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THESIS

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

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Environmental Engineering)
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Distillery industries is considered as one of the largest polluter in Thailand. The effluent from distillery wastewater treatment is high in organic carbon and dark brown in colour. It can cause the adverse effects if treated without proper treatment before release to environment.

This study investigated the effects of electrooxidation process on distillery wastewater. Distillery wastewater with initial COD of 1,000 mg/L was treated in a 5 L. batch reactor. Electrolytic cell in the reactor consisted of 17cm. x 17cm. x 1cm. graphite anode and an 17cm. x 17cm. x 1cm. iron cathode. The experiments were conducted under varying conditions of pH, electrical current and supporting electrolyte concentration. Experimental results, at pH 5.7, 2A, showed that with the use of graphite anode, electrooxidation was enhanced by electrolyte. Color could be removed to a greater extent while organic matter to a lower extent. Removal of color, COD and TOC increased from 9.06, 13.25, 1.63% without NaCl to 92.94, 45.82, 10.00% in the presence of 10g NaCl/L. Varying pH had only slight effect on color and TOC removal, but a stronger effect on COD. COD removal at pH 4 was found to be highest with 54.56% removal. The effect of electrical current was also noticeable, increased with increase in electrical current. At pH 4 with 10g NaCl/L, after 150min retention time, the lowest removals of 45.37% Colour, 25.06% COD and 7.35% TOC at 0.8A, increased to 96.58% Colour, 56.51% COD and 21.94%TOC at 8A.

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Student's signature Thesis Advisor's signature

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Wijittra Sansud

April 2013

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TABLE OF CONTENTS

Page

Copyright by Kasetsart University All rights reserved

LIST OF TABLES

Copyright by Kasetsart University All rights reserved

LIST OF FIGURES

Copyright by Kasetsart University All rights reserved

LIST OF FIGURES (Continued)

Copyright by Kasetsart University All rights reserved

LIST OF FIGURES (Continued)

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LIST OF FIGURES (Continued)

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LIST OF ABBREVIATIONS

A	=	Ampere
$AgSO_4$	=	Silver sulphate
BOD	=	Biochemical oxygen demand
COD	=	Chemical oxygen demand
Fe	=	Iron
Fe^{2+}	=	Ferrous ion
Fe(OH)2	=	Ferrous hydroxide
HOCl	=	Hypochlorite
H_2	=	Hydrogen
$HgSO_4$	=	Mercury sulphate
H_2SO_4	=	Sulphuric Acid
K_2Cr2O_7	=	Potassium dichromate
L	=	Litre
Mg	=	Milligram
NaCl	=	Sodium chloride
$(NH_4)_2Fe(SO_4)_2$	=	Ammonium ferrous sulphate
OH^-	=	Hydroxide ion
TDS	=	Total dissolved solid
TOC	=	Total organic compound
TSS	=	Total suspended solid
V	=	Volt

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

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 per 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, increasing 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 distillery wastewater such as biological process, chemical oxidation and 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.

Electrochemical processes have been successfully demonstrated for removing pollutants. Reaction can be electrocoagulation, electroflotation, electroprecipitation and electrooxidation. This processes can be applied successfully in wastewater treatment. Electrooxidation appears to be one of the promising technologies for

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treating recalcitrant compounds in industrial wastewater. This work was carried out to find the optimum condition of treating colour and COD in distillery wastewater by electrooxidation with use of graphite electrode and iron cathode. The effect of pH, electrical current, initial concentration, contact time and concentration of supporting electrolyte was investigated.

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OBJECTIVES

To determine effects of operating conditions (namely pH, contact time, electrical current and supporting electrolytes concentration) on colour and COD removal from distillery wastewater by electrooxidation.

Scope of study

1. The wastewater used for this study was collected from the Liquor distillery organization, Chachoengsao Province

2. The studies of electro oxidation werecarried out in 5L batch reactor using a graphite anode and an iron cathode with direct current (0.8 – 8A).

3. The factors under study include pH, contact time, electrical current and supporting electrolyte concentration.

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LITERATURE REVIEW

1. Distillery Wastewater

1.1 Alcohol production process

Alcohol can be produced from wide range of feedstock. These include sugar based (sugarcane and beet molasses, cane juice), starch based (corn, wheat, cassava, rice, barley) and cellulosic (crop residues, wood, municipal solid wastes) material. Molasses is the main byproduct of beet sugar process. It is one of the most important raw materials used in fermented industries due to its low cost and wide availability.

Alcohol production in distilleries consists of four main steps. The process includes feed preparation, fermentation, distillation and packaging as shown in Figure 1

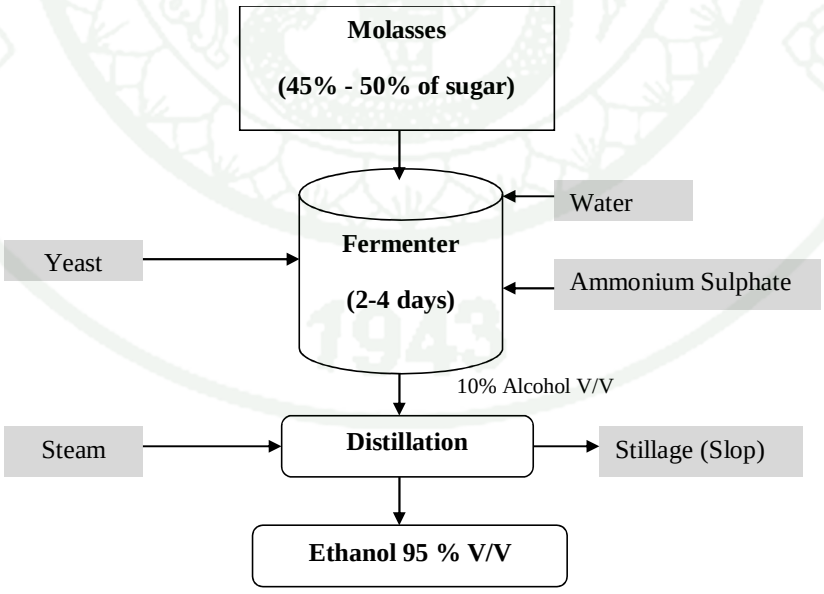

Figure 1 Alcohol production chart from molasses

Source: Scheitzer (1997)

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1.2 Distillery wastewater characteristic

Alcohol production from molasses generates large volumes of high strength wastewater that is of serious environmental concern. The aqueous effluent stream from distilleries wastewater is approximately 12-15 times the volume of the produced alcohol. The wastewater from distillery is high temperature in the range of 70-80 °C, deep brown in colour, acidic in nature (low pH) and has high concentration of organic material and solids and it is very complex. However, the pollution load of the distillery wastewater depends on the quality of molasses, unit operation for processing of molasses and process of recovery of alcohols. Table 1 summarizes the typical characteristics of distillery slop generated in Thai distilleries using molasses.

Table 1 Distillery wastewater characteristic from liquor distillery industry in Thailand

Parameter	**Range**	**Average**
Discharge volume (m^3/day)	23-400	90
pH	2.3–5.5	3.7
Temperature (°C)	53-100	88.6
BOD5 (mg/L)	17,500-45,000	27,475
COD (mg/L)	56,970-193,600	118,100
COD/BOD5	1.90-7.67	4.3
SS (mg/L)	5,240-23,830	11,319
TS (mg/L)	36,280-123,640	75,830
TVS (mg/L)	30,280-59,220	58,520

Source: The Excise Department (1983)

The recalcitrant nature of wastewater from sugarcane molasses is due to the presence of the dark brown colorants. During heat treatment, Maillard reaction takes place resulting in formation of melanoidins, one of the final products of the Millard reaction. Apart from melanoidins, the other recalcitrant compounds present in

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the waste are caramel, different products of sugar decomposition, anthocyanins, tannins and different xenobiotic compound. The unpleasant odor of the effluent is due to the presence of skatole, indole and other sulfur compounds, which are not decomposed by yeast during distillation.

1.3 Melanoidin

Melanoidin are brown recalcitrant compounds present in the effluent of fermentation processes that use molasses as carbon source, for instance those generated in ethanol production, bakery yeast processing and brewery industry. Melanoidin produced by non-enzymatic browning reaction called Maillard reactions, a complex reaction which occurs during the heating of sugars and amines. The resulting carbon chain is a cyclic based structure with nitrogen bound in amine rather than nitro form. The formation of the brown colour is not fully understood and the structure of melanoidin is largely unknown, which makes it difficult to quantify these compounds. It is assumed that it does not have a definite structure as its elemental composition and chemical structures largely depend on the nature and molar concentration of parent reacting compounds and reaction conditions as pH, temperature heating time and solvent system used.

The complexity of Millard reaction has been extensively studied during recent years and new important pathways and key intermediates has been established (Martins *et al*., 2001). A scheme of Maillard reaction is shown in Figure 2. Melanoidins are recognized as being acidic compounds with charged nature. With increasing reaction time and temperature, the total carbon content increases, thus promoting the unsaturation of the molecules. The colour intensity increases with the polymerization degree.

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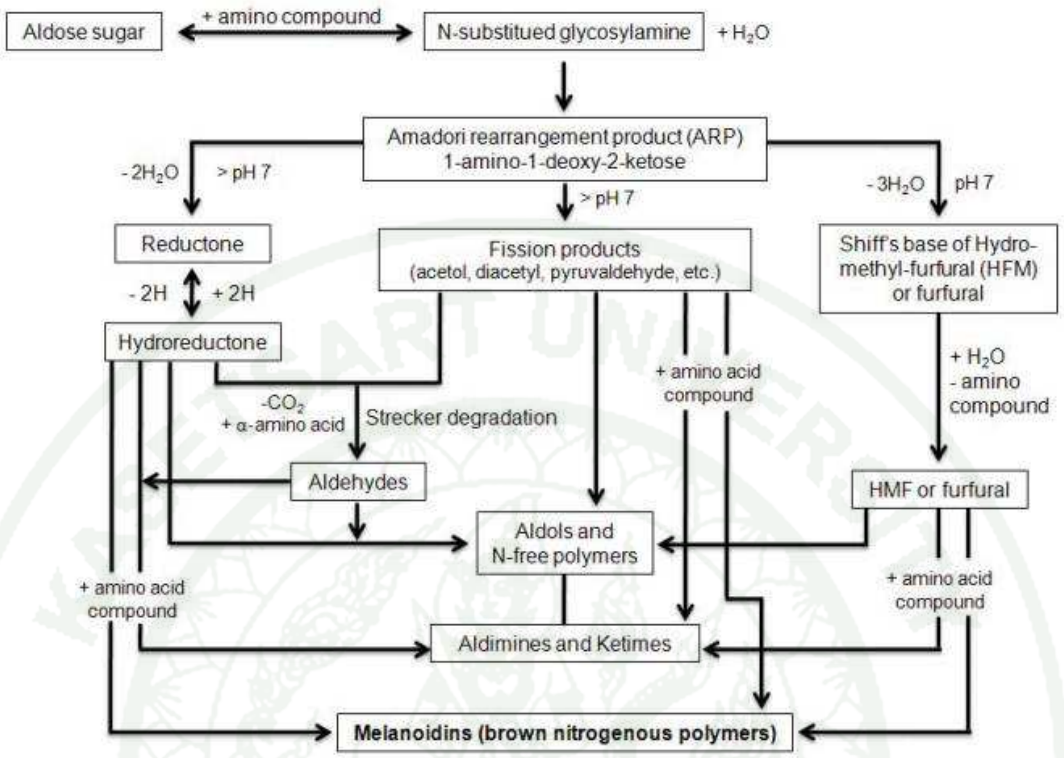

Figure 2 Scheme of Maillard reaction

Source: Martins *et at*. (2001)

The chemical structure of melanoidins is difficult due to the complexity of the Maillard reaction. Cammerer *et al*., 2002 proposed the general structure for melanoidins prepared from monosaccharides and glycine as shown in the Figure 3. Although the chemical structure of melanoidins is not cleary understood, most of the studies about melanoidin have been done on model melanoidins, since natural and synthetic melanoidins both have similar elemental (CHON) compositions, spectroscopic properties and electrophoretic mobilities at various values.

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Figure 3 Basic melanoidin structure formed from carbohydrates and amino acid

Source: Cammerer *et al*. (2002)

1.4 Environmental impact of distillery wastewater

The production and the characteristics of distillery wastewater are highly variable and depend on the raw material used and various aspects of the ethanol production process. Wash water used to clean the fermenters, cooling water blow down and water blow down further contribute to its variability. Distillery wastewater has very high biological oxygen demand (BOD), chemical oxygen demand (COD), and low BOD/COD raito. Its recalcitrant nature is due to presence of the brown polymer, melanoidin, these compound have antioxidant properties, which render them toxic to many microorganisms. The defiance of melanoidins to degradation is apparent from the fact that these compounds escape various stages of wastewater treatment plants and finally enters into the environment. The highly coloured components reduce sunlight penetration in river, lakes or lagoons which in turn decrease both photosynthetic activity and dissolved oxygen concentration.

Melanoidin have antioxidant properties, which render them toxic to aquatic micro and macro-organisms and conventional biological processes such as activated sludge. Biological treatment process is insufficient to treat melanoidin

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containing wastewater. Only 6% - 7% melanoidin has been degraded in conventional anaerobic-aerobic treatment processes (Pena *et al*., 2003), therefore, it is necessary to study about additional treatments required to decolourize distillery effluent.

Disposal of distillery wastewater on land is equally hazardous to the vegetation. It is reported to reduce soil alkalinity and manganese availability, thus inhibiting seed germination. Application of distillery effluent to soil without proper monitoring perilously affects the groundwater quality by altering its physic-chemical properties such as colour, pH electrical conductivity (EC), etc, due to leaching down of the organic and inorganic ion.

2. Distillery wastewater treatment

A number of technologies have been explored for reducing the pollution load of distillery effluent. All technologies that used can be classified as below;

2.1 Physical and chemical treatment

Physico chemical treatment is typically cost effective and can be completed in short time periods (in comparison with biological treatment). Equipment is readily available and is not engineering or energy-intensive. Treatment residuals from separation techniques will require treatment or disposal, which will add to the total project costs.

2.1.1 Coagulation – flocculation

This process transforms dissolved contaminants into an insoluble solid, facilitating the contaminant's subsequent removal from the liquid phase by sedimentation or filtration. The process usually uses pH adjustment. Chemical such as lime, alum, and ferric salt or polyelectrolyte are always involved in coagulation/flocculation which large amount of sludge would then be produced.

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Therefore, in order to lower the additional expense result from sludge removal, it is important to consider the amount of chemical used in the process

Migo*et et al*. (1993) used a commercial inorganic flocculant, a polymer of ferric hydroxyl sulphate for the treatment of distillery wastewater. The treatment result showed around 87% colour removal. These finding had been in disagreement with those of Inance *et al*, (1999) who reported the coagulation with alum and iron salt was not effective for colour removal.

2.1.2 Adsorption

The process of adsorption involves separation of substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

Adsorption operation employing solid such as activated carbon and synthetic resins are used wildly. Activated carbon, which can be prepared from lignite, charcoal, wood and cotton remnants, or coconut shell, is widely used in adsorption due to its high surface area (500-1,400 m^2/g). Adsorption on adsorbent surface can be expresses in a term of adsorption isotherm. This method is an efficient alternative used to remove low organic concentration in wastewater.

