TransMembrane ChemiSorption, an emerging solution for ammonia removal and recovery from microelectronics fabrication wastewater.

Remediation Synopsis:

The use of 3M™ Liqui-Cel™ Membrane Contactors for dissolved gas management in the production of ultrapure water has been a standard for semiconductor wafer manufacturing for over three decades. The utilization of membrane degassers for the treatment of wastewater effluent within this industry is a relatively new application for membrane degassing technology. This technical brief takes a closer look at remediation of ammonia wastewater effluent using 3M membrane degassing technology.

Introduction:

As global environmental regulations become more stringent and awareness grows, wastewater treatment prior to effluent release in the semiconductor wafer manufacturing process is increasingly critical to help support sustainable operations. An important consideration of wastewater effluent from microelectronic fabrication process is the treatment and recovery of ammonia from wastewater. Ammonia wastewater has been a byproduct of wafer cleans since the introduction of the RCA (SC-1 & SC-2) process in 1965. Wet cleaning steps, buffered oxide etch, chemical mechanical polishing (CMP), etc., are critical process steps in the fabrication of CMOS devices and display panels. These important fabrication steps are also significant contributors to the NH_4-N concentrations found in wastewater.

Traditional methods of ammonia waste treatment include air stripping and acid adsorption using packed columns or towers, pyrolysis and biological treatment options such as annamox and nitrification/denitrification to breakdown ammonium. An important and novel technology is the stripping and recovery of ammonia from wastewater using Liqui-Cel membrane contactors.

The use of membrane contactors combines the removal and recovery of ammonia into a single step and is known as Transmembrane ChemiSorption (TMCS). Liqui-Cel membrane contactors enable a process to effectively reduce, recover — and in some cases — recycle NH_4-N from wastewater streams.

Many microelectronic fabricators already utilize membrane contactors in the production of de-ionized and ultrapure water to remove dissolved oxygen and carbon dioxide, as well as to control levels of dissolved nitrogen and hydrogen in the production of functionalized water. These same membrane contactors can be utilized in lieu of other technologies to strip and recover ammonia from semiconductor wastewater effluent.

The availability of waste acid streams from other steps in wafer manufacturing makes it cost-effective for stripping ammonia. The familiarity of the use of these membrane contactors within other gas stripping operations, facilitates adoption of TMCS within the electronics segment. Additionally, the low particle content and ease of pretreatment makes this wastewater effluent an ideal stream to utilize a Liqui-Cel membrane contactors for ammonia abatement.

TransMembrane ChemiSorption Process Description:

Free ammonia gas can be removed from a feed 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 the membrane interface prevents aqueous liquid phases from entering the pores or flowing through the porous wall.

Because of the very low Henry constant and high solubility of NH_3 compared to other dissolved gases in water, 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 contactors used in ultra-pure water. The use of an acid solution will work effectively as a stripping solution for removing dissolved ammonia gas from wastewater. The low-pH acid solution will react with ammonia gas to form an ammonium salt thereby maintaining high driving force for ammonia transfer. Most commonly sulfuric acid is utilized as the stripping solution, but phosphoric acid is another waste acid stream commonly used in integrated circuit fabrication and has been demonstrated to maintain removal performance slightly better than sulfuric in TMCS characterization studies[1] (see figure 1).

Ammonia gas reacts according to Equation 1 below to form ammonium sulfate.

Equation 1:

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\,SO_4$$

This reaction will generate and maintain the concentration differential or driving force for removing ammonia gas from wastewater. This process is described as TransMembrane ChemiSorption or TMCS. Since TMCS relies on the transfer of dissolved ammonia gas through the membrane pores separating the ammonia rich wastewater and stripping streams, an elevated pH and temperature of the wastewater stream favors the ionization equilibrium (eq. 2) of ammonia nitrogen to free ammonia gas, as seen in figure 2.

