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Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate

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Abstract

Municipal landfill leachate, especially mature leachate, may disrupt the performance of moderately-sized municipal activated sludge wastewater treatment plants, and likewise tend to be recalcitrant to biological pretreatment. Recently, Fenton methods have been investigated for chemical treatment or pre-treatment of mature leachate. In this paper, the results of laboratory tests to determine the roles of oxidation and coagulation in reducing the organic content of mature leachate during Fenton treatment are presented. The efficiencies of chemical oxygen demand (COD) oxidation and coagulation were tested, and the ratio of COD removal by oxidation to that by coagulation was assessed, under various operating conditions. Low initial pH, appropriate relative and absolute Fenton reagent dosages, aeration, and stepwise addition of reagents increased COD removal by oxidation and the importance of oxidation relative to coagulation. Simultaneous aeration and stepwise reagent addition allowed comparable treatment without initial acidification pH, due to the generation of acidic organic intermediates and the continuous input of CO_2. On the other hand, high COD oxidation efficiency and low ferrous dosage inhibited COD removal by coagulation. At significantly high oxidation efficiency, overall COD reduction decrease slightly due to low coagulation efficiency. Under the most favorable conditions (initial pH 3, molar ratio $[H_2O_2]/[Fe^{2+}] = 3$, $[H_2O_2] = 240$ mM, and six dosing steps), 61% of the initial COD was removed, and the ratio of COD removal oxidation to coagulation was 0.75. Results highlighted the synergistic roles of oxidation and coagulation in Fenton treatment of mature leachate, and the role of oxidation in controlling the efficiency of removal of COD by coagulation.

Keywords: Fenton treatment; Landfill leachate; Oxidation; Coagulation; Organic contaminants

1. Introduction

Sanitary landfills have been suggested to be the most economical and environmentally acceptable method for disposal of municipal solid wastes, in the United States and throughout the world [1]. However, leachate produced from landfills is a high strength organic wastewater which, when discharged directly to a municipal wastewater treatment plant, may cause corrosion of the pump station, difficulty in maintaining constant effluent chlorine residual, and sludge bulking and settling problems. Biological methods are typically applied for treatment of young leachates (e.g., from landfills of less than 1–2 years age), characterized by high 5-day biochemical oxygen demand (BOD_5)/chemical oxygen demand (COD) ratios (>0.6) and high concentrations of low molecular weight organics [2]. However, such methods are not effective for treatment of mature leachates (e.g., from landfills of more than 5–10 years age), due to their low BOD_5/COD ratios (<0.3) and high fraction of high molecular weight, refractory organics. Hence, several physicochemical processes have been studied or used for pretreatment or full treatment of mature leachate [3–8].

Among potential physicochemical technologies for leachate treatment, the Fenton process has been extensively studied in recent years [9–17], and analyses indicate Fenton process to be one of the most cost-effective alternatives for this application [18]. Organic removal efficiency depends upon several operating parameters, including reaction pH, dosages of Fenton reagents, aeration, coagulation pH, mode of reagent addition, temperature, UV irradiation, and subsequent pH adjustment for coagulation. A detailed discussion on the effects of these operational factors is available somewhere [19]. The typical Fenton wastewater treatment process includes four stages: oxidation,

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neutralization, coagulation/flocculation, and solid–liquid separation [20,21]. Hence, organics are removed by both oxidation and coagulation. The oxidation is generally ascribed to generation of hydroxyl radical ($^{\bullet}OH$) according to Eq. (1), a strong and indiscriminant oxidant. However, other species including ferryl moieties are also candidate oxidants [22,23].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

Some of Fe^{3+} produced can be reduced to Fe^{2+} through Eq. (2), although the rate is several orders of magnitude slower than that of Fe^{2+} to Fe^{3+} conversion through Eq. (1).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}HO_2 + H^+ \quad (2)$$

The Fe^{2+} generated in Eq. (2) may react with H_2O_2 to produce more $^{\bullet}OH$ through Eq. (1). Coagulation is then due to precipitation of ferric-oxyhydroxides after the neutralization stage. However, most previous investigations focused primarily on the effects of operating parameters on overall organics removal efficiencies; how these parameters impact oxidation and coagulation and whether oxidation or coagulation predominates in terms of treatment under various conditions are not well recognized, and such understanding as pertains to treatment of landfill leachate is still more limited. Yoon et al. [24] concluded that coagulation played a primary role in Fenton removal of organics from leachate, based only on the observation that both Fenton treatment and simple coagulation removed high molecular organics more readily and selectively. Wang et al. [25] and Lau et al. [26] reported that oxidation and coagulation were responsible for approximately 20 and 80% of overall COD removal, respectively, in Fenton treatment of a biologically stabilized leachate. Kang and Hwang [27] found that pH and absolute dosages of Fenton reagents significantly affected the removal of COD from leachate by oxidation and coagulation, and that coagulation pH influenced the efficiency of coagulation. However, more required relationships particularly between oxidation and coagulation in terms of removal efficiency have not been clear.

