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Changes of absorption spectra, $SUVA_{254}$, and color in treating landfill leachate using microwave-assisted persulfate oxidation

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Abstract−We experimentally determined the effects of microwave-assisted persulfate oxidation (MAPO) on absorbance spectra, specific ultraviolet absorbance at a wavelength of 254 nm ($SUVA_{254}$), and color in treating landfill leachate. The effects of treatment temperature ($60 \le T \le 90$ °C) and sodium persulfate (SPS) concentration ($0.05 \le [SPS] \le 0.3$ M) were characterized. An absorbance band in the visible region disappeared after MAPO, but the absorbance in UV region remained. $SUVA_{254}$ of treated leachate varied from 2.3 to 14.7 L/mg·m. Color number (CN) removal of 99% ($CN = 0.004\ cm^{-1}$) was achieved within 30 min with MAPO at 80 °C and [SPS]=0.2 M. As T and [SPS] increased, CN and total organic carbon decreased, but $SUVA_{254}$ increased.

Keywords: Advanced Oxidation, Process Technology, Removal, Spectroscopy, Wastewater

INTRODUCTION

Leachate is a liquid released during decomposition of waste material and percolation of rainwater through the waste layers. It is a highly-variable heterogeneous mixture of high-strength organic and inorganic contaminants including humic acids, ammonia nitrogen, heavy metals, and inorganic salts [1-3]. Non-biodegradable (refractory) compounds formed by humic acids, fulvic acids, and the hydrophilic fraction [4] confer a strong coloring to the leachate. At old landfills, the organic fraction in the leachate becomes dominated by refractory compounds such as humic substances [5]. Biological processes to remove organic matter can be effective for young leachate in which the proportion of biodegradable organic matter is high [6], but their effectiveness decreases as the leachate ages, because during this process the proportion of refractory organic matter increases; therefore physicochemical treatments must be applied [7].

Advanced oxidation processes have been evaluated as methods to treat landfill leachate, because the principal oxidizing agents (hydroxyl or sulfate radicals) can chemically destroy molecules in target pollutants to reduce their toxicity and even transform them to water and carbon dioxide. Particularly, persulfate ($S_2O_8^{2-}$) oxidation has been used to decompose organic pollutants in contaminated wastewater [8]. $S_2O_8^{2-}$ is a strong oxidant (redox potential 2.2 V), but the sulfate free radicals ($SO_4^{\bullet-}$) have a redox potential of 2.6 V that can destroy refractory organic contaminants better than does $S_2O_8^{2-}$ [9]. The low cost of persulfate salt (0.93-2.65 US dollar/kg) [10,11] facilitates use of $S_2O_8^{2-}$ oxidation to treat wastewater. Sodium persulfate (SPS) has strong oxidative capacity, low cost, relatively high stability, and aqueous solubility, so it is widely used to degrade organic contaminants [10,12]. However, SPS must be activated before it becomes reactive [9]. Heating can transform SPS to $SO_4^{\bullet-}$ [13,14].

Microwave irradiation has a shorter reaction time and lower energy requirement than conventional heating [15,16]. Microwave heating has several advantages over conventional thermal processes, including non-contact heating, material-selective heating, and heating from interior to exterior [15,17]. Landfill leachate is a water-based solution. Water absorbs microwave energy readily, so landfill leachate can be heated well by microwave irradiation in a short time [9]. Free radicals can be generated by applying microwave irradiation simultaneously with oxidants [15]; in this case, the effects of microwaves can be thermal, athermal, or both. The thermal effects are associated with high temperature T and microwave fields (molecular vibration); the athermal effects are associated with $S_2O_8^{2-}$ oxidation and free-radical reactions. The use of microwave irradiation can increase the $S_2O_8^{2-}$ decomposition rate constant about three to four times compared to values obtained under conventional heating [16].

