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Application of response surface methodology to the advanced treatment of biologically stabilized landfill leachate using Fenton's reagent

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ABSTRACT

A Fenton process that uses $FeCl_2$ as the alternative catalyst was employed to deal with the biologically treated landfill leachate. Data obtained revealed that this Fenton process can provide an equivalent pollutant removal as the Fenton process that uses $FeSO_4$ as catalyst. Central composite design (CCD) and response surface methodology (RSM) were applied to evaluate and optimize the four key factors, namely initial pH, Fe(II) dosage ($[Fe^{2+}]$), H_2O_2/Fe(II) mole ratio ($[H_2O_2]/[Fe^{2+}]$ ratio) and reaction time, which affect the performance of the Fenton treatment. Chemical oxygen demand (COD) and color were selected as response variables. This approach provided statistically significant quadratic models, which were adequate to predict responses and to carry out optimization under the conditions studied. It was demonstrated that the interaction between initial pH and $[H_2O_2]/[Fe^{2+}]$ ratio has a significant effect on the COD removal, while the interaction between $[H_2O_2]/[Fe^{2+}]$ ratio and reaction time shows a large impact on color removal. The optimal conditions were found to be initial pH 5.9, $[Fe^{2+}]$ = 9.60 mmol/L, $[H_2O_2]/[Fe^{2+}]$ ratio = 2.38, reaction time = 5.52 h. Under this optimal scheme, the COD and color in the effluent were reduced to 159 mg/L and 25°, respectively, with an increase of BOD_5/COD ratio from 0.05 to 0.21.

1. Introduction

In the treatment of landfill leachate, biological treatment systems are frequently used (Atmaca, 2009), mainly due to their simplicity and cost-effectiveness for simultaneous removal of nitrogen and biodegradable organic carbon. However, given the progressively more stringent discharge standards in most countries and the poor efficacy on treatment of aged leachates, biological techniques alone are usually insufficient in degrading high-molecular-weight fractions and decoloring (Moraes and Bertazzoli, 2005). For biologically stabilized leachate to meet the standards for discharge into sewer or into natural waters, further advanced treatments are commonly required.

A variety of methods such as activated carbon adsorption, ozonation, microfiltration, ultrafiltration, nanofiltration, reverse osmosis and Fenton processes are usually used for the advanced treatment of stabilized landfill leachate. Among these, in particular, the Fenton process is the most widely used technique with low cost and simple operability as well as efficient performance.

In recent years, Fenton processes, including conventional Fenton (Gulsen and Turan, 2004; Hermosilla et al., 2009; Kim et al., 2001; Li et al., 2009; Primo et al., 2008b; Roddy and Choi, 1999; Wang et al., 2009), photo-Fenton (Hermosilla et al., 2009; Kim et al., 1997; Kim and Vogelpohl, 1998; Primo et al., 2008a), electro-Fenton (Atmaca, 2009; Lin and Chang, 2000; Mohajeri et al., 2009; Zhang et al., 2006b) and photoelectro-Fenton processes (Altin, 2008), have been successfully applied in landfill leachate treatment. The Fenton treatment can effectively reduce the concentrations of organic contaminants and color, as well as can increase the biodegradable fraction of organic constituents in leachate, particularly in mature or biologically recalcitrant leachate (Deng and Englehardt, 2006).

However, to achieve high treatment performances, the optimal operating conditions must be determined, and this is not an easy task because several factors affect Fenton treatment performance (Oliveira et al., 2006). Until now, in Fenton treatment of landfill leachate, most studies have only focused on the traditional one-factor-at-a-time approach, studying the effect of each factor on the response of process performance by keeping the remaining factors constant. However, this approach, which does not take into ac-

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count cross-effects from the factors considered, is time-consuming and results in a poor optimization result (Herney-Ramirez et al., 2008; Oliveira et al., 2006).

Alternatively, experimental factorial designs coupled with the analysis of results using e.g. the response surface methodology (RSM) have proven to be quite a reliable statistical method, allowing the use of the minimum experimental numbers. The RSM has an important application in the process design and optimization as well as in the improvement of existing designs (Zinatizadeh et al., 2006). The statistical approach based on the use of factorial designs is more practical compared to the one-factor-at-a-time approach, as it arises from experimental methodology which includes interactive effects among the variables and, eventually, it depicts the overall effects of the parameters on the process (Bas and Boyaci, 2007; Zinatizadeh et al., 2006). Although many reports (Abdessalem et al., 2008; Arantes et al., 2006; Herney-Ramirez et al., 2008; Martinez et al., 2005; Mohammed et al., 2009; Sleiman et al., 2007) have been found on the application of the RSM (Zhang et al., 2009) to wastewater treatment using Fenton processes, to our knowledge only few applications are available concerning biologically stabilized leachate treated with Fenton.

