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Advanced landfill leachate treatment using iron-carbon microelectrolysis- Fenton process: Process optimization and column experiments

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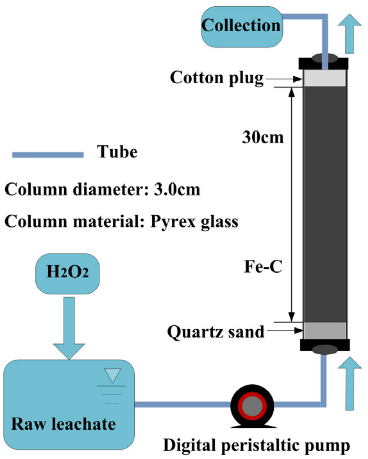
HIGHLIGHTS

- Fe-C microelectrolysis-Fenton process is proposed to pretreat landfill leachate.
- Operating variables are optimized by response surface methodology (RSM).
- 3D-EEMs and MW distribution explain the mechanism of enhanced biodegradability.
- Fixed-bed column experiments are performed at different flow rates.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel hydrogen peroxide-enhanced iron-carbon (Fe-C) microelectrolysis reactor was proposed for the pretreatment of mature landfill leachate. This reactor, combining microelectrolysis with Fenton process, revealed high treatment efficiency. The operating variables, including Fe-C dosage, H_2O_2 concentration and initial pH, were optimized by the response surface methodology (RSM), regarding the chemical oxygen demand (COD) removal efficiency and biochemical oxygen demand: chemical oxygen demand (BOD_5/COD) as the responses. The highest COD removal (74.59%) and BOD_5/COD (0.50) was obtained at optimal conditions of Fe-C dosage 55.72 g/L, H_2O_2 concentration 12.32 mL/L and initial pH 3.12. Three-dimensional excitation and emission matrix (3D-EEM) fluorescence spectroscopy and molecular weight (MW) distribution demonstrated that high molecular weight fractions such as refractory fulvic-like substances in leachate were effectively destroyed during the combined processes, which should be attributed to the combination oxidative effect of microelectrolysis and Fenton. The fixed-bed column experiments

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were performed and the breakthrough curves at different flow rates were evaluated to determine the practical applicability of the combined process. All these results show that the hydrogen peroxide-enhanced iron-carbon (Fe-C) microelectrolysis reactor is a promising and efficient technology for the treatment of mature landfill leachate.

1. Introduction

Landfill represents a key management strategy for solid waste disposal throughout the world, mainly due to its economic advantages [1]. The major problems caused by landfilling are related to the highly hazardous leachate generated by the decomposition of organic wastes and rainfall percolation through the waste material [2]. The composition of leachate varies greatly according to the type of waste, site hydrology, amount of precipitation, cover design, landfill age, and operational practice [3]. Stabilized leachate is characterized by a low biochemical oxygen demand: chemical oxygen demand (BOD_5/COD) ratio (<0.3) and a large fraction of high-molecular-weight organics (e.g. humic and fulvic acids) that is particularly challenging, especially for biological methods [4]. Therefore, single or combination of physicochemical processes is often used to improve the biodegradability of leachate as a pretreatment step to biological processes [5]. The physicochemical treatment processes usually consist of coagulation/flocculation [6], reverse osmosis, activated carbon adsorption [8] and advanced oxidation processes (AOPs) [6].

In the past decade, the AOPs, such as ozonation oxidation, electrochemical oxidation [7], Fenton oxidation and photocatalysis, have gained significant interest [5,9]. Among them, cost-effective Fenton process is considered as one of the most promising AOPs for leachate treatment. During the Fenton reaction, hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals (Eq. (1) [10]):

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

Highly reactive hydroxyl radicals ($^{\bullet}OH$) can significantly degrade recalcitrant and toxic organic compounds, and increase biodegradability of organic compounds [11]. However, the disadvantage of conventional Fenton process is a large amount of extra H_2O_2 and Fe^{2+} needed to keep the moderate hydroxyl radicals production. For this, some novel Fenton processes such as UV-Fenton, UV-H_2O_2 and Electro-Fenton were developed to improve the biodegradability and eliminate the color of landfill leachate [12]. Nonetheless, higher operational costs on account of UV and electric energy supply, limit the wide applications of these processes [13].

