Electrochemical Degradation of Reactive Orange 16 by using Charcoal-Based Metallic Composite Electrodes
(Penguraian Elektrokimia Reaktif Oren 16 Menggunakan Elektrod Komposit Logam Berasaskan Arang)

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ABSTRACT

The performance of charcoal composite electrodes, by using commercial activated charcoal and charcoals from coconut trunk, mangrove wood, rubber wood, and sugarcane, was compared in an attempt to fabricate effective and low cost electrodes for wastewater treatment in textile industries. Reactive Orange 16 was chosen as a model dye because of its high resistance towards conventional treatment methods, while sodium chloride was selected as a supporting electrolyte. The electrode efficiencies were determined based on the percentage of Reactive Orange 16 decolourisation. The charcoals used, duration of electrolysis, functional groups present in charcoals, Brunauer-Emmett-Teller surface area and production of hypochlorite ion that contribute to the effectiveness of the electrodes were examined. The coconut trunk, rubber wood, sugarcane, mangrove wood, and commercially available activated charcoals that were incorporated into tin composite electrodes were able to degrade Reactive Orange 16 until 98.5%, 96.2%, 83.0%, 71.2%, and 29.6%, respectively, after 20 min of electrolysis. The degradation increases with duration of electrolysis. This study illustrated that the production of hypochlorite ion from sodium chloride in solution was the main factor that enhanced the Reactive Orange 16 colour removal. Adsorption process on the electrode surface did not play any significant role in the dye decolourisation.

Keywords: Agricultural waste; composite; decolourisation; electrolysis; reactive orange 16

ABSTRAK

Prestasi elektrod komposit berasaskan arang dengan menggunakan arang teraktif komersial dan arang daripada batang kelapa, kayu bakau, kayu getah dan tebu telah dibandingkan dalam satu percubaan untuk menghasilkan elektrod yang berkesan dan berkos rendah bagi perawatan air sisa industri tekstil. Reaktif Oren 16 dipilih sebagai pewarna ujian kerana ketahanannya yang tinggi terhadap kaedah perawatan konvensional manakala natrium klorida dipilih sebagai elektrolit penyokong. Keberkesanan elektrod ditentukan berdasarkan peratus penyahwarnaan Reaktif Oren 16. Jenis arang yang digunakan, tempoh masa elektrolisis, kumpulan berfungsi yang wujud dalam arang, luas permukaan Brunauer-Emmett-Teller dan penghasilan ion hipoklorit yang menyumbang kepada keberkesanan elektrod tersebut telah dikaji. Arang daripada batang kelapa, kayu getah, tebu, kayu bakau, dan arang teraktif komersial yang dicampurkan dalam elektrod komposit tin mampu menguraikan Reaktif Oren 16 masing-masing sehingga 98.5%, 96.2% 83.0%, 71.2% dan 29.6% selepas 20 min elektrolisis. Penguraian ini meningkat dengan pemanjangan tempoh masa elektrolisis. Hasil kajian menunjukkan bahawa penghasilan ion hipoklorit daripada larutan natrium klorida merupakan faktor utama yang menyebabkan peningkatan dalam penyahwarnaan Reaktif Oren 16. Proses penjerapan pada permukaan elektrod tidak memainkan peranan penting dalam penyahwarnaan pewarna yang digunakan.

Kata kunci: Elektrolisis; komposit; penyahwarnaan; reaktif oren 16; sisa pertanian

INTRODUCTION

The Malaysian batik industry has been long established and is one of the important branches of the textile industry in Malaysia. The industry uses lots of water in the textile dyeing processes thus, leaves a great amount of effluents to be treated. This is because the effluents are toxic, mutagenic, have low ability to biodegrade, high COD value, pH and temperature (Liakou et al. 1997; Šíma & Hasal 2013). One of the most vivid indicators of textile industrial wastewater pollution is colour (Nigam et al. 1996). At very low dye concentrations, their strong colour are still visible and disturb the solubility of gas in water bodies (Chung & Stevens 1993). The highly coloured effluents can give severe problems when disposing and discharging the wastewater into the water system without proper treatment; hence this will cause serious problems to the environment (Zollinger 2003). The strong colour is caused by the unfixed dyes. The types of dye, fibre, mode of application and shade depth will affect the degree of dye fixation into fabric (Alvares et al. 2001). About 10,000 different dyes and pigments are produced annually (Doble & Kumar 2005). The most common commercial dyes used in the textile industry are azo dyes, which are characterized by the presence of nitrogen-nitrogen double bonds (N=N) (Lee et

al. 2006). Almost 50% of produced dyes contain azo group (Bauer et al. 2001). Azo dyes, which normally consist of aromatic hydrocarbons, derivatives of benzene, aniline, toluene, naphthalene and phenol, are the most toxic to aquatic organisms. They pose lethal effect, carcinogenicity, genotoxicity and mutagenicity to fish, algae, bacteria as well as animals (Puvaneswari et al. 2006). Besides, the azo dyes are able to decrease the penetration of light, creating interruption in photochemical activities in aquatic systems (Sharma et al. 2003). Dyes are bright coloured (orange and yellow) because of chromosphere and azo group (Lee et al. 2006). The most problematic dye to be treated is reactive, water soluble, acidic and brightly coloured. These kinds of dye cannot be treated by conventional treatment methods (Willmott 1998). The complexity of aromatic molecular structure of the dyes may affect the stability and biodegradability of compounds (Wang & Li 2007). C.I. Reactive Orange 16 (RO16), an anionic sulphonated reactive azo dye was chosen as the model dye because of its high resistance towards conventional treatment methods and difficult to biodegrade (Chen 2009). Other than dyes, effluent from *batik* industrial wastewater also consists of resin, wax and silicate (Rashidi et al. 2012).

