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Short review on membrane distillation techniques for removal of dissolved ammonia

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ABSTRACT

When ammonia discharged into water resources, it has a negative effect on aquatic life as a major water pollutant. Therefore, removing of ammonia from wastewaters has become an essential need for last decades concurrent with developing in the industry and agriculture. Hence there are emerged various techniques for removing the solvated ammonia which among them membrane distillation (MD) is the powerful technique for wastewater treatment. In the thermally process of membrane distillation, only volatile molecules are transferred through hydrophobic membrane. The microporous membrane is a barrier for separation of permeate (cool side-liquid or gas phase) from feed (hot side-liquid or gas phase). The vapor pressure gradient is a propulsion force for migration volatile molecules into the permeate side. In this short review paper, we summarized the surveys about membrane distillation techniques in removal of solvated ammonia.

Contents

1. Introduction

Ammonia (NH_3) penetrated into the natural waters by industrial, domestic and agricultural waste water discharges have become a major environmental problem. Small amounts of discharged NH_3 without any purification can have harmful effects on aquatic life. Due to the toxic nature of ammonia, the use of biological processes to purify wastewater from ammonia is not so simple.

The removing and recovery of NH_3 and its derivatives from wastewaters can be performed by biological, physical, chemical, or a combination of them such as adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification (Degermenci et al. 2012; Tchobanoglous et al. 1991). Recently there are much attention to membrane distillation (MD) for separation of volatile pollutants from wastewaters because of its potentially low energy necessity. The MD process has capability for recycling of industrial wastewaters, and can be advantageous for high-temperature wastewater streams with relatively low levels of volatile compounds (Xie et al. 2009).

In the thermally process of membrane distillation, only volatile molecules are transferred through hydrophobic membrane. The microporous membrane is a barrier for separation of permeate (cool side-liquid or gas phase) from feed (hot side-liquid or gas phase). The vapor pressure gradient is a propulsion force for migration volatile molecules into the permeate side (Xie et al. 2009; Banat et al. 1998). Finally, migrated volatile compounds are either condensed or removed in the vapor phase, depending on the configuration (Xie et al. 2009; El-Bourawi et al. 2006; Lawson et al. 1997). In this paper we try to review the membrane distillation techniques in the wastewater treatment in order to remove ammonia and considering their advantages and disadvantages.

2. Membrane distillation techniques
2.1. Direct contact membrane distillation

Structure of a Direct contact membrane distillation (DCMD) are illustrated schematically in Fig. 1. In the membrane, Evaporator and permeate sides are charged with liquid hot-feed water and cooled permeate, respectively. The vapors passing through the membrane condense directly inside the liquid phase at the membrane surface. The single membrane layer has the low insulating properties hence a disadvantage of DCMD is the high sensible heat loss between condenser and evaporator sides.

Hollow fiber membrane contactors nominate a suitable alternative to remove various volatile contaminants (Tan et al. 2006; Ozturk et al. 2003; Zhang et al. 1985). These membranes provide a barrier between liquid phase and volatile contaminants, and these volatile molecules penetrate to membrane pores in order to reach liquid phase. To achieve less mass transfer resistances, it is necessary that the membranes used to remove volatile pollutants usually have a hydrophobic structure. Because of good hydrophobicity and feasibility, Polyvinylidene fluoride (PVDF) is an attractive membrane material to form asymmetric membranes (Tan et al. 2006; Jian et al. 1997; Deshmukh et al. 1998).

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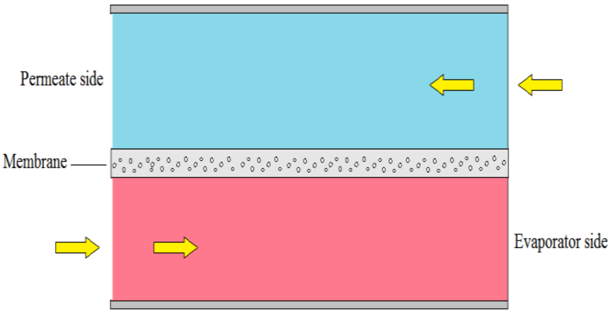

Fig. 1. Structure of direct contact membrane distillation (DCMD).

