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Ammonium recovery from process water of digested sludge dewatering by membrane contactors

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Abstract

Membrane contactors are a promising alternative for nitrogen removal and recovery from process water compared to other physicochemical and biological sidestream treatment processes. Münster wastewater treatment plant (WWTP) is the first municipal WWTP in Germany operating a full-scale membrane contactor system to improve the nitrogen elimination and recovery efficiency. Factors influencing the operation and membrane performance are investigated in an accompanying research project. Additional operational aspects of the applied membrane modules are investigated in detail using a bench-scale membrane contactor. First results of the full-scale application demonstrate a high nitrogen removal efficiency of >95%.

Key words: ammonium removal, membrane contactors, municipal wastewater, nitrogen recovery, process water treatment

INTRODUCTION

Process water deriving from the dewatering of digested sludge is an additional load for WWTPs due to high ammonium concentrations if returned to the biological wastewater treatment process. Investigating process water treatment technologies is of continuing concern with regard to the optimization of municipal WWTPs focusing on the increase of the nitrogen removal capacity, the reduction of the total energy demand as well as an enhanced nutrient recovery. Sidestream treatment of process water is applied in order to reduce the high ammonium load and to improve the WWTP's overall nitrogen elimination rate. Common methods are based on either biological processes; for example, partial nitritation and subsequent deammonification, or physicochemical principles; for example, air stripping or struvite ($MgNH_4PO_4 \cdot 6\ H_2O$) precipitation. Membrane contactors represent an innovative technology for the physicochemical sidestream treatment of process water. They are commonly used for industrial extraction, stripping or absorption processes and consist of hydrophobic hollow-fibre membranes (Melin & Rautenbach 2007).

While already being established in industrial applications (e.g. food and beverage or pharmaceutical industry), membrane contactors are not common in the treatment of process water at municipal WWTPs. Until now, only few operational experiences from pilot plants and bench-scale experiments have indicated their general applicability for the treatment of municipal process water (Darestani *et al.* 2017). Apart from laboratory studies with hollow-fibre membrane contactors for the removal of ammonium from synthetic process water (Ashrafizadeh & Khorasani 2010; Hasanoğlu *et al.* 2010), several case studies, pilot plant and bench-scale tests investigated the treatment of zeolite regenerant solutions, swine manure and slaughterhouse waste (Lauterböck *et al.* 2014; Garcia-González & Vanotti 2015; Sancho *et al.* 2017).

Licon Bernal *et al.* (2016) and Sancho *et al.* (2017) studied the applicability of hollow-fibre membrane contactors for the removal and recovery of ammonium from a synthetic regenerant solution, which was used as a surrogate for the liquid phase produced during the regeneration of loaded zeolites being applied in tertiary wastewater treatment. Results showed >95% ammonium recovery; therefore, the treated regenerate solution can be reused for zeolite regeneration (Sancho *et al.* 2017). Garcia-González & Vanotti (2015) investigated the nitrogen recovery from swine manure using hollow-fibre membranes directly submerged into the ammoniacal manure. The investigation of influences of pH adjustment and aeration of swine manure at different ammonium concentrations resulted in ammonium recovery rates up to 94% subsequent to pH increase by alkali addition or aeration (Garcia-González & Vanotti 2015; Garcia-González *et al.* 2015). Lauterböck *et al.* (2012) conducted similar investigations with submerged hollow-fibre membranes in laboratory scale reactors for a longer period of time. Ammonium was reduced by half using membranes submerged into particle-rich fermentation broth and the anaerobic digestion process was enhanced (Lauterböck *et al.* 2014).

Investigations with membrane contactor pilot plants have been conducted at Neugut WWTP (Switzerland). Process water from sludge dewatering deriving from different municipal WWTPs and a digester with co-digestion of meat waste processing and containing 700–3,400 mg/l NH_4-N was treated by a pilot plant including three membrane stages in series with 120 m^2 total membrane surface area (Boehler *et al.* 2015). Sulphuric acid was recirculated through the lumen side of the hydrophobic hollow-fibre membranes (Darestani *et al.* 2017). Boehler *et al.* (2015) achieved elimination rates between 80% and 99% depending on the adjustment of pH value and temperature (up to $pH = 10.5$ and $T = 54$ °C using caustic soda and heat exchange, respectively).