Equation 2:

$$NH_3 + H_2O \longleftrightarrow NH^+_4 + OH-$$

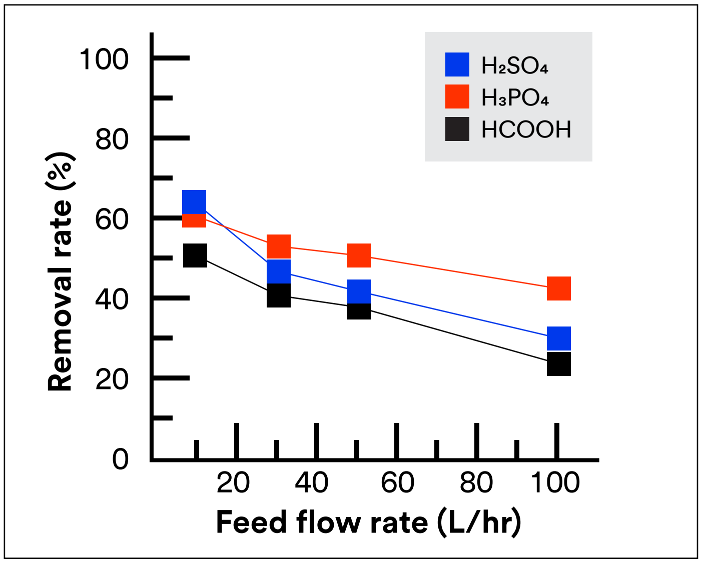


Figure 1: Ammonia removal stripping sorbent comparison by flowrate

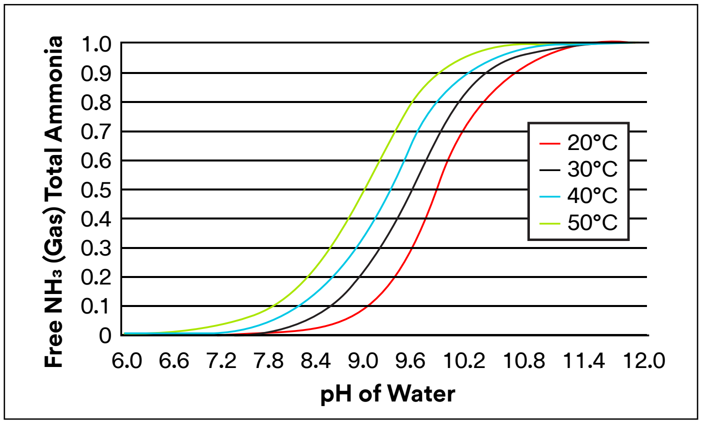


Figure 2: Ratio of free dissolved NH_3 to Total Ammonia Nitrogen in water as influenced by pH and Temperature

3M™ Liqui-Cel™ Membrane Contactors have a large contact area to volume ratio, accomplished by packing hundreds of thousands of hollow fiber membranes in a vessel. Figure 3 below describes the flow path of the wastewater within a Liqui-Cel membrane contactor during TCMS.

