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Removal of NH_3 from leachate by electrochemical oxidation treatment

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Abstract

Electrochemical oxidation process is a promising treatment technology for the degradation of organic pollutants in water samples. Few studies demonstrated that the electrochemical oxidation process plays a key role on the removal of NH3 from leachate. The removal efficiency of NH_3 increases with applied voltage very significantly, suggesting a very important role of mediated oxidation process. Furthermore, pH and electrolyte are also participated strongly to enhance the removal of NH_3 in leachate. To optimize the operating conditions, the effects of NaCl concentration, applied voltage, and pH of the solution were investigated statisticall by one-way ANOVA; all factors were found as a significant factor with $P = 0.05$ lower than 95% confidence level. However, the consumption energy was considered during electrochemical oxidation process. In chloride media, consumption energy is the lowest (33 kW h mg^{-1}), at 0.086 mol L^{-1} NaCl and 10 V, with high removal percentage of NH_3 which is 48%. In case of applied voltage, only 53% of NH_3 has been removed consuming more than 50 kW h mg^{-1} after 105 min at 0.043 mol L^{-1} NaCl and 20 V. All results are treated statistically by applying one-way ANOVA, interval confidence 95% and P-value 0.05.

1. Introduction

The sanitary landfill method for the ultimate disposal of solid waste material continues to be widely accepted and used [1, 2]. Leachate generated from municipal landfills is a toxic aqueous waste that often contains organic compounds, heavy metals, ammonium and many other soluble compounds. However, in landfill leachate, organic compounds and NH_3-N are the two dominant pollutants of environmental concern [3, 4]. In the past, the removal of NH_3 has attracted much attention due to the high concentration of untreated NH_3 in leachate can promote algal growth, deplete dissolved oxygen through eutrophication which is fatal to aquatic life, acute smell and carcinogenesis as well as obstacle to the disinfection of water supplies. Hence, NH_3-N has been identified not only as a major long-term pollutant but also as the main cause of a higher toxicity [5].

Untreated leachate is unsuitable for direct discharge into surface water sources because of its high NH_3-N concentration (2240 and 1235 mg L^{-1}) [6, 7]. Many treatment processes have been studied to control the pollution caused by landfill leachate. According to literature, biological (aerobic and anaerobic) and physico-chemical (air stripping, chemical precipitation) were the most widely used treatment methods for the removal of NH_3 from landfill leachate. Because of the change in the characterization of leachate with advancing years of the landfill, these methods have troubles such as decreasing treatment efficiencies and cost increasing. Further, biological and chemical methods produce large quantity of sludge which itself requires treatment [8, 9]. Hence, these methods are no longer adequate to achieve the levels of purification needed to reduce the negative effects of landfill leachate on ecology. Therefore, more effective treatment methods have been proved to treat leachate.

In recent years, the electrochemical oxidation process considered as a promising alternative for NH_3 removal from different types of waste water. In general, in electrochemical oxidation, pollutants can be destroyed by conducting a direct anodic oxidation or an indirect oxidation process. Many researchers have been focused on direct anodic oxidation of pollutants in an electrochemical process. It should be noted that the wastewater contain high concentration of chloride, ranging from 2000 to 18500 mg L^{-1} and potentially it can be oxidizing to form chlorine/ hypochlorite during an electrochemical process. Since, anodic oxidation of chloride is readily occurred, the indirect oxidation effect may take place during the electrochemical oxidation process of the wastewater containing chloride as reported by [10, 11]**.** The chlorine can be chemically converted to hypochlorous acid and hypochlorite ions depending on the pH of the solution which act as main oxidizing agents in the pollutants degradation

In the present work, electrochemical oxidation was studied to decrease the concentration of NH_3 in leachate which is obtained from a municipal landfill site using a graphite- PVC anode. This electrode has some advantages which are cheap, available and its electrical conductivity is acceptable compared to other materials.

2. **Experimental details**

2.1. *Chemicals and reagents*

NH_3-N reagent (Cat.26531-99) was provided by (Dusselderf, Germany). Sodium chloride (NaCl) was used as supporting electrolyte, hydrochloric acid and sodium hydroxide were used to adjust the pH of the solution. All these chemicals were purchased from Merck with purities of more than 99.5%. Acetone was supplied by Merck (Germany), tetrahydrofuran (THF) (CAS No. 109-99-9) was purchased from Sigma Aldrich.

