



## TOC reduction using Fenton and sono-Fenton process as membrane distillation pretreatment

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### ABSTRACT

Reduction of total organic carbon was focused in seawater with humic acid (HA) by one of the most important methods of advanced oxidation process. Among the advanced oxidation processes, Fenton processes are cost effective and use green oxidizing agent hydrogen peroxide, which is safer than other oxidizing agents, while sono-Fenton has shown some enhanced hydroxyl ion generation that results in faster oxidization of organic matter. Concentration of chemicals was varied as 2–4 mL L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> along with 0.2–0.4 g L<sup>-1</sup> of ferric sulfate as a catalyst considering ratio of ferric to H<sub>2</sub>O<sub>2</sub> as 1:10, which is optimized one found in previous research. Results showed that sono-Fenton is more effective than Fenton only in case of HA as well as in case of seawater with HA. Fenton produces large sludge while sono-Fenton did not show higher amount of sludge in this case. This is because of synergistic effects of ultrasonic waves, which have also effect on water molecules as well as boost up power of hydrogen peroxide oxidative species.

*Keywords:* Fenton; Sono-Fenton; Membrane distillation; Pretreatment; Humic acid

### 1. Introduction

Availability and quality of freshwater are the key factors in global sustainable growth. However, increase in human population [1], climate change [2,3], urbanization [4], and challenges for sustainable urbanization [5], food security [6], industrial growth, and development [7] are creating threats for preservation scarcity of freshwater. These areas can neither be stopped in their expansion nor leave their dependency over freshwater resources. Though efficient and cost-effective water treatments are still under development, efforts have been carried on to desalinate and decontaminate water (whether groundwater or seawater), and recycling of

water is nowadays under focus by industry for sustainable consumption and growth.

Among the various technologies of water treatments, advanced oxidation treatments and membrane processes for desalination of water have been dominating the conventional water and wastewater treatments over the past couple of decades. Water discharged from industrial wastewater contains lot of chemicals and heavy metals that can also be efficiently used by agriculture industry, which is achieved by membrane processes [8]. However, the main limitation of membrane processes is their installation and operational cost, membrane fouling, and requirement of very low suspended solids and total dissolved solids. The finest membrane process is reverse osmosis, which has even drawbacks of low water recovery and use of high pressure pumps those need heavy energy consumption [8].

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However, the latest membrane processes especially membrane distillation have various edges over reverse osmosis. Those include almost complete theoretical rejection of salts and non-volatile organic compounds, low pressure requirement for running the process, the use of solar heating [9–11] and utilization of waste heat energy as a preheating source to feed water [12]. However, since the principle relies on the phenomenon of difference of vapor pressure gradient between feed and permeate side of membrane distillation, this uses hydrophobic membranes, and the hydrophobicity should sustain in different types of feed water with temperature at about 70°C at feed side [12,13].

Membrane distillation suffers organic fouling that causes membrane wetting by penetration of water as water passes through the membrane resulting in transfer of contaminants from feed side to permeate side causing ultimate system failure [14]. Sometimes the fouling occurred by humic acid (HA), and other organic foulants are irreversible [15]. Recently pretreatments have been tried to prevent organic fouling for reverse osmosis membranes, like by granular activated carbon biofilter [16], submerged membrane bioreactors [17,18] and advanced oxidation processes including Fenton process [19]. However, for membrane distillation, so far there is no established pretreatment especially for organic fouling prevention.

The conventional Fenton process uses hydrogen peroxide and ferric salts as catalysts that result in transfer of electron between these two chemicals in order to yield hydroxyl ions ( $\text{-OH}$ ) [20,21], which is well known for its second highest powered redox potential to be used for degradation of organic matter. The basic mechanism of this reaction is shown in Eq. (1):



Reaction proceeds with regeneration of ferrous ion that takes place due to reduction of this oxidized ferric ion  $\text{Fe}^{3+}$  into its original form  $\text{Fe}^{2+}$ , which is shown by Eq. (2) [22]:



