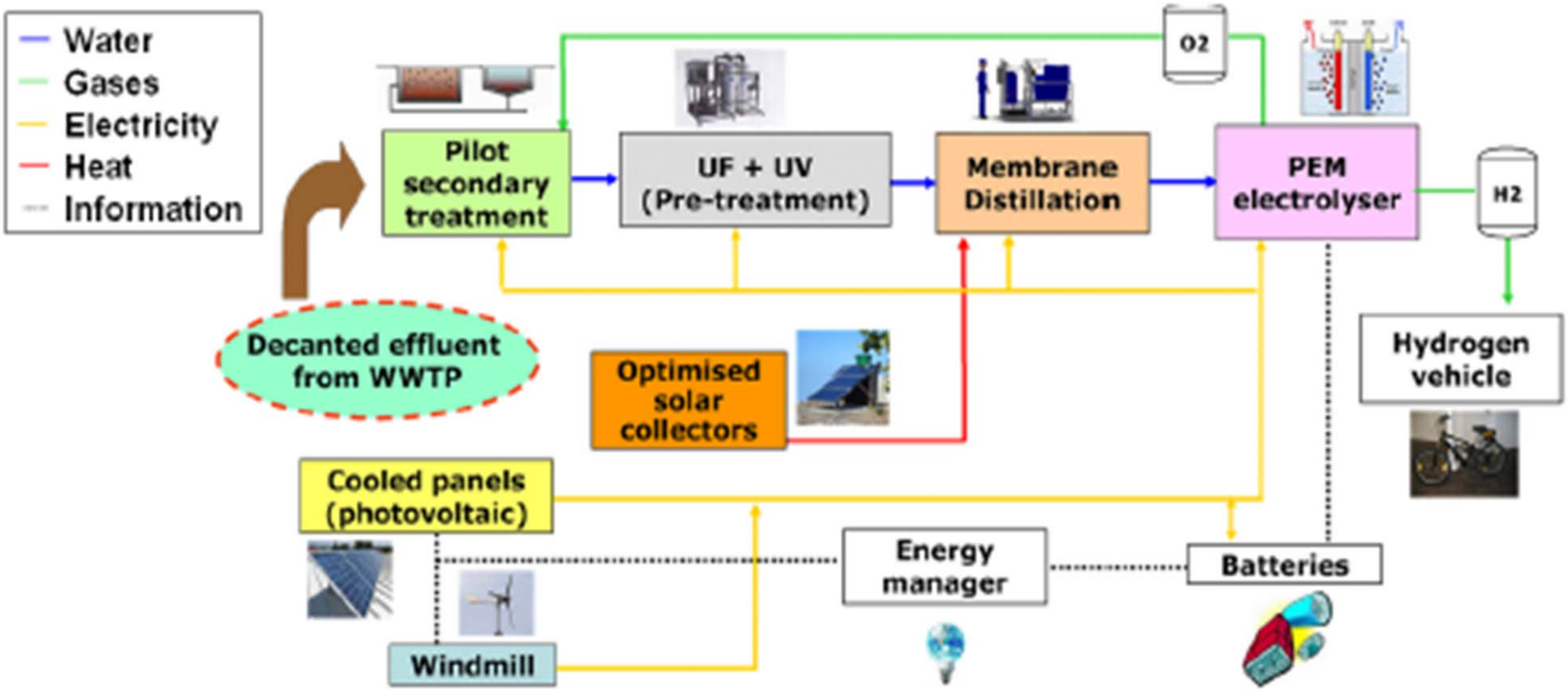
- In this Study the objective is to remove ammonium from water of a waste water treatment plant by a liquid-liquid membrane contactor.
- It will be applied in the Hydrogen and Oxygen production by electrolysis via renewable energies.



Introduction:

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Ammonia in water exists in free and ionic forms under equilibrium as:

$$NH_{3(aq)} + H_2O \Leftrightarrow NH_4^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$

For values below the pKa (9.3), ammonium is greater than ammonia. When pH is higher than the pKa, we found ammonia as predominant compound.