Fe-C microelectrolysis, an economical and environmentally friendly treatment method, is widely used in poor biodegradable wastewater treatment [14–16]. Basically, when a mixture of scraps iron is in contact with granular activated carbon (GAC) in solution, numerous microscopic galvanic cells are formed between the particles of iron (anode) and carbon (cathode) [16]. The electrode reactions can be illustrated as follows in Eqs. (2) and (3) [17]:

$$\text{Anode(iron)}: \quad Fe(s) - 2e^- \rightarrow Fe^{2+}(aq) \qquad (2)$$

$$\text{Cathode(carbon)}: \quad 2H^+(aq) + 2e^- \rightarrow 2[H] \rightarrow H_2(g) \qquad (3)$$

Microelectrolysis can enhance structural transformation of the organic pollutants due to the high potential difference (0.44 V) between Fe and C electrode. The generation of Fe^{2+} will trigger subsequent Fenton reaction without adjustment of solution pH. Recently, many studies have reported that H_2O_2 can be generated in internal microelectrolysis (IME) reactor with aeration, which subsequently combined with ferrous ions released by dissolution of iron scarps to form Fenton's reagent [16,18,19]. Zhang and his coworkers [20] also found that the addition of hydrogen peroxide at the end of internal microelectrolysis would improve COD removal efficiency. These results demonstrated that the combination of microelectrolysis and Fenton process can significantly improve removal efficiency of refractory organic pollutants and will be a potentially promising technology for the treatment of mature landfill leachate. However, to our knowledge, there are no reports on hydrogen peroxide- enhanced iron-carbon (Fe-C) microelectrolysis for landfill leachate treatment in one reactor as in continuous model, which maybe more appropriate to industrial application.

Dissolved organic matter (DOM) is a heterogeneous mixture of humic substances, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids, and hydrocarbons. It is noted that most of COD have been ascribed to the existence of DOM in leachate [21]. For the complexity of multi-components in landfill leachate, fraction of DOM is usually performed as a new and useful approach to differentiate and analyze the degradation of pollutants [22]. Correspondingly, a number of analyses in landfill leachate have been studied. Nevertheless, the characterization of leachate DOM fractions after treatments is even limited [23,24].

In this study, a novel hydrogen peroxide-enhanced iron-carbon (Fe-C) microelectrolysis reactor was employed to treat the mature landfill leachate. This reactor, combining microelectrolysis with Fenton process, revealed high treatment efficiency. Firstly, batch experiments were carried out to determine the optimal operational parameters including initial pH, H_2O_2 concentration, and Fe-C dosage through response surface methodology (RSM). Then the characteristic of DOM in leachate was analyzed by fluorescence spectroscopy and molecular weight (MW) distribution, and the mechanism of enhanced biodegradability was proposed. At last, the column experiments were conducted to explore the feasibility of the combined process for the leachate treatment in continuous model.

2. Materials and methods

2.1. Landfill leachate samples and chemicals

Leachate samples were obtained from Heimifeng refuse landfill of Changsha, China.The samples were immediately preserved in a refrigerator at 4 °C to minimize biological and chemical reactions. General characteristics of the leachate used in this study were as follow: pH 7.52 ± 0.2, COD 4980 ± 160 mg/L, BOD_5 548 ± 16 mg/L, the ratio of BOD_5/COD about 0.11 ± 0.1 and ammonia-nitrogen 1850 ± 18 mg/L, which indicated that the leachate was difficult to be treated biologically.

Hydrogen peroxide (30% solution, Sinopharm Chemical Reagent Co., Ltd) was analytical reagent (AR) grade. Scrap cast iron with a surface area of 0.3–0.4 $m^2 g^{-1}$ was obtained from Changpu Chemical Reagent Limited Company (Taizhou, China). To remove surface oil, scrap cast iron was rinsed with ethanol for 10 min. After being washed with distilled water, it was re-rinsed with 0.1 M H_2SO_4 and distilled water again. Granular active carbon (GAC) with a diameter of 2–4 mm was obtained from Morgan Carbon Company (Shanghai,

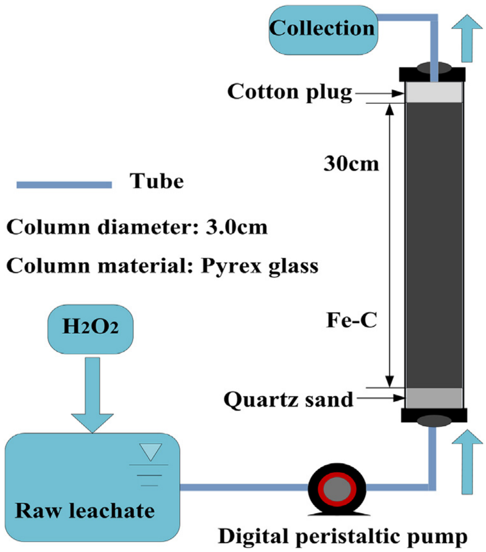

Fig. 1. Schematic diagram of column experiments.

Table 1
Levels of the variable tested in the Box-Behnken Design (BBD).

Independent variables	Symbol	Range and levels		
		−1	0	1
Fe-C dosage (g/L)	X_1	44	52	60
H_2O_2 concentration (mL/L)	X_2	10	12	14
initial pH	X_3	2	3	4

Table 2
Matrix of experimental design and the results of COD removal efficiency and the ratio of BOD_5/COD.

