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Treatment of Leachate Wastewater with Fenton Process

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Abstract Leachate wastewater produced from landfill areas contains high organic contents and heavy metals. Because of high concentration of organic pollutants and heavy metals, it can cause toxic effects on the environment. Advanced oxidation processes can provide a suitable treatment for leachate wastewater due to hydroxyl radical formation. The most appropriate advanced oxidation process is Fenton Process to achieve high removal efficiency for the treatment of leachate wastewater.

The main objective of the study was to determine the most favorable levels of the parameters for the treatment of leachate wastewater. The effects of hydrogen peroxide, ferrous ion concentrations and reaction time on the oxidation of leachate wastewater investigated by using a statistical design. In the Box-Behnken statistical experiment design method, hydrogen peroxide, ferrous ion concentrations and reaction time were selected as independent variables. As the dependent variables, total organic carbon and color removal efficiencies were examined by keeping the pH constant.

As a result of the experimental studies, maximum total organic removal efficiency obtained as 50% at the optimum reaction conditions that H_2O_2 concentration was 40000 mg/L, ferrous ion concentration was 3000 mg/L, reaction time was 40 minutes. At these conditions, color removal efficiency also achieved as 84%.

Keywords: Landfill leachate, Fenton process, Box-Behnken design

1. Introduction

Leachate wastewater occurred from municipal solid waste (MSW) in the landfill areas in cities. Landfill leachate which contains high concentrations of recalcitrant organic compounds, heavy metals (Cd, Cr, Pb), phenols, aromatic hydrocarbons, pesticides and other toxic contaminants, is a highly complex wastewater. Characterization of leachate wastewater is changed according to different conditions such as age of leachate (young or mature leachate), the municipal solid waste composition, landfilling technology (Liu et al., 2021).Due to highly complex characterization, leachate wastewater is one of the main pollution sources of groundwater and surface water (Long et al., 2017).

Different conventional treatment processes such as biological treatment can be used to remove organic pollutants in landfill leachate. However, refractory organic pollutants could be detected in the effluent from conventional treatment of leachate, especially, in leachate from mature leachate. In addition, a conventional treatment is not sufficient to obtain effective removal efficiencies and to achieve the environmental regulations (Escola et al., 2017). In addition, there is a possibility that leachate can reach to surface and ground water. The leachate wastewater cannot be treated easily by conventional treatment processes, discharge limits cannot be also achieved by these processes. For that reason, advanced treatment methods should be selected to treat leachate wastewater and to discharge in limitations.

Advanced oxidation process (AOPs) have gained increasing attention due to their simplicity and high efficiency to remove refractory organic compounds. Among the AOP$_S$, Fenton oxidation has been preferred for the treatment of landfill leachate. Fenton processes can be used as a pre-treatment process before biological treatment to improve efficiency of conventional treatment processes. The Fenton and photo-Fenton processes, combined with a biological treatment unit, have been successfully used to treat landfill leachates (Xi et al., 2017).

In this study, Fenton process applied to raw leachate wastewater as a pre-treatment process before biological treatment process in order to increase biodegradability of leachate. The UE Agency proposed multistage processes as the best available technology for treating landfill leachates (UE Agency, 2007).

The main objective of the study was to determine the most favorable levels of the parameters for the treatment of leachate wastewater. The effects of hydrogen peroxide (H_2O_2) and ferrous ion concentrations (Fe^{2+}) and reaction time on the oxidation of leachate wastewater investigated with total organic carbon (TOC) removal and color removal by using a Box-Behnken statistical experimental design and surface response methodology.

2. Materials and Method

The landfill leachate used in these experiments, was obtained from municipal solid waste in Turkey. The total organic carbon concentration of the raw leachate was around 2800 mg/L. pH value of the wastewater was around 7.8. Turbidity and color are very high, too. Color is 2.301 ABS at 570 nm.

2.1. Design of the Experiments

The effects of variables on the response generally evaluated by altering one factor at a time for multivariable systems. However, this technique is not sufficient to estimate responses at any experiment point. To optimize the reaction conditions and predict responses, several significant parameters are determined by response surface methodology (RSM). Among all RSM designs, Box-Behnken design needs fewer experimental runs and forecast to efficiency at intermediate levels not experimentally executed (Hamed and Sakr, 2001).

