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Original Research Paper

Performance of Electrochemical Oxidation in Treating Textile Industry Wastewater by Graphite Electrode

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ABSTRACT

This study was conducted to investigate the optimization and reduction of the toxicity level of the textile industry wastewater using electrochemical oxidation. We assessed the effect of current density and pH and found that the maximum removal of COD and colour was at the current density of 0.28A/cm^2 and at a pH of 5. The performance of graphite electrode for COD removal was also reached within 120th minute at 2.5M of NaCl concentration. The biodegradability was improved because ratio of BOD_5/COD was increased by 94.46% from 0.015 to 0.271 and the toxicity level was successfully reduced from 1.195% to 0.129%. It was observed that the removal of oil and grease can be up to 82.02%. It can be concluded that the graphite electrode is effective for treating textile wastewater.

INTRODUCTION

Batik textile industry is one of the most important textile manufacturing industries in Malaysia, especially in the East Coast of Peninsular Malaysia and Sarawak that is traditionally inherited from generation to generation. High skills coupled with the right equipment's and tools are needed in order to produce high quality batik. Nowadays, this industry has become very commercialized and contributed positively to the economic growth for the states of Kelantan and Terengganu (Ahmad 2002). The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes.

Wastewater from printing and dyeing units is often rich in colour, containing residues of reactive dyes and chemicals, such as complex components, aerosols, chroma, COD and BOD concentration as well as much more hard-degradation materials. The toxic effects of dyestuffs and other organic compounds, as well as acidic and alkaline contaminants from industrial establishments on the general public are widely accepted. Dyes are mainly aromatic and heterocyclic compounds with colour-display groups and polar groups. The structure is more complicated and stable, resulting in greater difficulty to degrade the printing and dyeing wastewater (Wang et al. 2011). The wastewater generated from textile industries is found to contain a high degree of pollutants with high total dissolved and suspended solids. The wastewater is highly coloured and viscous due to dyestuff and suspended solids. Sodium is the major cation due to high consumption of sodium salts in processing units, and chloride is the major anion found in the wastewater and high concentrations of bicarbonate, sulphate and nitrate. Heavy metals like chromium, iron, lead, zinc, copper, manganese are also present and the BOD/COD ratio is between 0.15-0.3, indicating the recalcitrant nature of organics present in the wastewater (Hussain et al. 2004).

During the dying process, about 5-20% of the dye is lost due to its partial adsorption on the fibres. Dyes are manufactured to have high chemical resistance because they are normally chemical species that are very difficult to degrade (aromatic dyes) and can badly affect the aquatic flora and fauna (Cerqueira et al. 2009). Furthermore, coloured effluents may contain considerable amounts of toxic compounds, especially azo dyes that are known to be highly carcinogenic (Daneshvar et al. 2007). The removal of dyes is therefore a challenge to both the textile industry and the wastewater treatment facilities. Dyeing wastewater is usually treated by conventional methods such as biological oxidation and adsorption. Because of the large variability of the composition of textile wastewater, most of these traditional methods are becoming inadequate (Mohan et al. 2001). A typical electrochemical treatment process consists of an electrolytic cell, which uses electrical energy to affect a chemical change. In simplest form, we can say that, an electrolytic cell consists of two electrodes, anode and cathode, immersed in an electrical conducting solution (the electrolyte) and are connected together, external to the solution, via an electrical circuit which includes a current source and control device. The chemical processes occurring in such cells are oxidation and reduction, taking place at the electrode/electrolyte interface (Chen 2004). Electrochemical oxidation is becoming an alternative wastewater treatment method and replacing the conventional processes, because many industrial processes produce toxic wastewaters, which are not easily biodegradable and required costly physical or physico-chemical pretreatments (Pulgarin et al. 1994). Many researchers have investigated the electrochemical oxidation of various types of wastewater containing 1,4 benzoquinone (Pulgarin et al. 1994), phenol (K¨orbahti et al. 2002, Iniesta et al. 2001, Comninellis et al. 1993, Gattrell & Kirk 1990), aniline (Kirk et al. 1985), olive oil (Gotsi et al. 2005, Israilides et al. 1997),vinasse (Vlyssides et al. 1997), chlorophenols (Polcaro & Palmas 1997), p-chlorophenol and p-nitro phenol (Borras et al. 2003), low level nuclear waste (Bockris & Kim 1997), human waste (Tennakoon et al. 1996) and tannery wastewater (Szpyrkowicz et al. 2005). Oil and grease which are present in excessive amounts may interfere with aerobic and anaerobic biological processes could lead to decreased wastewater treatment efficiency. Information about the quantity of oil and grease that is present is very helpful to design a proper operation of wastewater systems and to identify treatment difficulties (Pawlak et al. 2008).

