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Experimental investigation and techno-economic analysis of tetramethylammonium hydroxide removal from wastewater in nanoelectronics manufacturing via membrane distillation



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ABSTRACT

In nano-electronics manufacturing, tetramethylammonium hydroxide (TMAH) is extensively used in the photolithography and etching processes, leading to a waste disposal issue. The present study focuses on TMAH wastewater treatment in nano-electronics industries by using membrane distillation technology. Actual TMAH wastewater samples were collected at imec, Belgium. An air gap membrane distillation bench unit was employed to perform the experiments for different operating conditions i.e., feed temperatures and flow rates. High quality water is recovered after reducing the TMAH concentration to 1 ppm and lowering the TOC to 0.8 ppm from 8 ppm. For the industrial scale TMAH wastewater treatment, industrial waste heat driven and district heating driven membrane distillation systems are designed and analyzed. It is determined that 14 GWh thermal energy is required annually to treat 20,000 m³ of TMAH wastewater/year while considering 65 °C as the membrane distillation feed temperature. Expected unit water treatment cost is found as low as 16 \$/m³ of TMAH wastewater, roughly 80% lower than current disposal costs.

1. Introduction

Nano-electronics manufacturing continues to grow exponentially in concert with demand for a multitude of microprocessor-enabled devices. Ultrapure water is required for many of the fabrication facility (fab) processes and sub-processes, placing substantial demands on freshwater supplies. Moreover, various specialty chemicals are employed, thus necessitating wastewater treatment. In the EU various national and pan-European water policies including environmental directive 91/271/EEC [1] mandate that such wastewater streams cannot be released to the water bodies unless the contaminants are under the maximum allowable concentration. For example, wastewater from the photo-lithography and etching processes is subjected to special treatment before discharging due to the presence of tetramethylammonium hydroxide (TMAH, $C_4H_{13}NO$), a compound used as a photoresist developer, for silicon etching, and as an additive to cleaning [2,3]. TMAH is a highly water soluble, non-volatile strong organic alkali (pH ~ 12)

with a thermal decomposition temperature of > 65 °C (TMAH converts into methanol and trimethylamine above 108 °C) [4]. In its pure form, TMAH is considered as a hazardous material (HAZMAT class 8) and is corrosive to skin, eyes and respiratory tract. It exhibits high acute systemic toxicity based on oral and dermal LD50s [5]. Thus the alkalinity and toxicity of TMAH contaminated wastewater is harmful to humans and environment, also causing eutrophication in recipient water bodies [6]. Therefore, the EU directive 2010/75/EU [7] decrees the TMAH concentration limit of 7 ppm for adequate protection of aquatic ecosystems. Hence, the challenge for nano-electronics industries is to properly treat TMAH-based wastewater in a techno-economic way.

Technologies that are currently available for removal of TMAH include catalytic oxidation, electrodialysis, ion exchange, membrane bioreactor, reverse osmosis, and biological treatment (aerobic and anaerobic). Hirano et al. [8] developed an integrated technique based on two step decomposition method. The first step was pyrolyzing

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TMAH to TMA, which was further decomposed into nitrogen gas, water, and carbon dioxide in second step using base metal series catalyst (Pd-VO -WO catalysts supported on titania-silica). Ballard et al. [9] employed combination of aerobic biodegradation, advanced oxidation and biological denitrification for TMAH removal. The studies have reported TMAH removal of > 99% and total organic carbon (TOC) reduction of > 98%. Besides, Wang et al. [10] combined electrodialysis with ceramic filtration and activated carbon for concentrating, recovering and recycling TMAH. The researchers were able to concentrate TMAH in the range of 7.45–8.33%. Moreover, Huang et al. [11] established an oxidation degradation method of TMAH using ultraviolet light with activated persulfate which has shown TMAH concentration reduction up to 20 ppm. Another study, performed by Citraningrum et al. [6] shows that TMAH wastewater can also be treated using both strong and weak acid cation exchange resins. The selectivity coefficients of TMA + over proton was 5.16 for strong acid cation and 6.45×10^{-4} for weak acid cation. In addition, experiments were also conducted by S. Nishihama et al. [12] for separation and recovery of TMAH using different zeolites as adsorbents. The results predict that TMAH can be concentrated approximately 21 times using this method. You et al. [13] introduced a unique TMAH removal process using three different arrangements of reactors including membrane photoreactor, anoxic membrane bioreactor and combined membrane photoreactor and anoxic membrane bioreactor. The maximum achievable removal percentage of TMAH was nearly 80%. Alternatively, Chen et al. [14] validated the combined membrane bioreactor and reverse osmosis method for treating the nano-electronics wastewater. The research outcomes showed COD < 5 ppm, TOC \sim 2.5 ppm and conductivity \sim 150 μ S/cm in the treated water. In a related study, the authors performed anoxic/ aerobic process for biological treatment of high-strength organic nitrogen wastewater [15]. The investigation depicted 92–98% removal of carbon source, 80% reduction of organic nitrogen and ammonia and 70% deduction of total nitrogen. Chen et al. [16] demonstrated biodegradation method for treating the TMAH wastewater using completely the autotrophic nitrogen removal over nitrite (CANON) process in a mixed anoxic up-flow bioreactor. The removal efficiencies of total nitrogen were reached up to 90% in this research work.

