

Electrochemical Oxidation of Landfill Leachate: Investigation of Operational Parameters and Kinetics Using Graphite-PVC Composite Electrode as Anode

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The preparation of a new carbon composite electrode constructed from graphite-polyvinyl chloride (graphite-PVC) compressed mixtures was used for the first time to treat landfill leachate in Malaysia under electrochemical oxidation. The electrochemical oxidation of landfill leachate was studied on graphite-PVC and Pt electrodes as anode and cathode, respectively, with the presence of NaCl electrolyte in a batch electrochemical reactor. The highest chemical oxygen demand (COD) and color removals of 87% and 97%, respectively, were achieved at pH 3, 0.58% (m/v) + 2078 mg L⁻¹ electrolyte concentration, 15 V applied voltage, and 105 min electrolysis time. To confirm electrochemical oxidation, a field emission scanning electron microscopy (FESEM) was used to evaluate the surface of graphite-PVC electrode before and after treatment. The constant rate in terms of pseudo-first-order kinetics increased from 0.0015 min⁻¹ to 0.0186 min⁻¹ at 5 and 20 V applied voltage. The graphite-PVC composite exhibits favorable qualities as an electrode material because of its mechanical resistance, low cost, simple preparation, and easy renewal of the electrode surface.

Keywords: landfill leachate, composite electrode, graphite-PVC, electrochemical oxidation, kinetics study

Introduction

Increasingly affluent lifestyles and various developmental activities in several countries around the world has been accompanied by a rapid increase in both municipal and industrial solid waste generation.¹ In Malaysia, the generation of municipal solid waste (MSW) has increased by more than 91% over the past 10 years because of rapid urban development, increasing rural-urban migration, and increasing *per capita* income.² In most countries, sanitary landfilling is the most commonly used approach to eliminate MSW.^{3,4,5} Up to 95% of the MSW collected worldwide is disposed in landfills.⁶ After the waste is disposed in a landfill, MSW decomposes through a series of combined physicochemical and biological processes. During the decomposition process, a highly contaminated liquid called leachate is produced by excess rainwater percolating through the waste layers in the landfill.³ The leachate generated from sanitary landfill is generally a dark-colored liquid with a strong smell and

contains high rates of organic and inorganic pollutants.^{7,8} The discharge of leachate can lead to serious environmental problems because it may permeate to soils and sub soils, thus contributing to the pollution of ground and surface waters if left untreated.^{7,9}

Untreated landfill leachate is currently a major pollution source for surface and ground waters. Conventionally, landfill leachate is treated through biological methods such as anaerobic and aerobic processes or by physicochemical processes such as coagulation-flotation, precipitation, and flotation. Given the changes in the characteristics of leachate with advancing years in the landfill, the aforementioned methods will exhibit decreasing treatment efficiency and increasing cost with time. Moreover, biological and chemical methods produce considerable large quantities of sludge, which also requires treatment. Hence, developing a new treatment method is necessary.^{1,10,11} Electrochemical technology has been increasingly used to treat landfill leachate because of its safe and environmentally friendly nature. Electrochemical techniques are effective in treating wastewater that contains organic and inorganic compounds.¹² Since the late 1970s electrochemical

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oxidation has been successfully applied to treat textile wastewater,¹³ olive oil wastewater,¹⁴ tannery wastewater,¹⁵ coke-plant wastewater and phenol.^{16,17} This technique has been applied for landfill leachate treatment over the past 10 years.¹⁸

Electrochemical oxidation has several advantages such as easy operation, no chemical requirements, effective removal of organic and inorganic compounds, high color removal rate, and no sludge formation. Electrochemical oxidation is also able to oxidize organic pollutants to CO₂ and water, thus avoiding the problem of transferring the contaminants being converted from one phase to another. Moreover, the operation at room temperature and atmospheric pressure prevent volatilization and discharge of unreacted wastes.¹⁹ In general, during the electrolysis process of landfill leachate, organic contaminants will be removed by the indirect oxidation induced by the active chloride ions (Cl⁻) that originally exist or are added to the leachate; hence, organic contaminants are independent of the hydroxyl radicals.⁵ Different types of electrodes such as TiO₂, Ti, PbO₂/Ti, SnO₂/Ti and graphite have been investigated for electrochemical treatment.

Graphite-based electrodes have been used to treat landfill leachate. Graphite is an ideal electrode substrate in many aspects because of its wide anodic potential range, efficiency in wastewater treatment, low residual current, chemical inertness, and relatively low cost compared with other materials.^{20,21} Furthermore, graphite electrodes exhibit fast response and can be easily fabricated in different configuration sizes. Bashir *et al.*²⁰ used graphite electrodes for leachate treatment and found that the removal rates of COD and color were 68% and 84% during electrooxidation process, respectively.

