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Aged raw landfill leachate: Membrane fractionation, O_3 only and O_3/H_2O_2 oxidation, and molecular size distribution analysis

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ABSTRACT

Large molecular refractory organic compounds (i.e., humic substances) were the major chemical oxygen demand (COD) components of aged raw landfill leachate. To investigate the behaviours of the large molecular refractory organic compounds when they were subjected to oxidation with ozone only (O_3 only) and ozone combined with hydrogen peroxide (O_3/H_2O_2), the aged raw landfill leachate first was filtered with 0.8 and 0.45 μm pore size filters in series, then was sequentially fractionated with 10,000 MWCO; 5000 MWCO; and 1000 MWCO membranes, and four samples were formed: 0.45 μm–10,000 Da; 10,000–5000 Da; 5000–1000 Da; and <1000 Da. Mass distribution profiles of COD, 5-day biochemical oxygen demand (BOD_5), colour and metals in the aged raw leachate were developed through mass balance. After membrane fractionation of the aged raw leachate, the metals were fractionated with the humic substances. Each fractionated sample as well as the aged raw leachate was oxidised with O_3 only and O_3/H_2O_2. The H_2O_2 enhanced the reduction of COD and colour; while, the BOD_5 after O_3 only was always higher than that of O_3/H_2O_2. The addition of H_2O_2 improved the peak reduction of large molecules, but the effects of H_2O_2 on the fractions of 10,000–5000 Da and 5000–1000 Da were likely insignificant, which is in accordance with the COD results. No correlation was found between the BOD_5 increase and the area of new peak formed after oxidation. However, the BOD_5 of each sample after oxidation with O_3 only was the logarithmic function of its total peak area.

1. Introduction

The major components of the aged raw landfill leachate are large molecular refractory organic molecules; i.e., humic substances. This is due to the stabilization of most of its biodegradable fraction during the aging process. Humic substances include humins, humic acids and fulvic acids. Humins are insoluble in water at all pH values; therefore, the humic substances in the aged raw landfill leachates are mainly humic acids and fulvic acids (Chian, 1977; Lecoupannec, 1999). The molecular weight of the humic substances in the aged raw landfill leachate is within the range of 1000–10,000 Da.

Membrane fractionation has been applied to characterization of raw leachate (Park et al., 2001) and the leachates after electron-beam radiation process (Bae et al., 1999) or after

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biological treatment processes (Bae et al., 1999; Gourdon et al., 1989; Park et al., 2001).

Fractionation of landfill leachate with different molecular weight cut-off (MWCO) membranes can cause organic compounds of different molecular weights to end up in different fractions. Therefore, oxidation of such fractionated samples would reveal the behaviours of the organic compounds of different molecular weights during oxidation processes. In the research by Yoon et al. (1998), the aerobic lagoon effluents were fractionated with 1000 MWCO and 500 MWCO membranes. Then, coagulation and Fenton reaction were applied to the fractionated samples, respectively. In that study, only the TOC removal efficiency was investigated. To date, very little research work has been done with regard to oxidation of fractionated landfill leachate with only ozone (O_3) and ozone combined with hydrogen peroxide (O_3/H_2O_2).

Most of molecular size distribution analysis aimed at characterizing the molecular weight of organic compounds present in landfill leachate (Chian, 1977; Lecoupannec, 1999). Imai et al. (1998) analysed the molecular size distribution change of a landfill leachate before and after ozonation with high performance liquid chromatography (HPLC) equipped with gel filtration column and UV detector, the eluant was 0.3 M NaCl in 0.1 M pH = 7 phosphate buffer, and the flow rate was 0.8 mL/min. Wang et al. (2004) investigated the molecular size distribution of an aged raw landfill leachate before and after oxidation with O_3 only and O_3/H_2O_2. There is no information available regarding molecular size distribution change of fractionated landfill leachates before and after oxidation with O_3/H_2O_2.

