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# Optimization of COD and Colour Removal From Landfill Leachate by Electro-Fenton Method

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**Abstract:** The contamination of untreated leachate effluent is a potential source to effect of soil, surface and groundwater.In this study, the treatment of landfill leachate by electro-Fenton (EF) method was studied. The objectives of the study are to determine the optimum current density, the optimum treatment time, the optimum pH, the optimum hydrogen peroxide ($H_2O_2$) dosage and the optimum ferrous sulphate heptahydrate ($FeSO_4 \bullet 7H_2O$) dosage of landfill leachate samples using aluminium electrode. From the results, it is verified that electro-Fenton method (EF) can used efficiently to degrade leachate organics. The best removal efficiencies were obtained when current density value is 200 A/m$^2$, treatment time is 25 min and pH value is 4. The optimum dose of hydrogen peroxide ($H_2O_2$) is 800 mg/L which was obtained 78% and 96% of COD and colour removal efficiency respectively. The optimum ferrous ion ($Fe^{2+}$) is 1000 mg/L which was obtained 75% and 94% of COD and colour removal efficiency respectively.

**Key words:** landfill leachate, electro-Fenton, COD, colour, aluminium electrodes

## INTRODUCTION

Recently, the industrial and commercial growth in many countries has been affected in the increases of both municipal and industrial solid waste generations. Percentage composition of solid waste is different between areas because it is influenced by several factors such as location, community attitudes, frequency of collection, legal systems, population characteristics, socio-economic and lifestyle. Up to 95% of solid waste generated worldwide is currently disposed in landfill (Bohdziewicz and Kwarciak, 2008). Leachate is a high strength wastewater which has been recognized as one of the most concerned pollution sources. Landfill leachate is the hazardous and heavily polluted wastewater, formed as a result of percolation of rainwater and moisture through solid waste in the landfill site (Bohdziewicz and Kwarciak, 2008; Amuda, 2006). Landfill leachate contain high load of organic matter, high content ammonia nitrogen, heavy metals, inorganic salts and chlorinated organic. The composition of leachate depends on age of landfill, hydrogeology of the site, quality and quantity of solid waste, site climate, season, biological and chemical processes occurring in the landfill and the amount of precipitation and percolation of rainwater, landfill morpology, waste depth, landfill condition and operation of facilities (Li *et al.*, 2010). Lately, advanced oxidation processes (AOPs) have been studies because of their ability to generate radical intermediate compounds. The radical intermediate compounds contain highly oxidative species which are capability to oxidize toxic pollutants into harmless species. Technologies of oxidation processes such as Fenton oxidation, photo-oxidation and electro-oxidation are recurrently applied to increase efficiency of electro-chemical methods in order for degradation and decolourization of wastewater.

Today, there has been an increases focus on the use of electro-chemical methods which can produce OH• as the main oxidizing agent ( Brillas *et al.*, 2000; Kraft *et al.*, 2003; Mohajeri *et al.*, 2010). One of the promising of ability to degrade pollutants effectively is electro-Fenton (EF). Electro-fenton (EF) method has been applied with combination of fenton oxidation and electrochemical are carried out together and each of them is a powerful treatment method (Atmaca, 2009; Brillas and Casado, 2002; Mohajeri *et al.*, 2010). This process is use of electrically assisted Fenton reaction will produce more OH• radicals and the oxidation of the organics to $CO_2$ can be enhanced in the same period (Mohajeri *et al.*, 2010; Liu *et al*., 2007). Normally, there are two different electro-Fenton (EF) applications. In the first one the Fenton's reagents (Fe (II) and $H_2O_2$) are added to the reactor from outside and inert electrodes having high catalytic activity are used as anode material. In the second one, $H_2O_2$ is added from outside and Fe (II) is provided from sacrificial cast iron anodes. In the electro-Fenton process, hydrogen peroxide ($H_2O_2$) is produced in the required amount from the electrochemical reduction of oxygen. Hydroxyl free radical is generated by interaction of $H_2O_2$ with ferrous salts namely the Fenton reagent.

The objective of this study was to examine the efficiency of electro-Fenton process for removal of COD and colour from landfill leachate. The experiments involved with the determination of current density, treatment time, pH, dose of hydrogen peroxide ($H_2O_2$) and ferrous sulphate heptahydrate ($FeSO_4 \bullet 7H_2O$) on identification

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of the optimum experimental conditions for the efficient application of these processes. In this study, the used of aluminium plate as electrodes.

