Using 'TransMembraneChemiSorption' (TMCS) for Ammonia Removal from Industrial Waste Waters

Introduction

Dissolved gases like NH_3, H_2S or NOx in wastewater lead to contamination in the sewage system and high treatment costs for municipal wastewater treatment plants. This translates into high penalty fees that are paid by the company discharging these contaminates into the sewage stream. In many cases a membrane-based water treatment system can be justified because of a favorable pay back time.

Large-scale systems using conventional treatment processes such as extraction, stripping, or absorption can lead to several problems or issues. These issues may be overcome by using an alternate solution of Membrane Contactor technology. Membrane Contactors can remove ammonia from wastewater and recover it to a usable form in a single step.

It is therefore an adequate and desirable solution for treating the ammonia wastewater without polluting the air.

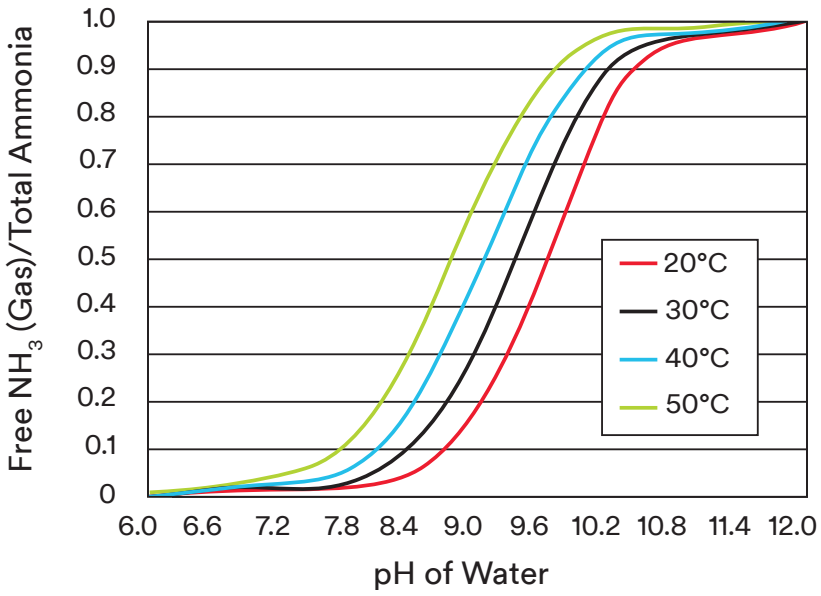
Process description

Ammonium ion (NH_4+) in water reacts with hydroxide ion (OH-) according to the following **Equation 1**.

$$NH_4^+ + OH^- \longleftrightarrow NH_3(g) + H_2O(l) \quad \textbf{Eq 1}$$

This reaction is reversible and can be driven forward or backward depending on the water pH as shown in **Figure 1**.

Fig. 1: Ionization Equilibrium of Free NH_3(g) in Water as Function of pH and Temperature



At a pH of 11.3 or higher, the equilibrium favors the formation of free ammonia gas which can be removed from a wastewater solution across the air filled pores of a microporous hydrophobic membrane when a proper driving force is maintained.
The small pore size and the hydrophobic nature of membrane prevents the liquid phase from entering into the pores or flowing through the porous wall due to surface tension effects.

Because of the very low Henry constant and high solubility of NH_3 compared to other dissolved gases in water, such as CO_2 or O_2, the free ammonia gas will be difficult to remove by applying vacuum or by using a sweep gas-vacuum combination as in typical degassing operations with Membrane Contactor technology.

However, an acid solution will work very effectively as a means of removing the ammonia gas from wastewater. The low-pH sulphuric acid solution will instantly react with ammonia gas according to **Equation 2** below to form ammonium sulphate. This will generate and maintain the concentration differential or driving force for removing ammonia from waste water.

$$2NH_3 + H_2SO_4 \longleftrightarrow (NH_4)_2\,SO_4 \qquad \textbf{Eq 2}$$

The process above generates a concentrated solution of up to 30% of ammonia sulphate, which is a fertilizer.

