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Removal and Recovery of Pollutants from Wastewater by Using Continuous Liquid Membrane System: A Review

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Abstract

Liquid membrane has received significant interest among the researchers as it provides efficient technology in treating wastewater. However the used of liquid membrane only available in batch and laboratory scale and only a few can be found in the industries. The restriction were related to the instability of liquid membrane such as small interfacial area for bulk liquid membrane (BLM), membrane swelling for emulsion liquid membrane (ELM) and membrane breakthrough for supported liquid membrane (SLM). Thus, this review will discuss on the work of researchers to overcome those problems mostly in batch and laboratory scale. A few applications on continuous liquid membrane in industry application also will be addressed. Eventually, this review will provide the prospective of liquid membrane as the future continuous treatment method in wastewater treatment.

Key words: Continuous liquid membrane, emulsion liquid membrane, supported liquid membrane, bulk liquid membrane, and future prospect

1 Introduction

The rapid industrialization and globalization have caused various environmental issues such as water pollution which containing organic matters, toxic elements, and heavy metals. These pollutants will pose a significant threat to the environment and even to human health. Industries that are producing a large amount of these pollutants-containing wastewater include electrical and electronics, metal plating and finishing, textiles and dyes, pulp and papers, automotive, foundries, oil refining and fertilizers (Bilal et al., 2013; Minhas, Memon, Qureshi, Mujahid, & Bhanger, 2013). The large amount of wastewater effluents containing toxic pollutants discharged into waterways pose a significant threat to groundwater which may cause acute or chronic poisoning to human health. However, these toxic pollutants, if recovered properly from wastewater prior to discharge, will not only prevent environmental pollution but will also help to reduce the disposal cost of industries through recycling and reusing.

Conventional methods for treating toxic pollutants from wastewater include adsorption, floatation, coagulation-flocculation, chemical precipitation, membrane filtration, electrochemical processes and ion–exchange (Bilal et al., 2013; Chang, Teng, & Ismail, 2011; Minhas et al., 2013). These methods have their own limitations such as produce secondary sludge, high capital and operating cost, inefficiency and difficulty in operating procedures (Wijers, 1996). Recently, considerable scientific attention has been devoted to liquid membrane due to its unique features such as simultaneous removal and recovery of solutes in a single unit operation, high selectivity and fluxes, less energy consumption and non-equilibrium mass transfer (Kocherginsky, Yang, & Seelam, 2007; Teng & Muthuraman, 2013). Liquid membrane consists of three main types which are Bulk Liquid Membrane (BLM), Emulsion Liquid Membrane (ELM), and Supported Liquid Membrane (SLM).

Liquid membrane can be operated in batch and continuous mode (Kislik, 2009). Almost all types of liquid membranes are still operating in batch system and laboratory scale because of membrane instability encountered (Kislik, 2009). Continuous system usually carried out in large scale production and designed for 24 h production throughout the year (Sinnot, 2005). However, only a few of liquid membrane operate in the continuous system in the industry. At present, emulsion liquid membranes (ELM) has been commercially available in the industries to remove and recover zinc from wastewater such as in the viscous fiber plant at Lenzing, Austria with the capacity of 75m^3/hr. Other industrial level plants in removal of zinc are located at Glanzstoff, AG, Austria (700 m3/h capacity) and CFK Schwarza, Germany (200 m3/h capacity) (a. L. Ahmad, Kusumastuti, Derek, & Ooi, 2011; Kamiński & Kwapiński, 2000; Kislik, 2009). However, according to Kocherginsky et

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al. (Kocherginsky et al., 2007), those three prominent types of liquid membranes are mostly under study in laboratory and batch scale. This is caused by some factors such as BLM which demonstrate small contact area and low process kinetics (Kamiński & Kwapiński, 2000; Kislik, 2009; Talebi, 2012). Second one, SLM faces the long-term stability due to support body and membrane breakage (Kislik, 2009; Talebi, 2012), and third one, ELM which has the big possibility of osmotic pressure and swelling (a. L. Ahmad et al., 2011; Sulaiman, Othman, & Amin, 2014). To be operated in the continuous mode, the formulation which are consist of carrier, stripping agent, diluents, phase modifier and surfactant for ELM system have an important effect on the mass transfer efficiency and continuous and stable operation of the liquid membrane (Othman, Goto, & Mat, 2004). Besides that, in SLM system, membrane support bodies also play an important role in maintaining a good operation and system stability. Continuous liquid membrane (CLM) provide higher recovery rate, more economic due to constant removal and recovery of selected solutes, less residence time and give less total operating cost for large scale and 24 h production when compare to the batch process (Kislik, 2009; Sinnot, 2005). Recent development of the CLM are the design of rotational and vibrational membrane devices, use of taylor-Couette column and the use of low-cost and good membrane support body (Kislik, 2009).