Hollow fiber membranes of PVDF with different morphological structures (Fig. 2) were prepared by Xiaoyao Tan et al. (Tan et al. 2006), to tailor for NH_3 separation from water. In order to accelerate ammonia removing, the aqueous solution of H_2SO_4 was utilized as stripping solution. The results revealed that increasing the pH is capable of promoting the NH_3 elimination. Post-treatment of PVDF membrane with ethanol was improved both the hydrophobicity and the effective surface porosity, and subsequently improved the NH_3 removal. In this process, the feed velocity of acid solution and initial concentration of NH_3 had little impacts on the NH_3 elimination.

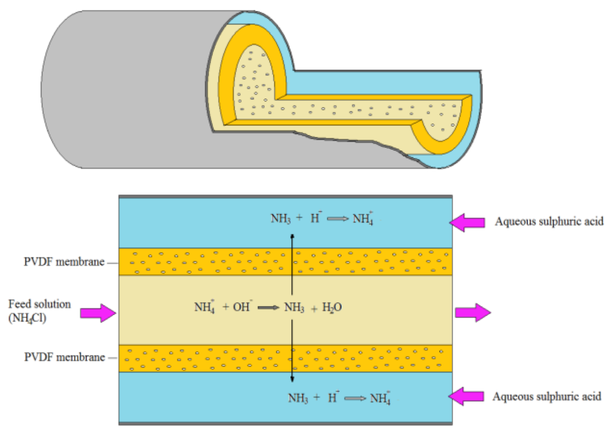

Fig. 2. PVDF hollow fiber membranes with different morphological structures.

In the other attempt, polypropylene hollow-fiber membranes were utilized to attain effective removal of dissolved ammonia (Ashrafizadeh et al. 2010). In order to accelerate ammonia removing, the aqueous solution of H_2SO_4 was utilized as stripping solution. Polypropylene membrane was shown to be very efficient in separating NH_3 from the wastewaters, in the best conditions, NH_3 removal of over 99 % was achieved. Attained results indicate that the velocities and initial concentrations of the NH_3 and H_2SO_4 solutions had insignificant effects on the NH_3 elimination. Increasing the pH of feed solution up to 10 enhanced the elimination of NH_3 meaningfully while insignificant improvements attained in upper than 10 value.

Increasing the feed velocity of NH_3 solution enhanced its removal in the range studied (Ashrafizadeh et al. 2010). Highly promising results can be attain using a submerged membrane contactor for NH_3 extraction. The direct NH_3 removal from particle rich substrates and less consuming input energy are the advantages of this method. B. Lauterböck et al. (2012) were utilized a hollow-fiber membrane contactor module for continuous NH_3 elimination in an anaerobic digestion process. The hollow-fiber membranes were directly immersed into the digestate of the anaerobic reactors.

The wastewater of slaughterhouse was used as feed for reactors with NH_4^+ concentrations ranging from 6-7.4 g/L. In this membrane reactor, the ammonia level was significantly decreased by about 70 %. The continuous ammonia removal causes to improve substrate conversion rates, a more stable process performance and an increased biogas yield (Lauterböck et al. 2012).

2.2. Sweeping gas membrane distillation (SGMD)

Sweeping gas membrane distillation (Fig. 3), uses a channel structure with an empty gap on the permeate side. The volatile compounds can be distilled with a low surface tension and an inert gas removes these vapor from the permeate side. Then condensation of vapors takes place outside the module by an external condenser.

