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Application of response surface method for coagulation process in leachate treatment as pretreatment for Fenton process: Biodegradability improvement

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ABSTRACT

Landfill leachate is a complex mixture containing toxic and recalcitrant substances with considerably low BOD_5/COD indicating the necessity and difficulty of its treatment. Amongst treatment processes, integrated separating-destructive processes are promising ones. In this way, suspended and colloidal particles get separated in a separating process while the soluble fraction undergoes a destructive process; probably an advanced oxidation process. In the present study, coagulation process using ferric chloride was employed as a pre-treatment process for landfill leachate. Design of experiment, modeling and data analysis were conducted using response surface method (RSM) considering COD, color and TSS removals as responses. In optimum conditions (pH = 7 and 1500 mg/L $FeCl_3$) the average COD, color and TSS removals were approximately 65%, 79% and 95%, respectively. Afterwards, Fenton process was applied for degradation of the leachate. Average oxidation state (AOS) and BOD_5/COD values increased from −0.51 and 0.11 to +1.7 and 0.4 respectively. Phyto-toxicity test was also conducted based on the germination index which was dramatically increased after coagulation and Fenton processes.

1. Introduction

Being categorized as high strength wastewater, landfill leachate is a complex mixture of organic and inorganic matters many of which are toxic and harmful. The composition of leachate depends on landfill age, percolation and precipitation and type of solid waste [1,2]. Landfill leachate is a source of pollution for groundwater and surface water resources. Therefore, it is essential to treat the leachate adequately. Complex quality and the presence of hazardous and toxic materials in landfill leachate along with low BOD_5:COD ratio limit the application of biological processes [3,4]. Hence, chemical processes are extremely used for landfill leachate as pretreatment or post-treatment based on chemical leachate quality. These processes can be categorized to destructive and non-destructive processes based on separation or degradation of organic pollutants. Non-destructive processes include coagulation–flocculation, adsorption and membrane processes that transfer pollutants from liquid to solid phase as sludge [5]. Destructive processes are commonly known as advanced oxidation processes (AOPs) that are based on the production of hydroxyl radical ($^{\bullet}OH$) which is non-selective and highly reactive; attacking most of organic molecules [6]. Since landfill leachate consists of both suspended/colloidal and dissolved matters in large amounts, combination of separation and destruction mechanisms is promising for efficient treatment of this mixture. Actually, large amounts of colloids and suspended particles disturb the AOPs performance and increase consumption of energy and reagents (e.g. H_2O_2 and Fe^{2+} in Fenton process) that is not appealing economically. Thus, application of a separating process as a pre-treatment before the destructive process enhances the overall treatment efficiency by eliminating the interferences of suspended and colloidal species and also by lowering the organic load for the destructive process [7]. Coagulation–flocculation is an efficient process in which inorganic metal salts such as aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate are added to generate high-valence cations within the solution thereby reducing the zeta potential [8,9]. Generally, salts of ferric ion are superior to those of the aluminum mainly due to more insolubility of ferric ion salts within a wider pH range [10]. After removal of suspended matters in pre-treatment, AOPs are supposed to be employed for degradation of soluble organic fraction of the leachate. Among AOPs, Fenton

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Table 1
Characteristics of raw leachate.

Characteristics	Unit	Value
Chemical oxygen demand (COD)	mg/L	11,280 ± 300
Biochemical oxygen demand (BOD)	mg/L	1300 ± 100
Total organic carbon (TOC)	mg/L	3750 ± 100
Electrical conductivity (EC)	mS/cm	12.50 ± 0.1
pH		6.21 ± 0.05
Total solid suspended (TSS)	mg/L	3940 ± 350
Apparent		Black

process has broadly been applied to oxidize organic pollutants in many cases, from purification of contaminated groundwater to treatment of different industrial wastewaters [11–13]. In Fenton process, H_2O_2 reacts with Fe^{2+}, resulting in the generation of hydroxyl radical and ferric ion according to Eq. (1) [14–16]:

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow HO^{\bullet} + Fe^{3+} + H_2O \quad (1)$$

Produced hydroxyl radicals can oxidize large molecules to smaller ones that their toxicity is less than the mother substance. In addition, the biodegradability of obtained by-products may increase due to the detoxification occurring in Fenton oxidation [17].

For the reduction of cost in integrated processes, optimization of the first process can be a vital practice for improvement of total efficiency. Response surface method (RSM) is a statistical tool for optimization of chemical processes in wastewater treatment which evaluates relative significance of independent variables. Moreover, RSM optimizes process parameters with limited number of experiments and offers an empirical model for the responses [10,18].

