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3M™ Liqui-Cel™ Membrane Contactors for the recovery of ammonia from municipal process waters

Technical Brief

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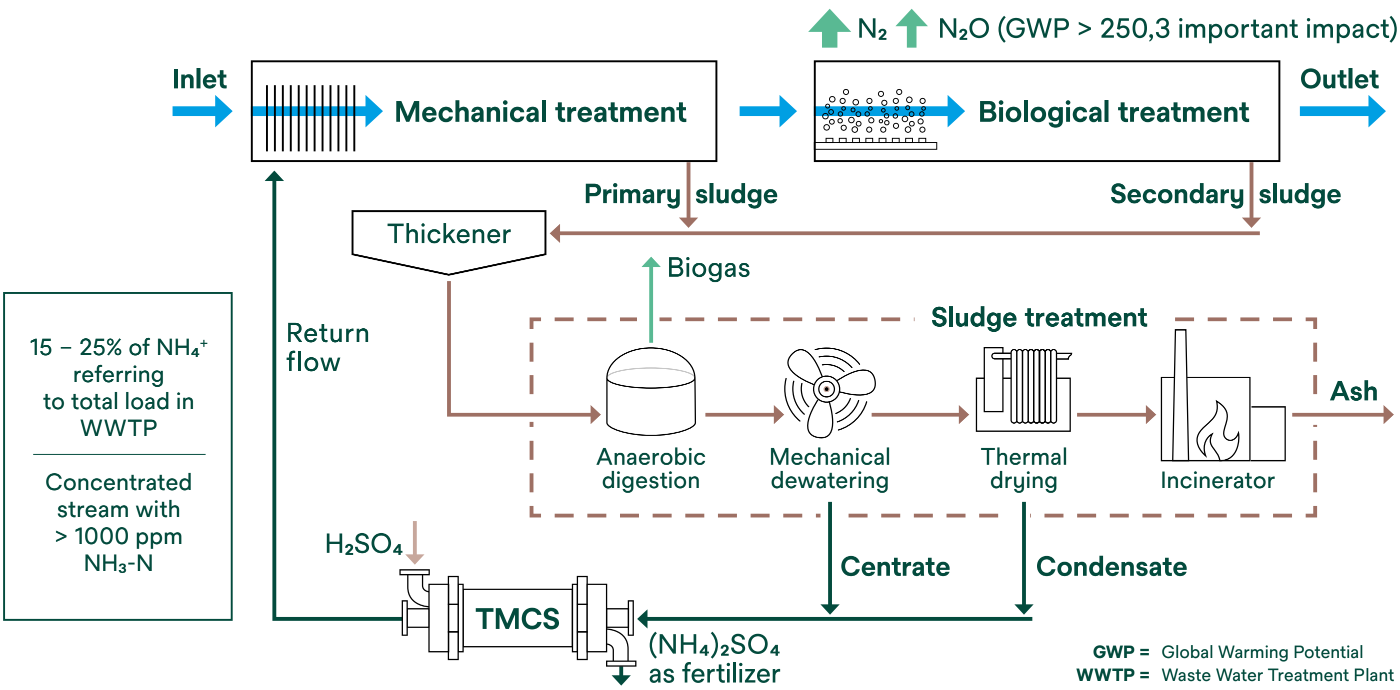
Abstract:
Process water or sludge dewatering effluent (SDE) in side stream of Large Wastewater Treatment Plants (LWWTP) provides a great potential for the nitrogen resource recovery and reuse as fertilizer. With more stringent nutrient discharge levels, growing capacity limits and requirement for more economic and sustainable treatment process, ammonia removal continues to receive growing attention. Compact membrane technology offers an energy efficient alternative to the traditional apparatus of physical or biological water treatment. Operational data from first existing industrial plants provides the framework for further developments towards circular economy at low carbon footprint.

Introduction

Common mechanical and biological treatment of the main-stream result in primary and secondary sludge. This sludge can be source of energy (in form of "biogas") and nutrients (in form of Phosphor and Nitrogen). [1-3] The return flow from sludge treatment in side-stream typically contains 15-20% of Ammonium-Nitrogen, referring to total load in a WWTP. [3,4] The concentrated stream is ideal for the recovery, due to high concentrations of Ammonia with more than 1000 ppm.

(See figure 1) Innovative solutions are being investigated, turning WWTPs in a bio-factory and avoid harmful release of ammonia with mainstream outlet for protecting the environment. [1] By ammonia abatement via TransMembrane ChemiSorption (TMCS) process in the side stream it could also be shown that the emissions of significant amount of Di-Nitrogenous-Oxide (N_2O) in the biological treatment of the mainstream could be avoided. [5,6] A gas with 250 times the Global Warming Potential (GWP) of Carbon-dioxide (CO_2) and with third important impact as greenhouse gas (GHG), being the main direct contributor in the operation of urban WWTP. [7]

