

## UNIVERSITI TEKNOLOGI MALAYSIA

BORANG PENGESAHAN  
LAPORAN AKHIR PENYELIDIKAN

TAJUK PROJEK : WET AIR OXIDATION (WAO) TREATMENT OF WASTEWATER  
FROM PAINT INDUSTRIES

Saya DR MOHD ARIFFIN BIN ABU HASSAN  
(HURUF BESAR)

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**1. PROJECT TITLE IDENTIFICATION :**

Wet Air Oxidation (WAO) Treatment of Wastewater From Paint Industries

Vote No:

78121

**2. PROJECT LEADER :**

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**3. DIRECT OUTPUT OF PROJECT (Please tick where applicable)**

Scientific Research	Applied Research	Product/Process Development
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| <input type="checkbox"/> No publications pending           | <input type="checkbox"/> Inventor team player            |
| <input type="checkbox"/> No prior claims to the technology | <input type="checkbox"/> Industrial partner identified   |

**5. LIST OF EQUIPMENT BOUGHT USING THIS VOT**

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**6. STATEMENT OF ACCOUNT**

a)	APPROVED FUNDING	RM : 34,000.00
b)	TOTAL SPENDING	RM : 32,638.60
c)	BALANCE	RM : 1361.40

**7. TECHNICAL DESCRIPTION AND PERSPECTIVE**

*Please tick an executive summary of the new technology product, process, etc., describing how it works. Include brief analysis that compares it with competitive technology and signals the one that it may replace. Identify potential technology user group and the strategic means for exploitation.*

a) Technology Description

The application of Wet Air Oxidation (WAO) for the destruction of organic pollutants in wastewater from paint industries has recently drawn much attention. Wet Air Oxidation (WAO) is one of the processes that have been used widely for wastewater treatment. Wet Air Oxidation (WAO) improved the overall efficiency of treating wastewater from paint industries (i.e TOC and COD) due to higher production of hydroxyl radicals.

b) Market Potential

Wet Air Oxidation (WAO) treatment of wastewater from paint industries is one of the promising alternative treatment methods that need to be explored. It is hoped that further research can be done for other type of wastewater as well as industrial sludge that is subjected to incineration process..

c) Commercialisation Strategies

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8. RESEARCH PERFORMANCE EVALUATION

a) FACULTY RESEARCH COORDINATOR

Research Status	( )	<input checked="" type="checkbox"/>	( )	( )	( )	( )
Spending	( )	<input checked="" type="checkbox"/>	( )	( )	( )	( )
Overall Status	( )	<input checked="" type="checkbox"/>	( )	( )	( )	( )
	Excellent	Very Good	Good	Satisfactory	Fair	Weak

Comment/Recommendations :

another  
 Proceed with e-science or FRGS  
 funds. Try other advanced technology  
 for better application of technology

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b) RMC EVALUATION

Research Status	( )	( )	( )	( )	( )	( )
Spending	( )	( )	( )	( )	( )	( )
Overall Status	( )	( )	( )	( )	( )	( )
	Excellent	Very Good	Good	Satisfactory	Fair	Weak

Comments :-

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Recommendations :

- Needs further research
- Patent application recommended
- Market without patent
- No tangible product. Report to be filed as reference

.....  
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Date : .....

## **ACKNOWLEDGEMENT**

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## **WET AIR OXIDATION (WAO) TREATMENT OF WASTEWATER FROM PAINT INDUSTRIES**

*(Keywords: textile industries, , WAO, COD, TOC)*

This research details an investigation of the Wet Air Oxidation (WAO) of wastewater from textile industries in order to develop a method for treating these wastewaters. The objective of this WAO treatment is to produce an effluent that is more aerobically biodegradable than the initial textile wastewater. WAO experiments were conducted on textile wastewaters, quantifying the effect on increasing the WAO temperature (180 – 220°C) for two hours at oxygen pressure of 20 bars. It was found that a greater WAO temperature significantly increased the Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) removals and turbidity reduction. A higher temperature gives a greater removal of TOC, COD and turbidity during the WAO of textile wastewater. For instance, WAO resulted in almost 63%, 75% and 85% TOC removals after 120 min of oxidation at 180°C, 200°C and 220°C respectively, 65%, 75% and 89% COD removals at 180°C, 200°C and 220°C respectively and 72%, 80% and 94% turbidity reductions were achieved after 120 min of oxidation at 180°C, 200°C and 220°C respectively. Additionally TOC and COD were not completely destroyed at the conditions studied, indicating that there were organics that are refractory to further oxidation. Thus, there is always proportionally more residual TOC than COD, indicating that there was more partial oxidation (to residual organics) than total oxidation to CO<sub>2</sub>.

