

Industrial solid waste landfill leachate treatment using electrocoagulation and biological methods

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a b s t r a c t

This paper aims to provide a treatment approach to the landfill leachate using electrochemical (EC) method and bio gas generation. The study mainly focused on the affecting parameters of the EC process, such as electrode material, initial pH, applied voltage, inter electrode distance, electrode reactive surface and insituperoxi-EC. The pH-7 has been observed to be the best for the removal of metals. Fe–Fe electrode pair with 1cm inter-electrode distance and electrode surface area of 40 cm² at an applied voltage of 7 V has been observed to be more efficient in the metal removal. The maximum removal percentage of the Ni, Zn, Pb, Cu, Fe and COD have been observed to be 95, 99.6, 98, 97.2, 73 and 60% respectively along with 13.4% of bio-hydrogen. Treatment cost also evaluated. This method has been observed to be very effective for the of landfill leachate.

Keywords: Land fill; Leachate; Electrocoagulation; Heavy metal; Bio-fermentation; Hydrogen

1. Introduction

Growing trend in global population, urbanization and industrialization towards achieving high quality of life and well-being of the population has resulted high amount of solid wastes being generated. The developing country like India has to develop the sustainable technology to manage industrial solid waste. The current solid waste disposal method is secure land filling. However, leachate is a promising problem from that land filling site, which has serious than that of industrial wastewater to the ecosystem [1] and contains both biodegradable and resistant organic compounds, heavy metals, suspended solids, chlorinated compounds and inorganic salts and exhibiting acute and chronic toxicity [2]. Some of the treatment methods such as biological treatment methods [3], membrane processes [4], advanced oxidation techniques [5], coagulation–flocculation methods [6], lagoon and wetland applications [7] have been examined in the literature. Because its characteristics change with advancing years of the landfill, these test methods have troubles such as decreasing treatment efficiencies and increasing cost [5,8]. Therefore, the implementation of a joint treatment comprising of a few treatment steps has been used to solve the problem. The electrochemical method followed by biological expected to be sufficient to treat such type of complex liquids.

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Electrocoagulation (EC) presents a robust novel and innovative alternative in which a sacrificial metal anode doses water electrochemically, which is applied for the treatment of many type of industrial wastewaters [8].

The reactions occurring in an electrochemical cell involving Iron (Fe) electrodes are as follows:

Reactions:

$$
\text{Fe} \to \text{Fe}^{2+} + 2^{\text{e-}} \tag{1}
$$

$$
2H_2O + 2^{e^-} \rightarrow 2H_{2(g)} + 3OH^-
$$
 (2)

$$
\text{Fe}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq}) \rightarrow \text{Fe (OH)}_{2(s)}
$$
 (3)

Fe metal ions immediately form hydroxides and/or poly hydroxides that finally transform into $Fe(OH)_{2}$ (S), as shown in Eqs. (1) and (3) (electrocoagulation). Hydroxides have strong affinity to capture the pollutants in the waste water, causing more pollutant removal than those conventional methods. Eq. (2) involves electro oxidation phenomena [9,10].

$$
Me^{n+} + nOH^{-} \rightarrow Me(OH)n(s)
$$
 (4)

The metal hydroxide floc formed from Fe electrode normally acts as adsorbents and/or traps for metal ions. Therefore, they would eliminate them from the solution. Simultaneously, the hydroxyl ions produced at the cathode increase the pH in the electrolyte and may induce co-precipitation of Fe, Cu, Pb, Ni, and Zn in the form of their corresponding hydroxides [Eqns. (3), (4)][9,11].

The organics present in the leachate will not be completely removed with single electrocoagulation method, however, addition of oxidizing agents can enhance the removal of organics. Hydrogen peroxide is most often used as chemical oxidant to improve the radical formation to degrade the organic pollutants.

$$
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}
$$
 (5)

With peroxide dosage the enhanced production of hydroxyl radicals [Eq. (5)] would degrade organic matter in the landfill leachate effectively [12].

Further, a combined electrocoagulation-biological treatment system results in high organic matter removal efficiency since it reduces the processing time and supply of water for dilution. Moreover, biological fermentation of organics with mixed consortia is also advantageous as it generates clean and renewable energy carrier gas at lowcost, thus attracting worldwide attention to sustain the future energy resources.

In the present study, the efficiency of electrocoagulation for the treatment of land fill leachate has been reported. The effect of electrode material, initial pH, applied voltage, inter electrode distance, reactive electrode area and insituperoxi EC on the treatment efficiency has been explored and discussed to determine the optimum operational conditions. Biological treatment has also been applied to enhance the COD removal at optimized electrocoagulation. The operating cost of treatment is also investigated, by considering the cost of consumption of electric power and electrode.