Another alternative to the previous graphite electrode is an electrode based on graphite-polymer composites, which can often be fabricated with great flexibility in size and shapes. Among commonly used polymers are polyvinyl chloride (PVC),²² polyethylene,²³ polyester,²⁴ polyurethane²⁵ and polyacrylic acid.²⁶ These polymers act as adhesives in the composite provided. Mamunya *et al.*²⁷ reported that the mixing of metal powders and polymer materials improved electrical conductivity of the composite prepared. Shen and Xu²⁸ reported that the use of pore electrode will increase the internal surface area, thus resulting in high electrocatalytic activity. A novel graphite oxide/poly(acrylic acid) nanocomposite was prepared and used by Kyzas *et al.*,²⁶ to remove dorzolamide as biomedical residues in wastewater. They showed that at pH 3, the removal rate was 90% to 95%. Kong *et al.*²⁹ studied the treatment of textile wastewater by using graphite/attapulgite composite materials as anode. Under optimum

experimental conditions, the decolorization rate was close to 100% and COD was 44%. In another study, a graphite-polyurethane composite electrode was used to determine furosemide, an antihypertensive drug, in pharmaceutical samples and to determine tetracycline in water through anodic oxidation.^{25,30}

This study used PVC as an adhesive in the preparation of graphite-PVC composite electrode by mixing graphite powder and PVC. This approach aims to produce cheap and homogeneous carbon/filler composite mixture solution.

This study also investigates the removal efficiency of COD and color of landfill leachate by using electrochemical oxidation with a graphite-PVC electrode. The effect of the operating variables, including the applied voltage, Cl⁻ concentration, and pH solution on the removal efficiency of COD and color in the solution wasted. The energy consumption and current efficiency of COD removal for the electrochemical cell were also calculated.

Experimental

Chemicals and reagents

Chemical oxygen demand (COD) reagent (cat. 21258.25) and total-P reagent (cat. 27427.45) were provided by Loveland (U.S.A). These reagents were used without further purification. 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 (Germany) with purities more than 99.5%. Acetone was supplied by Merck (Germany), tetrahydrofuran (THF) was purchased from Sigma Aldrich and deionized water (DIW) used was supplied by EASYPure RODI (U.S.A).

Site description and sampling

Raw leachate was collected monthly during the period from February to December in 2013, from Jeram sanitary landfill which is located in an oil palm plantation near Mukim Jeram, Kuala Selangor, Malaysia (Figure 1). The landfill area here is roughly rectangle in shape and occupied 64.7 hectares. Jeram sanitary landfill has been operated by Worldwide Holdings since January 2007. This landfill is designed with a capacity to hold 6 million tons of waste. Currently approximately 2000 tons of waste is disposed into the landfill every day, and to-date 4.1 million tons of waste has been added to the landfill. The operator estimated that the landfill will be completely filled in 2017. Hence the company is in planning stage to acquire 100 acre land

near the existing site in order to extend the lifetime of this landfill. All samples were collected in 1 L amber glass bottles with Teflon® lined caps to ensure sample integrity, using a stainless steel bucket previously rinsed with distilled water and methanol. The bottles head space was kept to a minimum by filling the bottles to the top. The bottles were rinsed in the field with sample and filled to the top on the second sampling. Disposable gloves were used to prevent any personal care products from contaminating. The samples were transported in ice cool container to the laboratory and filtered through a 0.7 µm GF/F filter obtained from Whatman to remove suspended solids and stored at 4 °C in order to keep the wastewater characteristics preserved.

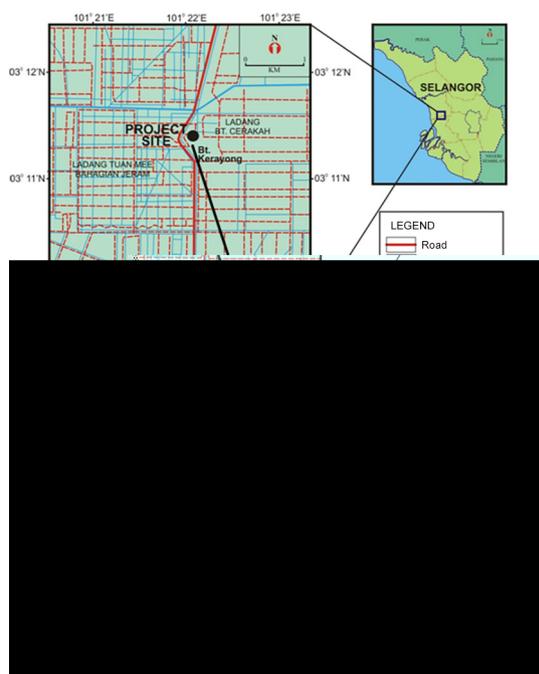


Figure 1. Map describes Jeram landfill leachate location.

