COLOUR AND COD REMOVAL OF DISTILLERY WASTEWATER BY ELECTROOXIDATION PROCESS WITH GRAPHITE ELECTRODE

Sansud Wijittra[1] and Suwanvitaya Patcharaporn[2]

[1,2]*Department of Environmental Engineering, Kasetsart University, Bangkok, Thailand.*

ABSTRACT

The objective of this research was to study the feasibility of colour and COD removal from distillery wastewater by using electrooxidation process. This work is carried out to find the optimum condition to treat colour and COD in distillery wastewater by applying the electrooxidation with graphite electrode. The effect of pH, electrical intensity, contact time and concentration of supporting electrolyte will be investigated. A maximum of 57.85% of chemical oxygen demand reduction , 96.62% colour reduction were obtained in the presence of sodium chloride as supporting electrolyte at pH 4 .Thus, electoroxidation process can be envisaged as an effective treatment process for decolourization of distillery wastewater.

KEYWORDS

Electrooxidation, graphite electrode, COD, colour

1. INTRODUCTION

Production of ethyl alcohol in distilleries based on cane molasses constitutes a major industry in Asia and South America. The world's total production of alcohol from cane molasses is more than 13 million m^3/annum. The aqueous distillery wastewater stream known as spent wash is approximately 12- 15 times by volume of the product alcohol. It is low in pH and dark brown in colour.The major coloured compound is Melanoidin which are the product of Maillard reaction between sugar and amino acid produced upon heating. This colour polymer is a major water pollutant which can increased load of recalcitrant organic material to natural water bodies and reduce the penetration of sunlight through the receiving water and dissolved oxygen concentration

Many processes have been developed to treat this waste such as biological process, evaporating process. However all this schemes on their own are either incomplete or are impractical, an example of biological treatment is the use of anaerobic digestion followed by an aerobic treatment prior to disposal, anaerobic-aerobic treatment generates methane gas and simultaneously creates other hazardous byproducts/pollutant such as sulfide, as well as relatively high biomass production and high cost in terms of energy. Therefore, it is worthwhile to find a promising sustainable approach to treat distillery wastewater effectively

with cost reduction. These facts make electrooxidation technologies as possible candidates for the treatment of these wastes

Electrooxidation of pollutants proceed either direct or indirect oxidation n. In direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In indirct oxidation process, strong oxidants such as hypochlorite/chlorine are generated in situ and are utilitzed immediately (D. Rajkumar, K. Palanivlu, 2004)

Electrooxidation appears to be one of the promising technologies for treated the industrial wastewater. This technique is more attractive, because the main reagent in electrochemistry is electron, which is called the "clean reagent" and degrades all the organics in wastewater without generating secondary pollutant by product. The experiments on electrooxidation by using graphite electrode of distillery wastewater were conducted at different condition. Percentage of COD and colour removal were investigated.

2. MATERIAL AND METHODS

2.1 Chemicals and wastewater sample

Distillery wastewater sample was sampled from equalization tank by grab sampling from Liquor distillery organization, Chachoengsao Province. The wastewater sample were analyze for pH, COD, TOC and colour. The distillery wastewater was diluted with distilled water to COD concentration 1,000 mg/L to each electrooxidation batches experiment. NaCl (Merck) in high purity was used as supporting electrolyte. Merck quality, $K_2Cr_2O_7$, $(NH_4)_2Fe(SO_4)_2$, $HgSO_4$, Ag_2SO_4 and H_2SO_4 were used for COD analysis.

2.2 Method of analysis

Variables in this study were initial pH of 4, 7, 10 by adjusted with sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4), retention time, and electrical intensity of 0.8, 2, 4, 6 and 8A. During the experiment, samples were collected at different time intervals and analyze for the various parameters. Parameter investigated included COD (close reflux method), colour measurement and TOC (Shimadzu TOC5000)
Colour measurements were carried out with UV-Visible spectrophotometer (Shimadzu) at 436 nm for Pt-Co Unit measurement. To estimate colour removal efficiency, colour removal ratio was calculated as follows

$$Abs\,(\%) = \frac{Abs_{(436)i} - Abs_{(436)t}}{Abs_{(436)i}} \; x\; 100 \qquad (1)$$

Where $Abs_{(436)i}$ is the value of absorbency at 436 nm. $Abs_{(436)t}$ is the value obtained at time t.