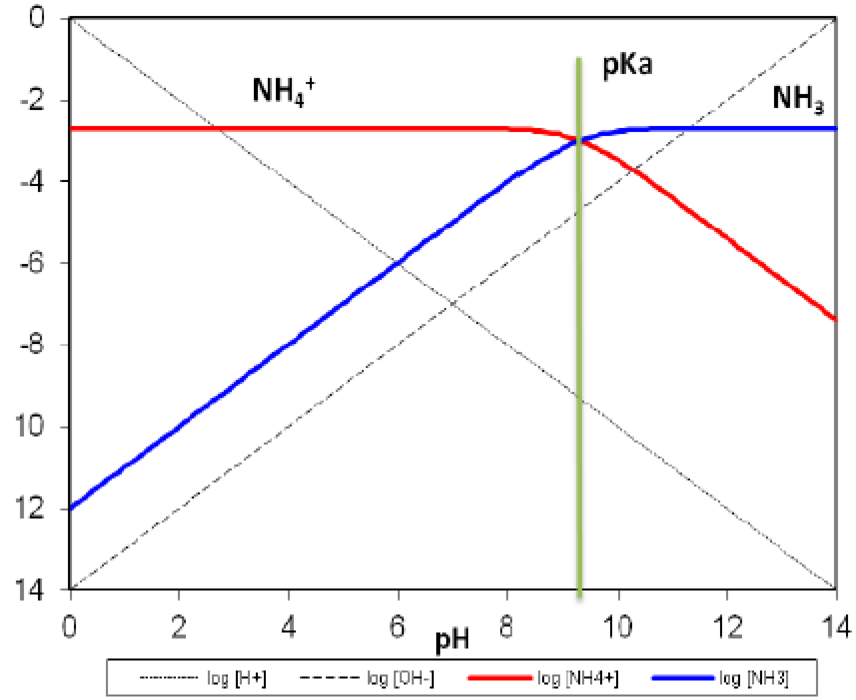

Figure 1. Dependence of the Ammonia-Ammonium equilibrium with respect to pH.

Experimental setup

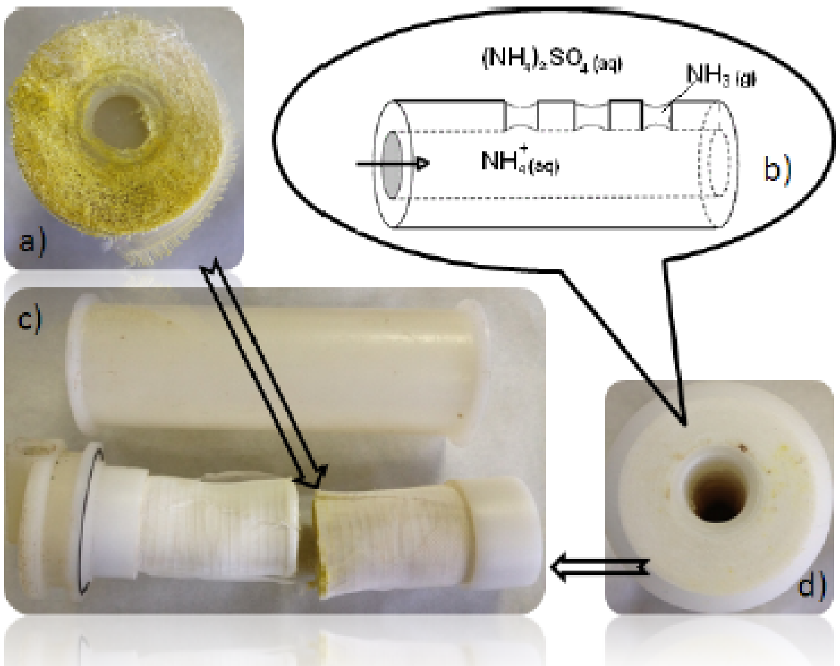

Figure 2. a) Cross section of a membrane module showing the fibers. b) Hollow fiber with the transport phenomena. c) Membrane contactor. d) Side view of the entrance to the hollow fibers.

Ammonia reacts with OH-ions present in the water, leading to gaseous ammonia molecule NH3.

This gas pass through the hydrophobic membrane porous and reacts with the acid solution, where it is immediately dissolved as is shown in Figure 2-b.