Most of the previous studies reported the possibility to recover solutes efficiently with CLM system but they still highlighted the need for further study to optimize the mass transfer for BLM, the condition and design of system to balance enrichment ratio, and degree of emulsion swelling for ELM and the proper type of support body to prevent membrane breakthrough for SLM. Then, the objective of this paper is to provide an overview on the removal and recovery of toxic pollutants from aqueous solution by using CLM system. A comparison of different types of CLM systems is outlined and their applications in removal and recovery of the pollutants are properly discussed. Major challenges and future prospects towards the utilization of CLM systems in removal and recovery of pollutants are also addressed.

2 Types and application of CLM system

Researchers have conducted many studies to develop an effective and cost-saving CLM. The attempts are being made by designing the reactors or columns that can give higher recovery rate, combination of the good characteristics of liquid membrane with one another and formulation of the good membrane phase and support body. All these attempts were reported to be under study or in laboratory scale. The first factor to be highlighted is the new design and modification of equipment. Fournier-Salaun et al. (Fournier-Salaün & Salaün, 2009) have proposed the new design of bulk liquid membrane to remove and recover chromium by using double extraction modules with rotating disc. Each module has two compartments of extracting and striping agent and continuously driven by peristaltic pumps. These compartments are equipped with rotating discs to increase mass transfer rate. They confirm the possibility of chromium recovery until 1 mole/L and made the conclusion that the volume of membrane and rotating discs speed did not have influence on percentage of chromium recovery. They also insisted that a rise of the flow rate will decrease the percentage of extraction due to less contact time. Lee et al. (Lee & Kim, 2011) also published a work about recovery of acetic acid by continuous emulsion liquid membrane by using the extraction column of Oldshue–Rushton type (multistage mixer column). The best effect of their study in batch process is applied in this continuous system. They obtained the percentage of acetic acid recovery as 93% and its enrichment ratio 4.2 under a specific operating condition because the total interfacial area for reaction capacity between feed phase and stripping phase was larger. They suggested the further study to optimize operating condition in this system and a better designed of extraction column for practical purpose. Besides that, the another work have been done by Ahmad et al. (A. L. Ahmad, Kusumastuti, Shah Buddin, Derek, & Ooi, 2014) to remove and recover cadmium from wastewater by using ELM in counter rotating Taylor-Couette column. This equipment will provide low and uniform fluid shear, help to stabilize the emulsion droplets and prevent membrane breakage and swelling. This equipment was found to recover more than 96% of cadmium by using high angular frequency ratio which provides high mixing activity with low shear stress.

The works to combine the good characteristics of several types of liquid membrane also have been conducted by the researchers. Recently, Belova et al. (Belova, Kostanyan, Zakhodyaeva, Kholkin, & Logutenko, 2014) have invented multistage three-phase extraction which consist of bulk and supported liquid membrane techniques and can be known as bulk-supported liquid membrane. This system was operated with three phases of mass transfer stages which interconnected with contact chambers which were extraction chamber and stripping chamber. The membrane phases were acted as mass transfer medium which counter currently in contact with feed and stripping phases in those chamber in closed circuit operation. The liquid membrane was held stationary circulating in the system while feed and stripping phases were flowing through all the stages as the mobile phase. This technique could help to improve the extraction and stripping processes of the metals. They found that the increasing flow rate of the membrane phases with respect to the flow of feed phase and the number of contact chambers will significantly increase the degree of recovery of metals. Meanwhile, Zheng et al. (Zheng, Chen, Wang, & Zhao, 2013) studied the effect of incorporating the hollow fiber supported liquid membrane with emulsion liquid membrane. The feed phase was pumped into the shell side of the hollow fiber membrane device with properly adjusted pH while the emulsion phase (containing H_2SO_4 solution with organic phase after treated with ultrasonic vibration) was pumped into tube side of the membrane device. The analyses outcome showed that, the stability of the emulsion phase was poor without any surfactant and the suitable phase ratio between organic and stripping phases to obtain the maximum recovery of copper was 1.0. Meanwhile, the pH of the feed stream required to achieve the maximum extraction of copper was determined as 3.0. With all supported result data, they claimed that this hollow fibre supported emulsion liquid membrane design gave an effective treatment technique in the recovery of copper-containing wastewater.

Other factors that contribute to development of continuous liquid membrane are the good formulation on the membrane phase and appropriate support body. Agtmaal et al. (Agtmaal, 2013) studied the effect of the extraction efficiency of phenol in continuous operation by using two type of supported liquid membrane which are PP (propylene) and PVDF (polyvinylidenefluoride). They found that using the membrane with less pore thickness will increase the extraction rate and minimize the drain of membrane solvent. Besides that Bhowal et al. (Bhowal, Bhattacharyya, Inturu, & Datta, 2012) have studied the removal of chromium (VI) from wastewater by using rotating spray column in continuous mode. They discovered that the volumetric mass transfer coefficient is depending on the emulsion (oil-in-water emulsion) flow rate, the rotational speed of column and flow rate of feed phase. From those results, they concluded that the preparation of emulsion reagents was important in order to increase the efficiency of the system as long as the smaller size of the rotating contactor was installed.