In the present study, in order to investigate coagulation process as a pretreatment for Fenton oxidation, a high strength leachate sample was selected having high total suspended solids (TSS) and low biodegradability (low BOD_5/COD).

Coagulation process was optimized by RSM with three responses of COD, color and TSS removals, and treatment of coagulation effluent was evaluated using Fenton process. Eventually, biodegradability of treated effluent was assessed by different indices. Phyto-toxicity test with germination index (GI) was studied for the evaluation of the final effluents.

2. Materials and methods

2.1. Landfill leachate sample

Landfill leachate samples were collected from Kahrizak landfill nearby Tehran, Iran. In Tehran, 3500 tons of solid wastes are being disposed daily at Kahrizak site. After sampling of the leachate, the samples were preserved in dark polyethylene containers and kept in temperature of 4 °C. Table 1 shows some of the characteristics of the leachate used in this study.

2.2. Chemicals

All chemicals used in this study were of analytical grade. H_2O_2 (30%), ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and NaOH were purchased from Merck Company. All reagents used in COD tests (potassium dichromate, sulfuric acid (98%), silver sulfate, mercury sulfate and ferrous ammonium sulfate) were provided from Sigma–Aldrich.

2.3. Coagulation process

2.3.1. Design of experiments

The coagulation process was designed and optimized using response surface method (RSM). The experimental design and optimization were conducted with Mini Tab 16 software. Central composite design (CCD) was used to optimize the two factors of pH and coagulant dose as main factors in coagulation process. The range of pH values selected was based on the best performance of $FeCl_3$ (pH = 4–9) as coagulant. The dosages of $FeCl_3$ are chosen on the basis of preliminary experiments. Thirteen experiments were carried out including 4 cubic points ($\alpha = \pm 1$), 4 axial points ($\alpha = \pm 1.41$) and 5 replicates at center points ($\alpha = 0$). The experimental levels of the independent variables (factors) are presented in Table 2.

Table 2
Coded and actual levels of independent variables.

	Coded levels				
Independent variable	−1.41	−1	0	+1	+1.41
	Actual levels				
pH (X_1)	4.1	5	7	9	9.8
Coagulant dose (mg/L) (X_2)	790	1000	1500	2000	2210

2.3.2. Coagulation experiments

The jar test experiments were performed using a series of 6 glass beakers and jar test apparatuses (Phipps and Bird jar test). A 800 mL leachate sample was poured in each of the jars. Then, the solution pH was adjusted to desired value by sulfuric acid and sodium hydroxide (4N). After that, ferric chloride ($FeCl_3$) in various dosages was added into each of the jars. Rapid mixing and slow mixing were conducted at 120 rpm for 90 s and 40 rpm for 20 min respectively. Settling time was 30 min for sedimentation of flocs driven from coagulation–flocculation process. The supernatant samples were taken for the measurement of TSS, color and COD. It should be notified that maximum care was considered for sampling in case of TSS measurement in order not to disturb the settled flocs.

2.4. Fenton process experiment

The effluent of optimized coagulation process was introduced to Fenton process. The Fenton experiments were carried out in a 500 mL glass vessel filled with 200 mL coagulation undergone effluent. The pH was set at 3.0 (ideal pH for Fenton process) by sulfuric acid [15,16]. Ferrous dosage at appropriate quantity was added to the solution. After that, hydrogen peroxide was introduced to solution to start Fenton's reaction while the solution was mixed at 150 rpm by magnetic stirrer during experiment. Sample was taken from solution and analyzed for COD. In order to remove residual hydrogen peroxide, thermal process was used similar with the study of Deng [19].

2.5. Phyto-toxicity study

The phyto-toxicity with germination index (GI) was studied on seeds of radish (*Raphanus sativus*), tomato (*Lycopersicum esculentum*) and cress (*Lepidium sativum*). 30 seeds were uniformly placed in a Petri dish which contained a Whatman paper filter. 10 mL sample from each stage of treatment was poured into Petri dish and incubated for 72 h at 25 °C. Distilled water was used for control tests. The GI was calculated based on Eq. (2) [20,21]. All experiments were carried out in triplicate and results are reported as mean with standard deviation.

$$GI(\%) = \frac{G_s}{G_c} \times \frac{L_s}{L_c} \times 100 \quad (2)$$

where G_s is the number of germinated seeds in effluent, G_c is the number of germinated seeds distilled water, L_s is radicle length in sample and L_c is radicle length in distilled water. A simple ruler was used for measurement of radicle length in millimeter unit.