2. Material and methods

2.1. Electroplating wastewater

Leachate has been collected from land filling site in Hyderabad, India. The initial characterization of the sample has been given in Table 1.

2.2. Methodology

Batch mode experiments have been carried in a 250 ml beaker with the working volume of 200 ml at room temperature (27°C). The three electrode materials (Fe, Al and stainless steel) have been used as anode and cathode with dimensions of 100 mm \times 50 mm \times 2mm. The pH of the leachate varied from 5–11 (4, 6 and 8), effective reactive surface area studied between $10-40 \text{ cm}^2 (10, 20 \text{ and } 40 \text{ cm}^2)$, distance between electrodes studied between 1–4 cm (1, 2 and 4 cm) and effect of applied voltage had been studied at 4 and 7 V, respectively. The adjustment of pH is made with 0.1 N/ 1.0 N solution of HCl or 0.1 N/ 1.0 N NaOH. Working electrodes are connected to a DC power supply (APLAB regulated DC power supply L6403) unit with 0–84 V voltage supply capacity. Hydrogen peroxide is added to the electrocoagulation unit at above optimized conditions dosages with variation of peroxide from 250–1250 ppm. The samples are collected at an interval of 10 min for 30 min and analyzed for pollutant content.

To enhance the organic matter removal, anaerobic biological fermentation in batch mode is combined with EC. The 320 ml batch reactor with working volume of 250 ml used for biological treatment of the leachate at room temperature under anaerobic conditions.

The active microbial innoculum is introduced in to the leachate and kept it for acclimatization for 20 d. The acclimatized mixed consortium is used for further treatment studies, where simultaneous biog as production is observed and analyzed using gas chromatography.

Table 1 Initial characterization of the landfill leachate

2.3. Analytical instruments

Physicochemical parameters such as pH, electrical conductivity, alkalinity, total hardness, calcium hardness, chlorides and chemical oxygen demand (COD) are determined accordance to standard methods (APHA 2005). The physico chemical instrumental analysis has been carried using double beam Shimadzu UV 2450 UV-Visible Spectrophoto meter, and metal analysis using Atomic absorption SensAA Spectrometer.

Hydrogen gas analysis carried using Gas ChromatographyAgilent-6890 equipped with a thermal conductivity detector (TCD) and a 2 m column packed with 5A molecular sieves. Nitrogen gas is used as the carrying gas at the flow rate of 30 ml/min. The operating temperatures of the column, detector and injector were 80, 100 and 100°C, respectively.

The pollutant removal percentage (%) is calculated as follows:

Removal of the pollutant
$$
(\%) = \frac{C_i - C_f}{C_i} \times 100
$$
 (6)

where *C_i* is the initial pollutant concentration (mg L^{−1}) and C_f is the final pollutant concentration (mg L^{−1}).

The hydrogen % present in the produced gas is calculated using the following formulae:.

%
$$
H_2 = \frac{A}{SA} \times \%S
$$
 (7)

where $A =$ sample area; $SA =$ standard area; $S =$ Purity of the standard.

2.4. Operation cost evaluation (OC)

One of the most important parameter affecting the application of any method is operating cost, which heavily determines cost of the treatment process. The OC of the EC is calculated [Eq. (8)] by including the material cost (mainly electrodes), utility cost (mainly electrical energy) and chemicals fixed costs [6,9].

$$
OC = aC
$$
 energy + bC electrode + cC chemicals (8)

where 'a' is the electricity consumed (kWh/m^3) , 'b' is the electrode material consumed $(kg/m³)$ and 'c' chemicals is consumption quantities of chemicals $(kg/m³)$ of the wastewater treated. The cost values (\$) of a, b and c calculated according to the Indian market (January, 2015). It is the energy price as 0.1 \$/kWh (6.40 Rs/kWh)), electrodes price as Fe-1.61\$/kg; Al-3.27\$/kg (97 Rs/kg and 197 Rs/kg)) and chemical cost (H_2O_2) as $9.07\frac{6}{572}$ Rs/l)).

The electrode and energy consumption were calculated using the following equations:

$$
C \text{ energy} = \frac{U I t_{EC}}{V} \tag{9}
$$

$$
C \, electrode = \frac{It_{EC}M}{ZFV} \tag{10}
$$

where *U* is cell voltage(V), *I* is the current (A), t_{EC} is the operating time (h), V volume of the sample (m^3) , \overline{M} is the molecular weight of electrode (for Fe-55.84 g/mol, Al-26.98 g/mol , *Z* is number of electrons transferred ($Z = 3$ for Al and 2 for Fe), F is the Faraday constant (96487C/mol).