Figure 3: Liqui-Cel Membrane Contactor EXF Series for TMCS Operation

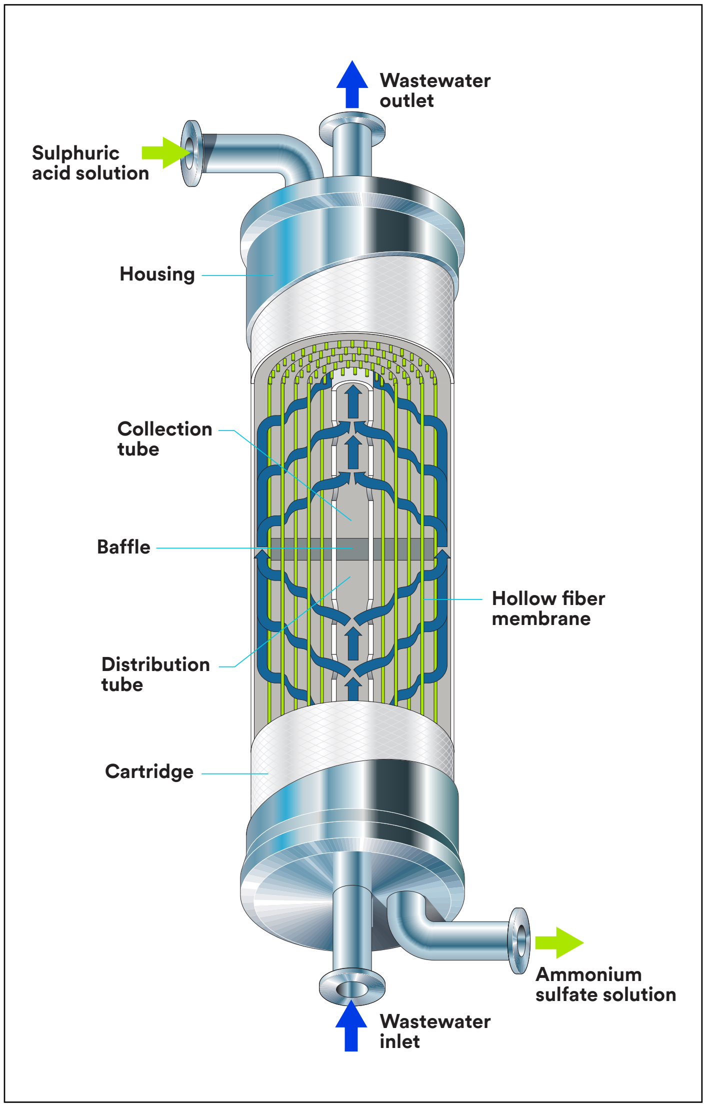
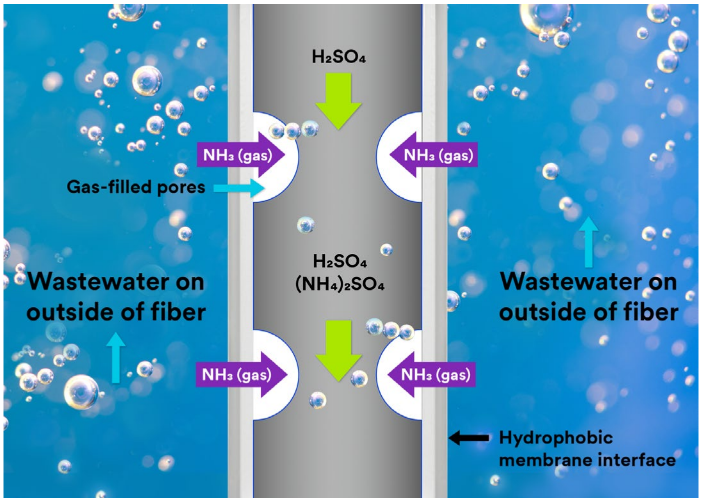


Figure 4 displays the gas diffusion path at the hollow fiber level. The ammonia rich water flows on the shell side (hollow fiber outer surface), while the stripping acid solution circulates on the lumen side (inside surface of the hollow fibers), reacting with the gaseous ammonia which diffuses through the porous membrane structure, without direct contact between the two liquid streams.

Figure 4: Single microporous hollow fiber showing mass transfer of ammonia gas molecules