In the statically experiments, the effects of hydrogen peroxide concentration (H_2O_2) and ferrous ion (Fe^{+2}) concentrations and reaction times as independent variables on the treatment of raw leachate wastewater were evaluated in terms of total organic carbon removal (TOC) as dependent variables in Box-Behnken design. In addition, color removal efficiency selected as other dependent variable.

2.2. *Experimental Procedure*

Fenton experiments carried out at room temperature (23±2ºC) using different hydrogen peroxide and ferrous ion concentrations at pH 3, which is suitable for Fenton process (Hsueh et al., 2005). Hydrogen peroxide (35% w/w) and ferrous sulfate obtained from Merck were used as an oxidant and catalyst, respectively.

All batch oxidation experiments were performed by using a jar test apparatus consisting of four beakers with a total volume of 1 L. The beakers were filled with 500 mL of leachate. First of all, pH of wastewater arranged as 3, then catalyst (ferrous ion) was added and mixed well with leachate wastewater before the addition of oxidant (hydrogen peroxide). Experiments were carried out at predetermined reaction times. At the end of the experiments carried out in the Box-Behnken experimental design; calcium hydroxide (10%) was added to arrange the pH value about 10 in order to observe settlement of wastewater. After 30 minutes, samples withdrawn from the beakers were analyzed immediately to avoid further reactions. TOC and color measurements were done. TOC-V/C-P-N Shimadzu analyzer for TOC parameter and Specol 1300 Analytical Jena spectrophotometer for color measurement were used.

3. Results and Discussion

Leachate wastewater used in these experiments only treated by biological treatment unit in wastewater treatment plant, however, discharge limits could not be achieved with only usage of biological treatment process. So, to evaluate effect of oxidation process on the treatment of leachate wastewater, to observe positive contribution on biological treatment unit and to reach discharge limits, Fenton process applied to leachate wastewater taken from at the beginning of biological treatment of leachate. Advanced oxidation experiments arranged by the response surface methodology.

Box-Behnken statistical experiment design used to investigate the effects of the three independent variables on the response function and to determine the optimal conditions maximizing the percent removals of color and TOC. The dependent variables (or objective functions) were the TOC (Y_1) and color (Y_2) removals.

The independent variables were hydrogen peroxide concentration (X_1), and ferrous ion concentration (X_2) and the reaction time (X_3). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively as shown in Table 1.

The values of the independent variables and the experimental results of dependent variables at each run are presented in Table 1. In addition, observed and predicted color and TOC removal efficiencies are also presented in Table 1.

The regression model

The application of RSM offers an empirical relationship between the objective function and the independent variables. The mathematical relationship between the objective function (Y) and the independent variables (X) can approximated by a quadratic polynomial equation (Eq 1) as follows:

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_2X_3+b_{11}X_1^2+b_{22}X_2^2+b_{33}X_3^2 \qquad \text{Eq (1)}$$

Coefficients in the regression model were determined by means of fifteen runs. Nine coefficients calculated such as one block term, three linear terms, three quadratic terms and three interaction terms. Different objective functions for independent variables with the determined coefficients are presented by Eqs. (2) to (3).

The objective function for TOC removal efficiency (Y_1) with the determined coefficient presented in Eq. (2).

$$Y_1= -83{,}058+0.000195X_1+0.064X_2+2.275\,X_3+4.0436E^{-07}X_1X_2+0.000011X_1X_3-0.000208X_2X_3-2.07347E^{-08}X_1^2-0.000013X_2^2-0.027X_3^2 \qquad R^2=0{,}996 \qquad \text{Eq (2)}$$

The objective function for Color removal efficiency (Y_2) with the determined coefficient is presented in Eq. (3).

$$Y_2=-92{,}271-0{,}0002X_1-0{,}0023X_2-0{,}334X_3+7{,}143E^{-09}X_1X_2+1{,}0E^{-05}X_1X_3-0{,}000033X_2X_3-5{,}33E^{-07}X_1^2+9{,}917E^{-07}X_2^2+0{,}0011X_3^2 \qquad R^2=0{,}9720 \qquad \text{Eq (3)}$$

Predictions obtained from the response functions were in good agreement with the experimental results, indicating the reliability of the method used. Objective functions with determined coefficients were used to estimate variations in response functions with the independent variables under different reaction conditions which were not carried out in experiments.

