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Evaluation of electro-oxidation of biologically treated landfill leachate using response surface methodology

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ABSTRACT

Box–Behnken statistical experiment design and response surface methodology were used to investigate electrochemical oxidation of mature landfill leachate pretreated by sequencing batch reactor (SBR). Titanium coated with ruthenium dioxide (RuO_2) and iridium dioxide (IrO_2) was used as the anode in this study. The variables included current density, inter-electrode gap and reaction time. Response factors were ammonia nitrogen removal efficiency and COD removal efficiency. The response surface methodology models were derived based on the results. The predicted values calculated with the model equations were very close to the experimental values and the models were highly significant. The organic components before and after electrochemical oxidation were determined by GC–MS.

1. Introduction

In the past decades, there has been increased interest in the use of electrochemical oxidation for the treatment of landfill leachate [1–13]. During the electrolysis, the destruction of pollutants can be achieved via two different oxidation mechanisms: direct anodic oxidation, where the pollutants are destroyed at the anode surface, and indirect oxidation, where a mediator is electrochemically generated to carry out the oxidation [1,14]. It is believed that contaminants in the leachate are primarily destroyed via indirect oxidation by strong oxidants such as hypochlorite generated from anodic oxidation of chloride, which originally exists or is applied in the leachate [15]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (3)$$

In this case, ammonia nitrogen in the leachate could be removed through the mechanism similar to "breakpoint reactions" [15]:

$$HOCl + NH_4^+ \rightarrow NH_2Cl + H_2O + H^+ \quad (4)$$

$$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O \quad (5)$$

$$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^- \quad (6)$$

$$NHCl_2 + NOH \rightarrow N_2 + HOCl + H^+ + Cl^- \quad (7)$$

Hydroxyl radicals or other reactive species may also be generated and participate in the electrochemical oxidation of organics [8].

Although electrochemical methods have been successfully applied to the treatment of landfill leachate, it is fairly expensive compared with biological treatment. Therefore, electrochemical oxidation is not considered as a full treatment for landfill leachate but as a finishing stage in a combined process or as an auxiliary unit in emergency situations [16]. Cossu et al. used Ti/PbO_2 and Ti/SnO_2 anodes to remove chemical oxygen demand (COD) and ammonia nitrogen from landfill leachate after pretreated by aerobic lagooning, denitrification, and activated sludge processes [16]. Sayadi and co-authors employed integrated membrane bioreactor (MBR)-electrochemical process to remove COD, ammonia nitrogen and color from the stabilized landfill leachate [8,9]. Ortiz and co-authors used boron-doped diamond (BDD) electrodes to remove COD and ammonia nitrogen from biologically/physicochemically pretreated leachates in both laboratory scale and pilot plant scale [3–6,11,12]. In these investigations, the traditional one-factor-at-a-time approach was used to study the effects of various factors on COD, ammonia nitrogen or color removal. This method estimates the effect of a single variable on electrochemical process while keeping all other variables at a fixed condition. But this classical approach is a time consuming method for multivariable systems and it cannot estimate the interactions among the

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Table 1
Average characterization of raw, biological pre-treated leachate.

Parameter	Raw leachate	Biological effluent
pH	8.10	8.85
NH_4^+-N (mg/L)	2470	520
COD (mg/L)	2400	560
BOD_5 (mg/L)	370	50
BOD_5/COD	0.154	0.089
Cl^- (mg/L)	2900	831
Alkalinity ($CaCO_3$ mg/L)	10,500	1500

variables [17–21]. Response surface methodology (RSM), a multivariate technique which mathematically fits the experimental domain studied in the theoretical design through a response function [22], is then proposed to solve these problems [17–21]. The main types of RSM designs include three-level factorial design, central composite design (CCD), Box–Behnken design and D-optimal design [17–19,23]. As one of the RSM designs, Box–Behnken design is known as a modified central composite experimental design [17–19,23]. It is an independent, rotatable quadratic design with no embedded factorial or fractional factorial points in which the variable combinations are at the midpoints of the edges of the variable space and at the center [17–19,23]. A comparison between Box–Behnken design and other RSM designs has demonstrated that Box–Behnken design is slightly more efficient than CCD, but much more efficient than the three-level full factorial designs [19]. Moreover, it requires fewer experiments than other RSM designs with the same number of factors [17–19,23]. For example, only 15 runs are needed for a three-factor experimental design. However, there was little report on the electrochemical oxidation of raw leachate or biologically/physicochemically pretreated leachate using RSM or other statistical experiment design approach [10,13,24–26]. As a result, RSM with Box–Behnken design was used in this study to verify the various interactions of responsible factors for the objectives such as ammonia nitrogen removal and COD removal, as well as to investigate the effects of three variables on the objectives during the electrochemical oxidation of biologically treated leachate. The three variables investigated include current density, inter-electrode gap and reaction time. The organic components before and after electro-oxidation were also investigated by GC–MS.

