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Microwave-enhanced persulfate oxidation to treat mature landfill leachate

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HIGHLIGHTS

- Kinetics of persulfate oxidation by MOP followed the first-order reaction.
- Adverse effects on reaction rates under higher MW powers and high persulfate doses.
- TOC/COD ratio dropped with oxidation time and an 86.7% reduction in ratio at pH 7.
- Solution pH has an insignificant effect on the fates of MA, LA, and AA.
- The energy cost of MOP (USD\$6.03/m^3) is similar to that of CHO (USD\$6.10/m^3).

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ABSTRACT

Microwave oxidation process (MOP) was evaluated for treatment of landfill leachate. Kinetics of persulfate oxidation in MOP, effects of pH and persulfate doses on fates of derivative organic acids, and the energy cost of MOP were evaluated. The results showed that total organic carbon (TOC) removal of 79.4%, color removal of 88.4%, and UV_{254} removal of 77.1% were reached at MOP 550 W/85 °C within 30 min. The kinetics of oxidation by MOP followed the first-order reaction. For a given persulfate dose, the reaction rate increased with the microwave power setting (775 W > 550 W > 325 W > 128 W) with reaction rate constants ranging from 10^{-5} to 10^{-2} min^{-1}. The adverse effects on reaction rates under higher microwave power settings and high persulfate doses are plausibly caused by excessive persulfate oxidation and self-scavenging termination of free radicals. During the MOP treatment, TOC/COD ratio dropped with time and an 86.7% reduction in TOC/COD ratio after 120 min at pH 7. Oxalic acid was the major derivative and its concentrations were higher under acidic conditions. Malic, lactic, and acetic acids were formed and soon degraded, and the solution pH has an insignificant effect on their fates. The energy cost of MOP (USD\$6.03/m^3) is essentially similar to that of conventional heating oxidation (CHO) (USD\$6.10/m^3).

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1. Introduction

Landfills are often the final destinations of municipal solid wastes. One of the main environmental concerns is associated with landfill leachate, and its composition depends on landfill age, refuse content, and climate conditions [1]. Leachate with a biological oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio larger than 0.4 is considered biodegradable [2], while that with a BOD_5/COD ratio less than 0.2 is considered recalcitrant [3]. Young landfills typically have higher COD concentrations (>10,000 mg/L), larger BOD_5/COD ratios (>0.5), and smaller TOC/COD ratios (<0.3); medium landfills have lower COD concentrations (500–10,000 mg/L), lower BOD_5/COD ratios (0.1–0.5), and larger TOC/COD ratios (0.3–0.5); and mature landfills (more than 10 years) have the smallest COD concentrations (<500 mg/L), the smallest BOD_5/COD ratios (<0.1), and the largest TOC/COD ratios (>0.5) [4–10].

Lots of treatment processes have been developed to minimize leachate's adverse environmental impacts [11]. They include aerobic biodegradation [12], anaerobic biodegradation [13], Fenton treatment [14,15], physical and chemical processes [16,17], membrane processes [18,19], catalytic oxidation [20,21], ozonation [22], electro-dialysis [23], electro-chemical oxidation [24], ultrasonication [25], and others.

Microwave technology receives lots of attention recently as a treatment alternative because of its shorter reaction time and

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lower energy requirement. Microwaves are electromagnetic waves. Microwave energy (E) in the frequency range of 1–100 GHz is about 0.4–40 J mol^{-1} [26]. A dipole would align with an oscillating electric field by rotation [27]. The dipoles within dielectric materials realigned themselves 2.45 billion times per second to heat promptly and effectively [28,29]. Free radicals would be generated from applying microwave irradiation simultaneously with oxidants [30–32]. The chemical reaction rate increases in the microwave field due to microwave-specific effects, which considered as athermal by some, but thermal by others [27,33]. Heretofore, athermal or thermal effects are still being debated [34,35].

Persulfate is one of the common oxidants used in microwave oxidation researches and often used in in-situ chemical oxidation (ISCO) [36,37]. Zhang et al. [38] compared microwave irradiation assisted by hydrogen peroxide, peroxymonosulfate or persulfate, and showed that persulfate was most effective in COD reduction in landfill leachate. Microwave-activated persulfate accelerated the oxidation rates, and the rate increased with powers [31,39]. The rate constant (k) can be determined from the Arrhenius equation [$k = A \times \exp(-\Delta G/RT)$]. The microwave field increases molecular vibrations due to orientation of polar molecules that enlarges the value of the constant A [40]. The reaction rates of persulfate increased with temperature from 10^{-6} min^{-1} at 25 °C to 10^{-2} min^{-1} at 90 °C [41]. Over or under microwave powers caused the adverse effects on reaction rates [42], but this microwave phenomenon was seldom discussed based on kinetics.

In our previously study, we have compared TOC and COD removals by CHO and MOP, and investigated the microwave-specific effects [42]. Besides, some of derivative organic acids are toxic, but they may still possess economic value. Existing researches on MOPs seldom delineated the effects of pH on derivative mechanisms of organic acids [43] and estimated the cost of MOP. The objectives of this study were to (i) perform a kinetic analysis of persulfate oxidation in MOP to evaluate the effects of microwave power settings, (ii) investigate the effects of pH and persulfate doses on formation and degradation behaviors of derivative organic acids, and (iii) estimate the energy cost of using MOP for mature landfill leachate treatment.