A full-scale membrane contactor facility was implemented at Yverdon-les-Bains WWTP (Switzerland). The facility includes several pre-treatment steps (alkali addition, heat exchanger and multiple filtration steps) and membrane modules in series (Boehler 2018). First operational experiences revealed about 70% nitrogen elimination when the pH value and temperature of the process water were adjusted to $pH = 9.7$ and $T = 40$ °C, respectively (Boehler 2018).

Manufacturing effluent (550–2,000 mg/l NH_3, $pH > 9$, $T = 40$–50 °C) from the Membrana GmbH (3M) production site in Wuppertal (Germany) was treated by a full-scale membrane contactor facility including two membrane modules in series over a two-year period (Ulbricht *et al.* 2013). Ammonia removal rates up to 95% were achieved in this industrial application.

While these investigations indicate that membrane contactors may be used for the treatment of municipal process water, only limited data in terms of full-scale and long-term operation as well as factors influencing the membrane performance is available.

A full-scale membrane contactor facility was installed at Münster WWTP in 2018 in order to reduce the municipal process water's high ammonium concentration by more than 90%. The objective is to accomplish a stable long-lasting operation and to investigate influences on the membrane performance under full-scale operational conditions. Within the scope of this study, the influence of varying operating parameters (e.g. pH of process water and absorbent solution, flow rates, temperature) on membrane performance as well as process water and absorbent quality have been investigated by online monitoring and chemical analyses.

MATERIAL AND METHODS

Full-scale set-up

Prior to entering the membrane modules, the process water is pre-treated by caustic soda dosage to adjust the pH value to pH ≥ 10; a subsequent lamella clarification and three filtration steps remove particulate matter from the process water. The pre-filtration includes a depth filtration stage, disc filters (30 μm)and a bag filter (1–3 μm). Figure 1 shows a simplified process flow sheet of the full-scale membrane contactor facility.