Among these techniques, catalytic oxidation and biodegradation are the most relevant for today's nano-electronics manufacturing. Although the processes have merits, there are still some intrinsic disadvantages. Catalytic oxidative treatment is quite expensive due to high cost of platinum and other catalysts [10]. Biodegradation involves relatively large equipment, long residence times for TMAH degradation, requires a high degree of monitoring and control, and leads to N₂O emissions [15,17]. Moreover, inhibition of TMAH biodegradation process can be observed above 150 mg/L whereas the process may cease when the concentration reaches 450 mg/L [18]. Owing to these limitations, many nano-electronics fabs simply collect TMAH wastewater for off-site thermal destruction. Therefore, there is a clear need to find new approaches for the cost-efficient and environmentally friendly handling of TMAH wastewater.

This study focuses on the introduction of a novel TMAH wastewater treatment method based on using membrane distillation water purification technology. Membrane distillation (MD) is a promising thermally driven technology which is capable of achieving extremely high environmental performance while using low grade heat sources [19]. MD uses a micro-porous, hydrophobic membrane that allows only volatiles (i.e., water vapor) to permeate through membrane, and its separation efficiency is largely insensitive to feed concentration and pH. Investigations have shown that it provides nearly 100% rejection of contaminants while operating at relatively mild temperature and pressure [20,21]. The properties of TMAH wastewater are compatible with MD technology, and suggest that water recovery and reconcentration are achievable goals. We believe that this is the first work that shows the potential of MD technology for treatment of TMAH wastewater. In this study, experimental investigations are considered for evaluating the performance of MD bench scale unit. Moreover, technoeconomic assessment of an industrial waste heat-integrated MD system is also performed for TMAH wastewater treatment in the nano-electronics industries and is also compared with district heating-integrated MD system, for the same purpose. The evaluation centers on the facility owned and operated by imec in Belgium.

2. Methodology

Establishing the performance of MD technology with real wastewater samples constitutes the first part of the investigation. Section 2.1 provides the details. This is followed by information on process integration and economic considerations.

2.1. Experimental procedures

2.1.1. Pretreatment

At the imec fab, TMAH wastewater from photo-lithography and etching processes is released with a combined flow rate of 200-300 L/h and subsequently collected. From the collection tank, the TMAH wastewater sample (550 L) was taken and analyzed which contained mainly hydrogen peroxide (8000 ppm), ammonium hydroxide (1409 ppm), TMAH (646 ppm) and hydrogen fluoride (158 ppm). Since TMAH wastewater contained hydrogen peroxide, 175 g of 60 µm mesh powdered manganese dioxide (MnO₂) catalyst was added in the sample of TMAH wastewater for catalytic reduction of hydrogen peroxide during first pretreatment step. The decomposition rate was monitored over time. The first pretreatment step continued for 8 h to achieve an acceptable hydrogen peroxide concentration. After the catalytic reduction, 350 L of pretreated sample was decanted and filtered (solid manganese dioxide was deposited at the bottom of the first pretreatment tank) and then pumped for the second pretreatment step for pH correction. In this step, a total 572 mL of 98% sulfuric acid was added in stages for 110 min and the pH reduction was observed. Eventually, the



Fig. 1. Schematic diagram of proposed TMAH wastewater treatment system.



Fig. 2. Xzero air gap membrane distillation bench scale setup with specifications of its main components [22].

pretreated TMAH wastewater sample of 15 L was filled in the hot water tank of the MD system. Fig. 1 shows the schematic diagram of employed TMAH wastewater treatment system.