Run	Variables			Experimental responses	
	X_1 Fe-C(g/L)	X_2 H_2O_2(mL/L)	X_3 pH	Y_1 COD removal (%)	Y_2 BOD_5/COD
1	60	12	2	66.33	0.41
2	44	14	3	62.11	0.37
3	52	14	2	65.67	0.40
4	60	12	4	66.11	0.42
5	52	10	2	57.44	0.33
6	52	12	3	73.33	0.49
7	52	12	3	74.00	0.50
8	44	12	4	60.56	0.37
9	60	14	3	73.11	0.48
10	60	10	3	63.00	0.38
11	44	12	2	58.11	0.34
12	52	12	3	72.75	0.49
13	52	14	4	66.00	0.40
14	52	12	3	72.33	0.48

China). Sulfuric acid and sodium hydroxide were used to adjust the pH of solution.

2.2. Experimental procedure

2.2.1. Batch experiments

Batch experiments were performed at ambient temperature (30 °C) in conical flasks with a 100 mL leachate sample. Orbital Shaker (Jerel HY-8 Rotatest Shaker) was used for sample shaking. The initial solution pH was adjusted to desired values (2.0, 3.0, 4.0) by 2 M H_2SO_4 and 2 M NaOH. Then H_2O_2 was added to achieve the concentrations of 10, 12, 14 mL/L. Meanwhile the dosage of Fe-C with a mass ratio of 3:1 was attained intended values (44, 52, 60 g/L). After 60 min reaction time on the Shaker at 350 rpm, sodium hydroxide solution was added to quench the reaction by increasing the pH to around 9.0. After settling 30 min, the supernatant was taken for the COD and BOD_5 analysis. Under the optimum conditions, the amount of iron in solution, molecular weight distribution and three-dimensional excitation and emission matrix (3D-EEM) fluorescence spectroscopy were measured before and after treatment.

2.2.2. Column experiments

Column experiments were performed to investigate the treatment efficiency of the microelectrolysis-Fenton reactor operated continuously and automatically. Optimal operating parameters obtained in above batch experiments were used, including an initial pH of 3.12, H_2O_2 12.32 mL/L, Fe/C mass ratio of 3:1. Based on the above conditions, leachate was fed into the columnar reactor (Φ3cm × 30 cm, Pyrex glass, Fig. 1) by a peristaltic pump (Model HL-1, China) with different flow rates of 1.0, 1.5, 2.0, 3.0, 6.0 mL/min. At pre-selected time intervals (2 h), 20 mL effluent was collected, and its pH value was adjusted to 10. After 30 min-settlement, the supernatant was taken for the COD analysis.

2.3. Analytical methods

The ammonia-nitrogen, BOD_5 were determined using colorimetric method, dilution and seeding method (after five days), respectively, according to the Standard Methods [25]. Chemical oxygen demand (COD) was determined by using microwave assisted potassium dichromate method. pH was monitored using a pH meter (Orion 710A, TX, USA). The ratio of BOD_5/COD was calculated to analyze the biodegradability of leachate. Fe^{2+} in the solution was measured by 1,10-orthophenanthroline colorimetric method at a wavelength of 510 nm [26]. Total iron was analyzed according to following procedure: firstly hydroxylamine hydrochloride was added into the sample under acidic conditions to reduce the iron ion in solution to Fe^{2+}, and then measured the Fe^{2+} in the solution [27].

Three-dimensional excitation and emission matrix (3D-EEM) fluorescence spectroscopy and molecular weight (MW) distribution of the leachate were measured after filtration with a 0.45 μm filter. 3D-EEM Fluorescence spectroscopy was recorded on an F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) with a xenon lamp as the excitation source. The EEM spectroscopy was obtained by measuring the emission spectra from 200 to 550 nm repeatedly, at the excitation wavelengths from 200 to 550 nm, spaced by 3 nm intervals. The scanning speed was set at 1200 nm/min for all measurements. Excitation and emission slit widths were 5 nm. The MW distribution of the leachates was determined by an ultra-filtration apparatus with different molecular-weight cutoffs of 1 kDa, 3 kDa, 5 kDa, 10 kDa. The molecular weight fractions were characterized by COD values of filtrate.

