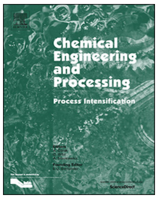
Chemical Engineering & Processing: Process Intensification 133 (2018) 148–159

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep



Intensification of landfill leachate treatment by advanced Fenton process using classical and statistical approach

Pranav H. Nakhate, Hrushikesh G. Patil, Kumudini V. Marathe*

Department of Chemical Engineering, Institute of Chemical Technology, Mumbai 400019, India

A R T I C L E I N F O

Keywords:
Advanced Fenton process (AFP)
Landfill leachate
One factor at a time (OFAT)
Box-Behnken design model (BBD)
Response surface methodology (RSM)

A B S T R A C T

The intensification of complex landfill leachate treatment using advanced Fenton process (AFP) (H_2O_2 + Fe(II) + Ozone) was investigated with classical One Factor At a Time (OFAT) and Statistical Experimental Design (SED) approach. The Classical OFAT was employed to identify the range of operating parameters whereas SED using the Box-Behnken Design model (BBD) with Response Surface Methodology (RSM) was employed to optimise the operating parameters. In the OFAT model, the optimum dosage of operating parameter viz. Fe(II) (0.06 mol/L), H_2O_2 (0.6 mol/L), ozone (30 gm/m^3) and pH (3) have shown COD and colour removal efficiency of 89.74% and 81.33% respectively within 120 min of reaction. Furthermore, in BBD, the optimum dosage at operating parameter viz. Fe(II) (0.06 mol/L), H_2O_2 (0.55 mol/L), ozone (25 gm/m^3) and pH (3) have shown COD and colour removal efficiency of 89.74% and 82.9% respectively. SED model also confirms the correlation between factors and their responses in line with OFAT. The present intensification approach has helped to achieve efficient way for complex landfill leachate treatment compared to other published studies.

1. Introduction

The human aggravation has consistently contributed to waste formation but this fact has been realized as a prominent issue only after massive demographic changes and industrialisation. The lack of solid waste management through proper channeling leads to some serious health concern [1]. Landfill waste disposal is the essential management strategy used by many countries due to its economic benefits [2,3]. According to central pollution control board India (CPCB), 7.80 million tonnes/annum of waste generated in India out of which 3.37 million tonnes/annum of waste goes to landfill (43.2%) [4]. This means roughly 0.2 to 0.6 kg per capita per day waste generated in India during 2014-15, depending upon the demographic size and shape and estimated to increase by 1.33% annually [4]. Despite that, one of the major environmental concern about landfill is the generation of leachate or water of precipitation which gets formed by rainwater draining through waste layer during the decomposition process [5]. Leachate may also get formed due to underground water which has been in contact with deposited waste as well as due to the biological activities carried out because of organic components from deposited waste [5,6].

Leachate is one of the hazardous effluent characterised by high concentrations of chemical oxygen demand (COD) (30,000–60,000 mg/L) [7], biochemical oxygen demand (BOD) (4,000–6,000 g/L) [8,9], colour, heavy metals, ammonia (500–2000 mg/L) [9], humic acid, and toxic organic and inorganic salts [10]. The leachate composition may vary depending on the origin of wastes, types of waste, waste management and landfill age [11]. As the landfill age increases, the biodegradability ratio changes accordingly [8,12]. The juvenile leachate ($<$ 5 years) usually characterised by having high BOD, COD and organic content values as well as higher biodegradability index (0.15-0.25) [9,12,13]. Matured leachate ($<$ 5–7 years) on the other hand have much lower concentrations of biodegradable organic components due to anaerobic degradation, therefore, having lower biodegradability index ($<$ 0.1) [6,14]. These complex characteristics of leachate cause hurdle in developing a comprehensible technique that can treat variously aged leachate, therefore combined sequential techniques have been studied recently, including flocculation-coagulation-adsorption, aerobic-anaerobic degradation and chemical oxidation [15–17]. Biological wastewater treatment processes like up-flow anaerobic sludge bioreactors (UFASB) etc. have been implemented for treatment of high strength effluents including juvenile leachate due to their cost-effective nature, high organic loading as well as their ammonia removal efficiency [18]. However, large COD quantity consumes a large amount of dissolved oxygen from effluents whereas colour being unamenable, blocks the sunlight leads to highly anaerobic condition [19].

