



REDUCTION OF COD IN NAM SON LANDFILL LEACHATE BY ELECTRO-FENTON AS SECONDARY TREATMENT AFTER ELECTROCOAGULATION PRETREATMENT

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Abstract. The unstable composition and properties of pollutants, together with very high concentration of pollutants such as ammonia nitrogen, COD and especially persistent compounds such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals, so leachate is the object that is very difficult to deal with. In fact, after a pre-treatment as electrocoagulation, over 73 % of COD has been treated from Nam Son landfill leachate, however the output value of COD still exceeds the QCVN 40:2011/BTNMT, column B. So, using electro-fenton technique as secondary treatment, just after an electrocoagulation pre-treatment was studied. This electro-fenton system using Pt gauze and carbon felt as an anode and a cathode respectively in order to electrochemically produce *in situ* hydrogen peroxide and regenerate Fe²⁺ catalyst, currently applied on the effectiveness in reducing COD in Nam Son landfill leachate was examined. At the optimal condition: pH 3, applied current of 1A, Fe²⁺ concentration of 0.1 mM, Na₂SO₄ concentration of 0.05 M, 77.2 % COD decrease could be reached within 60 min and the output value of COD is 130.9 mg.L⁻¹, according to QCVN 40:2011/BTNMT, column B. The research results indicated that the combination of an electro-coagulation with an electro-fenton process can effectively reduce the level of COD in Nam Son landfill leachate.

Keywords: landfill leachate, COD reduction efficiency, electro-fenton, felt carbon, hydroxyl radical.

Classification numbers: 3.3.3, 3.4.2, 3.7.3.

1. INTRODUCTION

In recent years, the population growth and socio-economic development in Vietnam have increased the demand for goods, raw materials and energy, and also raised the amount of solid waste, especially municipal solid waste (MSW) with an average of 12% per year [1]. Among different MSW disposal technologies, landfilling has been widely used because of its low investment cost and simple operation. Landfill leachate is the type of wastewater generated in landfills, which is formed due to the percolation of rainwater through the landfill or due to the moisture content of buried waste [2]. It is highly toxic liquid with heavy metals, different soluble materials and dissolving organic compounds, in particular significant quantities of humic acid and fulvic as refractory organic pollutants [3–5]. The leachate composition is usually unstable and varies according to landfill time, type of waste, seasonal weather variations, precipitation level and landfill temperature. All these factors make leachate treatment difficult and complicate. Many methods have been applied to treat the leachate, such as coagulation–flocculation, advanced oxidation processes, membrane technology, and biological treatment [6]. A technique based on the combining an electrolytic processes occurring on electrodes with chemical coagulation and flotation, called electrocoagulation (EC), a simple, efficient and economical technology because the capability of adsorbing contaminants onto the surface of metal hydroxides produced ‘*in situ*’ by this technology are 100 times greater than on superficies of metal hydroxides produced by hydrolysis of metal salts during traditional chemical coagulation [8]. However, our previous studies have shown that in the optimal conditions, the EC process removes only 73.21% of COD from Nam Son landfill leachate and so, it is necessary to have a secondary treatment process after EC [9].

Advanced oxidation processes (AOPs) is a group of techniques using hydroxyl radical ($\bullet\text{OH}$) as a powerful oxidizing agent (2.8 V oxidation potential) which can degrade organic pollutants, even persistent compounds until its complete mineralization, seems to be promising post treatment technique of leachate [10]. Electro-Fenton (EF) is an AOP technique in which $\bullet\text{OH}$ radical is generated by the reaction (1) between Fe^{2+} ions (introduced into the solution at the start) and H_2O_2 (produced continuously on the cathode by electrochemical reduction of oxygen molecule in acidic medium) [11-13]. The electrochemical reduction of Fe^{3+} on cathode helps to regenerate Fe^{2+} catalyst [13].



The decomposition efficiency of pollutants in water by EF technique is determined by the parameters: pH (optimal range 2 – 3), Fe^{2+} concentration (optimal range 0.1- 1.5 mM), current density and initial concentration of pollutants [14].