A study to determine the best method, in terms of efficiency, easiness and cost saving procedure to treat textile wastewater, has been carried out by many researchers. Generally, wastewater treatment methods can be divided into three main categories, which are mainly biological, chemical and physical processes with their own advantages and disadvantages (Robinson et al. 2001). As an example, although ozonation is useful to quickly degrade dye, it is a very expensive method (Tizaoui & Grima 2011; Xu et al. 1999). Biological treatment is inefficient for azo compound degradation because of the large degree of aromatic groups present in the dye molecule. Under anaerobic and aerobic conditions, azo compounds are non-biodegradable. However, they are able to be degraded by Phanerochaete chrysosporium (Paszczynski & Crawford 1995; Saxe et al. 2006). Chemical and physical techniques can be used to remove dye, but are limited only to small effluent volume (Robinson et al. 2001). The most interesting method to treat wastewater is by using electrochemical technology methods, which include electrooxidation, electrocoagulation, electrodeposition and electroflotation (Chen 2004). However, this paper is focused on the electrochemical oxidation technique which is proven to be a very effective method in textile wastewater treatment. The technique is able to completely oxidize organic pollutants to water and carbon dioxide (Parsa et al. 2009). Electron is the main reagent utilised in electrochemical technologies and it is called as 'clean reagent' (Maljaei et al. 2009). The risk of volatilization and releasing untreated residues could be minimized because electrolysis is conducted at atmospheric pressure and room temperature. During electrolysis, there were no consumption of additional reagents and no by-product or sludge was produced (Andrade et al. 2009). Furthermore, only a low consumption of energy is needed to degrade chromophore groups present in dyes from textile wastewater for a short period of electrolysis and the electricity cost is equivalent to the chemicals prices (Chatzisymeon et al. 2006; Robinson et al. 2001). Moreover, this method is safe for the environment as the breakdown of metabolites were mostly harmless. Hence, the treated wastewater can be released back into the nature and can also be efficiently reused for colouring application (Mohan et al. 2007; Ogutveren & Koparal 1994; Pelegrini et al. 1999).

The electrode material selections are very important to obtain the desired result in the electrochemical oxidation process. In this study, charcoal was used as the main ingredient in electrode fabrication. It is known as a charcoal-based metallic composite electrode since metals are also used to increase colour removal efficiency. Five types of charcoal which are commercially available activated charcoal, coconut trunk, mangrove wood, rubber wood and sugarcane charcoals, are selected. Wood charcoal can be defined as a black porous solid that is made up of amorphous carbon and residual ash, cheap and can be obtained from burning wood (Abdollahi & Hosseini 2014; Ahmedna et al. 2000). Application of wood charcoals in water treatment is not a new discovery. Activated charcoal from bamboo are utilized in wastewater treatment as adsorbents and can eliminate Zn(II) and Ni(II) efficiently from aqueous solution (Lalhruaitluanga et al. 2011). It was reported that carboxylic, hydroxyl and lactone groups present, for example, in coconut shell can cause sorption properties that have high affinity for metal ions and ensure heavy metal removal potential (Tan et al. 1993). Other report showed that polluting substances, such as arsenic, humic acid and phenol, can be removed by using activated carbon from rice husk and bagasse (Kalderis et al. 2008).

The objectives for this research were to fabricate low cost and environmental friendly charcoal-based metallic composite electrodes by using charcoals obtained from four different types of agricultural waste (rubber and mangrove woods, sugarcane and coconut trunk charcoals) and also commercially activated charcoals to study on factors that contribute to the RO16 dye degradation.

MATERIALS AND METHODS

CHEMICALS, CHARCOAL AND DYESTUFF

Deionized water was used as solvent throughout the experiment. A 200 mg/L of RO16 (C.I. 17757) as the chosen model dye and 1 M of NaCl were prepared as stock solutions. The chemical structure of RO16 is as shown in Figure 1. NaCl and an activated charcoal powder were purchased from respective R&M Chemicals and BDH Chemicals, and used without further purification. The working solution was prepared by adding 64 mL RO16 stock solution with 1 M NaCl to give 80 mL working solution, containing 160 mg/L RO16 and 0.2 M NaCl. Mangrove wood charcoal was bought from the local

grocery store. Fresh rubber woods, coconut trunk as well as sugarcane were obtained from local villages. These three materials were openly burned to obtain charcoals and washed with water to get rid of ashes, dried overnight at 100°C (including mangrove wood charcoal), and ground (all four charcoals) to finely divided charcoal powder. All the five powdered charcoals were passed through a 45 μm sieve. Powder graphite, tin, and polyvinyl chloride (PVC) were bought from Loba-Chemie, Riedel-de-Häen, and BDH Chemicals, respectively. Silver paint was purchased from RS Component and DEVCON epoxy-adhesive was bought from a local hardware store.
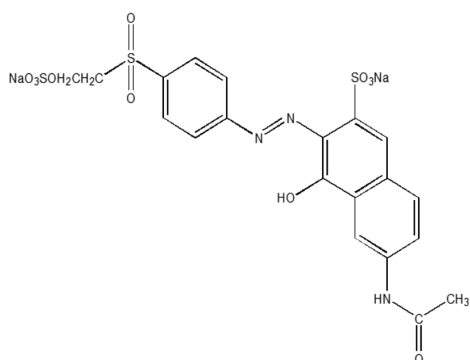

