Journal of Hazardous Materials B95 (2002) 153–159

Journal of Hazardous Materials

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Landfill leachate treatment by a coagulation–photooxidation process

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Received 21 November 2001; received in revised form 18 April 2002; accepted 19 April 2002

Abstract

This experimental study was conducted to investigate the effect of treatment of landfill leachate by a coagulation–photooxidation process. The effects of different dosages of coagulant and different pH values on the coagulation processes were compared. The effect of different concentrations of sodium oxalate ($Na_2C_2O_4$) on the treatment process was also studied after the coagulation was performed using $FeCl_3{\cdot}6H_2O$. The experimental results show that in the pH range of 3–8, the lower the pH value, the higher the efficiency of the treatment. A 24% removal of COD (chemical oxygen demand, mg(O_2) l^{-1}) can be attained by the addition of 1000 mg l^{-1} $FeCl_3$. A 31% removal of COD can be attained after 4 h of irradiation alone, and a 64% removal of COD can be attained after 4 h irradiation at pH 3 with the addition of 500 mg l^{-1} $FeCl_3{\cdot}6H_2O$.

Keywords: Coagulation; Photooxidation; Landfill leachate; Treatment

1. Introduction

Landfill leachate is generated as a result of precipitation, surface run-off, and infiltration or intrusion of groundwater percolating through a landfill. The discharge of landfill leachate can lead to serious environmental problems, since the leachate contains a large amount of organic matter (both biodegradable and non-biodegradable carbon), ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts. Although some of these pollutants can be degraded by microorganisms, the limitation of common biological processes

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PII: S0304-3894(02)00116-4

(degradation is only a part of COD and limited removal of bio-refractory organic pollutants) has made it difficult to meet the correlative discharge standard (GB8978 (1996), China, COD $<100\,mg\,l^{-1}$). The treatment of landfill leachate by a photooxidation processes has become popular during the last 5 year, owing to the short reaction time and acceptable costs [1–3]. The mechanism of photooxidation is based on the production of powerful free radicals ($^{\bullet}OH$) that oxidize, degrade, and even mineralize organic pollutants [1].

Landfill leachate treatment by a photochemical process has been studied widely during the past 20 year. A γ-ray irradiation system can lead to increases in BOD_5 (bio-chemical oxygen demand in 5 days) and degradation of some COD [4]. A 90% cyanide removal can be attained by an UV irradiation system [5]. The landfill leachate treatment by UV/oxidation process had been reported [6–8]. The $UV/H_2O_2 + O_3$ process was the most effective for TOC (total organic carbon) removal and a UV/H_2O_2 process had been utilized in Germany in a full-scale plant [3]. For toxic compounds the UV/O_3 process can also be regarded as an effective method of treatment. The photo-Fenton process ($Fe(II) + H_2O_2$ with UV-light) can obtain a 70% COD and 83% TOC removals in the treatment of landfill leachate [1,5,9]. The COD removal rate is related to irradiation intensity, the amount of H_2O_2 and Fe(II) added, pH value and COD loading. A 70% TOC removal can be obtained in treatment of landfill leachate by UV/TiO_2 process [10].

$FeCl_3{\cdot}6H_2O$ is a widely used coagulant. Hydrolytic iron species are good photocatalysts. For example, ferric chloride has been used to degrade azo dye [11,12]. The coagulation process is effective for removing high concentration organic pollutants, whereas, the photooxidation process is suitable for low concentration organic pollutants. Iron species used as coagulants in the treatment of landfill leachate have been reported [13,14]. There is a large quantity of hydrolytic iron(III) in the effluent of coagulation treatment process under conditions of low pH, which is an abundant source of active radicals for advanced photooxidation treatments. Using the same coagulant with a photocatalytic process has advantages such as easier operation and lower costs. Therefore, we utilized simultaneous coagulation and photooxidation to design a coagulation–photooxidation process for leachate treatment.

In the experiments reported here on the treatment of landfill leachate, a coagulation–photooxidation process was investigated. The relative effects of different operational schemes such as different coagulant dosages, pH values, and irradiation times were studied.

2. Materials and methods

2.1. Leachate

The leachate was collected from Wuhan Qingshan landfill (China). Characteristics of the leachate sample were $COD = 5800\,mg\,l^{-1}$; $BOD_5 = 430\,mg\,l^{-1}$; pH = 7.6. The leachate was stirred 7 min after the addition of $FeCl_3{\cdot}6H_2O$. HCl and NaOH were used to adjust the pH value to the desired value. The source of light (UV–VIS) was a 250 W high-pressure mercury lamp ($\lambda > 313\,nm$).

2.2. Analyses

The sample was transported to the laboratory in sealed plastic barrels, then stored at 4 °C before being used and analyzed. The pH was determined by a pH meter. The COD was determined by titration (ASTM-D1252-67, 1974). The color was determined by a dilution method (the sample was diluted by distilled water until the sample had the same color as distilled water).