2.2. *Landfill leachate*

Raw leachate samples were collected from Jeram sanitary landfill which is located in an oil palm plantation near MukimJeramKuala Selangor Malaysia (Figure 1). All samples were collected in 1L amber glass bottles. The collected landfill leachate was filtered through a 0.7µm GF/G filter obtained from Whatman (UK) to remove suspended solid and stored at 4°C in order to keep the leachate characteristics unchanged. The concentration of NH_3 in landfill leachate was varied between 2800 and 9800 mg L^{-1}. Furthermore, the concentration of chloride ion was 2078 mg L^{-1} in the same collected samples of leachate.

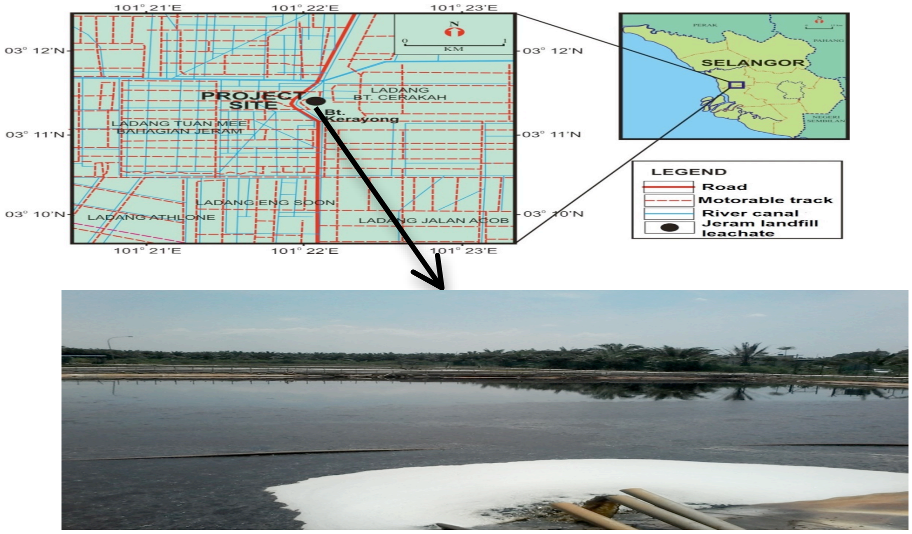

Figure 1: A map to describe the sampling area

2.3. *Electrochemical treatment process*

The electrolytic oxidation experiments of leachate were carried out in a 100 cm^3 glass beaker. The anode was graphite-PVC composite electrode and the cathode was Platinium. The preparation of anode was described elsewhere [12]. The cathode was Pt supplied by Aldrich chemical company. A 0.5 mm-thick Pt foil was cut into approximately (1 cm × 1 cm) piece, the inter-electrode gap was about 2.5 cm. The Pt foil was then connected to a silver wire with silver conducting paint and then sealed to a glass rod. Subsequently, epoxy gum was applied to cover the silver wire connecting surface. Graphite-PVC electrode was selected from many electrodes as reported by Mussa et al. (2013) [13].

Lab-scale electrolyses of 40 cm^3 of leachate sample were carried out to investigate the efficiency of electrochemical oxidation process on removal of leachate. Several parameters have been examined including, applied voltage (5, 10, 15 and 20 V), pH of the media (3, 7 and 9) and sodium chloride concentration (0.000, 0.043 and 0.086 mol L^{-1}). All experiments were repeated three times. Solutions were always kept at 22–25℃, which was the maximum temperature that can be used in the cell without significant water evaporation during prolonged electrolysis. All the experiments were carried out under vigorous stirring with a magnetic bar at 200 rotations per minute (rpm) to ensure mixing and the transport of reactant toward/from the electrode.