Preparation of electrodes

Preparation of Pt electrode

The Pt metal foil electrode was prepared by using a Pt metal foil (99.98% purity from Aldrich chemical company). A 0.5 mm-thick Pt foil was cut into approximately 1 cm × 1 cm piece. 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.²²

Preparation of a graphite-polyvinyl chloride electrode

The graphite-PVC electrode was prepared by mixing a weighed portion of graphite powder (100 mesh in size and 99.9% purity from Aldrich Chemical Company) and PVC in

4 mL tetrahydrofuran solvent. The graphite-PVC electrode was then swirled flatly to homogeneous consistency followed by drying in an oven at 50 °C for 3 h. The mixture was placed in 1cm diameter stainless steel mold and pressed at 10 ton cm⁻² by using hydraulic machine. A typical pellet contained approximately 95% of graphite and 5% of PVC. The total weight of the pellet was approximately 1.5 g. The graphite-PVC pellet was connected to a silver wire with silver conducting paint and sealed to a glass rode. Subsequently, epoxy gum was applied to cover the silver wire connecting surface.²²

Reactor setup

The reaction was connected by using a 100 mL pyrex glass inserted into a Pyrex glass vessel with two points, namely, an inlet and outlet water stream to control the temperature. The Pyrex glass electrochemical cell (reactor) was placed on a magnetic stirring block to keep its contents well mixed during the experiment. The graphite-PVC pellet and Pt plate were used as anode and cathode, respectively. The distance between the electrodes was approximately 2.5 cm. The electrodes were then connected to a direct current power supply (DC) (CPX200 DUAL, 35 V 10 A PSU).

Analytical techniques of physicochemical landfill leachate

The physicochemical characteristics of landfill leachate were determined on the basis of common physicochemical properties according to the standard methods for analysis of wastewaters and surface water developed by the American Public Health Association.³¹ The analyzed parameters (COD, color, and total-P) were measured by a spectrophotometer (Hach Odyssey DR/2400). The pH was measured by a pH meter (PH700 EUTECH Instruments). Total dissolved solids (TDS) and conductivity (Cond.) were measured by using a conductivity meter (cond610). The concentrations of some heavy metals were measured by using inductively coupled plasma optical emission spectrometry (ICP-OES optima 4300DV) and Cl⁻ was measured by using Metrohm 850 professional ion chromatography (IC). The average values of the physicochemical parameters of the landfill leachate from the Jeram landfill prior to treatment were analysed as listed in Table 1. UV-Vis absorption spectrophotometric analysis with an absorbance measuring from 230 nm to 400 nm was also connected by using a Shimadzu UV-2450 spectrophotometer. The surface morphology of the graphite-PVC electrode was analyzed before and after the electrochemical oxidation process by using a

Field Emission Scanning Electron Microscopy (FESEM) (ZEISS, Merlin compact model).

Treatment procedure

Samples of raw landfill leachate were filtered by using a 0.7 μm GF/F filter. Approximately 40 mL of sample was then transferred into the electrochemical cell. The sample in the electrochemical cell was mixed at 200 rpm by a magnetic stirrer during the experiments to keep the sample homogeneous. The effect of pH was studied by using 1 mol L⁻¹ of HCl or NaOH to adjust the pH value. The effect of sodium chloride concentration as the supporting electrolyte was also tested. The reaction was started by applying the specified voltage. The recycling water for temperature control (23-25 °C, i.e., ambient lab scale) was pumped through the reactor jacket. Samples were collected from the reactor at regular time intervals and analyzed to determine the COD and color removal rates during electrochemical treatment with respect to their initial values. After each run, electrodes were polished by using sand papers and washed by using distilled water and acetone. The operational conditions of the experiments are given in Table 2.

Table 1. Physicochemical properties of raw leachate (mean \pm SD)^a

Parameter	Average value (n = 9) ^b
COD / (mg L ⁻¹)	8833 \pm 4343
Color (Pt-Co) ^c	13522 \pm 5535
Total-P / (mg L ⁻¹)	147 \pm 43
pH	8.3 \pm 0.1
TDS / (mg L ⁻¹)	24958 \pm 3826
Cond. / (mS cm ⁻¹)	27 \pm 4
Cl ⁻ / (μg L ⁻¹)	2078 ^d
Ba / (μg L ⁻¹)	97 \pm 54
Cd / (μg L ⁻¹)	6 \pm 2
Cu / (μg L ⁻¹)	36 \pm 24
Pb / (μg L ⁻¹)	525 \pm 90
Zn / (μg L ⁻¹)	17 \pm 5

^aSD: standard deviation; ^bn: number of samples; ^cPt-Co: hazen color unit; ^done sample only.

The removal percentage for COD and color was calculated according to equations 1 and 2.³²

$$R\% = \frac{[\text{COD}]_0 - [\text{COD}]_t}{[\text{COD}]_0} \times 100 \quad (1)$$

where R% is the removal percentage for (COD) parameter, [COD]₀ is initial value of COD, and [COD]_t is the value of COD at time t.

Table 2. Experimental conditions

Parameter	Value
Raw landfill leachate / mL	40
Electrolyte amount (m/v) / %	0 + 2078 mg L ⁻¹ , 0.25 + 2078 mg L ⁻¹ , 0.58 + 2078 mg L ⁻¹
Applied voltage / V	5, 10, 15, 20
pH	3, 7, 9
Temperature / °C	23-25, ambient (lab scale)
time / min	15, 45, 75, 105

$$R\% = \frac{[\text{C.I.}]_0 - [\text{C.I.}]_t}{[\text{C.I.}]_0} \times 100 \quad (2)$$

where R% is the removal percentage for the color parameter, [C.I.]₀ is initial value of the color intensity, and [C.I.]_t is the value of the color intensity at time t.