Experimental setup

- **Materials**
  - The hydrophobic membrane contactor HFMC, (Liqui-Cel X30HF, Celgard, USA).
  - Ammonium chloride
  - NaOH,
  - H_2SO_4
  - Borax
  - Ion Chromatography (ICS-1000 Dionex, USA).

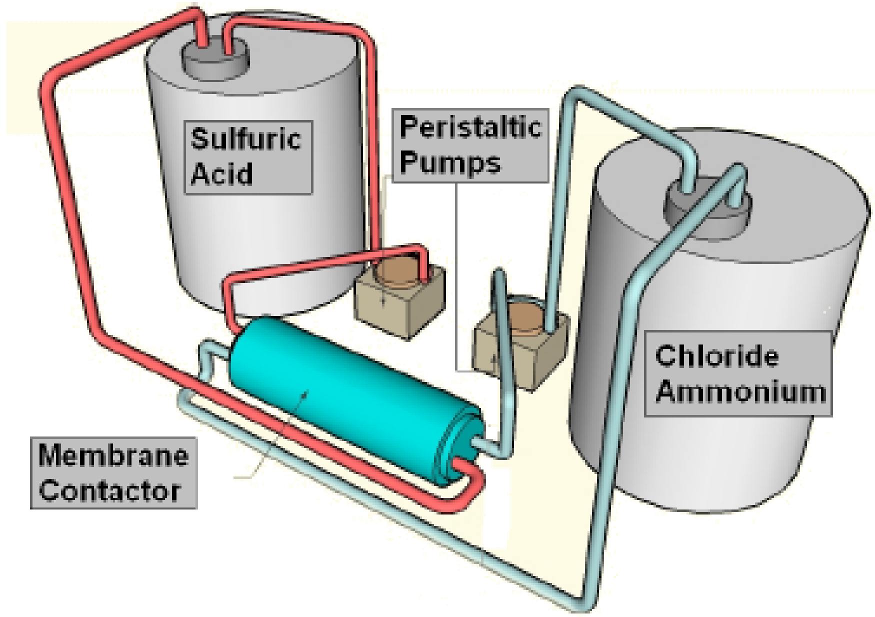

Figure 3. Experimental setup.

- **Set-up and procedure**

The pH of the feed solutions was set higher than the usual value of pKa with NaOH. Borax buffer has been used to keep the pH.

Equations

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Following assumptions that have been made for some authors [1-4]:

- Unsteady state and isothermal conditions.
- Henry's law is applicable for solution-membrane interface.
- No pore blockage
- The reaction of ammonia with the sulfuric acid is instantaneous and always occurs in excess
- Flow rates of both ammonia solution and sulfuric acid are constant.
- Feed tank operates at the perfect mixing.

$$\frac{\partial C_j}{\partial t} + U_z \frac{\partial C_j}{\partial Z} = D_j \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_j}{\partial r} \right) + \frac{\partial^2 C_j}{\partial Z^2} \right\}$$

$$C_{j,Z=0} = C_{tank} \qquad \left(\frac{\partial C_j}{\partial r} \right)_{r=0} = 0$$

$$-D_j \left(\frac{\partial C_j}{\partial r} \right)_{r=r_{hf}} = k_{g,pore} \left(\frac{p^g{}_{a,\text{int}}}{R_g T} \right)$$

Use of COMSOL

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One single hollow fiber is simulated using a 2D axisymmetric model with the PDE coefficient form

The equations were normalized in terms of the aspect ratio of the fiber.

Recirculation is taken into account as a boundary condition in Z=0, where a ODE describes the concentration in the tank as a global equation

$$d_a \frac{\partial C_j}{\partial t} + \beta \cdot \nabla C_j = c \nabla^2 C_j$$

$$-D_j \left(\frac{\partial C_j}{\partial R} \right)_{R=1} = \frac{k_{g,pore}}{r_{hf}} \left(\frac{p^g{}_{a,\mathrm{int}}}{R_g T} \right)$$

$$d_a = 1 \qquad \beta = \begin{bmatrix} -D / r_{hf} \\ 2\overline{U}\left(1 - R^2\right) / L \end{bmatrix}$$

$$p^g{}_{a,\mathrm{int}} = \frac{H_a C_{j,R=1}}{\left(1 + \frac{K_b}{10^{pH-14}}\right)} \qquad c = \begin{bmatrix} \frac{D}{r_{hf}^2} & 0 \\ 0 & \frac{D}{L^2} \end{bmatrix}$$

$$V \frac{dC_{\tan k}}{dt} = Q\left(C_{j,z=L} - C_{\tan k}\right)$$

$$C_{j,Z=0} = C_{\tan k}(t)$$

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$$pH(t) = pH_0 + \frac{(pH_{end} - pH_0)t^{3/2}}{6.58*10^4 + t^{3/2}}$$