This cycle takes place and gets fast to degrade organic species in water. Though Fenton process is conventional technique, however, sono-Fenton process is a novel technique and getting importance in degradation of dyes and bisphenol as organic pollutants [23]. This method uses ultrasonic waves, which are able to make very high pressure at specific points and very hot localized points along with microbubbles giving synergistic effects [23]. Ultrasonic waves have also dynamic effect on hydroxyl and other  $\text{H}_2\text{O}_2$  based oxidizing species and radicals [24]. Natural organic matter has also been reduced by combined hydrogen peroxide and ultrasonic treatments [25]. Though as per our knowledge and literature search, yet reduction of organic matter especially HA along with seawater has not been treated by either Fenton or sono-Fenton process.

The objectives of this study were: (a) to reduce natural organic matter especially HA in seawater for process

improvement in desalination and as a pretreatment for membrane distillation, (b) to check influence of other factors over performance and degradation efficiency of HA by  $\text{H}_2\text{O}_2$  oxidizing treatments, and (c) to optimize the conditions. For this purpose, Fenton and sono-Fenton process were applied on HA solution, seawater, and HA-containing seawater. Investigations over the concentration of hydrogen peroxide, temperature effect, and effect of process time were evaluated in both treatments in order to compare the performance of both and optimize conditions.

## 2. Experimental procedure

### 2.1. Chemicals and reagents

All chemicals used in these experiments were reagent grade and extra pure. Hydrogen peroxide, ferric sulfate, anhydrous calcium chloride, strontium chloride hexahydrate, sodium bicarbonate, potassium bromite, boric acid, sodium fluoride, and HCl were purchased from Daejung Chemical, South Korea. Potassium chloride, HA, and sodium hydroxide were purchased from Sigma Aldrich, South Korea. Magnesium chloride hexahydrate was purchased from Samchun, South Korea.

### 2.2. Equipment

Shimadzu TOC analyzer (TOC-L CPH 638-91112-58, Japan), magnetic hot plate stirrer (SMHS-6, Wise-Stir), JAC ultrasonic bath (4020P, KODO) having frequency of 40 kHz and power of 400–500 W, and vacuum filtration device (J070346, South Korea) was used in this research study.

### 2.3. Methods

#### 2.3.1. Experimental setup

Three different solutions were made: first by HA in deionized water with 10 mg  $\text{L}^{-1}$  concentration, second with mixture of same concentration of HA and seawater, and the last with seawater only. Seawater was prepared using ASTM D-1141-98 (reapproved 2003). The pH was kept 8.2 to simulate as a real seawater. For Fenton process, hydrogen peroxide concentration was kept 2–4 mL  $\text{L}^{-1}$  and ferric sulfate 0.2–0.4 g  $\text{L}^{-1}$ , with keeping ratio of  $\text{H}_2\text{O}_2$  to Fe as 1:10. Though Fenton treatments are carried on from acid to neutral pH, we kept pH of solution 8.2 as to resemble to that of seawater.

#### 2.3.2. Experimental procedures and recipes

First of all, duplicate set of solutions of each HA, seawater with HA, and seawater only were prepared in order to evaluate the effect of Fenton and sono-Fenton with ferric sulfate as a catalyst. Three beakers were treated inside sonication bath, and the other comparable three was kept on magnetic stirrer keeping temperature at 35°C while that of was made. The treatment was carried out with 2 mL  $\text{L}^{-1}$  of  $\text{H}_2\text{O}_2$  and 0.2 g  $\text{L}^{-1}$  ferric sulfate. After observing and evaluating results of these trials, two more sets of beakers of seawater with HA solution were treated by increasing concentration of  $\text{H}_2\text{O}_2$  as well as catalyst as to optimize performance in case of seawater with HA.

### 3. Results and discussion

#### 3.1. Effect of variation in time over degradation of HA

From Fig. 1 it is revealed that in case of sono-Fenton process whose removal efficiency is 70.8%, the reduction percentage is 20% higher than in case of Fenton process in early 5 min while after 15 min this reduces 68% while simple Fenton reaches to 70%. Though it is the case of HA solution only, however, this indicates that sono-Fenton is effective for a very quick degradation of organic matter and accelerates the efficiency of hydrogen peroxide. However, the presence of inorganic ions affects this, which is explained in section 3.2.