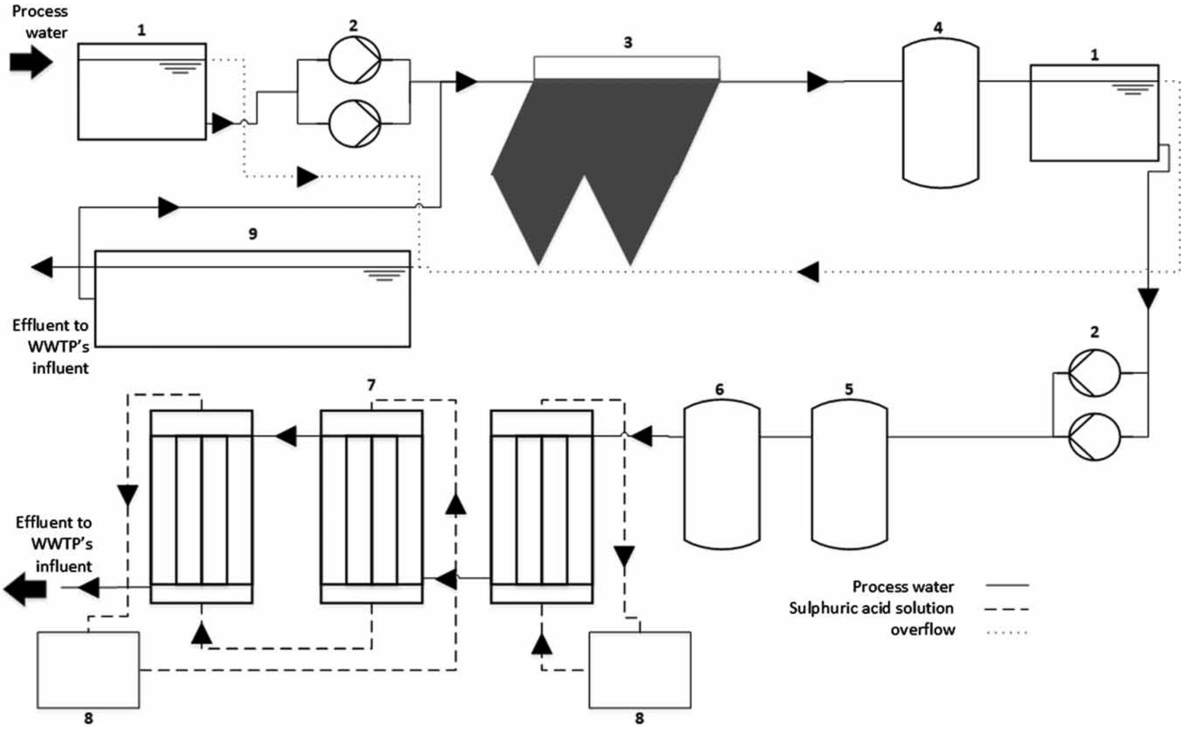

Figure 1 | Process flow sheet of full-scale membrane contactor facility: 1: process water reservoir; 2: pumps; 3: lamella clarification; 4: depth filtration stage; 5: disc filters (30 μm); 6: bag filter (1–3 μm); 7: three-stage membrane contactor; 8: sulphuric acid reservoir.

The three-stage membrane contactor includes 16 14 × 28 Liqui-Cel® hollow-fibre membrane modules (polypropylene, 0.02–0.1 μm pore size) providing 3,520 m^2 total membrane surface area and 30 m^3/h maximum treatment capacity (3M Company 2015). Nitrogen is recovered from the process water as ammonium sulphate solution by using sulphuric acid as the absorbent phase within the membrane contactor process. Unloaded sulphuric acid (pH = 2–3) is applied to the second and third membrane stages (1st acid cycle); the partially loaded sulphuric acid (pH = 4.5) is subsequently fed to the first membrane stage (2nd acid cycle) to further increase the nitrogen loading of the acid. Process water flows on the shell side, while sulphuric acid is applied on the lumen side of the membrane module. Due to the increased pH value, ammonium (NH_4^+) dissociates to ammonia (NH_3), which diffuses through the membranes and is absorbed by sulphuric acid. Therefore, a permanent concentration gradient between both sides of the membrane is maintained as the driving force for ammonia diffusion through the membranes.

Bench-scale set-up

In addition to the investigation and optimization of the full-scale plant, the operation and chemical cleaning of membrane contactors have been studied by means of a bench-scale facility with one smaller 2.5 × 8 Liqui-Cel® hollow-fibre membrane module (polypropylene, 0.02–0.1 μm pore size). The applied module provides 1.4 m^2 membrane surface area and 0.7 m^3/h maximum treatment capacity (3M Company 2017). Pre-treatment steps comparable with the pre-treatment of the full-scale plant were not necessary because of using synthetic or pre-treated process water. Figure 2 shows a simplified process flow sheet of the laboratory membrane contactor.