2.1.2. Membrane distillation prototype

An air gap membrane distillation (AGMD) unit provided by Xzero AB and located at imec's fab has been employed to treat and reconcentrate the pretreated TMAH wastewater. Fig. 2 shows the facility with specifications of its main constituents [22]. The main component of the system was the MD module, divided into feed (hot) and permeate (cold) sides by means of PTFE membrane. The membrane was supplied by Donaldson having following characteristics: thickness 254 µm; area 0.194 m²; pore size 0.2 µm; porosity 80%; and liquid entry pressure of 6.89 kPa [23]. The pretreated wastewater (feed water) was heated and recirculated in the feed channel (hot side) of the module, with water used as a coolant on the cold side. Feed water and coolant temperatures were measured with temperature sensors (pT100) and flow rates were controlled by FIP FlowX3 (paddlewheel flow sensors f3.00/f6.30). All the temperature and flow sensors, and alarms were monitored and organized by a Crouzet logic unit. A handheld conductivity meter determines the permeate quality, with grab samples of 500 mL taken for subsequent analysis.

The experiments were performed for different MD feed inlet temperatures i.e., 60 °C, 65 °C and 70 °C. Table 1 presents the considered trials, which were studied during this work. The permeate samples were collected and analyzed, and the concentrate volume was also measured in order to calculate the reduction rate of TMAH wastewater. Fig. 3 represents the process flow diagram of Xzero air gap membrane distillation bench scale system.

2.1.3. Analytical methods

During the tests, concentration, pH, conductivity, total organic carbon (TOC), inorganic carbon (IC) and total carbon (TC) of feed and permeate samples were determined. The pH was measured with a combined electrode (Yokogawa FU20) connected to a transmitter (Yokogawa EXA pH-402) with display. The electrode was mounted in the circulation line from the hot water tank before the modules and the pump. The conductivity was measured with a WTW LF3000 conductivity meter with appropriate measuring probe (K = 0.1). The TOC (as well as IC and TC) was measured with Sievers 900 TOC-analyzer. The anions (fluoride, chloride, nitrite, nitrate and sulfate) and cations (sodium, potassium, ammonium and tetramethylammonium) were measured with ion chromatography after adequate dilution on ThermoFischer ICS-5000 Capillary System. Metals (aluminum, chromium, copper and zinc) were analyzed on ICP-OES from PerkinElmer.

2.2. Industrial scale membrane distillation integrated system

As reported in the literature, the amount of TMAH wastewater varies from $0.2 \text{ m}^3/\text{h}$ for small fabs up to $5 \text{ m}^3/\text{h}$ for large fabs [8,24]. A challenge in an industrial case is to cost-effectively supply the substantial amount of thermal energy required by the MD system. There are several waste heat sources available in fabs, and three of them were considered in this study: (1) condenser outlet water stream (~35 °C) from heat recovery chiller having thermal power of ~3.5 MW [25]; (2) hot air stream (~350 °C) from VOCs abatement systems having thermal power of ~0.41 MW (reference to 80 °C, considering the dew point of VOCs exhaust) [26]; and (3) process cooling water exhaust stream (~85 °C) released from manufacturing tools having thermal power of

Table 1

Feed and coolant flow rates and temper	atures in three	trials of TMAH	wastewater treatment.
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	-			
Trials	TMAH wastewater inlet temperature (°C)	Coolant inlet temperature (°C)	TMAH wastewater flow rate (kg/s)	Coolant flow rate (kg/s)
1	60	20	0.20	0.26
2	65	32	0.20	0.26
3	70	30	0.12	0.14



Fig. 3. Process flow diagram of Xzero air gap membrane distillation bench scale system.

 \sim 2.44 MW [27,28]. Using above mentioned heat sources, the industrial scale waste heat driven MD setup was designed and analyzed in order to fulfil energy requirement of MD system for treatment of TMAH wastewater of flow rate 2.5 m³/h (corresponding to 20,000 m³/year) from a generic nano-electronics manufacturing facility. The number of the desirable MD modules were calculated based on the TMAH wastewater flow rate and previously reported specific thermal energy demand to heat the MD feed [29]. Moreover, it was assumed that the specific thermal energy demand is not a function of TMAH wastewater concentration under values of 10% (w/v %). The industrial waste heat driven MD system (case 1) was further compared with district heating driven MD system (case 2) for TMAH wastewater treatment.

2.3. Process economy

Capital, operational and maintenance expenditures (CAPEX & OPMEX) were calculated based on literature and communication with manufacturers. The economic evaluation was performed for treating 20,000 m³/year of TMAH wastewater. For calculating the total equipment cost, design specifications of the main equipment were determined. Moreover, in order to calculate the annual CAPEX, some assumptions were taken i.e., 1) plant life and membrane lifetime were selected 20 years and 5 years, respectively; 2) the annual interest rate was set to 5%; 3) retrofitting cost was considered as 4% of the CAPEX; and 4) land and startup costs were not assessed. When waste heat was considered as the thermal energy source, only the capital cost of heat exchangers was taken into consideration. Other costs including chemicals, cooling water, insurance, labor, concentrate disposal, service and maintenance and electricity were accounted as the annual OPMEX. Operational costs were calculated according to the TMAH wastewater