V.O. Ojijo*et et al*. (2010) investigated decolourization of melanoidin containing wastewater using the abundantly available coal fly ash. Maximum colour removal was achieved around pH 6, whereas increasing sorbent mass from 10g/L to 200 g/L enhanced colour reduction from 25% - 86% and the coal fly ash had maximum sorption capacity of 53g/g and could be used as adsorbent in melanoidin removal.

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2.1.3 Membrane technology

The principle of micro filtration and ultra filtration is physical separation. The substances that are larger than the pore in membrane are totally removed. Micro filtration and ultra filtration are pressure-dependent process, which remove dissolved solid and other substances from water to a lesser extend than nano filtration and reverse osmosis.

Smita *et al*. (2010) studied on the effect of electrooxidation on combine physicochemical and membrane treatment process. The overall COD removal efficiency is around 73% – 93% and total solid removal efficiency is 82% – 87% respectively.

2.1.4 Ozonation

Ozone was formerly applied for odor removal in drinking water and also uses to oxidize melanoidin compound. The oxidizing power of ozone is higher than chlorine. Moreover ozone generator has no remaining while chlorination produced chlorinate organic.

Sumaeth (1998) used iron oxide as catalyst to enhance ozone oxidation process. From the experimental result of both with and without iron oxide catalyst, increase in either hydraulic retention time and ozone flow rate resulted in increasing the treatment efficiencies of both COD and colour removal.

2.1.5 Fenton's reagent

Fenton's reagent, a combination of hydrogen peroxide (H_2O_2) with ferrous and ferric (Fe^{2+} and Fe^{3+}), is used as catalyst radical reaction which can generated hydroxyl radical ($HO^{\cdot}$). Hydroxyl radical is a stronger oxidant compare to ozone and chlorine.

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Pala and Erden (2005) studied decolourization of a baker's yeast industry effluent by fenton oxidation. The best Fe^{2+}/ H_2O_2 dosage was 1200 mg/L Fe^{2+}/800 mg/L H_2O_2 at pH 4 and in reaction time of 20 min,the maximum color removal efficiency was obtained as 99% and COD removal efficiencies were obtained as 88%.

2.2 Biological Process

Biological method (aerobic and anaerobic) is the feasibility of decreasing BOD, COD and TOC of distillery wastewater and probably the most inexpensive but inadequate for the treatment of color removal, because high molecular weight compounds are not easily degrade by bacteria.

2.3 Electrochemical process

Electrochemical process is another alternative applied to treat wastewater from distillery. The method has been applied successfully to treat wastewater such as protein wastewater, yeast wastewater, restaurant wastewater, landfill leachate and wastewater containing heavy metal. Hence, it is expected that the electrochemical would be an ideal choice for decolourization of wastewater.

Tassanaraphan (2009) studied treatment of distillery wastewater by electrocoagulation. The properties of sample were 1,018 – 1,129 mg/L COD, 510 – 550 mg/L BOD and 920 – 950 Pt-Co unit for colour. For the batch experiment, the cell voltage of 10 V yielded the best result. The values for COD, BOD and colour reduced to 254 mg/L, 185 mg/L and 32 Pt-Co unit, respectively.

3. Electrochemical process

Treatment of wastewater by electrochemical process had been practiced for most of 20^{th} century with limited success. In the last decade, this technology has been

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increasingly used in South America and Europe for treatment of many kinds of wastewater.

Electrochemical treatment is effective in treatment of wastewater from domestic and landfill areas, paper industries, metal coating manufactures, and textile industries. It can be applied to remove large amount of contaminants such as BOD, COD, TOC, TDS, TSS and colour.

3.1 Principle of electrolytic cell

Electrolysis is a basic electrochemical process of evolution of gas or decomposition of material on the electrodes due to the decomposition of solution under the influence of an electrical current. The solution which is used in this process is called electrolyte. This unit is named electrolytic cell as shown in Figure 4.

The electrode connected to the negative source behaves as cathode and the other as anode. If the electrode at anode is a metal like iron or aluminum, the metal will move away from the electrode into the solution as ion. On the other hand, if the electrode is inert like platinum, gases such as hydrogen or oxygen will be liberated, depending upon the type of electrolyte.

In treatment system, electrolyte solution would be wastewater while oxidation- reduction occurs at anode and cathode, respectively.

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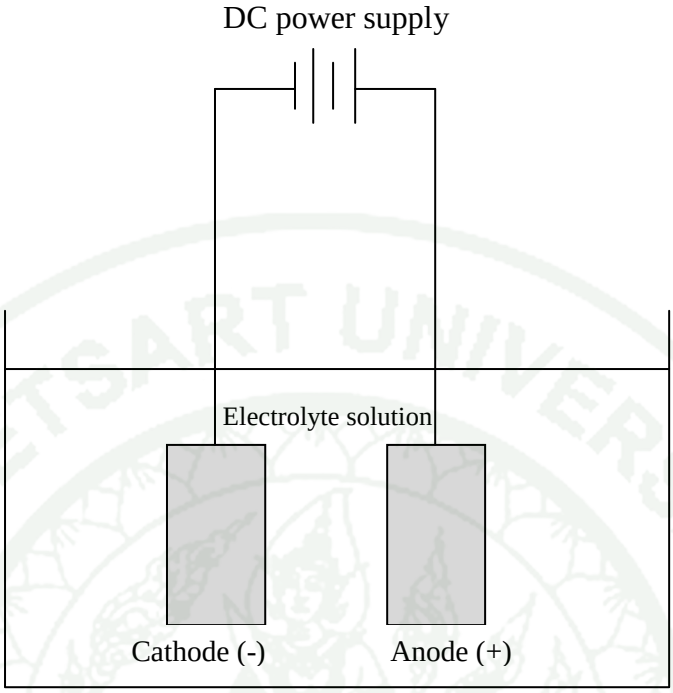

Figure 4 Schematic Diagram of Electrolytic Cell with DC Power Supply

Source: Duangta (2004)

3.2 Redox reaction induced by electrical current

In this process, the metal electrodes are forced to corrode by mean of a direct electrical current at anode. The metal is flocculated by hydroxide that comes from the reduction reaction of cathode. For example, by dissolution of iron, the following electrochemical reactions occur.

Anode (oxidation)	Fe	$\longrightarrow$	$Fe^{2+} + 2e^-$	(1)
Cathode (reduction)	$2H_2O + 2e^-$	$\longrightarrow$	$H_2 + 2OH^-$	(2)
Redox reaction	$Fe + 2H_2O$	$\longrightarrow$	$Fe(OH)_2(s) + H_2(g)$	(3)

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3.3 Faraday's Law

Michael Faraday first quantified the relationship between charge passed and amount of a substance oxidized or reduced at an electrode in the 1830s. His ideas are embodied in two statements pertinent to electrolytic processes.

3.3.1 The amount of product formed is directly proportional to the charge passed.

3.3.2 For a specified quantity of charge passed, the masses of products formed are proportional to the electrochemical equivalent weights of the product.

These two principles can be concisely stated in on equation

$$m = \frac{\mathrm{s\,M\,I\,t}}{\mathrm{n\,F}} \qquad (4)$$

Where
- m = the mass of substance (g)
- s = stoichiometric coefficient of the species
- M = atomic or molecular weight (g/mol)
- I = current (ampere)
- t = time (second)
- n = number of electrons participating in the redox reaction
- F = Faraday's constants = 96,485 Coulomb/mole

3.4 Electrochemical cell configuration

The simplest electrochemical cell consists of a cathode and an anode, however, the large electrode must be employed to treat wastewater when electrochemical cell is used. Therefore, several cell banks, units in which contain a lot of single electrochemical cells, are practically used to generate redox reactions in wastewater treatment system which current supplying depend on resistance.

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There are two main classes of electrode configuration which are monopolar and bipolar. A monopolar cell consists of an anode (direct current positive charged member) and cathode (direct current negative charged member) each join to the power source by a separate power connection. These electrodes are separated by a space that allows the electrolyte solution to flow between the plates for electrolysis to occur. Multiple electrodes may be connected to a common input connection in a parallel configuration within each electrolyzer assembly. Each electrode polarity is defined by its connection polarity, anodes only on the positive connection and cathodes only on the negative connection. In bipolar electrodes differ from monopolar, each electrode will serve as both an anode and a cathode. The different charges would be generated on the surface of the inner electrode as shown in the Figure 5.

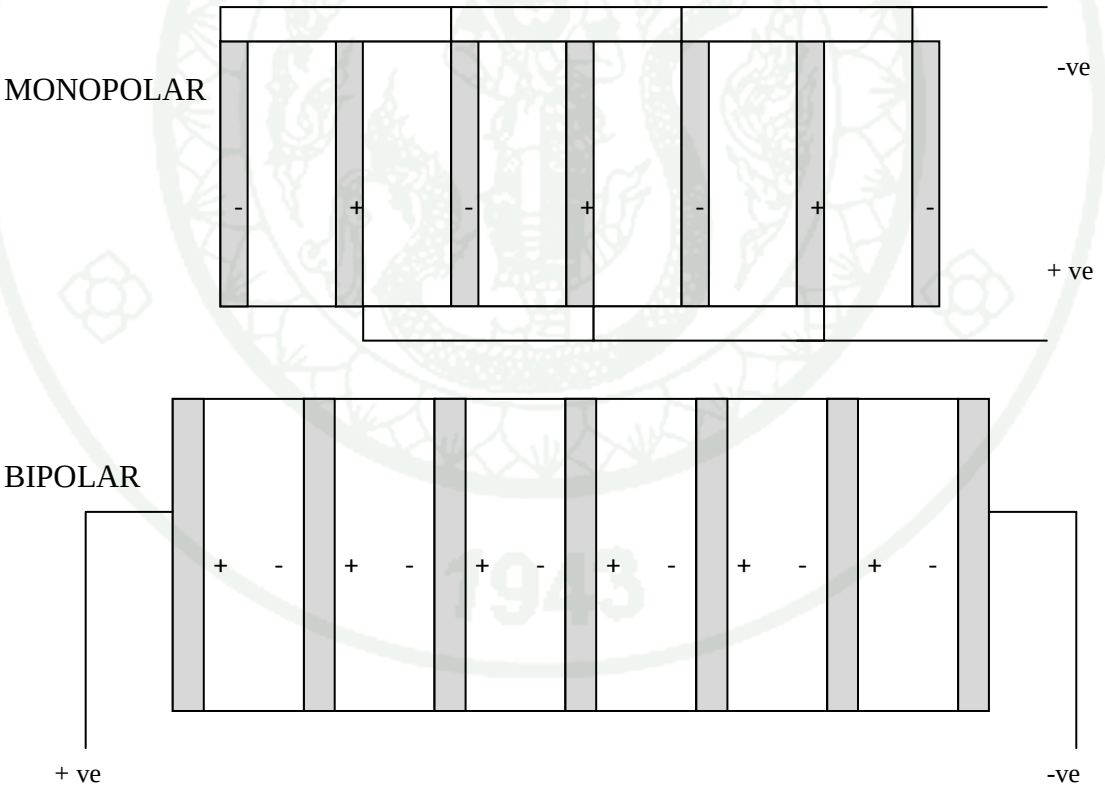

Figure 5 Monopolar and bipolar connection of electrode

Source: Duangta (2004)

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There are variations of multiple cell arrangements have been proposed such as monopolar electrode single cell, monopolar electrode with cell in series, monopolar electrode with cell in parallel and bipolar electrode with multiple cell in series as shown in the Figure 6.

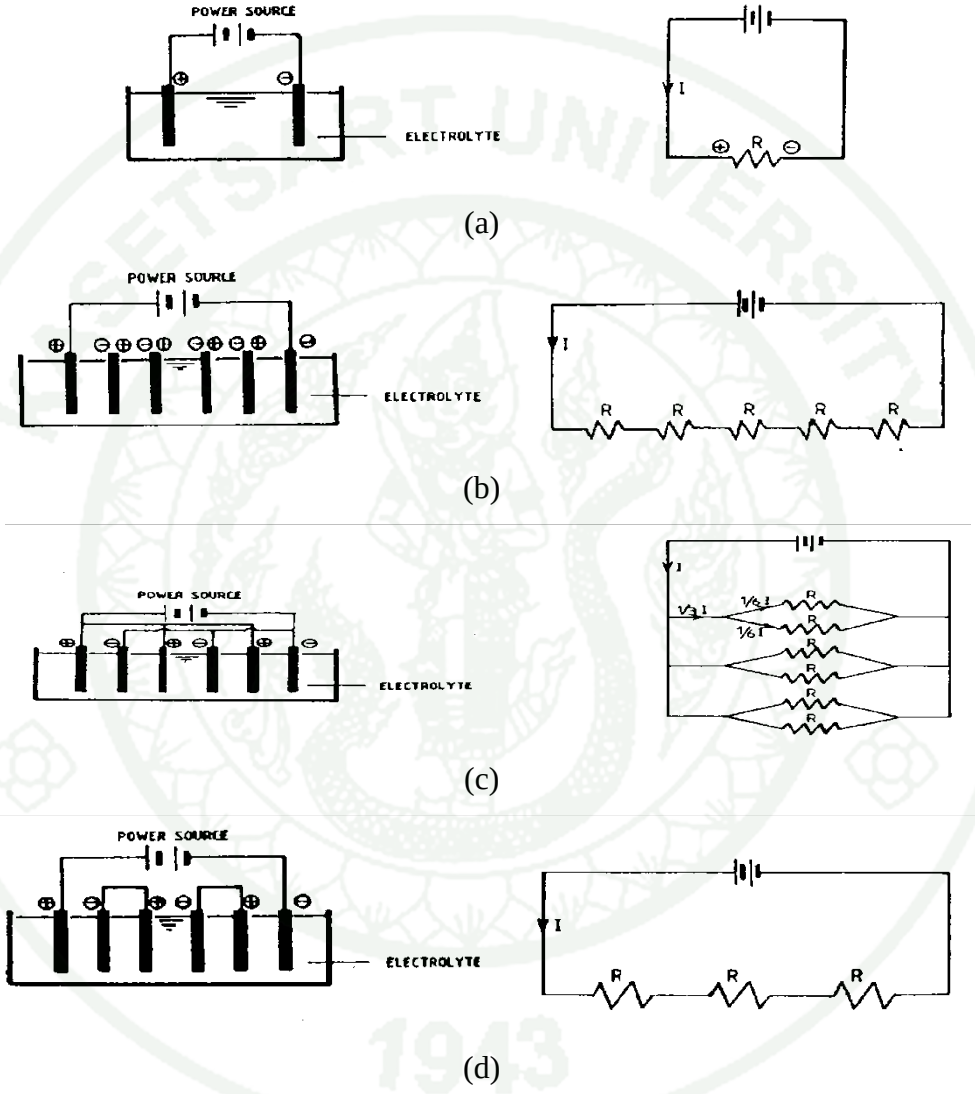

Figure 6 Electrolytic cell arrangements

(a) Monopolar electrode single cell

(b)Monopolar electrode with cells in series

(c)Monopolar electrode with cells in parallel

(d) Bipolar electrode with cells in series

Source: Anawat (2002)

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3.5 Electrode material

Electrode is a component of a half-cell acting as a conductor connecting electrolyte solution and a voltmeter. There are two types of electrodes, active electrodes and inert electrodes. Active electrodes take place in the process its self. Inert electrodes are just there to conduct the current without interfering. Inert electrodes can be (Ti), Platinum (Pt) or graphite but graphite is widely used because it is cheaper. Metal electrodes are categorized by materials of which they are made of. Metal commonly used as active electrodes are .Aluminum (Al) and Iron (Fe). The common electrode materials used are as shown in the Table 2.