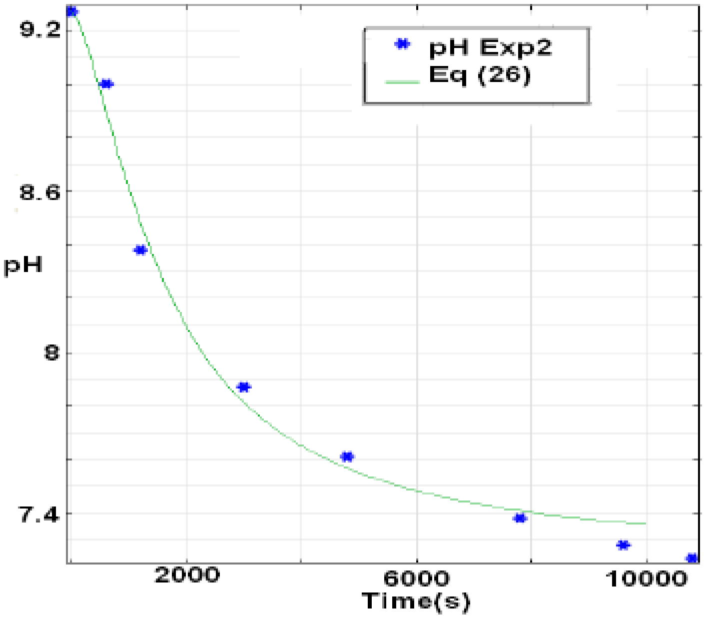

Figure 4. Evolution of pH in an experiment without buffer solution.

The pH of the solution in the tank was considered as a time dependant function, fitted in a previous step in MATLAB from experimental results

Results

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In the Figure 5 is shown how the concentration is decreasing when the fluid pass the lumen of a fiber, at R=1 the transport of the ammonia trough the membrane to the acid solution is occurring.