Since the past two decade, physicochemical techniques for

---

* Corresponding author.
E-mail address: kv.marathe@ictmumbai.edu.in (K.V. Marathe).

https://doi.org/10.1016/j.cep.2018.10.004
Received 22 June 2018; Received in revised form 1 October 2018; Accepted 7 October 2018
Available online 09 October 2018
0255-2701/

wastewater treatment have gained significant importance due to their high efficiency and low-cost approach. In 1980, the concept of an advanced oxidation process (AOP) was introduced for wastewater treatment after its successful implementation in potable water treatment [20,21]. AOP produces hydroxyl radicals $OH^{\bullet}$ which are the most reactive oxidizing agent having an oxidation potential of 2.80 V against calomel electrode (reference electrode) [22]. Deng Y. and Zhao R. (2015) have done a detailed review on various AOP's, their principles and their impacts on wastewater treatment, in which they mentioned that $OH^{\bullet}$ are non-selective and reacts with various species with rate constants of 10^{8}-10^{10} $M^{-1}s^{-1}$. The main AOP which involves generation of $OH^{\bullet}$ include ozone (O_3), hydrogen peroxide (H_2O_2), etc. [21]. The integration of powerful oxidizing agents like oxygen (O_2), O_3, H_2O_2, Ultra-violet (UV) light, solar light, radiation, ultrasound, Fenton along with semiconductor catalysts [22–24] can be effective in increasing biodegradability as well as reducing COD and colour intensity of mature landfill leachate [6].

Fenton process has been widely used for the oxidation of different organic components from various wastewater stream as it contains high oxidation potential of 2.72 V [25]. It basically includes the mixture of H_2O_2 and ferrous salts (Fe(II)) from ferrous sulphate ($FeSO_4$) which form a high concentration of $OH^{\bullet}$ with rate constant between 53–76 $M^{-1}s^{-1}$ [25,26]. Other AOP's are compelling in effluent treatment, however, Fenton process has significant performance as it can be operated at ambient temperature, the reagents can be available radially, safe to handle and do not require illumination [25]. The combination of Fenton process along with other oxidizing agents can improve the formation of $OH^{\bullet}$ and can be termed as advanced Fenton process (AFP) [27]. A combination of Fenton process with UV radiation is called photo-Fenton process (PFP), incorporation of biological methods with electro-Fenton process, termed as Bio-electro-Fenton [28,29], whereas, in an electro-Fenton process (EFP) [30], both Fe(II) and H_2O_2 are electro generated via reduction on electrodes [31]. Extensive research can be observed in literature where PFP or EFP as a part of AFP was used for the treatment of landfill leachate [31–33], As discussed earlier, ozone itself has higher oxidation potential and selectivity towards organic pollutants but very few research articles have considered ozone as an oxidizing agent in association with Fenton process. several research papers have carried out ozonation either as a pre-treatment for Fenton experiments or post-Fenton experimentation to improve the treatment efficiency [34]. Composition and subsequent complexity of the effluent may hamper the utilisation quantity of ozone or Fenton process, if used as a single entity [35]. Moreover, use of AFP for the effluent treatment may decrease the operational cost based on energy consumption, enhance $OH^{\bullet}$ availability and increase the COD reduction.

Abu Amr, S. A. and Aziz Hamidi carried out the optimisation of stabilized landfill leachate using ozone/Fenton's reagent in a single process for the first time. They studied operating parameters including ozone dosage, Fenton's reagent ratio, pH and reaction time where the highest COD and colour reduction of 65% and 98% was observed respectively [36]. Abu Amr, S. A., and co-workers also carried out experiments to treat 20 L landfill leachate in order to investigate the efficiency of ozone/Fenton process in which they observed the highest COD and colour reduction of 78% and 98% respectively [35]. Therefore, it can be beheld that, in presence of Fenton's reagent and ozone the rate of formation of $OH^{\bullet}$ can be accelerated resulting into the degradation of organic components from landfill leachate [37].