2.4. Experimental design via response surface methodology

Response surface methodology (RSM) was a powerful statistical tool used to construct models, analyze and optimize operation parameters, and evaluate the influences of several individual factors. The Box-Behnken Design (BBD) was applied to evaluate the effects of Fe-C dosage (X_1), and H_2O_2 concentration (X_2), initial pH (X_3), and their interactions on COD removal efficiency and the ratio of BOD_5/COD. In Table 1, X_1, X_2, X_3 were varied over the ranges 44–60 g/L, 10–14 mL/L, 2–4, with corresponding central values of 52 g/L, 12 mL/L, 3.0. The experimental design was listed in Table 2. Experimental data were fitted to a polynomial quadratic equation

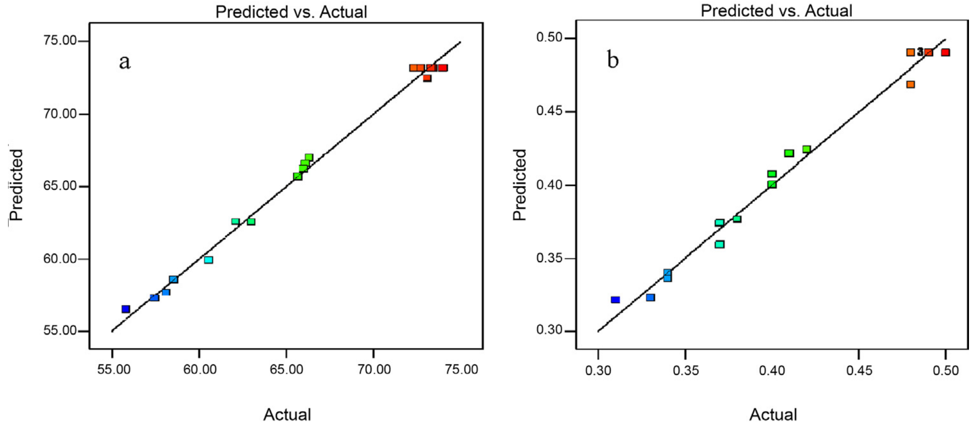

Fig. 2. Correlation of actual and predicted values of response for (a) COD removal efficiency, (b) BOD_5/COD.

Table 3
Analysis of variance tables for COD removal efficiency and BOD_5/COD.

Source	COD removal		BOD_5/COD	
	F Value	P-value Prob > F	F Value	P-value Prob > F
Model	119.04	<0.0001	59.35	<0.0001
X_1	209.49	<0.0001	90.00	<0.0001
X_2	211.20	<0.0001	84.10	<0.0001
X_3	2.76	0.1406	2.50	0.1579
X_1X_2	5.92	0.0452	3.20	0.1168
X_1X_3	2.92	0.1311	0.80	0.4008
X_2X_3	0.25	0.6328	0.20	0.6682
X_1^2	133.74	<0.0001	64.47	<0.0001
X_2^2	191.29	<0.0001	126.37	<0.0001
X_3^2	247.83	<0.0001	126.37	<0.0001
Lack of Fit	2.08	0.2461	4.50	0.0901

to correlate each response with an independent variable. Quadratic equation for the variable was described as follows in Eq. (4):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i \le j}^{k} \sum_{j}^{k} \beta_{ij} X_i X_j \tag{4}$$

Where Y is the response variable, X_i and X_j are the variables, β_0 is a constant, β_i, β_{ii} and β_{ij} were coefficients, k is the number optimized in the experiment.

The Design Expert software (version 8.05b) was used for the statistical design of experiments and data analysis. The three-dimensional (3D) response surface plots constructed for each polynomial equation was evaluated using analysis of variance (ANOVA) tests. The quality of the fit polynomial model was expressed by the correlation coefficient (R^2 and Adj R^2), and its statistical significance was examined by the *F*-test. Model terms were evaluated on the P value (probability) with 95% confidence level. Furthermore, the adequacy of the regression equations was checked by comparing the experimental data with predicted values obtained from the equations [28].

3. Results and discussion

3.1. Statistical analysis of the response surface models

The complete design matrix with the independent variables (X_1-X_3) and the response values (Y_1-Y_2) obtained from the experiment was presented in Table 2. In addition, Table 3 and 4 illustrated the analysis of variance (ANOVA) and polynomial quadratic equations that incorporated the interactions between the three variables.

As shown in Table 2, the very low values of Prob > F (<0.0001) of two models implied that terms were significant in all models. There was only 0.01% chance that a model F-value could occur due to noise. Moreover, based on the values Prob > F (<0.05), two variables (X_1, X_2) were found to be significant model terms. This indicated that Fe-C dosage (X_1), H_2O_2 concentration (X_2) had prominent effects on COD removal and B/C. The lack of fit F-values of two models (2.08, 4.50) showed that the variation of the data around the fitted model were not significant relative to the pure error, implying significant model correlation between the variable and process response.

The ANOVA results and final quadratic models (Table 3 and 4) indicated the adequacy of the model successfully describing the correlation between the factors and the response. The fitness of the models was investigated by determining the R^2 coefficient. High R^2 values of 0.9935, 0.9871, respectively, ensured the suitability of the quadratic models to the experimental data. Meanwhile, the coefficients of variance (CV) for COD removal and B/C were found to be 1.19%, 2.72%. The models can be considered well reproducible and reliability of the experiments at these low CV values [29]. Besides, the plots of the predicted values versus the actual values for COD removal and B/C help us judge the model suitability. As presented in Fig. 2, the plots indicated adequate agreement between the actual and predicated data obtained from the model. In conclusion, the predicted models were proved appropriate to navigate the design space defined by the BBD.