Chemical Oxygen Demand tests were performed according to Standard Methods of Examination of Water and Wastewater (APHA, 2000). The percentage of COD removal efficiency was calculate as follow

$$COD\,(\%) = \frac{COD_i - COD_t}{COD_i} \times 100 \qquad (2)$$

Where COD_i corresponds to the initial value and COD_t is the value obtained at time t

2.3 Experiment setup

The schematic diagram of experiment apparatus was shown in Figure 1. The electrooxidation reactor consists with two parallel electrodes having an inter electrode gap of 50 mm. The reactor tank made from acrylic plate with a dimension of 15 x 17 x 15 cm^3 (width x length x depth) and 15 x 17 x 10 cm^3 (width x length x depth, settling part) with and effective volume about 5 L. The iron cathode and graphite anode plates were placed vertically and parallel to each other. Each electrode plate has a dimension of 17 x 17 x 1 cm^3 (width x length x thickness). For all batch experiments a working volume of 4 L of distillery wastewater were used. Between two batches, reactor and both electrode were cleaned with 10% v/v hydrochloric acid at least 2 hour and then rubbed with a sponge and rinsed with tap water. The anode and cathode sets were connected; respectively to the positive and negative outlets of a dc power supply (KAIWA ,PS 304-III). The eletrooxidation reactor was equipped with a speed controller mixer (100 rmp) in order to keep the electrolyte well mixed.

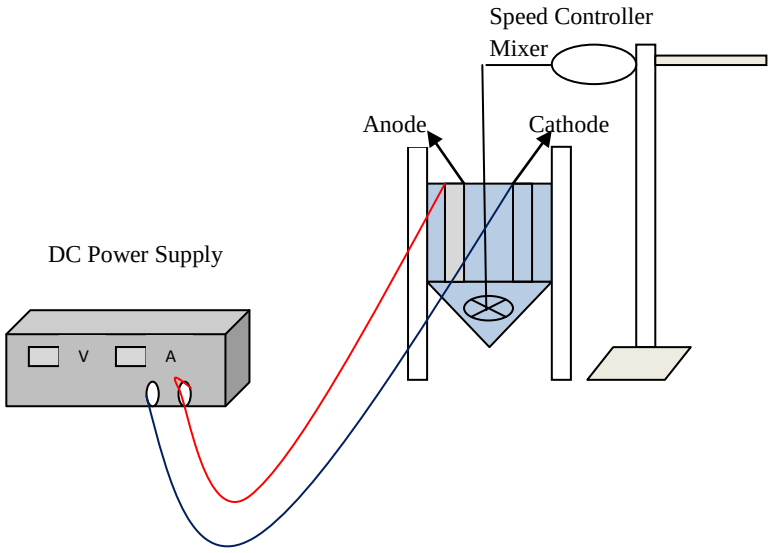


Figure 1: The experimental setup of electro oxidation process

3. RESULTS AND DISCUSSION

3.1 Preliminary Study

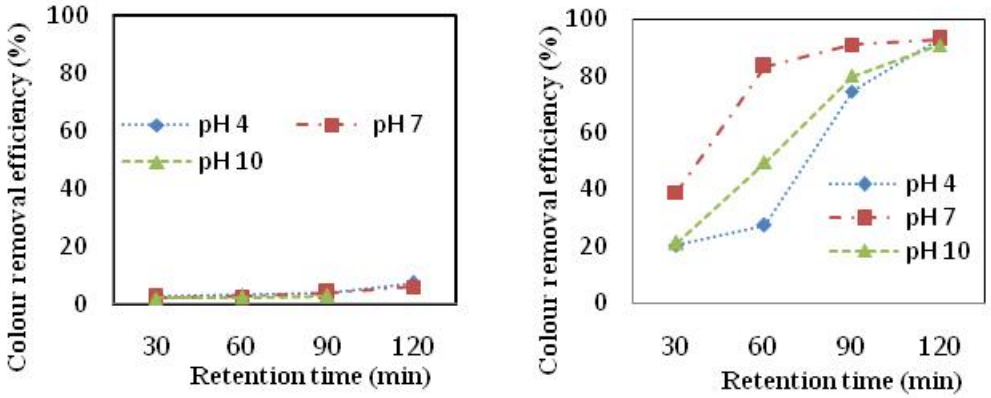
The presence of supporting electrolyte such as chloride can promote the degradation of organic pollutants in wastewater due to the formation of the strong oxidizing agent called chloric acid (HOCl) in the process. This species can destroy the molecules of organic pollutants to non-pollute species such as CO_2 (Szpyrkowicz et al., 2001).