2.4. *Chemical analysis*

The pH of solution was measured by a pH meter (PH700 EUTECH Instruments, Singapore). NH_3-N was measured by a spectrophotometer (Hach Odyssey DR/2400). Chloride ions (Cl^-) were measured by Metrohm 850 professional Inductive Plasma (IC.UV-visible absorption spectrophotometric) instrument with an absorbance measuring from 230 nm to 400 nm was also connected by using a Shimadzu UV-2450 spectrophotometer.

2.5. *Statistical analysis*

The statistical analysis of variance (one-way ANOVA) was achieved for applied voltage, pH effect and sodium chloride concentration by using Minitab Version 17, Tukey with
$P = 0.05$ and 95% as interval confidence.

3. Result and Discussion

3.1. *Effect of NaCl concentration*

Figure 2 shows the effect of NaCl concentration on NH_3-N removal at different concentrations of NaCl (0.000, 0.043 and 0.086 mol L^{-1}). The results demonstrated that the removal percentage of NH_3 increased directly with the increasing of concentration of NaCl. The removal percentage of NH_3-N was 34% without NaCl added, while its removal was 48% in the presence of 0.086 mol L^{-1} NaCl after 105 min electrolysis time. Similarly, many studies showed that a higher chloride concentration leads to an increase production of OCl^- then oxidation of NH_3 [14-16].

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \tag{2}$$

$$HOCl \leftrightarrow H^+ + OCl^- \tag{3}$$

$$OCl^- + leachate \rightarrow CO_2 + H_2O + Cl^- + P\ (products) \tag{4}$$

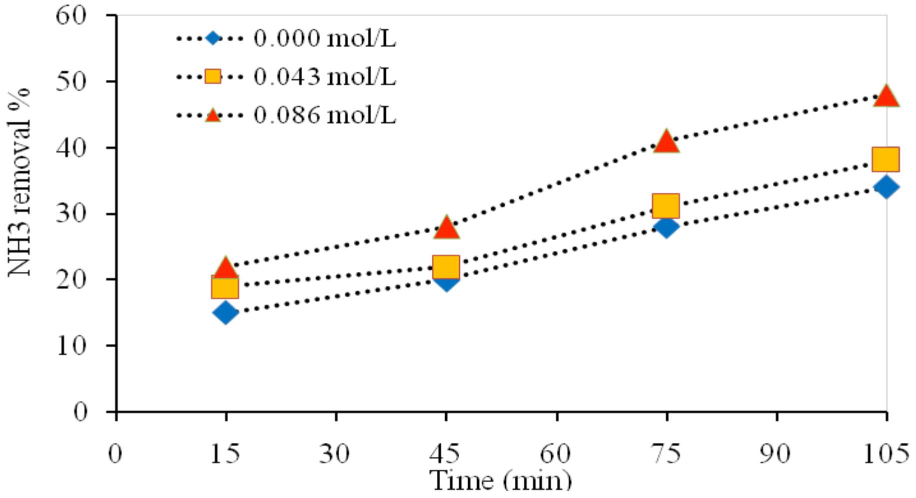

Figure 2: Effect of NaCl concentration on the removal of NH_3 from leachate at different electrolysis times, applied voltage 10 V and pH 8.3. Particle size distribution of silver nanoparticles from dynamic light scattering measurements

3.2. *Effect of NaCl on energy consumption*

The energy consumed in the electrochemical oxidation of the landfill leachate by using a constant voltage was calculated according to (Eq 5) [17]. The obtained results are presented in Figure 3. Energy consumption was influenced by the voltage, however, the increasing of voltage from 15 V to 20 V did not reflect enhancement of NH_3 removal:

$$EC = \left[\frac{VI\Delta t}{\Delta[NH_3]}\right] \tag{5}$$

where *EC* is energy consumption in kWh per kg of NH_3 reduced in the process (kWh/kg NH_3), V is the cell potential in V, I is the current in A, Δt is the electrolysis time in hours, and $\Delta\,[NH_3]$ is the amount of NH_3 reduction during the time t.