3 Application of continuous liquid membrane in wastewater treatment

Wastewater treatment is the major problem of the most proportion of the industrial sectors. Liquid membrane is seen to be promising technology in wastewater treatment since it has the similar established working principle with solvent extraction but provide the advantage of cost reduction and recovery process. There are a number of on-going research studies to employ liquid membrane in continuous mode for wastewater treatment. Only a few of those works have been reported and applied for continuous application either in the pilot plants or industrial applications such as the recovery of zinc, phenol and copper. For an instance, the removal and recovery of zinc have been introduced by using ELM pertractions at the several plants in the district of Galvano Techniek Veenendaal and Loko Gramsbergen, Netherlands by a research company (Kislik, 2009). The treatment plant can be operate at the maximum capacity of $1500 dm^3/h$. The operation of this plant has lower down the volume of wastewater produced to six fold reduction and saving the company operation cost totaling 30,000 Euros per year (Kislik, 2009). This ELM pertraction technology offers a good potential for commercialization in the future. Another industrial plant have been built in China which can treat about 0.5tons/h wastewater that containing approximately 1000mg/L of phenol (Kamiński & Kwapiński, 2000). This system was described as permeation column which consists of kerosene, extractants and surfactant as organic phase and sodium base as a receiving phase. Wastewater has to be maintained in the range of pH 9 to achieve the good separation (Kamiński & Kwapiński, 2000). The inventor has claimed that the recovery of phenol in the receiving phase was good as 0.5mg/L (Kamiński & Kwapiński, 2000). Besides that, Yang et al. (Yang & Kocherginsky, 2006) have developed the pilot plant to recover the copper from the industrial spent etchant (Cu^{2+} in aqueous solutions with ammonia). They manage to build the efficient and economic system to regenerate the spent etchant for reuses while simultaneously recover the copper product. The system consists of hollow fiber supported liquid membrane with 130 m^2 effective surface area. That pilot plant could offer the recovery of copper as much as 60 kg/day while regenerated back the spent etchant up until 100 L/day. However to the best author knowledge there is still lack of CLM application neither in the public wastewater treatment nor industrial wastewater treatment.

4 Major challenges and future prospects

Liquid membrane is the treatment method that has been widely study and extensively investigate in various fields of industries such as industrial wastewater, metal recovery, bio-separation, gas separation, pharmaceutical and food and beverage production (Kislik, 2009; Pabby, Rizvi, & Requena, 2008). Since the treatment of industrial wastewaters required the good promising technique, liquid membrane can be regarded as potentially powerful solution for removal and recovery of pollutants in this context. However, most of the researchers faced the difficulties on the application and commercialization of liquid membrane due to instability of membrane occurs. Thus, most of the recent research studies have been focusing on the minimizing those problems. Their research studies mainly involve in maximizing the contact area to increase the mass flux, minimizing the membrane leakage or rupture, and improving the pore support structure to avoid the loss of carrier and solvent which are associated to BLM, ELM and SLM respectively. Besides that the successful application of liquid membrane in continuous mode is also related to good membrane formulation and proper operating conditions. These can be achieved from suitably designed computer–aided flow system to fully control the whole extraction and recovery processes (Ma, Shen, Luo, & Zhu, 2004). With full commitment from researchers to further the research studies, it is undeniable that CLM will be extensively used in future either in public domain or industrial sectors.

5 Conclusions

The development of science and technology around the world in positive way undeniable, but at the same time it will produce the side effect to the environment. The discharge of wastewater containing hazardous pollutants without proper treatment will result the future generations into environmental red zone. Liquid membrane is the prospective treatment method in the removal and recovery of the pollutants from wastewater. The use of liquid membrane in continuous mode is more preferred as it provide higher and constant recovery rate, more selectivity, less residence time and less operating cost compared to the batch mode. Nevertheless, there are a number of obstacles that encountered by researchers to commercialize liquid membrane as it demonstrate the instability problems. Thus, many studies have been conducted to find the solutions regarding to those problems such as combination of the good characteristics of liquid membrane with one another, formulation of the good membrane phase and support body and modification on the reactors or columns. These studies were mostly available in batch or laboratory scale. Only a few industrial applications of CLM can be found the industrial scale such as the recovery of zinc, phenol and copper. As the recent studies on CLM were showing the positive and concrete results, it has a bright future to be use in the wastewater treatment.

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