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Optimization of stabilized leachate treatment using ozone/persulfate in the advanced oxidation process

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ABSTRACT

The objective of this study was to investigate the performance of employing persulfate reagent in the advanced oxidation of ozone to treat stabilized landfill leachate in an ozone reactor. A central composite design (CCD) with response surface methodology (RSM) was applied to evaluate the relationships between operating variables, such as ozone and persulfate dosages, pH, and reaction time, to identify the optimum operating conditions. Quadratic models for the following four responses proved to be significant with very low probabilities (<0.0001): COD, color, NH_3–N, and ozone consumption (OC). The obtained optimum conditions included a reaction time of 210 min, 30 g/m^3 ozone, 1 g/1 g $COD_0/S_2O_8^{2-}$ ratio, and pH 10. The experimental results were corresponded well with predicted models (COD, color, and NH_3–N removal rates of 72%, 96%, and 76%, respectively, and 0.60 (kg O_3/kg COD OC). The results obtained in the stabilized leachate treatment were compared with those from other treatment processes, such as ozone only and persulfate $S_2O_8^{2-}$ only, to evaluate its effectiveness. The combined method (i.e., $O_3/S_2O_8^{2-}$) achieved higher removal efficiencies for COD, color, and NH_3–N compared with other studied applications. Furthermore, the new method is more efficient than ozone/Fenton in advanced oxidation process in the treatment of the same studied leachate.

1. Introduction

Continuous population growth and industry development have led to an increase in waste generation. To date, landfilling is the preferred option for the disposal and management of urban solid wastes (Tengrui et al., 2007). Despite the advantages of this disposal method, the produced highly polluted leachate elicits significant concern, especially because landfilling is the most common solid waste disposal technique (Ghafari et al., 2005). Landfill leachate is defined as liquid that seeps through solid waste in a landfill, producing extracted, dissolved, or suspended materials (Christensen et al., 2001). Leachate, recognized as a potential source of groundwater and surface water contamination, contains high amounts of organic compounds, ammonia, heavy metals, a complex variety of materials, and many other hazardous chemicals (Christensen et al., 2001; Alslaibi et al., 2010; Scotish Environment Protection Agency (SEPA), 2003; Schrab et al., 1993). Regardless of changes in the concentration of landfill leachate, its complexity can be categorized based on the four major groups of pollutants, depending on a complex set of interrelated factors: dissolved organic matter, inorganic macro-components, heavy metals, and xenobiotic organic compounds (Aziz et al., 2004).

One of the main problems encountered in landfill management is the establishment of efficient treatment methods for large quantities of polluted leachate. The environmental effect of leachate is influenced by its strength, proper collection, and efficiency of treatment. Leachate requires treatment to reduce the amount of pollutants to an acceptable level prior to discharge into water sources (Aziz et al., 2007). A number of leachate treatment techniques, including biological, physical, and chemical processes, have been applied (Goi et al., 2009; Baig et al., 2001). Ozone is one of the chemical processes that have recently received considerable attention in landfill leachate treatment because of its oxidation potential and ability to reduce leachate strength and the amount of non-biodegradable organics (Bila et al., 2005; Rice et al., 1997; Huang et al., 1993). Several applications of ozone on landfill leachate treatment have been conducted. Tizaoui et al. (2007) obtained 27% and 87% removal rates for chemical oxygen demand (COD) and color, respectively, during the ozonation of leachate. Hagman et al. (2008) obtained a 22% COD reduction, whereas Rivas et al. (2003) achieved a 30% reduction in COD. Accordingly, the performance of ozone alone in stabilized leachate treatment is low; its effectiveness can be improved using advanced oxidant materials and techniques. Using hydrogen peroxide (H_2O_2) in advanced oxidation process (AOP) during the ozonation process, Tizaoui et al. (2007) reported 50% COD removal, whereas Hagman et al. (2008) achieved a COD removal rate ranging from 22% (ozone alone) to 50%. Goi

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et al. (2009) achieved a COD removal rate ranging from 24% to 41% at varying pH of 4.5–11. Using ozone/Fenton in AOPs, Abu Amr and Aziz (2012) improved the COD and color removal from 15% and 27% to 65% and 98%, respectively. However, the use of ozone and ozone/persulfate in AOPs still has low ammonia removal efficiency, which exists in high level in stabilized leachate and is extremely toxic to the environment and aquatic organisms (Bashir et al., 2011). Persulfate ($S_2O_8^{2-}$) is the newest oxidant used in chemical oxidation of groundwater and soil cleanup (Huling and Pivetz, 2006) and recently received attention in landfill leachate treatment because of its effectiveness in removing organics and ammonia (Deng and Ezyske 2011), which has standard oxidation potential (E^0 = 2.01 V) compared with ozone (E^0 = 2.07 V) (Kolthoff et al., 1947). Furthermore, $S_2O_8^{2-}$ has an ability to initiate sulfate radical based-AOPs that are strong oxidants (E^0 = 2.7 V) (House, 1962). Consequently, the current study investigates the effectiveness of cooperatively employing $S_2O_8^{2-}$ and $O_3/S_2O_8^{2-}$ in stabilized landfill leachate treatment. The scope and benefit of this new method is the increase in the oxidation potential using $S_2O_8^{2-}$ in the advanced oxidation processes during the ozonation of stabilized leachate as one treatment reactor stage. In the present study, the interaction and statistical relationships among four independent factors (ozone dosage, $S_2O_8^{2-}$ dosage, pH variance and reaction time) for the treatment of semi-aerobic stabilized leachate were assessed through response surface methodology (RSM). The RSM is a mathematical and statistical technique that is useful for the optimization of chemical reactions and industrial processes, and is commonly used for experimental designs. The main objectives of the present study include the following:

1. To investigate the efficiency of ozone/persulfate in (AOPs) for treating semi-aerobic stabilized leachate.
2. To build up the equations of COD, ammoniacal nitrogen, and color removal efficiency from stabilized leachate and ozone consumption with respect to operational conditions (i.e., ozone dosage, $S_2O_8^{2-}$ dosage, pH variance and reaction time using RSM and CCD).
3. To determine the optimum operational condition of the studied application.