Results and Discussion

Effect of different parameters on the electrochemical oxidation processes of landfill leachate

Effect of NaCl concentration

The influence of supporting electrolyte (NaCl) concentration on the pollutant degradation rate was tested for three dosages (0% (m/v) + 2078 mg L⁻¹, 0.25% (m/v) + 2078 mg L⁻¹ and 0.58% (m/v) + 2078 mg L⁻¹) at 10 V applied voltage. The rate of degradation of COD and color increased with the increasing of supporting electrolyte concentration (Figures 2a and 2b). When the concentration of NaCl was at the level of (0% m/v + 2078 mg L⁻¹) (i.e., without adding NaCl), the removal rates of COD and color were 27% and 39%, respectively. This result could be attributed to the chloride content in landfill leachate, as mentioned in Table 1. The removal efficiencies of COD and color were 40% and 50%, respectively, at the level of 0.58% (m/v) + 2078 mg L⁻¹ NaCl. This result was caused by the increasing formation of OCl⁻.

During electrochemical oxidation, Cl⁻ was discharged at the anode to generate Cl₂. Thereafter, Cl₂ was chemically converted to OCl⁻ to effectively oxidize the pollutants (equations 3 to 6). In the light of the above results, 0.58% (m/v) + 2078 mg L⁻¹ NaCl was selected for further experiments.



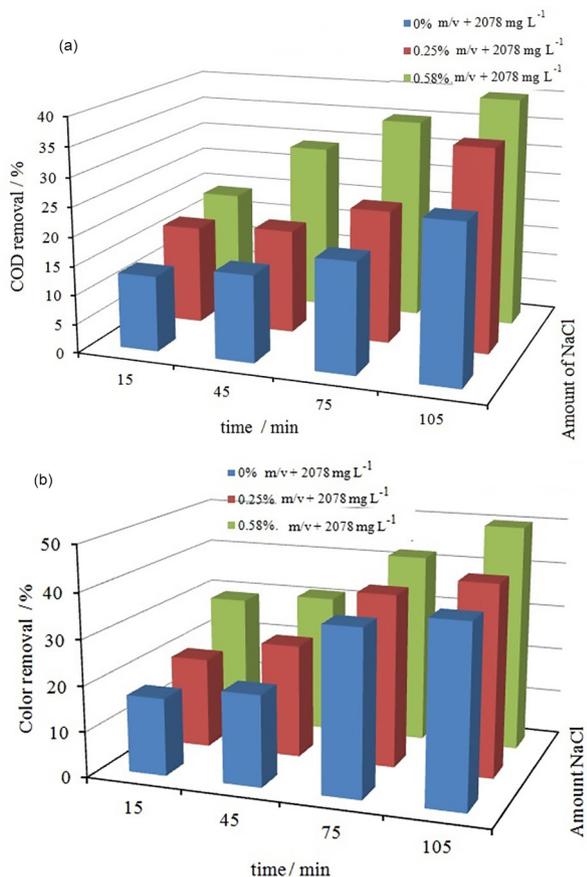


Figure 2. Effect of NaCl concentration on the removals: (a) COD and (b) color from leachate at different electrolysis times (applied voltage: 10 V; pH: 8.3).



In a separate experiment, OCl^- formation was investigated by adding 0.58% (m/v) NaCl to 40 mL of deionized water. During electrolysis, OCl^- was produced because of the presence of Cl^- , which was responsible for the formation of hypochlorite ions to degrade the pollutants in the leachate. The formation of OCl^- in the aqueous solution was monitored using UV-Vis spectrophotometer (Figure 3).

Effect of applied voltage

One of the most important parameters that can affect the removal efficiency in the electrochemical process is the applied voltage.³³ Thus, 5, 10, 15 and 20 V were applied. Figures 4a and 4b show the effect of applied voltage on COD and color removal efficiencies under the following conditions: 0.58% (m/v) + 2078 mg L⁻¹ NaCl as supporting electrolyte and at pH 8.3. At any time during the electrolysis, increasing the applied voltage

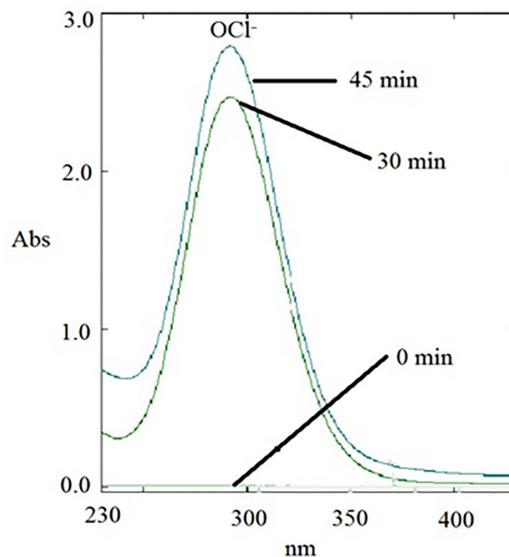


Figure 3. UV-Vis spectra of OCl^- in aqueous media: concentration of NaCl: 0.58% (m/v); applied voltage: 10 V.