Fig. 4. Effect of Catalytic reduction on hydrogen peroxide concentration over the function of time.

flow rate or as the percentage of the total equipment cost as followed in relevant studies. For instance, insurance as 5% of CAPEX [30], labor cost as 0.03 m^3 of MD feed [30–32], service and maintenance cost as 0.033 m^3 of MD feed [30], electricity price as 0.05 m^3 of MD feed [33] and annual membrane replacement cost was considered 15% of total membrane cost per year [34]. Pretreatment chemicals cost 500 fm of manganese dioxide and 200 m^3 for 98% sulfuric acid [35]. The concentrate disposal cost is taken as 130 m^3 of the concentrated brine. Furthermore, unit water treatment cost was also calculated using annual CAPEX and OPMEX and was used as the main criterion for selecting the better of the two above-mentioned cases. The price of the district heating was taken as 18 GJ (1 fm = 1.19 fm) [36]. Besides this, in order to realize the extent of the economic benefit of the proposed method, different TMAH wastewater treatment technologies cost was also compared.

3. Results and discussion

3.1. Pretreatment analysis

3.1.1. Catalytic reduction

Fig. 4 shows the effect of manganese dioxide (MnO_2) addition on hydrogen peroxide (H_2O_2) concentration as a function of time. During 8 h of catalytic reduction, the initial concentration of hydrogen peroxide (3000 ppm) was reduced to < 100 ppm. After each manganese dioxide intake, the trend showed exponential decrease of hydrogen peroxide concentration which gradually stabilized over the time. Moreover, it was also observed that the reduction rate of hydrogen peroxide has a direct positive relation with increasing concentration of manganese dioxide and decreasing concentration of hydrogen peroxide [37]. The sample was continuously mixed during the pretreatment step.

The catalyst manganese dioxide speeds up the decomposition rate of hydrogen peroxide by 1000 times as compared to the uncatalyzed reaction [38]. Due to adding manganese dioxide, the following decomposition reaction of hydrogen peroxide occurs:

$$MnO_2 + 2H_2O_2 \to MnO_2 + O_2 + 2H_2O$$
 (1)

$$2H_2O_2 \to O_2 + 2H_2O \tag{2}$$

This catalytic reduction reaction is spontaneous and exothermic which reduces the activation energy to $\sim 58 \text{ kJ/mol}$ from $\sim 75 \text{ kJ/mol}$ [39]. During the catalytic reduction, foaming at the surface of the TMAH wastewater was also observed due to oxygen gas bubbles, which were produced and released during the decomposition reaction. Downward displacement of the water sample was also observed. The



Fig. 5. Representation of hydrogen fluoride and ammonium hydroxide equilibriums as function of pH [40].

TMAH wastewater filtration (after catalytic reduction) resulted in complete separation of manganese dioxide. For a continuous process, the catalyst manganese dioxide can be reused, although catalyst degradation and losses would occur to various degrees. In order to avoid the catalyst inactivity, occasionally i.e., during a complete maintenance and shutdown of such an installation, the catalyst might need to be replaced.

3.1.2. Neutralization

The performance of the MD system is significantly affected by the volatility of the TMAH wastewater inlet sample, which is strongly dependent on pH value. The TMAH wastewater sample contains both ammonium hydroxide (NH₄OH) and hydrogen fluoride (HF) which have adverse effect on the volatility as a function of the pH as shown in Fig. 5 [40]. In order to handle the volatile nature of ammonia, sulfuric acid was added and resultantly the pH of the wastewater was lowered to 2.94 in accordance to the pKa value (3.18) of hydrogen fluoride while considering Henderson-Hasselbach equation ($pH = pK_a + log \frac{|A^-|}{|HA|}$ where [A⁻] is conjugate base concentration and [HA] is the conjugate acid concentration). The reduction in pH of the wastewater sample has effected the ammonium hydroxide equilibrium since the volatility of the ammonia solution changes due to change of the pH as shown in the following reversible reaction [41]:

$$NH_3 + H_2 O \rightleftharpoons NH_4^+ + OH^- \tag{3}$$

Along with change in ammonium hydroxide equilibrium, the chemical equilibrium of hydrogen fluoride (stated below) has also been pushed towards hydrogen fluoride gas that can be released from TMAH wastewater sample.

$$H^+ + F^- \rightleftharpoons HF$$
 (4)

With pH reduction, the ammonia (volatile) was converted to ammonium ions (nonvolatile), however, more hydrogen fluoride gas (volatile) was formed instead of fluoride ion (nonvolatile). This allowed hydrogen fluoride gas to pass through the membrane to the distillate (See section 3.2.). Fig. 6 shows the effect of sulfuric acid concentration

with time on pH of the TMAH wastewater.