Table 2 Common electrode materials

Cathodes	Anodes
Mercury (Hg), Lead (Pb), Copper (Cu) Nickel (Ni)	Platinum (Pt), Platinum/Titanium (Pt/Ti), Iron/Titanium (Fe/Ti)
Graphite and other forms of C sometimes treated thermally or with organics to modify porosity, density, corrosion resistance	Graphite and other forms of C (treated cathodes)
	Lead (Pb) in acid sulfate media
Steels	Lead dioxide (PbO_2) on Titanium or Niobium(Nb)
Coating of low H_2over-current materials on steel, e.g. Nickel (Ni),	Nickel in alkaline media
Nickel/Aluminum (Ni/Al), Nickel/Zinc (Ni/Zn)	Dimensionally stable anode (DSA)
	Other oxide coating

Source: Pletcher D. (1984)

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3.5.1 Aluminium

Aluminium, the most abundant metals in the earth's crust, is used for many applications especially lightweight structures requiring high strength because of its flexibility. Al^{+3}, and active substance, which reacts with non-metallic substances, in water undergoes hydration and hydrolysis. Sulfate, nitrate, and halide aluminum salts are soluble in water while aluminum hydroxide is not.

Large amount of suspended solids deriving from corroded aluminium is generated through electrical decomposition when aluminium is used as an electrode.

3.5.2 Iron

Iron is an active metal, which has high melting and boiling points. Iron within in compounds has oxidation state of +2 and +3. Although higher oxidation state can also be found, they are strong oxidants and unstable, therefore, iron rust is then found when they are exposed to moisture. Rust protection approaches such as metal coating in which Zinc, and Chromium are commonly used or metal adding are applied in order to achieve rust-free iron.

When iron electrode is used as electrochemical cell, hydroxide iron deposition. Therefore, it is necessary to change the iron plates in the electrochemical cell periodically.

3.5.3 Titanium

Titanium, a transition metal, which has the lowest density among all transition metals, is stable around the room temperature. However, when the temperature is higher than 500° C, it reacts vigorously with other metals and forms compounds such as $TiCl_4$ and TiO_2 or reacts with steam to form dioxide and hydrogen gas. The oxidation states of titanium are +2, +3 and +4, which is the most common

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oxidation state and Ti^{+4} is the most stable form of titanium. Tue to the high strength and high melting point, Ti^{+4} is always used in jet engine.

Titanium is non-corrosive when it is used as an electrode in the electrochemical cell because of its lowest density, high boiling and melting points, inert characteristic, and good electrical conductivity. Due to the electrical conductivity property of titanium, high electron transfer is achieved, therefore, clear solution remain.

3.5.4 Platinum

Platinum, a glossy white metal, is more flexible than other metals, therefore, it can be bended like Gold (Au), and Silver (Ag). Although platinum has wide range of oxidation state, from +2 to +8, the important oxidation states are +2, +3 and +4. In nature, platinum can be found as a free element or combined with other elements or as a mixture when it is blended with other metals. Platinum can also be found with Copper (Cu), silver and gold. Due to its heat and electrical conductivity and inert characteristic, platinum is typically used to make an electrode and container, which is resistant to high temperature and corrosion.

When platinum is used as an electrode for electrochemical process, small amount of residues and clear solution would be achieved.

4. Electrooxidation

Study on electro oxidation for wastewater treatment goes back to the 19^{th}century. During the last two decades, research works have been focused on the efficiency in oxidizing various pollutants on different electrodes, improvement of the electro catalytic activity and electrochemical stability of electrode materials, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutant degradation.

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Pollutants can be destroyed by conducting a direct anodic oxidation or an indirect oxidation process. The schem of these two processes is illustrated in Figure 7 and 8.

4.1 Direct anodic oxidation

Electrooxidation of pollutants can also occur directly on anodes. Physically adsorbed “active oxygen” (adsorbed hydroxyl radicals, °OH) or chemisorbed “active oxygen” (oxygen in the oxide lattice, MO_{x+1}) is generated. This process is usually called anodic oxidation or direct oxidation. The physically adsorbed active oxygen causes the complete combustion of organic compounds (R), and the chemisorbed active oxygen (MOx+1) participates in the formation of selective oxidation products.

$$R + MO_x(^{\circ}OH)_z = CO_2 + zH^+ + ze^+ MO_x \quad (5)$$

$$R + MO_{x+1} = RO + MO_x \quad (6)$$

The direct electrooxidation rate of organic pollutant is dependent on the catalytic activity of the anode, diffusion rate of organic compounds in the active points of the anode and the applied current intensity.

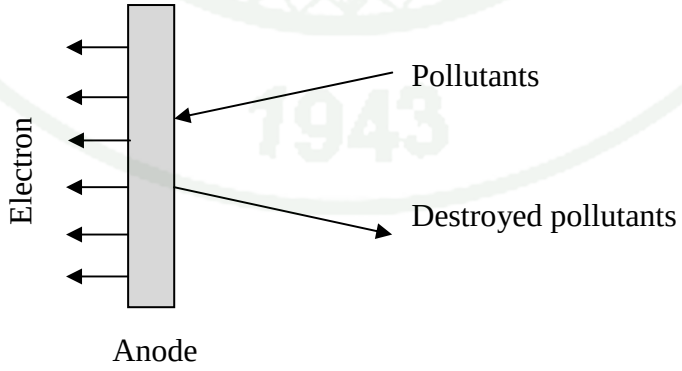

Figure 7 The scheme of pollutant removal pathway in direct oxidation mechanism

Source: W. Miled*et al*. (2010)

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4.2 Indirect electrooxidation process

Indirect electrooxidation of pollutants which was observed to be most efficient method on decolourization and mineralization, can be conducted when strong oxidant such as chloride, ferric or silver are present. The indirect electrooxidation rate is dependent on the diffusion rate of strong oxidants electroformed into solution which are able to completely convert all organics into water and carbon dioxide.

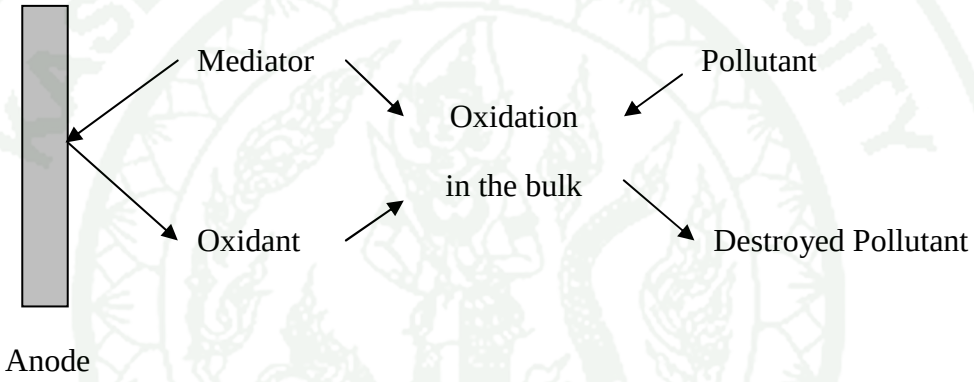

Figure 8 The scheme of pollutant removal pathway in indirect oxidation mechanism

Source: W. Miled*et al*. (2010)

W. Miled *et al*. (2010) studied on decolorization of highly polluted textile wastewater by indirect electrochemical oxidation process. The best removal of organic compounds contained in the waste has been obtained at pH 13, low electrolyte concentration and current intensity (0.1 M and 200 mA, respectively). COD and percentage colour removal were 75% and 43% respectively.

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Previous Study

A number of previous researches were conducted on electro oxidation of various types of organic pollutants. Several researches have reported that manytypes of pollutants could be removed by electrooxidation effectively. In addition the electro oxidation technique is also effective for recalcitrant compounds. The operating conditions used in electro oxidation process are dependent on the type of industry and the kind of wastewater.

An experiment on treatment of landfill leachate by electrochemical oxidation was carried out by Yang Deng and Englehardt (2006). It was found that anode materials, pH, current density, chloride concentration and electrolytes added all influence removal efficiencies of pollutants. During electro oxidation of leachate, COD reduction efficiency ranges from 70% up to above 90% and NH_3-N removal efficiency almost reaches 100% under appropriate conditions. Cho *et al* (2010) conducted a research on effect of voltage and sodium chloride on electrooxidation of swine wastewater. The system consisted of titanium anode coated with iridium oxide and stainless steel cathodes. The results obtained indicated that 7 V and 0.05% (8.56 mM) NaCl level would be the optimum conditions for the designed electrolysis process. Under these conditions, the average removal efficiencies of NH_4-N, soluble nitrogen, PO_4-P, soluble total organic carbon and color were 99%, 94%, 59%, 64%, and 93%, respectively.

Ivonne *et al*. (2010) conducted research on combined electrocoagulation – electrooxidation treatment for industrial wastewater. Samples of wastewater were collected from a treatment plant located at the end of an industrial park. It was found that the sample was completely mineralized after 21 hour of electoxidation treatment. Higher current densities resulted in a faster rate of COD reduction and the faster rate for complete mineralization occurred at pH 8. Bhaskar *et al*. (2009) also studied on combined electrocoagulation-electrooxidation of textile effluents. The textile wastewater was initially treated by electrocoagulation to remove the suspended solids. After the electrocoagulation the wastewater was further treated by electrooxidation

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with two different electrodes. COD was removed to the extent of 90% to 93% using graphite and 54% with $RuO_2/IrO_2/TaO_2$ coated titanium electrodes.

Canizares P. *et al.* (2009) studied on comparison between conductive diamond electrochemical oxidation (CDEO), ozonation and Fenton oxidation for the treatment of synthetic melanoidins. The results showed that CDEO removal efficiency seem to strongly depended on the addition of electrolyte salt. Sodium chloride (NaCl) was used as supporting electrolyte to improve the removal percentage of organic load, indicating the important role of mediated oxidation process. The concentration of NaCl solution ranging from 0 to 86 mM, COD remaining is about 20% of initial COD in electrolysis without addition of NaCl while electrolyses with NaCl electrolyte obtain the complete removal of COD.

Several authors have reported about the effectiveness of indirect electrochemical oxidation for organic pollutants removal. Ata M. *et al* (2009) studied on decolourization of coloured textile wastewater using indirect electrochemical oxidation method. Decolourization of Reactive Yellow 3 (RY3) was performed using a 0.2 L solutions containing specified concentration of dye and NaCl as supporting electrolyte. The results showed that increase in NaCl concentration until 2 g/L leads to increase in the decolourization rate of RY3. Aquino.and Andrade (2009) also reported that for glyphosate herbicide (GH) degradation by electrooxidation system seems to be significant in the absence of chloride. At 30 $mAcm^{-2}$ and 4 hour of electrolysis, complete GH removal from the electrolyzed solution has been achieved.

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MATERIALS AND METHODS

Experiment was performed in a laboratory scale batch system, 5L acrylic reactor with wastewater from Liquor distillery organization, Chachoengsao Province

Materials

1. Lab scale electrooxidation process

Lab scale electrooxidation system (Figure 9) was 5L acrylic tank equipped with electrolytic cell of monololar electrode. Electrolytic cell consisted of 17 x17 x 1cm^3 graphite anode and 15x17x1 cm^3 iron plate cathode connected to DC power supply adjustable to 0.8 – 8 A. The electrooxidation reactor was equipped with an over head mixer (100 rpm).

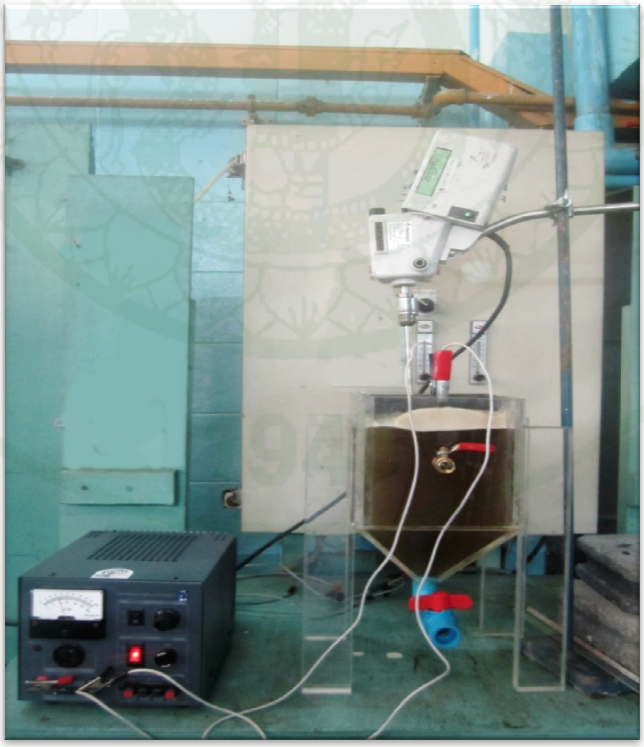

Figure 9 Batch electrooxidation experiment reactor

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2. Equipment and material for laboratory analysis

2.1 Analytical equipment

- UV-Visible Spectrophotometer (Shimadzu)
- Total Organic Carbon Analyzer model 5000,Shimadzu
- pH meter
- Thermometer

2.2 Chemical reagent

- Potassium dichromate ($K_2Cr_2O_7$)
- Sulphuric acid (H_2SO_4)
- Mercury sulphate ($HgSO_4$)
- Silver sulphate ($Ag2SO_4$)
- Ammonium ferrous sulphate ($(NH_4)2Fe(SO_4)_2$)
- Ferroin indicator
- Sodium Hydroxide (NaOH)
- Sodium Chloride (NaCl)
- Hydrochloric Acid (HCl)

3. Preparation of Wastewater Sample

Distillery wastewater sample was collected from equalization tank by grab sampling from Liquor distillery organization, Chachoengsao Province. The wastewater were refrigerated at 4° C to preserve the physical and chemical properties of wastewater.

The distillery wastewater was diluted with distilled water to initial concentration of 1,000 mg/L of COD for further analysis.

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Analytical method

Chemical analysis was conducted in accordance with Standard Method for the Examination of Water and Wastewater 20th Edition 2000. Parameters and analytical methods are summarized in Table 3

Table 3 Analytical method

Parameter	**Method**
pH	pH meter
COD	Closed Reflux, Titration (5220D)
TOC	TOC analysis
Colour	Platinum-Cobalt and ADMI
Temperature	Thermometer

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Methods

The experiments were performed in a laboratory scale batch system, 5 L reactor, using initial wastewater with COD concentration of 1,000 mg/L

1. Preliminery test of distillery wastewater from Liquor distillery organization, Chachoengsao Province

The distillery wastewater samples were collected from equalization tank by grab sampling and put into the plastic container. The wastewater were analyzed for pH, COD, TOC, SS and colour.