was accompanied by an increase in the percentage of COD and color removal (Figures 4a and 4b). This result can be explained by the fact that the rate of hypochlorite ions generation increased with applied voltage, thus, eventually increasing pollutant degradation. The removal efficiencies of COD and color at 5 V were 11% and 39%, respectively. When the applied voltage was increased to 20 V, the removal efficiency dramatically increased to approximately 90% of COD. The color was also completely removed at 105 min. The difference between the rate of degradation in terms of COD removal for applied voltage at 105 min of 15 V and 20 V was approximately 8%. Hence, choosing 20 V as the best applied voltage was unreasonable because this study was restricted to enhancing the potential by energy consumption consideration. These results are in agreement with the previous study.¹⁹ On the basis of these results, 15 V was selected as the optimum voltage for further experiments.

Determination of the optimum cell voltage based on current efficiency (CE)

The results of current efficiencies were shown in Figure 5 and calculated on the basis of equation 7.¹⁹ The highest current efficiency was observed at 15 V. Increasing the cell voltage from 15 V to 20 V insignificantly affected COD removal (only 8%) (Figure 4a). The reason behind this result might be corrosion of graphite material at high voltage (20 V). Therefore, at high voltage, the strong wear of the graphite anode during leachate electrolysis was most likely caused by the graphite solubilization enhanced by the

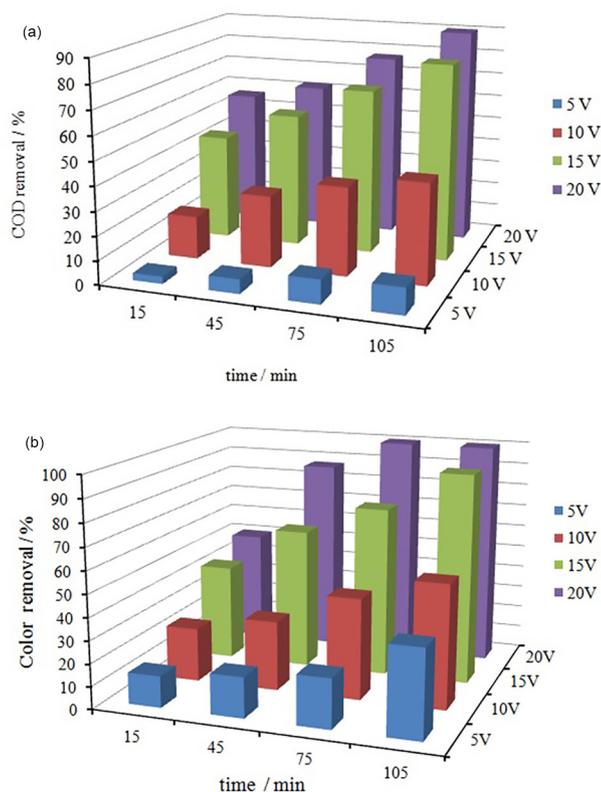
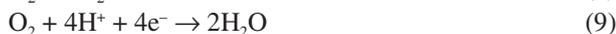


Figure 4. Effect of applied voltage on the removals: (a) COD and (b) color from leachate during difference electrolysis times (0.58% (m/v) + 2078 mg L⁻¹; pH 8.3).

presence of active chlorine. The maximum use of graphite electrode was experienced between 5 and 7 h of operation depending on toughness of reaction conditions.

$$CE = \frac{[(COD)_0 - (COD)_t]}{8I\Delta t} \times FV \quad (7)$$

where CE is current efficiency; (COD)₀ and (COD)_t are the CODs at initial time and t time, respectively (g O₂ L⁻¹); I is the current (A); F is Faraday's constant (26.8 Ah); V is the volume of the treated leachate (L), the numerical constant (8) considered the equivalent weight taken into account the equivalent weight of O₂ because of the cathodic reactions.³⁴



Effect of voltage on energy consumption (EC)

The energy consumed in the electrochemical oxidation of the landfill leachate by using a constant voltage was calculated by using equation 10.¹⁹ The results obtained are presented in Figure 6. Energy consumption increases with voltage, but the increasing of voltage from 15 V to 20 V did

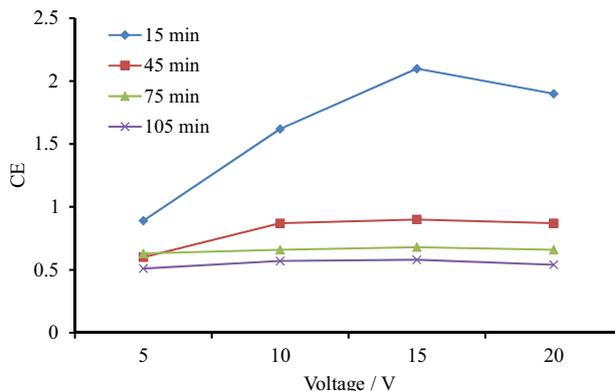


Figure 5. Effect of applied voltage on current efficiency (CE) in electrochemical process at different times (0.58% (m/v) + 2078 mg L⁻¹ NaCl; pH 8.3).

not enhance COD removal (Figure 4a). This finding was in line with the previous CE, hence, 15 V was considered the optimum value for further experiments.

$$EC = \frac{VI\Delta t}{\Delta COD} \quad (10)$$

where EC is energy consumption in kWh per kg of COD reduced in the process (kWh kg⁻¹ of COD), V is the cell potential in V, I is the current in A, Δt is the electrolysis time in h, and ΔCOD is the amount of COD reduction during the time t.