The resulting ammonium ions were reacted with sulfate ions (SO_4^{-2}) and produced the ammonium sulfate $((NH_4)_2SO_4)$ which is soluble inorganic salt. The reaction is exothermic with standard molar enthalpy of -1180 kJ/mol [42]. The chemical reaction is listed below.

$$2NH_4^+ + SO_4^{-2} \rightleftharpoons (NH_4)_2 SO_4 \tag{5}$$

The solubility of ammonium sulfate increases at elevated temperature which is favorable for MD separation process.

3.2. Performance of membrane distillation

Table 2 shows the chemical analysis of real TMAH wastewater sample, wastewater sample after catalytic reduction and acid neutralization, pretreated wastewater sample after heating at 60 °C and distillate samples at various feed temperatures. The noticeably high concentration of sulfate ions was observed in the pretreated TMAH wastewater owing to the addition of 98% sulfuric acid during acid neutralization. Along with sulfate ions, concentration of other ions including fluoride, nitrate, ammonium and TMAH was also considerably high after the pretreatment steps. It is noteworthy to mention that nitrite was formed and appeared in the wastewater due to oxidation of ammonium hydroxide during the storage in the collection tank. Compared to pretreated wastewater, the hot feed (pretreated TMAH wastewater) sample shows higher concentration of TMAH and the reason might be higher water evaporation rate due to elevated temperature; no thermal decomposition of TMAH was observed. However, the fluoride concentration was reduced due to marginal degassing of hydrogen fluoride gas at elevated temperature. The concentration change of other contaminants was minimal and was not of interest at this point. After the MD separation process, an acceptable result was obtained concerning the removal of ammonium hydroxide and TMAH, and even the concentration of hydrogen peroxide, nitrite and sodium ions along with metals were under the detection limit. However, the fluoride concentration in the distillate was quite high i.e., 125 ppm to 147 ppm. High concentration of fluoride was due to presence of volatile hydrogen



Fig. 6. Effect of acid neutralization on pH as function of time.

Table 2

Concentration of contaminants in 1) real TMAH wastewater sample 2) wastewater sample after catalytic reduction and neutralization 3) pretreated wastewater sample after heating at 60 °C and 4) distillate samples after the MD separation process while varying the wastewater temperature. ($^{\circ}$ < $^{\circ}$ indicates a value below the respective detection limit).

Contaminants	TMAH wastewater	Pretreated	Pretreated wastewater after	After CR + AN + MD			
		wastewater		Trial 1	Trial 2	Trial 3	
				Distillate, 60 °C	Distillate, 65 °C	Distillate, 70 °C	
_	Concentration (ppm)	Concentration (ppm)	Concentration (ppm)	Concentration (ppm)	Concentration (ppm)	Concentration (ppm)	
Hydrogen peroxide	8000	< 100	< 50	< 50	< 50	< 50	
Aluminum	0.1	0.1	0.3	< 0.0004	< 0.0004	< 0.0004	
Chromium	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	
Copper	0.3	0.1	0.1	< 0.004	< 0.004	< 0.004	
Zinc	0.7	0.1	0.1	< 0.002	< 0.002	< 0.002	
Fluoride	158.1	162	150.5	124.2	133.5	147	
Chloride	12.3	10.4	11.6	0.1	0.1	0.1	
Nitrite	9.8	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
Nitrate	37.4	80.4	80.3	1.1	0.6	0.4	
Sulfate	28.3	3529.7	3731.3	201.7	11.5	9	
Sodium ion	1.2	0.6	0.7	< 0.05	< 0.05	< 0.05	
Potassium ion	15.6	7	7.2	0.3	0.1	0.1	
Ammonium ion	1409.5	895	980.8	4.7	3.9	3.5	
Tetramethylammonium	646.1	637.5	732.6	1.6	1.2	1	
рН	10.55	2.94	2.89	2.81	2.81	2.80	

CR + AN + MD = Catalytic reduction + acid neutralization + membrane distillation.

fluoride gas in MD feed that was able to pass through the membrane to the distillate (Other ions i.e., chloride, nitrate, sulfate and potassium ions have reasonably low concentration.). Moreover, it is noteworthy to mention that manganese (from catalyst manganese dioxide) was not found in the distillate. While comparing different feed temperatures, the trend shows that higher temperatures lead to slightly improved contaminant retention in the MD feed due to higher driving force (vapor pressure difference). For instance, sulfate and nitrate are present in the distillate and the concentration of these ions has been reduced with increasing feed temperature due to increase of solubility of these ions in the feed, thus favoring the removal of these contaminants. Since the separation is not fully complete, it is possible that these contaminants became adsorbed and/or permeated through the membrane. (Follow-on studies would be needed to study this effect in more detail.) For all the trials, the pH value was around 2.8 for the distillate. After 8 h of MD separation process, the initial volume (350 L) was lowered to 108.5 L. This results in concentration factor of 3.2.