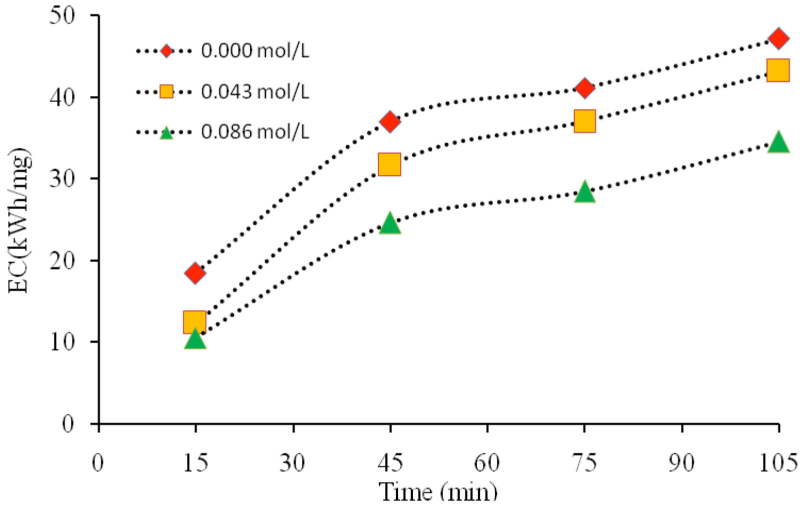

Figure 3: Effect of NaCl concentration on the energy consumption for removal of NH_3 from leachate at different electrolysis times, applied voltage 10V and pH 8.3.

3.3. *Effect of applied voltage*

Figure 4 shows the relationship between the applied voltage and NH_3 removal percentage in the electrochemical oxidation treatment of raw landfill leachate. When the applied voltage increased from 5 to 20 V, the removal of NH_3 increased also. The removal of NH_3 was 22%, 41%, 48% and 53% at 5, 10, 15 and 20 V of applied voltage after 105 min, respectively. This is due to increasing of the generation hypochlorite ions with increasing of applied voltage.

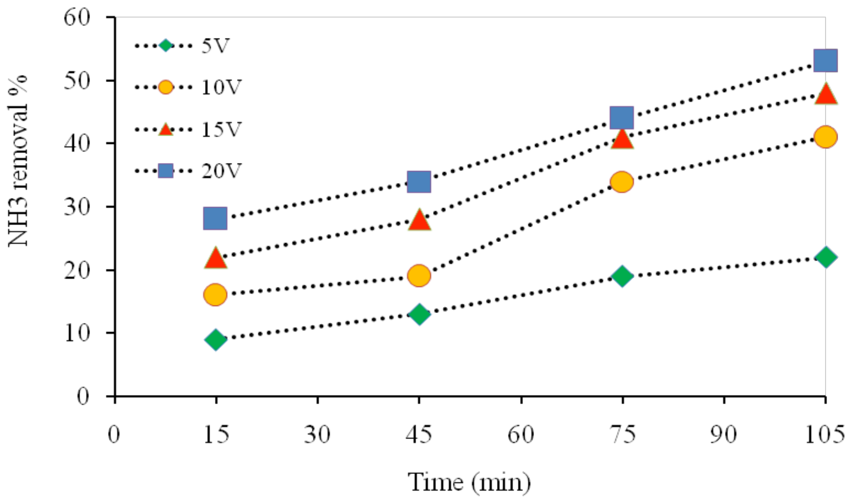

Figure 4: Effect of applied voltages on the removal of NH_3 from leachate at different electrolysis times, 0.043 mol L^{-1} NaCl and pH 8.3.

3.3. *Effect of applied voltage on energy consumption*

In this study, energy consumption for the electrochemical oxidation process of leachate was evaluated at different applied voltages. The results were presented in Figure 5. Energy consumption increases with applied voltage, furthermore, the increasing of applied voltage from 15 V to 20 V enhanced NH_3 removal significantly (Figure 4). Consequently, the difference between 10 V and 15 V in the efficiency of the removal is significant. However, the difference in energy consumption between 10 V and 15 V is very significant and observed. This finding was in line with our previous study on removal of COD from leachate **[12]**, hence, 10 V was considered the optimum value for further experiments because good removal was obtained at low energy consumption.