Our previous study examined the effects of T, SPS concentration ([SPS]), and pH on the total organic carbon (TOC) removal of landfill leachate using microwave irradiation [18]. Absorbance spectra, ultraviolet absorbance at a wavelength λ=254 nm (UV_{254}), and specific UV_{254} absorbance ($SUVA_{254}$) are also often used as proxies for the level of organic matter [19]. $SUVA_{254}$ value can reveal the relative content of aromatic structures in the dissolved organic matter [20]. The persulfate oxidation has also been considered to be a promising and attractive treatment technology for decolorization of wastewaters [11]. However, no experimental study on spectroscopic characterization in treating landfill leachate using microwave-assisted persulfate oxidation (MAPO) has been reported to our best knowledge. Here, we present an experimental study to investigate changes of these factors with MAPO of landfill leachate.

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MATERIALS AND METHODS

1. Landfill Leachate and Material

Landfill leachate was collected from a landfill (>10 years old) in Gangwon-do, South Korea, and stored at 4 °C until use. To minimize interference by suspended solids, all leachate samples were allowed to settle under gravity; only the supernatants were used in experiments. Oxidation was initiated by adding SPS ($Na_2S_2O_8$, >98%, Shinyo Pure Chemical, Japan).

2. Experimental Set-up

A microwave accelerated reaction system (MARS, CEM Corporation, 0-1,600 W power output, 2,450-MHz frequency, 0≤T≤330 °C) equipped with a T sensor was used to heat the leachate, which was contained in a 250-mL flat-bottom flask with ground glass joint neck and equipped with magnetic stirrer (120 rpm). The total liquid volume was 200 mL. MARS at the highest output power (1,600 W) was used to maintain T because applying high-power microwave irradiation can reduce reaction time significantly without changing the amount of energy provided [16,21]. Two factors (60≤T≤90 °C and 0.05≤[SPS]≤0.3 M) that affect spectroscopic characterization were used.

3. Specific Ultraviolet Absorbance

$SUVA_{254}$ is a useful parameter because it provides information about the chemistry and treatability of organic matter [22]. For example, $SUVA_{254}$ is directly correlated with the aromatic carbon content of organic matter [23-25] and represents the contributions of microbial ($SUVA_{254}$<3 L/mg·m) and terrestrial ($SUVA_{254}$>4 L/mg·m) organic material [23]. $SUVA_{254}$ is defined as the UV absorbance of a water sample at a given wavelength normalized to dissolved organic carbon (DOC) concentration (Eq. (1)).

$$SUVA_{254}\ (\mathrm{L/mg\cdot m}) = \frac{UV_{254}\ (\mathrm{cm^{-1}})}{DOC\ (\mathrm{mg/L})} \times 100\ (\mathrm{cm/m}) \quad (1)$$

4. Color Number

The visible region of the leachate spectrum showed no limited absorption maxima, so the color number (CN) (Eq. (2)) was used to characterize color [26]. The CN relies on the measurement of the spectral absorption coefficient (SAC) in the visible range at λ=436, 525, and 620 nm [27].

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \quad (2)$$

SAC is determined by the absorption value (Abs) in a cell of thickness x as

$$SAC_i = \frac{Abs_i}{x} \quad (3)$$

5. Analytical Methods

TOC was determined by using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). UV absorbance was analyzed by UV-Vis spectrophotometer (Libra S60, Biochrom., UK). The pH, alkalinity, conductivity, solids, chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and NH_4^+-N and NO_3^--N concentrations were determined according to the procedures in Standard Methods [28].

