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Effect of persulfate and persulfate/H_2O_2 on biodegradability of an anaerobic stabilized landfill leachate

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ABSTRACT

The current study investigated the effects of $S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$ oxidation processes on the biodegradable characteristics of an anaerobic stabilized leachate. Total COD removal efficiency was found to be 46% after $S_2O_8^{2-}$ oxidation (using 4.2 g $S_2O_8^{2-}$/1 g COD_0, at pH 7, for 60 min reaction time and at 350 rpm shaking speed), and improved to 81% following $S_2O_8^{2-}/H_2O_2$ oxidation process (using 5.88 g $S_2O_8^{2-}$ dosage, 8.63 g H_2O_2 dosage, at pH 11 and for 120 min reaction time at 350 rpm). Biodegradability in terms of BOD_5/COD ratio of the leachate enhanced from 0.09 to 0.1 and to 0.17 following $S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$ oxidation processes, respectively. The fractions of COD were determined before and after each oxidation processes ($S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$). The fraction of biodegradable $COD_{(bi)}$ increased from 36% in raw leachate to 57% and 68% after applying $S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$ oxidation, respectively. As for soluble $COD_{(s)}$, its removal efficiency was 39% and 78% following $S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$ oxidation, respectively. The maximum removal for particulate COD was 94% and was obtained after 120 min of $S_2O_8^{2-}/H_2O_2$ oxidation. As a conclusion, $S_2O_8^{2-}/H_2O_2$ oxidation could be an efficient method for improving the biodegradability of anaerobic stabilized leachate.

1. Introduction

Sanitary landfill is recognized as the most common and desirable method of urban solid waste management and as the most economical and environmentally acceptable method of municipal and industrial solid waste disposal (Tengrui et al., 2007). However, the large quantity and highly polluted leachate that is produced from landfilling is recognized as a potential source of environmental contamination. Leachate contains large amount of organics, ammonia, heavy metals, and many other hazardous materials (Ghafari et al., 2005; Christensen et al., 2001). There are many important factors that affect leachate characteristics such as age and type of landfill and leachate. Stabilized leachate is generated from old landfills (>10 years) with stable characteristics. Stabilized leachate is characterized by a very strong organic content, has a high ammonia concentration and very low biodegradability (BOD_5/COD < 0.1), which is difficult to be treated biologically thus increasing the risk on the environment (Schiopu and Gavrilescu, 2010; Renou et al., 2008; Aziz et al., 2004). Leachate requires an efficient treatment to reduce the high concentration of contaminants to an acceptable level prior to ultimate discharge to the environment (Aziz et al., 2010; Goi et al., 2009). Different leachate treatment methods, including physical, chemical and biological processes have been reported (Abu Amr and Aziz, 2012; Abu Amr et al., 2013a,b; Baig and Liechti, 2001; Hagman et al., 2008).

Chemical oxygen demand (COD) is the most important factor in determining and evaluating the leachate quality. COD measures only the total amount of organic matter without differentiating between biodegradable and non-biodegradable fractions. Therefore, the total value of COD cannot reflect the real data that can be used for further research or deeper analysis (Orhon and Cokgor, 1997). Abu Amr et al. (2014) evaluated the biodegradation and characterization of different COD fractions in stabilized landfill leachate. Total COD can be divided into four main fractions, namely, biodegradable, non-biodegradable, particulate and soluble fractions, which are further subdivided into biodegradable soluble $COD_{(bsi)}$ and non-biodegradable soluble $COD_{(ubsi)}$ (Doğruel et al., 2011; Wentzel et al., 1999).

Persulfate is one of the reagents used in chemical treatment processes and can be used in leachate treatment. Recently it has received an attention in water and wastewater treatment (Huling and Pivetz, 2006; Shiying et al., 2009). Several studies have been

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reporting on persulfate applications for color and COD removal, as well as biodegradability improvement for different types of landfill leachate (Shiying et al., 2009; Yang et al., 2011). Because the effectiveness of persulfate alone in leachate treatment is relatively weak (Abu Amr et al., 2013a), persulfate requires additional advanced oxidation techniques to enhance its effectiveness for high organic content removal from old leachate. The mechanisms of persulfate activation is to initiate sulfate radical which has high oxidation potential ($E^\circ = 2.7$ V) (Renaud and Sibi, 2001). Different applications on persulfate activation have been reported. Xu et al. (2012) employed activated carbon combined with persulfate to enhance biodegradability and improve organic removal in stabilized leachate. Abu Amr et al. (2013a) used ozone gas to initiate sulfate radical from persulfate during ozonation of stabilized leachate. Ozone cannot react directly with persulfate; however, at high pH (11), significant amount of ozone applied will dissociate and produce hydroxyl radicals which will be involved in the activation of persulfate during ozonation (Abu Amr et al., 2013a,b).

The performance of employing H_2O_2 directly to activate persulfate reagent for stabilized leachate treatment is not well documented. The effect of persulfate and combined $S_2O_8^{2-}/H_2O_2$ treatment methods on the fractions of total COD in the landfill leachate is never reported in literature. In addition, the performance of activated persulfate in improving biodegradability, solubility, and biodegradable soluble COD in the leachate is still not well documented.