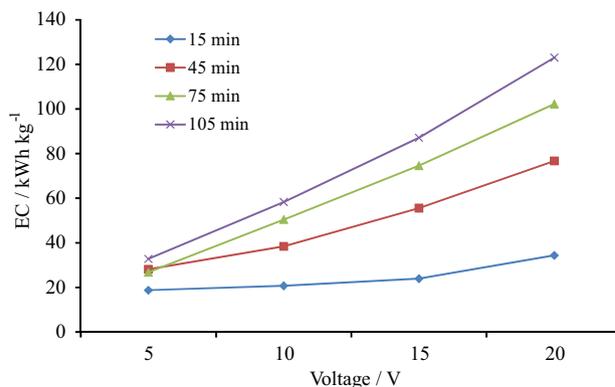


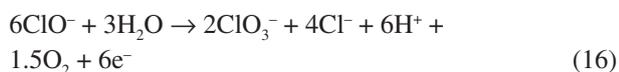
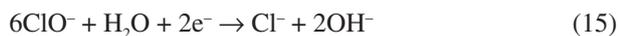
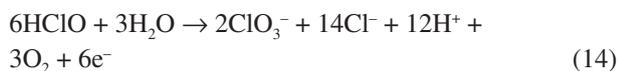
Figure 6. Effect of applied voltage on energy consumption (EC) in electrochemical process at different times (0.58% m/v + 2078 mg L⁻¹ NaCl; pH 8.3).

The energy consumption of real samples is very different, thus, comparing the results obtained with other papers that used different real samples, anode materials, volume of samples, and time of treatment will be unreasonable. To the best of our knowledge, a comparative study on the treatment of landfill leachate has not been reported yet. For example, Panizza and Martinez-Huitle¹² evaluated energy consumption during treatment of landfill leachate by using three types of

anodes: TiRuSnO₂, PbO₂ and BDD. The researchers found that the energy consumption of TiRuSnO₂, PbO₂, and BDD were 250, 275, and 140 kWh/m³ at 8 h electrolysis time, respectively. However, Bashir *et al.*²⁰ found that the energy consumption was 1.1 kWh kg⁻¹ of 600 mL leachate when using graphite electrode. Another study reported that the energy consumption was influenced by the volume of the leachate sample.³⁵ The energy consumption was reduced from 90.1 kWh kg⁻¹ to 55.7 kWh kg⁻¹ when the volume was increased from 5 L to 10 L.

Effect of pH

In the electrochemical oxidation process, the pH of the solution plays an important role in the removal efficiency of pollutants.¹⁹ To investigate the effect of pH on COD and color removal, the experiments were conducted under pH 3, 7, and 9. The results in Figures 7a and 7b showed that the maximum removal of COD and color was obtained at pH 3, whereas the lowest removal was obtained at pH 9. The reason behind this result was the low production of chlorine/hypochlorite ion in alkali medium, which favors the formation of chlorate or perchlorate. In acidic medium, the COD and color removal percentages were high because the chlorine/chloride that present in the solution was in the form of hypochlorous acid, which possesses high oxidation potential compared with hypochlorite (equations 11 to 18). Therefore, pH 3 was the optimum value for the treatment of landfill leachate because it had the highest COD and color removal percentage compared with other pH values (Figures 7a and 7b).



where R is pollutants and P is product.

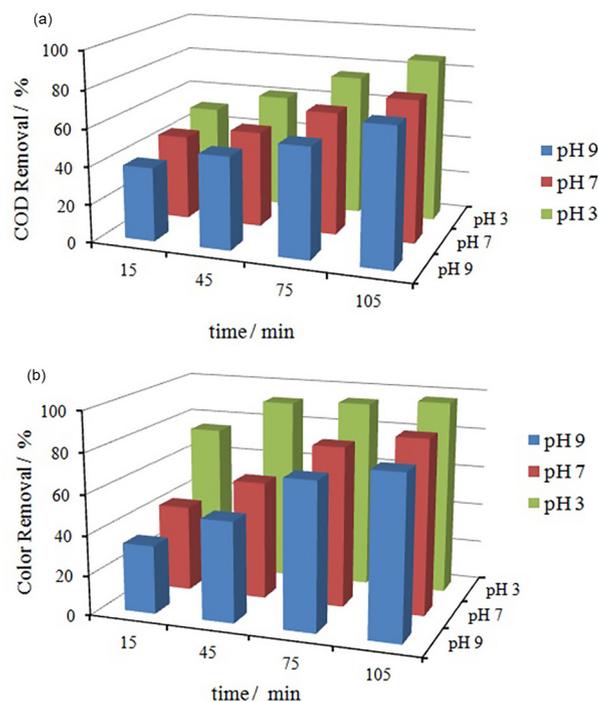


Figure 7. Effect of pH on the removal: (a) COD and (b) color from leachate at different electrolysis times (applied voltage: 15 V; 0.58% m/v + 2078 mg L⁻¹ NaCl).