The aim of this study is to characterize the physico-chemical properties of the homemade textile industry wastewater and to determine the efficiency of the electrochemical oxidation process on homemade textile industry wastewater by using graphite electrodes.

MATERIALS AND METHODS

Sampling: Samples were taken as an origin and were replicated into two replicates. The samples were taken in the high density polyethylene (HDPE) barrels and kept in the room temperature for the characterization method. The batik wastewater samples were collected from Master Wan batik industry located in Taman KajangUtama, around Kajang area in Selangor, Malaysia.

Wastewater characterization: The electrolysis cells were built by using a container PVC measuring 11 × 11 × 8 cm. Four electrodes that arranged in pairs were arranged vertically in electrolysis cell used as anode and cathode. Electrodes were on the end of left, and right hand side, on the other hand, need to be connected to the current generator source by using an alligator clip that has positive and negative labels for smooth current flow and voltage. Basically, this method would consequently produce a complete electrolysis cell. This electrochemistry oxidation process was done by using galvanostatic condition method where static current limitation was kept and used in the electrolyte in the process. Electric current energy source was used and produced from the Dual DC power supply tool (35D Textronix, 0-15V, 0-10A). The most effective electrolyte used in this electrolysis cell is sodium chloride (NaCl) and hence sodium chloride was used as electrolyte to maintain the current conductivity due to fixed frequency.

The wastewater samples were characterized according to certain parameters or experimental scales such as BOD testing, COD testing, colour and toxicity testing and finally biodegradation index testing. It shows that the COD/BOD_5 ratio was less than 0.1 indicating that the samples were non-biodegradable. Besides that, the *in-situ* parameter tests such as pH and temperature of the wastewater samples from the batik industry were taken into consideration. The treated wastewater samples were characterized again by using electrochemical oxidation method with graphite electrodes. The parameters or experimental scales such as BOD testing, COD testing, colour, toxicity testing and also finally biodegradation index testing were included where the ratio of the COD/BOD_5 was more than 0.1 which simply means that the samples are easily biodegradable.

The batch electrochemical oxidation reactor used in the experimental study was made of high density polyethylene with an approximate volume of 1000 mL. The electrodes were connected to a direct current power supply (35D Textronix, 0-15V, 0-10A). The reactor consisted of four electrodes that have the same dimensions and merged in a beaker. For each electrode in the system, the immerged surface was $30 cm^2$ (0.64 cm × 6.00 cm × 8). The efficiency of the electrolytic cell was studied with different current densities (current density i.e. the current per area of electrode).

Each experiment was of batch operation with duration of 180 min and samples were drawn for every 30 minutes and COD, BOD, colour was measured. Before each run, electrodes were rinsed with tap-water, dried at 103°C, cooled and weighed. At the end of each run, the electrodes were washed thoroughly with water to remove any solid residues on the surface, dried and reweighed. When too large current is used, there is a high chance of wasting electrical energy in heating up the water. More importantly, a too large current density would result in a significant decrease in the current efficiency. In the present study, current densities of 12 A/m^2, 24 A/m2 and 48 A/m^2 were selected and evaluated for many parameters.

RESULTS AND DISCUSSION

Preliminary study: During the preliminary investigation, the undivided cell with graphite electrodes was selected as the working cell and the anode/cathode respectively. The results also showed the percentage of colour removal with different type of parameters and its best optimization state. The electrolysis time was also fixed at 120 minutes.