2. Study on factors affecting treatment efficiency of electro oxidation process for the removal of colour and COD from liquor wastewater

All experiments were conduct in a batch system. The batch electro oxidation apparatus consists of DC power supply, reaction tank and speed controller mixer. Initial COD concentration of wastewater sample was 1,000 mg/L. Initial pH of wastewater samples was adjusted at 4, 7 and 10 with NaOH or H_2SO_4 solution to determine the effect of parameters for this process

2.1 Determination of effects of supporting electrolyteon electrooxidation process of distillery wastewater

Determination the effects of supporting electrolyte for colour and COD removal was perform as preliminary study. The wastewater with original pH used electrical current at 2A with and without supporting electrolyte. (Use NaCl as electrolyte by adding 10g/L), allow the electro oxidation process to treat the wastewater for 30, 60, 90 and 150 minute. Collect the treated water 200 mL in each operating time. The COD, TOC, SS, colour and temperature were analyzed. Change the initial wastewater pH value to 7 and 10 and repeat the same treatment as pH 4.

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2.2 Determination of effects of supporting electrolyte concentration

Determination the effect of supporting electrolyte concentration on electrooxidation was perform with wastewater pH 4 initial COD concentration of 1,000 mg/L with 6A electrical current and NaCl concentration of 1g/L. Allow the electrooxidation process to treat the wastewater for 30, 60, 90 and 150 minute. Collect the treated water 200 mL in each operating time. The COD, TOC, SS, colour and temperature wereanalyzed. Change the supporting electrolyte concentration to 5, 7, and 10g/L of NaCl and repeat the same treatment as supporting electrolyte concentration 1g/L of NaCl.

2.3 Determination of effects of pH on electrooxidation process of distillery wastewater

Determination the effects of pH for electrooxidation process of distillery wastewater was perform. The wastewater with pH4 used electrical current at 2A with 10 g/L NaCl as supporting electrolyte., allow the electro oxidation process to treat the wastewater for 30, 60, 90 and 150 minute. Collect the treated water 200 mL in each operating time. The COD, TOC, SS, colour and temperature were analyzed. Change the initial wastewater pH value to 7 and 10 and repeat the same treatment as pH 4.

2.4 Determination of effects of electrical current on electrooxidation process of distillery wastewater

The optimum pH of wastewater that obtains from 2.1 was fixed to determine the electrical current effecting colour and COD removal. Adjust the electrical currentat 0.8 A, allow the electro oxidation process to treat the wastewater for 30, 60, 90 and 150 minute. Collect the treated water 200 mL in each operating time. The COD, TOC, SS colour and temperature wereanalyzed. Change the electrical currentto 2, 4, 6 and 8A and repeat the same treatment as electrical current 0.8A.

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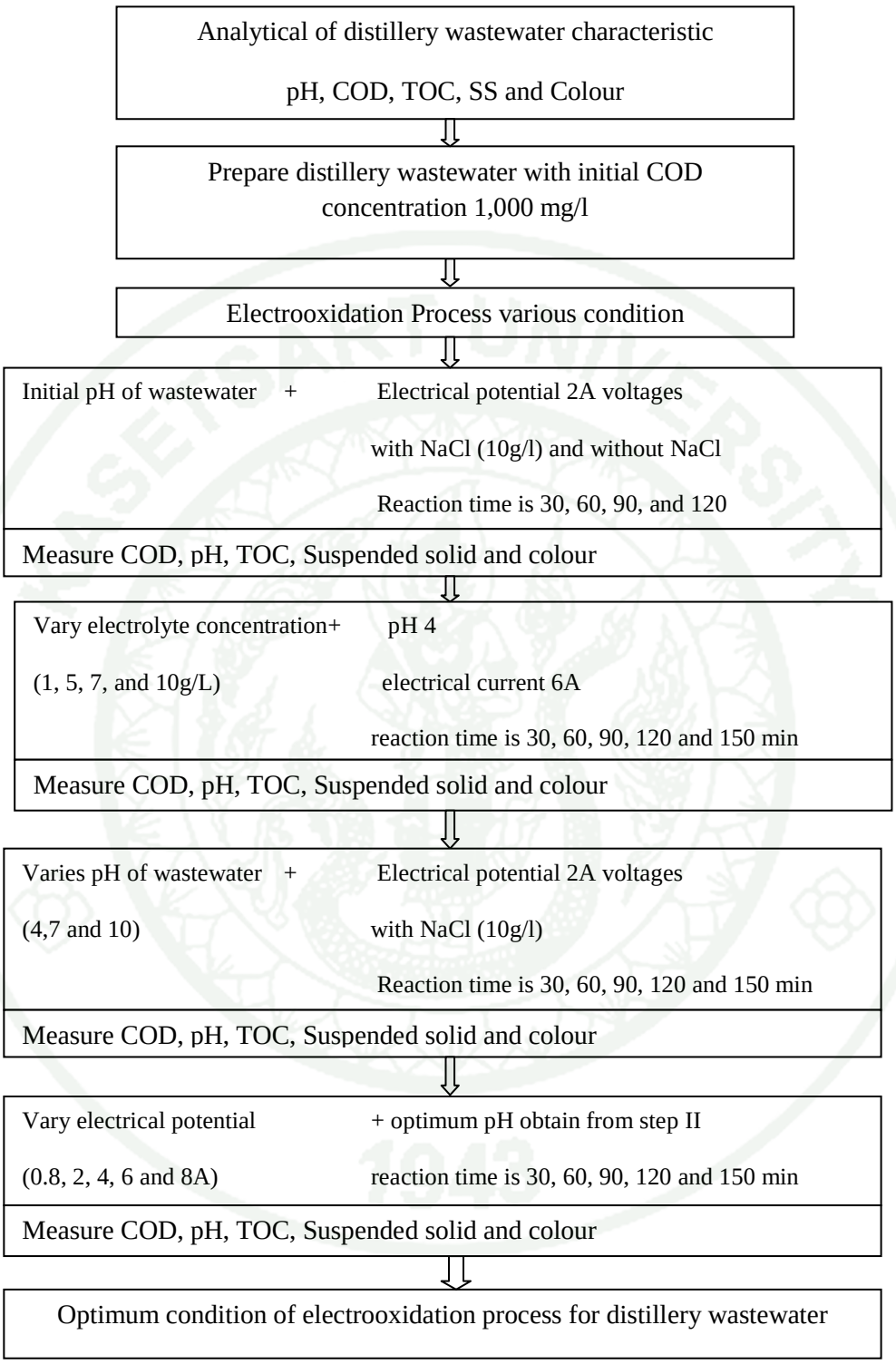

Figure 10 Experiment step for determination of optimum condition of electrooxidation process for distillery wastewater

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RESULTS AND DISCUSSION

1. Preliminary test of distillery wastewater

Table 4 shows the result of analysis of distillery wastewater characteristic from Liquor distillery organization, Chachoengsao Province. Generally the wastewater is acidic, brown in colour and high concentration of COD, TOC and suspended solid.

Table 4 The distillery wastewater characteristic

Parameter	Unit	Value
pH		3.80 – 4.60
COD	mg/l	96,000-124,000
Suspended solid	mg/l	5,600 – 12,600
TOC	mg/l	32,100 – 36,000
Colour	Pt-Co unit	2,200-2,500

2. Effect of electrooxidation on COD and colour removal of distillery wastewater

The efficiency of electrooxidation in the removal of COD and colour in the distillery wastewater depends on several parameters including pH, supporting electrolyte concentration and electrolyte current. The experiment was conducted with distillery wastewater with 1,000 mg/l of initial COD concentration, pH vary of 4, 7 and 10, the electricalcurrent vary of 0.8, 2, 4, 6 and 8 A and the supporting electrolyte concentration vary of 1, 5, 7 and 10 g/l of NaCl. The concentration of COD, TOC, SS and colour were analyze at vary time of 30, 60, 90, 120 and 150 min.

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2.1 Preliminary study of effects of electrolyte on electrooxidation of distillery wastewater

The experiments were conducted with distillery wastewater with 1,000 mg/L of initial COD, original pH of 5.7 and 2A electrical current. The presence of 10g NaCl/L electrolyte was compared to non-electrolyte condition. Figure 11 - Figure 14 shows the results of electrooxidation of distillery wastewater with and without supporting electrolyte. At 120 min retention time, without NaCl, removal percentage of COD, TOC, SS and colour were 13.25%, 1.63%, 12.43% and 9.06% respectively. Additional of NaCl increased removal percentage of COD, TOC, SS and colour. The highest reduction in COD (45.82%), TOC (10.00%), SS (46.80%) and colour (92.24%) were achieved at 120 min retention time.

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).

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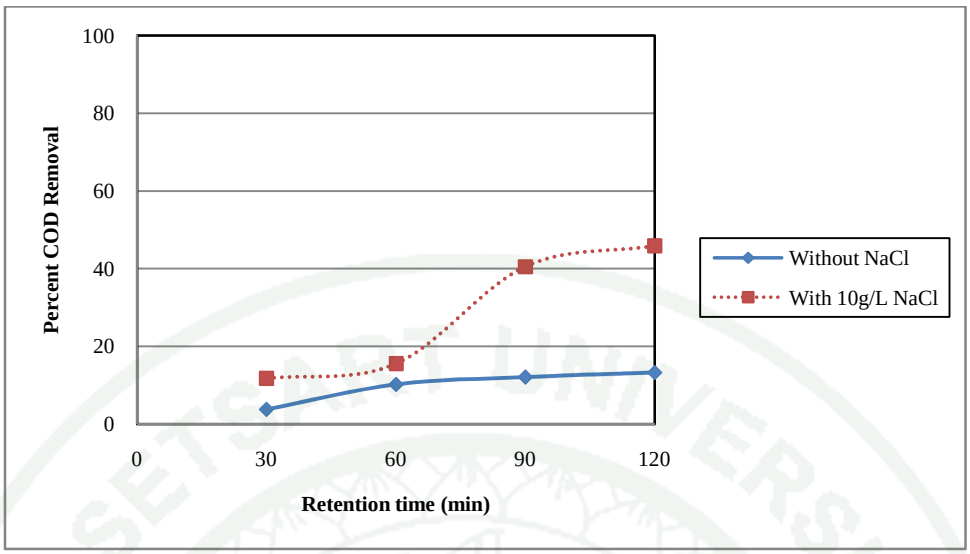

Figure 11 COD removal percentage achieved at various time by electrooxidation with and without NaCl

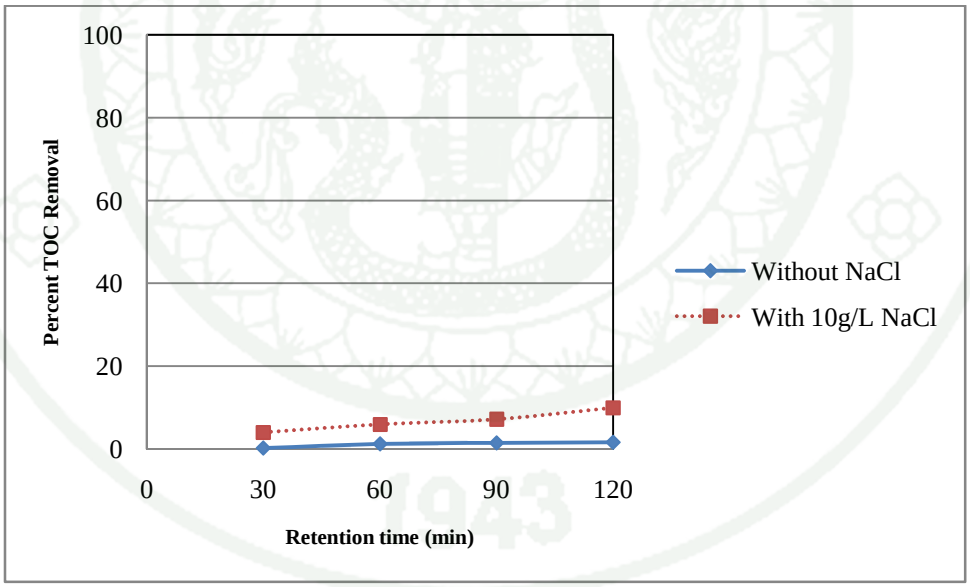

Figure 12 TOC removal percentage achieved at various time by electrooxidation with and without NaCl

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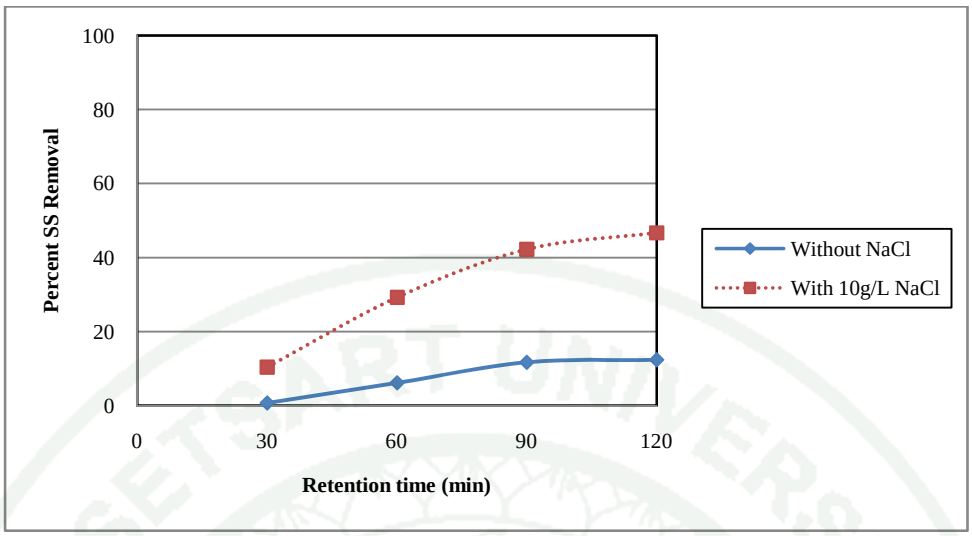

Figure 13 SS removal percentage achieved at various time by electrooxidation with and without NaCl

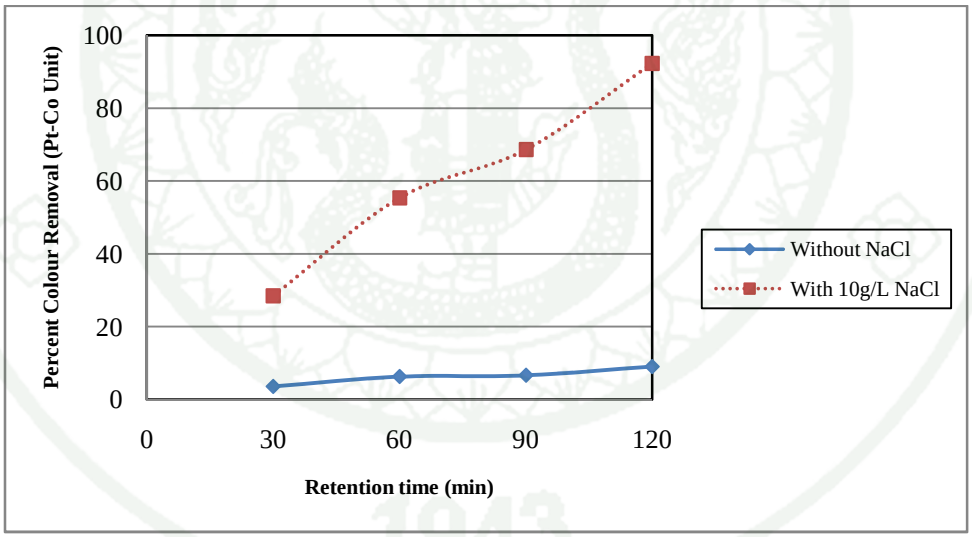

Figure 14 Colour (Pt-Co Unit) removal percentage achieved at various time by electrooxidation with and without NaCl

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2.2 Effect of electrolyte concentration on electrooxidation of distillery wastewater

The purpose of adding NaCl was to enhance indirect oxidation that can promote the degradation of organic pollutant in wastewater. In this step, experiments on various electrolyte concentrations were conducted. The experiment condition was 6A electrical current at varying NaCl concentration of 1, 5, 7 and 10g/L. The result obtained from varying NaCl concentration is as shown in Figure 15 – Figure 19. It was found that increasing the electrolyte concentration resulted in increase in COD, TOC, SS and colour reduction.