The use of electric current has offered EF some absolute advantages over chemical fenton, as follows: (1) In situ generation of hydrogen peroxide leads to a reduction in chemical use, so cost savings and safety risks of transportation, storage; (2) The continuous regeneration of Fe^{2+} results in the initial addition of a very small amount of the catalyst, approximately $10^{-4} \text{ mol.L}^{-1}$, thus reducing chemical costs and the amount of produced sludge. This value is lower than allowable discharge limits of iron so it is not necessary to remove the iron from water after treatment [11 - 13]. Recently, new generations of catalysts based on iron or transition metals with high catalytic activity and low cost have been developed. Besides, three-dimensional electrodes or iron-graphite, iron-carbon composite electrodes with high Faraday efficiency,

corrosion resistance, long life and low cost have been successfully manufactured. All of these have contributed to increasing the efficiency of organic wastewater treatment and reducing operating costs. Another advantage of EF technique is the ability to easily couple with other processes such as: coagulation in order to treating wastewater from rubber production [15], electro-chlorination for treatment of wastewater from food industry [16], nanofiltration to deal pharmaceutical effluent [17], active sludge process for the removing sulfamethazine in pharmaceutical wastewater [18], membrane bioreactor (MBR) in order to handle landfill leachate [19]. Consequently, the coupling of electrocoagulation and EF can remove the color, organic compounds, small quantity of aromatic substances and EF process can degrade most persistent organic pollutants.

In this paper, COD reduction in Nam Son landfill leachate by an EF process as secondary treatment after EC pre-treatment will be discussed. The effects of pH, Fe^{2+} catalyst concentration and applied current on the COD reduction efficiency were also investigated.

2. MATERIALS AND METHODS

2.1. Landfill site description and leachate characteristics

This study used leachate taken from the reservoir of Nam Son landfill located in Soc Son district. being the largest landfill in Hanoi, in April, 2019. The samples were pre-treated by EC batch reactor before treatment by EF reactor. Some characteristic parameters of the leachate are shown in Table 1.

Table 1. The characteristics of Nam Son landfill leachate used in this study.

No.	Parameters	Unit	Raw leachate	Leachate after EC
1	pH	-	7.9-8.1	8.5 - 8.9
2	COD	mg.L^{-1}	2308.5 – 2865.6	461.88 - 574.23
3	Color	Pt-Co	12432 – 1329	890 -1080
6	TSS	mg.L^{-1}	280 - 320	95 - 106

2.2. Electrochemical system

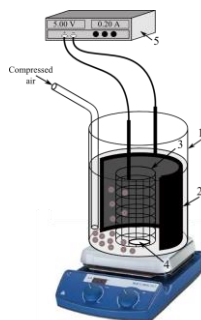


Figure 1. Scheme of EF experiment system: (1) cylindrical beaker-type reactor of 250 mL capacity, (2) carbon-felt cathode, (3) platinum anode, (4) magnetic stir bar, (5) digital DC generator.

Experiments were performed at room temperature in a simple cylindrical beaker-type reactor of 250 mL capacity (Figure 1). The EF system used Pt anode (9 cm × 5 cm) and carbon felt cathode (12 × 5 cm) in which Pt gauze and carbon piece rolled up into cylinder, anode on the inside, cathode on the outside and two electrodes stood 1 cm apart.

The aqua reaction system was added with small quantity of ferric ion as catalyst and continuously supplied with oxygen to produce H₂O₂ (reaction (2)) by aeration of compressed air at a constant flow rate of 1 L / min, starting 30 minutes before the beginning of electrolysis. In order to ameliorate the mass transfer, system was vigorously stirred with a magnetic bar. Sulphuric acid was added to adjusting the pH of reaction system. The direct current used for experiments was provided by a digital DC generator VSP4030 (B&K Precision, CA, US).

2.3. Materials and analysis

The carbon felt used in these experiments was commercial product of A Johnson Matthey Co., Germany. FeSO₄·7H₂O (99.5 %, Merck) was used to provide Fe²⁺ catalyst, and Na₂SO₄ (99 %, Merck) was supporting electrolyte. H₂SO₄ (98 %, Merck) was used to adjusting the pH of reaction system.

Since the pyridine concentration in landfill leachate is usually very small in comparison to COD value (about 0.02 mg.L⁻¹ [20]), so the COD was determined by the dichromate method (TCVN 6491:1999, corresponding to ISO 6060:1989) without significant difference. The pH meter (HANNA HI 991001) was used for monitoring pH of solution. The chemicals used for COD analysis were pure and all the experiments were carried out at room temperature of 25°C.