Considering that no reduction of total COD was observed, organochlorides might have been formed. The main drawback of the indirect electrochemical degradation process was the formation of chlorinated organic compounds as hazardous compounds. Naumczyk *et al.*³⁶ found that several organic chlorides formed in high concentration during the electrooxidation of textile wastewater contains high concentration Cl⁻. Chiang *et al.*¹⁶ conducted experiments with lignin, tanning acid, and chlorotetracycline. All three compounds produced high concentration of total organic halides (TOX) at the beginning of electrolysis, but the level of TOX decreased with electrolysis time. However, Deng and Englehardt¹⁸ reported that investigation on the formation of chlorinated organic compounds during leachate electrooxidation was lacking.

Investigation of surface morphology of graphite-PVC

The surface morphology of graphite-PVC was investigated by using field emission scanning electron microscopy (FESEM) to evaluate the effectiveness of electrochemical oxidation before and after treatment (Figures 8a and 8b).

To validate the electrochemical oxidation, two batches of experiments were conducted. The first experiment was for the blank electrode (i.e., without treatment) (Figure 8a),

and the second experiment was specified for the electrode after treatment (Figure 8b).

The electrochemical oxidation affected graphite-PVC and created several holes on the graphite surface (Figure 8b). However, Figure 8a shows soft and hole-free surface because electrochemical oxidation did not occur.

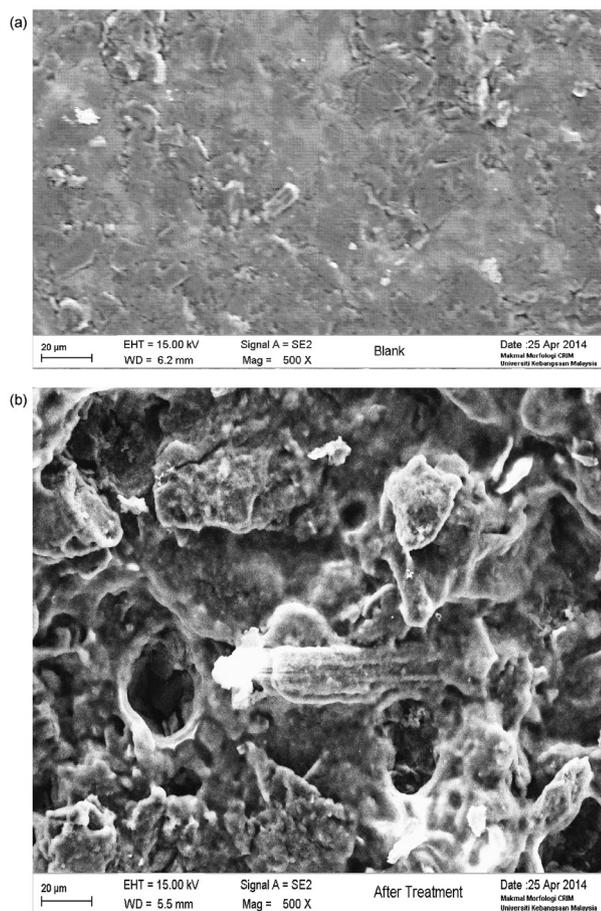


Figure 8. Scanning electron microscope: graphite-PVC (a) before and (b) after treatment.

Kinetic investigations

In electrochemical oxidation, the COD removal rate is proportional to the pollutant and chlorine/hypochlorite concentrations. Considering that pollutant removal occurs via indirect oxidation (when chloride is used as supporting electrolyte), the effect of chlorine/hypochlorite and the kinetics of COD removal may be derived as follows (equations 19 to 27):



$$[\text{COD}]_0 = 0 \quad (20)$$

$$[\text{COD}]_t = \times \quad (21)$$

$$r = k[\text{COD}][\text{Cl}_2] \quad (22)$$

$$k[\text{Cl}_2] = k^- \quad (23)$$

$$\frac{d[\text{COD}]}{d[t]} = -k^- [\text{COD}] \quad (24)$$

$$\frac{-d[\text{COD}]}{d[t]} = k^- [\text{COD}] \quad (25)$$

$$\int_{[\text{COD}]_0}^{[\text{COD}]_t} \frac{d[\text{COD}]}{[\text{COD}]} = -k^- \int_0^t dt \quad (26)$$

$$\ln \frac{[\text{COD}]_t}{[\text{COD}]_0} = -k^- t \quad (27)$$

where r is the rate of reaction, k is the rate constant, $[\text{COD}]_0$ is the initial concentration of pollutant, and $[\text{COD}]_t$ is the concentration after a certain reaction time (t).