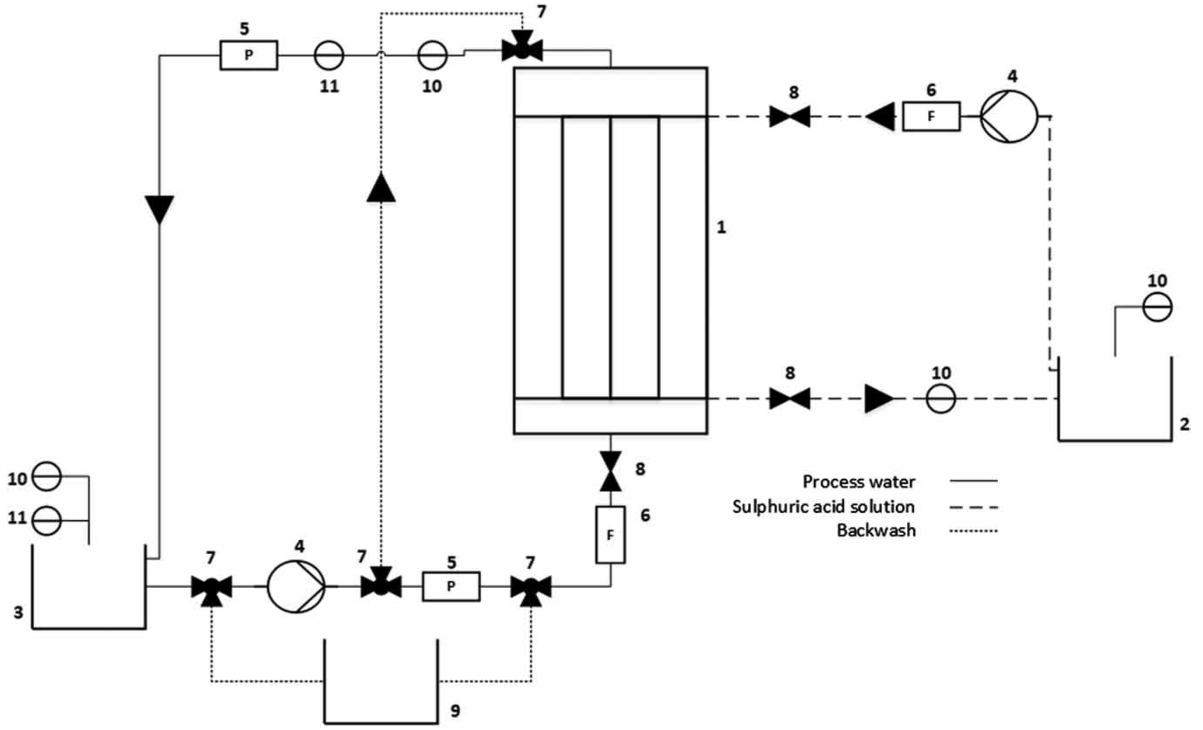

Figure 2 | Process flow sheet of bench-scale membrane contactor facility: 1: membrane contactor; 2: acid reservoir; 3: feed reservoir; 4: gear pump; 5: pressure transmitter; 6: flowmeter; 7: 3-way valve; 8: valve; 9: backwash/cleaning reservoir; 10: pH meter; 11: ammonium sensor.

Process water (on the shell side) and sulphuric acid (on the lumen side) are fed to the vertically mounted membrane module in countercurrent flow. Eighty litres of process water and 3 litres of sulphuric acid are recirculated into a 100-litre feed reservoir and a 5-litre acid reservoir, respectively, by gear pumps (Cole-Parmer GmbH, Wertheim, Germany). The membranes are backwashed and chemically cleaned in counter-current flow. Flow rates are continuously measured by flow meters (ASV Stübbe GmbH & Co. KG, Vlotho, Germany). Temperatures and pH values of process water and sulphuric acid are measured by pH sensors before entering and after leaving the module (Xylem Analytics Germany GmbH, Waldheim, Germany). Additionally, system pressure and ammonium concentrations are measured in process water influent and effluent (pressure: KTE/KTU6000, First Sensor AG, Berlin, Germany; ammonium: PRONOVA Analysentechnik GmbH & Co. KG, Bad Klosterlausnitz, Germany). A control program is conducted by a BlueBox system and software and can be adapted individually (GO Systemelektronik GmbH, Kiel, Germany).

Synthetic process water

First bench-scale investigations have been conducted using synthetic process water based on a sodium bicarbonate/carbonate buffer solution ($c = 0.01$ mole/l) and containing ammonium chloride ($c = 1{,}150$ mg/l NH_4-N). The temperature and pH values were $T = 21.1 \pm 0.3$ °C and $pH = 9.2 \pm 0.05$. A 50-percent sulphuric acid solution ($pH = 0.97$) was used as absorbent.

RESULTS AND DISCUSSION

The full-scale membrane contactor facility has been successfully implemented at Münster WWTP. In the first operation phase after commissioning, the membrane contactors were operated at $14.25 \pm 4\ m^3/h$. The treatment resulted in $96.4 \pm 3\%$ nitrogen elimination efficiency (see Table 1). The sulphuric acid was recirculated in two separate cycles until the maximum pH value or saturation concentration of ammonium sulphate solution was achieved. Analyses of the absorbent solution revealed increased ammonium sulphate concentrations. These results suggest that the ammonium concentration of process water from digested sludge dewatering can be significantly reduced by means of membrane contactors.