3. Experimental procedure

1. Add 100, 250, 500, 750 or 1000 mg $FeCl_3{\cdot}6H_2O$ to a 1000 ml leachate sample. After stirring and clarifying, the supernatant is sampled to determine the COD and color, so that one can study the effect of coagulant dose on coagulation.
2. Adjust the pH value of 1000 ml leachate sample to a pH of 3–8, respectively, before adding 500 mg $FeCl_3{\cdot}6H_2O$ to the sample. After stirring and clarifying, the supernatant is sampled to determine the COD and color, so that one can study the effect of pH on coagulation.
3. Place a 500 ml sample filtrated from 1000 ml raw leachate under irradiation using a 250 W high-pressure mercury lamp. After 0.5, 1–4 h irradiation, take a sample to determine the COD and color, so that one can study the effect of irradiation on treatment leachate.
4. Adjust the pH value of 1000 ml raw leachate to 3, 5 or 8, respectively, and add 500 mg $FeCl_3{\cdot}6H_2O$. After stirring and clarifying, the 500 ml supernatant are irradiated using a mercury lamp. After 0.5, 1–4 h, the supernatant is sampled to determine the COD and color, so that one can study the effect of the combination coagulation–photooxidation process.
5. Add 500 mg $FeCl_3{\cdot}6H_2O$ to the 1000 ml raw leachate. After stirring and clarifying, 500 ml supernatant is combined with 0, 5 or 20 ml 10^{-3} mol l^{-1} sodium oxalate ($Na_2C_2O_4$) solution, the resulting solutions contained 0, 10^{-5}, 4×10^{-5} mol l^{-1} $Na_2C_2O_4$, respectively, and are irradiated using a mercury lamp. After 0, 0.5, 1–4 h irradiation the supernatant is sampled to determine the COD and color, so that one can study the effect of addition of $Na_2C_2O_4$ on the coagulation–photooxidation process.

4. Results and discussions

4.1. Effect of coagulant dose on coagulation

The effect of different doses of $FeCl_3{\cdot}6H_2O$ is as shown in Fig. 1. The removal of COD and color increased with increasing concentration of $FeCl_3{\cdot}6H_2O$. We observed that when the dose of $FeCl_3{\cdot}6H_2O$ was greater than 500 mg l^{-1}, the removal of COD increased slowly. The removal of color increased with the addition of coagulant as a line.

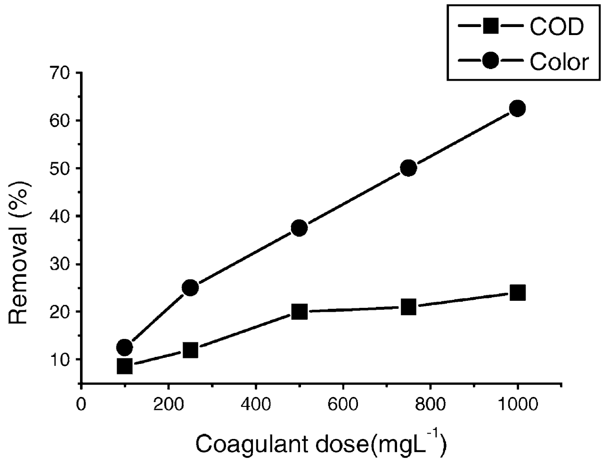

Fig. 1. The effect of coagulation dose on the removal of COD and color from landfill leachate.

4.2. *Effect of pH on coagulation*

Fig. 2 presents the effect of pH values on the coagulation. The lower the pH, the higher removal of COD and color in the pH range of 3–8. The removal of COD and color decreased with the pH value increasing in the pH range of 3–8, but the percentage removal of color was obviously higher than that of COD. We conclude that the complex leachate contains some conjugated acidic or alkali matter, which turned into colorless conjugated structure and did not precipitate under acidic condition.

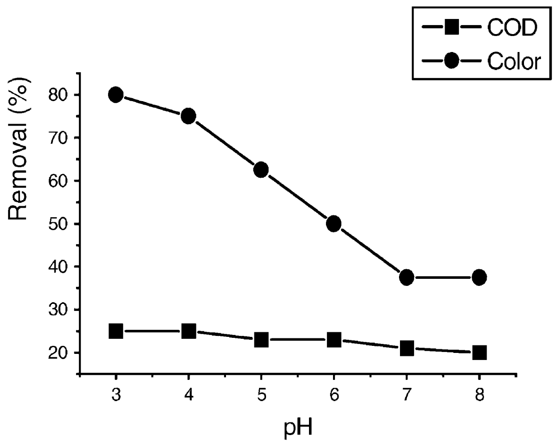

Fig. 2. The effect of pH values on the removal of COD and color from landfill leachate.