Optimization of sodium chloride (NaCl) concentration: The general chloride reaction involved in electrochemical oxidation was presented as the following:

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode: $2e^- + 2H_2O \rightarrow 2OH^- + H_2$

Overall: $2OH + Cl_2 \rightarrow Cl + OCl^- + H_2O$

Chlorine (Cl_2), hypochlorous acid (HClO) and hypochlorite ions (ClO^-) are strong oxidizing species and often referred to as "active chlorine" (Miled et al. 2010). Besides using sodium chloride as the supporting electrolyte, the other parameters were also stated at pH 13; distance between electrode at 1 cm and the current density at 0.2 A/cm^2. The removal of the colour percentage was plotted against NaCl concentration to determine the operating value. The effect of changing the electrolyte concentration (0.5M, 1.0M, 1.5M, 2.0M, 2.5M and 3.0M) on colour and COD removal is illustrated in Fig. 1. Experiments showed that in the electrolysis of batik wastewater samples with chloride, an indirect electrochemical oxidation effect of chlorine/hypochlorite is the main pathway of removal of the pollutants. The superior effect of chloride may be due to the indirect oxidation effect of chlorine and the *in-situ* generation of the hypochlorite ions which seems to be the most effective oxidation method due to the fragmentation of the batik wastewater samples. The results indicated that the best colour removal was with the concentration of 2.5M of the sodium chloride (NaCl). The concentrated 3.0M of the NaCl showed that the level of colour removal is low. An electrolyte concentration of 2.5M was selected as the best NaCl concentration owing to the toxic effects in the electrochemical oxidation process. Electrolyte concentration higher than 0.5M does not have major effect on the colour removal nor the COD removal but the concentration which is higher than 2.5M of NaCl has the major effects on the colour and the COD removal.

Colour removal is most important for the textile industry's wastewater treatment. It is clear from Fig. 1 that the electrochemical oxidation process has effectively reduced the colour in the homemade textile industry wastewater samples. At pH 13, the indirect oxidation effect of chlorine/hypochlorite is the predominant mechanism for the decolorization (Miled et al. 2010). As for the COD removal, the highest percentage of sodium chloride shows the low percentage of COD removal, which is the 3.0M of NaCl concentration. This is probably because all the COD has been used up and there is no more colour changes observed. The optimum concentration of NaCl was 2.5M, where the colour and COD removal both showed as 79.67% and 75.12%, respectively.

Determination of optimum pH value: To examine the effect of pH on the decolorization process, the batik wastewater samples were initially adjusted to the desired pH for each experiment, using the optimized concentration of sodium chloride of 2.5M in standard. The experiments were carried out at pH 1, 3, 5, 7, 9, 11, and 13. Following Miled et al. (2010), the distance of the electrode and the current density was standardized to 1cm and 0.2A/cm^2 respectively. The effects of electrochemical oxidation in different pH parameters of homemade textile industry wastewater samples are illustrated in Figs. 2a and 2b. The experiments were carried

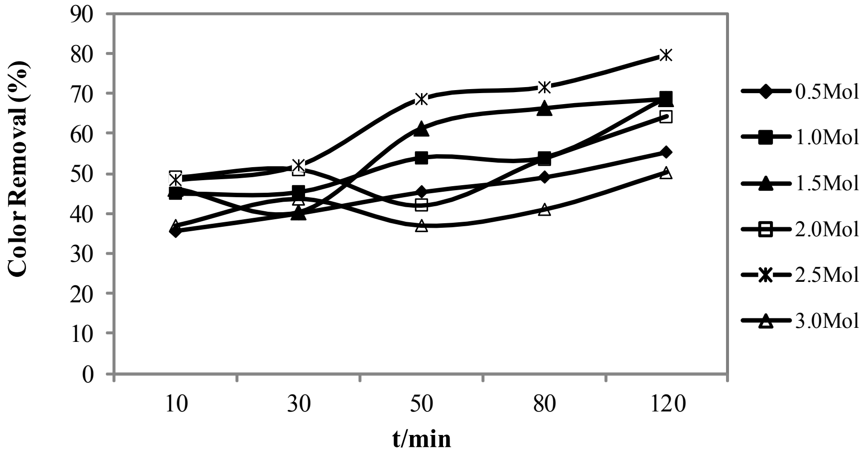

Fig. 1: Percentage of colour and COD removal at different electrolyte concentrations.