3.2. Process optimization and analysis

To enhance the understanding of the impacts of the three selected variables (Fe-C dosage, H_2O_2 concentration, initial pH) on COD removal efficiency and the ratio of BOD_5/COD, the predictive models were presented as three-dimensional response surface plots in Fig. 3. The plots were approximately symmetrical in shape with circular contours. All response plots showed clear peaks, implying that the optimum conditions for maximum values of the responses were attributed to Fe-C, H_2O_2 and initial pH inside the design boundary. Response surface plots in Fig. 3 indicated optimum points to be at about Fe-C 55.72 g/L, H_2O_2 12.32 mL/L and pH 3.12 for COD removal efficiency 74.59% and B/C 0.50. These optimum experiment efficiencies were selected from the economic considerations, meaning that insignificant increase were observed with excessive Fe-C dosage and H_2O_2 concentration.

Fig. 3 (a) (d) showed that the dosages of Fe-C and H_2O_2 had significant effect on COD removal efficiency and the ratio of B/C. In Fig. 3 (b) (e), the COD removal efficiency and the ratio of B/C improved with increasing Fe-C dosage by 55.72 g/L, then main-

Table 4
ANOVA results for response parameters.

Response	Final equation in terms of coded factors	R^2	Adj R^2	C.V (%)
Y_1	$73.17 + 4.00X_1 + 4.01X_2 + 0.46X_3 + 0.95X_1X_2 - 0.67X_1X_3 - 0.20X_2X_3 - 4.40X_1{}^2 - 5.26X_2{}^2 - 5.99X_3{}^2$	0.9935	0.9852	1.19
Y_2	$0.49 + 0.038X_1 + 0.036X_2 + 0.00625X_3 + 0.010X_1X_2 - 0.005X_1X_3 - 0.0025X_2X_3 - 0.044X_1{}^2 - 0.061X_2{}^2 - 0.061X_3{}^2$	0.9871	0.9704	2.72