3. RESULTS AND DISCUSSIONS

3.1. Effects of pH

In EF process, the initial pH plays an important role because it controls the production of the hydroxyl radical and the concentration of ferrous ions [21]. To study the effect of pH on the COD reduction efficiency by using Fenton process, 200 ml of landfill leachate was added with Na₂SO₄ salt (0.05 M) for increasing conductivity, FeSO₄ (0.1 mM) for catalysis and acidified to pH values of 2 – 6 by sulphuric acid, then electrolyzed with a current of 0.5 A.

Figure 2 shows the effect of pH on reducing the COD of leachate. It could find that when the pH increases from 3 to 6, COD treatment efficiency decreases, the cause may be at pH above 3, the higher pH was, the more Fe²⁺ was converted into precipitate Fe(OH)₃, which reduced the concentration of Fe²⁺ catalyst, so decreased the amount of hydroxyl radicals generated (according to Eq. (1)). Moreover, the colloid precipitate Fe(OH)₃ could adhere to the cathode surface preventing the electronic reception of Fe³⁺ to regenerate Fe²⁺ catalyst (Eq. (3)). In addition, increase of pH could decrease the oxidation potential of the •OH radical which caused the COD treatment efficiency reduce [22]. Furthermore, amount of H₂O₂ could be diminished by its decomposition to oxygen at high pH [23].

In the opposite direction, when the pH decreased from 3 to 2, the reduction of COD removal efficiency was observed. The reason may be that at a pH lower than 3, the amount of H₂O₂ in the reaction system has been significantly diminished due to the reaction of H₂O₂ with H⁺ to form oxonium ion (H₃O₂⁺) (Eq. (4)) [24] or H₂O (Eq. (5)) [25], resulting in reducing the amount of the •OH radical generated by Fenton reaction (Eq. (1)). In addition, the low pH also

promoted the reduction reaction of H^+ to H_2 gas according to Eq. (6) which was a competitive reaction with H_2O_2 generation reaction (Eq. (2)) [26].

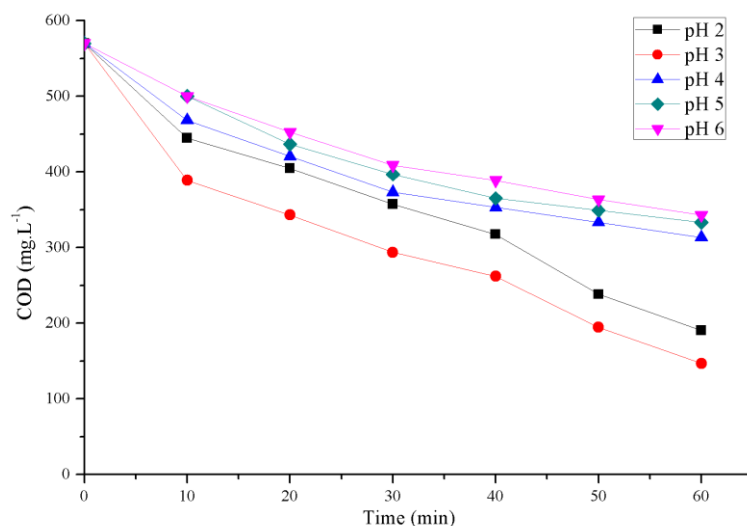


Figure 2. Variation of the COD value in Nam Son landfill leachate with time and pH for EF experiments. EF performed at conditions: $[Fe^{2+}] = 0.1$ mM, $I = 0.5$ A and $V = 200$ ml.

This result is similar to the result obtained by Ozcan *et al.* [27] when COD in landfill leachate of municipal solid waste landfill in Kermanshah city (Iran) was treated by EF. From the above results, the optimal pH 3 was chosen for subsequent experiments.