FIGURE 1. Structure molecule of Reactive Orange 16 (RO16)

ELECTRODES PREPARATION

The electrodes preparation was carried out according to the common procedure used elsewhere (Riyanto et al. 2007; Zakaria et al. 2015). The homogenized mixtures of charcoal-graphite-tin-PVC and graphite-PVC (by weight composition of $C_{30}C^G_{18}Sn_{12}PVC_{40}$ and $C^G_{60}PVC_{40}$) were placed in two different evaporating dishes. About 5 mL of THF was added and the mixtures were stirred by using a glass rod. This was to dissolve PVC in the mixture until the solvent evaporated to dryness. Then, the mixtures were oven dried at 100°C for 3 h and finely ground with a mortar and pestle. The two homogenized mixtures were added one after another into a 13-mm diameter mould in 85:15 weight ratio and later pressed at 10 tonne cm^{-2} to form two-layer round-cylindrical pellets of approximately 0.8 g. Then, the pellets were attached to the U-bent end of a silver wire at the centre of the round thin layer surface of the two-layer pellets by using silver paint. From observation, it was obvious the graphite layer was shinier as compared to the charcoal layer. The straight part of the silver wire was enclosed in glass tube. After the paint had dried, DEVCON epoxy-adhesive was applied all over the pellets, except for the front surface of the thick layer parts of the two-layer pellets. Then the modified pellet (at the surface where epoxy-adhesive was applied) was attached to a glass-slide (22mm × 22 mm) and the end of the glass tube to strengthen the fabricated electrode. This modification is to ensure that the fabricated electrode was completely closed to prevent the solution from coming

in touch with the wire during the experiment (Zakaria et al. 2015).

DECOLOURISATION OF REACTIVE ORANGE 16 DYE (RO16)

The study on RO16 decolourisation was conducted at room temperature. A 100 mL Pyrex glass beaker was used as an electrolysis undivided cell. The five charcoal composite electrodes were used as anode while the stainless steel rod (d=10 mm) was used as cathode. The 80 mL working solution was stirred throughout the experiment by using a magnetic stirrer to ensure a uniform concentration and increase the mass transport of the electrolyte. Direct current power supply (TTi PSU Bench CPX400) was used as power supply at a fixed voltage of 10 V for 2 h. The experimental set-up is as shown in Figure 2. About 3 mL of electrolytic solution was taken at every 10, 20, 40, 60, 90, and 120 min for measuring absorbance by using a UV-visible spectrophotometer.
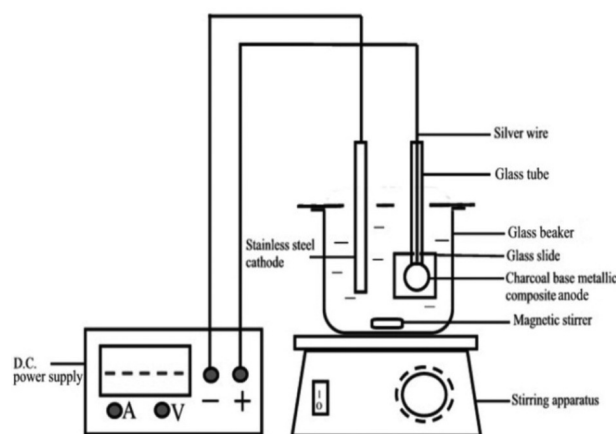

FIGURE 2. Experimental set-up for electrolysis process

INSTRUMENTATION

The decolourisation of RO16 was determined by the changes in absorption intensity of azo chromophore (-N=N-) at a wavelength of 493 nm by using UV-visible spectrophotometer while Chemical Oxygen Demand (COD) was measured by using Hach spectrophotometer (DR/2400) according to Method 8000, as suggested by the *DR/2400 Procedure Manual* (Hach 2004). The electrode effectiveness was evaluated by the percentage of RO16 colour removal. This paper will focus on two RO16 absorption bands which were located at 388 nm (due to π-π* transition due to the aromatic rings bonded to the azo group) and 493 nm (due to chromophobic azo compound n-π* transitions). Both bands contributed to the strong orange colour appearance (Migliorini et al. 2011). The spectra of the charcoals were recorded by using Fourier Transform Infrared Spectrometer (FTIR) to identify the functional groups present in the charcoals, which may be responsible for decolourisation and COD removal efficiency. The Scanning Electron Microscope

(SEM) was performed to observe porosity of the charcoals. The surface area of the charcoals was verified by using Brunauer-Emmett-Teller analysis (BET).

RESULTS AND DISCUSSION

The colour removal experiments were conducted for 2 h and the results obtained are as summarized in Table 1 as well as in Figures 3 and 4. As mentioned previously, the charcoals used in the composite electrodes were from coconut trunk, rubber wood, sugarcane, mangrove wood and the commercial charcoal. They were able to reduce RO16 colour up to 98.5%, 96.2%, 83.0%, 71.2% and 29.6%, respectively, after 20 min of electrolysis and increased up to 99.8%, 99.0%, 99.5%, 99.2%, and 83.3%, respectively, after 2 h. In Figure 3, the UV-visible spectra showed that both maximum peaks at 388 and 493 nm decreased in absorbance, in tandem with the decrease in RO16 colour intensity. The decrease signifies the breakage of azo bonds (N=N) and degradation of aromatic rings (Migliorini et al. 2011). Rapid decrease of the two absorption bands can be observed with the coconut trunk charcoal composite electrode as it removed 75.2% and 98.5% of RO16 colour in 10 and 20 min, respectively. The efficiencies of rubber wood, sugarcane and mangrove wood charcoal composite electrodes in degrading azo chromophore were also proven since the two bands were almost vanished in respective 20, 40 and 60 min of