In addition, we observed that Fenton processes have the drawback of introducing large amounts of sulfate, which is caused by adding $FeSO_4$ as the catalyst and by adding sulfuric acid for pH adjustment as well. Regarding the sulfate content, although the Chinese legislation does not directly limit their concentration for effluent discharge, it is safer to minimize their content in the effluents. High sulfate concentrations can unbalance the natural sulfur cycle (Kioussis and Kofinas, 2005; Silva et al., 2002; Yang et al., 2009). The accumulation of sulfate-rich sediments in lakes, rivers and seas may cause the release of toxic sulfides that can provoke damages to the environment, such as odor and corrosion (Ghigliazza et al., 2000; Gonzalias et al., 2007). Being aware of the fact that $FeCl_2$ has similar chemical properties in the Fenton reactions compared with $FeSO_4$, and that the chloride introduced may be more acceptable than sulfate, the use of $FeCl_2$ as the catalyst in place of $FeSO_4$ may be a good option. However, the performance of the Fenton treatment using $FeCl_2$ as an alternative catalyst needs to be evaluated.

Our work aims (i) to compare the Fenton performance for the treatment of biologically treated leachate using $FeCl_2$ or $FeSO_4$ as catalysts, (ii) to evaluate the Fenton treatment of the stabilized leachate by using a central composite factorial design (CCD) coupled with RSM for data analysis, in order to estimate the joint effects of four independent factors, namely initial pH value, Fe(II) dosage, H_2O_2/Fe(II) mole ratio and reaction time, where COD and color were selected as the response variables, (iii) to optimize the factors based on the overlay plot.

2. Materials and methods

2.1. Leachate characteristics

The municipal landfill site has been in operation for 11 years and is located in Jiangmen, a city in Southern China. Leachate samples were obtained from an in situ sequencing batch reactor (SBR). The samples were preserved in a refrigerator at 4 °C. This storage technique had no detectable effect on its composition. The physicochemical characteristics of the SBR-treated leachate used in this test are listed in Table 1. It was a dark brown alkaline mixture, with small amounts of suspended solids (SS) and sulfate; chloride also showed appreciable concentrations. The average BOD_5/COD ratio was below 0.05, indicating a low biodegradability. Both COD and color failed to meet local discharge standards (COD $\leqslant$ 100 mg/L, color $\leqslant$ 40°), therefore further treatment using physicochemical technique was required.

2.2. Analytical methods and experimental procedure

All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water. The solution pH was measured with a pHS-9V digital instrument. Sludge production was determined by suspended solids (SS). Chloride, COD, BOD_5, color, sulfate and SS were measured by using standard methods (APHA, 1995). The residual hydrogen peroxide concentration was monitored by iodometric titration. All parameters were measured in duplicate with an experimental error below 5%. In order to prevent the interference of H_2O_2 in the COD analysis, the measured COD value was corrected according to the methods recommended by Talini and Anderson (1992) and Benatti et al. (2006).

All runs were conducted at room temperature (26 ± 1 °C) and atmospheric pressure. The initial pH of the leachate was adjusted to the desired value with sulfuric acid (98%) and sodium hydroxide solution (30%). Subsequently, 1 L of the leachate was added to the 2 L beaker. The leachate was stirred with a magnetic stirrer throughout the experiments. The designed amount of $FeSO_4{\cdot}7H_2O$ or $FeCl_2{\cdot}4H_2O$ was added and then the Fenton reaction was initiated by adding the required amount of H_2O_2 (30%, w/w). After the designated reaction time, a NaOH solution was added to adjust the pH to approximately 7.5, and then a small amount of polyacrylamide (PAM: 0.2%, w/w) was added to enhance the flocculation performance. Final samples of supernatant in the beakers were taken after 1 h clarification for water quality measurements.

In the comparative experiments, $FeCl_2$ and $FeSO_4$ were used as different catalysts. In both cases, the Fe^{2+} concentrations were varied on four levels (6, 9, 12 and 15 mmol/L), while the other conditions including the initial pH of 4.0 (suggested by Lau et al. (2002)), the $[H_2O_2]/[Fe^{2+}]$ ratio of 1.9 and the reaction time of 4 h (based on one-factor-at-a-time experiment, data not shown) were kept unchanged. The COD, color, sulfate, chloride and SS concentrations were measured at the end of each experiment. The average sedimentation rate, which describes the sludge settleability until the sludge sedimentation ceased, was measured by transferring the mixing liquid to the 100 mL volumetric cylinders immediately after the PAM was added.

2.3. Experimental design and statistical model

The Design Expert Software (version 7.1.3) was used for the experimental design and data analysis. In this study, the CCD coupled with the RSM for data analysis were applied to optimize the four major operating factors: initial pH value, $[Fe^{2+}]$, $[H_2O_2]/[Fe^{2+}]$ ratio and reaction time. Table 2 shows the factor levels in this experiment. In order to evaluate the performance of the Fenton treatment, COD and color removal, the important water quality parameters in which the single biological treatment failed to meet the discharge requirements, were selected as response variables.

Table 1
Characteristics of the SBR-treated leachate.

Parameters	pH	SS (mg/L)	Color (°)	COD (mg/L)	BOD_5 (mg/L)	Alkalinity (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
	8.15–8.20	5–10	520	570–585	10–20	1800–1850	10–15	1150–1200