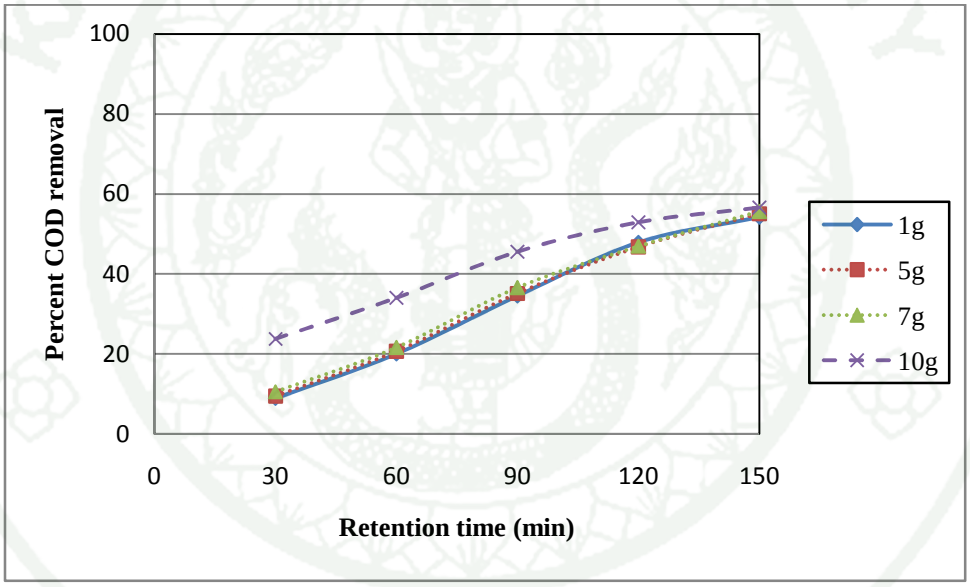

Figure 15 COD removal percentage achieved at various time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 6A electrical current

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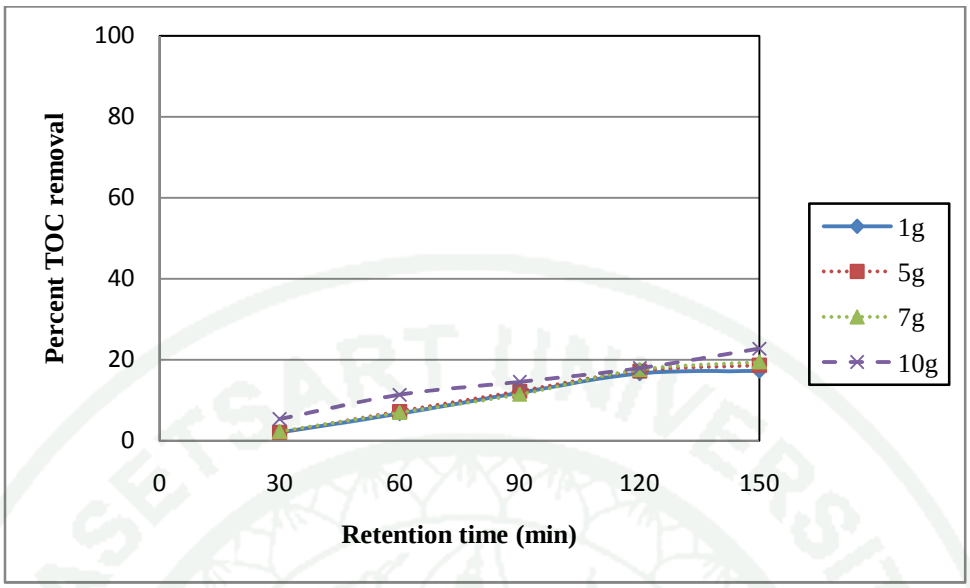

Figure 16 TOC removal percentage achieved at various time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 6A electrical current

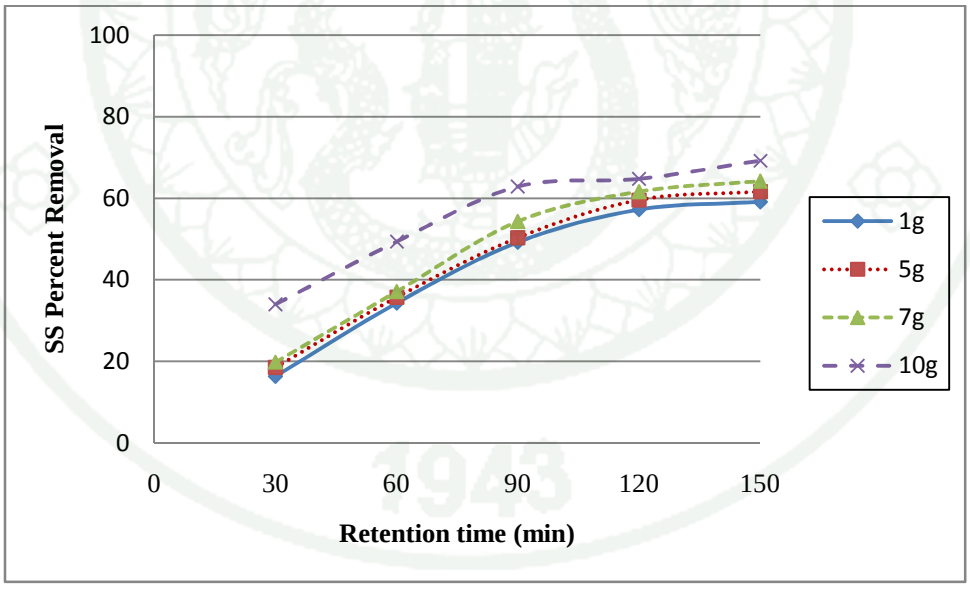

Figure 17 SS removal percentage achieved at various time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 6A electrical current

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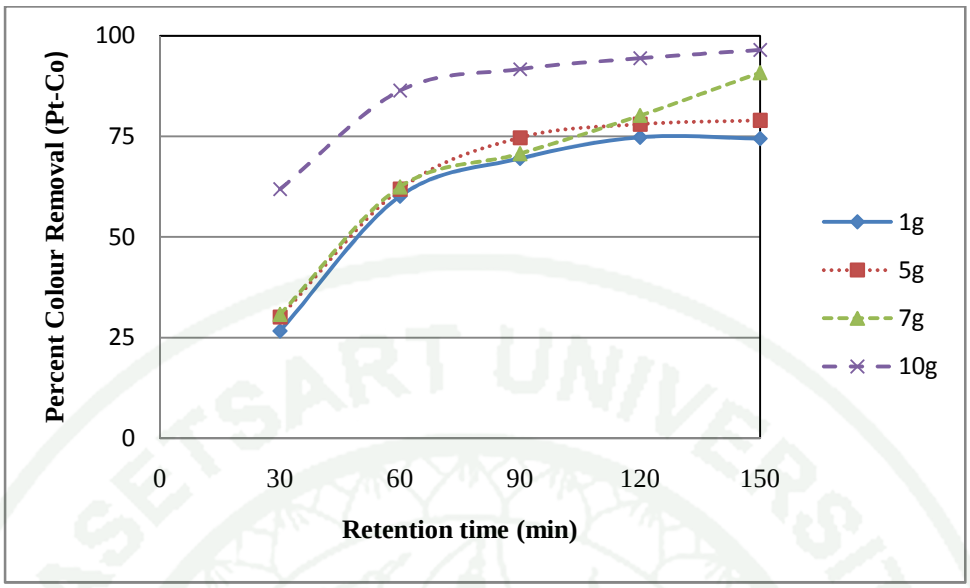

Figure 18 Colour removal percentage (Pt-Co Unit)achieved at various time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 6A electrical current

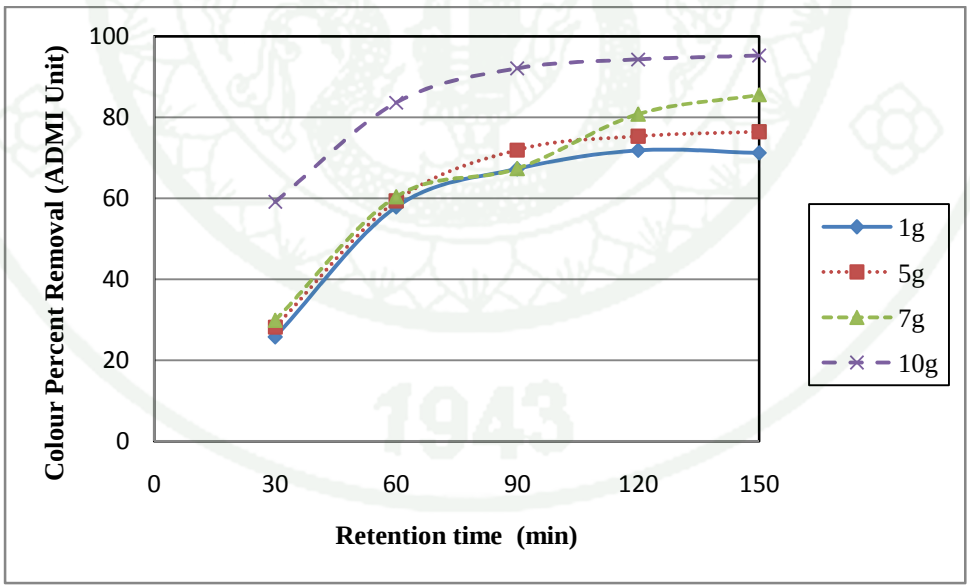

Figure 19 Colour removal percentage (ADMI Unit)achieved at various time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 6A electrical current

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It could be noted that the effect of NaCl concentrations on removal of COD and TOC were not as clear as those on colour removal. The condition with addition of 10g NaCl/L was therefore selected for the next step.

2.3 Effect of pH

In this step, pH was brought into consideration. The experiment was conducted with 2A electrical current at various pH of 4,7 and 10. The result obtained from varying pH is as shown in Fig 20 – Figure 24. It was found that pH had only a slight effect on removal of TOC, SS and colour. For COD removal, pH 4 was distinctive giving highest removal of 54.56%.

Since the original pH of distillery wastewater sample was in the acidic condition , further study related to the influence of electrical current were carried out under pH4 with additional of supporting electrolyte NaCl 10g/L.

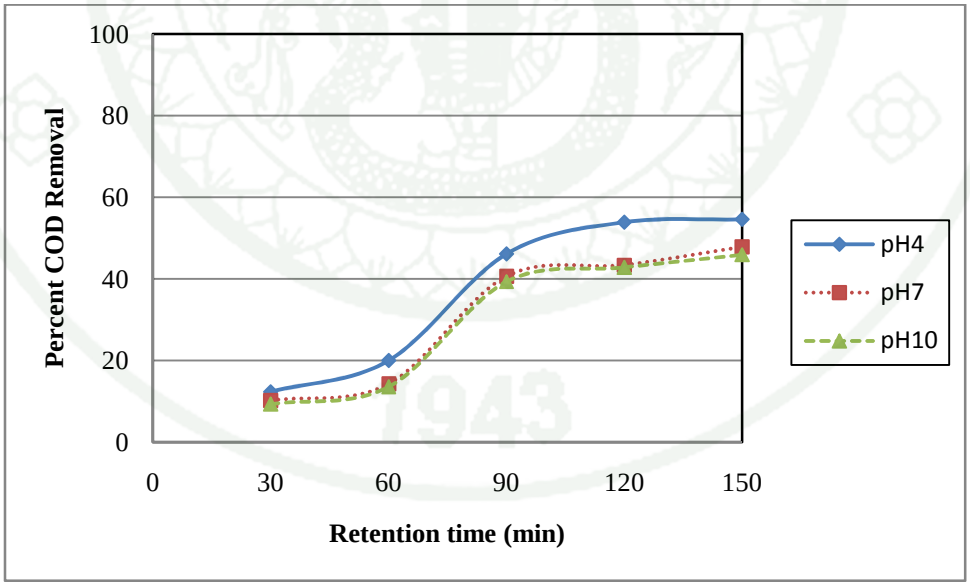

Figure 20 COD removal percentage achieved at various pH and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 2A electrical current

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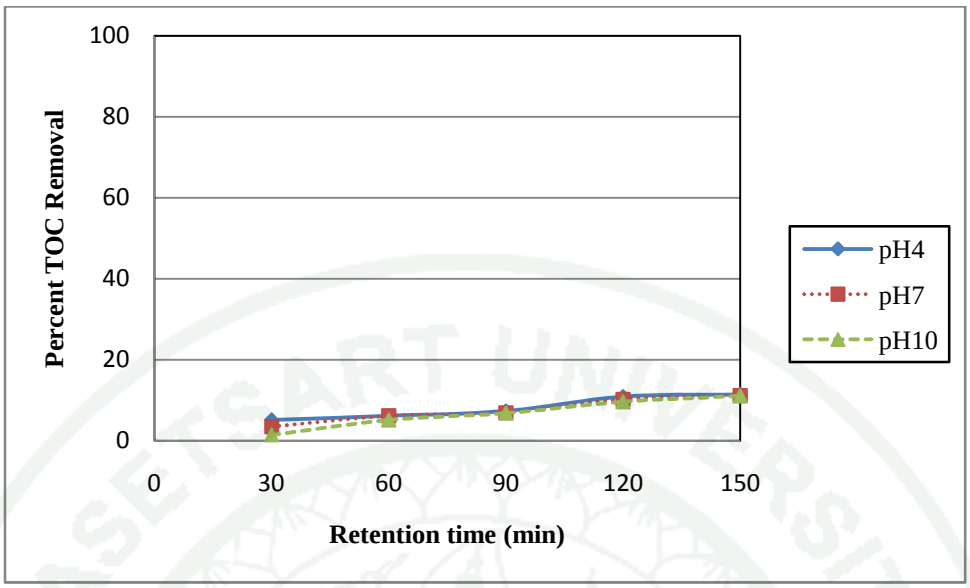

Figure 21 TOC removal percentage achieved at various pH and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 2A electrical current