Rubber wood charcoal

Coconut trunk charcoal

Sugarcane charcoal

Mangrove wood charcoal
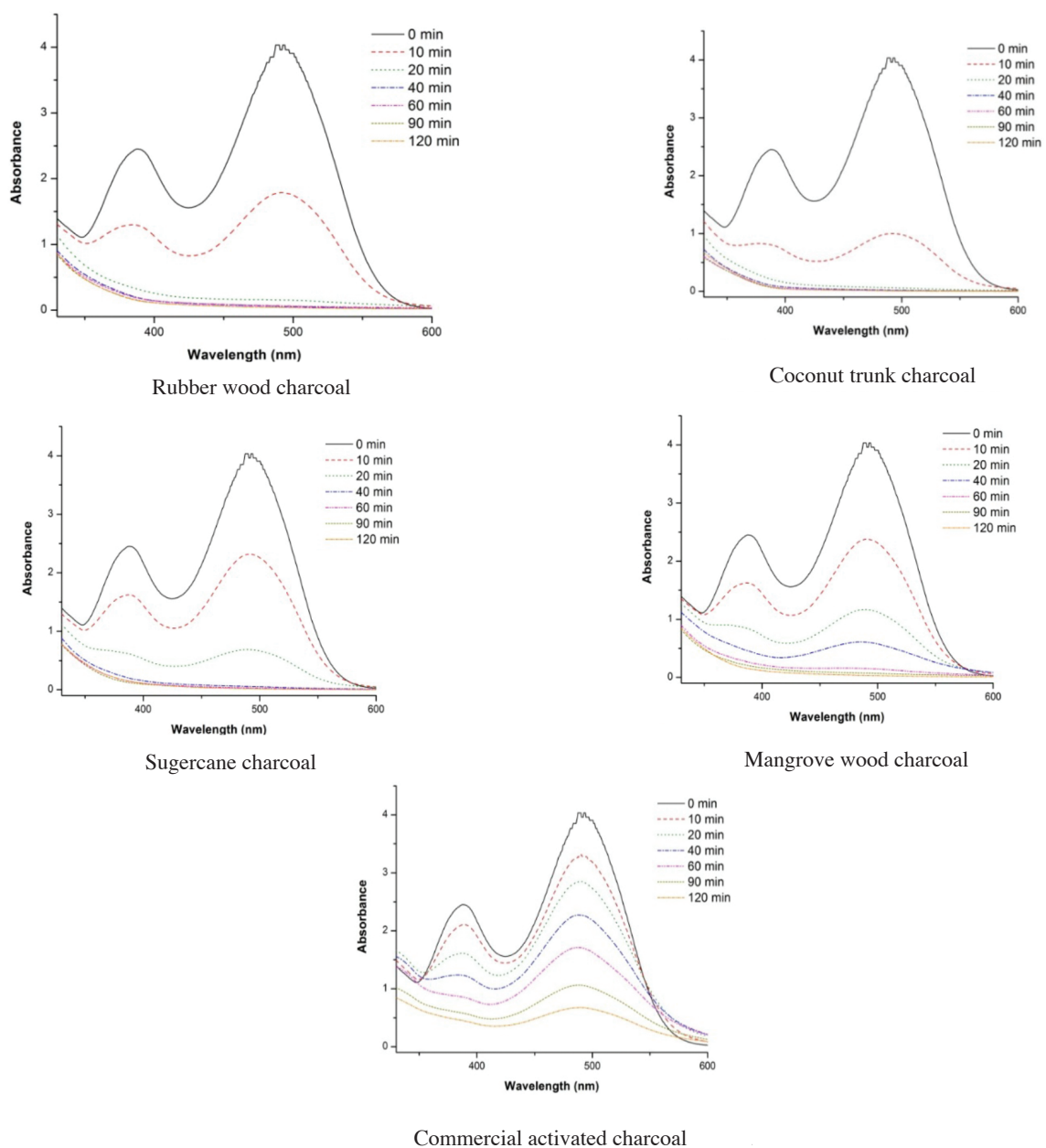

Commercial activated charcoal

FIGURE 3. UV-visible spectra of RO16 degradation by electrolysis using composite electrodes with different sources of charcoals

electrolysis. However, the commercial activated charcoal composite electrode needed 120 min to degrade RO16 dye to 83.3%. The percentages of colour removal increase proportionally with the duration of electrolysis.

