SONOELECTROCHEMICAL DEGRADATION OF NAPHTHALENE AND 2,4-DICHLOROPHENOL

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Introduction

Advanced oxidation process (AOP) has attracted huge attention due to its strong oxidative potential induced by hydroxyl radical (·OH) that can abate the extensive range of micropollutants[1]. Each process under AOPs features its own characteristics depending on driving force to generate ·OH. Of AOPs, electrochemical and sonochemical process have an advantage of consuming no additional chemicals but only electrical energy to treat pollutants.

Several researchers reported the improvement of degradation rate for certain pollutants when these two processes were combined[2, 3] while others did contrastively for different pollutants[4]. These conflicting results are thought to be due to the physicochemical properties of pollutants.

In this study, sonoeletrochemical degradation efficiency of two pollutants featuring different physicochemical properties were compared and discussed.

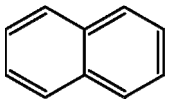
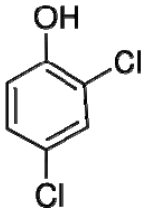
Materials and methods

Chemicals

Naphthalene of extra pure grade ($C_{10}H_8$) was purchased from Samchun Pure Chemical Co., Ltd and was used as received. 2,4-Dichlorophenol ($C_6H_4Cl_2O$) was obtained in analytical grade from Sigma-Aldrich and used in the form of solid powder as it was. Sodium sulfate (Na_2SO_4) as the supporting electrolyte was extra pure grade from Samchun Pure Chemical Co., Ltd. Aqueous solution of naphthalene and 2,4-dichlorophenol was prepared at room temperature with deionized water obtained from Millipore Milli-Q. Dichloromethane (CH_2Cl_2) as a solvent to extract naphthalene was special grade (>99.8 %) from Samchun Pure Chemical Co., Ltd.

Physicochemical properties considered, Henry's law constant and water diffusivity, are shown in Table 1.

Table 1. Physicochemical properties of two pollutants considered in this study

	Naphthalene	2,4-Dichlorophenol
Structure		
Henry's Law Constant (atm-m^3mol^{-1})	4.83×10^{-4}	3.16×10^{-6}
Water Diffusivity (cm^2s^{-1})	7.50×10^{-6}	8.77×10^{-6}

Sonoelectrochemical Procedure

Experimental devices are described schematically in Fig. 1. Cylindrical reactor (diameter: 10 cm, height: 15 cm, solution volume: 1 L) with water jacket was made of stainless steel and sealed with cover.

For sonochemical degradation experiment, ultrasonic waves were generated through tranducer installed at the bottom of reactor powered by ultrasound generator (35 kHz, 64 W/L, Flexonic 4, Mirae Ultrasonic Tech, Bucheon, Republic of Korea).

For electrolysis experiment, Pt anode (coated on Ti, mesh type, width: 6 cm, height: 7 cm) and stainless steel cathode (mesh type, width: 8 cm, height: 7 cm) were used. Regulated DC power supply from PNCYS (EP-3010) was used to apply voltage (30 V in potentiostat mode) to electrodes.

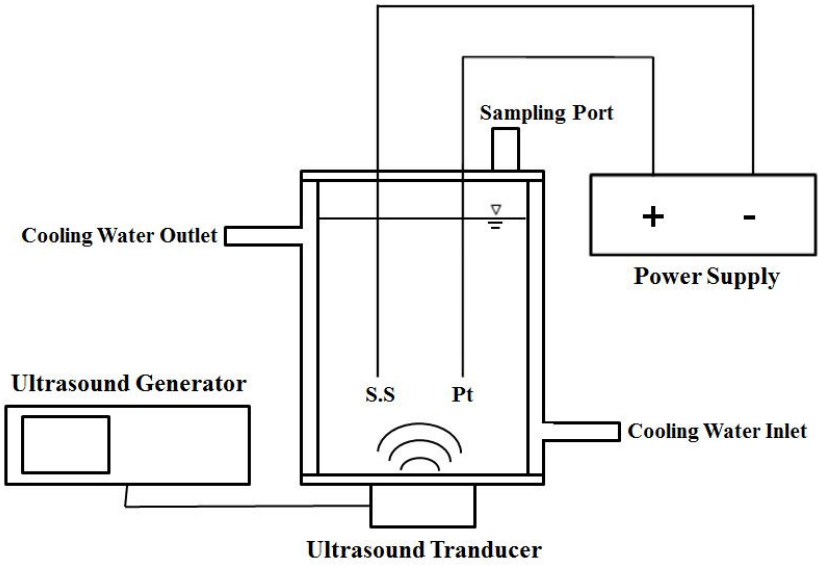


Fig. 1. Schematic diagram of experimental sets; S.S:Stainless Steel

Analytical Method

Concentration of naphthalene was determined by GC-MSD (Agilent 7890A 5975C inert XL MSD with Triple-Axis Detector) with CombiPAL Autosampler (CTC Analytic AG). DB-5MS Column (3 m length×0.25 mm I.D.×0.25 μm film thickness) was used. GC-MSD was operating with 55 ℃ of initial temperature for 0.4 min and ramping to 300 ℃ at 50 ℃min^{-1}. Samples were drawn from the reactor with syringes and were mixed with dichloromethane.