The general chloride reactions involved in elcetrooxidation are present as follow

$$\text{Anode:} \quad 2Cl^- \longrightarrow Cl_2 + 2e^- \qquad (3)$$
$$\text{Cathode:} \quad 2e^- + 2H_2O \longrightarrow 2OH^- + H_2 \qquad (4)$$
$$\text{Overall:} \quad 2OH^- + Cl_2 \longrightarrow Cl^- + OCl^- + H_2O \qquad (5)$$

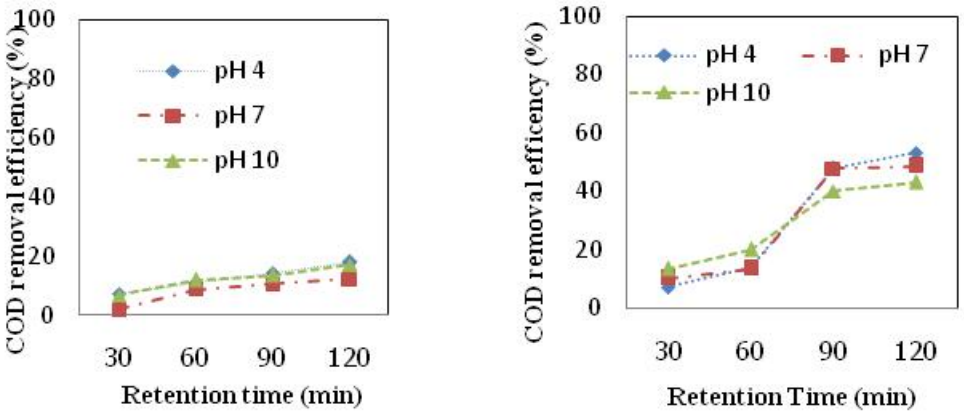
The experiments dealt with the initial pH 4, 7 and 10 by adjusted with sodium hydroxide and sulphuric acid and initial COD 1000 mg/L at the electrical potential 2A and adding NaCl as supporting electrolyte 10 mg/L. The results showed that colour and COD removal efficiency were higher in the presence of NaCl.

In the absence of NaCl the colour removal efficiency varied from 0.00% to 9.53% (Pt-Co Unit), 1.38% to 7.23% (ADMI unit) and COD removal efficiency varies from 1.75% to 17.86%. A maximum of 9.53% (Pt-Co unit) and 7.23% (ADMI unit) colour removal, 17.86% COD removal were obtain at the pH 4 within retention time 120 min, as shown in the figure 2 and 3. The results revealed that the presence of supporting electrolyte, NaCl, had more efficiency to reduce colour and COD as shown in figure 2 and 3. By using 10 mg/L of NaCl, 92.81% (Pt-Co Unit) and 93.50% (ADMI unit) of colour removal efficiency and 53.33% of COD removal efficiency were obtain at pH 4 within retention time 120 min.



(a) (b)

Figure 2: Effect of NaCl on colour removal efficiency at various pH value
(a) colour removal efficiency (ADMI unit) without presence of NaCL and
(b) colour removal efficiency (ADMI unit) with presence of NaCl 10 mg/L



(a) (b)

Figure 3: Effect of NaCl on COD removal efficiency at various pH value.
(a) COD removal efficiency (ADMI unit) without presence of NaCL
(b) COD removal efficiency (ADMI unit) with presence of NaCl 10 mg/L

3.2 Effect of pH on COD and colour removal efficiency by electrooxidation

Experiments of COD and colour removal by electrooxication have been studied at the initial COD concentration of 1000 mg/l, pH 4, 7 and 10 by applied the electrical potential 7 V with NaCl as supporting electrolyte (10g/L). The result revealed that at pH 4, ,the higher removal efficiency, 53.93 % (COD), 95.81% (colour in Pt-Co unit) and 96.50% (colour in ADMI unit), of COD and colour were remove within 150 min retention time which had shown in the figure 4 and 5. This result is in accordance with previous studies (P.Piya Areetham et al., 2006) where it was found that the oxidation of organic contaminates in distillery wastewater was significantly observed in the acid condition.