Figure 4 shows the effects of decolourisation percentages against time for various charcoal composite electrodes. Generally, from five charcoal-based composite electrodes, four were effective in decolourising the RO16 textile dye. The coconut trunk charcoal composite electrode was the most efficient as compared to others while the commercial activated charcoal gave the lowest degradation efficiency since it took a longer time to degrade azo bonds in RO16.
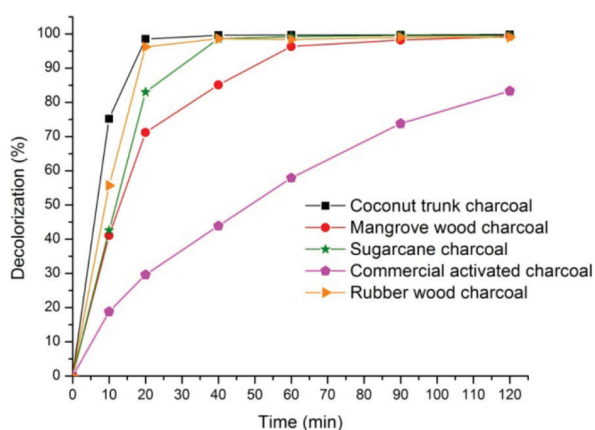

FIGURE 4. Effects of electrolysis time on decolorization percentages of RO16 using composite electrodes with different sources of charcoals

This study focused on charcoal as the main anode component for the oxidation process. Only one-layer charcoal-graphite-tin-PVC as anode fabricated electrode was used in the decolourisation of RO16 textile dyes. However, since the pellets contained charcoal as the main component, the resulting pellet became less dense; thus, allowing the solution to penetrate through where the silver wire cannot be attached to the pellets completely (Zakaria et al. 2015). Connection between silver wire and fabricated electrode are very important because silver wire acts as an electrical lead in the electrochemical set-up (Kartick et al. 2017).

Nevertheless, no connection is discovered between colour removal and COD removal (Rajkumar & Kim 2006). According to the results obtained, as summarized in Table 1 and as shown in Figure 5, mangrove wood charcoal composite electrodes gave the highest COD removal percentage after 2 h of electrolysis (56.4%), followed by charcoals of coconut trunk, commercially activated, sugarcane and rubber wood composite electrodes with 53.9%, 43.7%, 37.6%, and 32.2% COD removal, respectively. Even though colour removal shown by the commercial activated charcoal composite electrode was the lowest, COD removal for this electrode was better than sugarcane and rubber wood charcoal composite electrodes. The capability of all charcoal composite electrodes in COD removal was not very efficient even though the colour removal rate was comparatively high, demonstrating that the breakage of the azo bonds was the first step of electrochemical degradation, followed by degradation of aromatic rings which led to the continuation of COD removal (Fernandes et al. 2004). All charcoal composite electrodes showed an increase in COD removal percentages against time, except for the sugarcane and rubber wood charcoal composite electrodes.
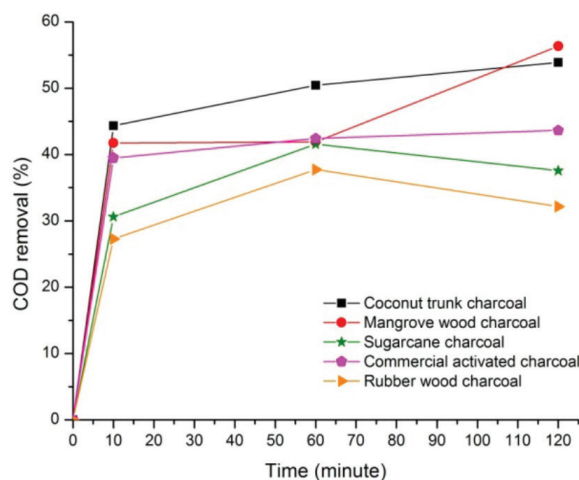

FIGURE 5. COD removal percentages of RO16 solution with time in electrolysis using composite electrodes with different sources of charcoals

TABLE 1. Percentage color and COD removal of RO16 by electrolysis using composite electrodes with different sources of charcoals

Electrolysis time (min)	Coconut trunk		Sugarcane		Rubber wood		Mangrove wood		Commercial activated	
	Color	COD	Color	COD	Color	COD	Color	COD	Color	COD
10	75.3	44.4	42.6	30.6	55.7	27.3	41.1	41.7	18.8	39.5
20	98.5	-	83.0	-	96.2	-	71.2	-	29.6	-
40	99.6	-	98.6	-	98.6	-	85.1	-	43.9	-
60	99.7	50.4	99.2	41.6	98.4	37.7	96.3	41.9	57.9	42.4
90	99.7	-	99.5	-	99.0	-	98.2	-	73.8	-
120	99.8	53.9	99.5	37.6	99.0	32.2	99.2	56.4	83.3	43.7

Anode material is one of the vital part of an anodic oxidation process (Chen 2004). SEM was utilized to study the topography of the charcoals, which give useful information on surface features (Achaw 2012). Figure 6 shows the SEM images of all raw charcoals used. The non-uniformity in sizes and shapes of the particles were observed. The porosity of charcoals enhanced the value of surface area; hence, increased the saturation capacity per unit mass of charcoals. To investigate the surface area of these charcoals, BET analysis was used.