During electrochemical oxidation, chlorine/hypochlorite is produced by the anodic oxidation of chloride and is converted to chloride as the pollutants are oxidized. Thereafter, the chloride will be anodically oxidized to form chlorine/hypochlorite, which oxidizes the pollutant again. Accordingly, the concentration of chlorine/hypochlorite could be assumed constant, and $[\text{Cl}_2]$ and k in equation 22 might be merged into a pseudo-first-order kinetic constant (k^-) (equation 23). By plotting $\ln[\text{COD}]_0/[\text{COD}]_t$ against time k^- can be obtained. The effect of applied potential and pH on the rate constant was investigated. The results are shown in Figure 9, Figure 10 and Table 3.

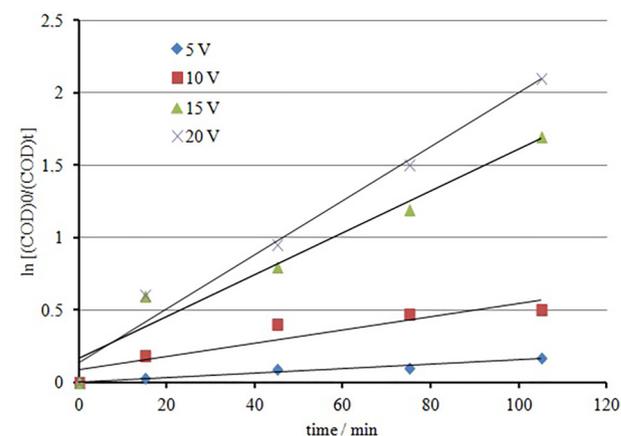


Figure 9. Kinetic analysis for pseudo-first-order COD removal using different applied voltage (0.58% m/v +2078 mg L⁻¹ NaCl; pH 8.3).

The results in the Table 3 showed that voltage had an enhancing effect on rate constant because of the increase in the concentration of active oxidant species such as Cl_2/OCl^-

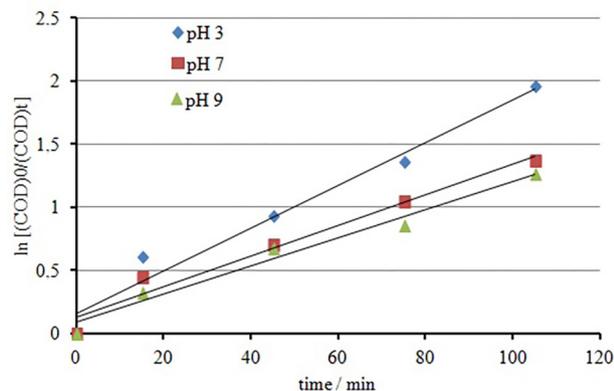


Figure 10. Kinetic analysis for pseudo-first-order COD removal using different pH values (0.58% m/v + 2078 mg L⁻¹ NaCl; applied voltage: 15 V).

Table 3. Rate constant for the removal of COD at different applied voltages and pHs

Operating parameter	Value	k ⁻ / min ⁻¹
Applied voltage / V	5	0.0015
	10	0.0046
	15	0.0145
	20	0.0186
pH	3	0.017
	7	0.012
	9	0.011

in the solution. Rate constant was directly increased with increasing applied voltage from 0.0015 to 0.0186 min⁻¹ within 5 V to 20 V. However, increasing the cell voltage from 15 V to 20 V insignificantly changed the rate constant.

The effect of pH on the rate constant for removal of COD was also studied. The kinetics at all pH values follow the first pseudo model with good linearity ($R^2 = 0.97$). The highest rate constant was observed at pH 3, 0.017 min⁻¹. This value confirmed the optimum pH, as discussed in the COD removal section. All rate constants were 0.011, 0.012, and 0.017 min⁻¹ at pH 9, 7, and 3, respectively.

Conclusion

The present investigation illustrates the following results:

Graphite-PVC composite was successfully used as a low-cost alternative for the removal of hazardous compounds from landfill leachate. Electrochemical oxidation can significantly reduce concentrations of organic contaminants and color in the leachate. Voltage applied, chloride concentration, and pH can considerably influence performance. The FESEM study supported the results on electrochemical oxidation process by showing

the morphological difference in the graphite-PVC electrode before and after the electrochemical oxidation of landfill leachate.

Although the removal efficiency increased with increasing applied voltage and the optimal applied voltage was 15 V, considering the removal efficiency, energy consumption, and current efficiency, simultaneously. The observed difference in the kinetics of COD removal at different value of voltage might be attributed to the increasing hypochlorite concentration.

Acknowledgments

The authors would like to thank the ALIR staffs at faculty of Science and Technology for providing ultrapure water and facilities for sampling. This work was financially supported by UKM-DLP-2012-024 and FRGS/2/2013/SG01/UKM/01/1.

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Submitted: October 31, 2014

Published online: March 10, 2015