3.2. Effect of Fe^{2+} concentration

According to Eq. (1) it is clear that the concentration of Fe^{2+} catalyst is another important parameter impacting on the amount of hydroxyl radical generated, so indirectly effecting on COD treatment efficiency. To study this effect, 200 ml of landfill leachate was added with Na_2SO_4 salt (0.05M) for increasing conductivity, acidified to pH values of 3 by sulphuric acid, $FeSO_4$ salt was injected to adjust the amount of Fe^{2+} catalyst at different concentration values from 0.05 to 0.5 mM, then electrolyzed with a current of 0.5 A. The results are shown in Figure 3. As can be seen, when the concentration of Fe^{2+} increases, the efficiency of COD treatment increases, but when the concentration of Fe^{2+} exceeds 0.1 mM the effectiveness of COD treatment decreases without increase. This can be explained as follows: at low Fe^{2+} concentrations, according to Eq. (1), the higher concentration of Fe^{2+} was, the greater the amount of radicals $\bullet OH$ was produced; which means the higher COD removal efficiency was. When Fe^{2+} concentration was too high, above 1 mM, Fe^{2+} could react with radical $\bullet OH$ (Eq. (7)) reducing the amount of this radical [29]. In addition, too much Fe^{2+} could lead to too much Fe^{3+} generated. Excess Fe^{3+} could react with H_2O_2 (Eq. (8) and (9)) to form the free radical $HO_2\bullet$ [30], which was less active than $\bullet OH$ [31]. These things indicate that COD treatment efficiency decreases when Fe^{2+} concentration exceeds 0.1 mM.

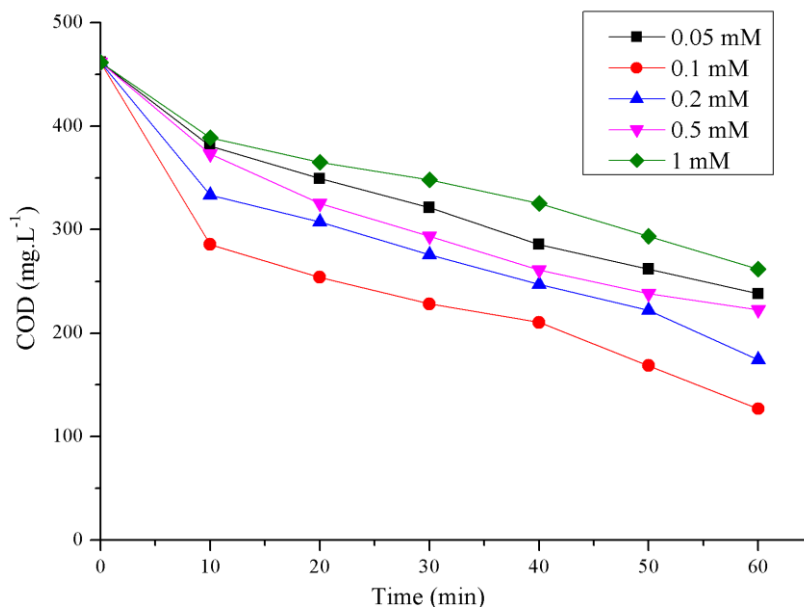


Figure 3. Variation of the COD value in Nam Son landfill leachate with time and initial Fe^{2+} concentration for EF experiments. EF performed at conditions: pH = 3, I = 0.5 A and V = 200 ml.

Furthermore, use over high concentration of Fe^{2+} can generate a large quantity of ferric oxide sludge, resulting in much more requirement of separation and disposal of the sludge. Consequently 0.1 mM of ferrous ions has been chosen for the subsequent experiments. This result differs from that obtained by Daud *et al.* [32] for the reduction of COD in landfill leachate of Simpang Renggam municipal landfill, Malaysia, in which the optimal Fe^{2+} dosage for EF process is 1000 mg.L^{-1} . This might be caused by the high difference in initial COD concentration of landfill leachates, initial COD in this study was only 462 mg.L^{-1} whereas in Daud's research it was about 13.200 mg.L^{-1} .

3.3. Effect of applied current

In electrochemical processes in general, EF in particular, the applied current is one of the most important parameters impacting on the degradation process. In order to investigate the effect of this parameter on the COD reduction efficiency, 200 ml of landfill leachate was added Na_2SO_4 salt (0.05 M) for increasing conductivity, acidified to pH values of 3 by sulphuric acid, FeSO_4 (0.1 mM) for catalysis FeSO_4 , then electrolyzed with different current values from 0.1 A to 2 A. According to Figure 4, the higher current is, the greater COD reduction rate is. This is reasonable because, according to Faraday's law of electrolysis, the amount of substances electrolyzed on the electrodes is directly proportional to the applied current, so when the current increased, the amount of H_2O_2 produced in Eq. (2) raised, at the same time, regeneration speed of Fe^{2+} catalyst from Eq. (3) could be faster, leading to up the amount of radicals $\bullet\text{OH}$ produced by Eq. (1). This trend is also observed in other studies on landfill leachate [27, 32]. However, at current above 0.5 A, increase in current only caused a slight raise in COD reduction efficiency

(Figure 5), while brought many disadvantages such as high electric consumption, eroding the surface of carbon felt electrodes and so reduces their service life. So, in order to meet the discharge Vietnamese standard (according to QCVN 40:2011/BTNMT, column B, $\text{COD} < 150 \text{ mg.L}^{-1}$), a current of 1 A is sufficient to treat the COD in Nam Son landfill leachate.