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## **PENGOKSIDAAN SECARA UDARA LEMBAP (WAO) BAGI RAWATAN SISA AIR DARI INDUSTRI CAT**

*(Katakunci: industri tekstil, WAO, COD, TOC)*

Penyelidikan ini adalah untuk mengenalpasti keberkesanan proses pengoksidaan secara udara lembap (WAO) bagi rawatan sisa air dari industri tekstil di dalam membangunkan kaedah rawatan sisa air sebegini. Objektif rawatan WAO adalah untuk menghasilkan efluen yang biodegradasi secara aerobic berbanding sisa air tekstil sebelum dirawat. Eksperimen WAO terhadap sisa air tekstil telah dijalankan untuk mengetahui kesan secara kuantitatif apabila suhu rawatan ditingkatkan (180 - 220°C) selama dua jam dan tekanan oksigen pada 20 bar. Hasil kajian menunjukkan bahawa dengan peningkatan suhu akan meningkatkan penyingkiran TOC, COD dan juga menurunkan kekeruhan sisa air. Suhu yang lebih tinggi meningkatkan penyingkiran TOC, COD dan juga pengurangan kekeruhan sisa air selepas rawatan WAO. Sebagai contoh, WAO memberikan sebanyak penyingkiran TOC sebanyak 63%, 75% and 85% selepas dua jam rawatan pada suhu 180°C, 200°C and 220°C masing-masing, penyingkiran COD sebanyak 65%, 75% and 89% pada 180°C, 200°C and 220°C masing-masing dan pengurangan kekeruhan sebanyak 72%, 80% and 94% diperolehi selepas dua jam rawatan WAO pada 180°C, 200°C and 220°C masing-masing. Tambahan lagi penyingkiran TOC and COD tidak berlaku sepenuhnya pada keadaan penyelidikan, menunjukkan bahawa masih terdapat lagi bahan organik yang tegar untuk melalui proses pengoksidaan seterusnya. Dengan itu, secara perkadarannya, baki TOC melebihi COD, menunjukkan bahawa pengoksidaan separa (terhadap baki organik) berbanding pengoksidaan sepenuhnya menghasilkan CO<sub>2</sub>.

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## NOMENCLATURE

WAO	Wet Air Oxidation
$\cdot\text{OH}$	Hydroxyl radical
$^{\circ}\text{C}$	Temperature
TOC	Total organic carbon
COD	Chemical Oxygen Demand

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Research

Paint industrial sector is one of the most important industrial sectors of Malaysia. Environmental problems of the paint industry are mainly caused by discharges of wastewater. Paint processing employs a variety of chemicals, depending on the nature of the raw material and product. Some of these chemicals are different enzymes, detergents, dyes, acids, sodas and salts. Industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to acceptable levels that have been set by the Department of Environment (DOE) before discharging them into environment.

In recent years Wet Air Oxidation (WAO) is an emerging technology for treating wastewater containing organic pollutants that may not readily biodegradable. WAO is an alternative attractive treatment for waste streams which are too dilute to incinerate and too concentrate for biological treatment (Mantzavinos et al. 2000). Considerable attention has also been given to the WAO for paint industry. Our previous work has also shown that WAO treatment can be employed effectively for the degradation of detergents (Abu-Hassan et al. 2003).

## **1.2 Problem statement**

In this study, the effect of the WAO treatment of wastewater from paint industries will be discussed. WAO is one of the processes that have been used widely for wastewater treatment. Paint wastewater from a company in Kulai, Johor will be used as the wastewater sample.

## **1.3 Objective of Study**

The aim of this research is to study the treatment of wastewaters from paint industries, by means of Wet Air Oxidation. The objectives of this project are: (1) To study the effectiveness of WAO treatment for paint wastewater (in terms of turbidity, TOC and COD). (2) To investigate the WAO of LAS with respect to the impact of various operating conditions (temperature and reaction time) on the overall degradation (in terms of TOC and COD).

## **1.4 Scope of Study**

Experiments were carried out at temperatures from 180°C to 220°C, and an oxygen pressure of 20 bars was maintained for all the experiments. For those experiments in which relatively small liquid volumes were required for further analysis (e.g. for turbidity, TOC and COD measurements), 100-200 mL were withdrawn after 30, 60 and 90 minutes oxidation. For those experiments in which a final (after 120 min oxidation) liquid sample was needed, the reaction vessel contents were collected at the end of each run.

## **CHAPTER 2**

### **LITERATURE**

#### **2.1 History of Wet Air Oxidation (WAO)**

More than 40 years ago, Zimmermann (Zimmermann 1954) was looking for an alternative method to treat special black liquors from papermills. In view of their very high silica content, the usual evaporation and combustion method (Kraft process) was unsuitable. Zimmermann found he could burn pulpmill liquors, and described a method using air at high pressure leading to the combustion of organic compounds at relatively low temperatures, as long as oxygen was present.

Wet air oxidation (WAO) was beginning to take off. Zimmermann added that this new method was quite similar to incineration as the organic residues were mainly burned to carbon dioxide, nitrogen (ammonia or molecular) and to ashes, together with a limited amount of acetic and traces of carbon monoxide. When the temperature was about 300°C, the organic matter removal efficiency exceeded 95% and enabled the mineral fraction of the oxidised liquor to be recycled. Due to the vapour pressure of water (86 bar at 300°C) and because of nitrogen from the air, the total pressure figure came to 175 bar, and therefore WAO was obviously an important feature to consider.



### **2.1.1 The Wet Air Oxidation Process**

Wet air oxidation can be defined as the oxidation of organic and inorganic substances in an aqueous solution by means of oxygen or air at elevated temperatures and pressures. Typical conditions for WAO range from 440 K and 2 MPa to 600 K and 14 MPa (Luck et al. 1995). WAO is an alternative attractive treatment for waste streams which are too dilute to incinerate and too concentrated for biological treatment (Donlagic and Levec 1998). High temperature conditions convert the organic matter to carbon dioxide. The liquid phase is maintained by a high pressure, which also increases the concentration of dissolved oxygen (Debellefontaine and Foussard 2000) and thus the oxidation rate. Although WAO technology has shown its great potential for treating different varieties of waste streams containing pollutants, this is usually an expensive process when used to achieve complete oxidation of all organic materials present to carbon dioxide (Wilhelmi and Knopp 1979).