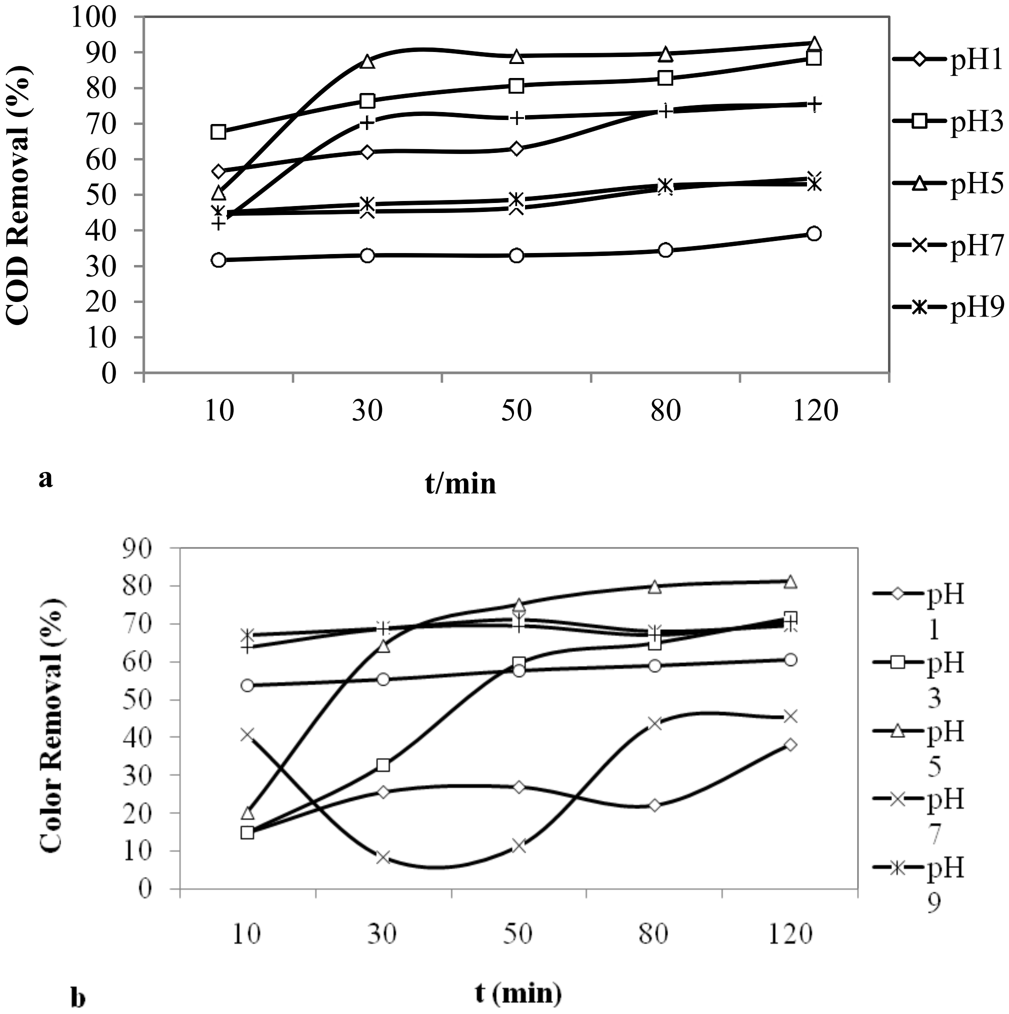

Fig. 2: Percentage of (a) COD removal and (b) colour removal at different pH at 120 minutes of electrochemical oxidation.

out with 2.5M of sodium chloride, (NaCl) concentration due to the optimized standardization. The results of electrolysis that have been done at pH 1, 3, 5, 7, 9, 11, and 13, were compared with the terms of colour and COD removal. From Figs. 2a and 2b, it is a clear evidence that the effect of pH value on the colour and COD removal in homemade textile industry wastewater is remarkable under slightly basic conditions. The optimum pH in the study was identified as pH 5 and the highest percentage of colour and COD removal were 92.02% and 86.67%, respectively.

Determination of optimum current density (A/cm²): The pollutant removal rate increased initially with increase of current density. However, the optimum current density is 0.28A/cm^2 which gives 93.89% of colour removal and 85.38% for COD removal. The optimum current density is 0.28A/cm^2 due to the decrease in percentage colour and COD removal at the current density of 0.51A/cm^2. This is due to the fact that the colour and COD have been fully removed.