This process, also described as: "TransMembraneChemi-Sorbtion" (TMCS), is shown schematically on a single fiber in **Figure 2.**

The wastewater flows through the shellside of the contactor (outside of the membrane), while an acid solution, such as sulphuric acid, circulates on the lumenside. (**Figure 3** shows the flow paths of both streams.)

Fig. 2: Cutaway of a Single Microporous Hollow Fiber Showing TMCS of Ammonia

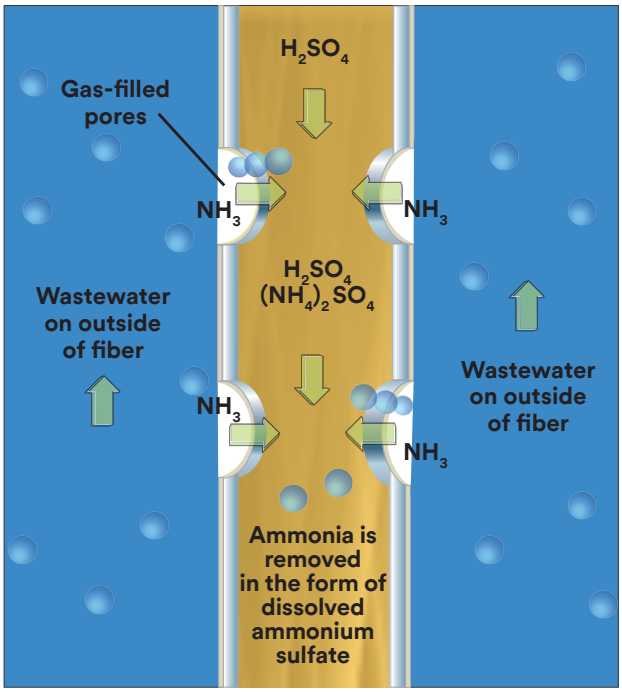
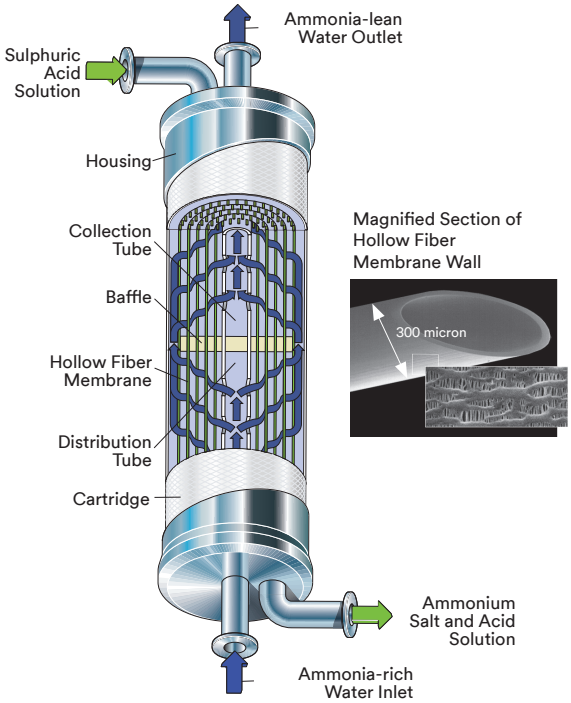