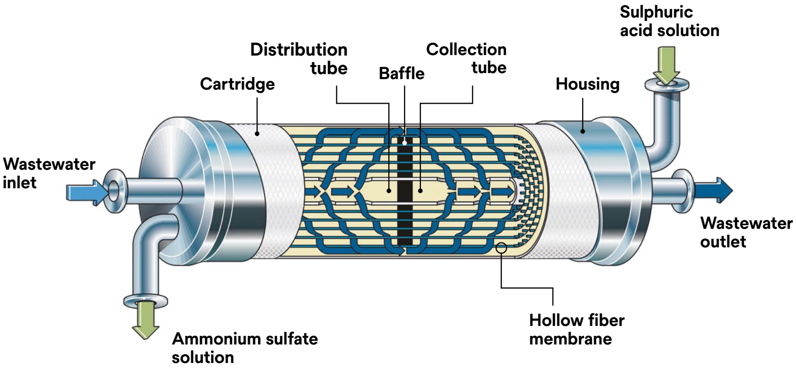
Figure 1. Sample of TransMembrane ChemiSorption (TMCS) process in municipal process water.



Hollow Fiber Membrane Contactors could be established in different industries for the efficient gas transfer from or to liquid streams. [8] Initially proven as successful separation technology in the clean water environment, advances purification techniques also allow for use in municipal process waters. Research and development in academic settings have paved the way for large-scale implementation, with commercial installations progressing from pilot projects to full-size references. [9] Growing experience from long-term operation provides basis to process evaluation and improvement.

Methods

The most widely used EXF-Series design of 3M™ Liqui-Cel™ Membrane Contactor modules can be described as a Radial-Flow device with a four-port configuration and a center baffle (See Figure 2, left). A hollow fiber configuration does provide a large surface area for the gas transfer. The polypropylene membrane is not wettable by water within the specified operating pressure, because material repels water droplets from its surface and a small pore size does not allow liquid water to pass through. The proposed TransMembrane ChemiSorption (TMCS) process uses this hydrophobic membrane as barrier between two aqueous liquids (See Figure 2, right).



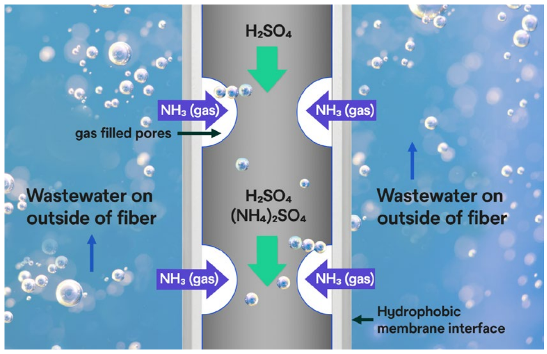


Figure 2. 3M™ Liqui-Cel™ Membrane Contactor EXF-Series for TMCS operation (left) and Single microporous hollow fiber showing mass transfer of ammonia gas molecules (right)

During operation, the Ammonia (NH_3)-loaded wastewater flows along the outside (shell side) of the hollow fibers, while a countercurrent flow of acid solution is introduced to the inside of the hollow fibers (lumen side). Gases pass the gas-filled pores of the microporous membrane to chemically react with the receiving phase. Driving force to this process is the difference in ammonia gas concentration between the wastewater stream and the acidic solution. By recirculation of the absorption fluid, the transferred NH_3 (gas) converts to an ammonium (NH_4+)-salt solution until saturation limit is reached. However, there is also water vapor transfer to dilute acid and avoid scaling and blocking the hollow fiber lumen.

First industrial TMCS system with commercial Liqui-Cel membrane contactors for ammonia recovery was installed already in 2004 at the Membrana GmbH site in Wuppertal, Germany. [10] The goal of the process water treatment to reduce the NH3 concentration from 1,5g/L by at least 90% was achieved. This was followed by further large-scale installations for the treatment of flue gas condensate in fossil fueled power stations or condensate polishing effluent from regeneration of ion exchangers. Currently, the largest systems for ammonia recovery from process wastewater for flow rates above 100m³/h are in operation in the semiconductor industry in Asia. First successful SDE treatment by Hollow Fiber Membrane Contactors to recover the ammonia are running since 2016 in Yverdon-Les-Bains, Switzerland. [11]

Results

For TMCS treatment of municipal process water, appropriate pre-treatment is required to protect the membranes from hardness precipitation, particle blocking and biofouling. In addition, care must be taken to avoid or remove additives that lead to wetting of the hydrophobic membrane. The following process scheme (See Figure 3, left) shows an installation example, with coagulation/flocculation, followed by lamella sedimentation and sand filter. Additional filter steps are then required and savings on the caustic consumption are realized by CO_2-stripper and temperature increase by heat exchanger.