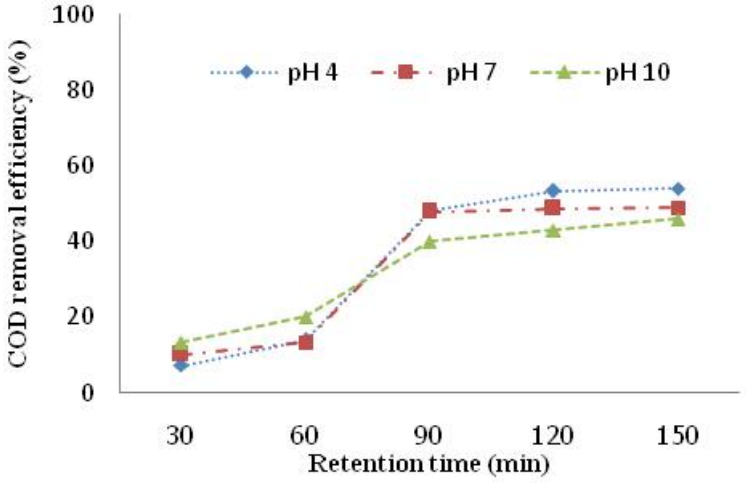


Figure 4: Effect of pH value with different initial pH for COD removal efficiency.

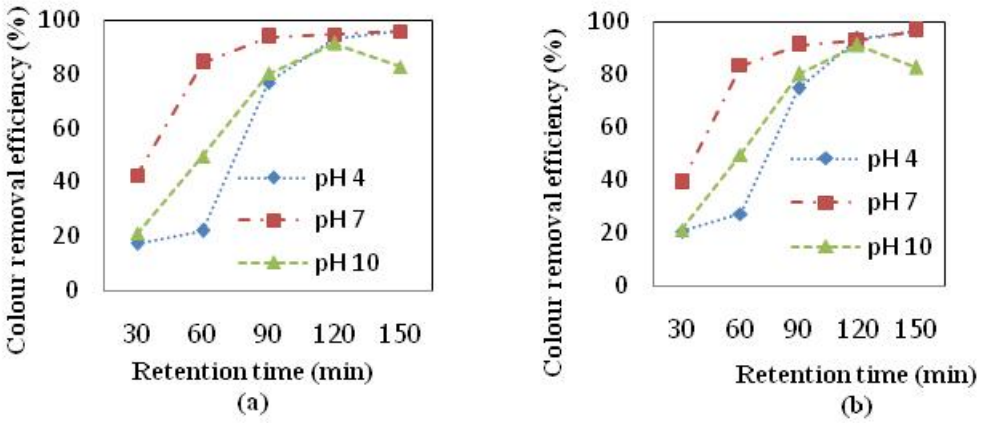


Figure 5: Effect of pH value with different initial pH for colour removal efficiency.
(a) Colour removal efficiency (Pt-Co unit)
(b) Colour removal efficiency (ADMI unit)

In acidic condition, hypochlorous acid was predicted to be the most species in the solution. Therefore higher rate of decolourization in acidic condition maybe due to higher oxidation potential of hypochlorous acid rather than hypochlorite (A. Maljaei et al., 2009)