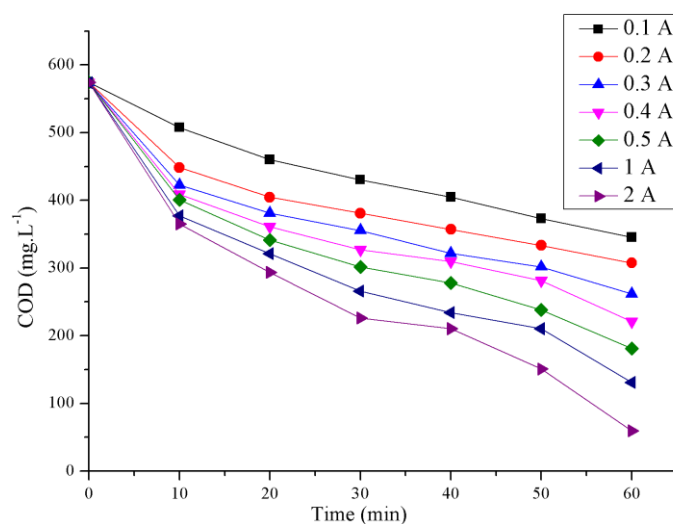


Figure 4. Variation of the COD value in Nam Son landfill leachate with time and current for EF experiments. EF performed at conditions: $\text{pH} = 3$, $[\text{Fe}^{2+}] = 0.1 \text{ mM}$ and $V = 200 \text{ ml}$.

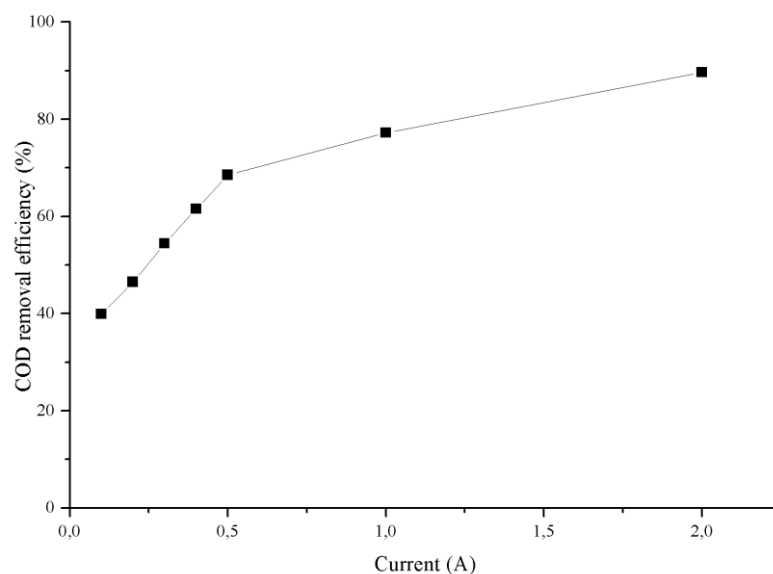


Figure 5. Variation of the COD value in Nam Son landfill leachate with current for EF experiments. EF performed at conditions: $\text{pH} = 3$, $[\text{Fe}^{2+}] = 0.1 \text{ mM}$, $t = 60 \text{ min}$ and $V = 200 \text{ ml}$.

4. CONCLUSION

The results obtained have shown that pH , Fe^{2+} concentration and current intensity had great influences on the COD reduction efficiency in Nam Son leachate by EF technique. An

electrocoagulation pre-treatment could only reduce the COD of Nam Son landfill leachate from 2308.5 – 2865.6 mg.L⁻¹ to 461.88 - 574.23 mg.L⁻¹, which required an EF process as secondary treatment. Under the optimal conditions for EF process: pH = 3, [Na₂SO₄] = 0.05 M, [Fe²⁺] = 0.1 mM, I = 1 A, approximately, 77.2 % COD reduction can be reached within 60 min and the output value of COD is 130.9 mg.L⁻¹, according to QCVN 40:2011/BTNMT, column B.

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