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Removal of COD from landfill leachate by an electro/Fe^{2+}/peroxydisulfate process

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HIGHLIGHTS

- An electro/Fe^{2+}/peroxydisulfate process was used to remove COD from landfill leachate.
- An empirical correlation between persulfate concentration and COD value was obtained.
- COD removal by oxidation and coagulation was quantitatively determined.
- Effects of pH_0, current density, Fe^{2+} and PDS dosage on COD removal were investigated.
- 62.2% COD was removed at 60 min, $[PDS]:[Fe^{2+}] = 62.5$ mM:15.6 mM, pH 3 and $j = 13.89$ mA/cm^2.

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ABSTRACT

Electrochemical method was used to enhance COD removal during treatment of landfill leachate by ferrous ion activated peroxydisulfate (PDS) process. The contribution of oxidation and coagulation to COD removal was quantitatively determined. The effects of initial pH, current density, PDS and ferrous ion dosage on COD removal were investigated. The COD removal by oxidation increased with PDS concentration and current density, but decreased with initial pH. There existed an optimal Fe^{2+} dosage for the oxidative degradation of leachate. The COD removal by coagulation increased with Fe^{2+} dosage, but decreased with current density. The overall COD removal efficiency was significantly improved with respect to ferrous ion activated PDS process.

1. Introduction

An increasing amount of solid waste is generated on account of the growing population, industrialization, living standards, which has resulted in the deterioration of environment. Sanitary landfilling is now the most common way to dispose solid waste. The decomposition of waste and percolation of rainfall in the landfill will produce landfill leachate, which is a highly polluted wastewater containing large amounts of organic pollutants and other contaminants. The removal of organic matter based on chemical oxygen demand (COD) and so on is the usual prerequisite before discharging the leachates into natural water bodies [1,2]. Therefore, various technologies have been proposed for the treatment of landfill leachate, among which advanced oxidation processes (AOPs) are regarded as one of the most effective techniques to remove recalcitrant organic pollutants from landfill leachate [1,3–5]. Generally, AOPs are defined as the oxidation processes that generate hydroxyl radicals in sufficient quantity to affect leachate treatment [3,6]. Similar to hydroxyl radicals, sulfate radicals have a high redox potential ($E^0 = 2.6$ V), and sulfate radical-based AOPs have been applied to the treatment of landfill leachate [7–10]. Basically, sulfate radicals can be generated by the activation of peroxymonosulfate (PMS) or peroxydisulfate (PDS) with transition metal, heat, UV or ultrasound (US) [11–16]:

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + M^{(n+1)+} \quad (1)$$

$$HSO_5^{-} + M^{n+} \rightarrow SO_4^{\cdot -} + OH^{-} + M^{(n+1)+} \quad (2)$$

$$S_2O_8^{2-} + \text{heat/UV/US} \rightarrow 2SO_4^{\cdot -} \quad (3)$$

$$HSO_5^{-} + \text{heat/UV/US} \rightarrow SO_4^{\cdot -} + {}^{\cdot}OH \quad (4)$$

Sun et al. [7] reported that a 56.9% of COD removal efficiency was achieved by Co^{2+} activated PMS process. Over 90% COD was removed from the leachate when thermal persulfate oxidation

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was employed [8]. Recently, persulfate was combined with other oxidants such as ozone for the treatment of stabilized leachate and 72% of COD removal efficiency was obtained [9,10].

Because of its being inexpensive and nontoxic, ferrous iron has been widely used to mediate the activation of PMS or PDS [13,17,18]:

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot -} \tag{5}$$

$$HSO_5^- + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\cdot -} + OH^- \tag{6}$$

However, the slow regeneration of Fe^{2+} after conversion to ferric ion is usually considered as one of the drawbacks of iron-mediated advanced oxidation processes [19]. This problem can be solved by coupling electrochemical process and iron activated PMS/PDS process, and ferrous ions are electro-regenerated via cathodic reduction of ferric ions [20]:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{7}$$