$$OCl^- + H_2O \quad HOCl + OH^- \qquad (4)$$

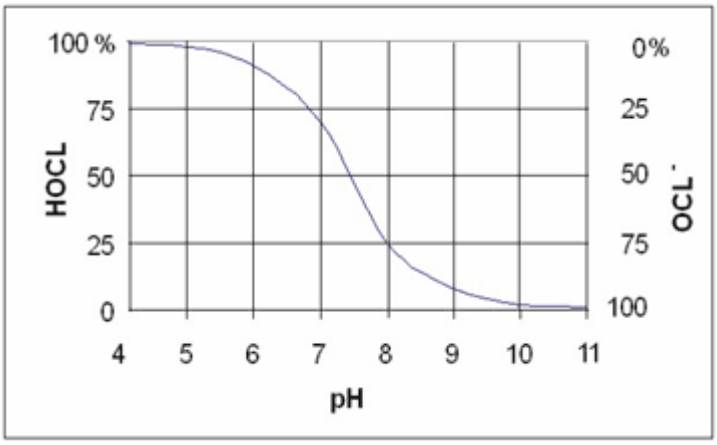


Figure 6 Distribution of main chlorine species as a function of pH

Since the removal efficiency of colour and COD which the higher efficiency obtained at pH 4 in presence of NaCl 10 g/L further study related to the influence of electrical potential were carried out under the same condition.

3.3 Effect of electrical intensity on COD, TOC and colour removal efficiency

Effect of electrical potential was also investigated by applied electrical potential from 0.8 to 8A at initial pH 4 with supporting electrolyte (NaCl 10g/L), increasing electrical intensity led to the increase of COD and TOC removal efficiency which the result had shown in figure 7. By using electrical intensity 4A, the results had show that 57.85% and 15.32% of COD and TOC were removed within retention time 150 min. In addition the COD/TOC ratio decreased from 3.57 to 1.78 during the course of retention time, which was similar to that observed in some previous works (Rajkumar and Palanivelu, 2004; Ribordy et al., 1997). This phenomenon indicated the formation of stable compounds.

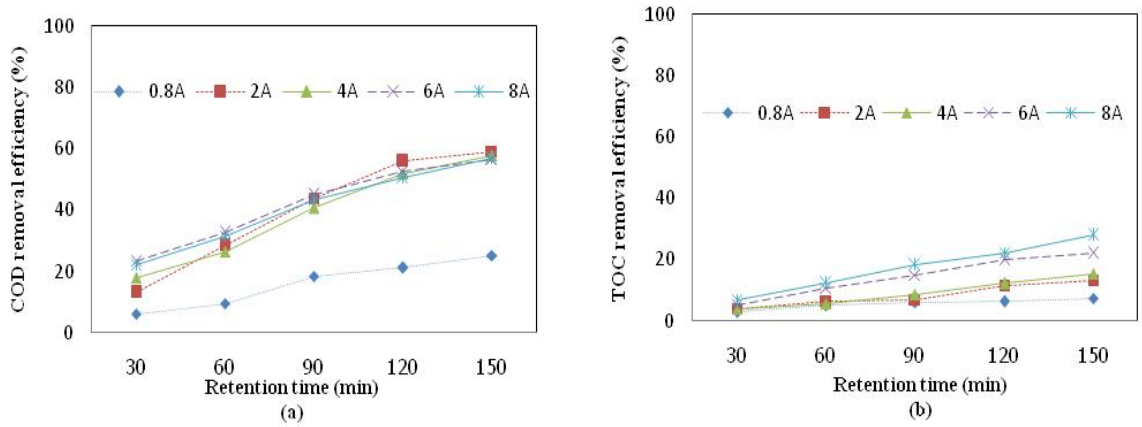


Figure 7 Effect of electrical intensity on COD and TOC removal (a) COD removal efficiency (b) TOC removal efficiency

It was notice that when the temperature of electrooxidation process is higher than 40°C, colour removal efficiency was decrease gradually. With electrical intensity 8A, percentage of colour removal efficiency were reduce from 87.09 (at 90 min) to 83.24 (at150 min) when the temperature were increase from 35° C (at 90 min) to 45°C (at 150 min).