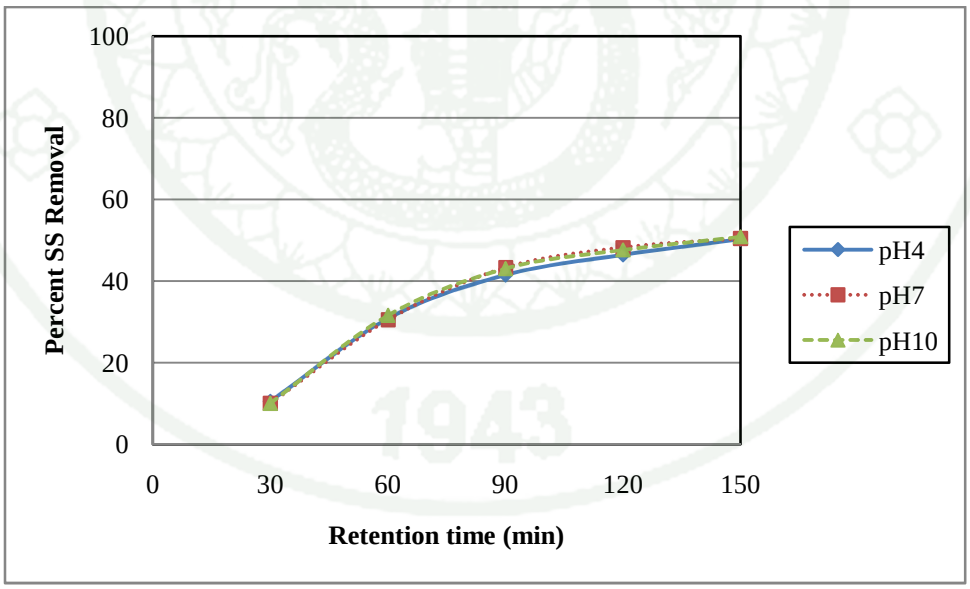

Figure 22 SS removal percentage achieved at various pH and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 2A electrical current

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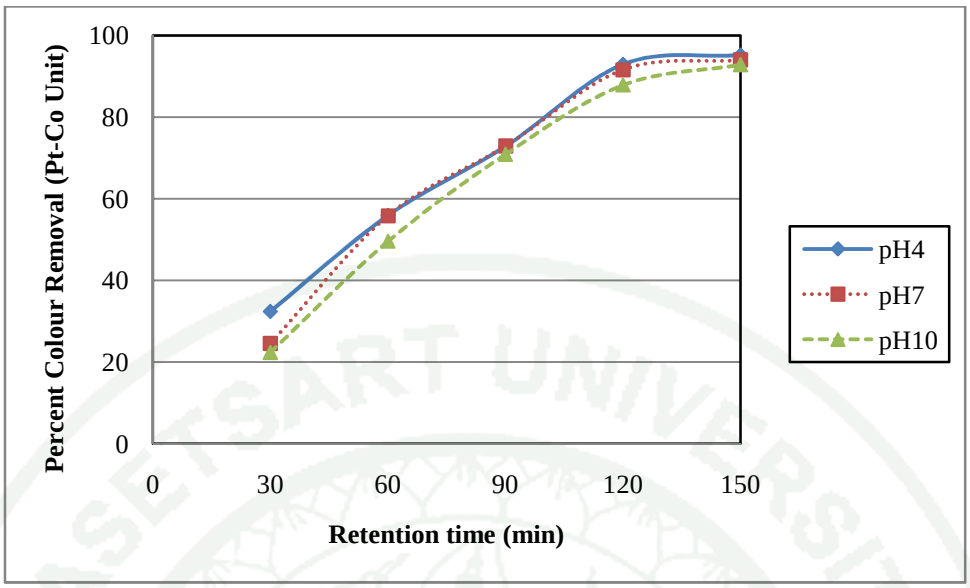

Figure 23 Colour removal percentage (Pt-Co Unit) achieved at various pH and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 2A electrical current

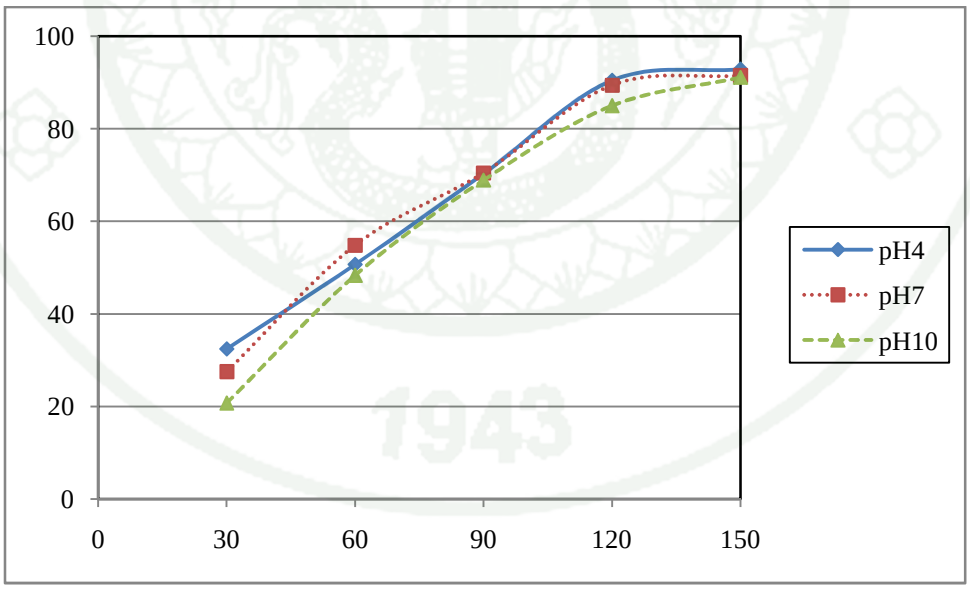

Figure 24 Colour removal percentage (ADMI Unit) achieved at various pH and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration at 2A electrical current

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Figure 25 Effect of pH on colour removal at 30 – 150 min retention time

2.4 Effect of electrical current

In this step, various electrical current was brought into consideration. The experiment was conducted at pH 4 with initial COD of 1,000mg/L, various electrical current of 0.8, 2, 4, 6 and 8A. The result obtained from varying electrical current is as shown in Figure 26 – Figure 30. It was found that increase in electrical current led to the increase in COD, TOC, SS and colour removal.

Colour removal was very low at 0.8A (6.23% – 45.16% at 30-150 min retention time), with and increasing electrical current , the colour removal (Pt-Co Unit) was considerably enhance, 26.23%-93.25%, 34.43% – 95.13%, 62.73% - 96.58% and 57.77% - 83.49% at 30-150 min retention time with electrical current 0.8, 2, 4, 6, and 8A respectively. This agreed with previous study of Piya-areetham *et al*. (2006) which found that colour and COD removal in distillery wastewater increased from 30% and 25% at 1A to 61% and 52% with 9A respectively within 360 min retention time.

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Only for COD that increasing in electrical current to higher than 0.8A, higher COD removal could be achieved, but only a slight difference could be observed among the various conditions.

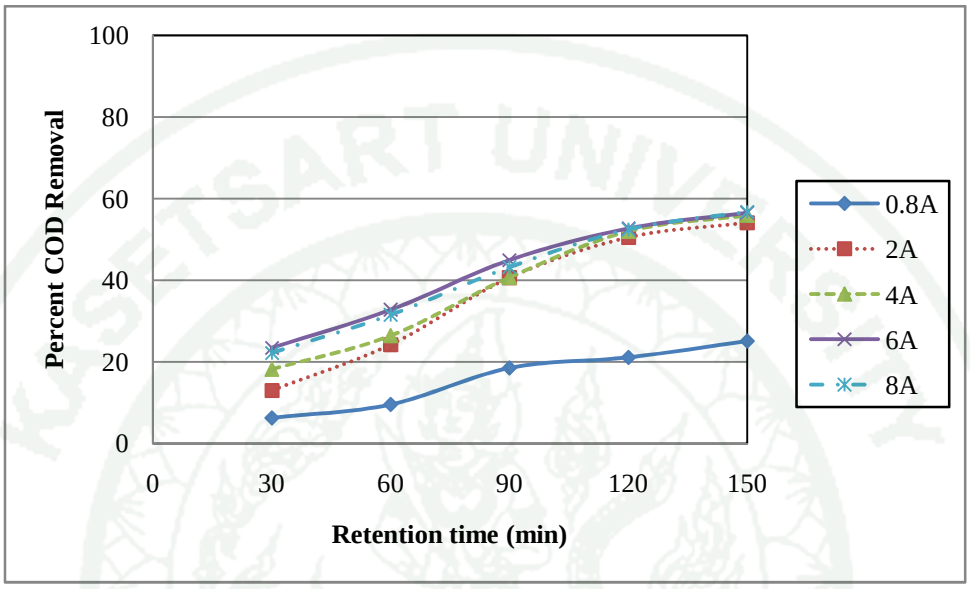

Figure 26 CODremoval percentage achieved at various electrical current and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration

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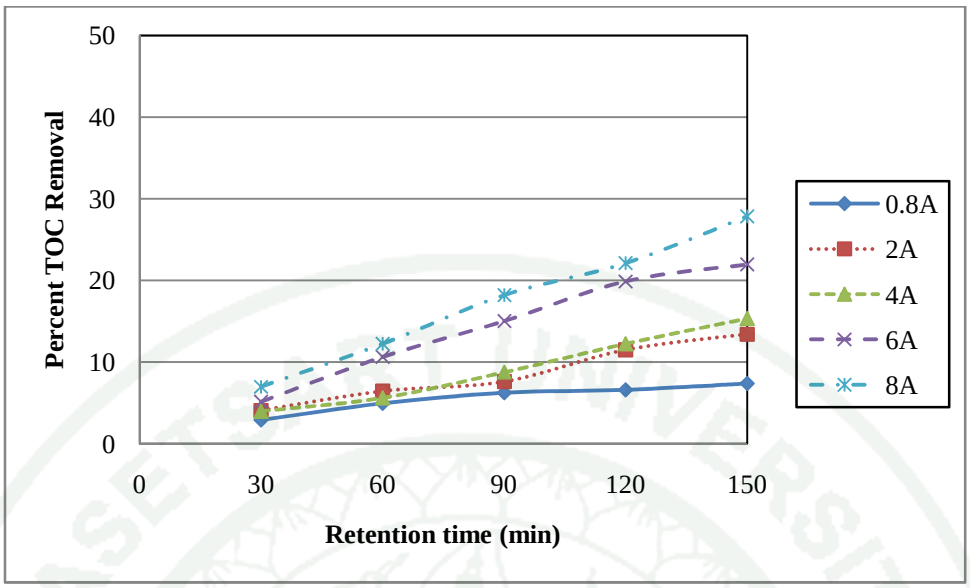

Figure 27 TOC removal percentage achieved at various electrical current and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration

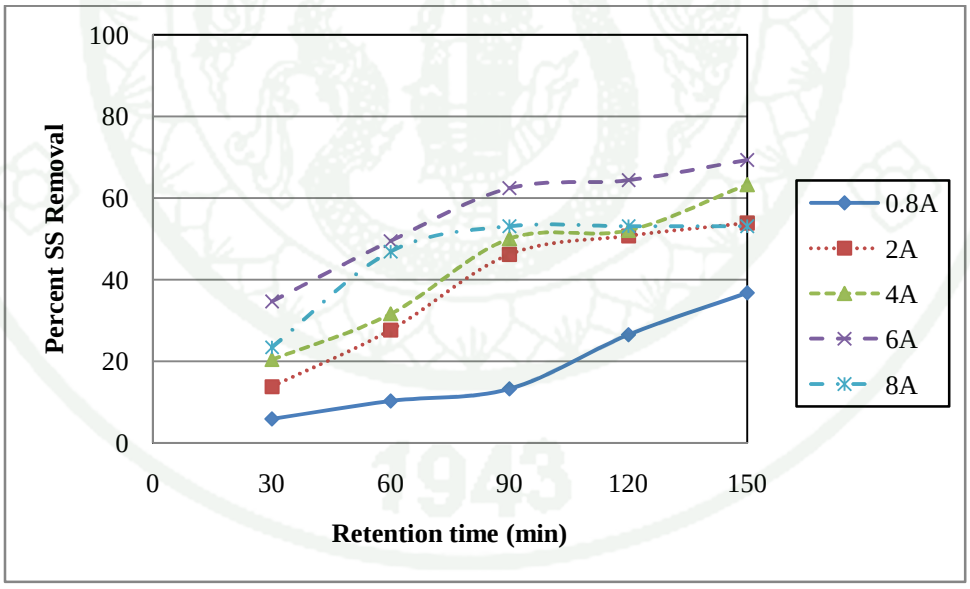

Figure 28 SS removal percentage achieved at various electrical current and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration

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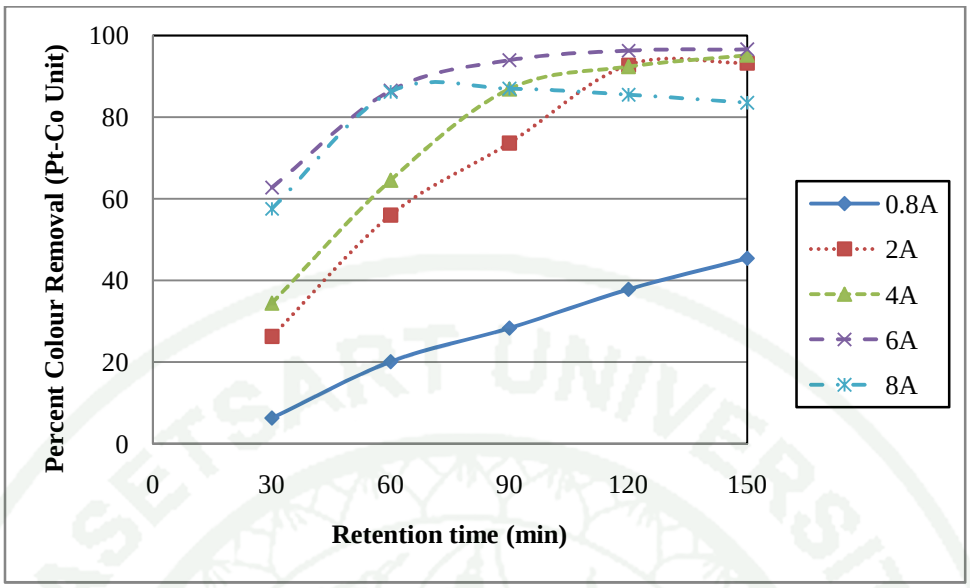

Figure 29 Colour removal percentage (Pt-Co Unit) achieved at various electrical current and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration

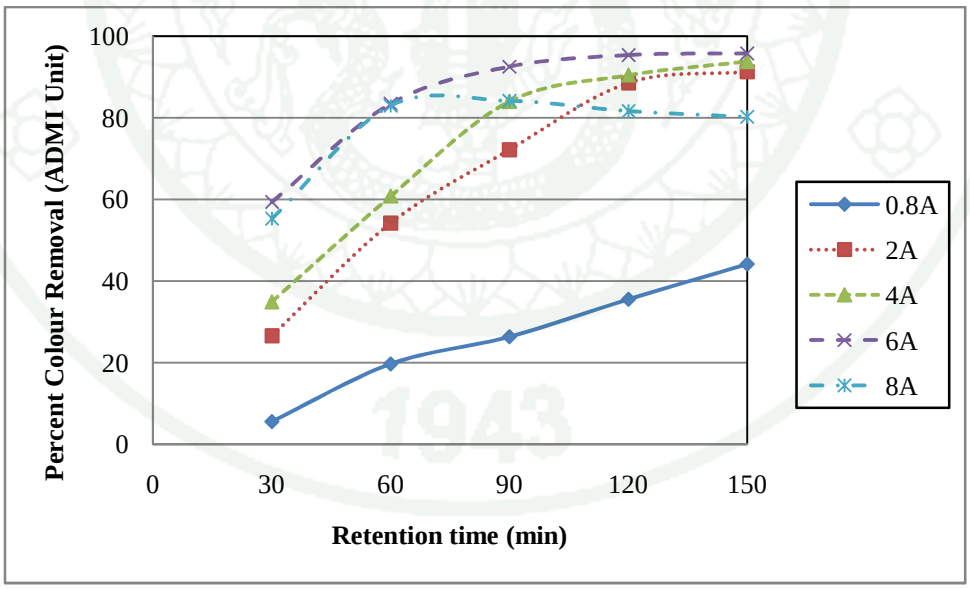

Figure 30 Colour removal percentage (ADMI Unit) achieved at various electrical current and time by electrooxidation with initial pH 4, 1000 mg/L COD concentration

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It was noticed that at the electrical current 8A after 90 min retention time, the colour removal percentage had decrease from 86.95% at 90 min retention time to 83.49% at 150 retention time as can be seen in Figure 31.