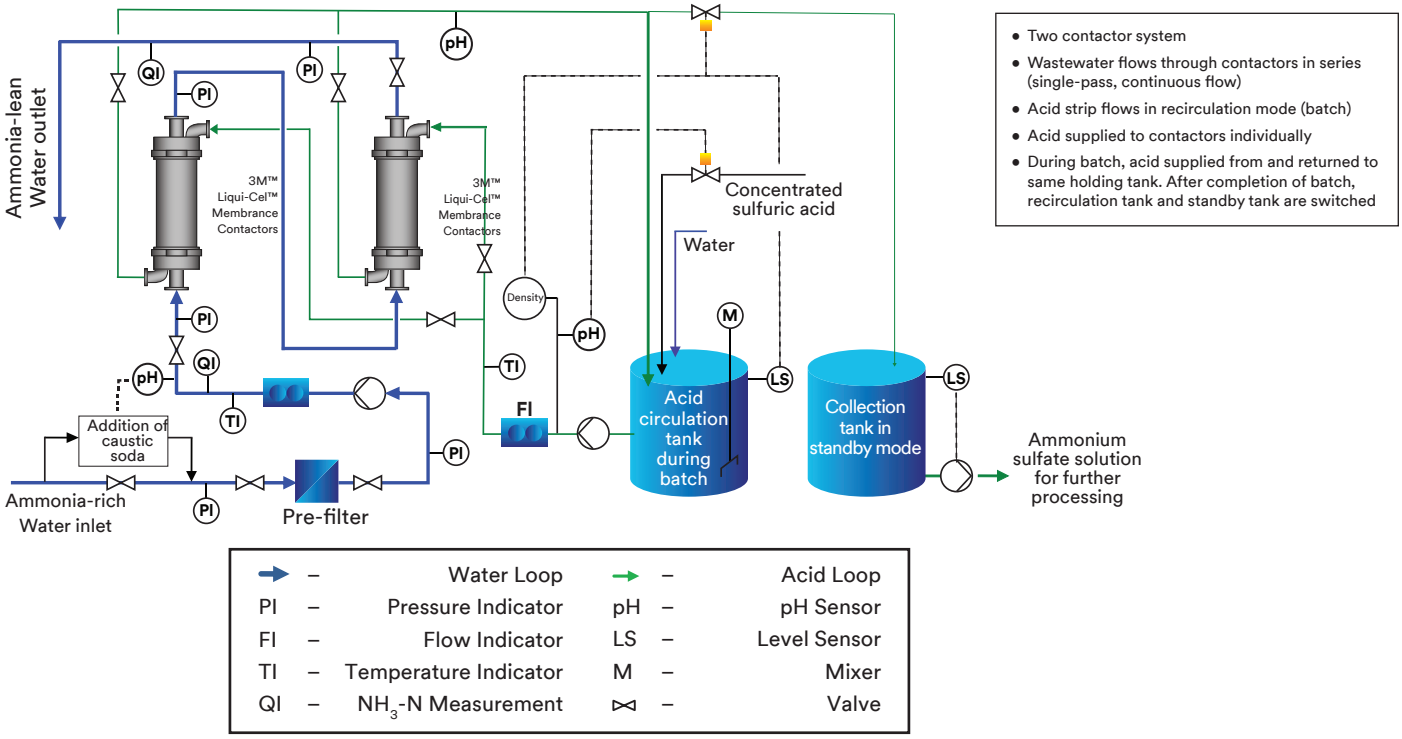
Fig. 3: 3M™ Liqui-Cel™ Membrane Contactor EXF Series for TMCS Operation



System design

A schematic process diagram of a typical plant for TMCS of ammonia is shown in Figure 4. For each contactor, the wastewater flows from bottom to top through the shell side of vertically installed membrane contactor. The acid solution flows through the lumen side of contactor from top to bottom. Feed water flows through the contactors in series, while acid should always be fed to contactors in parallel. The ammonium salt solution is pumped from circulation tank in batch mode. If the maximum level of the circulation tank is reached, the solution is redirected to the collection tank.

Fig. 4: Generic P&ID with Two Membrane Contactors in Series for TMCS of Ammonia



Successful operation of a 3M™ Liqui-Cel™ Membrane Contactor system in the TMCS mode depends on a well-designed fluid path. It is important to follow these recommendations when designing a system.

Ideal Process Parameters for Ammonia Removal

- NH_3 (g) inlet concentration > 200 ppm (mg/L)
- Wastewater pre-filtration (absolute) < 5 µm absolute
- Temperature range > 35-50 °C (95-122) (F)
- Wastewater stream pH ≥ 11
- Acid stream pH ≤ 1-2

The acid and caustic consumption depends on the inlet water, the pH, the water temperature and the ammonia content. When the inlet parameters are closest to being in the free ammonia state, with concentrations suitable for membrane contactor treatment that fit within the operating window of the TMCS process, less acid and caustic will be required.

Conclusion

Single-step TransMembrane ChemiSorption (TMCS) facilitated by 3M™ Liqui-Cel™ Membrane Contactors can enable resource recovery and process flexibility, as well as help reduce environmental impacts. When compared to traditional steam or air stripping, they can provide:

- Compact, modular and scalable designs
- Combined processes and in-line operation
- Operation at lower temperatures for reduced energy consumption

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