## MATERIALS AND METHODS

### *Preparation of Sample:*

The study was conducted on leachate samples from Simpang Renggam municipal landfill site in Johor. This site located at latitude $1^0$ 53'41.64" North and longitude $103^0$ 22'34.68" East in Kluang district, Johor State, Malaysia. Sample has been taken and stored according to the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF, 2005). Leachate samples were taken from landfill site by using a submersible pump is submerged at a depth 1500 mm from the surface leachate site. Landfill leachate samples are collected and stored in bottles and kept in a room at 4°C prior to use to avoid degradation or changes to its characteristics. The initial characteristics of COD and colour for landfill leachate samples were determined. **Table 1** were shown the initial characteristics of the raw landfill leachate.

**Table 1:** Characteristics of landfill leachate collected from Simpang Renggam Municipal Landfill Site

| Parameter | Initial Characteristics |
|---|---|
| Chemical Oxygen Demand (COD) | 13166-13500 |
| Suspended Solids (SS) | 270-1200 |
| Ammonia Nitrogen ($NH_3$-N) | 755-2670 |
| Colour | 2393-12400 |
| pH | 8.31-8.47 |

*All units are in mg/L except for pH and Pt.Co for colour

### *Experiment Set Up:*

The electro-Fenton experiments were using 1000 mL beakers as reactors with the diameter of 11 cm by vertically positioned Al-Al electrode spaced by 5 cm which carried out on laboratory scale. The electrodes dimension of each electrode was 200 mm × 50 mm × 1 mm made of aluminium are connected to a digital direct current (DC) power supply (MPS 3030DD Model) in bipolar (Al-Al) electrode modes. A direct current (DC) power supply was used to provide the desired current. Initial leachate pH was adjusted to the desired values with concentrated sulphuric acid or sodium hydroxide before adding Fenton reagents. The anodes and cathodes are connected to the positive and negative outlets of a DC power supply. The total effective working areas are 0.010 $m^2$ when immersed 10 cm into the leachate sample. In each run, a pre-decided amount of ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide ($H_2O_2$) were added into leachate samples to activate electro-Fenton reactions before the electrical current was turned on. The leachate was stirred thoroughly with a magnetic stirrer. At an appropriate time intervals, DC power supply was turned off and the reactions was terminated. At the end of each run, the sample were allowed to stand 30 minutes settling time and the supernatant was then taken for water quality measurements. COD was measured using a DR5000 spectrophotometer (HACH spectrophotometer) and colour was measured using same spectrophotometer at 465nm wavelength.

### *Apparatus:*

### *Reactor (glass tank):*

One liter glass beaker is used as the reactor tank in the experimental studies.

### *Electrodes:*

Aluminum electrodes are used in the electrocoagulation process as plates for the anodes and cathodes with the dimension of 200 mm high × 50 mm wide × 1 mm thick.

### *pH:*

HACH Sension3 pH meter is used to determine the pH of the POME samples. To obtain the optimum pH value, the pH of landfill leachate samples was adjusted by adding sodium hydroxide (NaOH) or sulphuric acid ($H_2SO_4$).

### *Chemical Oxygen Demand and Colour Analyses:*

COD and colour analyses are performed in accordance to the standard methods described in (APHA, AWWA, WEF, 2005) with the use of DR 5000 spectrophotometer.

## RESULTS AND DISCUSSION

***Optimum Current Density:***

Figure 1 was shown the optimum current density on the removal efficiency of COD and colour for Al-Al. In this study, the optimum current density is 200 A/m$^2$ which was obtained 74% and 96 % of COD and colour removal respectively. Amount of current density is an important operation condition to electrodes. According to Atmaca (2009), since the current was applied to electrodes increases, production of Fe (II) required for Fenton oxidation becomes higher. Nevertheless, under high DC current applying, the efficiency may not change significantly while energy consumption of the method increased. From the results, there are closed readings each other of 150 A/m$^2$, 200 A/m$^2$ and 250 A/m$^2$. As expected, it was found that the removal efficiency increased with the increase of current density.