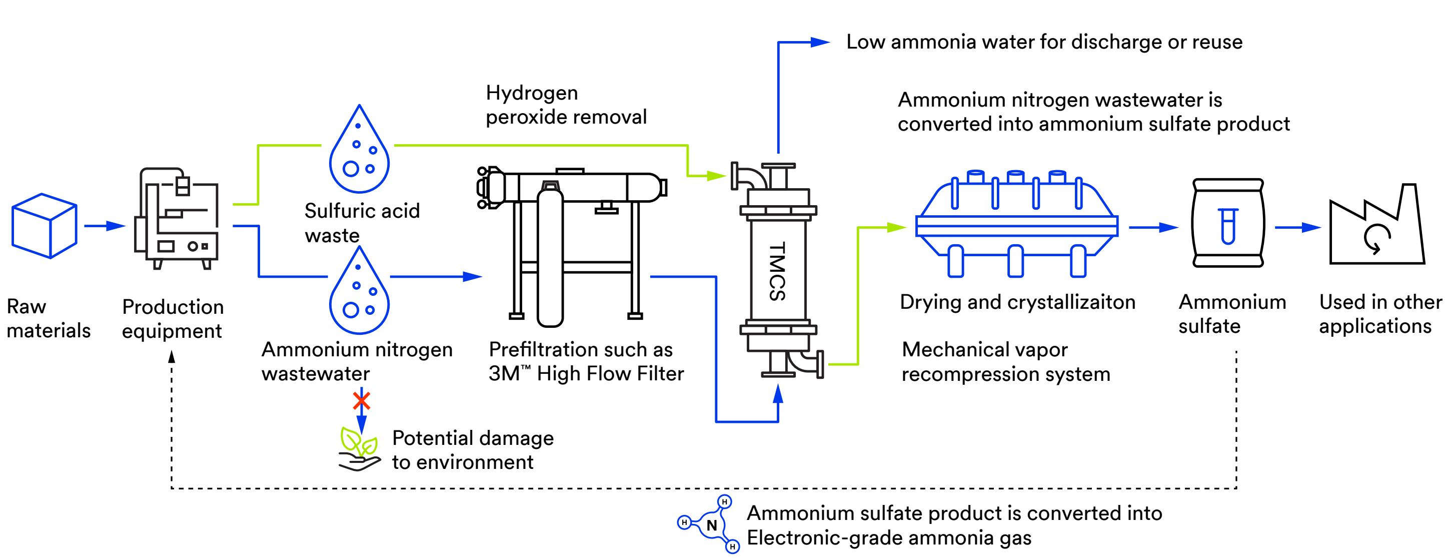


Practical Recycling of Ammonia using Waste Acid Streams:

TransMembrane ChemiSorption has an attractive value proposition in the semiconductor segment by providing recycling of waste acid streams and production of ammonium salts that can have can be further processed into usable byproducts. F. Zhenggui, et al., from Taiwan Semiconductor, describes the use of TransMembrane ChemiSorption to recycle ammonia nitrogen from discarded alkaline recycle (CWD-N), alkaline scrubber discharge (AEX-N) and ammonium fluoride fab discharge (NH4F-N)[2]. This system utilizes sulfuric acid waste recycle as the stripping media.

Ammonia removal efficiencies of 95-99% and ammonium sulfate concentrations of 30%, have been achieved with multiple Liqui-Cel membrane contactors in series. Ammonium sulfate can have economic value with further processing, recycled into industrial or electronic grade ammonia gas and used to generate gypsum board. While ammonium sulfate could be used as a fertilizer, there are restrictions when the byproduct emerges from industrial processes. These regulations vary by region.