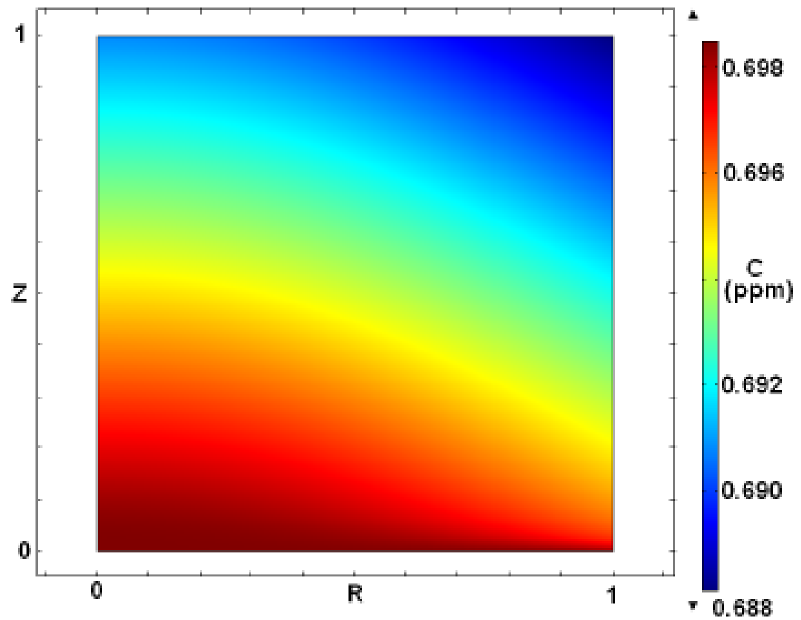
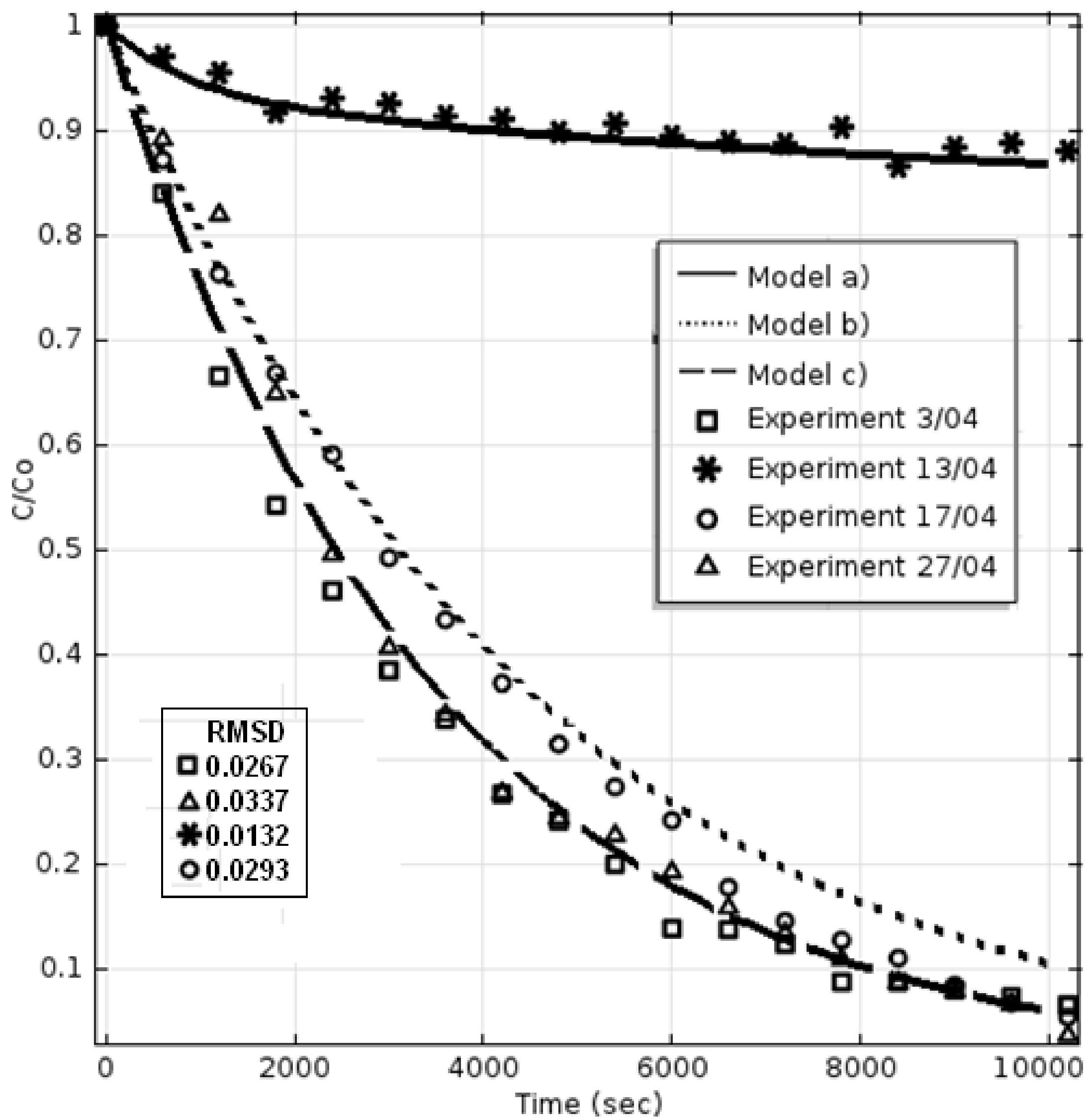


Figure 5. Distribution of Cj over plane inside the fiber for a t=10000 seconds.