3.2.1. Organic substances and conductivity

TOC, IC and TC provides significant information on organic and inorganic carbon content, therefore these water quality parameters were also examined. Fig. 7a and b shows the TOC, IC, TC and conductivity of pretreated sample, heated sample after pretreatment and distillate/permeate samples at different feed temperatures. As there were no organic acids used, the carbon content may come from the decomposition of TMAH (forming volatile methanol), organic additives (which are quite low in concentration) and carbon dioxide dissolved in the wastewater.

The outcomes show that TOC, IC, and TC concentration in the distillate were reduced to quite sufficient levels as compared to the amount in TMAH wastewater heated samples after pretreatment. However, while comparing the carbon content in distillate at different MD feed inlet temperatures, there was no clear trend observed with changing temperatures which means TMAH thermal decomposition was not observed. Nevertheless, it is known that TMAH thermal decomposition temperature is above 65 °C, therefore the recommended optimum MD feed temperature for TMAH wastewater treatment is \leq 65 °C. At 65 °C, concentration of TOC ~0.8 ppm, IC ~0.1 ppm, and TC ~0.9 ppm was observed. Similarly, there was no significant change observed in conductivity while varying the MD feed temperatures between 60 and 70 °C. The resulting permeate quality meets most local standards for release to the recipient with the exception of fluoride concentration. Usage of strong base anion resin/activated alumina can be a potential method to handle fluoride concentration before disposal



Fig. 7. Water quality analysis varying with wastewater feed temperature in MD system a) TOC, IC and TC concentration and b) Conductivity. AP refers to after pretreatment and HAP refers to heated samples after pretreatment.





Table 3

Cases	Low grade heat sources	Mass flow rate across heat recovery exchanger, kg/s		Temperature across heat recovery exchanger, °C			Heat transfer area,m ²	Thermal power provided, MW	
		Feed	Source	Feed		Source			
				Inlet	Outlet	Inlet	Outlet	_	
1	Heat recovery chiller VOCs abatement exhaust Cooling water exhaust	0.69 9.17 30.97	0.69 1.5 12.42	20 54.57 54 57	30 65	35 350 85	25 85	11.61 150.94 207.66	0.03 0.4
2	District heating supply line	40.84	16.39	54.40	65	85	58.6	278.32	1.80

or reuse of the permeate [43,44].

3.3. Industrial scale membrane distillation integrated system

Fig. 8 shows the industrial scale semi-batch MD system configurations (waste heat driven and district heating driven), which were designed for treating TMAH wastewater through MD while employing catalytic reduction and acid neutralization as the pretreatment techniques. The calculations show that for reaching the aimed temperature of 65 °C, thermal power demand was 0.13 MW for heating the TMAH wastewater in the first pass. However, depending on the configuration, the total thermal power demand has increased up to 1.78-1.8 MW due to higher flow rate of the concentrate/retentate in the continuous cycles. In case 1, integrated approach of combining industrial waste heat sources i.e., condenser outlet water from heat recovery chiller (0.03 MW), hot air stream from VOCs abatement systems (0.4 MW) and process cooling water exhaust from manufacturing tools (1.35 MW) has been used for fulfilling the thermal energy requirement of the MD system. However, in case 2, district heating supply line of 85 °C was considered as the main thermal energy source to fulfil the MD heating requirements. The proposed schemes are capable of providing required amount of thermal power, thus both of the cases are technically promising options for industrial scale TMAH wastewater treatment through MD. Table 3 compares the characteristics of the selected energy sources and MD feed in these integration cases in terms of flow rate (m^3/h) and temperature (°C) across heat recovery exchangers, the provided thermal power and heat transfer area required.

As mentioned above, along with treating the TMAH wastewater the other objective is to reconcentrate the TMAH wastewater stream,

Table 4

Design specification of industrial scale MD integrated system.