#### 3.2. Effect of variation in time over degradation of seawater with HA

Since seawater has variety of ions including sodium, magnesium calcium, strontium, and potassium cations, while chloride, carbonate, bicarbonate, bromide, borate, and fluoride as anions [26]. In Fig. 2, degradation efficiency reduced drastically and reaches below 50%. In this case, at 5 min the removal efficiency of Fenton is 48% while that of sono-Fenton is 50%, and 15 min later, this Fenton become 45% and sono-Fenton also to 48%. However, after that, it goes to further decline. Here also, the trend of rapid reduction of total organic carbon (TOC) remained valid by sono-Fenton

but after 15 min this changes to reverse as in the previous case. The reduction in removal efficiency may be due to complexation of organic and calcium ion as mentioned already in previous research [27].

#### 3.3. Effect of variation in time over degradation of seawater

Fig. 3 shows that Fenton process has better removal efficiency for the first 15–20 min later it reduced. While sono-Fenton process has given an optimum removal efficiency at 30 min. This could be because of the vibrational energy introduced by sound waves in the system, which brought change in TOC. However, the removal efficiency remained as low as at 15 min around 35%, which may be due to chemistry of seawater interfering with degradation species and possibly could made complexes [28].

#### 3.4. Effect of increase in concentration of hydrogen peroxide and catalyst

Fig. 4 shows a dramatic change in behavior of TOC reduction when concentration of  $H_2O_2$  was increased at  $4\text{ mL L}^{-1}$  keeping concentration of catalyst same as before. This increase brought adverse effect in Fenton process, but due to increase in oxidizing power, removal efficiency remained 50% on an average. The decrease in TOC removal

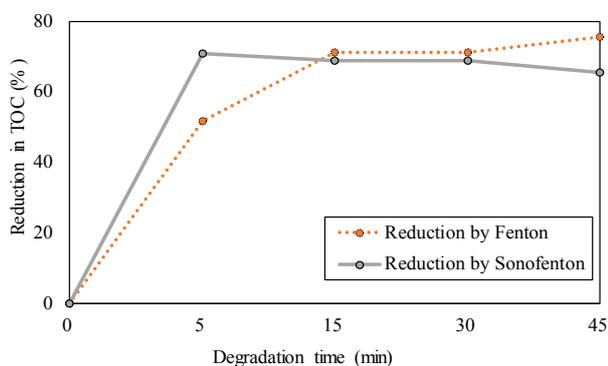


Fig. 1. Effect of time on reduction of TOC in HA solution by Fenton and sono-Fenton process.

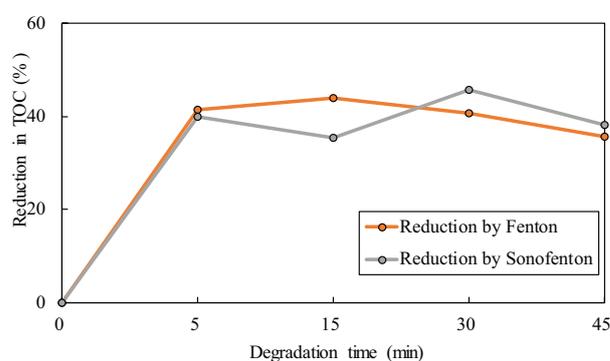


Fig. 3. Effect of time on reduction of TOC in seawater by Fenton and sono-Fenton process.