#### **2.1.1.1 Process Description**

Figure 2.1 depicts a typical WAO treatment system. The wastewater is brought to the system pressure, using a high pressure pump. The compressed wastewater then flows through a heat exchanger to raise the temperature of the wastewater. Air is added to the reactor using a compressor. The feed temperature is adjusted such that the exothermic heat of reaction raises the mixture temperature to the operating temperature (Mishra et al. 1995). The reactor effluents can be cooled by cooling water. Liquid and non-condensable gases are disengaged in a separating vessel. The gases can be treated further to reduce the concentration of the undesirable pollutants by incineration (Wilhelmi and Knopp 1979) or catalytic oxidation (Luck

1999). The liquid phase from the separating vessel can be treated either by a chemical or biological oxidative process.

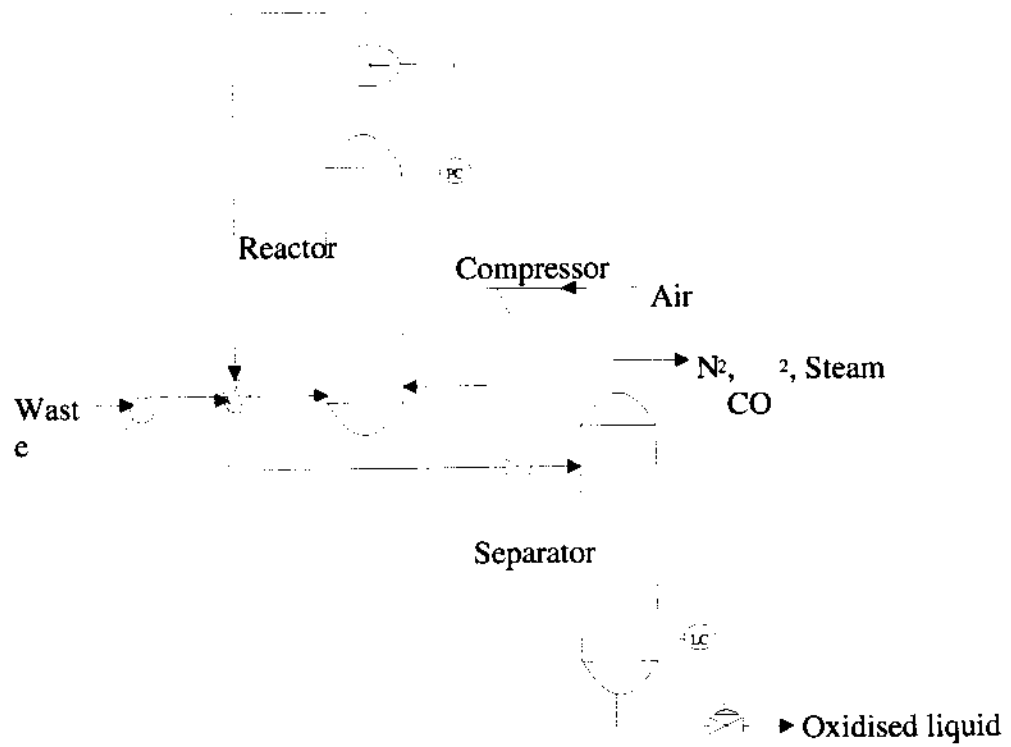


Figure 2.1. Basic WAO Process Flow Diagram

### **2.1.2 Advantages and Disadvantages of WAO**

A significant advantage of a WAO process is that WAO is capable of oxidising high-concentration organic compounds in the chemical wastewaters (Mishra et al. 1995). Furthermore, the oxidant (oxygen) for WAO processes is cheap compared to other advanced oxidation technologies, such as Fenton's Reagent (hydrogen peroxide) treatment. Additionally, a WAO process creates minimal air pollution problems since contaminants tend to stay in the aqueous phase. The small amount of gas that is discharged consists mainly of spent air or oxygen and carbon dioxide.

As mentioned earlier, typical operating pressures and temperatures of a WAO treatment process can easily exceed 100 MPa and 300°C respectively (Mishra et al. 1995). Due to its severe operating conditions, the WAO treatment process does have several inherent disadvantages. Maintaining the WAO treatment process at these operating conditions is energy consuming, implying that it is a relatively costly process in comparison with other conventional wastewater treatment methods (Lin and Ho 1996). Additionally, severe temperature and pressure are also employed, requiring expensive reactors (Baillod et al. 1985). Therefore, from a practical standpoint, it is highly desirable to operate the WAO treatment process at a sufficiently lower temperature which still enables good oxidation efficiency of the WAO process.

## **2.2 Paint Wastewater**

The main environmental problems of the paint manufacturing plants are generation of wastewater, air emission and solid waste. Wastewater generation contains both process and domestic wastewater. Paint industries wastewater is generated due to washing of process vessels from water-based paint manufacturing,

water-based resin manufacturing, and solvent-based resin manufacturing areas. However, at some paint industries wastewater is also generated from laboratory due to washing of utensils and from precipitation tanks of pigment manufacturing.

Table 2.1 below shows the source and type of process wastewater from paint industry. Equipment cleaning wastes make up 80% of the waste generated in paint manufacture (EPA, 1999).