Components		Specification					
MD Modules		N = 196					
Membranes		Area = 451 m^2					
Heat Exchangers	Case 1	Heat Transfer area = 370 m^2					
	Case 2	Heat Transfer area = 278 m^2					
Pumps	Case 1	N = 10, Capacity 1–660 m ³ /h					
	Case 2	N = 6, Capacity 1–660 m ³ /h					
Water tanks		Capacity = $150 \text{ m}^3/\text{h}$, N = 6;					
		Capacity = $5 \text{ m}^3/\text{h}$, N = 1					
Pretreatment tanks		Capacity = $5 \text{ m}^3/\text{h}$, N = 2					
Auxiliaries		140 $/m^3$ of MD feed					
Raw material		Amount					
Chemicals	Manganese dioxide	5 kg/year					
	Sulfuric acid	55 m ³ /year					
Cooling Water		$1.2 imes 10^6 \mathrm{m^3/year}$					

therefore, in order to reduce the TMAH wastewater volume, the concentrate/retentate stream should be recycled back from the MD pilot plant unit. However, to avoid the scaling and caking on the membrane surface, blowdown has been considered. It was assumed that when the concentration of TMAH reached 5% (w/v) in the concentrated wastewater, the solution was purged in order to satisfy the safety limitations.

Depending on the flow rates and thermal energy requirements, the equipment design was done for the industrial scale MD integrated system for both cases. Considering 147 m³/h of MD feed, the calculated number of MD modules were 196, having dimensions of $730 \times 630 \times 165$ mm³. The specific electrical energy consumption was approximately 0.5 kWh/m³ of permeate. The heat exchangers area has been calculated according to the maximum thermal power demand/ available thermal power to fulfill the MD modules' requirement. In case 1, three heat exchangers were connected in order to exploit the maximum potential of the industrial waste heat available while in case 2, only one heat exchanger was required. Moreover, case 1 accounts for higher heat exchanger area due to lower heat transfer coefficient of air $(10 \text{ W/m}^2\text{K})$ as compared to heat transfer coefficient of water (250 W/ m²K) in case 2. Commercial pumps and water tanks were considered according to the flow rates and required storage. Moreover, the annually required chemicals and cooling water amount were also determined for both cases. Table 4 shows the specifications of the main components and necessary amount of raw materials. These cases have been used further for determining the industrial system economics.

3.4. Economics of industrial waste treatment systems

Fig. 9 shows the summary of the economic comparison of the industrial scale MD integrated systems. The results of the CAPEX show that MD modules and heat exchangers are the two key cost driving equipment in both cases. In these schemes, MD modules were responsible for the major CAPEX share (\sim 55–59%). Heat exchangers have occupied the second place (case 1: \sim 30%; case 2: \sim 25%), which was further followed by tanks (\sim 7%) and pumps (\sim 3%). Membranes and other auxiliaries were accountable for approximately 2% of the total CAPEX.

However, while using district heating as heat source (case 2), the capital cost of the same configuration was reduced by 7%, mainly due to low level of system complexity. Annual CAPEX was also calculated for both cases i.e., ~ 64 K\$ for case 1 and 60 K\$ for case 2. It was assumed that the wastewater treatment plant was effectively operated for 91% all year round. For these cases, the annual operating and maintenance expenditure includes mainly thermal energy cost (case 1: 0%; case 2: ~80%), chemicals (case 1: ~3%; case 2: ~1%), insurance (case 1: ~15%; case 2: ~3%), electricity (case 1: ~21%; case 2: ~4%), cooling water (case 1: ~9%; case 2: ~2%), service and maintenance, labor and membrane replacement (case 1: ~28%; case 2: ~5%) and concentrate disposal (case 1: ~24%; case 2: ~5%). It is noteworthy to emphasis here that Case 1 is self-sufficient system in terms of thermal



Unit water treatment cost (\$/m3)

Fig. 9. Process Economy of both cases, Top: Capital expenditure; Middle: Operating and Maintaining expenditure; Bottom: Unit water treatment cost.

energy demand.

For the case of district heating driven MD system for TMAH wastewater treatment, the annual CAPEX was approximately similar to the case 1, however, the annual OPMEX was increased more than fivefold. So, eventually approx. 1.1 M\$ could be saved annually while considering the industrial waste heat as the main thermal energy source. The estimated unit water treatment cost was 16.79 \$/m³ for Case 1 and 72 $/m^3$ for case 2. Thus, the comparison of total annual expenditures and unit water treatment cost of these two cases demonstrate the economic benefit of the use of industrial waste heat over the district heating. The estimated unit wastewater treatment cost is roughly 80% lower than the cost of current disposal practices (offsite thermal destruction cost: 130 \$/m3 [45]) and about 50% lower than other potential methods costs (electrodialysis cost: 36 \$/m³ [10]). Payback periods are estimated to be 4 years for Case 1 and 7 years for case 2. The comparison depicts that the promising TMAH wastewater treatment technology is membrane distillation using industrial waste heat from nano-electronics industries, as thermal energy source.