Figure 5: Recycle of ammonia in microelectronics with value added byproducts

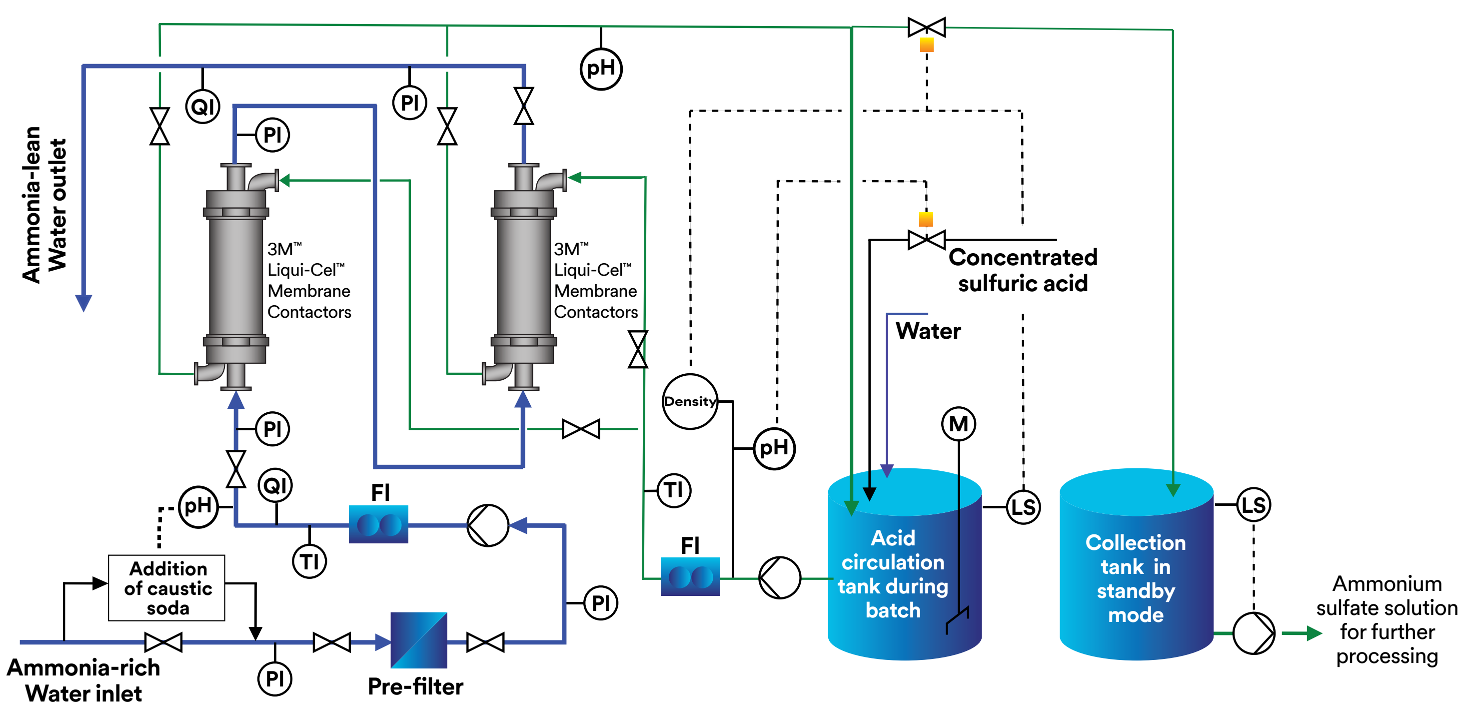


Basic TMCS System Design:

A schematic of a general TMCS process flow for 3M™ Liqui-Cel™ Membrane Contactors used in the treatment of ammonia wastewater is shown in Figure 6. For each contactor, the wastewater flows from bottom to top through the shell side of vertically installed Liqui-Cel membrane contactors. The acid solution flows through the lumen side of the contactors from top to bottom, or countercurrent to the ammonia rich wastewater.

The ammonia wastewater feed flows through the contactors in series, while acid should always be fed to the Liqui-Cel membrane contactors in parallel. The ammonium salt solution is pumped from a circulation tank in batch mode. A steady pH setpoint is maintained by adding fresh acid to the recirculation tank during the batch. If the maximum level of the circulation tank is reached, the solution is redirected to the collection tank.