**Table 2.1 : Source and Type of Process Wastewater from Paint (EPA, 1999)**

Sources	Types of process wastewater
Water-based paint manufacturing area	Cleaning or washing water of process vessels water
Water-based resin manufacturing area	Washing of kettle and cooling water from condenser for reaction kettle
Solvent or oil-based resin manufacturing area	Sprinkling water (to cool down) from heated kettle
Lead chromate pigment manufacturing	Supernatant lead chromate after precipitation and filtration of pigment slurry

Wastewater from paint industry like water-based paint wastewater can be highly toxic to the environment as well. It harms fish, wildlife and contaminates the food chain if poured down a storm drain. It can also pollute groundwater if dumped onto the ground. Excessive paint pouring down the drain disrupts microbes and causes sewage treatment to be less effective (Gondal, 2007).

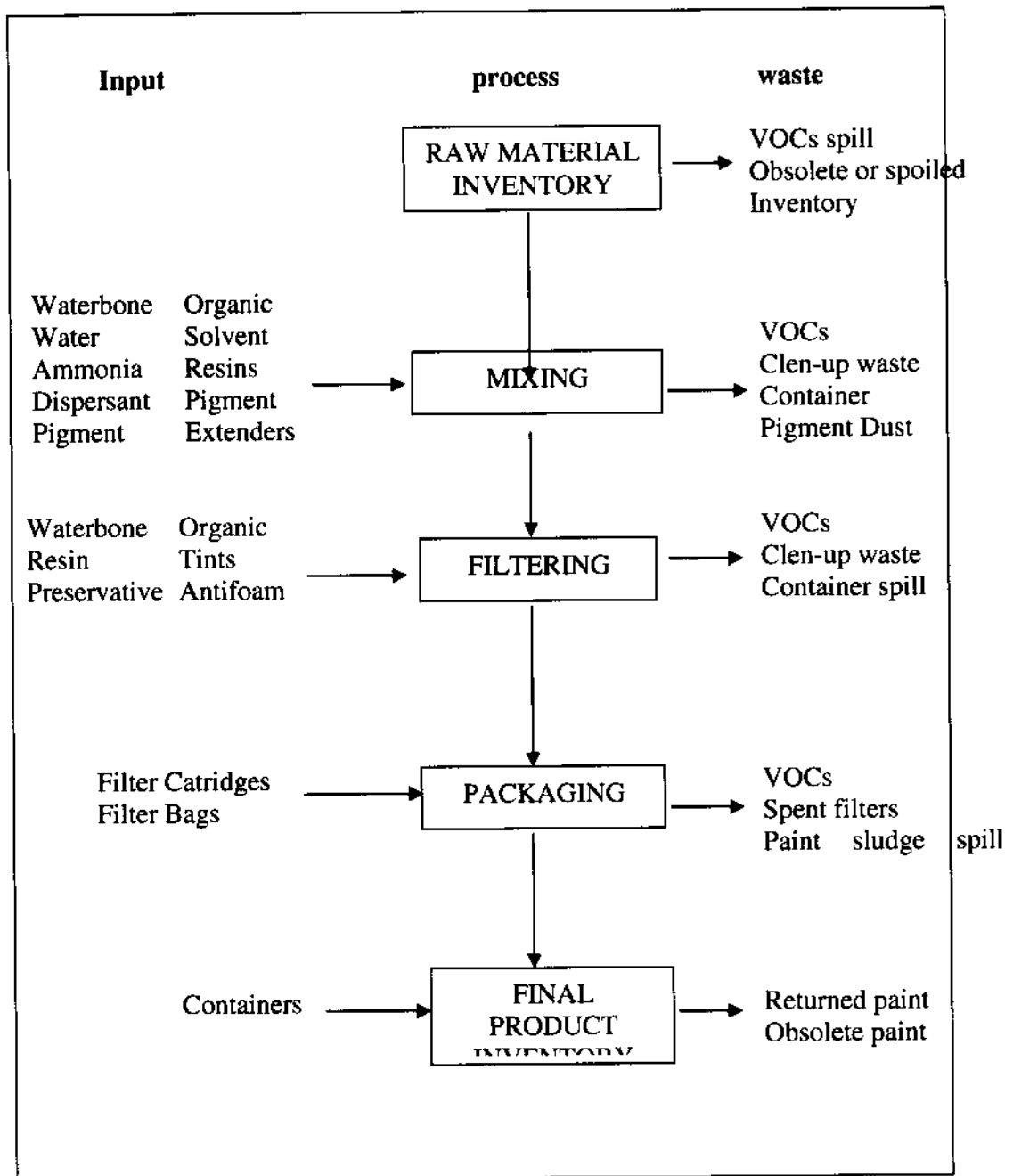
Paint has also adverse effects on human health occupant. If used in closed area, its chemical components can irritate eyes, skin and lungs and causes headaches and nausea. It can also contribute to respiratory problems, muscle weakness, liver and kidney damage. The other metals along with lead which are present in paint such as chromium

and cadmium also pose many health risks (Gondal, 2007). The wastewater must be treating appropriately before discharge to the environment to minimize the hazardous effects of paint on environment and human health.

