Ceramic membrane ozonator for soluble organics removal from produced water

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Abstract. In this work, the performance of ozonation for degradation of soluble organic compounds in produced water was investigated. Tubular ceramic membrane diffuser (with and without a static mixer in the lumen side) was used to facilitate contact between ozone and produced water. The ozonation was conducted at ozone flow rate of 8 L.min⁻¹, ozone concentration of 0.4 ppm, original pH of the solution, and pressure of 1.2 bar, while the flow rates of the produced water were varied (192, 378 and 830 mL.min⁻¹). It was found that the reduction of benzene, toluene, ethylbenzene, and xylene were 85%, 99%, 85%, and 95%, respectively. A lower liquid flow rate in a laminar state showed a better component reduction due to the longer contacting time between the liquid and the gas phase. The introduction of the static mixer in the lumen side of the membrane as a turbulence promoter provided a positive effect on the performance of the membrane diffuser. The twisted static mixer exhibited the better removal rate than the spiral static mixer.

1. Introduction
Produced water is the largest waste stream co-produced during oil extraction in oil production operations [1,2]. The properties of produced water depend on geological formation, geographical location of the reservoir, and residual production chemicals [3]. The major compounds of produced water include dissolved and dispersed oil compounds, dissolved formation minerals, production solids, dissolved gases, and production chemical compounds [4]. The most soluble organic compounds in produced water are BTEX (benzene, toluene, ethylbenzene, and xylene) and phenols [5]. Organic acids such as formic acid and propionic acid, aliphatic hydrocarbons, phenols, carboxylic acid, and low molecular weight aromatic compounds are also included as soluble compounds [1,6]. Dissolved organics, especially BTEX, are necessary to be removed when the option of produced water management is discharge, reuse, or consume in beneficial use [7]. BTEX is considered a serious problem since it has some acute and long term toxic effects [8]. Thus, numerous studies and methods have been explored in attempts to remove soluble organic compounds from produced water [9–12].

Ozone as a strong oxidant is easily dissolved in water and is able to dissociate soluble toxic organic compounds into harmless compounds. The aqueous reaction between ozone and substances to be treated is known to be a complex process, including the direct reaction of molecular ozone and indirect reaction in which OH radicals formed as an oxidizing agent during ozone auto-decomposition [13]. Because of strong oxidation properties, ozone has become a superior agent for disinfection, detoxification, deodorization, and organic removal of water and wastewater [14–16]. As a strong oxidant, ozone can be used to treat a dissolved organic with low concentration (e.g. BTEX in produced water) effectively which can hardly be achieved by other methods. Ozone ability to oxidize organics matter makes it compatible to treat produced water, which contains many organic compounds.
It has been found that the main limitation in ozonation system is the low mass transfer rate of ozone from the gas to the liquid phase [17,18]. The mass transfer efficiency depends on the mixing characteristics of the gas-liquid contactor used, the kinetics of ozone reaction in the water, and the number and size of bubbles produced [17–19]. The efficacy can be increased by creating a higher surface-area-to-volume ratio for the contact of ozone with the solution through the generation of smaller bubbles [20]. A smaller bubble size results in a higher surface-to-volume ratio. In addition, smaller bubbles have higher residence times in contactor, leading to higher gas volume fractions [21]. The floating of bubbles and the possible additional mechanical agitation of the liquid create shear forces at the boundary layer which improve the local mass transfer and also keep the bubbles from coalescing [22].

Membrane technology has been considered as the promising alternative for conventional technologies in various processes including separation, purification, chemical reaction, and contacting processes [23–34]. Membrane technology offers interesting features such as lower energy consumption, relatively low operating expenditure, smaller footprint, easy to scale-up, and easy to operate [35–38]. Recently, the use of a membrane as a contacting device between two process streams has been widely studied [39–41]. Ozonation through membrane contactor has been used in several studies for organics treatment such as ozonolysis of hazardous organic compounds [42], decolorization of NOM and indigo [43], and degradation of organic pollutants in the wastewater [14]. The inorganic membranes are more suitable for ozone contactor rather than polymeric membranes because of its higher durability and oxidation resistance [44].

Although ozonation process has been applied in many wastewater treatments, the use of ozonation process to remove soluble organic compounds from produced water still has not been investigated in detail. The aim of this study is to investigate the ozonation of soluble organic compounds from produced water. A ceramic membrane module was used as a contactor (ozonator) to increase the ozone mass transfer rate during the ozonolysis of soluble organic compounds.

2. Materials and method

Chemicals used in this experiment involved benzene, toluene, ethylbenzene and xylene as a model solution. In addition, acetonitrile (CH₃CN) was used as solvent for UV spectrophotometer analysis. Tubular ceramic membrane was used as diffuser in ozonation process (ozonator). The specification of the membrane is shown in Table 1. The High Efficiency Ozonizer (O₃&W OWA-200; AC 110/220 V 50/60 Hz) was used to generate ozone.

| Parameter          | Description         |
|--------------------|---------------------|
| Material           | Ceramic membrane    |
| Module type        | Tubular             |
| Module number      | 1                   |
| Membrane length (cm)| 34                  |
| Number of tube     | 7                   |
| Tube diameter (mm) | 4                   |
| MWCO (kDa)         | 100                 |
| Surface area (m²)  | 0.1                 |