In this paper, overall COD removal efficiency, and COD reduction by oxidation and by coagulation under various operating conditions are reported for a mature leachate. The ratio of COD removal by oxidation to that by coagulation was used to determine whether oxidation or coagulation played a predominating role under the tested conditions. Specifically, the effects of initial pH, molar ratio and absolute dosages of Fenton reagents, aeration, and mode of stepwise reagent addition on oxidation and coagulation are described. In addition, the interaction between oxidation and coagulation in terms of treatment efficiency is characterized. Finally, the interactive effects of aeration and stepwise addition of reagents on both oxidation and coagulation are described.

2. Experimental

Landfill leachate was collected from the Polk County North Central Landfill collection tank (Winter Haven, FL, USA). The mean BOD_5/COD was less than 0.05, typical for mature leachate. The collected leachate was stored in a zero headspace plastic bottle in refrigerator at 4 °C until use. The average composition of the tested landfill leachate is listed in Table 1. All chemicals were at least analytical grade and were used as received, except as noted. The raw landfill leachate was prefiltered through a glass filter paper (934-AH, Whatman, Cifton, VA, USA) to remove large particles and debris, and maintain uniformity of tested samples. All runs were conducted at room temperature and atmospheric pressure. Initial leachate pH was adjusted to the desired value with concentrated sulfuric acid (H_2SO_4, 96%, FishChemical, Fair Lawn, NJ, USA). Subsequently, 200 mL of prefiltered leachate was dispensed to a 1-L beaker. The leachate was stirred thoroughly with a magnetic stirrer. In the aerated Fenton tests, injected air was supplied by a small air pump (20 L/h, Tetratec, China). The height from the leachate table to the beaker brim adequately avoided the overflow due to foaming occurring at initial stage of reaction under aeration. In the experiments to investigate effects of aeration and stepwise feeding of Fenton reagents, Fenton oxidation proceeded for 9 h, and the total reagent dose was added incrementally at each designated addition time. In other experiments, Fenton oxidation proceeded for 2 h. Reagents addition was as follows. First, granular ferrous sulfate ($FeSO_4{\cdot}7H_2O$, heptahydrate, FishChemical, Fair Lawn, NJ, USA) was added. Subsequently hydrogen peroxide solution (H_2O_2, 30% w/w, VWR, West Chester, PA, USA) was added. After the designated oxidation time, NaOH pellets were added to the rapidly stirred solution, to increase the pH to approximately 6.5. A solution of 10 M NaOH solution was then added dropwise, to a pH of 8.0. The beaker with leachate was transferred to a Phipps & Bird Stirrer (Model 7790, Richmond, VA, USA) for a period of 20 min flocculation at 20 rpm. Overall COD removal, and COD removal by oxidation and by coagulation were measured by a slight modification of the method of Kang and Hwang [27]. Accordingly, 100 mL aliquot of uniformly mixed solution was immediately dispensed to a glass cylinder and heated in a 50 °C water bath (8851, Cole Parmer, Chicago, IL, USA) for 30 min to remove any residual H_2O_2 in solution, and the sample was brought to the room temperature for a 90 min sedimentation period. Then, the volume of the settled iron sludge was recorded. After that, the COD values of the supernatant and the settled sludge samples were measured separately. The former indicated COD in the effluent after the overall process, and the latter indicated the COD of the solid phase that was contributed from these organics coagulated. COD removal by oxidation was the difference between COD reduction by the overall process and the COD

Table 1
Average composition of the tested landfill leachate

Parameters	COD (mg/L)	BOD_5/COD	Electrical conductivity (ms/cm)	pH	NH_3-N (mg/L)	Alkalinity ($CaCO_3$ mg/L)
	1100–1300	<0.05	8.30	8.18	300	3050