3. Results and discussion

3.1. Effect of reaction time on leachate treatment by EC

The reaction time for metal removal from leachate has been investigated at different reaction time intervals (10–30 min) with Fe–Fe electrodes. From the results it is observed that, a maximum of 24% COD removal has been achieved at 30 min while the maximum removal of metal has been observed (Fig. 1) to be 53, 53, 73, 95 and 50% of Ni, Zn, Pb, Cu and Fe respectively at the reaction time of 20 min. After 20 min, removal rate has not increased to a considerable range, which might be due to passivation layer on the electrode material. Similar results have been also observed by Bazafshan et al., [13] and Sepideh et al., [14]. Therefore, to avoid excess operational cost, the reaction time has been optimized to 20 min.

3.2. Effect of electrode metal on leachate treatment by EC

The identification of the electrode material is also an important parameter to know the coagulant affinity. The materials most widely tested for their effectiveness are iron, aluminum and stainless steel as they are cheap and readily available. The maximum metal removal has been achieved with the Fe–Fe electrodes and hence considered as the optimum choice. Moreover, the settle ability of particle formed by Fe–Fe electrode combination by $Fe(OH)_{3}$ is better than that formed by $\mathrm{Al(OH)}_3$. Similar results were observed by Li et al., [15]. The COD removal has been observed to be better with the SS electrode, which is of 40% (Fig. 2). This might be due to the OH radicals released from the SS surface.

3.3. Effect of applied voltage on leachate treatment by EC

Applied voltage is one of the operating parameters directly affecting the performance and the operating cost.

Fig. 1. Effect of reaction time on leachate treatment by EC. Experimental conditions: electrode material: Fe; applied voltage: 6V; pH: 6; area of the electrode: 40 cm²; volume of the sample: 200 ml; inter electrode distance: 2 cm; reaction time 10, 20, 30 min.

Fig. 2. Effect of electrode metal on leachate treatment by EC. Experimental conditions: electrode material: Fe, Al, SS; applied voltage: 6 V; pH: 6; area of the electrode: 40 cm²; volume of the sample: 200 ml; inter electrode distance: 2 cm; reaction time: 20 min.

Fig. 3. Effect of applied voltage on leachate treatment by EC. Experimental conditions: electrode material: Fe; applied voltage: 4 V, 5 V, 6 V, 7 V; pH: 6; area of the electrode: 40 cm²; volume of the sample: 200 ml; inter electrode distance: 2 cm; reaction time: 20 min.

EC experiments have been carried out at 4 V, 5 V, 6 V and7 V (Fig. 3). At 7 V the maximum removal of metals had been found to be 74, 65, 94, 95, 62 and 29% of Ni, Zn, Pb, Cu, Fe and COD respectively. With increase in voltage, treatment efficiency also increased which might be attributed to increase in both the coagulant dose and bubble generation rate [16]. Akbal et al., [17] also observed the same order of removal while treating the metal plating wastewater.

3.4. Effect of initial pH on leachate treatment by EC

The initial pH of the solution shows considerable effect on the removal efficiency of the electrocoagulation process. In the present study, it has been observed (Fig. 4) that metal removal efficiency is optimum at neutral conditions. At pH 7 the maximum removal was observed to be 95, 99.4,

Fig. 4. Effect of initial pH on leachate treatment by EC. Experimental conditions: electrode material: Fe; applied voltage: 7V; pH: 5, 6, 7, 9, 11; area of the electrode: 40 cm^2 ; volume of the sample: 200 ml; inter electrode distance: 2 cm; reaction time: 20 min.

98, 97, 69 and 40% of Ni, Zn, Pb, Cu, Fe and COD respectively. However, with increase or decrease in pH from 7, the removal rate decreased which might be due to the solubility of discharged metal ions [18]. Same trend has been observed by Liet al., [15].

3.5. Effect of Inter electrode distance on leachate treatment by EC

The inter-electrode distance has been studied as a parameter to minimize electricity consumption for the treatment of leachate. Inter-electrode distance varied at 1 cm, 2 cm and 4 cm. The removal percentage of metals has been observed to be decrease with increase in inter-electrode distance from 1 to 4 cm (Fig. 5). The maximum removal achieved were Ni (95%), Zn (99.4 %), Pb (98 %), Cu (97 %), Fe (69%) and COD (40%) at the shortest distance (1 cm) between the electrodes with electrode area of 40 cm². Similar observations have also been reported by Ashok Kumaret al., [19] and Ghosh et al., [20].That removal efficiency increase might be due to the faster anion discharge at the anode and improved oxidation. It also reduces resistance, the electricity consumption and consequently, the cost of the wastewater treatment [9,21].