The lower conductive heat loss and reduced mass transfer resistance are the advantages of sweep gas MD towards other configurations (El-Bourawi et al. 2006). In addition, this module provides a superior permeate flux and evaporation efficiency (Xie et al. 2009). Therefore, among various membrane distillation methods, the SGMD was indicated to be prominent method for the removing volatile components from wastewaters (Xie et al. 2009; Khayet et al. 2003; Rivier et al. 2002). Also membrane wetting is minimized when SGMD has less condensation of water droplets in the membrane pores (Franken et al. 1987). The ammonia elimination from wastewaters with high NH_3 concentration (500-10,000 mg/L) has been studied (Ding et al. 2006; Zhu et al. 2005). The mass transfer coefficient for SGMD was indicated to be similar to vacuum membrane distillation (VCMD) at NH_3 concentrations of up to 3200 mg/L while the selectivity was found 27-100 % higher (Ding et al. 2006). Some industries discharge the wastewater containing lower ammonia concentrations and we know that the feed concentration has influence on MD performance. The ammonia elimination from wastewater containing low value of NH_3 (100 mg/L) has been simulated in experiments with SGMD (at pH 11.5) by Zongli Xie et al (Xie et al. 2009). It has found that the raising of feed temperature causes to enhance in the permeate flux meaningfully, but reducing the selectivity. Also increasing in flow rates of feed and sweep gas promoted NH_3 removal efficiency and permeate flux. Up to 97 % ammonia removal could be achieved in the best of conditions, to give a purified water containing only 3.3 mg/L of NH_3 (Xie et al. 2009).

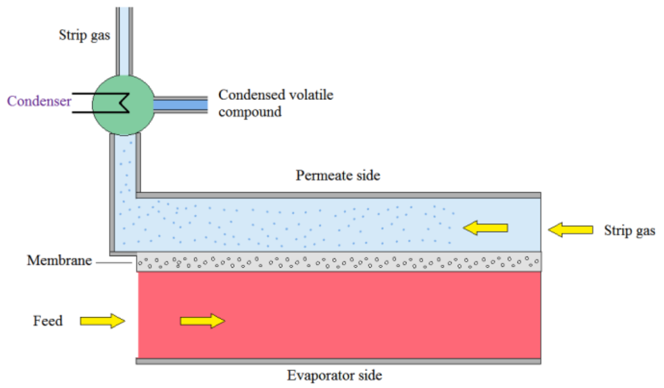

Fig. 3. Schematic of sweeping gas membrane distillation.

2.3. Vacuum membrane distillation (VCMD)

In Vacuum membrane distillation includes an air gap channel configuration (Fig. 4). The volatile compounds that have transferred through the membrane, are sucked out by the vacuum from permeate channel and condenses outside the module. The advantages of VCMD are that leaving a larger effective membrane surface active and a reduction of the boiling point. However, providing the technical equipments for generation of a vacuum is a disadvantage to this method (https://en.wikipedia.org/wiki/Membrane_distillation). pH is a critical factor for NH_3 removal applications by VCMD when increasing the feed pH caused to enhancing ammonia removal efficiencies. EL-Bourawi et al. (2007) were investigated the applicability of VCMD for NH_3 removal from its aqueous solutions. The results showed that higher value for feed temperatures, pH and initial feed concentrations and lower value for downstream pressures promote NH_3 removal efficiency.

This is found that the pH value is to be a most effective factor. Mass transfer significantly affected by temperature and concentration polarization between feed border layers. Increasing in feed flow velocity is caused to decreasing in temperature and concentration polarizations. The resistance to mass transfer is shown to change from being mainly

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located in the feed side at low flow velocities and feed temperatures to be closely located through the membrane pores at 55.7 °C and logically higher feed flow velocity of 0.84 m/s. Although higher feed temperatures and lower downstream pressures increase remarkably the total trans membrane flux and the NH_3 removal rate, the corresponding ammonia separation factors were decreased. Ammonia removal efficiencies higher than 90 % with separation factors of more than 8 were achieved by El-Bourawi team (El-Bourawi et al. 2007).

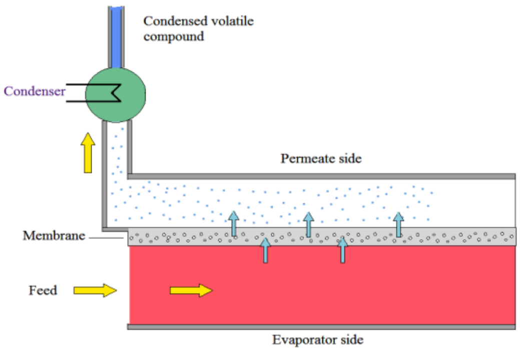

Fig. 4. Vacuum membrane distillation includes an air gap channel configuration.