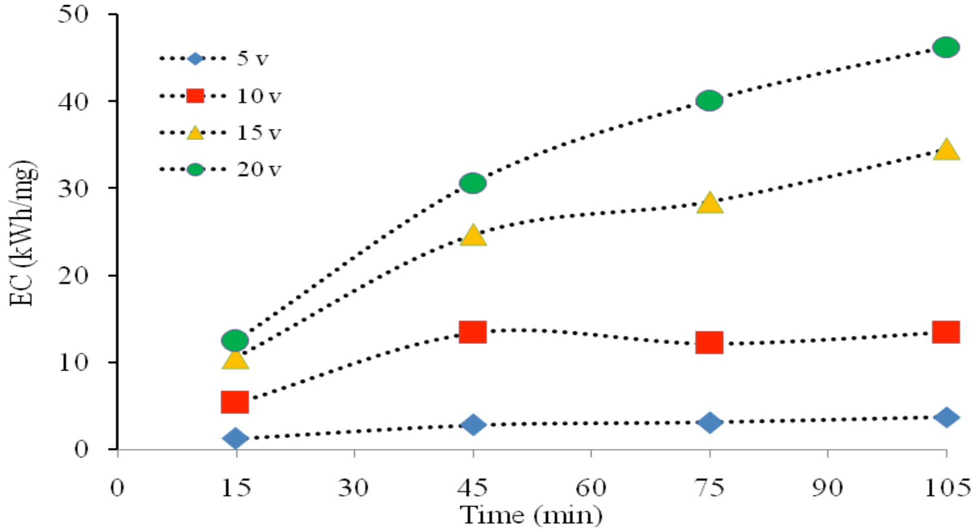

Figure 5: Effect of applied voltages on the energy consumption for removal of NH_3 from leachate at different electrolysis times, 0.043 mol L^{-1} NaCl and pH 8.3.

3.4. *Effect of pH*

In the electrochemical oxidation process, pH of the solution plays an important role in the removal efficiency of pollutants. The effect of pH was continued on evaluation of NH_3-N removal. Figure 6 shows the relationship between pH and the removal which is inversely. At pH 3 the removal percentage of NH_3-N was 61%, while 48% NH_3-N was removed at pH 9. This is also due to the production of HOCl in acidic medium which act as strong oxidizing agent to oxidize NH_3-N as reported by **Anglada et al. (2011) [7].**

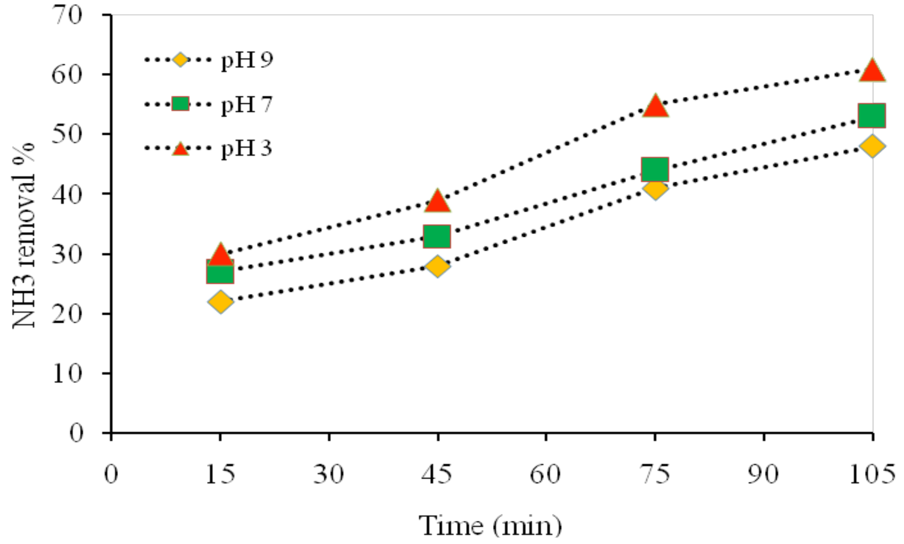

Figure 6: Effect of pH on the removal of NH_3-N from leachate at different electrolysis times, applied voltage 10 V, 0.043 mol L^{-1} NaCl.