### **2.2.1 Paint Manufacturing and Processing**

Manufacturing of solvent-based paint involves grinding and mixing of raw material. No chemical reaction takes place in this process. In the first step, raw materials are charged into ball-mill or attritors for dispersion. Usually ball-mill is used when it is required to reduce the particle size of certain raw materials. The attritor is used when simple dispersion is needed without reducing particle size. This is followed by refining machine to remove over size particles from the mixed materials. During these processes, quality is checked regularly by the laboratory to ascertain that the required dispersion has been achieved. In the second step this refined, dispersed material is diluted with solvent to the required viscosity. This is done in mixers. Dilution is controlled through laboratory testing. After final finishing the finished product is filled in the containers of desired sizes, which are ultimately sealed to avoid any loss of solvent (Dey, 1999).

After completion of each batch, usually equipment are washed and cleaned by using solvent and cotton rags. However sometime, new batches are charged without cleaning when the very next batch is of same color as previous batch or with lighter shade. If cleaning is carried out, cotton waste and used solvent is generated as waste (Dey, 1999). Figure 2.2 below shows the paint manufacturing process and waste generation source. There are five main processes including raw material inventory, mixing, filtering, packaging and final product inventory.



**Figure 2.2 : Paint Manufacturing Process and Waste Generation Source**  
(Flick, 1989)

Therefore, Figure 2.3 shows one of the typical paint manufacturing schematic. In this process, resins, solvents and pigment dispersion are mix in the mixing reactor.

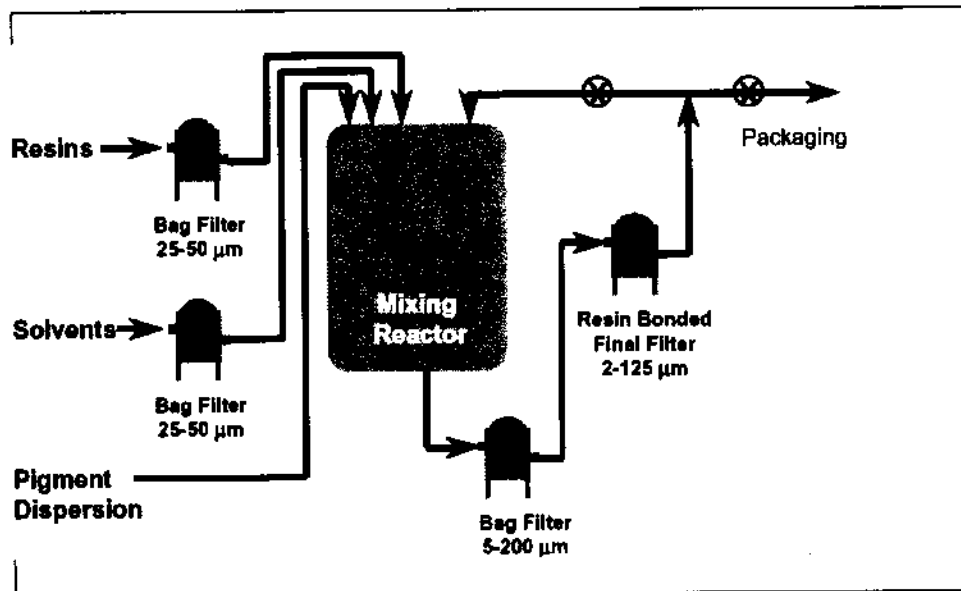


Figure 2.3 : Typical Paint Manufacturing Schematic (Dey, 1999)

### 2.2.2 Raw Material

The paint industry uses about 300 different types of raw materials for producing various kinds of paints. About 15 percent raw materials of the industry are petroleum-based (Flick, 1989). Paint is categorized in two broad classes namely water-based paint and solvent-based paint. The main difference between them is the medium which is either water or solvent. Other difference is of solubility of auxiliary chemicals which are added to give certain properties to the paint. Chemicals are soluble in water and not necessarily soluble in solvent.

Usually, the raw materials used at paint industries are pigments, resins, extenders, solvent, additives, water and filler. Raw materials such as resin, pigments, extenders and additives can be further classified as water soluble and those which are soluble in the solvent (Flick, 1989).

- i. Pigments are those compounds that impart color in the products. Hundreds of different pigments, both natural and synthetic are exists. The basic white pigment is titanium dioxide, selected for its excellent concealing properties and black pigment is commonly made from carbon black. Other pigments used to make paint include iron oxide and cadmium sulfide for reds, metallic salts for yellows and oranges. Iron blue and chrome yellows for blues and greens.
- ii. Resin to bond the paint into a protective skin. The natural resins most commonly used are lin-seed, coconut and soybean oil while alkyds, acrylics, epoxies and polyurethanes number among the most popular synthetic resins.
- iii. Solvent which keeps paint in liquid until applied or used it on material. Solvents are various low viscosities and volatile liquids. They include petroleum mineral spirits and aromatic solvents such as benzol, alcohols, esters, ketones and acetone.
- iv. Additives serve as everything from fillers to antifungicidal agents. Additives serve many purposes. For example, calcium carbonate and aluminum silicate are simply fillers that give the paint body and substance without changing its properties. Other additives produce certain desired characteristics in paint such as the thixotropic agents that give paint its smooth texture, driers, anti-settling agents, anti-skinning agents, defoamers and a host of others that enable paint to cover well.
- v. Extenders provide a consistency in the properties of the paint such as gloss.
- vi. Filler such as clay and chalk are used to provide body to the paint.



### 2.2.3 Paint Wastewater Characteristic

Wastewater characterization is essential to the design of a treatment process. The main source of process wastewater in any paint industry is the manufacturing plant of water-based paint (Jubete *et al.*, 2007). This plant is equipped with mixing machines including dispersers and kneaders. Wastewater is generated due to washing of these machines. Washing of machines depends highly on the colour of the paint which is being manufactured.