The innovativeness of the present study lies in the incorporation of Fenton process with ozonation (H_2O_2 + Fe(II) + Ozone) in a single step to intensify "juvenile" landfill leachate treatment using OFAT for optimization of operating parameters including Fe(II) dosage, H_2O_2 dosage, ozone dosage, pH and reaction time. The statistical correspondence amongst individual factors like Fe(II) dosage, H_2O_2 dosage, and ozone dosage were evaluated using BBD with RSM. The treatment efficiency was evaluated in terms of COD and colour reduction. Moreover, lab scale dataset was developed along with approximate cost estimation based on power dissipation, for future scale-up studies at effluent treatment plant (ETP) which may help in commercializing the process.

2. Materials and methodology

2.1. Materials

The chemical required for the AFP procedure viz. H_2O_2 (30% w/v), Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), Sulfuric acid (H_2SO_4), and Sodium hydroxide (NaOH) were obtained from SD fine chemicals limited, India. Ozonator of model Zeon 100 from Waterhouse, India was used for ozone generation with a constant output of 0.5 g/h (Max. 10 W electricity consumption). The Chemicals required for analysis purpose including Potassium Iodide (KI), Silver Sulphate (Ag_2SO_4), Mercury Sulphate ($HgSO_4$), Potassium Dichromate ($K_2Cr_2O_7$), Ferroin Indicator (0.025 M), Glucose, etc. were also purchased from SD fine chemicals Limited, India.

2.2. Leachate sampling

The leachate sample was collected from Deonar dumping ground, located at eastern suburb of Mumbai city, India. It is India's oldest and largest dumping ground with 132 ha (ha) of area and collection of almost 9000 tonnes of landfill wastes per day. Initial COD of landfill leachate was around 25,000 mg/L which was brought down to around 4000 mg/L (± 400) at end of UFASB in ETP using initial techniques. The landfill leachate sample was collected after UFASB reactor operation therefore, the sample was filtered prior to experimentation and stored in a dark area in order to avoid further decomposition. The collected leachate effluent contained high COD concentration of 3744 mg/L, total dissolved solids (TDS) concentration of 12,089 mg/L, the conductivity of 18.46 mS/cm, pH of 7.8 and reddish dark brown coloration due to the presence of complex landfill components showing the absorbance of 3.6 at 240 nm.

2.3. Experimental procedure

The AFP experiments were performed employing both classical OFAT and SED approach. A jacketed three-neck glass reactor with a net volume of 500 mL incorporate with a gas inlet and outlet facilities were designed for AFP experimentation. The chemicals required for AFP were used without any further purification. The Fenton's reagent was freshly prepared at every individual experiment by addition of appropriate amount of H_2O_2 and $FeSO_4.7H_2O$ whereas ozone was generated from atmospheric oxygen via corona discharge technique using laboratory scale ozone generator. Firstly, 200 mL of landfill leachate sample with initial COD 3744 mg/L was taken into glass rector. Secondly, a known quantity of $FeSO_4.7H_2O$ (for generation of Fe (II)) was added into the reactor followed by immediate addition of a known volume of H_2O_2. The sample was stirred vigorously at 1000 rpm on a magnetic stirrer for Fenton process whereas ozone was added into the closed reactor for AFP. The AFP experimentation was performed under constant stirring and at ambient temperature (303 K) whereas excess ozone was trapped in 1% KI solution outside the glass reactor. In classical OFAT approach, the impact of individual components was studied by varying their concentration. The Fe (II) concentration was varied from 0.02 mol/L to 0.1 mol/L, H_2O_2 concentration was varied from 0.1 mol/L to 1 mol/L, ozone dosage was varied from 10 g/m^3 to 40 g/m^3 whereas initial pH was varied from 3 to 9 using digital pH meter. After an appointed reaction time, 0.1 N NaOH was added to sample to adjust final pH at 7 approximately. The treated leachate sample was then filtered through 0.45 μm filter prior to analysis.