RESULTS AND DISCUSSION

1. Characteristics of Landfill Leachate

The COD concentration of landfill leachate was 666 mg/L and alkalinity was 3,328 mg $CaCO_3$/L (Table 1). The leachate was slightly

Table 1. Characteristics of the raw landfill leachate in this study

Parameter	Value
pH	8.4±0.1
Alkalinity (mg $CaCO_3$/L)	3,328±104
Suspended solids (mg/L)	22.2±1.9
Chemical oxygen demand (mg/L)	666±11
Total organic carbon (mg/L)	437±1
Kjeldahl nitrogen (mg/L)	1,252±35
Ammonia nitrogen (mg/L)	1,246±20
Nitrate nitrogen (mg/L)	5.6±0.1
Conductivity (mS/cm)	17±1
UV_{254} (cm^{-1})	4.44
$SUVA_{254}$ (L/mg·m)	1.5
Color number (cm^{-1})	0.381

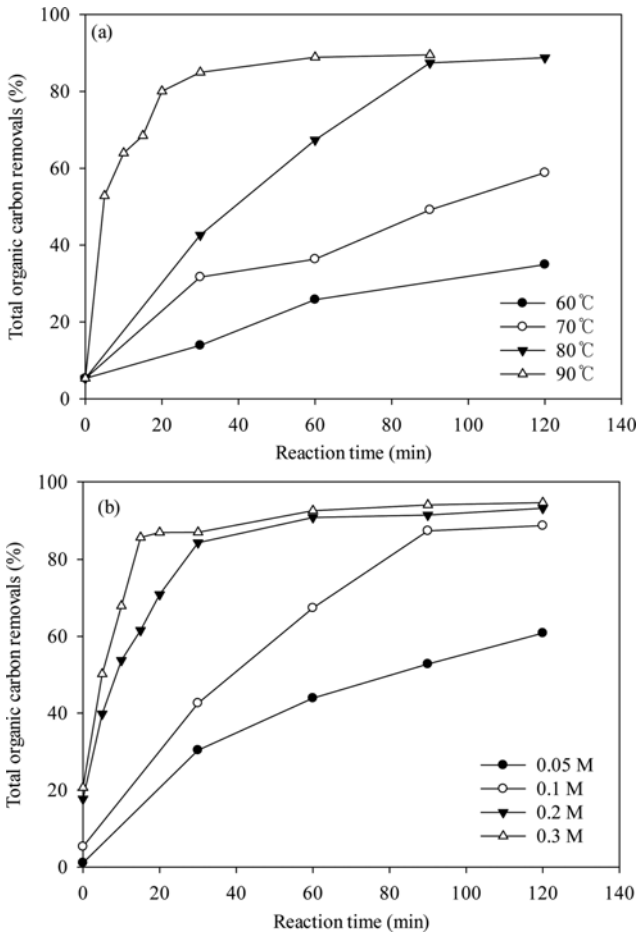

Fig. 1. Change in total organic carbon removal vs. (a) temperature (sodium persulfate concentration=0.1 M) and (b) sodium persulfate concentration (temperature=80 °C) with microwave-assisted persulfate oxidation.

alkaline (pH=8.4), partly due to the biological activity [29]. In an alkaline solution SO_4^{2-} may play a role in scavenging hydroxyl radical and slowing down organic degradation rate [30]. The leachate had high concentration of TKN (1,252 mg/L) [26,29,31,32]; most of the TKN was NH_4^+-N (1,246 mg/L). The presence of NH_4^+-N and organic nitrogen was mainly due to their generation during decomposition of organic matter. Older leachate with refractory contaminants and high content of NH_4^+-N is not appropriate for biological processes due to inhibition of the microorganisms in activated sludge [33-35]. Landfills more than 10 years old have fairly high NH_4^+-N [29]. The $SUVA_{254}$ was 1.5 L/mg·m and CN was 0.381 cm^{-1}. These properties are consistent with the properties of stabilized leachate [22,29].

2. Total Organic Carbon Removals with Microwave Assisted Persulfate Oxidation

Our previous study showed that TOC removal efficiency generally increased with T and [SPS] [18]. TOC removal after 30 min with [SPS]=0.1 M was 14% at 60 °C, 32% at 70 °C, 43% at 80 °C, and 85% at 90 °C (Fig. 1(a)). At final T=80 °C, TOC removal after 30 min was 30% at 0.05 M, 43% at 0.1 M, 84% at 0.2 M, and 87% at 0.3 M (Fig. 1(b)).