Based on the BET studies, the commercial activated charcoal powder recorded the highest surface area (871.3), and followed by charcoals from coconut trunk (161.4), sugarcane (109.5), rubber wood (13.2) and mangrove wood (2.0 m^2g^{-1}) (Table 2). The values of surface area of the charcoals may vary, depending on the sources of samples (Salehin et al. 2015). Although the commercial activated charcoal provides the highest surface area, the decolourisation rate of RO16 dye by using this electrode was the lowest.
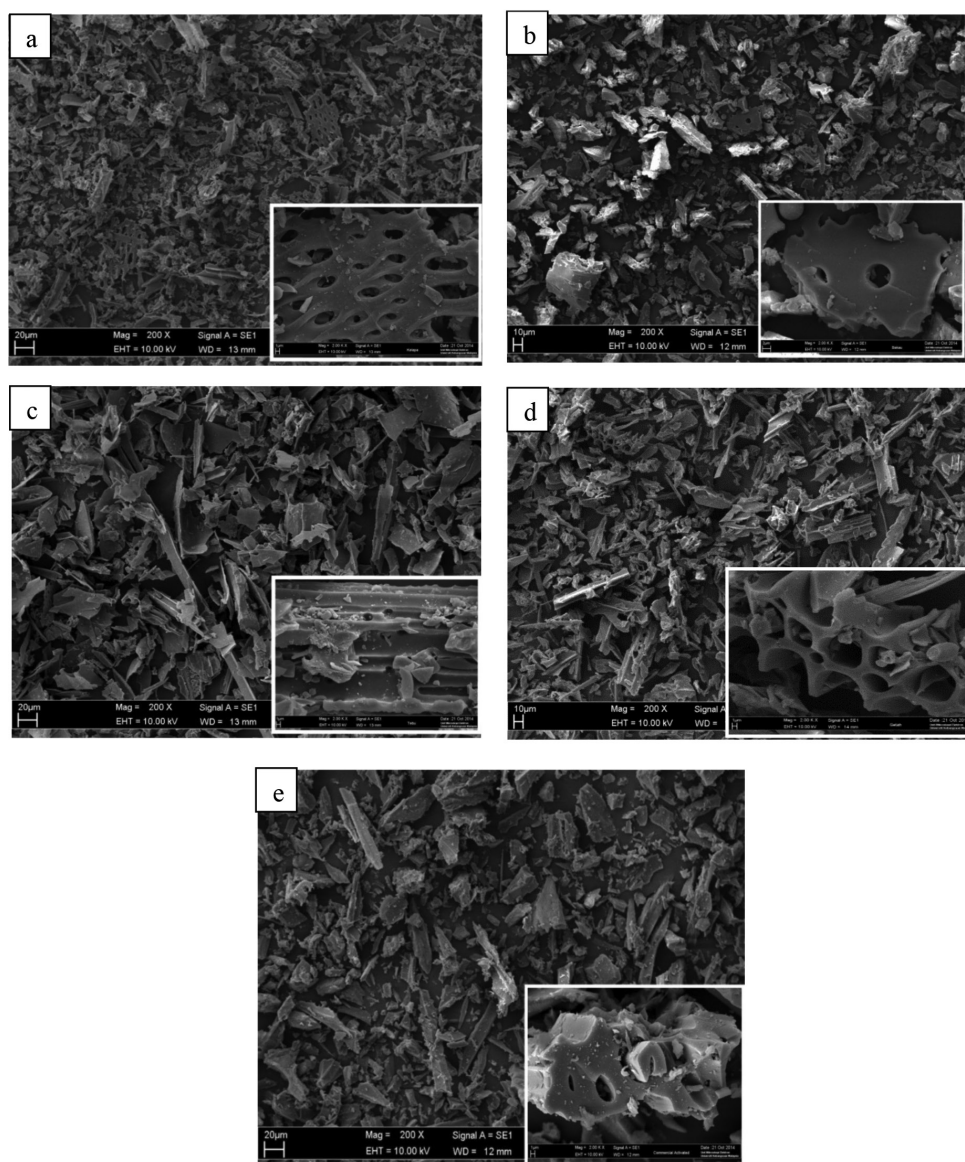

FIGURE 6. SEM images of charcoals powder from, a) coconut trunk b) mangrove wood c) sugarcane d) rubber wood and e) commercial activated charcoal

TABLE 2. BET surface area obtained from different sources of raw charcoals

Source of charcoal	Coconut trunk	Rubber wood	Sugarcane	Mangrove wood	Commercial activated charcoal
Surface area (m^2g^{-1})	161.4	13.2	109.5	2.0	871.3

Generally, adsorbent with a higher surface area would have a higher adsorption capacity (Nahil & Williams 2012; Pourmand et al. 2015). However, in many cases, surface area is inadequate to explain the adsorption properties of carbons; hence, the characteristic and quantity of surface functional groups present in charcoals should also be considered (Nahil & Williams 2012; Timur et al. 2010). The most crucial and usual groups affecting the adsorption and surface characteristics of charcoals are functional groups containing oxygen that elevate the adsorption of polar species (Avgul et al. 1970).

To study the functional groups responsible for RO16 dye degradation, FTIR spectroscopy was used to compare the five different sources of charcoals used. The FTIR spectra of the charcoals showed that the peak patterns for all charcoals were close to each other, which indicated that their functional groups were also quite similar (Tsai et al. 2006) (Figure 7). The broad band at around the wavenumber of 3,396 cm^{-1} denoted the presence of hydroxyl groups in charcoals. All charcoals showed C-H band around 2,926 cm^{-1}, except for the commercial activated charcoal. The existence of C=O group can be seen

around the wavenumber at 1,687 cm^{-1}. The C=C stretching band appeared around 1,586 cm^{-1} in all spectra, except for the commercial activated charcoal, indicating the existence of aromatic rings. This can be proven by the presence of out-of-plane C-H aromatic bending vibration region (900-690 cm^{-1}) (Pavia et al. 2008). The band around 1,619 cm^{-1} implied the presence of C=C alkene in mangrove wood and commercial activated charcoals and this is proven by out-of-plane =C-H bending that occurred in the range of 1000 to 650 cm^{-1} (Pavia et al. 2008). The absorption band around 1,193 cm^{-1} confirmed the presence of C-O in all charcoals.