$$RMSD = \sqrt{\frac{\sum\left(y_{\exp} - y_{est}\right)^2}{n}}$$



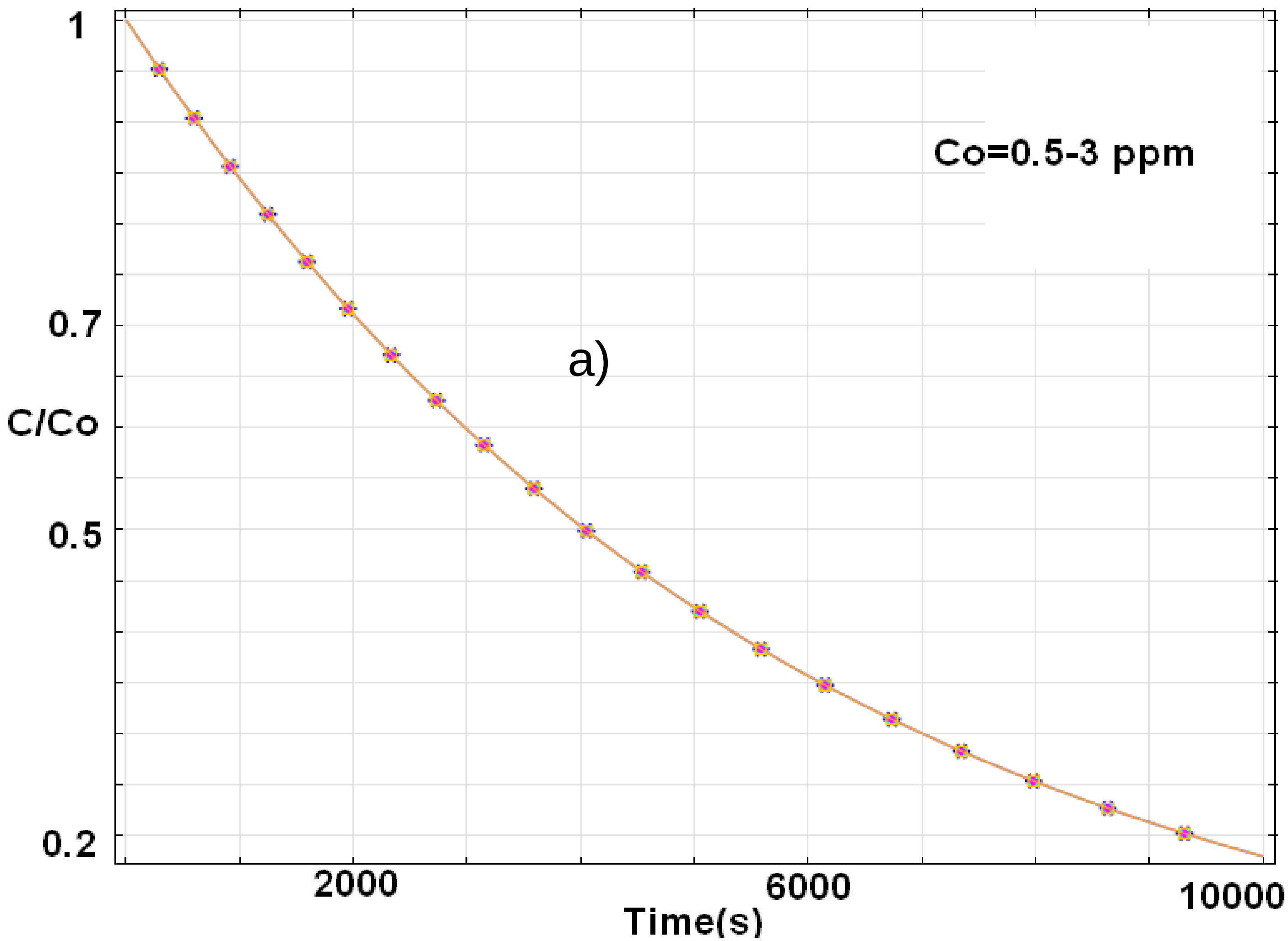
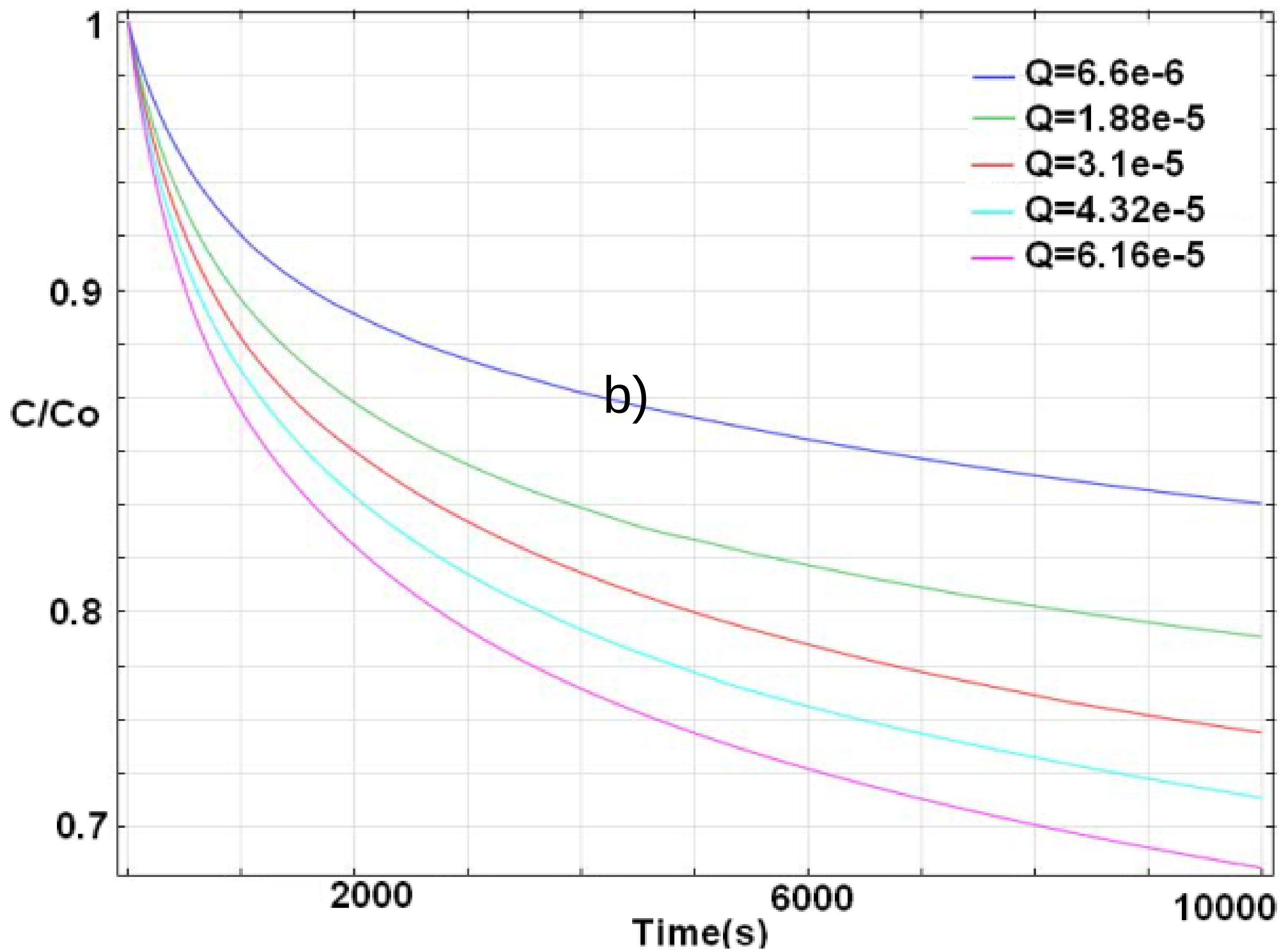
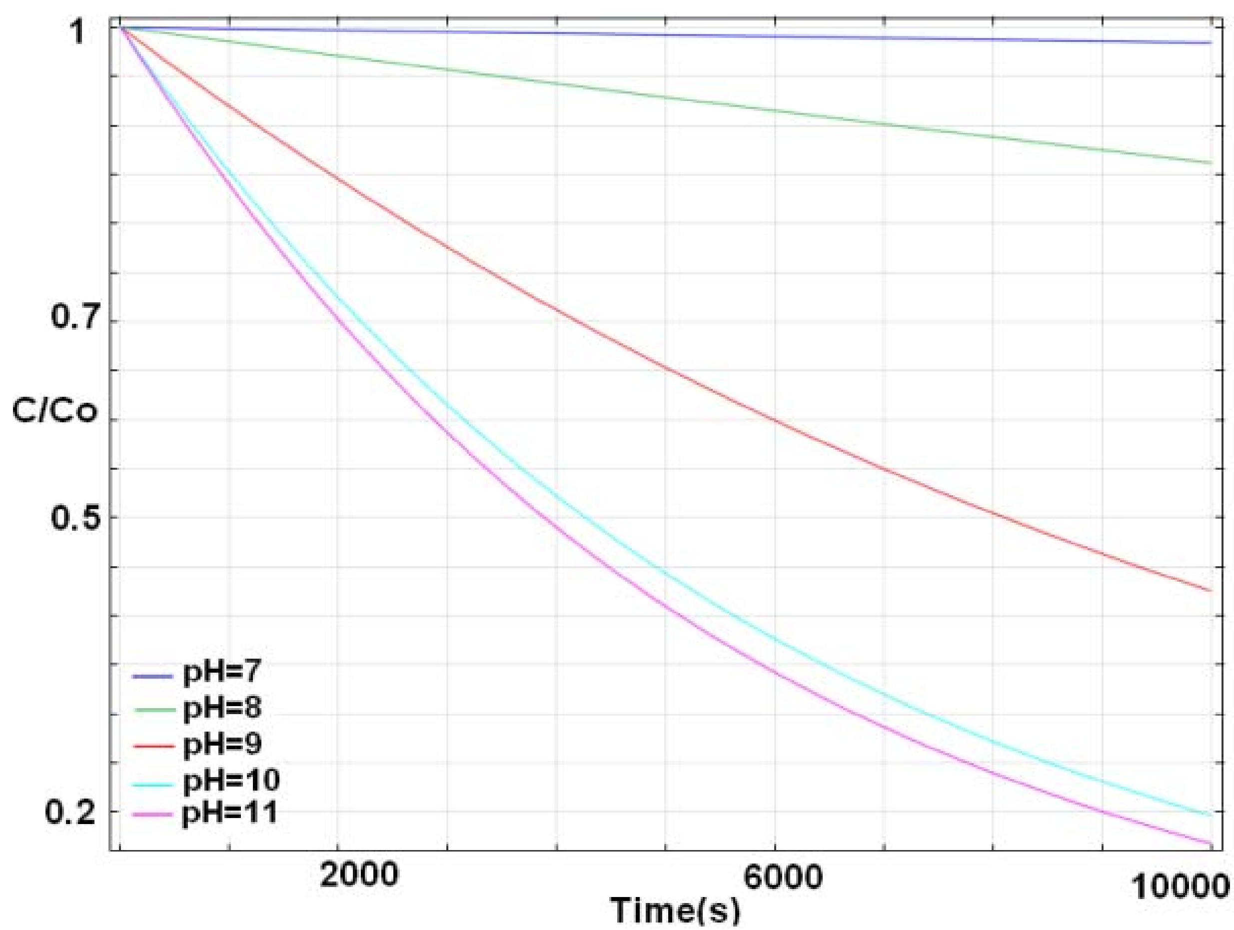


Figure 7. Evolution of concentration in the feeding tank at different conditions.



1
0.9
0.8
0.7
C/Co
2000
6000
10000
Time(s)
Q=6.6e-6
Q=1.88e-5
Q=3.1e-5
Q=4.32e-5
Q=6.16e-5
b)



1
0.7
C/Co
0.5
0.2
pH=7
pH=8
pH=9
pH=10
pH=11
2000
6000
10000
Time(s)

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Conclusions

- The membrane contactor model can be used to evaluate the hollow fiber membrane contactors performance for ammonia removal from aqueous solutions under different conditions and to define the operational parameters.

- This model is suitable for prediction of ammonium removal in view the minimal deviations when compared to the experimental data.

- The most important parameters to control during the experiment are the flow rate and the pH, mainly the last one, due to the high dependence in the chemical equilibrium of ammonium reaction to ammonia.

- More rigorous approaches will be taken in to account in further works where the model include the solution for the hydrodynamics inside the membrane contactor.

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Acknowledgments

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Thank you for your attention.

Questions suggestions and comments are welcome.