3. Spectrum Change During Microwave-assisted Persulfate Oxidation

Humic substances generally absorb strongly in the UV-Vis range (190-800 nm) [36,37]. To reveal the effect of T and [SPS] on landfill leachate composition, changes in the absorbance spectra (190-700 nm) of the landfill leachate with MAPO were investigated. The samples exhibited a featureless decrease in absorbance with increasing wavelength in UV-Vis spectra; the peaks decreased gradually and the full spectrum scanning pattern significantly changed as T and [SPS] increased (Fig. 2). The attenuation and final disappearance of absorption peaks clearly indicate that the leachate was degraded [7]. No new absorption bands, especially those of aromatic moieties and other similar intermediates, appeared in the visible or ultraviolet region; this observation indicates that the main chromophores and aromatic moieties in the original leachate solution were destroyed under oxidation and that the leachate can be decolored effectively [7,26]. Absorption in the visible region (400-700 nm, responsible of color) disappeared after MAPO, so this treatment decolorizes the leachate effectively. However, absorbance in the UV region (190-400 nm) remained; this is a sign that aromatic compounds survived after the treatment [37-39].

4. Change of Specific Ultraviolet Absorbance with Microwave-assisted Persulfate Oxidation

In a previous study, leachate had $1.9 \leq SUVA_{254} \leq 7.4$ L/mg·m, although the leachate was uniformly characterized to have stabilized [22]. In this study, the raw leachate had $SUVA_{254}$=1.5 L/mg·m (Table

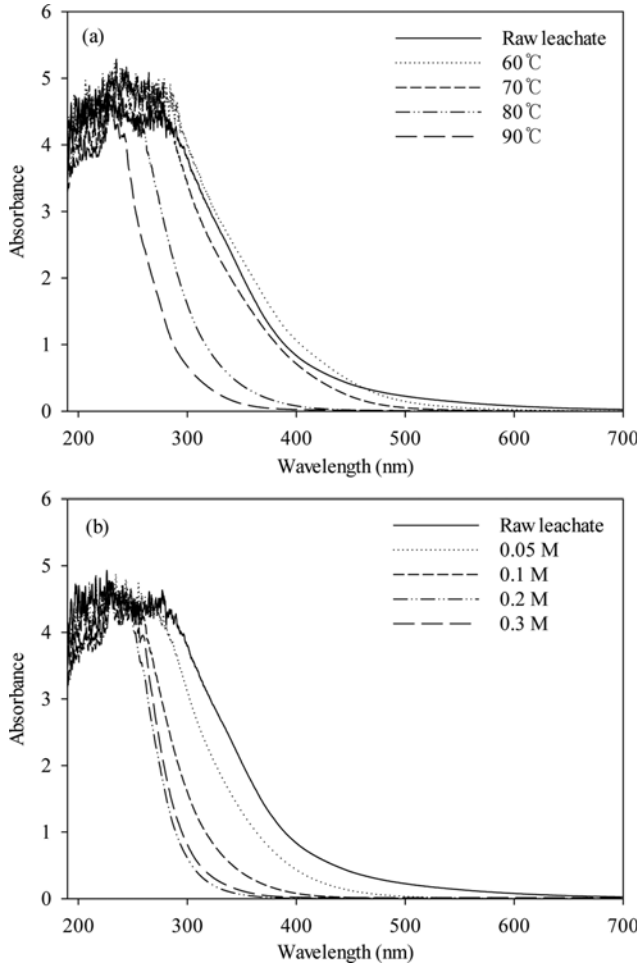

Fig. 2. Spectrum change with (a) temperature (sodium persulfate concentration=0.1 M) and (b) sodium persulfate concentration (temperature=80 °C) with microwave-assisted persulfate oxidation at 30-min reaction time.