Paint industry wastewater is one of the major contributors for polluting the soil and water resources with the poisonous such as plumbum, cromium and cadmium. Effluent from paint wastewater finds an Absorbable Organic Halogen (AOX). Some of the organic halogen compounds are highly toxic, carcinogeric, bio-accumulative and persistent (Flick, 1989).

Level of pollution also varies from industry to industry, depending mainly on the types of process and the size of the industry. Table 2.2 shows the typical range environmental parameters based on the basis of the data collected during the three environmental audits. It is clear from the table that the levels of COD, BOD, TSS and Settleable Solids as pollutants are much higher than the prescribed NEQS. This is mainly due to the presence of inorganic pollutants.

**Table 2.2 : Characteristic of Effluent from Paint Industries (Dovletoglou *et al.*, 2002)**

Environmental Parameters	Measured Range in Paint Industries	NEQS standards		
		Into inland Water	Into sewage Treatment l	Into sea
pH	8 - 13	6 - 9	6 - 9	6 - 9
TDS (mg/L)	500 - 1100	3500	3500	3500
COD (mg/L)	6500 - 11500	150	400	400
BOD (mg/L)	100 - 500	80	250	200
TSS (mg/l)	2800 - 3800	200	400	200
Copper (mg/l)	1 - 35	1.0	1.0	1.0
Zinc (mg/l)	0.07 - 0.15	5.0	5.0	5.0

#### 2.2.4 Environmental Impact

Wastewater generated from most of the paint manufacturing industries is discharged into sewerage line outside the factory. The sewerage line usually ends up in water bodies ultimately leading to rivers or sea. Most paint industries wastewater is discharged without any treatment. This wastewater does not meet NEQS for COD, BOD, TSS, TDS, lead and chromium.

Gondal (2007) studied the determination of poisonous metals in wastewater collected from paint manufacturing plant using Laser-Induced Breakdown Spectroscopy (LIBS). The plasma was generated by focusing a pulsed Nd:YAG laser at 1064 nm on the solid residue from wastewater collected from paint industry. The concentration of different elements of environmental significance like lead, copper, chromium, calcium, sulphur, magnesium, zinc, titanium, strontium, nickel, silicone, iron, aluminum, barium, sodium, potassium and zirconium in paint wastewater were 6, 3, 4, 301, 72, 200, 20, 42, 4, 1, 35, 120, 133, 119, 173, 28 and 12 mg kg<sup>-1</sup>, respectively.

Impacts of wastewater generated from paint manufacturing industries are evaluated while keeping in mind the final destination. The study of Gondal (2007) about these impacts of pollutant wise are discussed below :

i. Organic pollutants

High COD causes depletion of dissolved oxygen in the water body. This deficiency of oxygen could cause adverse effects on aquatic environment. In the worst case this can result in the total depletion of oxygen in some places causing an anaerobic environment. This would be fatal to aerobic life. The depletion of oxygen at coastal areas may impact adversely on the growth of mangrove causing disturbance of a habitat especially for fishes. It is difficult to predict the extent but in the long run it may adversely affect the local fishing industry.

ii. Particulate and Sediments

Suspended solids present in wastewater are partially organic in nature. Upon settling in the bottom of water body, they decompose aerobically as well as an aerobically, depending on prevailing condition. Usually they first consume all the dissolved oxygen available and then start decomposing an aerobically. They clog the gills of fishes.

iii. Lead

As a heavy metal, lead in water bodies can enter into food chain. Lead may affect several organs of the human body including the nervous system, blood forming system, the kidney, cardiovascular and reproductive system. One of the major concerns is the adverse effect it has on the nervous system. Lead often causes irreversible damage by reducing intelligence causing attention deficit, hyperactivity and behavioural abnormalities.

iv. Chromium

The toxicity of chromium salts is variable for plant and animal life. Algae have been shown to be particularly sensitive. Although apparently of estuarine molluscs unaffected in their own metabolism, it is accumulate trivalent chromium also. Trivalent chromium has the potential of oxidation and conversion into highly toxic and carcinogenic hexavalent chromium.

v. Waste Solvent

Waste solvent is sold for down stream uses but it is feared that finally it ends up in the water or soil environment causing pollution.

vi. Total Dissolved Solids (TDS)

Dissolved solids are undesirable in receiving water. Dissolved minerals and organic constituents may produce aesthetically displeasing color, tastes and odor. Some chemicals may be toxic and some of the dissolved organic constituents have been proven to be carcinogenic.

### 2.3 Treatment Technologies for the Paint Wastewater

Wastewater from paint factories is a dangerous source of environmental contamination. Pollutants are characterized by high levels of chemical and biochemical oxygen demand, color, concentration of suspended solids and so on. Much researcher has been carried out to determine the most appropriate methods to solve the problem, with some successful applications in the real world nowadays.

(Dovletoglou *et al.*, 2002). There are several ways in which wastewater are treated. Alternatively, the wastewater is partially treated on site before it released to the sewage treatment work (Aris, 2004). There are three stages of wastewater treatment for paint industry basically like below ;

- i. Preliminary and Primary treatment, which removes percent to 60 percent of the solids.
- ii. Secondary treatment, which removes about 90% of pollutants and completes the process for the liquid portion of the liquid portion of the separated wastewater.
- iii. Sludge (biosolids) treatment and disposal.