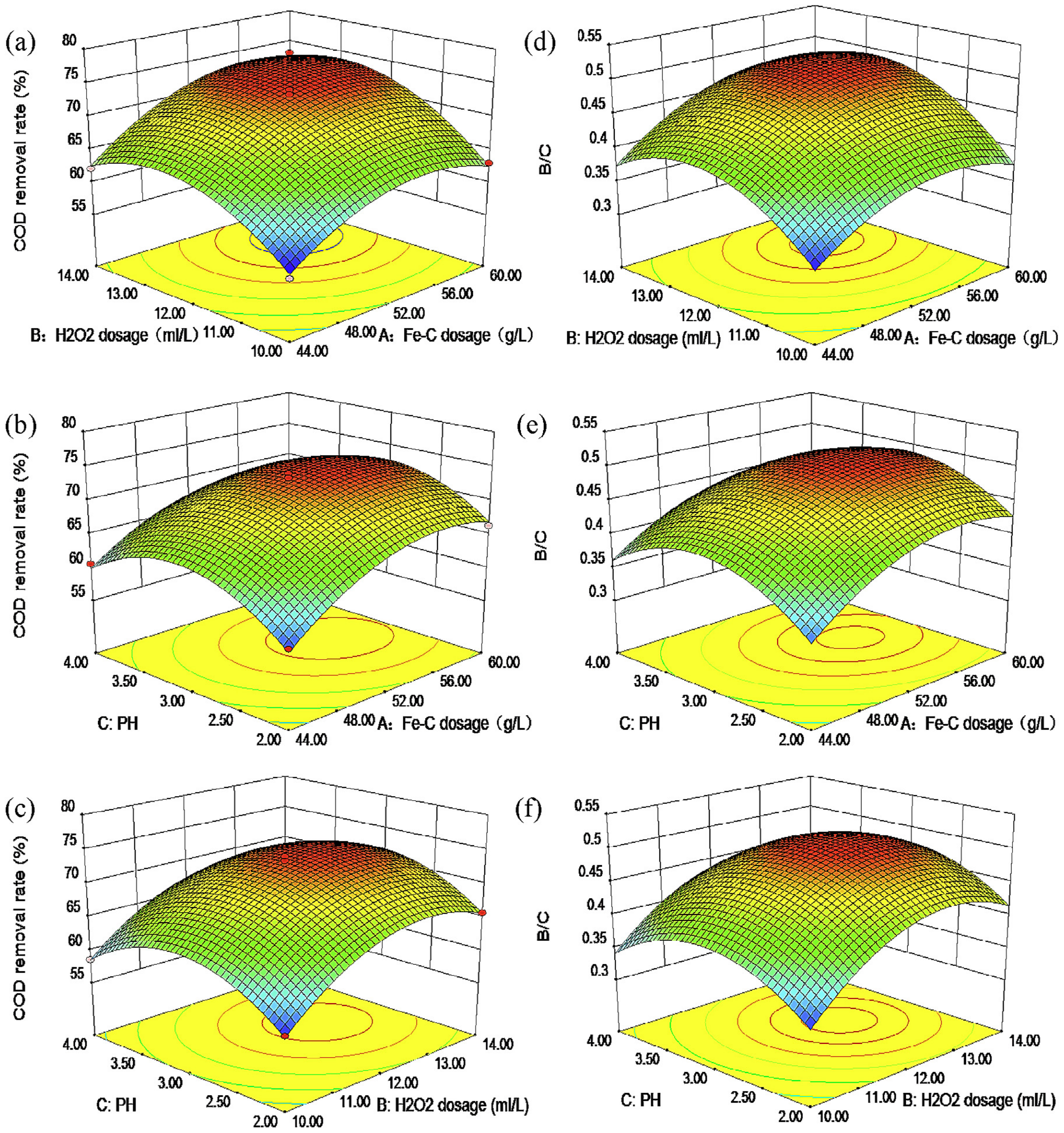

Fig. 3. Three-dimensional contour plots of the quadratic model for COD removal rate (a–c) and B/C (d–f) (temperature: 30 °C; reaction time: 60 min).

tained this efficiency basically. Furthermore, excess Fe^{2+} produced by Fe-C microelectrolysis could lead to the rise in the hydroxide sludge amount, and generated sludge needed proper disposal that imposed undesirable operational costs [30]. In Fig. 3 (c) (f), likewise, excess H_2O_2 was not necessarily the best feasible choice for leachate treatment. Hydroxyl radical ($^{\bullet}OH$) scavenging effect by excess H_2O_2 presumably became stronger as the H_2O_2 dosage rapidly increased. Consequently, the less reactive radical $HO_2{}^{\bullet}$ was formed as shown in Eq. (5) [31]:

$$H_2O_2 + {}^{\circ}OH \rightarrow H_2O + HO_2{}^{\bullet} \quad (5)$$

pH also played an important role according to Fig. 3 (b) (c), a pH below optimum can inhibit oxidation reaction because at extremely low pH values, the Fe^{2+} formed reacts relatively slowly with H_2O_2, less $^{\bullet}OH$ radical production resulting in the reduction of COD removal efficiency. On the other hand, a pH above optimum, the removal efficiency of COD also reduced because of the formation of ferric oxyhydroxide hindered the microelectrolysis reaction between Fe and C [32].

Two additional experiments were conducted applying the optimum conditions to confirm the agreement of the results achieved from models. Results indicated that 74% COD removal efficiency

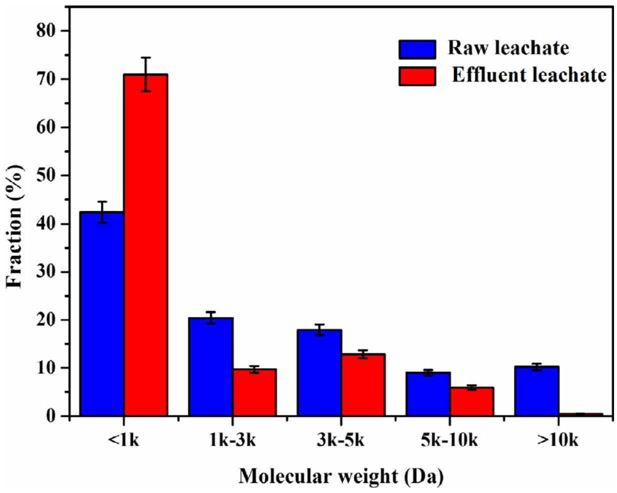

Fig. 4. Molecular weight distribution of the raw and effluent leachate (Fe-C dosage: 55.72 g/L; H_2O_2 concentration: 12.32 mL/L; initial pH: 3.12; reaction time: 60 min; temperature: 30 °C).

and 0.49 B/C obtained from the experiments and the consequences estimated by models were in close agreement.

3.3. The transformation of iron valence

To investigate the transformation of iron during Fe-C microelectrolysis-Fenton process, the amount of iron in solution after treatment under the optimum conditions were measured. Experimental results showed that the mass concentration of Fe^{2+} and Fe^{3+} were 0.45 and 5.25 g/L, respectively. Fe^{2+} in the solution was quickly transformed into Fe^{3+} according to Eq. (1). In turn, the quick consumption of Fe^{2+} promoted its continuously generation from the Fe-C microelectrolysis system. With the consistent production of $^{\bullet}OH$, residual Fe^{2+} and Fe^{3+} were precipitated as iron oxyhydroxides due to the increasing of pH (about 9 at the end).