Figure 31 Colour removal at different retention time with 8A electrical current

2.5 Effect of electrooxidation on total organic compounds

While COD is a surrogate parameter indicating amount of organic compound, TOC is the amount of organically bound carbon. The reduction of TOC results from the loss of carbon complete oxidation. Figure 32 – Figure 36 shows the reduction percentage of COD and TOC during oxidation process at different electrical condition. COD and TOC reduction followed the same trend, increased with increase in retention time. However, COD removal was much higher than TOC removal. At 150 min retention time, COD removal were 25.06%, 54.13%, 55.88%, 56.51% and 56.80% while TOC removal were 7.35%, 13.41%, 15.32%, 21.94% and 27.83% at 0.8, 2, 4, 6 and 8A respectively. This indicated that the organic matter was partially oxidized to other organic forms.

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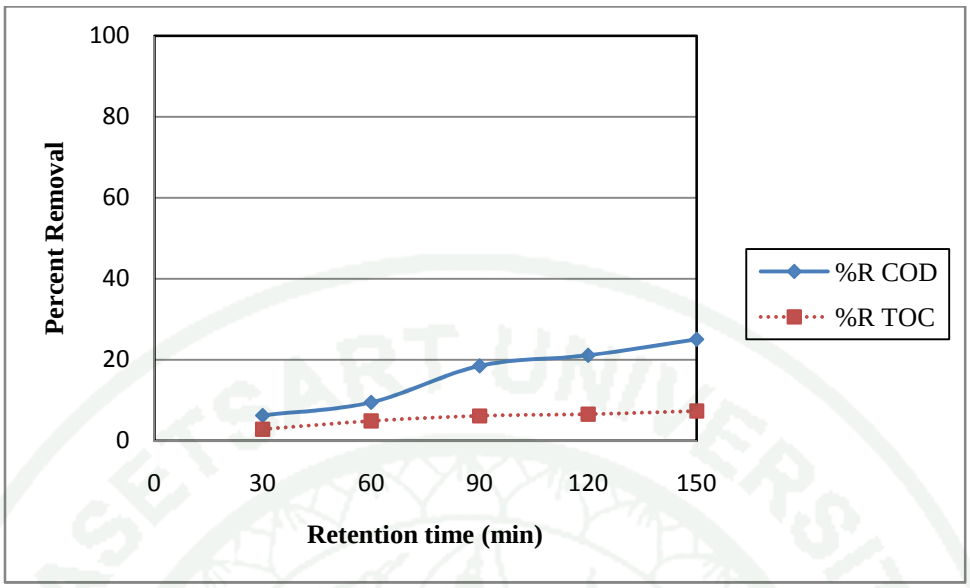

Figure 32 Comparison of COD and TOC removal of initial COD concentration of 1,000 mg/L, pH of 4 with 0.8 A electrical current at various time

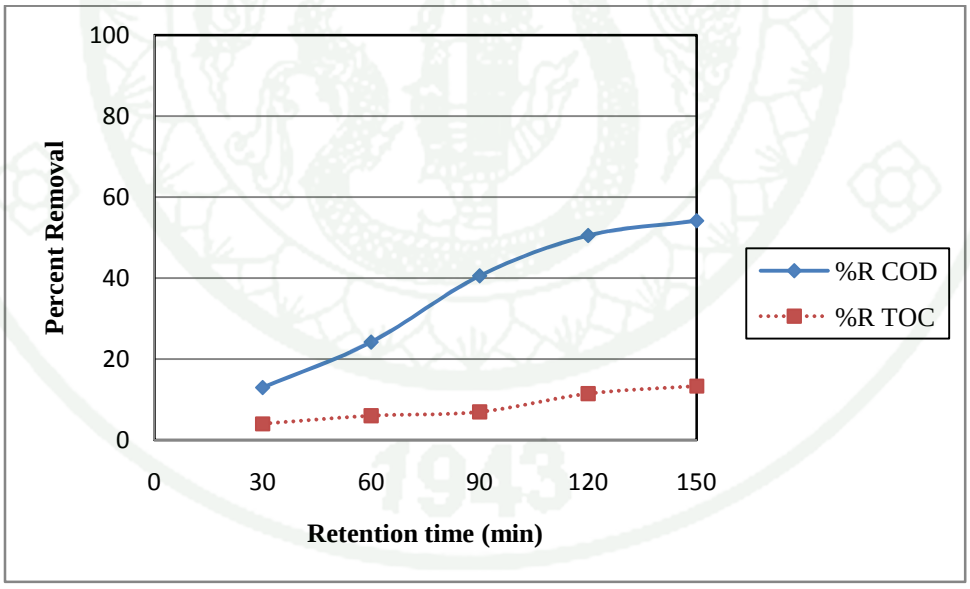

Figure 33 Comparison of COD and TOC removal of initial COD concentration of 1,000 mg/L, pH of 4 with 2A electrical current at various time

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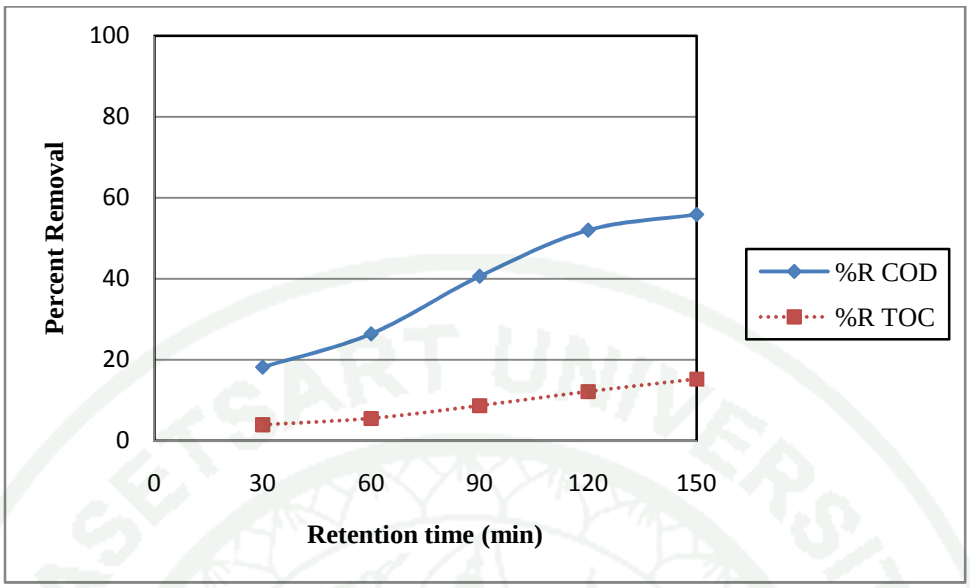

Figure 34 Comparison of COD and TOC removal of initial COD concentration of 1,000 mg/L, pH of 4 with 4A electrical current at various time

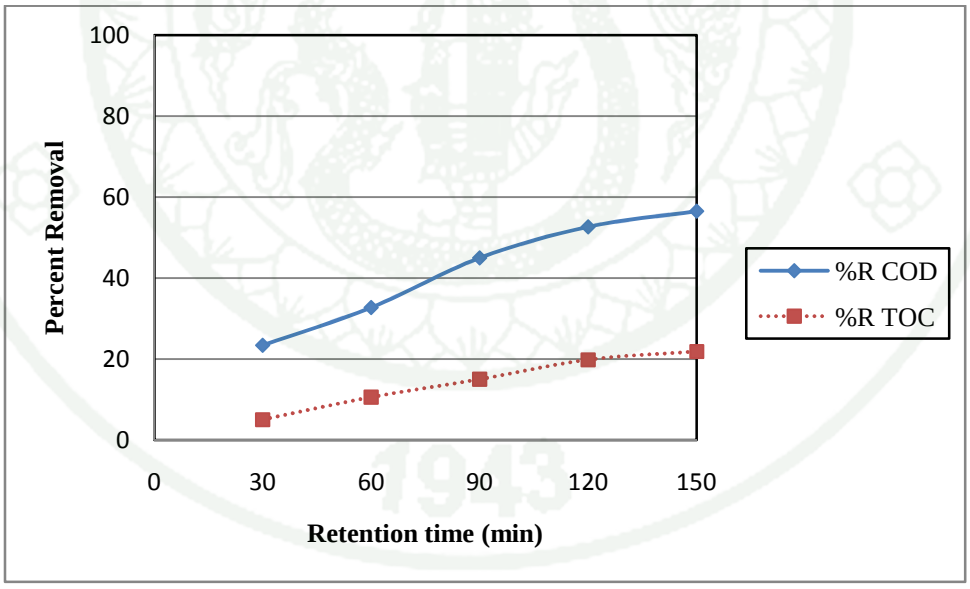

Figure 35 Comparison of COD and TOC removal of initial COD concentration of 1,000 mg/L, pH of 4 with 6A electrical current at various time

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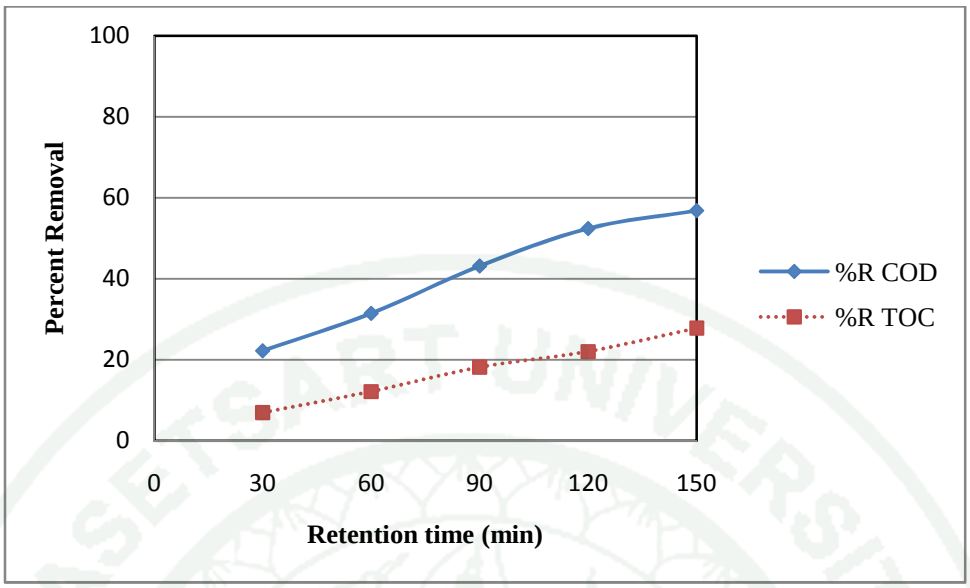

Figure 36 Comparison of COD and TOC removal of initial COD concentration of 1,000 mg/L, pH of 4 with 8A electrical current at various time

The TOC concentration is decrease during the course of electrolysis time as shown in the Figure 37. It was notice that when TOC concentration is reduce, increasing in IC concentration value as shown in the Figure 38. This confirmed that organic compound was change to inorganic compound oxidized to other inorganic form.

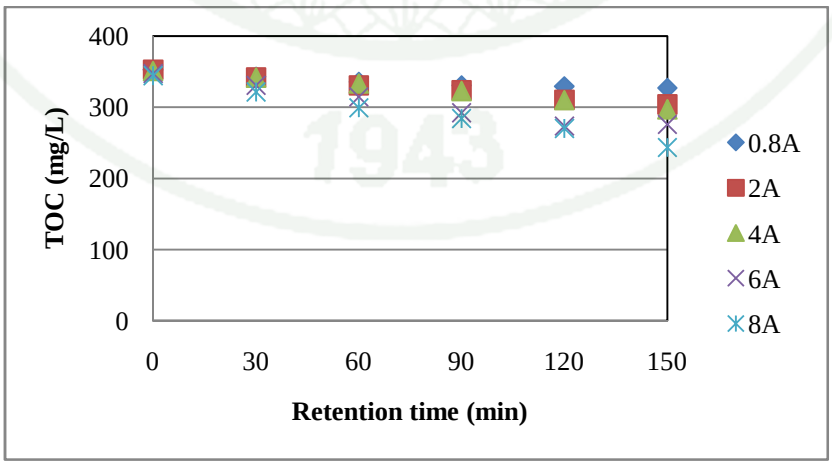

Figure 37 TOC concentration at the different electrical current with initial COD concentration of 1,000 mg/L, pH of 4 at various time

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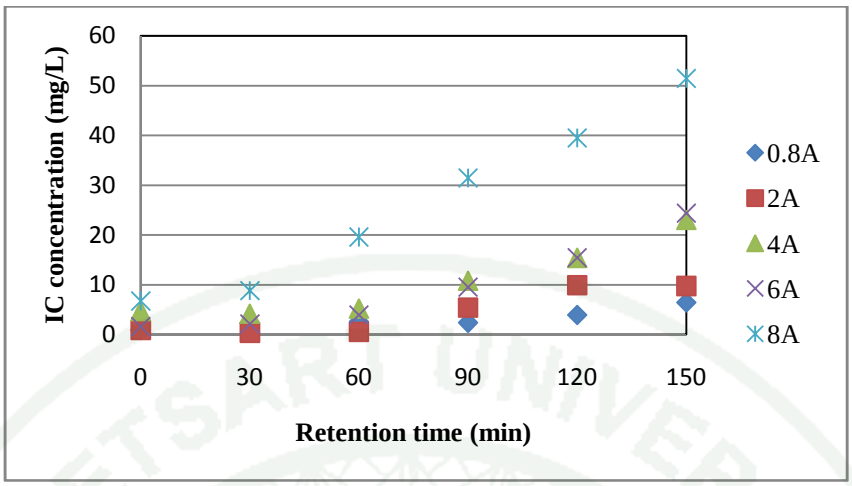

Figure 38 IC concentration at the different electrical current with initial COD concentration of 1,000 mg/L, pH of 4 at various time

CONCLUSION AND RECOMMENDATION

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Conclusion

This study examined the treatment of distillery wastewater using electro oxidation with graphite anode. From the experiment results and discussion of this study, the following conclusions can be drawn.

Presence of NaCl as supporting electrolyte enhanced electrooxidation of distillery wastewater. Very low removal could be achieved without NaCl. Increase in NaCl concentration resulted in increase in removal percentage. COD removal of 56.56% and colour removal (Pt-Co Unit) of 96.47% could be achieved with 10g/L NaCl at 6A.

No significant different in removal percentage with pH variation. The best condition in this study was at pH 4 which is the condition close to pH of raw wastewater.