Figure 6: Generic P&ID with two Liqui-Cel Membrane Contactors in Series for TMCS of NH_3



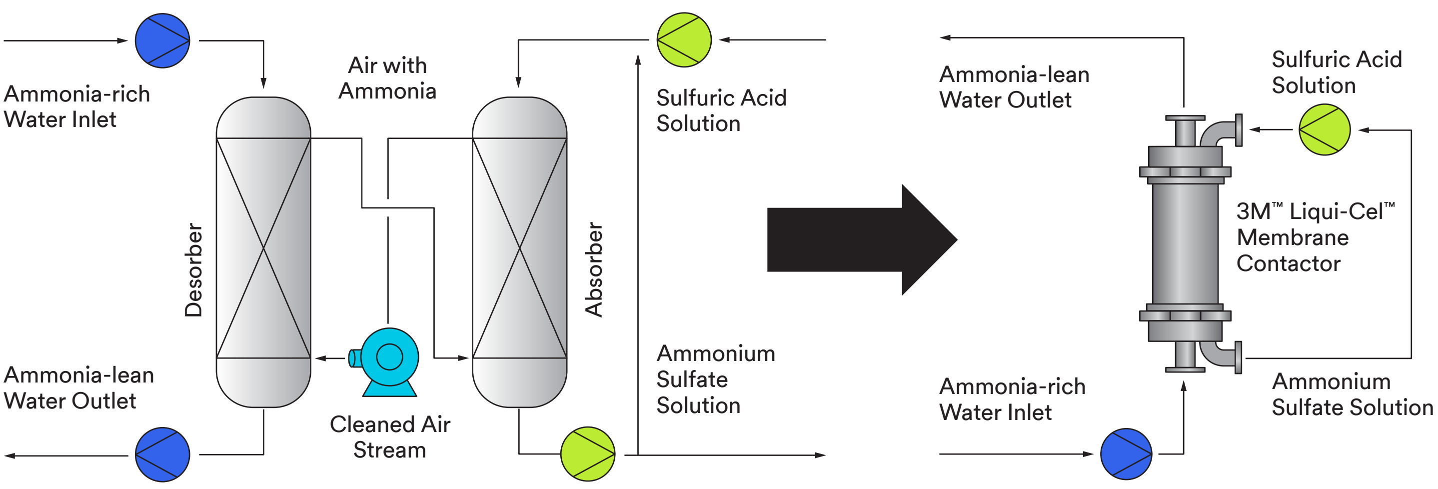
The optimum process parameters and pretreatment for successful operation of a TMCS system for ammonia removal are found to be:

- NH_3(g) inlet concentrations > 200 ppm (mg/L)
- Wastewater prefiltration with ≤5 um absolute filter rating, such as a 3M™ High Flow Series Cartridge
- Pre-treatment of oxidizing agents present in the ammonia wastewater feed stream. Peroxide levels not to exceed 10 ppm
- The ammonia-rich inlet wastewater temperature range should be 35-50°C
- The ammonia-rich inlet wastewater stream should be pH > 10, this will usually require dosing with caustic injection to reach target pH
- The strip acid stream pH ≤ 1-3
- TDS <2 ppm

TMCS and Conventional Technology Contrast:

A common technology for treating microelectronic ammonia wastewater streams is the use of packed or tray towers (columns) to remove ammonia. The use of towers involves a two-stage process of stripping the ammonia from the liquid stream into an air stream, followed by an acid scrub of the air to produce an ammonium salt. By contrast TMCS is a single stage process with high specific contact area, providing a single stage ammonia removal process in a compact volume footprint — see figure 7.