The experimental set up used in this study is depicted in Figure 2. BTEX solution was introduced into the membrane lumen and air stream contains ozone was passed through the shell side in dead-end mode. Ozone gas passed through membrane pores from shell side toward membrane lumen side creating micro bubbles. The contact between ozone and BTEX solution occurs in the bubbles surface, where the micro bubble can be assumed to be completely soluble in the liquid state inside membrane lumen. The gas flow rate is set at 8 L.min⁻¹, 0.4 ppm of ozone concentration, and 1.2 bar of pressure. The flow rates of produced water were varied at 192, 378, and 830 mL.min⁻¹ to determine the effect of
different liquid capacity on the removal of BTEX. The effluent of ceramic membrane reactor was treated into separator vessel to give an adequate degassing time for the gas to be separated from the liquid. Unreacted residue gas was discharged from the top of separator while the effluent liquid was recirculated into the membrane diffuser system. A static mixer was introduced into membrane lumen to provide better hydrodynamic and increase the performance of BTEX reduction. The effect of static mixer addition was determined by comparing the BTEX reduction for each configuration at constant flow rate of 378 ml min⁻¹. Two different shapes of the static mixer, namely spiral and twisted static mixer, were used in this study. The shapes of both static mixers are shown Figure 1.

BTEX concentration was analyzed with UV Spectrophotometer based on Thomas method (Thomas and Burgess, 2007). BTEX concentration has been analyzed using UV spectra with the wave length of 256, 262, and 264 nm respectively. The standard solution used in UV spectrophotometer was prepared from 5%-volume of CH₃CN (Acetonitrile) solution. This standard solution was also used as a solvent for the sample with the ratio of solvent to sample was 1:1, in order to compare the BTEX concentration with the pure standard solution.

![Figure 1. Experimental set-up of ceramic membrane ozonator](image)

3. Results and discussion

3.1. Removal of BTEX

The contact of ozone and BTEX solution inside lumen membrane leads to the reaction of BTEX dissociation into the harmless compounds. The reduction of BTEX concentration within solution has been observed and the result is shown in Figure 2. The initial benzene concentration was 4095 ppm, which is reduced to the final concentration of 557 ppm after 250 minutes of ozonation. Total reduction of Benzene concentration reaches 86.4%, with the highest reduction rate occurred at 120 until 210 minutes. Toluene concentration decreased from initial concentration of 937 ppm to the final concentration of 6 ppm, with the total reduction of toluene reaches 99.4%. At the same time, ozonation process performance within membrane diffuser for ethylbenzene reduction reaches 85% for 94 ppm initial concentration. As for xylene concentration with the initial value of 4024 ppm, the concentration reduction after 210 minutes of ozonation process reaches 95%.

From Figure 2 it is observed that the concentration reduction of each component shows a similar trend. The difference in reduction rates is mainly due to the different initial concentration of the component in the solution. Higher initial concentration leads to the faster reduction of component following the reaction equilibrium rule. In addition, ethyl benzene is easier to destroy compared to the
other organics. It is because ethyl benzene has ethyl groups attached to the benzene, which may be easier to cut by oxidant than the aromatic ring.

![Figure 2. BTEX concentration at various operating time](image)

3.2. The effect of liquid flow rate

In order to determine the effect of feed flow rate into the reduction performance of the BTEX component, three different flow rates were introduced into membrane diffuser, and the removal of toluene was observed for each flow rates. Toluene was chosen as the model for the following study because it has the best percent reduction. The flow rates of the liquid phase were 192 ($Q_1$), 378 ($Q_2$), and 830 ml/minute ($Q_3$). The effect of different feed flow rate on toluene reduction can be seen in Figure 3.

As shown in Figure 3, higher feed flow rate leads to lower toluene reduction rate. It was found that the toluene reduction rate follows the following order: $Q_1 > Q_3 > Q_2$. It can be explained by the decrease of contacting time between the liquid and the gas phases as the flows increase. As a result of short contacting time in a higher flow rate, the longer time is needed for the reaction to reach its equilibrium. Thus, for a larger feed capacity (larger produced water stream) a higher membrane area will be required. However, flow rate $Q_3$ showed the better performance compared to $Q_2$, although $Q_3$ is higher. It could be associated with the increased Reynolds number at the higher flow rate. When the liquid stream on a turbulence regime, a better dispersion and mixing of gas in the liquid could be achieved. As the results, a better reaction of ozone and toluene was obtained.

![Figure 3. Removal of toluene at various liquid flow rates and operating time](image)
3.3. The effect of static mixer

The main limitation in ozonation system is the low mass transfer rate of ozone from the gas phase to the liquid phase. In order to increase ozone mass transfer rate, higher turbulent flow is desired. The effect of static mixer presence on the lumen of ceramic membrane diffuser to the removal of toluene is shown in Figure 4. Figure 4 shows that the addition of static mixer into the lumen of ceramic membrane diffuser can increase toluene reduction rate. The liquid turbulent flow can increase the ratio of surface area to ozone volume within the solution.

Figure 4 also shows that SM2 (twisted static mixer) generate better toluene reduction performance compared with SM1 (spiral static mixer). The ability of twisted static mixer to increase the mass transfer rate of ozone from gas phase to liquid phase was better than spiral static mixer due to the higher turbulence induced by a spiral fluid channel.

![Figure 4. Toluene removal at various static mixer types and operating time](image)

4. Conclusions

The performance of ozonation through ceramic membrane diffuser was investigated during the removal of BTEX from a synthetic produced water solution. The effect of ozonation time, liquid flow rate, and static mixer were investigated. The removal rate of benzene, toluene, ethyl benzene and xylene were 86%, 99%, 85%, and 95%, respectively (ozonation time: 250 min.; liquid flow rate: 378 mL.min⁻¹; without static mixer). A lower liquid flow rate in a laminar state showed a better component reduction due to the longer contacting time between the liquid and the gas phase. The introduction of static mixer in the lumen side of the membrane as the turbulence promoter provided a positive effect on the performance of the membrane diffuser. The twisted static mixer exhibited the better removal rate than the spiral static mixer.

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