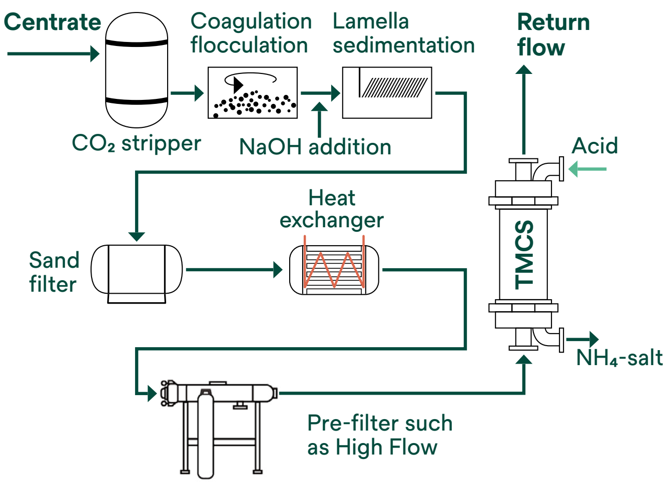


Figure 3. Process scheme for installation example of a pre-treatment to TMCS process (left) and photo of an EXF-8×20 TMCS system for ammonia recovery in sludge dewatering plant (right)

The compact, modular and scalable technology uses only little space (See Figure 3, right) to enable containerized systems that can be mobile, does not require dedicated areas of land as with biological treatment and allows to quickly adapt to capacity changes or scale-up from pilot programs. Process flexibility is an advantage due to short start-stop times, running continuous or batch mode, operating within a wide range of ammonia concentrations, tolerating rapid fluctuations in inlet ammonia concentrations, and providing excellent turn down ratio for wastewater flow.

Due to the hygroscopic behavior of acid causing water vapor transfer, the ammonium salt solution is becoming diluted. Depending on the inlet ammonia levels and the temperature gradient, additional post-concentration may be required. A new approach is proposed to integrate Membrane Contactor Technology for osmotic distillation with the caustic soda used in the pre-conditioning process. The resulting ammonium-salt achieved fertilizer quality in composition and concentration, so the product was used in near farming for ammonia-nutrient crop-feed. [11,12]

Discussion

When comparing 3M™ Liqui-Cel™ Membrane Contactors for ammonia removal vs Stripping and Scrubbing technology, three key differences can be observed. (See Figure 4) Firstly, the ability for the NH_3 gas to transfer from the wastewater phase, through the membrane pore and react with the acid phase, leads to a single step operation. In conventional tower stripping the NH_3 gas is desorbed into an air stream in one tower. A second tower is used to scrub NH_3 from the air by reacting it with an acid stream. Secondly, the tower technology requires a larger building footprint to provide the contact area necessary for the separation task. The membrane contactor enables very high area to volume ratio, providing more compact solution. Finally, since stripping and absorption occurs simultaneously during TMCS, the amount of auxiliary equipment such as air blowers and pumps is reduced.

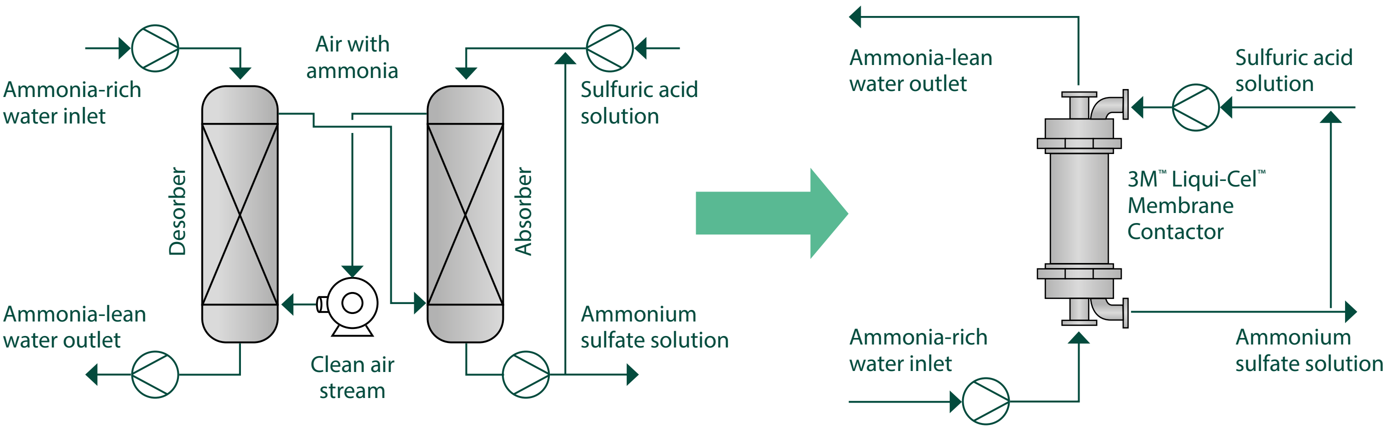


Figure 4. Technology comparison of conventional Two-Stage Stripping + Scrubbing Process (left) to Single Stage TMCS Process (right)

Conclusions

The TMCS process intensification combines several treatment steps in a single apparatus, which offers a smaller equipment footprint compared to traditional columns. The membrane acts as a barrier against contamination of the uptake phase to produce a high-quality ammonium salt solution that can be reused. The modular design of a membrane system offers additional advantages for scale-up, control and redundancy. The TMCS process is a promising solution when space is limited, and energy consumption is critical. In addition to the energy-saving recovery of valuable compounds and thus optimized material cycles of important resources, greenhouse gas emissions (nitrous oxide) from biological treatment processes can be reduced.

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