2. Material and methods

2.1. Characteristics of the landfill leachate

The Sanjuku landfill is located in Taipei, Taiwan. The landfill began its operations in 1994 to accept raw garbage, cement-stabilized fly ash, and bottom ash. The landfill has a tipping area of 30 ha with a design capacity of 6,170,000 m^3. Raw garbage was no longer accepted since 2002. Since 2003 the cement-stabilized fly ash from the incinerators of municipal solid waste became the main feed to the landfill and the bottom ash was no longer landfilled since 2005. Leachate is being collected and subjected to conventional secondary treatment.

The characteristics of raw leachate from 1/2011 to 1/2014 are (mean concentration ± standard deviation): pH (7.4 ± 0.3), BOD_5 (49 ± 32 mg/L), COD (204 ± 86 mg/L), BOD_5/COD ratios (0.24 ± 0.1), and TOC (55 ± 19 mg/L), as shown in Fig. 1. The concentrations of the chemical compounds are ammonia nitrogen(187 ± 110 mg/L), chromium ions (0.006 ± 0.003 mg/L), lead ions (0.023 ± 0.080 mg/L), cadmium ions(0.002 ± 0.007 mg/L), mercury ions (0.0002 ± 0.0004 mg/L), copper ions (0.002 ± 0.006 mg/L), zinc ions (0.035 ± 0.073 mg/L), arsenic ions (0.0025 ± 0.0016 mg/L), oxalic acid (OA) (42.8 ± 13.2 mg/L), acetic acid (AA) (0.5 ± 0.4 mg/L), malic acid (MA) (16.8 ± 14.7 mg/L), lactic acid (LA) (11.1 ± 0.6 mg/L), and formic acid (FA) (13.6 ± 13.1 mg/L). All the data, except the organic acids, were obtained from the Sanjuku landfill.

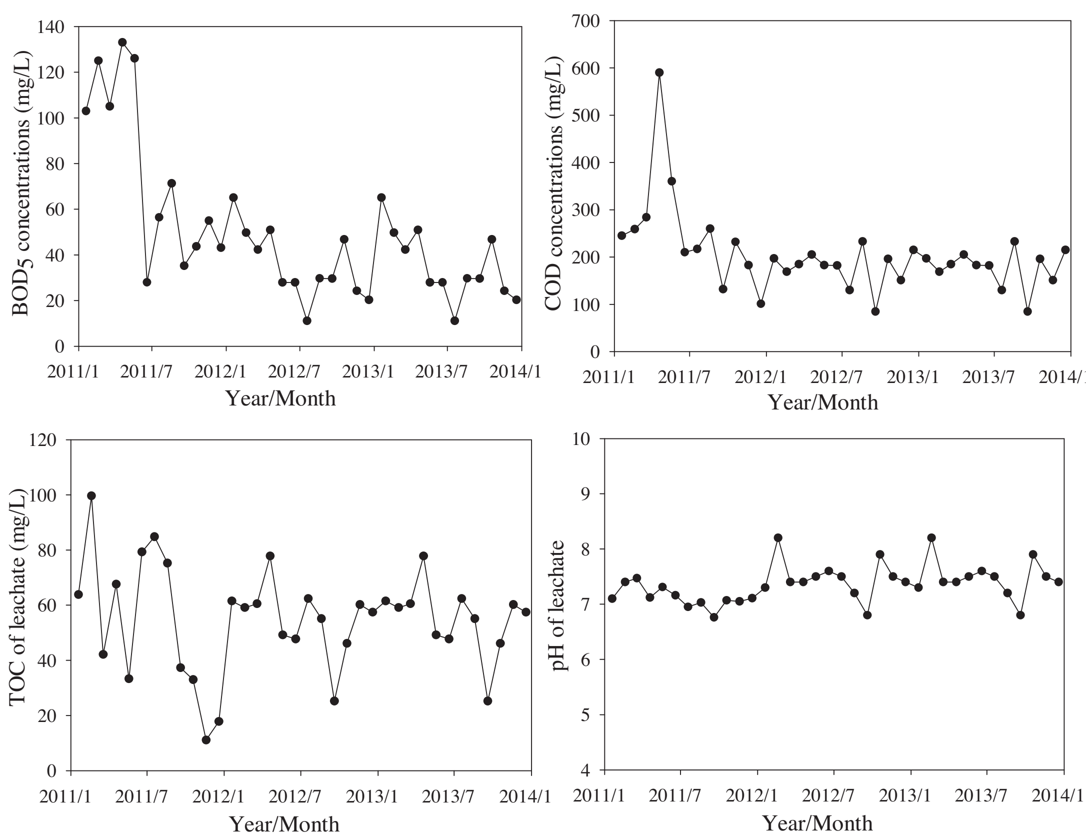

Fig. 1. Characteristics of raw leachate from 01/2011 to 01/2014 (data were obtained from the Sanjuku landfill).