However, after 200 A/m$^2$ the removal efficiency for COD and colour was decreased. COD removal increases when the high of current use but speed of the COD removal will be slow down when the current higher than 200 A/m$^2$. There is similar result with Atmaca (2009) and Zhang *et al., (*2006). This phenomenon was caused by the interfere reactions. However, interfere reactions can be reduced by using the proper Fe (II)/$H_2O_2$ and Fe (III)/$H_2O_2$ ratios and initial pH. According to Boye (2003) and Brillas *et al.,* (2004) the decreased in current efficiency is because of the formation of hardly oxidizable products.

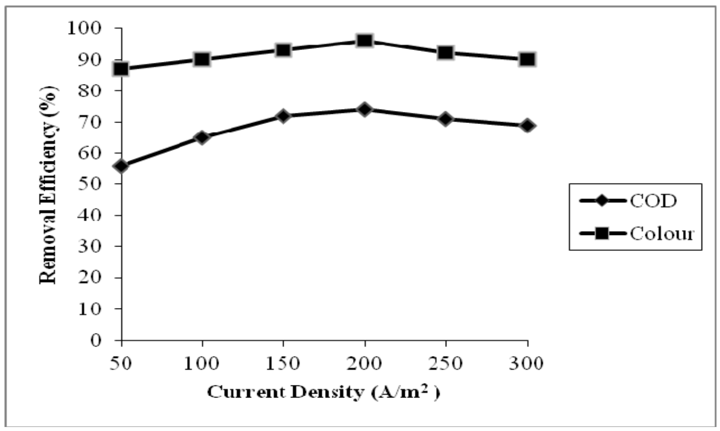


**Fig. 1:** Effects of current density on COD and colour for Al-Al at pH 3, treatment time 30 minutes, $H_2O_2$ 600 mg/L, $Fe^{2+}$ 600 mg/L, distances between electrodes 5 cm and settling time 30 minutes.

***Optimum Treatment Time:***

Figure 2 were shown the optimum treatment time on the removal efficiency of COD and colour for Al-Al.The best removal efficiencies were obtained when treatment time is 25 minutes. COD and colour were achieved 73 % and 95 % removal respectively. The results showed that the removal efficiency of COD and colour has decreased when treatment time over than 25 minutes. Zhang (2007) has been investigated of hydrogen peroxide added in a single step and in a continuous mode with feeding time. From their results, the initial COD removal rate increased with the decreasing feeding time and it reached highest when hydrogen peroxide was applied all at once. Also that, the decrease of feeding time, the concentration of hydrogen peroxide during the initial period would increase.

This phenomenon will be more hydroxyl radicals would be generated resulting from the chain reaction between hydrogen peroxide and ferrous ion. According to Lin and Chang (2000) the treatment time is to complete the oxidation reaction largely due to the dosage of $H_2O_2$. In general, the time to terminate the electro-Fenton can vary significantly with the increases amount of $H_2O_2$. Besides that, Zhang *et al.,* (2006) was indicated the process of electro-Fenton very fast in the first 15- 30 minutes and then slowed down till it was complete in 75 minutes.

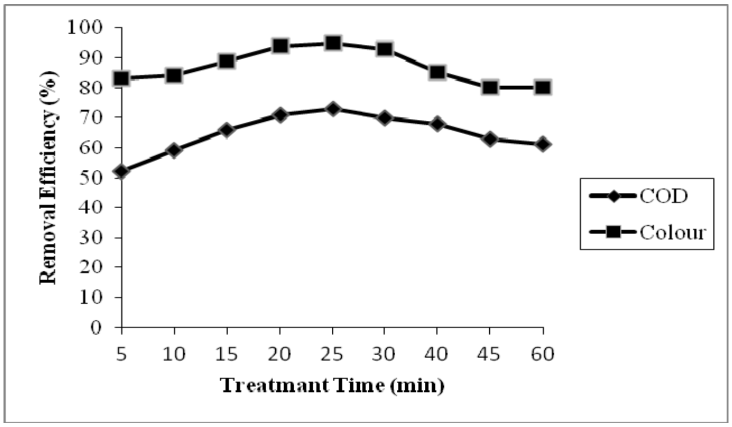


**Fig. 2:** Effects of treatment time on COD and colour removal efficiency for Al-Al at current density 200 A/m$^2$, pH 3, $H_2O_2$ 600 mg/L, $Fe^{2+}$ 600 mg/L, distances between electrodes 5 cm, and settling time of 30 minutes.