Apart from economic benefit, as compared to other options MD clearly provides the opportunity to treat TMAH wastewater onsite and can recycle high-quality water back into the fab for other industrial operations. Moreover, it provides the environmental benefit over other methods since it uses industrial waste heat and reduces the carbon dioxide emission linked to primary energy demand.

3.4.1. Sensitivity analysis

The sensitivity analysis was performed using standard spreadsheet software (Microsoft[®] Excel[©]) in order to determine the effect of technoeconomic factors on unit water treatment cost. For the purpose, plant capacity (5000, 20,000 and 30,000 m³/year), plant life (10, 20 and 30 years), interest rate (2, 5 and 10 %), membrane price (50, 90 and 200 $/m^2$), chemicals price (400, 700 and 1000 /ton) and brine saturation concentration value (2.5, 5 and 10 w/v %) were varied under the techno-economic limitations. Fig. 10 shows the sensitivity of the unit water treatment cost considering variation of different techno-economic factors for the two above mentioned cases.

It was determined that the plant capacity and concentrate saturation value are the two most critical techno-economical parameters for the unit water treatment costs. For decreasing the concentrate saturation limit from 5% to 2.5%, the estimated water treatment cost was increased by 20% for Case 1 and 5% for case 2. The reduction of plant capacity from 20,000 m3/year to 5000 m3/h was accountable for 32% increase in unit water treatment cost for Case 1 and 6% for case 2. (The reason of the observed inverse relation among the plant capacity and unit water treatment cost was the considered capacity method where the degression coefficient (m) was used for MD modules (m = 0.8), heat exchangers (m = 0.8) and pumps (m = 0.0667).) Furthermore, with decreasing the plant life from 20 years to 10 years, the unit water treatment cost was increased by approximately 11% for Case 1 and 2.5% for case 2. It is notable that the variation in membrane and chemical prices do not have significant effect on the unit water treatment cost. However, increase of interest rate up to 10% leads to increase in the unit water treatment cost by 8% for Case 1 and 2% of case 2. The results show that Case 1 (heat source: industrial waste heat) is more sensitive to the variation in the considered parameters as compared to case 2 (heat source: district heating). For case 2, the effect is not significant due to higher operating cost mainly the heat cost.



Fig. 10. Sensitivity analysis of TMAH wastewater treatment cost for different techno-economic parameters.

4. Conclusions

This study was focused on introducing a novel industrial application of MD system for the treatment of TMAH wastewater in nano-electronics industries. For the purpose, experimental tests using bench scale MD prototype were performed for determining the separation efficiency of TMAH and other contaminants. Moreover, techno-economic analysis of the industrial scale system has been performed for the continuous flow rate of 20,000 m³/year of TMAH wastewater. The summary of the major findings is listed below.

- 1. The experimental tests results show that high quality water was recovered having TMAH concentration $\sim 1 \text{ ppm}$, ammonium hydroxide concentration $\sim 3.5 \text{ ppm}$ and TOC $\sim 0.8 \text{ ppm}$.
- 2. The optimal MD feed temperature is 65 °C which is a compromise while considering the quality of the treated water and thermal power demand for TMAH wastewater treatment. However, when industrial waste heat sources are selected as the main heat source, the conclusive factor is treated water quality. It is noteworthy that above 65 °C the TMAH decomposition starts happening.
- 3. Considering clean water production rate as $20,000 \text{ m}^3/\text{year}$, the annual thermal power demand was 14 GWh when the MD feed temperature was considered 65 °C. The thermal energy demand can be fulfilled using industrial waste heat sources in nano-electronics industries or district heating.
- 4. The process economy shows that the industrial waste heat driven MD system is the best considerable option, the specific water treatment expense can be as low as ~16 $/m^3$. However, with the sensitivity analysis, it was determined that the expenditure can be varied up to ~32% of the unit water treatment cost. The estimated

payback period is almost 4 years for this system.

5. Since the proposed industrial waste heat driven MD system design does not only treat wastewater in nano-electronics industries under environmental regulations but also reduces carbon dioxide emissions since it operates mainly using industrial waste heat as the thermal energy source. So, it may consider as dual benefit system in terms of environmental aspects.

Apart from this, for disposing the treated water in the surface water or other water bodies, it is recommended to perform some post treatments including pH adjustment and fluoride ions adsorption etc. in order to observe the strict environmental regulations. The treated water could also be recycled back to the fab after satisfying the standards for the purpose of reuse in the industrial processes. The additional system cost for the mentioned post treatment methods is expected to be ~10 $/m^3$, associated with the consumables (chemicals). Nevertheless, the cost of the TMAH wastewater treatment through industrial waste heat integrated MD system can be further reduced by developing the commercial MD modules which are suitable for industrial scale applications.

Conflicts of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2019.02.067.

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