2. Materials and methods

2.1. Landfill leachates sampling

Leachate samples were taken with polyethylene bottles from April 2009 to May 2009 from a landfill at Wuhan (China), which has been in operation since 2003. Samples taken were preserved in refrigerator at 4 °C in accordance with the Standard Methods [27]. The physicochemical characteristics of the raw leachate are shown in Table 1.

2.2. Sequencing batch reactor (SBR)

Biological pretreatment of raw leachate was carried out in a SBR with a working volume of 10 L. An air-compressor was used for aeration, and a mechanical stirrer with 150 rpm was used to provide the mixing of substrate and biomass in the reactor. Effluent and sludge were drawn by siphon, and the solid residence time was controlled at about 20 days. The SBR system was operated in the following sequential phases: 0-h feeding (3.5 L leachate was fed instantaneously), 8-h aeration, 3-h mechanical agitation, 6-h aeration, 5-h mechanical agitation, 1-h settling, and 0.25-h decant. Initially, the seeding sludge from a landfill leachate treatment plant was acclimatized to the landfill leachates. Organic loading was increased progressively till the influent COD reached 1720–1727 mg/L. Then the SBR system was operated for six cycles and the results are presented in Fig. 1. The mixed liquor suspended solids (MLSS) concentration was within the range of 3500–4000 mg/L during the experiments. The effluent from the SBR system was stored in a reservoir and its characteristics were analyzed (Table 1) before used in the electro-oxidation experiments.

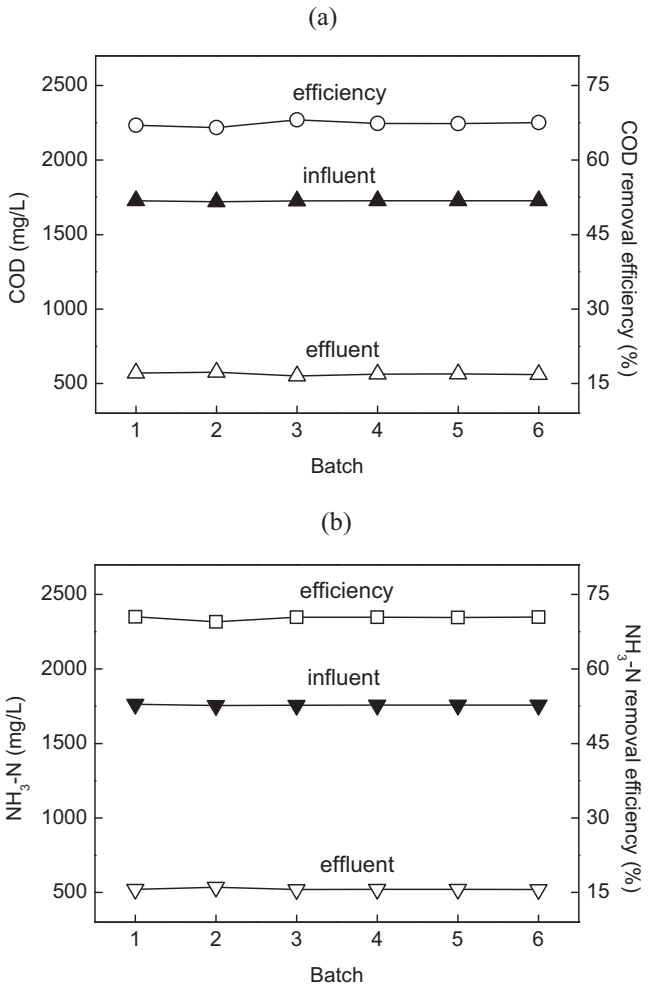

Fig. 1. The ammonia nitrogen (a) and COD (b) removal for various SBR treatment cycles.

2.3. Electrochemical reactor

The electrochemical oxidation experiments were conducted in a rectangular electrolytic cell which has been used in our previous studies [28–30]. The reactor containing 200 mL leachate was immersed in a water bath to maintain the temperature at 35 ± 2 °C. Electrolyses were operated under constant current conditions using a direct current (DC) power supply (Model WYK-305, Yangzhou Jintong Source Co., Ltd., China). A 5 cm × 11.9 cm plate anode (Ti/RuO_2–IrO_2) and a plate cathode (stainless steel) of the same dimensions were arranged parallel to each other and were dipped in the leachate. The working surface area of the electrode was 31.5 cm^2. A magnetic stirrer (Model 78-1, Hangzhou Instrument Motors Factory, China) provided mixing of the solution in the reactor.