3.5. *Statistical analysis*

The most significant results were obtained with applied voltage, pH effect and effect of NaCl. The significance value in terms of P-value was 0.000 in all cases which means high significant results were obtained. In case of applied voltage, four values of voltage were tested by one-way ANOVA 20, 15, 10 and 5 V. Applied voltages were not shared with same latter which means it was significant in all values. pH effect was statistically treated and exhibited very high significantly difference in terms of removal% as shown in Table 1. Effect of electrolyte (NaCl) was also investigated statistically then all amounts were significant.

Table 1. Statistical Analysis of Variance for the different independent factors using Tukey method and 95% confidence. P value less than 0.05.

Applied voltage, V						
Factor value	N*	Mean	Grouping			
20	3	53	A			
15	3	48		B		
10	3	41			C	
5	3	21				D
pH effect						
Factor value	N	Mean	Grouping			
3	3	61	A			
7	3	52		B		
9	3	48			C	
Effect of NaCl, mol L^{-1}						
Factor value	N	Mean	Grouping			
0.086	3	48	A			
0.043	3	38		B		
0.000	3	34			C	

* N is the number of replication.

Conclusions

The electrochemical removal of NH_3 using graphite-PVC as anode was presented well with suitable efficiency for NH_3 removal. The present study investigates that the most suitable conditions for treatment of landfill leachate in terms of NH_3 removal are supporting electrolyte; NaCl, applied voltage and pH of solution. However, the high concentration of NaCl exhibited the highest NH_3 removal compared to other concentrations. The high applied voltages 20 and 15 V resulted high NH_3 removal as well but not too big significant. pH of the solution was also tested reffering to the highest NH_3 removal was accompanied to acidic media (pH 3). The obtained results were treated statistically to state that all experiments were significant according to Minitb Version 17, Tukey with P=0.05 and 95% as interval confidence. Some suggestions should me mentioned here which are the possibility to use different electrolytes as supporting electrochemical catalysts for NH_3 and other organic pollutants removal.

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References

1. E. Diamadopoulos, *Water Res.*, 28 (1994) 2439.
2. P.B. Moraes, R. Bertazzoli, *Chemosphere*, 58 (2005) 41.
3. S. Top, E. Sekman, S. Hoşver, M.S. Bilgili, *Desalination*, 268 (2011) 158.
4. J. Schwarzbauer, S. Heim, S. Brinker, R. Littke, *Water Res.*, 36 (2002) 2275.
5. D. Fatta, A. Papadopoulos, M. Loizidou, *Environ. Geochem. Heal.*, 21 (1999) 175.
6. F. Ilham, M. Gonullu, E. Arslankaya, U. Kurt, O. Apaydin, *First international workshop on application of Redox Technologies in the environment, İstanbul, Turkey*, (2009).
7. Á. Anglada, A. Urtiaga, I. Ortiz, D. Mantzavinos, E. Diamadopoulos, *Water Res.*, 45 (2011) 828.
8. J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, *Chemosphere*, 54 (2004) 997.
9. N. Mohan, N. Balasubramanian, C.A. Basha, *J. Hazard. Mater.*, 147 (2007) 644.
10. Al-Qaim F.F., Mussa Z.H., Othman M.R., Abdullah Md. P., *J. Hazard. Mater.,* 300 (2015) 387.
11. Z.H. Mussa, F.F. Al-Qaim, Md.P. Abdullah, M.R. Othman, *J. Env. Chem. Engin.*, 4 (2016) 3338.
12. Z.H. Mussa, M.R. Othman, Md.P. Abdullah, *J. Brazil. Chem. Soci.*, 26 (2015) 939.
13. Z.H. Mussa, M.R. Othman, Md.P. Abdullah, N.A. Nordin, *Int. J. Chem. Sci.*, 11 (2013) 1636.
14. L.C. Chiang, J.E. Chang, T.C. Wen, *Water Res.*, 29(1995), 671.
15. X.L. Ma, R.P. Wang, W.Q. Guo, H. Yang, Z. Liang, C. Fan, *Int. J. Electrochem. Sci.*, 7 (2012) 6012.
16. A. Cabeza, A. Urtiaga, M.J. Rivero, I. Ortiz, *J. Hazard. Mater.*, 144 (2007) 715.
17. J.B. Parsa, M. Rezaei, A.R. Soleymani, *J. Hazard. Mater.*, 168 (2009) 997.