Increase in electrical current resulted in increase in COD, TOC reduction. At pH 4 with 10g NaCl/L, after 150min retention time, the lowest removals of 45.37% Colour, 25.06% COD and 7.35% TOC at 0.8A with, increased to 96.58% Color, 56.51% COD and 21.94%T OC at 8A.

Recommendation

Detailed cost estimation for oxidation of distillery wastewater should be conducted in the future, and a comparison of this cost should be done with alternative technologies.

LITTERATURE CITED

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APHA, AWWA and WEF. 2000. **Standard Methods for the Examination of Water and Wastewater.** 20th ed., APHA, Washington DC.

Aquino, S., A.R. de Andrade. 2009. Electrooxidation of glyphosate herbicide at different DSA composition pH, concentration and supporting electrolyte effect. **Electrochimica Acta** 54: 2039-2045.

Ata, M., A. Mokhtar and M.M. Niyaz. 2009. Decolourization and aromatic ring degradation of colored textile wastewater using indirect electrochemical oxidation method. **Desalination** 249: 1047-1078.

Bhaskar, G., M. Thalamadai, S.S. Latha, D. Latha, S. Parvathy and S. Prabhakar. 2009. Electrochemical pretreatment of textile effluents and effect of electrode materials on the removal of organics. **Desalination** 249: 167-174.

Cammerer, B., J. Valentina and W. Lothar. 2002. Carbohydrate structure as part of the melanoidin skeleton. **International Congress Series** 1245: 269-273/

Canizares, P., M. Hernandez Ortega, M.A. Rodrigo, C.E. Barrera Ciaz, G. Roa Morales and C. Saez. 2009. A comparison between conductive diamond electrochemical oxidation and other advance oxidation process for the treatment of synthetic melanoidins. **J ournal of Hazardous Materials** 164: 120-125.

Cho, J.H., J.E. Lee and C.S. Ra. 2010. Effects of electric voltage and sodium chloride level on electrolysis of swine wastewater. **Journal of Hazardous Materials** 180: 535-541.

Deepak, P. and A. Alok. 2007. Biological approaches for treatment of distillery wastewater : A review. **Bioresource Technology** 98: 2321-2334.

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Fernandes, A., M.J. Pacheco, L. Ciriaco and A. Lopes. 2012. Anodic oxidation of a biologically treated leachate on a boron doped diamond anode. **Journal of Hazardous Materials** 199-200: 82-87.

Guido, S., S. Lisa, A. Riccardo, S. Vito and M. Mario. 2000. Electrochemical oxidation of organic pollutants at low electrolyte concentration. **Electrochimica Acta** 46: 373-380.

Inanc, B., F. Ciner and I. Ozturk. 1999. Colour removal from fermentation industry effluent. **Water SciTechnol** 40: 331-338.

Ivonne, L., B. Carlos, B. Bryan, G. Pablo and C. Eduardo. 2010. A combined electrocoagulation electrooxidation treatment for industrial wastewater. **Journal of Hazardous Materials** 175: 688-694.

Kitkaew, D. 2004. **Color removal from textile dye wastewater by electrochemical process**. M.S. Thesis, Mahidol University.

Luc, F., B. Pascal and D. Georges. 2006. Water wastewater and waste management in brewing industries. **Journal of Cleaner Production** 14: 463-471.

Martins, I.F.S., M.F. Wim., and A.J.S. Martinus. 2001. A review of Miallard reaction in food and implications to kinetic modeling. **Trends in Food Science & Technology** 11: 364-373

Manisankar, P., C. Rani and S. Viswanathan. 2004. Effect of halides in the electrochemical treatment of distillery effluent. **Chemosphere** 57: 961-966.

Masid, S., S. Waghmare, N. Gedam, R. Misra, R. Dhodapkar, T. Nandy and N.N. Rao. 2010. Impact of electrooxidation on combined physicochemical and membrane treatment processes: Treatment of high strength chemical industry wastewater**. Desalination** 259: 192-196.

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Metcalf and Eddy. 2003. **Wastewater Engineering.** 4th ed. McGraw-Hill, Inc., New York.

Miled, W., A. Haj Said and S. Roudesli. 2010. Decolorization of high polluted textile wastewater by indirect electrochemical oxidation process. **Journal of Textile and Apparel Technology and Management** 6: 1-6.

Migo, V.P., M. Matsumara, E.J.D. Rosaria and H. Kataoka. 1993. Decolourization of molasses wastewater using an inorganic flocculant. **J. Fermentation Bioeng** 75: 438-442.

Ojijo, V.O., M.S. Onyango, A. Ochieng and F.A.O. Otieno. 2010. Decolourization of melanoidin containing wastewater using South African coal fly ash. **International Journal of Civil Environmental Engineering** 2 (1): 17-23.

Onofrio, S., R. Serena, G. Alessandro and S. Giuseppe. 2009. Electrochemical oxidation of organic in water role of operative parameters in the absence and in the presence of NaCl. **Water Research** 43: 2260-2272.

Pala, A., G. Erden. 2005. Decolorization of a baker's yeast industry effluent by fenton's oxidation. **Journal of Hazardous Materials** 127: 141-148.

Pena, M., M. Coca, G. Gonzalez, R. Rioja and M.T. Garcia. 2003. Chemical oxidation of wastewater from molasses fermentation with ozone. **Chemosphere** 51: 839-900.

Pinisakul, A. 2002. **Application of electrochemical process for treatment of arsenic contaminated water**. Ph.D. Thesis, Asian Institute of Technology.

Piya, P., K. Shenchunthichai and M. Hunsom. 2006. Application of electrooxidation process for treating concentrated wastewater from distillery industry with a voluminous electrode. **Water Research** 40: 2857-2864.

Copyright by Kasetsart University All rights reserved

Pletcher, D. 1984. **Industrial Electrochemistry**. Chapman and Hall., London.

Radhika A., S. Lata, M. Gupta and P. Singh. 2010. Removal of melanoidin present in distillery effluent as a major colorant: A review. **Jounal of Environment Biology** 31: 521-528.

Ram, C., B. Ram and R. Vibhuti. 2008. Melanoidins as major colourant in sugarcane molasses based distillery effluent and its degradation. **Bioresource Technology** 99: 4648-4660.

Sarayu, M., K. Bhavik and M. Datta. 2009. Distillery spent wash: treatment technologies and potential applications. **Journal of Hazardous Materials** 163: 12-25.

Scheitzer, P.A. 1997. **Handbook of Separation Techniques of Chemical Engineers**. McGraw-Hill, New York.

Tassanaraphan, A. 2009. **Treatment of Distillery Wastewater by Electrocoagulation**. M.S. Thesis, Kasetsart University.

Yang, D., E.D. James. 2006. Electrochemical oxidation for landfill leachate treatment. **Waste Management** 27: 380-388.

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APPENDICES

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Appendix A

Removal percentage calculation

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1. COD removal percentage

$$\% \text{ COD removal} = \frac{(C_{t=0} - C_{t=t})}{C_{t=0}} \times 100\%$$

Where $C_{t=0}$ = Initial COD concentration (mg/L)

$C_{t=t}$ = COD concentration at oxidation time

2. TOC removal percentage

$$\% \text{ TOD removal} = \frac{(T_{t=0} - T_{t=t})}{T_{t=0}} \times 100\%$$

Where $T_{t=0}$ = Initial TOD concentration (mg/L)

$T_{t=t}$ = TOD concentration at oxidation time

3. SS removal percentage

$$\% \text{ SS removal} = \frac{(SS_{t=0} - SS_{t=t})}{SS_{t=0}} \times 100\%$$

Where $SS_{t=0}$ = Initial SS concentration (mg/L)

$SS_{t=t}$ = SS concentration at oxidation time

4. Colour removal percentage

$$\% \text{ colour removal} = \frac{(\text{Colour}_{t=0} - \text{Colour}_{t=t})}{\text{Colour}_{t=0}} \times 100\%$$

Where $\text{Colour}_{t=0}$ = Initial colour concentration

$\text{Colour}_{t=t}$ = Colour concentration at oxidation time

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Appendix B

Effect of supporting electrolyte

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Appendix Table B1 COD, TOC,SS and Colourpercentremoval without adding NaCl at 1,000 mg/L COD initial concentration with 2A electrical current

Retention time (min)/Parameter	Percent Removal				
	1	2	3	Mean	SD
COD					
30	3.57	3.33	4.45	3.78	0.48
60	9.52	10.00	11.11	10.21	0.67
90	11.90	12.22	12.22	12.12	0.15
120	13.10	13.33	13.33	13.25	0.11
TOC					
30	0.11	0.28	0.18	0.19	0.07
60	1.11	1.12	1.35	1.20	0.11
90	1.43	1.40	1.36	1.40	0.03
120	1.62	1.71	1.55	1.63	0.07
SS					
30	0.00	2.00	0.00	0.67	0.94
60	6.52	6.00	6.12	6.21	0.22
90	10.87	12.00	12.24	11.70	0.60
120	13.04	12.00	12.24	12.43	0.45
Colour (Pt-Co Unit)					
30	3.62	3.50	3.70	3.61	0.08
60	6.43	6.23	6.06	6.24	0.15
90	6.64	6.71	6.51	6.62	0.08
120	8.91	8.96	9.30	9.06	0.17

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Appendix Table B2 COD, TOC,SS and Colour percent removalwith NaCl 10g/L at 1,000 mg/L COD initial concentration with 2A electrical current

Retention time (min)/Parameter	Percent Removal				
	1	2	3	Mean	SD
COD					
30	11.90	11.11	12.22	11.75	0.47
60	16.67	13.33	16.67	15.56	1.57
90	41.67	40.00	40.00	40.56	0.79
120	45.24	45.56	46.67	45.82	0.61
TOC					
30	4.22	3.75	4.18	4.05	0.21
60	5.93	6.03	6.00	5.99	0.04
90	7.15	7.26	7.06	7.16	0.08
120	10.32	9.79	9.88	10.00	0.23
SS					
30	10.91	10.20	10.00	10.37	0.39
60	29.09	28.57	30.00	29.22	0.59
90	41.82	42.86	42.00	42.23	0.45
120	45.45	46.94	48.00	46.80	1.04
Colour (Pt-Co Unit)					
30	28.13	27.93	29.32	28.46	0.61
60	55.84	54.76	55.24	55.28	0.44
90	67.47	69.67	68.75	68.63	0.90
120	92.00	93.03	91.69	92.24	0.57

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Appendix C

Effect of pH on electro oxidation process

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Appendix Table C1 COD, TOC,SS and Colour percent removal at various pH with NaCl 10g/L at 1,000 mg/L COD initial concentration with 2A electrical current

Retention	**Percent Removal (Mean value)**				
time(min)/pH	**COD**	**SS**	**TOC**	**Pt-Co**	**ADMI**
pH 4					
30	12.27	10.49	5.14	32.39	32.40
60	20.01	30.82	6.21	55.92	50.68
90	46.14	41.46	7.35	72.81	70.25
120	53.83	46.39	10.90	92.93	90.41
150	54.56	50.26	11.52	95.18	92.85
pH 7					
30	10.16	10.01	3.51	24.52	27.50
60	14.24	30.49	6.19	55.84	54.85
90	40.61	43.28	7.01	72.89	70.47
120	43.39	48.25	10.34	91.60	89.43
150	47.79	50.3876	11.19	93.98	91.48

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Appendix Table C1 (Continued)

Retention time(min)/pH	Percent Removal				
	COD	SS	TOC	Pt-Co Unit	ADMI unit
pH 10					
30	9.30	10.01	1.49	22.31	20.74
60	13.56	31.58	5.16	49.59	48.31
90	39.31	43.05	6.87	70.87	68.89
120	42.78	47.62	9.67	87.84	84.95
150	45.89	50.83	11.13	92.82	91.07

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Appendix D

Effect of electrical current on oxidation process

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Appendix Table D1 COD, TOC, SS and Colour percent reduction at different electrical current (initial pH 4 and 1,000 mg/L of initial COD concentration)

Retention time/ parameter	**Percent removal**				
	0.8V	**2A**	**4A**	**6A**	**8A**
COD					
30	6.27	13.03	18.17	23.46	22.20
60	9.55	24.24	26.43	32.74	31.50
90	18.53	40.60	40.68	44.96	43.20
120	21.12	50.50	51.98	52.66	52.44
150	25.06	54.13	55.88	56.51	56.80
TOC					
30	2.89	4.10	3.95	5.13	6.99
60	4.95	6.05	5.60	10.60	12.23
90	6.24	6.98	8.75	15.01	18.18
120	6.59	11.48	12.23	19.90	22.10
150	7.35	13.41	15.32	21.94	27.83

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Appendix Table D1 (Continued)

Retention time/ parameter	Percent removal				
	0.8V	**2A**	**4A**	**6A**	**8A**
SS					
30	5.88	13.83	20.41	34.65	23.46
60	10.29	27.70	31.63	49.50	46.91
90	13.24	46.16	50.00	62.38	53.09
120	26.47	50.76	52.04	64.36	53.09
150	36.76	53.84	63.27	69.31	53.09
Colour (Pt-Co)					
30	6.26	26.23	34.43	62.73	57.57
60	20.06	55.97	64.49	86.49	86.16
90	28.34	73.61	86.88	93.91	86.95
120	37.76	92.78	92.34	96.30	85.45
150	45.37	93.25	95.13	96.58	83.49
Colour (ADMI)					
30	6.23	26.18	34.43	62.90	57.77
60	19.97	56.39	64.49	86.64	86.16
90	27.19	73.21	86.88	93.96	87.09
120	37.59	92.77	92.34	96.26	85.06
150	45.16	94.12	95.13	96.62	83.24

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Appendix E

Effect of electrolyte concentration on electro oxidation process

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Appendix Table E1 COD, TOC, SS and Colour percent reduction at different supporting electrolyte concentration (initial pH 4 and 1,000 mg/L of initial COD concentration)

Retention time/parameter	**NaCl concentration**			
	1g/L	**5g/L**	**7g/L**	**10g/L**
COD				
30	8.89	9.42	10.49	23.79
60	20.01	20.63	21.59	34.00
90	34.45	35.16	36.57	45.53
120	47.87	46.74	46.93	52.89
150	54.14	55.07	55.62	56.56
TOC				
30	2.08	2.06	2.31	5.42
60	6.73	7.33	7.01	11.43
90	11.86	12.30	11.51	14.58
120	16.66	17.29	17.60	17.96
150	17.28	18.69	19.50	22.80

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Appendix Table E1 (Continued)

Retention time/parameter	NaCl concentration			
	1g/L	5g/L	7g/L	10g/L
SS				
30	16.30	18.48	19.79	33.94
60	34.27	35.68	37.10	49.32
90	49.16	50.29	54.30	62.81
120	57.18	59.59	61.59	64.74
150	59.12	61.59	64.18	69.24
Colour (Pt-Co Unit)				
30	26.68	30.19	30.78	61.86
60	60.14	61.86	62.43	86.37
90	69.51	74.69	70.69	91.71
120	74.77	78.03	80.20	94.39
150	74.47	78.98	90.81	96.47
Colour (ADMI Unit)				
30	25.81	25.88	29.90	59.09
60	57.89	57.98	60.40	83.63
90	67.28	66.89	67.31	92.05
120	71.81	71.09	80.74	94.30
150	71.25	72.03	85.53	95.21

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