As an analogue to electro-Fenton process with a sacrificial iron anode, a novel "Electro–Fe(II)/Oxone" process was put forward and applied to the degradation of 2,4,5-trichlorophenoxyacetic acid in aqueous solution [19]. This process was further enhance by introducing the UV light [21,22]. Based on Fered-Fenton process, another novel "electro/iron (Fe^{2+}, Fe^{3+})/PDS (PMS)" process was proposed and evaluated in our previous studies. It exhibited better performance than iron (Fe^{2+}, Fe^{3+})-catalyzed activation of PDS (PMS) process in the removal of Acid Orange 7 [20], bisphenol A [23] and clofibric acid [24]. Unfortunately, this process has not been applied to the real wastewater treatment. In the iron activated persulfate process, the organics could be removed by the oxidation with reactive radicals generated from the activation of persulfate and by the coagulation with iron salts. Nevertheless, only the overall COD removal was concerned in the transition metal activated persulfate process and the contribution of oxidation and coagulation to COD removal has not been investigated. COD is one of the most important wastewater characteristics and the dichromate reflux method of COD determination is widely used [25]. Like H_2O_2 in Fenton process, the residual persulfate would interfere with COD measurement. Therefore, an empirical correlation between persulfate concentration and COD value was determined first in this study. Then the electro/Fe^{2+}/peroxydisulfate method was applied to the leachate treatment. The overall COD removal efficiencies as well as COD removal by oxidation and by coagulation under various operating conditions such as initial pH, peroxydisulfate concentration, Fe^{2+} concentration and current density were investigated.

2. Materials and methods

2.1. Leachate collection and characterization

Landfill leachate samples were collected with polyethylene bottles from a municipal sanitary landfill located in Wuhan, China. Samples were stored in a refrigerator at 4 °C in accordance with the Standard Methods [25]. Its characteristics were pH 9.5, COD 1900 mg/L, NH_4^+–N 2150 mg/L, Cl^- 3822 mg/L and total Fe 78.9 mg/L.

2.2. Chemical reagents

Sodium peroxydisulfate ($Na_2S_2O_8$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), potassium dichromat ($K_2Cr_2O_7$), silver sulfate (Ag_2SO_4), and mercury sulfate ($HgSO_4$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with deionized water.

2.3. Experimental procedures

The experiments were carried out in a rectangular electrolytic reactor (plexy glass) of 12 cm × 10 cm × 20 cm with 1000 mL of working volume. A 10 cm × 15 cm plate anode (Ti/IrO_2–RuO_2–TiO_2) and a plate cathode (titanium) of the same dimensions were arranged parallel to each other at a distance of 2.0 cm. The reactor was immersed in an ice-water bath to keep the temperature constant at 20 °C. Electrolysis was conducted under constant current conditions using a direct current (DC) power supply (LW-3030KD) from Shanghai Wenkai power equipment Co. Ltd. (China). A magnetic stirrer (Model DW-3, Yingyu Yuhua Instrument Plant, China) provided mixing of the solution in the reactor. The initial pH value of the leachate was adjusted using concentrated sulfuric acid and sodium hydroxide before the leachate was transferred to the electrolytic reactor. The DC power supply was turned on when PDS and Fe^{2+} solutions were applied to the electrolytic cell. At the pre-selected time interval, 10 mL of samples were withdrawn from the reactor and neutralized by sodium hydroxide to precipitate iron ions. The neutralized samples were centrifuged for 10 min at 2000 rpm using a centrifuge (TDL-5Z, Hunan Xingke, China). The COD value of the supernatant indicated the residual COD in the effluent after the overall process [20]. At the end of the each run, another sample of 10 mL aliquot solution was taken, neutralized by sodium hydroxide and mixed uniformly prior to COD analysis. It indicated the residual COD in the effluent after oxidation process. COD removal by coagulation was the difference between the overall COD removal and COD removal by oxidation [26]. Since PDS would interfere with COD measurements, the COD values of PDS solutions at different concentrations were measured. A linear relationship between COD value and PDS concentration was observed with a determination coefficient R^2 of 0.998. Then the ratio of COD to PDS concentration (f) was determined and COD values of all the samples could be corrected for the residual PDS concentrations according to the following correlation equation:

$$COD = COD_m - f[PDS] \tag{8}$$

with

$$f = 30.52[PDS] + 22.21 \tag{9}$$

where f is the correction factor which means the ratio of the COD value to the PDS concentration in g/L and COD_m is the measured COD value in mg/L.

The COD removal was calculated according to the following equation:

$$\text{COD removal } (\%) = \frac{COD_0 - COD_t}{COD_0} \times 100 \tag{10}$$

where COD_0 and COD_t are the COD values of the sample at time 0 and t min, respectively.

2.4. Analytical methods

The pH value of solutions was measured by a Mettler-Toledo FE20 pH meter (Mettler-Toledo Instruments Co., Ltd. Shanghai). The PDS concentration was analyzed using an iodometric titration method [27]. COD was determined using a fast digestion-spectrophotometric method based on the Standard of the People's Republic of China for Environmental Protection [28]. Chloride was measured using silver nitrate titration method [29]. Total iron was determined using phenanthroline method [30]. Ammonium nitrogen was analyzed using Nessler's reagent colorimetric method [31].