3.6. Effect of reaction area on leachate treatment by EC

Reaction surface area has been studied at 10, 20 and 40 cm2 to minimize reactive surface area and electrode consumption for the treatment. The metal removal efficiency decreased with decrease in electrode reaction area from 40 cm^2 to 10 cm². The maximum % removal efficiency of Ni, Zn, Cu, Pb, Cu, Fe and COD were observed (Fig. 6) to be 95, 99.4, 98, 95, 69 and 40%, respectively. This might be attributed to a greater electrode area that produced larger amounts of anions and cations from the electrodes. The larger the electrode surface,the increased rate of floc's formation, which in turn influenced the removal efficiency. Similar results were observed by Ashok Kumar et al., and Ghosh, et al., [19,20].

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Fig. 5. Effect of inter electrode distance on leachate treatment by EC. Experimental conditions: electrode material: Fe; applied voltage: 7 V ; pH : 7 ; area of the electrode: 40 cm^2 ; volume of the sample: 200 ml; inter electrode distance: 1 cm, 2 cm, 4 cm; reaction time: 20 min.

Fig. 6. Effect of reaction area on leachate treatment by EC. Experimental conditions: electrode material: Fe; applied voltage: 7 V; pH: 7; area of the electrode: 10 cm^2 , 20 cm^2 , 40 cm^2 ; volume of the sample: 200 ml; inter electrode distance: 1 cm; reaction time: 20 min.

3.7. Effect of insitu- peroxide EC on leachate treatment

The effect of different hydrogen peroxide dosages (250 ppm–1250 ppm) on the treatment efficiency has been shown in Fig. 7. The metal removal has not been significantly influenced by the addition of peroxide. However, the COD removal efficiency increased with increased hydrogen peroxide dosage, where maximum COD removal efficiency of 56% at 750 ppm peroxide dosage was observed. Similar results were observed by Merve Oya Orkun [21]. Addition of excess peroxide above 750 ppm of the dosage did not increase the removal rate which might be attributed to the formation of hydroperoxyl radical $HO_{2'}^-$ a much weaker oxidizing radical than hydroxyl radical [Eq. (11)] [22,23].

Fig. 7. Effect of insitu- peroxide EC on leach at treatment. Experimental conditions: electrode material: Fe; applied voltage: 7 V; pH: 7; area of the electrode: 40 cm²; volume of the sample: 200 ml; inter electrode distance: 1 cm; reaction time: 20 min, hydrogen peroxide dosage: 250, 500, 750, 1000, 1250 ppm.

Table 2

Operational cost for the treatment of leachate

$$
H_2O_2 + OH \rightarrow HO_2^- + H_2O \tag{11}
$$

The treatment cost for the leachate at optimum condition has been observed to be $10.4 \text{ US} \$/\text{m}^3$ (Table 2).

3.8. Biogas production and treatment of leachate

In the biological treatment of leachate samples, the degradation of organic matter has been observed to be 20%, where hydrogen production of 13.4% has been achieved at room temperature. The peak area for the standard hydrogen, acclimatization stage and fermentation of leachate has been observed to be 265, 2.3 and 36.5 respectively. During acclimatization studies only 2.3% of hydrogen has been observed. However with leachate fermentation process the production of hydrogen of 134 ml out of 1000 ml biogas has been observed. After biological treatment, pollutant removal carried with EC and the removal of Ni, Zn, Cu, Pb, Cu, Fe and COD observed to be 95, 99.6, 98, 97.2, 73 and 60% respectively.

4. Conclusions

This study concluded that biological fermentation followed by EC is efficient and effective for the removal of pollutants from industrial solid waste landfill leachate. The maximum removal of metal is observed at a reaction time of 20 min, initial pH of 7, electrode material as Fe–Fe, electrode reaction area of 40 cm², applied voltage of 7 V and electrode spacing of 1 cm. Iron electrodes are found to be most ideal electrodes, compared to aluminum and SS electrodes. Metal removal rate increased with increasing current applied voltage and electrode surface area. However, it decreased with increasing inter-electrode distance. Under optimum treatment conditions % removal of metal has been found to be 95, 99.6, 98, 97.2, 73 and 60% of Ni, Zn, Cu, Pb, Cu, Fe and COD respectively along with 13.4% of bio hydrogen.

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