After evaluation of results in Box-Behnken design, optimum hydrogen peroxide concentration for the TOC removal obtained as nearly 40000 mg/L resulted in mineralization. For that reason, effects of other independent parameter variation at constant optimum hydrogen peroxide concentration showed in Figure 1.

Table 1. Observed and predicted percent removals of the Box-Behnken experiments at the pre-determined experimental points.

Run No	Actual and coded levels of variables			Observed percent removals		Predicted percent removals	
	X_1 H_2O_2, (mg/L)	X_2 Fe^{2+} (mg/L)	X_3 (Time) (min)	Y_1 TOC	Y_2 Color	Y_1 TOC	Y_2 Color
1	(0) 22500	(0) 2000	(0) 45	43.5	79.3	43.50	78.77
2	(0) 22500	(+1) 3000	(+1) 60	25.3	79	26.59	78.63
3	(-1) 5000	(-1) 1000	(0) 45	9.8	78	11.11	77.69
4	(+1) 40000	(-1) 1000	(0) 45	16.6	78	16.54	77.94
5	(+1) 40000	(0) 2000	(-1) 30	41.2	76.5	42.55	76.19
6	(+1) 40000	(+1) 3000	(0) 45	52	78.5	50.69	78.81
7	(0) 22500	(+1) 3000	(-1) 30	41.8	82	41.76	82.00
8	(0) 22500	(-1) 1000	(+1) 60	12.8	79	12.84	79.00
9	(0) 22500	(0) 2000	(0) 45	43.5	79	43.50	78.77
10	(+1) 40000	(0) 2000	(+1) 60	39.3	79	39.33	79.06
11	(0) 22500	(0) 2000	(0) 45	43.5	78	43.50	78.77
12	(-1) 5000	(0) 2000	(+1) 60	15.4	73	14.05	73.31
13	(-1) 5000	(0) 2000	(-1) 30	28.7	81	28.68	80.94
14	(-1) 5000	(+1) 3000	(0) 45	16.9	78	16.96	78.06
15	(0) 22500	(-1) 1000	(-1) 30	16.8	80	15.51	80.38

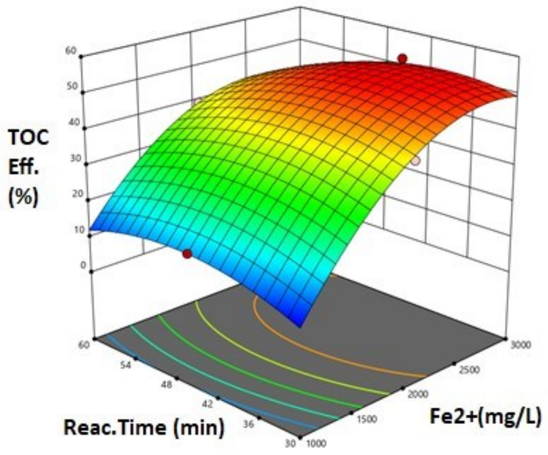

Figure 1. TOC removal efficiencies achieved with different ferrous ion concentrations and reaction times at the constant concentration of hydrogen peroxide (pH:3, H_2O_2: 40000 mg/L)

Figure 1 shows the effect of different ferrous ion concentrations and different reaction times on TOC removal efficiency when initial concentration of hydrogen peroxide was 40000 mg/L.