### **2.3.1 Biological Treatment**

Biological treatment is an important means by which toxic or hazardous organic compounds can be economically converted to less noxious materials. Biological processes are type of oxidation processes which transform the contaminants to simpler and harmless form. Depending on oxygen consumption, they can be classified into aerobic (with oxygen) and anaerobic (without oxygen) processes (Brown and Weintraub, 1982).

Engineering studies conducted in the laboratory with activated sludge reactors and Rotating Biological Contactors (RBC) demonstrated that both suspended and attached growths can be effective biological methods to treat this paint stripping wastewater when blended with domestic wastewater up to about 50% by volume.

The different bacterial strains that were isolated in microbial analyses of US Navy aircraft paint stripping wastewater indicated that such wastewater is able to support bacterial populations as large as those found in the treatment of domestic wastewater. These large populations suggest high levels of bacterial activity in the paint stripping wastewater treatment systems (Brown and Weintraub, 1982).

Gotvajn and Koncan (2005) suggested that the bacterial community remained stable during the toxic shock and that bacteria able to biodegrade the wastes were present at all times in the population along with bacteria unable to biodegrade the wastes but not inhibited by them. The former bacteria were responsible for the reductions in the concentrations of the potentially toxic organic compounds.

### 2.3.2 Coagulation and Flocculation

In recent years, with the technological advancements in polymer chemistry and the increasing interest in nutrient control in addition to the rising construction and energy costs, substantial interest has developed in chemically enhanced wastewater treatment methods (Dovletoglou *et al.*, 2002).

Coagulation and flocculation has always attracted considerable attention for yielding high removal efficiency in wastewater treatment. This process can be directly applied to wastewaters to remove organics together with suspended solids without being affected by the toxicity in the wastewater. In addition, the main advantage of the conventional processes like coagulation and flocculation is the decolourization of the waste stream due to the removal of dye molecules from the effluents and not due to a partial decomposition of dyes which can lead to an even more potentially harmful and toxic aromatic compound (Dovletoglou *et al.*, 2002).

The coagulant iron chloride and the flocculants Polysep 3000 (natural cationic flocculant), Superfloc A-1820 (synthetic anionic polymer) and Praestol 2515 TR (anionic flocculant) have been used in this study to show the efficiency of coagulation and flocculation process in the chemical precipitation method for the removal of organic and colouring matters from the paint industry wastewater (El-Gohary *et al.*, 2002)

El-Gohary *et al.* (2002) study also includes the amount of produced sludge. The results indicate that  $\text{FeCl}_3$  is efficient at pH range 8 to 9 and at optimal dose of 650 mg/L. Iron chloride allows the removal of 82 percent of Chemical Oxygen Demand (COD) and 94 percent of colour. However, sequential addition of coagulant and polymeric additives enhance clearly pollutant removal and produces less decanted sludge compared to the results obtained when the coagulant is used alone. The removal efficiency of COD reaches 91 percent and that of colour 99 percent.

Coagulation and biflocculation process is more effective than the coagulation and monoflocculation one. The sequential addition of iron chloride, Polysep 3000 (cationic flocculant) and Praestol 2515 TR (anionic flocculant) seems to be the most suitable combination for the treatment of the paint industry wastewaters (El-Gohary *et al.*, 2002).

### 2.3.3 Microfiltration

Dey (2004) study focuses on the tertiary treatment of effluent by enhanced chemical coagulation and crossflow microfiltration to produce water that is of sufficient quality for reuse in various production stages. In this study, the effluent from a modern paint manufacturing plant in Kuala Lumpur was used for this purpose. The filtrate was subjected to cross-flow microfiltration and permeate was tested for necessary quality attributes. Screening of aerobic microbes and fungi were conducted by streaking the samples on nutrient agar and malt extract agar, respectively. Iron sulfide agar tubes were used for screening anaerobic microbes or the sulfate reducing bacteria. The tests showed that permeate was free from microorganisms. The process was implemented in a paint manufacturing plant in Malaysia, which resulted in 55 percent reduction in water consumption (Dey, 2004).

The efficiency of treatment of paint is strongly influenced by the effluent pH. In the pH range of 4.0 to 4.5 the flocculation formation was minimal, however when the

pH was increased to between pH 7.0 and 7.5 flocculations were easily formed. The studies showed that the optimum pH for the treatment was 7.5 (Dey, 2004). Effective treatment of the effluent can only be achieved by employing alum in combination with polyelectrolytes. Treatability of the effluent improved with the use of polyelectrolytes in combination with alum compared with the use of only alum. Maximum COD and turbidity removal rates of 74 and 99.6 percent were recorded (Dey, 2004).

It was also found that pre-treatment of the effluent was necessary as untreated effluent had an adverse effect on the limiting flux of the membrane filtration process. It was deduced that limiting flux increased by 100 percent when the effluent was chemically treated (Dey, 2004).

#### **2.3.4 Electrochemical Treatment**

In recent years, electrochemical oxidation is becoming an alternative for wastewater treatment and starting to replace traditional processes. It is because many industrial processes produce toxic wastewaters which are not easily biodegradable and requiring costly physical or physico-chemical pretreatments (Pulgarin *et al.*, 1994). However, there is a lack of research dealing with electrochemical treatment of paint wastes in literature, present publications are only related to conventional treatment methods. The electrochemical oxidation of water-based paint wastewater was investigated batch-wise in the presence of NaCl electrolyte with carbon electrodes for the first time in literature studied by Bahadir *et al.* (2007).