The complexation of cadmium (Cd) by organic components in landfill leachates has been known for more than 20 years (Knox and Jones, 1979). This complexation was attributed to the organic compounds with phenolic hydroxyl groups (Knox and Jones, 1979; Livens, 1991) having stability constant towards Cd at the order of 105. Lun and Christensen (1989) further confirmed the complexation of organic compounds in landfill leachates with Cd ions by spiking Cd solution into five Danish municipal landfill leachates, and then determined free divalent Cd and complexed Cd. Christensen et al. (1996) found the ability of dissolved organic carbon in a landfill leachate-polluted groundwater to form complexes with heavy metals Cd, nickel (Ni) and zinc (Zn) was in the order of Zn < Cd < Ni. Jensen and Christensen (1999) investigated the distributions of metals in the colloidal fractions and dissolved fractions of four Danish landfill leachates. From their research, calcium (Ca), manganese (Mn) were about equally distributed between the dissolved fractions and the colloidal fractions, whereas iron (Fe) was found mostly in the colloidal fractions; 10–60% of the total content of Ni, 0–95% of the total content of Zn, and 30–100% of the total content of copper (Cu) were associated with the colloidal fractions; Cd was found primarily in the truly dissolved fraction (26–100%); and lead (Pb) and chromium (Cr) that distributed between colloidal and dissolved species varied among the leachate samples. Jensen et al. (1999) found that dissolved Cd, Cu, and Pb were mainly associated with dissolved organic carbon, while Ni was also present as carbonate complexes, and Zn as carbonate complexes and free divalent Zn. Moreover, Jensen et al. (1999) reported that very little metal was found in colloids larger than 0.40 μm. It has been reported that fulvic acids could complex with Ca (Ephraim and Allard, 1994a), Cd (Ephraim and Xu, 1989), Cu (Ephraim and Allard, 1994b), Fe (Ephraim, 1992a), Strontium (Sr) and europium (Eu) (Norden et al., 1993) and Zn (Ephraim, 1992b).

In this research, the fractionated samples as well as the aged raw leachate were oxidised with O_3 only and O_3/H_2O_2. Chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), colour and metals of each sample were measured. The mass distribution profiles of COD, BOD_5, colour and metals were developed through mass balance analysis between the aged raw leachate and the fractionated leachate samples. The results can unfold the correlation between the organic compounds and the metals in the aged raw leachate. Meanwhile, the molecular size distribution of each sample before and after oxidation was also analyzed. These data can reveal the behaviours of the organic compounds in the aged raw leachate with molecular weight of 0.45 μm–10,000 Da; 10,000–5000 Da; 5000–1000 Da; and < 1000 Da during the oxidation processes.

2. Materials and methods

2.1. *Landfill leachate*

The aged raw landfill leachate was collected from an equalization storage tank of the Clover Bar Landfill Leachate Treatment Plant, Edmonton, Alta., Canada. This landfill leachate had been stabilized in the equalization storage tank for about one year due to the pipeline modification for the five-stage rotating biological contactors (RBCs). The volume, UV absorbance at 254 nm and UV absorbance at 280 nm, and average water quality parameters of the aged raw leachate are shown in Table 1.

The process of membrane fractionation is illustrated in Fig. 1. Five litre (5000 mL) aged raw leachate was filtered with 0.8 and 0.45 μm pore size filters, sequentially. Thirty-two (32) mL and 18 mL were lost in the 0.8 and 0.45 μm pore size filters, respectively, and 4,950 mL filtrate was obtained. This filtrate was further fractionated with 10,000 MWCO regenerated cellulose membrane (PLGC, 10k, Millipore Corporation, Bedford, MA, Catalogue #: CDUF001LG) at 124.2 kPa. After the fractionation, the pressure of membrane cell was reduced to zero, the inlet tubing and retentate tubing were taken out of the feed flask and put into a beaker containing 200 mL ultra pure water (conductivity^{-1} > 18 MΩ). This ultra pure water was run for 2 min to wash out the organic compounds retained in the membrane cell. Then, the pressure was increased to 124.2 kPa, and the filtrate was also collected into the filtrate flask during this washing period. The retentate in the beaker was poured into the retentate flask, and the volumes of retentate and filtrate were measured with graduated cylinders. Then, the retentate (330 mL) was diluted to 1000 mL with a volumetric flask and the sample of 0.45 μm–10,000 Da was formed to supply enough samples for the oxidation with O_3 only and O_3/H_2O_2.

The process of the fractionation with 5000 MWCO regenerated cellulose membrane (PLCC, 5k, Millipore Corporation, Bedford, MA, Catalogue #: CDUF001LC) and 1000 MWCO