3.4. Evolution of the DOM characteristics

3.4.1. MW distribution of the DOM

The apparent MW distribution of DOM in the raw and treated leachate under optimal condition was shown in Fig. 4. The result indicated that the major part (80.8%) of DOM in raw leachate distributed in a molecular weight region of <5 kDa, of which the organic matters with MW < 1 kDa were the main composition. Furthermore, high molecular weight organic matters with MW > 10 kDa accounted for 10.22% of DOM.

After microelectrolysis-Fenton combined process, the organic matters with MW > 10 kDa were almost completely degraded, while those with MW < 1 kDa increased from 42.37% to 70.97%. This indicated that most large molecules of DOM were mineralized or transformed to smaller ones. Recent study showed that high molecular weight organic matters revealed the major resistant against biodegradation, and were the main components of leachate treatment [33]. Therefore, in this combined process, the efficient removal of high molecular weight organic matters was of great significance in improving the biodegradability of leachate.

3.4.2. 3D-EEM fluorescence spectroscopy of the DOM

The EEM spectra of DOM before and after leachate treatment were illustrated in Fig. 5. There were three principal EEM peaks in the raw leachate DOM (Fig. 5a).The peak A at Ex/Em of 240–270/370–440 nm, labeled as fulvic-like compound [34], was characterized as the components derived from lignin and other degraded plant materials [35]. The peak B at Ex/Em of 275/340 nm was derived from the protein tryptophan-like substance [36]. The peak C at Ex/Em of 230/340 nm was also related to the protein tryptophan-like substances [37]. The two peaks B and C had been ascribed as protein-like peaks [38]. The multiple peaks in EEM spectrum of raw leachate DOM showed that the sample was composed of complex components associated with fulvic-like organic compounds. The fluorescence intensity of three components was expressed as the color of the peaks. As shown in Fig. 5a, the fluorescence intensity of peak A was the highest, suggesting that the fulvic-like compound comprised mainly of DOM. This result indicated the poor biodegradability of the raw leachate.

After microelectrolysis-Fenton combined process, two primary peaks D1 and D2 were observed at Ex/Em of 270/260 and 225/300 nm (Fig. 5b). Both peaks were stronger, and the locations were blue-shifted to shorter wavelength than those of the raw leachate. Furthermore, there was no obvious peak ascribed as fulvic-like compound. Such the differences implied the decreases of molecular size, aromatic polycondensation, level of conjugated chromophores, and humification degree of DOM when the leachate was treated [35,39].

From these results, it was deduced that the fulvic-like substances were efficiently decomposed after treatment, suggesting the significant improvement of the biodegradability of leachate.

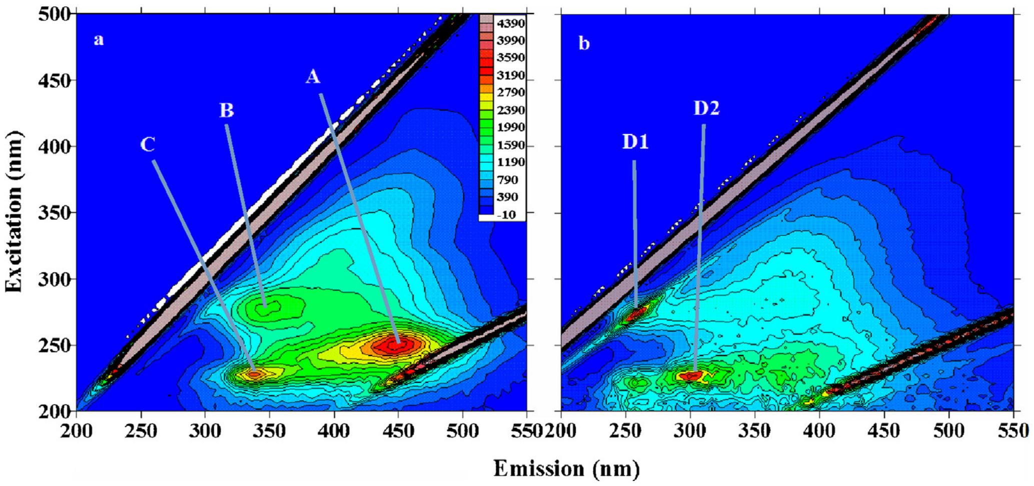

Fig. 5. Three-dimensional excitation and emission matrix (3D-EEM) fluorescence spectroscopy: (a) the raw leachate and (b) after the microelectrolysis-Fenton process (Fe-C dosage: 55.72 g/L; H_2O_2 concentration: 12.32 mL/L; initial pH: 3.12; reaction time: 60 min; temperature: 30 °C).