Surface phenomenon results in forces of binding between the adsorbent surface and molecules, atoms and ions of adsorbate are called adsorption process (Lokman 2006). All charcoal composite electrodes showed the potential to adsorb and degrade RO16 dye. The major functional groups in the charcoals (hydroxyl and carboxyl) caused the sorption properties, which helped to bind the dye (Tan et al. 1993). The presence of hydroxyl and carbonyl groups was able to form Van der Waals bonding with the RO16 molecule. The Van der Waals forces may occur
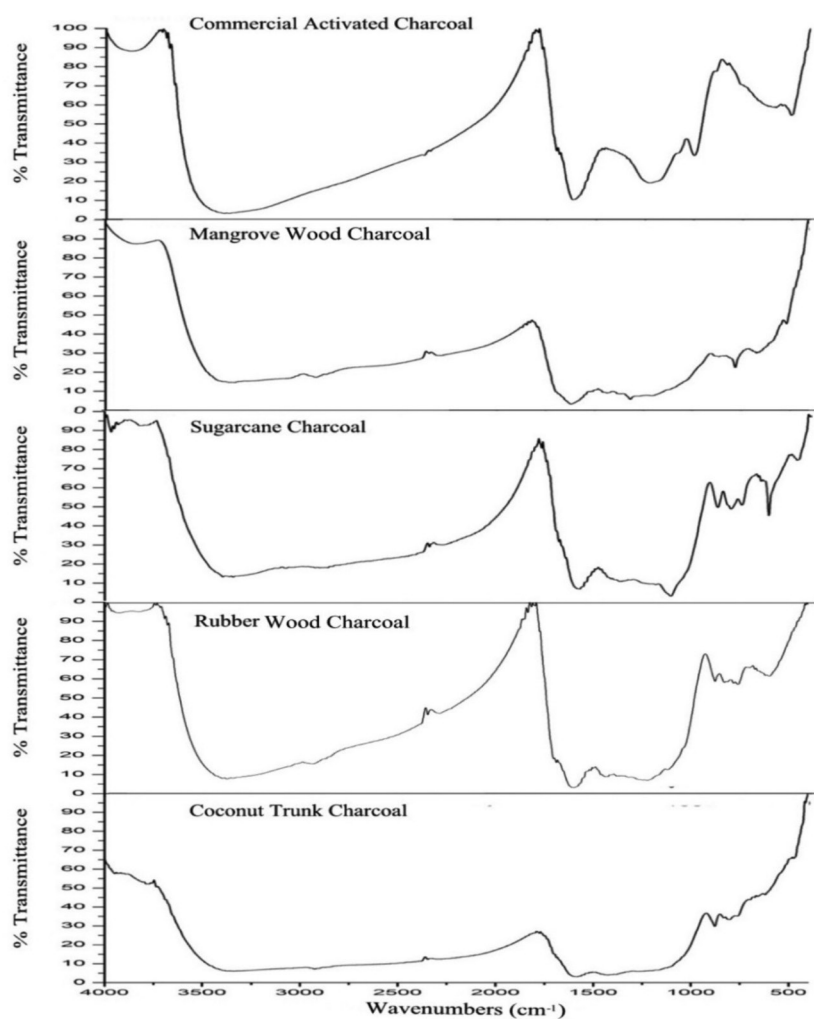

FIGURE 7. FTIR spectra of raw charcoals powder obtained from different sources

between the azo group of the dye and the functional groups of the charcoals (alone or as electrodes) and destruct some of the dyes (Sakkayawong et al. 2005).

Other than charcoal, graphite and tin were used in the mixture of the electrode pellets at certain weight ratio. Graphite and tin are known as good electric conductors. Additionally, graphite has potential as electrocatalyst (Iqbal & Ashiq 2007; Moore et al. 2004). The charcoal-based composite electrodes fabricated in this study had good quality as working electrode since they could degrade RO16 dye, cheap and easily prepared.
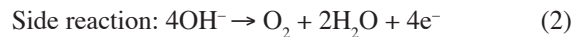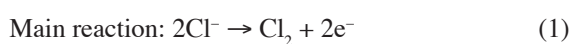
Since the FTIR spectra showed that functional groups for the charcoals were quite similar, the reason behind each electrode efficiency is still unknown. The results obtained from BET and SEM studies also showed no relation with the difference in efficiency of the electrodes. The results indicated that adsorption capacity is not the main factor affecting the electrodes capability to degrade RO16 dye molecule.

In this study, where NaCl was used as the supporting electrolyte, indirect oxidation played an important role in the degradation of RO16 dye molecule. Here, the dye molecule was destroyed in the bulk solution through oxidation by a strong electrochemically generated oxidant, such as hypochlorite ion and chlorine. Sodium chloride is most commonly used in textile processing industries since it is inexpensive and quite efficient (Rajkumar & Kim 2006). The hypochlorite/chlorine was produced from chloride ion from NaCl by applying electrical current to the solution (Raghu et al. 2009). The oxidant was generated *in situ* and utilised promptly (Rajeshwar & Ibanez 1997). The RO16 dye (pollutant) was oxidized and the hypochlorite/chlorine was reduced back to chloride ion (Raghu et al. 2009).
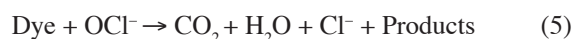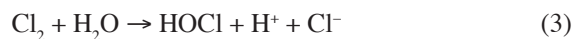
The existing or the formation of hypochlorite ion in degradation of the dye molecule was confirmed by the electrolysis of 0.2 M NaCl solution alone with different sources of charcoals in charcoal-based composite electrodes for 20 min. The UV-visible spectra obtained showed a single maximum peak absorption of hypochlorite ion at 291 nm (Figure 8). Electrode contained charcoal that is originated from coconut trunk gave the highest intensity of hypochlorite ion after 20 min, followed by rubber wood, sugarcane, mangrove wood and commercial activated charcoal.