2.4. Air gap membrane distillation (AGMD)

In air-gap MD (http://en.wikipedia.org/wiki/Evaporator), the evaporator channel resembles that in DCMD, while the permeate gap filled with air exists between the membrane and a cooled wall (Fig. 5). Before condensation on the cooler wall surface, the vapor diffusing through the membrane must additionally overcome this air gap. The advantage of this method is the high thermal insulation (http://en.wikipedia.org/wiki/Thermal_insulation) near the condensation channel, therefore reducing heat conduction losses. However, the disadvantage is that the air gap acts as an extra barrier for mass transport, reducing the surface- related permeate output compared to DCMD. A further advantage towards DCMD is the fact, that volatile (http://en.wikipedia.org/wiki/Volatility (chemistry)). Substances such as alcohol or other solvents (with a low surface tension) can be separated from diluted solutions, because there is no contact between the liquid permeate and the membrane with AGMD (https://en.wikipedia.org/wiki/Membrane_distillation). Hasanoğlu et al. (2010) were used polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes so that contact the NH_3 solutions and the receiving solution (Diluted solutions of H_2SO_4). The hydrophobic hollow-fiber separates the feed including aqueous ammonia on the shell side and the receiving solution on the lumen side. The pores of hydrophobic membrane filled by an air gap which is not wetted by the aqueous solutions. First, NH_3 molecules penetrates from the feed into the feed-membrane interface. NH_3 volatilizes through the feed-membrane interface, diffuses across the air-filled pore of the membrane, and finally it reacts immediately with sulfuric acid on the interface to form nonvolatile component, ammonium sulfate. Therefore, the NH_3 concentration in the acid solution is essentially zero.

Theoretically total NH_3 removal could be possible under this separation system, whereas difference in ammonia partial pressure between the feed and the receiving solution is a driving force for this membrane contactor process (Hasanoğlu et al. 2010).

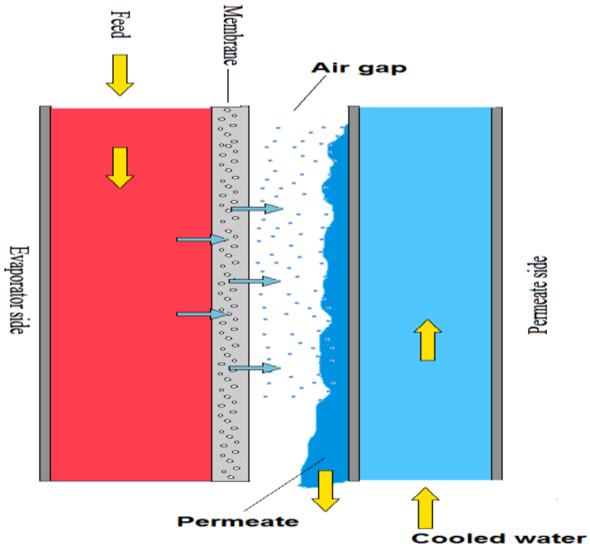

Fig. 5. Schematic of air-gap membrane distillation.

3. Conclusions

In this short review paper we summarized the surveys about membrane distillation in removal of solvated ammonia. The MD process has capability for recycling of industrial wastewaters, and can be advantageous for high-temperature wastewater streams with relatively low levels of volatile compounds. The various techniques have utilized in membrane distillation such as direct contact, sweeping gas, vacuum and air gap membrane distillation which can be led to ammonia treatment from wastewater. The single membrane layer has the low insulating properties hence a disadvantage of DCMD is the high sensible heat loss between condenser and evaporator sides. The lower conductive heat loss and reduced mass transfer resistance are the advantages of sweep gas MD towards other configurations. The advantages of VCMD are that leaving a larger effective membrane surface active and a reduction of the boiling point. The advantage of AGMD is the high thermal insulation near the condensation channel, therefore reducing heat conduction losses.

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