Table 1 | Process data and results of the first operation phase at Münster WWTP

Process parameter and results	Value	Unit
Flow rate of process water	14.25 ± 4	m^3/h
Influent ammonium concentration	816 ± 45	mg/l NH_4-N
pH value before NaOH addition	7.6	–
Temperature of inlet process water	20–22	°C
NaOH addition	4.05 ± 0.25	l/m^3
pH value inlet after NaOH addition	10.3 ± 0.30	–
Effluent ammonium concentration	29 ± 24	mg/l NH_4-N
Removal efficiency	96.4 ± 3	%
NH_4-N concentration in $(NH_4)_2SO_4$ produced	4.1	% by weight

The process stability of the full-scale facility was temporarily affected by increased particle concentrations in the process water derived from sludge dewatering by centrifuges. Since the initial two-stage microsieve pre-filtration proved insufficient for the adequate removal of particulate matter, an additional depth filtration stage has been included in the pre-treatment process, resulting in the stable operation of the membrane contactors.

The bench-scale membrane contactor has initially been operated at $0.02\ m^3/h$ process water flow rate and $0.01\ m^3/h$ sulphuric acid flow rate. Table 2 presents the experimental data of the first operation phase. The pH value of the process water was maintained at 9.2 ± 0.05 by continuous addition of 2 mole/l caustic soda solution, while the pH value of the absorbent solution remained constantly at $pH = 0.97$. During the first 2-hour operation of the bench-scale plant, the synthetic process water's ammonium concentration was reduced from 1,150 mg/l NH_4-N to 940 mg/l NH_4-N, thus resulting in 18% nitrogen removal efficiency.

Table 2 | Process data and results of the first operation phase of the bench-scale facility

Process parameter and results	Value	Unit
Flow rate of process water	0.02	m^3/h
Flow rate of sulphuric acid	0.01	m^3/h
Initial ammonium concentration	1,150	mg/l NH_4-N
pH of process water	9.2 ± 0.05	–
Temperature of inlet process water	21.1 ± 0.3	°C
Final ammonium concentration	940	mg/l NH_4-N
Removal efficiency	18	%
pH of sulphuric acid	0.97	–

The differences between the influent and effluent ammonium concentrations were relatively low. Increased removal efficiencies are expected in future tests; however, the removal rates observed in the full-scale facility will not be achievable by the bench-scale plant due to its single-stage membrane contactor and lower sulphuric acid concentration. Furthermore, the pH value of the sulphuric acid did not increase during the short operation time as is theoretically expected due to the absorption of ammonia by sulphuric acid. However, it is expected that the pH value of the sulphuric acid and the ammonium removal of the process water will increase with longer operation.

After the successful implementation of the bench-scale set-up, a first operation phase dealt with a long-term operation for 21 hours. Synthetic process water and sulphuric acid were fed to the contactor with flow rates of 0.02 m^3/h and 0.01 m^3/h for all investigations, respectively.

Temperatures, pH values of process water and acid solution and ammonium concentrations of process water have been monitored online during the investigations by the BlueBox system. Additional chemical analyses via rapid tests have been conducted regarding ammonium concentrations of the process water. All other operational parameters; for example, flow rate and pressure, were monitored with the BlueBox system.

Ammonium concentration and pH value of the influent process water were maintained constant by continuous addition of 2.5 mole/l caustic soda solution and 100 g/l ammonium chloride (NH_4Cl) solution. The synthetic process water's pH value and NH_4-N concentration were maintained at 9.3 ± 0.1 and $1{,}099 \pm 176$ mg/l NH_4-N, respectively, in order to achieve conditions close to the full-scale operation at Münster WWTP. Within the investigation, the pH value of the sulphuric acid solution remained constant at $pH = 0.94$. A nitrogen removal efficiency of approximately 21% was achieved with an effluent ammonium concentration of 867 ± 163 mg/l NH_4-N during operation. Figure 3 shows the NH_4-N concentrations of the influent and effluent process water. Table 3 sums up the experimental data of the long term operation.