The production of hypochlorite ion is in agreement with the decolourisation rate demonstrated by all electrodes, therefore, verifying that the production of hypochlorite ion was the main aspect influencing the electrode effectiveness in this research. Therefore, based on this study the formation of hypochlorite ion played the most important role rather than the adsorption process in the degradation of RO16 dye molecule. The reactions are assumed to happen in the bulk solution (Raghu et al. 2009; Rajkumar & Kim 2006).

Anode:

$$\text{Main reaction: } 2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$\text{Side reaction: } 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{2}$$

Bulk solution:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{4}$$

$$\text{Dye} + OCl^- \rightarrow CO_2 + H_2O + Cl^- + \text{Products} \tag{5}$$

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{6}$$

The enhancement in removal efficiency of the dye was attributable to the increment in chloride ions in the electrolyte. The complete breakdown of RO16 dye was achieved through the involvement of active chlorine, namely hypochlorous acid, chlorine, and hypochlorite ion. These oxidants react with the dye molecules and finally lead to their complete conversion to carbon dioxide, water and other smaller molecules (Martinez & Ferro 2006).

Based on results obtained, as summarized in Figure 4, Table 2 and Figure 8, it is confirmed that the oxidation of RO16 dye molecule mostly occurred in the bulk solution. The composite electrode functions as a hypochlorite ion generator only. Adsorption process on the electrode surface did not play any significant role in decolourisation of the dye.

Energy consumption, current efficiency and operating cost were also taken into consideration as one of the objectives to fabricate low cost electrodes (Table 3). The energy consumptions and current efficiencies were measured per g of COD removed. The energy consumptions and current efficiencies for all electrodes fabricated were compared, and from the results obtained, it can be seen that there was a connection between energy consumption and current efficiency. The application of electrode with high current efficiency reduced energy usage. Current efficiency and energy consumption of commercially available charcoal-based composite electrode are, respectively, the highest and the lowest, even though its capability to
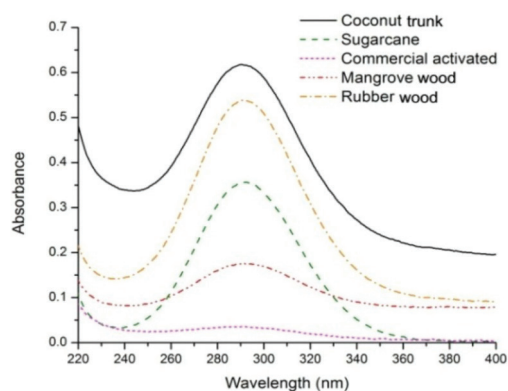
FIGURE 8. UV-visible spectra for the formation of hypochlorite ion using composite electrodes originated from different sources of charcoals

TABLE 3. Cost, energy consumption and current efficiency

Charcoal base metallic composite electrode ($C_{30}C^G_{18}Sn_{12}PVC_{40}$- $C^G_{60}PVC_{40}$)	Current efficiency (%)	Energy consumption (kWh/g)	Cost		
			Electrode material (USD)	Electricity (USD/g)	Operating (USD)
Coconut trunk	37.01	0.0905	0.53	0.01	0.54
Mangrove wood	46.14	0.0726	0.53	0.01	0.54
Rubber wood	38.77	0.0864	0.53	0.01	0.54
Sugarcane	42.70	0.0785	0.53	0.01	0.54
Commercial activated	59.45	0.0564	0.59	0.01	0.60

Current efficiency and energy consumption were calculated based on 60 min electrolysis. Current electricity rate is 0.01 USD/kWh

degrade RO16 dye is the lowest than other electrodes. The objective of this research was achieved since the range of operating cost for all the fabricated electrodes was only within USD0.54 to USD0.60.

There are a number of research were done to study the degradation of reactive dyes by using electrochemical method (Neti & Misra 2012; Wu et al. 2008; Xiong et al. 2001; Xu et al. 2008). The use of coconut trunk charcoal composite electrode in the degradation of dyes in this study showed good performance as compared to the previous studies. In this study, about 98.5% of RO16 dyes (200 mg/L) was achieved in 20 min, while Neti and Misra (2012) can degrade about 85% from 50 mg/L of RB4 solution in 6 h.

CONCLUSION

The comparative study of five different charcoal sources in the fabrication of charcoal composite electrodes in the decolourisation of RO16 dye was successfully performed, in which the discolouration rates of charcoals were in the following order: coconut trunk > rubber wood > sugarcane > mangrove wood > commercial activated. The formation of hypochlorite ion was discovered as the main factor that influence the results. The surface area and the presence of carbonyl and hydroxyl groups in the charcoals increased the adsorption capacity of charcoals, and thus contributing to the efficiency of dye removal. From the results obtained, it can see that there is no connection between colour and COD removal. The results concluded that all charcoal composite electrodes had good potential in decolourising RO16 textile dye. The oxidation process of RO16 dye molecule mostly occurred in the bulk solution and not on the electrode surface. The composite electrode functions only as a hypochlorite ion generator. Adsorption process on the electrode surface did not play any significant role in decolourisation of the dye. This research is crucial since it proved that agricultural wastes, as the main element in charcoal-based electrode, can treat water pollution caused by textile industries.

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