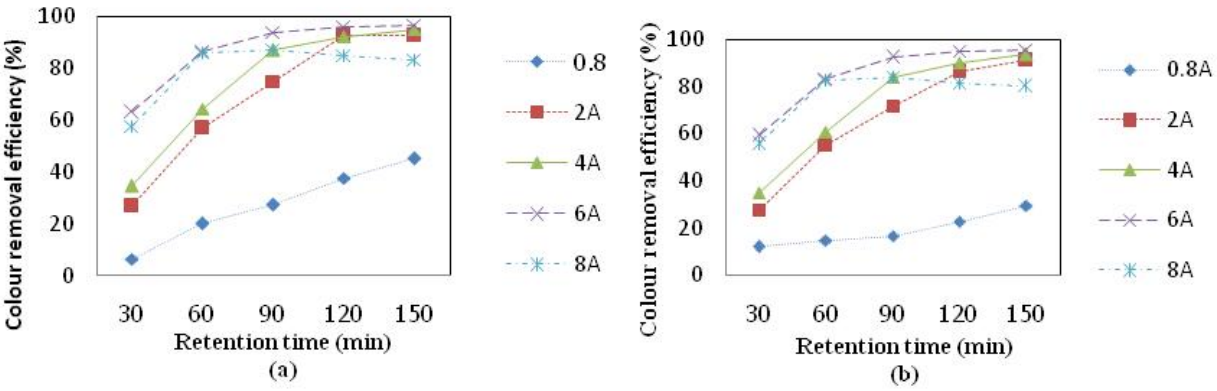


Figure 8 Effect of electrical intensity on colour removal efficiency
(a) Colour removal efficiency (Pt-Co Unit)
(b) (b) colour removal efficiency (ADMI unit)

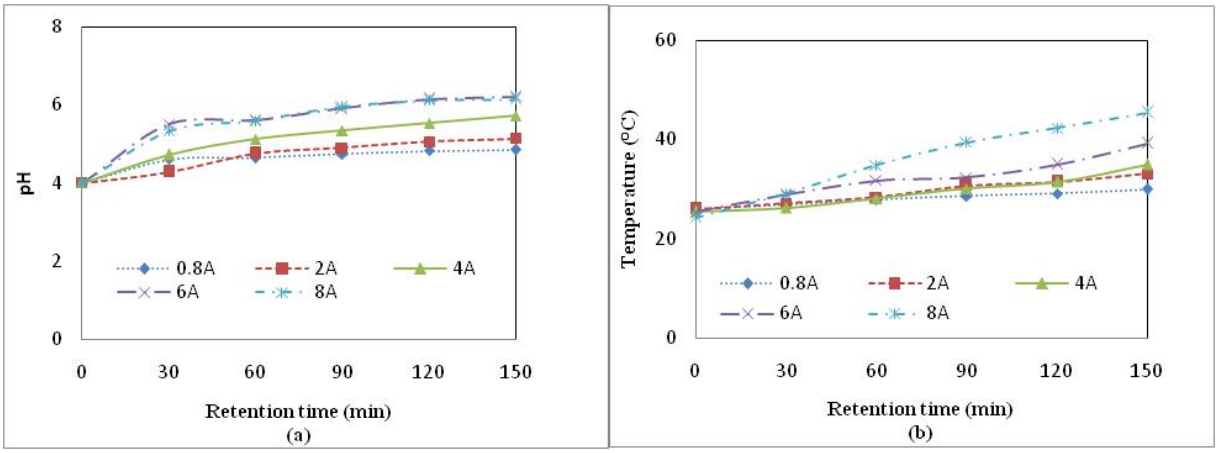


Figure 9 Effect of electrical intensity on (a) pH at different retention time
(b) temperature of different at different retention time

4. CONCLUSION AND PERSPECTIVES

The possibility of the oxidation process of distillery wastewater was first investigated by using graphite electrode. The distillery wastewater was diluted to COD concentration 1,000 mg/L with various pH at electrical intensity 2A. For the treatment the effect of supporting electrolyte was include. The results demonstrated that in the presence of supporting electrolyte had high potential of colour and COD removal. Effect of pH, contact time and electrical intensity on the electrooxidation process was investigated.

It is concluded from this study that initial pH and electrical intensity had effect on the removal efficiency of COD, TOC and colour. Initial pH 4 in the presence of NaCL 10g/L and electrical intensity 2A, approximately 53.33%, 92.81 and 93.50 of COD, colour (Pt-Co unit), and colour (ADMI unit) were remove respectively. This was attributed to the fact that in acidic condition, hypochlorous acid was predicted to be the most species in the solution, therefore higher rate of oxidation in maybe due to its higher oxidation potential. The overall experimental results indicated that electrooxidation process has the potential to be a feasible technique for colour and COD removal in distillery wastewater. The further studies of optimum condition for electrooxidation of distillery wastewater in other aspects will be needed.

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