2. Materials and methods

2.1. Leachate sampling and characteristics

Leachate samples were collected from an aeration pond of a semi-aerobic stabilized landfill at the Pulau Burung Landfill Site (PBLS), byram forest reserve penang, Malaysia. The PBLS has an area of 62.4 ha, of which 33 ha are currently operational, receiving approximately 2200 t of municipal solid waste daily. The site is equipped with a natural marine clay liner and three leachate collection ponds (Bashir et al., 2011). On April 19, 2012, the leachate samples were collected manually and placed in 20 L plastic containers. The samples were immediately transported to the laboratory, characterized, and cooled at 4 °C to minimize the biological and chemical reactions. Landfill leachate used in the experiments was characterized with high organic contents (COD 2480 mg/L and Color 3450 (Pt. Co.), very low biodegradability (BOD_5 93, BOD_5/COD 0.038) and quite high NH_3–N (792 mg/L). Sample collection and preservation were performed in accordance with the standard methods for the examination of water and wastewater (APHA, 2005).

2.2. Experimental procedures

For each run, persulfate reagent as sodium persulfate ($Na_2S_2O_8^{2-}$M = 238 g/mol) was employed for advanced oxidation during stabilized leachate ozonation. Persulfate dosage was determined as $COD_0/S_2O_8^{2-}$ ratio (g/g) with different ratios and gradually added to the leachate sample in the ozone reactor to determine the optimum $S_2O_8^{2-}$ dosage for the efficiencies of COD, color, and NH_3–N removal. This reagent was then added to the leachate sample in the ozone reactor. All experiments were carried out using 2 L samples in an ozone reactor with a height of 65 cm, an inner diameter of 16.5 cm, and a cross-column ozone chamber support for enhancing ozone gas diffusion (Fig. 1). Ozone was produced by a BMT 803 generator (BMT Messtechnik, Germany) fed with pure dry oxygen at the recommended gas flow rate of 200–1000 mL/min under 1 bar pressure. Input and output ozone gas concentrations ranged from 30 g/m^3 to 80 g/m^3 NTP and were measured by an ultraviolet gas ozone analyzer (BMT 964). Before each run, the gas flow meter was adjusted to obtain the desired ozone gas concentration. A water bath and cooling system maintained the internal reaction temperature in the ozone reactor at <15 °C as an optimal half-life of the dissolved ozone (30 min) in water (Lenntech, 2012). The process variables included ozone dosage, persulfate dosage, reaction time, and variation in pH. The ozone consumed (OC) during the removal of a certain amount of COD during ozonation under the experimental conditions is given in the following equation:

$$\mathrm{OC} = \frac{Q_G}{V} \times \frac{\int_0^t (1 - \frac{C_{AG}}{C_{AG0}})dt}{(\mathrm{COD}_0 - \mathrm{COD})} \quad (1)$$

where Q_G is the gas flow rate (mL/min), V is the sample volume (mL), C_{AG} is the off-gas ozone concentration (g/m^3), C_{AG0} is the input ozone concentration (g/m^3), t is the time (min), and COD_0 and COD correspond to the initial and final COD (mg/L), respectively.

2.3. Analytical methods

COD, color, NH_3–N, and pH were immediately tested before and after each run in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). The NH_3–N concentration was measured by the Nessler method using an HACH DR 2800 spectrophotometer. The pH was measured by a portable digital pH/Mv meter. The COD concentration was determined by the closed-reflux colorimetric method using a DR2800 HACH spectrophotometer. The color concentration was measured using a DR 2800 HACH spectrophotometer. Test values are presented as the average of three measurements, and the difference between measurements was less than 3%. The removal efficiency of COD, color, and ammonia were obtained using in the following equation:

$$\mathrm{Removal}(\%) = \left[C_i - \frac{C_f}{C_i}\right] \times 100 \quad (2)$$

where C_i and C_f respectively refer to the initial and final COD, color, and ammonia concentrate.

2.4. Experimental design and analysis

Design Expert software (version 6.0.7) was used for the statistical design of the experiments and data analysis. In the present study, a central composite design (CCD) and RSM were applied to optimize the experimental parameters and assess the relationships between four significant independent variables, as presented in Table 1: (1) ozone dosage, (2) persulfate dosage, (3) variation in pH, and (4) reaction time. Persulfate dosage was determined as $COD_0/S_2O_8^{2-}$ ratio (g/g). The COD, color, and NH_3–N removal and OC were the dependent variables (responses) during ozonation. Performance was evaluated by analyzing the COD, color, and NH_3–N removal efficiencies. Each independent variable was varied over three levels between −1 and +1 at the determined ranges