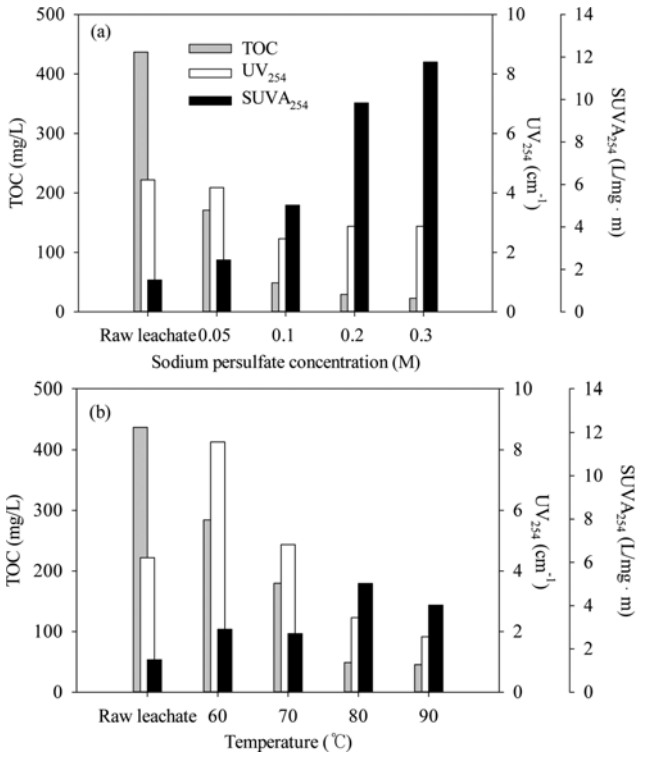

Fig. 3. DOC, UV_{254}, and $SUVA_{254}$ changes with (a) temperature (sodium persulfate concentration=0.1 M) and (b) sodium persulfate concentration (temperature=80 °C) at 120-min reaction time.

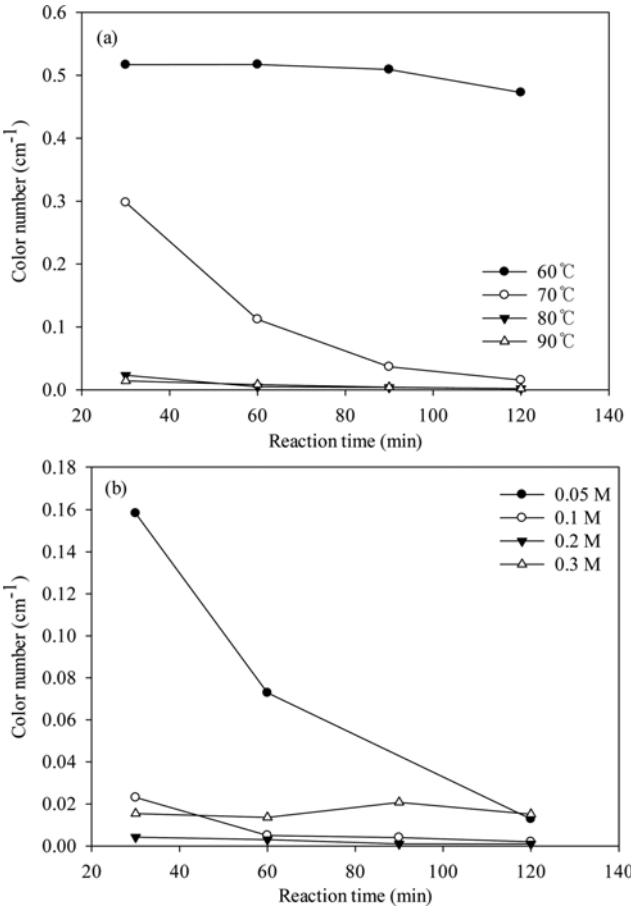

Fig. 4. Color number change with (a) temperature (sodium persulfate concentration=0.1 M) and (b) sodium persulfate concentration (temperature=80 °C) with microwave-assisted persulfate oxidation.