Determination of optimum distance between electrodes (cm): The distance between electrodes from 1cm, 3cm, 5cm and 7cm is taken into consideration to determine the optimum electrode distance. To determine the effect in the distance between the electrodes due to the decolorization process, different distance between the electrodes such as 1, 3, 5 and 7 cm were placed in order to run the electrochemical oxidation process. The distance of 3cm is optimized to be the best distance between the electrodes in the process of colour and COD removal. The highest percentage obtained in 3cm distances between electrodes which are 76.03% and 75.76%, respectively. This clearly shows that the optimized distance between electrodes was one of the main parameters in the electrochemical oxidation process. The distance of 1cm

Table 1: Characteristic of optimized rate of wastewater from batik industry.

Parameter	Optimized Rate
pH	5
Distance between electrode (cm)	3
Concentration of sodium chloride (NaCl) (Mol)	2.5
Current density (A/cm^2)	0.28

Table 2: The toxicity level of inhibition effect against time.

Duration of time (min)	Toxicity Inhibition (%)
0	1.195
50	-0.697
120	0.129

is closer between each electrode compared to the distances of 5cm and 7cm for the electrodes to mix well and homogenize to produce the current and perform the decolorization process with the COD removal.

Determination of optimum in time: The duration of electrochemical oxidation from 10 min, 30 min, 50 min, 80 min, 120 min and 170 min is taken into consideration. To determine the optimum time due to the decolorization process, different parameters of time were used to run the electrochemical oxidation process. The effects of time showed that the 120 minutes was the optimum time in this process. This is clearly proved in the results where the colour and COD removal were 60% and 65.43%, respectively. At the 170th minute, the percentage of colour and COD was decreasing and there were no changes in colour and COD in the end of the electrochemical oxidation process.

Optimum condition of electrochemical oxidation: The optimum condition of an electrochemical oxidation process was run at pH 5, 0.28A/cm^2, 3cm of distance between electrodes and finally 2.5M of sodium chloride (NaCl) concentration. The percentage of colour and COD removal are 93.89% and 89.71%, respectively.

Table 1 illustrates the characteristics of optimized batik industry wastewater. It was found that the best optimization of batik industry wastewater is pH 5, 0.28 A/cm^2, distance between electrodes which is 3 cm, the 120 minutes as the optimization time and 2.5 M of NaCl concentration. The values of COD and BOD_5 were stated before and after electrochemical oxidation process has been carried-out. The batik wastewater samples can be degraded biologically and the biodegradability index increases from 0.015 before the electrochemical process to 0.0271 after the electrochemical process. The percentage of removal was up to 94.46%.

The toxicity level was evaluated and the result showed that before the electrochemical oxidation process, the samples were slightly toxic, but reached non-toxic level after the electrochemical oxidation process. The percentage of inhibitions is illustrated in Table 2. At the 0 minute, the toxicity inhibition level was 1.195% and it was reduced to -0.697 at the 50th minute and finally at the 120th minute, the level of inhibition was increased to 0.129.

The data that were obtained clearly stated that the value which decreased and increased later on shows that the samples were slightly toxic and reduced to non-toxic level (Liu, 1981). The percentage removal of oil and grease were valued before and after the electrochemical oxidation process. This indicates that the batik wastewater samples contain high level of oil and grease where it can decrease from 1351.42 mg/L before electrochemical process to 242.97 mg/L after the electrochemical process and degrade up to 82.02%. This result also indicates that the process of batik needs high usage of wax that leads to the highest removal in oil and grease (Susanti et al. 2013).

CONCLUSIONS

Indirect electrochemical oxidation of the batik wastewater samples were studied using graphite anodes and cathodes in the presence of sodium chloride (NaCl) and an electrolyte. Methods of changing electrolyte concentration, pH, distance between electrodes and current density were taken as parameters of optimization to improve the degradation. The percentage of COD and colour removal were 89.71% and 93.89%, respectively, at the pH of 5, 0.28A/cm^2 of current density, the distance of 3cm between electrodes, 120th minute as the optimized time and 2.5M of concentrated sodium chloride (NaCl). The Biodegradability Index also showed that the samples are 94.46% biodegradable and at the same time the samples are reduced to non-toxic level and the removal of oil and grease was up to 82.02%. It can be concluded that the electrochemical oxidation technique can be used effectively as a pre-treatment stage prior to conventional treatment in the homemade textile wastewater industry.

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