In this study, hydrogen peroxide is used to activate persulfate ($S_2O_8^{2-}/H_2O_2$). The objective of the study is to investigate the effects of $S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$ oxidation processes on the COD fractions of anaerobic stabilized landfill leachate. The fractions of biodegradable, non-biodegradable, soluble, and particulate COD were determined before and after both $S_2O_8^{2-}$ and $S_2O_8^{2-}/H_2O_2$ oxidation processes.

2. Materials and methods

2.1. Leachate sampling and analysis

Leachate samples were collected from a collection pond at Deir El-Balah Landfill Site (DBLS), at Deir El-Balah City, Middle Governorate in Gaza Strip, Palestine. DBLS is classified as an anaerobic stabilized landfill. The DBLS has an area of 7 ha, it receives approximately 450 tons of municipal solid waste daily (Solid Waste Management Council (SWMC), 2012). In this study, the leachate samples were collected 4 times manually from February 2014 to June 2014 and were placed in 2 L plastic containers. The samples were immediately transported to the laboratory, characterized, and cooled to 4 °C to minimize the biological and chemical reactions. General characteristics of the leachate used in this work are summarized in Table 1. Leachate contains high content of organics and ammonia and has very low biodegradability (BOD_5/COD 0.43–0.09), which classifies it as old (stabilized) leachate. Leachate samples were collected, transferred and preserved according to the Standard Methods for the Examination of Water and Wastewater (2005).

2.2. Experimental procedure

All experiments were conducted at room temperature (28 °C) with a 50 mL leachate sample volume in polyethylene bottles with a 250 mL volume capacity. Orbital Shaker (Luckham R100/TW Rotatest Shaker 340 mm X 245 mm) was used for sample shaking at 350 rpm. For persulfate oxidation alone, $S_2O_8^{2-}$ as sodium persulfate ($Na_2S_2O_8$) (molecular weight = 238.09 g/mol) was utilized and the process variables included different $S_2O_8^{2-}$ dosage, pH and reaction time. For $S_2O_8^{2-}/H_2O_2$ oxidation system; hydrogen peroxide (H_2O_2 37%) was utilized to activate persulfate oxidation. The process variables included $S_2O_8^{2-}$ dosage, H_2O_2 dosage, pH and reaction time. Persulfate and persulfate/H_2O_2 oxidation processes were carried out using optimum experimental conditions determined through a set of preliminary experiments. These were 4.2 g of persulfate per gram of COD ($COD_0/S_2O_8^{2-}$), pH 7, reaction time 1 h and shaking speed 350 rpm for persulfate oxidation alone, and 5.88 g ($S_2O_8^{2-}$), 8.63 g H_2O_2, pH 11 and 120 min reaction time at 350 rpm for combined $S_2O_8^{2-}/H_2O_2$. pH was adjusted using 5 M sulfuric acid solution and 5 M sodium hydroxide solution. Following the oxidation processes, the effect of combined $S_2O_8^{2-}/H_2O_2$ was compared with that of $S_2O_8^{2}$ alone on leachate biodegradability.

Table 1
General characteristics of landfill leachate from DBLS.

Parameter	Results
COD (mg/L)	19,180–20,448
BOD (mg/L)	830–1821
BOD/COD ratio	0.043–0.09
EC (μS)	39,200–40,800
TDS (mg/L)	22,356–25,296
Nitrate (mg/L)	2020–3602
Ammonia (mg/L)	2450–3400
Chloride (mg/L)	6150–6953
Sulfate (mg/L)	780–856
Alkalinity (mg/L)	22,500–24,000
Hardness (mg/L)	6980–7283
Calcium (mg/L)	1246–1620
Magnesium (mg/L)	715–785
Potassium (mg/L)	3980–4345.5
Sodium (mg/L)	5586–6000
pH	7.9–8.42
Turbidity NTU	476–537.5
Cupper (Cu)(mg/L)	0.36–0.44
Lead (Pb)(mg/L)	0.143
Nickel (Ni)(mg/L)	4.63
Manganese (Mn)(mg/L)	0.08
Cadmium (Cd)(mg/L)	0.259
Zinc (Zn)(mg/L)	5.84

2.3. Analytical method

COD, BOD_5, and pH, were immediately tested before and after each run of the experiments according to the Standard Methods for the Examination of Water and Wastewater (2005). Leachate was stirred well before being analyzed. COD concentration was determined by the open reflux method No. (5220). BOD concentration was examined by the 5-Day BOD Test No. (5210). pH was measured using a portable digital pH/Mv meter. The COD removal efficiencies were obtained using the following Eq. (1):

$$\text{Removal } (\%) = \left[(C_i - C_f)/C_i\right] \times 100 \quad (1)$$

where C_i and C_f refer to the initial and final COD concentrations.

Biodegradability in term of BOD_5/COD ratio, was also determined. The fractions of biodegradable and non-biodegradable COD were determined through the aeration of 1000 mL leachate sample (before and after persulfate and persulfate/H_2O_2 oxidation processes); an air pump (model – AP-3500, power: 5 W, pressure: 0.012 MPa, output: 2 × 2 L/min, voltage: AC 220 V, frequency: 50 Hz) was used. Mechanical mixer using magnetic stirrer was supplied to provide sufficient mixing. The sample size was maintained at 1000 ml during aeration, and water loss (by evaporation) in the sample was compensated by adding distilled water (Abu Amr et al., 2014). Before aeration; COD was measured as an initial (COD_i). COD value was monitored and examined after each 24 h of aeration time (for 17 days) and the lowest value was measured as a