1); thus, the aromaticity within natural organic matter was not high. This result is reasonable considering that the landfill was operated as a bioreactor and that the leachate is >10 years old [22].

After treatment, the leachate in this study had $2.3 \leq SUVA_{254} \leq 14.7$ L/mg·m (data not shown). $SUVA_{254}$ increased as TOC removal by oxidation increased (Fig. 3). Other researchers [22,25] have also observed this trend. Increase in $SUVA_{254}$ generally indicates increased humification, aromaticity, and hydrophobicity of organic matter and, hence, reduced biodegradability [25]. The increase in $SUVA_{254}$ occurred because TOC removal exceeded UV_{254} removal (Fig. 3); this difference in rate indicated that recalcitrant compounds are present in the leachate [19].

5. Color Number Removals Using Microwave-assisted Persulfate Oxidation

The CN removal within 30 min with [SPS]=0.1 M was 22% at 70 °C, 94% at 80 °C, and 96% at 90 °C (Figs. 4 and 5). At 60 °C, CN was higher than in raw landfill leachate and did not decrease within 120 min. At 80 and 90 °C, CN decreased rapidly during the first 30 min, and then slowed. This result means that two processes occur: a fast one that lasts ~30 min, and a slow one that continues beyond 30 min to an asymptote; the latter process corresponds to slow discoloration rates [26]. At 80 °C, the CN removal within 30

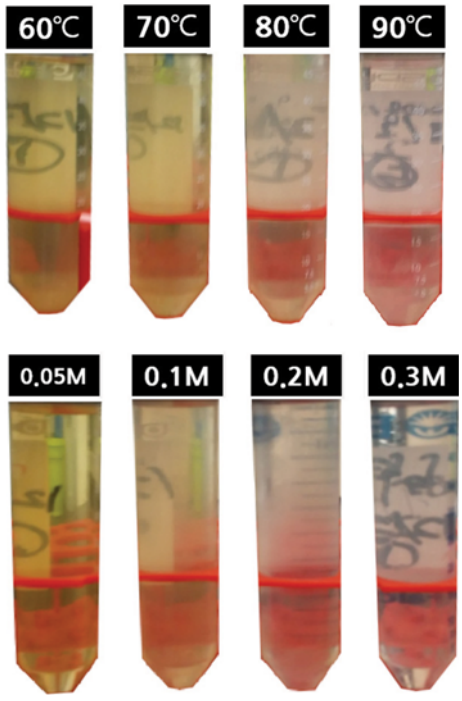

Fig. 5. Decolorization with temperature and sodium persulfate concentration with microwave-assisted persulfate oxidation.

min was 58% at [SPS]=0.05 M, 94% at [SPS]=0.1 M, 99% at [SPS]=0.2 M, and 96% at [SPS]=0.3 M; at $0.1 \leq [SPS] \leq 0.3$, CN decreased rapidly during the first 30 min.

CN reduction increased as T and [SPS] increased (Figs. 4 and 5). CN removal of 99% ($CN=0.004\ cm^{-1}$) was achieved within 30 min using MAPO at T=80 °C and [SPS]=0.2 M. This efficacy exceeds that obtained in a previous study that used ozone/hydrogen peroxide (2 g/L H_2O_2) (94%; $CN \fallingdotseq 0.2\ cm^{-1}$ within 60 min) [26].

CONCLUSIONS

The full spectrum scanning pattern significantly changed with increasing T and [SPS]. $SUVA_{254}$ value increased as TOC removal efficiency increased. During the process, CN and TOC reduction increased with T and [SPS]. The relationships described will guide optimization of MAPO to treat landfill leachate.

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