***Optimum Initial pH:***

In the electro-Fenton process, pH is an important operation parameter on removal of COD and colour. The function of pH is to controls the production of the hydroxyl radical and the concentration of ferrous ions in the solution. Figure 3 were shown the optimum pH on the removal efficiency of COD and colour for Al-Al. The optimum pH was found at pH 4 which was achieved 74 % and 96 % of COD and colour respectively. From the results, the low removal COD and colour decreased at pH>4. It is similar by Lin and Chang (2000) were obtained the removal decreased for initial pH>4. From this results, it is clearly seen that pH 3, 4 and 5 is very closed each other on removal efficiency of COD and colour. In general, many researcher have been found that Fenton's reaction occur in low pH values between 2 and 4 (Mohajeri *et al.*, 2010; Atmaca, 2009; Zhang *et al.*, 2006; Gosh *et al.*, 2011; Aziz *et al.*, 2012; Lopez *et al.*, 2004; Deng, 2007).

When the pH value has been increased, the iron ions of $Fe^{3+}$ precipitate, which slow down the regeneration of ferrous ions. As a result, the amount catalyst of Fenton's reaction will be decreases. In fact, hydrogen peroxide is unstable in basic solution and possibly will itself rapidly decompose to water and oxygen as pH >5 (Mohajeri *et al.*, 2010; Nidheesh and Gandhimathi, 2012). It is show that the stable hydroxyl radicals are produced at pH values of 2-4 and that high oxidizing potential was exhibited in this pH range ( Zhang, 2007; Badawwy and Ali, 2006). According to Zhang (2006) and Rivas *et al.*, (2004) the pH>4, $H_2O_2$ decomposes in a different manner without any contribution to oxidation reactions.

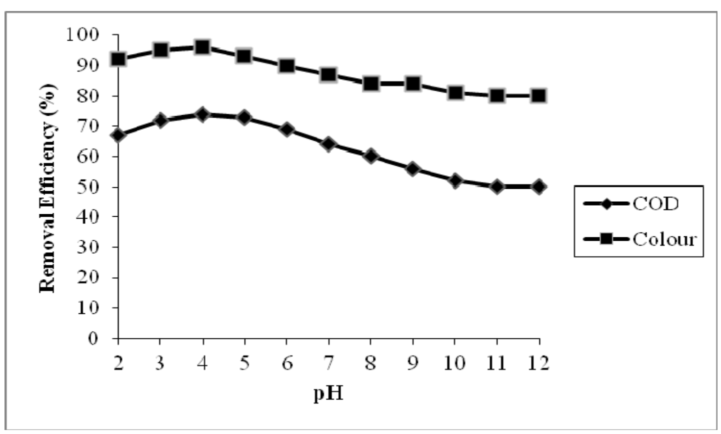


**Fig. 3:** Effects of pH on COD and colour removal efficiency for Al-Al at current density 200 A/m$^2$, treatment time 25 minutes, $H_2O_2$ 600 mg/L, $Fe^{2+}$ 600 mg/L, distances between electrodes 5 cm and settling time of 30 minutes.

***Effect of $H_2O_2$ Dosage:***

The dosage of $H_2O_2$ is an important part in the electro-Fenton process. The increased of $H_2O_2$ concentration ability to remove more pollutants in wastewater. It is due to the increase in hydroxyl radical concentrations as a result of the addition of $H_2O_2$. According to Zhang (2007) the efficiency of hydrogen peroxide for degrades organic pollutants in the leachate decreased with the increase of Fenton's reagent dosage. At the high dosage of $H_2O_2$, the decrease in removal efficiency was due to the hydroxyl radical scavenging effects of $H_2O_2$ and the recombination of the hydroxyl radical. The results showed that the best removal efficiency of COD and colour is 800 mg/L of $H_2O_2$ dosage which are obtained 78% and 97% of COD and colour removal respectively. It is seen that, the removal efficiency were increased when the dosage has been increased. However, a higher oxidant doses higher than optimum dose cannot provide adequate results. It is similar results reported by Ghosh *et al.*, (2011). From their study, they were obtained 1530 mg/L of optimum $H_2O_2$ dosage and a higher oxidant dose of 3825 mg/L did not lead to higher COD reduction.