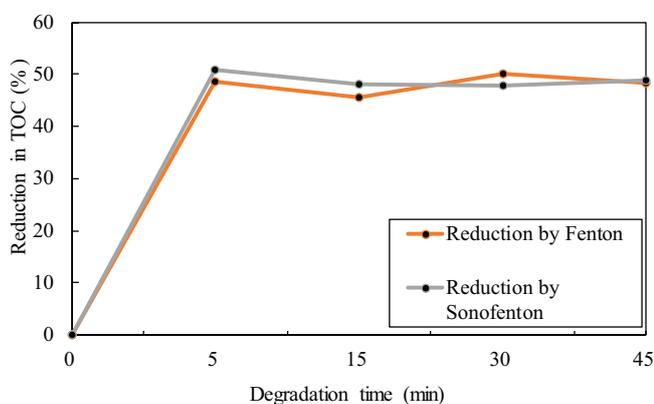


Fig. 2. Effect of time on reduction of TOC in HA and seawater solution by Fenton and sono-Fenton process.

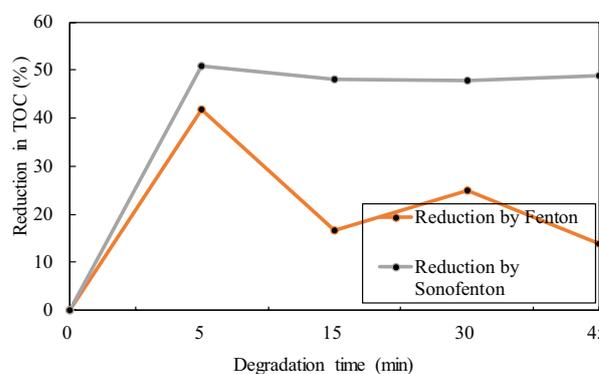


Fig. 4. Effect of increase in concentration of  $H_2O_2$  on reduction of TOC in seawater with HA by Fenton and sono-Fenton process.

efficiency of  $H_2O_2$  could be due to scavenging effect of its excess amount as shown in previous researches [29,30].

Fig. 5 shows a different behavior in case of sono-Fenton process when catalyst concentration is increased. Though initial rate of TOC removal is almost similar, but after 5 min sono-Fenton efficiency increased by 3% while over the middle period 10–32 min sono-Fenton efficiency remained below Fenton. This could be due to accelerated scavenging effect of wither  $H_2O_2$  or Fe ion itself in presence of ultrasonic waves. However, after around 35 min removal efficiency of sono-Fenton increased sharply and reached at around 70% by the end of process.

### 3.5. Effect of variation in temperature on process

Initial temperature of all samples was  $22^\circ C$ , and temperature slowly raised up on both magnetic hot plate stirrer and sonication bath with almost same ratio; however, sonication has a bit sharp rise in temperature due to heating effect of ultrasonic waves. The final target temperature was  $35^\circ C$ . Fig. 6 shows the enhanced heating effect of ultrasonic waves, which accelerates generation of hydroxyl ions and other oxidizing radicals. The vibrational energy brought rapid degradation of HA and reduced TOC in comparison with Fenton

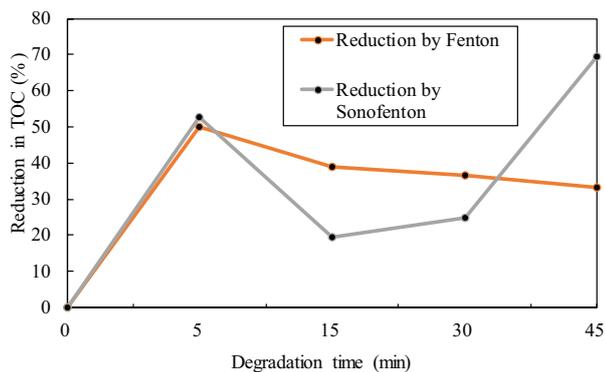


Fig. 5. Effect of increase in catalyst dosage reduction of TOC in seawater with HA by Fenton and sono-Fenton process.