Results of the long-term bench-scale investigation revealed a stable operation for 21 hours. With operating parameters of $pH = 9.3$ and ambient temperatures, the removal efficiency of circa 21% is low compared to the results of the full-scale set-up. During the long-term operation, the pH value of the sulphuric acid did not increase. Reasons for the stable pH value are the relative short operation time and the low removal efficiency, which mean that not enough ammonia has been absorbed by the sulphuric acid for an increase in the pH value. High removal rates comparable

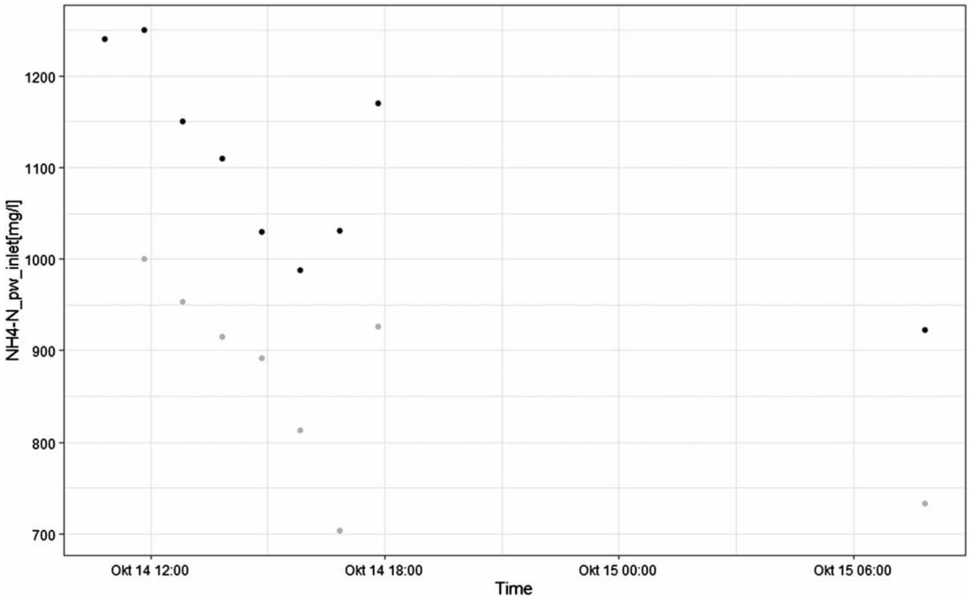

Figure 3 | NH_4-N concentrations of influent and outlet process water.

Table 3 | Process data and results of the long-term operation phase of the bench-scale facility

Process parameter and results	Value	Unit
Flow rate of process water	0.02	m^3/h
Flow rate of sulphuric acid	0.01	m^3/h
Initial ammonium concentration	1,099 ± 176	mg/l NH_4-N
pH of process water	9.3 ± 0.1	–
Temperature of inlet process water	21.3 ± 0.9	°C
Final ammonium concentration	867 ± 163	mg/l NH_4-N
pH of effluent process water	9.0 ± 0.8	–
Temperature of effluent process water	21.8 ± 0.9	°C
Removal efficiency	21 ± 12	% NH_4-N
pH of sulphuric acid	0.94	–
Temperature of sulphuric acid	22.0 ± 0.7	°C

to the full-scale facility will not be achieved because of the single-stage design and lower acid concentration.

There is abundant room for further progress in operation optimization of the bench-scale membrane contactor facility. Prospective investigations of operation and chemical cleaning of the module will be studied as well as the influences on the membrane performance.

CONCLUSIONS

The results of the initial operation phases of the full-scale as well as bench-scale membrane contactor facilities indicate the general applicability of membrane contactors for an efficient nitrogen elimination from municipal process water. However, experiences from the operation of the large-scale plant highlight the relevance of an efficient and reliable particle removal in order to ensure long-term membrane performance. Future studies using both the full-scale and bench-scale facilities will investigate the impact of varying operational parameters on the membrane performance. An appropriate membrane cleaning strategy will be developed by testing different backwash/cleaning cycles and chemicals (e.g., alkaline and acid solutions) in order to ensure reliable long-term operation. An increased energy efficiency compared to alternative physicochemical process water treatment technologies is expected.

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