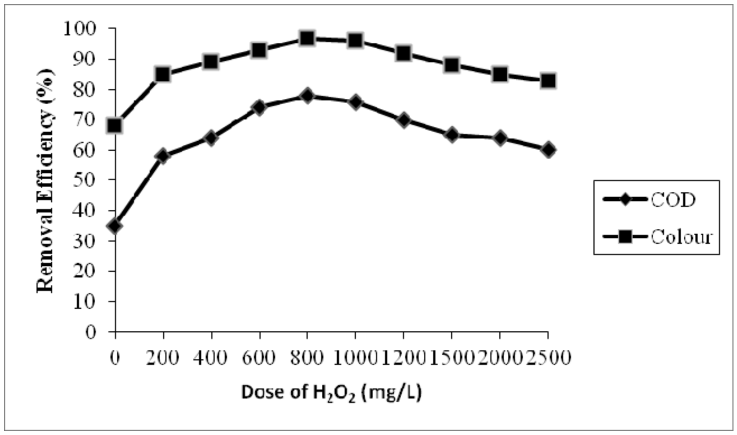


**Fig. 4:** Effects of $H_2O_2$ dosage on COD and colour removal efficiency for Al-Al at current density 200 A/m$^2$, treatment time 25 minutes, pH 4, dose of $Fe^{2+}$ 1200 mg/L, distances between electrodes 5 cm and settling time of 30 minutes.

### *Effect of $Fe^{2+}$ Dosage:*

In electro-Fenton process, ferrous ion concentration is requirement to generate this process (Zhou *et al.*, 2007). Figure 5 has been showed the effect of $Fe^{2+}$ concentration on removal of COD and colour. The optimum $Fe^{2+}$ concentration is 1000 mg/L for 75% of COD and 95% of colour removal respectively. Usually, the efficiency of electro-Fenton process increases with $Fe^{2+}$ concentration because the concentration hydroxyl radical (Wang *et al.*, 2010). The main oxidizing agent ($H_2O_2$) in the electro-Fenton process increases with the increase in $Fe^{2+}$ concentration. The excess of ferrous ion use in the electrolyte solution can consume the hydroxyl radicals and affect the extent of degradation (Nidheesh and Gandhimathi, 2012). After the electro-Fenton process the excess amount of $Fe^{2+}$/ $Fe^{3+}$ will be contamination for soil and groundwater because the excess amount of $Fe^{2+}$/ $Fe^{3+}$ produces extra amount of sludge and increase total dissolved solids and electrical conductivity.

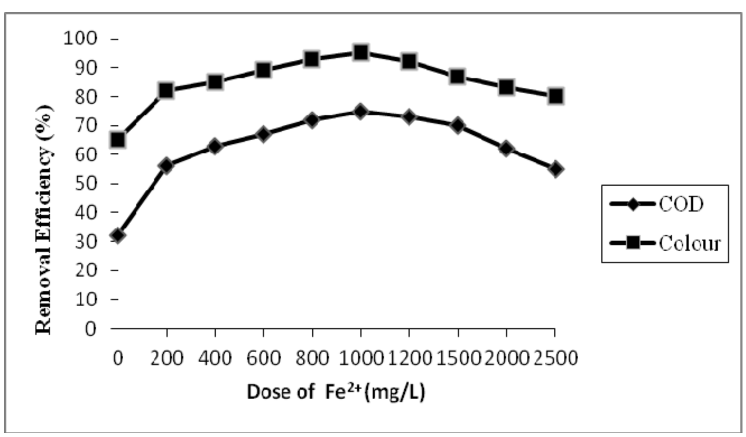


**Fig. 5:** Effects of $Fe^{2+}$ dosage on COD and colour removal efficiency for Al-Al at current density 200 A/m$^2$, treatment time 25 minutes, pH 4, dose of $H_2O_2$ 1200 mg/L, distances between electrodes 5 cm, and settling time of 30 minutes.

***Conclusion:***

Optimum condition for electro-Fenton process were found at current density 200 $A/m^2$, treatment time 25 minutes, pH 4, $H_2O_2$ dosage 800 mg/L and $Fe^{2+}$ dosage 1000 mg/L. Hence, electro-Fenton is recommended as a powerful technique for the degradation and decolorization of landfill leachate.

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