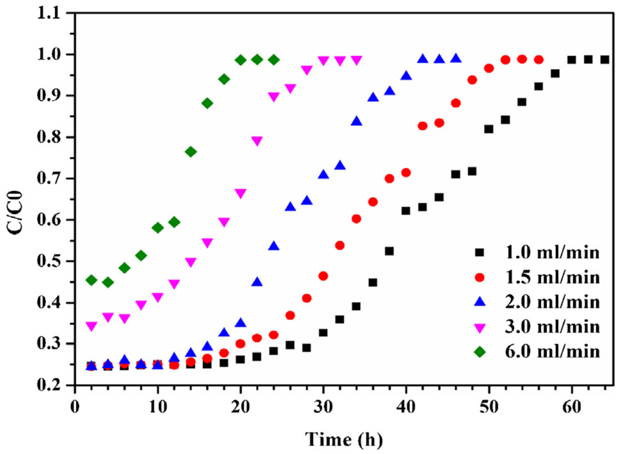

Fig. 6. Breakthrough curves at different flow rates (column height: 30 cm; H_2O_2 concentration: 12.32 mL/L; initial pH: 3.12; temperature: 30 °C) (C_0 and C (mg/L) are the inlet and outlet COD).

3.5. Column experiments

In this study, column experiments were carried out at different flow rates (1.0, 1.5, 2.0, 3.0, 6.0 mL/min) to evaluate the practical applicability of the combined process. In this section, other parameters such as initial pH, H_2O_2 concentration were fixed at 3.12, 12.32 mL/L, respectively, which were verified to be optimum conditions. The breakthrough curves at different flow rates are illustrated in Fig. 6. It was noticed that more processing time was required to reach the breakthrough for low flow rate. The minimum initial C/C0 (0.25) occurred at flow rate of 2.0 mL/min or less than 2.0 mL/min. Initial C/C0 rose sharply to 0.55 when the flow rate increased to 6.0 mL/min. These behaviors could be explained in the following way: if the flow rate is too fast, the solutes in the column have not enough residence time to contact and react reciprocally. Therefore, lower flow rate would be beneficial for achieving high COD removal efficiency. However, for flow rate, it was not that the lower the better. As the C/C0 staying at the ultimate value of 0.25, the reaction time and input of the leachate were found to be 16, 12, 10 h and 0.96, 1.08, 1.2 L for flow rate at 1.0, 1.5 and 2.0 mL/min, respectively, with corresponding retention time of 120, 80 and 60 min. The results demonstrated that a decrease in flow rate caused the decrease of the capacity of leachate treatment. The longer time solutes stayed, the more redundant reactions of microelectrolysis made the faster consumption of Fe-C, thus resulting in lower COD removal efficiency in the subsequent reaction. As a consequence, an appropriate flow rate holding 60 min retention time would be beneficial for COD efficient removal in column experiments.

3.6. Economic analysis

Based on the optimal experiments of Fe-C microelectrolysis-Fenton process, 1000 mL landfill leachate (COD 4980 ± 160 mg/L) treatment needs about GAC 13.93 g, iron 41.79 g, H_2O_2 (30%) 12.32 mL and H_2SO_4 (2 M) 3 mL. In China, the prices of H_2O_2 (30%), iron, GAC and H_2SO_4 (98%) were 166, 226, 150 and 90 US$ per 1000 kg, respectively. So the cost of this technology as well as considering the essential energy consumption was estimated to about 3.7 US$ for 1 kg COD. Compared with the cost of the conventional Fenton method, 5 US$ for 1 kg COD [40], the Fe-C microelectrolysis-Fenton process has a great potential in landfill leachate treatment.

4. Conclusions

This paper provided a novel and effective design idea of combining Fe-C microelectrolysis and Fenton in one reactor for mature landfill leachate treatment. The operational parameters, including Fe-C dosage, H_2O_2 concentration and initial pH were optimized using the RSM. The prediction results of the model generally agreed with the experimental results. The optimal conditions were identified as Fe-C dosage 55.72 g/L, H_2O_2 concentration12.32 mL/L and initial pH 3.12, which resulted in 74.59% COD removal and B/C 0.50. The major part (70.97%) of DOM fraction distributed in the molecular weight region of <1000 Da after treatment, demonstrating the efficient removal of high molecular weight fractions by the combined processes. The analyses of 3D-EEM fluorescence spectroscopy before and after treatment showed refractory fulvic-like substances were efficiently degraded, with only protein-like substances left in the effluent. The column experiments in different flow rates demonstrated that an appropriate retention time, nearly 60 min was considered to be beneficial for efficient COD removal from landfill leachate. These results illustrated the potential of hydrogen peroxide-enhanced iron-carbon (Fe-C) microelectrolysis process for the pretreatment of mature landfill leachate.

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