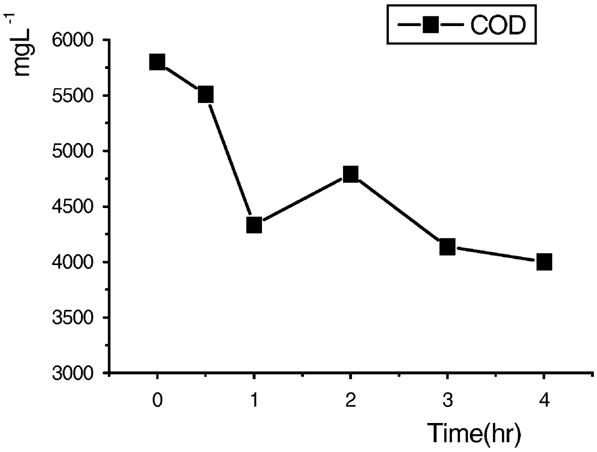

Fig. 3. The effect of direct irradiation on the removal of COD from landfill leachate.

4.3. Effect of irradiation

The effect of irradiation is as shown in Fig. 3. After 4 h irradiation, a 31% removal of COD and 70% removal of color were attained. Kim et al. [5] reported that irradiation process alone was ineffective for the removal of COD (the COD removal was only 10–20%), possibly because of the existence of iron(III) or some other photocatalytic matter in the leachate of this study.

4.4. Effect of pH on irradiation

The effect of irradiation at pH 3, 5 and 8 is as shown in Fig. 4. The irradiated sample volume was 500 ml after coagulation using 500 mg l^{-1} $FeCl_3{\cdot}6H_2O$. The trend of COD concentration at different pH values is similar. The COD concentration slightly decreased during the first hour of irradiation, but increased during the next hour of irradiation. After 2 h irradiation, the COD concentration decreased again but did not change after 4 h period of irradiation. This result is mainly due to the fact that the easiest-degraded material was degraded during the first hour of irradiation. The COD concentration increased after the first hour of irradiation because the photochemical reaction oxidized some organic matter which could not be oxidized by $K_2Cr_2O_7$ and induced the formation of short-lived intermediates [6]. The percentage removal of COD was different at different pH values after 4 h irradiation, and the removal is highest at pH 3 and lowest at pH 8. This result is attributed to the fact that the concentration of iron(III) is lowest at pH 8.

The color varied at different pH values after coagulation and irradiation. The color was totally reduced after 4 h irradiation, but the higher the color before irradiation, the better the percentage removal of the color. The color removal after 4 h irradiation at pH 3, 5 or 8 is 37.5, 50 or 75%, respectively.

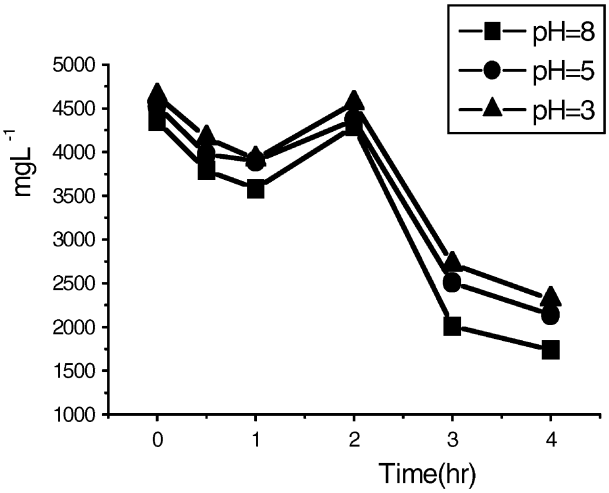

Fig. 4. The effect of irradiation on the removal of COD from landfill leachate at different pH values after coagulation.

4.5. *Effect of addition $Na_2C_2O_4$*

Deng et al. [11,12] reported that Fe(III) oxalate complexes were photoreactive, and used them to study on the discoloration, the optimal molar ratio of $C_2O_4^{2-}$:Fe(III) = 10–20:1. We added $Na_2C_2O_4$ solution in the effluent of landfill leachate treated by 500 mg l^{-1} $FeCl_3{\cdot}6H_2O$ coagulation, the molar ratio of $C_2O_4^{2-}$:Fe(III) is about 10:1. The result indicated no remarkable effect was attended by the addition of $Na_2C_2O_4$.

5. Conclusions

Experiments to treat landfill leachate collected from Wuhan Qingshan Landfill (China) by coagulation–photooxidation process were carried out. The following are the major findings:

1. treatment of landfill leachate from Wuhan Qingshan Landfill (China) by coagulation–photooxidation process was effective. A 64% removal of COD and 90% removal of color were obtained;
2. treatment using a coagulation–photooxidation process was affected by pH. In the pH range of 3–8, the lower pH value was the most effective;
3. no marked effect was attained by the addition of $Na_2C_2O_4$;
4. a 31% removal of COD and 70% removal of color could be obtained by UV–VIS ($\lambda >$ 313 nm) irradiation process alone.

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