At a constant hydrogen peroxide concentration of 40 g/L, TOC removal efficiency increased from 10% to 50% when ferrous ion concentration increased from 1000 to 3000 mg/L. In order to obtain more than 40% TOC removal efficiency at a constant peroxide concentration of 40 g/L, ferrous ion should be above 2000 mg/L and reaction time should be arranged nearly 40 min. As shown in Figure 1, TOC removal efficiencies were 5, 37, and 54% when Fe^{+2} concentrations of 1000, 2000 and 3000 mg/L, respectively at a hydrogen peroxide concentration of 40000 mg/L and reaction time of 40 min.

In addition, TOC removal efficiencies were 50, 54, and 30% when reaction time of 30, 45 and 60 min, respectively at a hydrogen peroxide concentration of 40000 mg/L and ferrous ion concentration of 3000 mg/L.

When optimum hydrogen peroxide concentration as nearly 40 g/L used for maximum TOC removal, color removal efficiencies obtained as nearly 80% that is the maximum color removal efficiency in the experiments. For that reason, effects of other independent parameter variation on color removal efficiency at constant optimum hydrogen peroxide concentration like that total organic carbon removal efficiency presented in Figure 2.

Figure 2 shows the effect of different ferrous ion concentrations and different reaction times on color removal efficiency at when initial concentration of hydrogen peroxide 40000 mg/L.

At a constant hydrogen peroxide concentration of 40 g/L, color removal efficiency increased from 72% to 84% when ferrous ion concentration increased from 1000 to 3000 mg/L.

In order to obtain more than 70% color removal efficiency at a constant hydrogen peroxide concentration of 40 g/L, ferrous ion should be above 1000 mg/L and reaction time should be nearly 30 min.

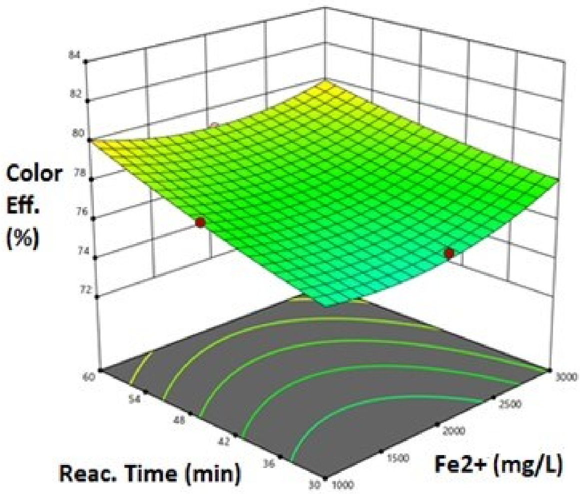

Figure 2. Color removal efficiencies achieved with different ferrous ion concentrations and reaction times at the constant dose of hydrogen peroxide (pH:3, H_2O_2: 40000 mg/L)

As shown in Figure 2, color removal efficiencies were 72, 76 and 84% when reaction time of 30, 45, and 60 min, respectively at a hydrogen peroxide concentration of 40 g/L and ferrous ion concentration of 1000 mg/L.

Based on the results, maximum total organic removal efficiency obtained as 50%. At the optimum reaction conditions that H_2O_2 concentration was 40000 mg/L, Fe^{+2} concentration was 3000 mg/L, reaction time was 40 minutes. At these conditions, color removal efficiency also achieved as 84%.

3.Conclusion

Fenton Process as an advanced oxidation process applied to landfill leachate wastewater in order to treat raw wastewater, to reach discharging limits and to increase biodegradability of leachate wastewater. Hydrogen peroxide and ferrous ion concentrations and reaction time were chosen as independent variables while TOC removal efficiency and color removal efficiency were selected as dependent variables in Box-Behnken design. In the statistical method, operating conditions for independent variable; hydrogen peroxide concentration was 5000-40000 mg/L (X_1), ferrous ion concentration was 1000-3000 mg/L (X_2), reaction time was determined as 30-60 minutes (X_3).

Concentration of independent variables (oxidant and catalyst) significantly affected on dependent variables. TOC removal efficiency increases with the ferrous ion concentration (X_2). The reaction time variable has also a more significant effect on TOC removal efficiency.

Maximum TOC removal efficiency (50%) and color removal efficiency (84%) and were obtained with a H_2O_2/Fe (II)/reaction time ratio of 40000/3000/40.

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