2,4-Dichlorophenol concentration was analyzed with HPLC equipped with Eclipse XDB-C18 (4.6 mm ID × 250 mm, 5 μm) and G4212B 1260DAD Detector (λ=202 μm). Temperature of the column was kept at 25 ℃ constantly. The mobile phase was phosphoric acid, deionized water and acetonitrile in the volumetric ratio of 1:39:60 with a flow rate of 1mLmin^{-1}.

Kinetic constants were calculated with assumption of pseudo first reaction.

Results and discussion

Kinetic constants for each pollutant in different degradation processes are summarized in Table. 2.

In sonochemical degradation process, the removal efficiency of naphthalene was 56 % in an hour while that of 2,4-dichlorophenol was only 29 % in same period of time. Kinetic constants also show a huge difference. This result follows the fact that pollutants with high volatility are more degradable than ones with low volatility. It is because more solutes diffuse into the bubbles and experience extremely high temperature and pressure which is called supercritical condition[5].

In electrochemical process, 86 % of naphthalene was removed in an hour and showed 3.13×10^{-2} min^{-1} of kinetic constants. However, 2,4-dichlorophenol showed 28 % removal in same period of time and 6.3×10^{-3} min^{-1} of kinetic constant.

Table 2. Comparison of kinetic constants in three different processes; US: Sonochemical process, EC: Electrochemical process, US/EC: Sonoelectrochemical process

	k_{US} (min^{-1})	k_{EC} (min^{-1})	$k_{US/EC}$ (min^{-1})
Naphthalene	1.42×10^{-2}	3.13×10^{-2}	3.18×10^{-2}
2,4-Dichlorophenol	4.8×10^{-3}	6.3×10^{-3}	3.3×10^{-2}

In combined system, very similar removal rate and kinetic constant were obtained, 89 % and 3.18×10^{-2} min^{-1} for naphthalene, 73 % and 3.3×10^{-2} min^{-1} for 2,4-dichlorophenol. For naphthalene, electrochemical effect seems to hold big portion in degradation according to Fig. 2 and Fig. 3.

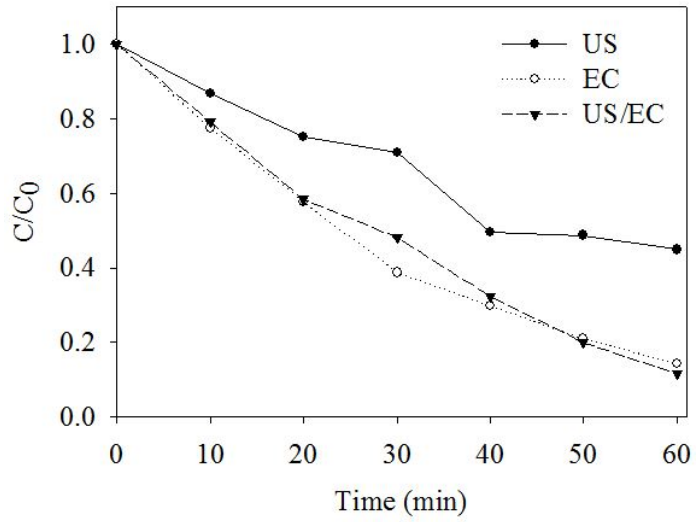


Fig. 2. Degradation of naphthalene in different treatment processes; US: Sonochemical process, EC: Electrochemical process, US/EC: Sonoelectrochemical process

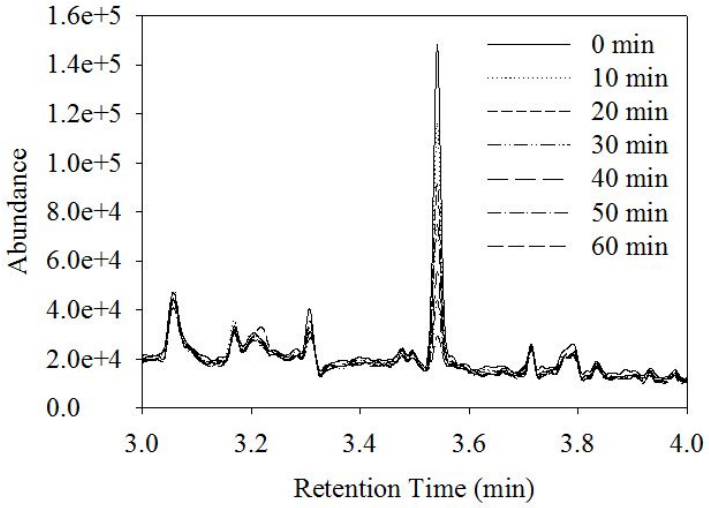


Fig. 3. GC/MS chromatogram for naphthalene in sonoelectrochemical treatment

In case of 2,4-dichlorophenol, whereas, the result definitetly implies that two degradation mechanisms, electrochemical and sonochemical mechanisms, affect each other during the process and draw positive synergistic effect[6]. This synergistic phenomena has been reported by several researchers such as Yan-ze Ren et al[6]. In electrochemical degradation process, diffusion is one of the most important mechanism that can influence on mass transfer especially through diffusive layer around electrode and ultrasound can decrease the layer leading a better mass transfer of pollutant[7]. Since 2,4-dichlorophenol has a higher water diffusivity, it takes more advantages by ultrasound than naphthalene.

With these results, we can conclude that it is highly necessary to consider physicochemical properties of target pollutant to drive out the best performance of sonoelectrochemical system.

Acknowledgements

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