Figure 7: Tower technology and TMCS comparison



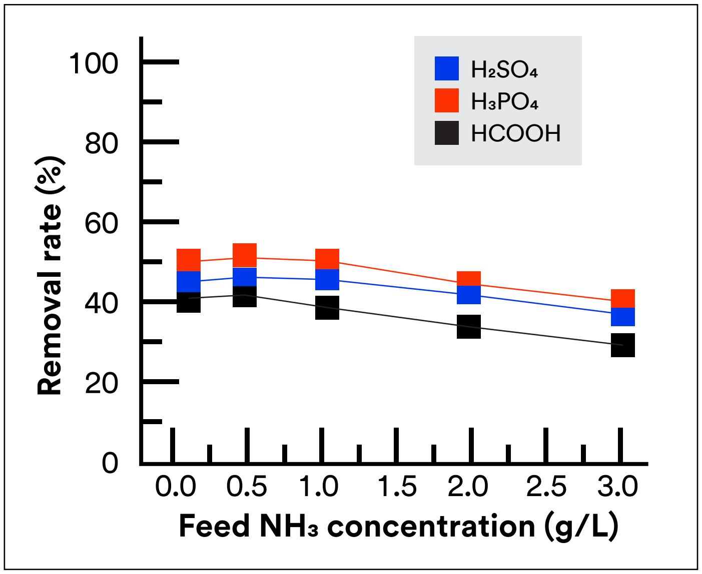
Conventional Two-Stage Stripping + Scrubbing Process **Single-Stage TMCS Process**

Tower scrubbing technology's total gas-liquid contact area is determined by the droplet concentration within the scrubbing column. Appropriate selection of nozzles/atomizers has a significant impact on the contact surface area between the liquid and gas phase. The spray tower scrubbing liquid (acid) pressure, also plays a significant role in the efficiency of ammonia removal. Optimal operating pressures vary depending on spray nozzle design. Characterization studies by M.J. Jafari et al., have found that high pressures, ranging from 9 to 12 bars, are necessary to achieve NH_3 removal efficiencies >85%[3]. Liqui-Cel membrane contactors degassing modules require lower operating pressures (3 bars maximum) to generate similar removal rates, reducing operating costs, and reducing the overall footprint necessary for the gas-liquid separation.

Biological nitrogen removal is another technology used for NH_4-N removal within the microelectronics industry. Biological methods are attractive due to the low initial investment costs. This process involves two microbial steps, nitrification and denitrification. Nitrification is the oxidation of ammonium to nitrite, followed by further oxidation of nitrite to nitrate. The nitrite and nitrate are then reduced via bacterial denitrification into dinitrogen gas.

A key unit operation of semiconductor manufacturing is chemical-mechanical planarization (CMP) of copper films using slurries that are then cleaned in alkaline solutions containing azoles[4]. These azole compounds provide effective corrosion inhibition of the planarized metal layers but can be toxic to microorganisms and inhibitory to nitrification microbes, disrupting the bio-nitrogen removal process[5]. Biological processes can be disrupted by large shifts within incoming effluent ammonia concentrations and are best suited for operations where the ammonia concentrations are in the tenths to hundreds of ppm. TMCS poses an advantageous physicochemical alternative to biological nitrogen removal without sensitivity to high ammonia concentrations or presence of compounds that disrupt the microbial decomposition of ammonia in wastewater streams. TMCS performance is stable and no significant performance degradation has been observed at ammonia concentrations >1000 ppm, providing a flexible operation plan without concerns of decaying process performance, see figure 8[1].

Figure 8: Ammonia inlet concentration vs. removal rate



Conclusion:

As the microelectronics industry adapts to tackle sustainability challenges, exploring new methods of handling ammonia-rich effluent streams are being more enthusiastically considered. While each ammonia removal and recovery solution may have its place, depending on overall system design and goals, the TMCS process offers a unique and powerful solution that helps electronics producers meet these challenges in a single-step process and more compact space. With demonstrated efficiency in ammonia reduction and recovery, along with the potential to re-use waste streams, the TMCS process with 3M™ Liqui-Cel™ Membrane Contactors is enabling organizations to meet local regulations, achieve sustainability goals and protect our environment.

References:

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5. K.V. Jog, et al., Effect of chemical structure on the microbial nitrification inhibition and copper corrosion inhibition properties of azole compounds, Journal of Cleaner Production 366 (2022)

For more information, contact your 3M sales representative.

3M Company
3M Separation and Purification Sciences Division
13840 South Lakes Drive
Charlotte, North Carolina USA 28273
Phone: +1 980 859 5400
3M.com/Liqui-Cel

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