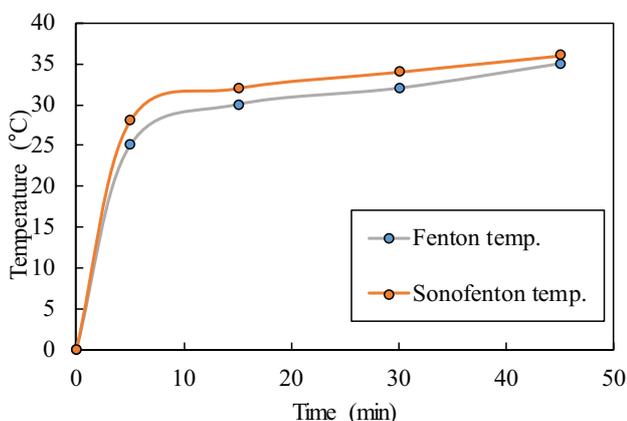


Fig. 6. Effect of variation in temperature per unit time by Fenton and sono-Fenton process.

process carried on over magnetic hot plate. This is because of the microbubbles and very high localized temperature and pressure.

## 4. Conclusions

Pretreatment for removal of organics or reduction of TOC from seawater was carried out for prevention of organic fouling in membrane distillation. Seawater with HA was treated by Fenton and sono-Fenton process. A comparison was made for reduction of TOC with HA solution and seawater only. The optimum time at which maximum removal efficiency obtained in case of seawater with HA was 5 min with  $2 \text{ mL L}^{-1}$  of  $H_2O_2$  along with  $0.2 \text{ g L}^{-1}$  of catalyst. Sono-Fenton has a quicker degradation of organics and has a better removal of TOC in short time as compared with Fenton process only.

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## References

- [1] E.S. Parish, E. Kodra, K. Steinhäuser, A.R. Ganguly, Estimating future global per capita water availability based on changes in climate and population, *Comput. Geosci.*, 42 (2012) 79–86.
- [2] J.A. Duran-Encalada, A. Paucar-Caceres, E.R. Bandala, G.H. Wright, The impact of global climate change on water quantity and quality: a system dynamics approach to the US–Mexican transborder region, *Eur. J. Oper. Res.*, 256 (2017) 567–581.
- [3] S.J. Murray, P.N. Foster, I.C. Prentice, Future global water resources with respect to climate change and water withdrawals as estimated by a dynamic global vegetation model, *J. Hydrol.*, 448–449 (2012) 14–29.
- [4] V. Srinivasan, K.C. Seto, R. Emerson, S.M. Gorelick, The impact of urbanization on water vulnerability: a coupled human–environment system approach for Chennai, India, *Global Environ. Change*, 23 (2013) 229–239.
- [5] P. Wu, M. Tan, Challenges for sustainable urbanization: a case study of water shortage and water environment changes in Shandong, China, *Procedia Environ. Sci.*, 13 (2012) 919–927.
- [6] M.A. Hanjra, M.E. Qureshi, Global water crisis and future food security in an era of climate change, *Food Policy*, 35 (2010) 365–377.
- [7] M. Flörke, E. Kynast, I. Bärlund, S. Eisner, F. Wimmer, J. Alcamo, Domestic and industrial water uses of the past 60 years as a mirror of socio-economic development: a global simulation study, *Global Environ. Change*, 23 (2013) 144–156.
- [8] C.A. Quist-Jensen, F. Macedonio, E. Drioli, Membrane technology for water production in agriculture: desalination and wastewater reuse, *Desalination*, 364 (2015) 17–32.
- [9] F. Suárez, J.A. Ruskowitz, S.W. Tyler, A.E. Childress, Renewable water: direct contact membrane distillation coupled with solar ponds, *Appl. Energy*, 158 (2015) 532–539.
- [10] Y.-D. Kim, K. Thu, N. Ghaffour, K. Choon Ng, Performance investigation of a solar-assisted direct contact membrane distillation system, *J. Membr. Sci.*, 427 (2013) 345–364.
- [11] Y.-D. Kim, K. Thu, S.-H. Choi, Solar-assisted multi-stage vacuum membrane distillation system with heat recovery unit, *Desalination*, 367 (2015) 161–171.
- [12] P. Wang, T.-S. Chung, Recent advances in membrane distillation processes: membrane development, configuration design and application exploring, *J. Membr. Sci.*, 474 (2015) 39–56.

- [13] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: recent developments and perspectives, *Desalination*, 356 (2015) 56–84.
- [14] G. Naidu, S. Jeong, S.-J. Kim, I.S. Kim, S. Vigneswaran, Organic fouling behavior in direct contact membrane distillation, *Desalination*, 347 (2014) 230–239.
- [15] G. Naidu, S. Jeong, S. Vigneswaran, Interaction of humic substances on fouling in membrane distillation for seawater desalination, *Chem. Eng. J.*, 262 (2015) 946–957.
- [16] G. Naidu, S. Jeong, S. Vigneswaran, S.A. Rice, Microbial activity in biofilter used as a pretreatment for seawater desalination, *Desalination*, 309 (2013) 254–260.
- [17] S. Jeong, S.-J. Kim, L. Hee Kim, M. Seop Shin, S. Vigneswaran, T. Vinh Nguyen, I.S. Kim, Foulant analysis of a reverse osmosis membrane used pretreated seawater, *J. Membr. Sci.*, 428 (2013) 434–444.
- [18] S. Jeong, G. Naidu, S. Vigneswaran, Submerged membrane adsorption bioreactor as a pretreatment in seawater desalination for biofouling control, *Bioresour. Technol.*, 141 (2013) 57–64.
- [19] N. Savchuk, P. Krizova, Membrane and AOP processes—their application and comparison in treatment of wastewater with high organics content, *Desal. Wat. Treat.*, 56 (2015) 3247–3251.
- [20] A. Matilainen, M. Sillanpaa, Removal of natural organic matter from drinking water by advanced oxidation processes, *Chemosphere*, 80 (2010) 351–365.
- [21] E. Basturk, M. Karatas, Advanced oxidation of Reactive Blue 181 solution: a comparison between Fenton and Sono-Fenton process, *Ultrason. Sonochem.*, 21 (2014) 1881–1885.
- [22] A. Babuponnusami, K. Muthukumar, A review on Fenton and improvements to the Fenton process for wastewater treatment, *J. Environ. Chem. Eng.*, 2 (2014) 557–572.
- [23] M. Cai, J. Su, G. Lian, X. Wei, C. Dong, H. Zhang, M. Jin, Z. Wei, Sono-advanced Fenton decolorization of azo dye Orange G: analysis of synergistic effect and mechanisms, *Ultrason. Sonochem.*, 31 (2016) 193–200.
- [24] A.J. Exposito, J.M. Monteagudo, A. Duran, A. Fernandez, Dynamic behavior of hydroxyl radical in sono-photo-Fenton mineralization of synthetic municipal wastewater effluent containing antipyrine, *Ultrason. Sonochem.*, 35 (2017) 185–195.
- [25] H. Pourzamani, MAJD A.M.S., H.M. Attar, B. Bina, Natural organic matter degradation using combined process of ultrasonic and hydrogen peroxide treatment, *Yearbook of the Institute of Geosciences UFRJ*, 38 (2015) 63–72.
- [26] H. Elderfield, *Seawater chemistry and climate*, *Science*, 327 (2010) 1092–1093.
- [27] Y. Yu, S. Lee, S. Hong, Effect of solution chemistry on organic fouling of reverse osmosis membranes in seawater desalination, *J. Membr. Sci.*, 351 (2010) 205–213.
- [28] L.G. Devi, S.G. Kumar, K.M. Reddy, C. Munikrishnappa, Effect of various inorganic anions on the degradation of Congo Red, a di azo dye, by the photo-assisted Fenton process using zero-valent metallic iron as a catalyst, *Desal. Wat. Treat.*, 4 (2009) 294–305.
- [29] J. Wei, Y.H. Song, X.G. Meng, J.S. Pic, Optimization and analysis of homogenous Fenton process for the treatment of dry-spun acrylic fiber manufacturing wastewater, *Desal. Wat. Treat.*, 56 (2015) 3036–3043.
- [30] H. Xu, M. Li, F.M. Wu, J. Zhang, Optimization of Fenton oxidation process for treatment of hexoxygen industrial wastewater using response surface methodology, *Desal. Wat. Treat.*, 55 (2015) 77–85.