The electrochemical treatment conditions were optimized using response surface methodology where potential difference, reaction temperature and electrolyte concentration were to be minimized while chemical oxygen demand (COD), color and turbidity removal percents and initial COD removal rate were maximized at 100 percent pollution load (Bahadir *et al.*, 2007).



The optimum conditions were satisfied at 35 g/L external electrolyte concentration, 30 °C reaction temperature and 8V potential difference (64.37 mA/cm<sup>2</sup> current density) realizing 51.8 percent COD, complete color and turbidity removals and 3010.74 mg/L initial COD removal rate. According to these results, the electrochemical method could be a strong alternative to conventional physicochemical methods for the treatment of water-based paint wastewater (Bahadir *et al.*, 2007).

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Introduction**

Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) analyses used to investigate the effects of WAO treatment of wastewater from paint industries. From the COD and TOC analyses it is vital to see the contents of organic and oxygen throughout the research.

#### **3.2 Materials**

The sample of paint wastewater is taken from American & Efird (Malaysia) Sdn. Bhd located in Kulai, Johor. The paint wastewater with turbidity of 52,500 NTU, TOC and COD concentrations of 52,500 mgL<sup>-1</sup> and 86,800 mgL<sup>-1</sup> respectively.

### 3.3 Experimental Set-up and Procedures

#### 3.3.1 WAO Experiment

A 20-L high pressure reactor (CEPP) is capable of performing semibatch or continuous experiments at pressure up to 40 bars and temperatures up to 300°C. A schematic diagram of the reactor system is shown in Appendix 1. In a typical semi-batch run, 20 L of the paint wastewater was batch loaded into the reactor. The reactor was then heated up to the operating temperature. Experiments were carried out at temperatures from 180°C to 220°C, and an oxygen pressure of 20 bars was maintained for all the experiments. As soon as the operating temperature was reached, oxygen was continuously fed into the reactor while being stirred to start the reaction. For those experiments in which relatively small liquid volumes were required for further analysis (e.g. for TOC and COD measurements, 100-200 mL of wastewater were withdrawn. For those experiments in which a final (after 120 min oxidation) liquid sample was needed, the reaction vessel contents were collected after the temperature was down to the ambient temperature at the end of each run. Samples that were collected were immediately analysed or refrigerated.

To minimise the extent of reaction time, the following procedure was utilised. When the final reaction time had been reached (120 min), the oxygen was shut off and the vessel was depressurised (through relief valve) to remove most of the oxygen from the reactor and to stop the reaction. As soon as the temperature dropped to ambient temperature, the vessel was opened and its contents were collected for further analysis.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 The Effect of WAO Temperature on the WAO of the Paint Wastewater

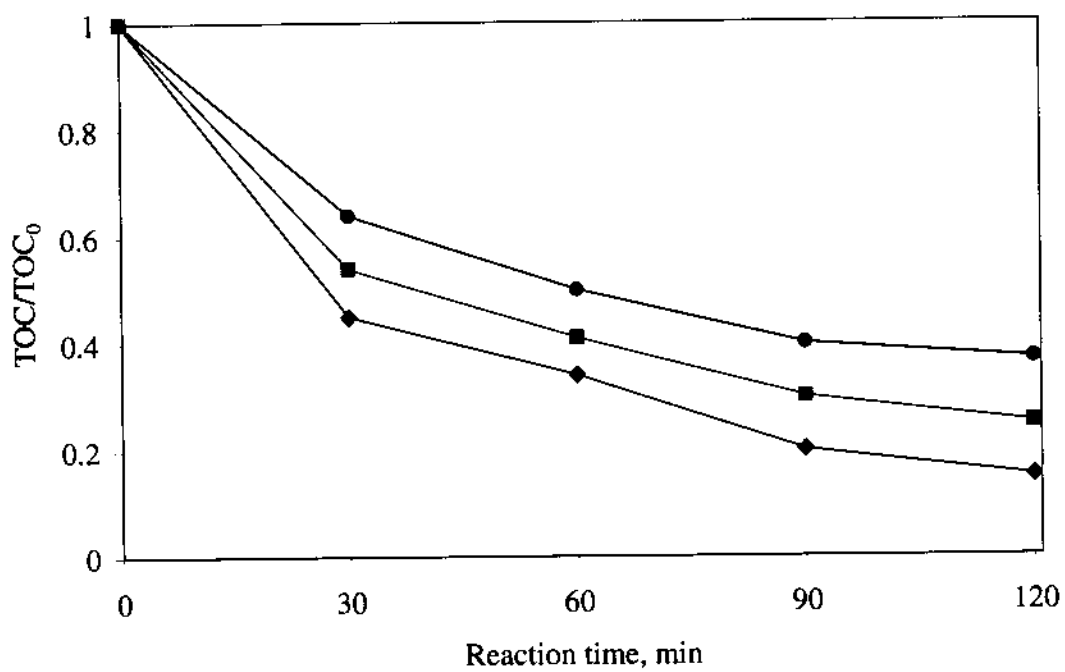
It is known that temperature is one of the parameters affecting the WAO of paint wastewater. The objective of this chapter is to investigate the treatment of paint wastewater, with respect to the effect of operating temperature between 180°C and 220°C and reaction time on the overall degradation (in terms of turbidity, TOC and COD).

#### 4.2 Turbidity, TOC and COD Removals

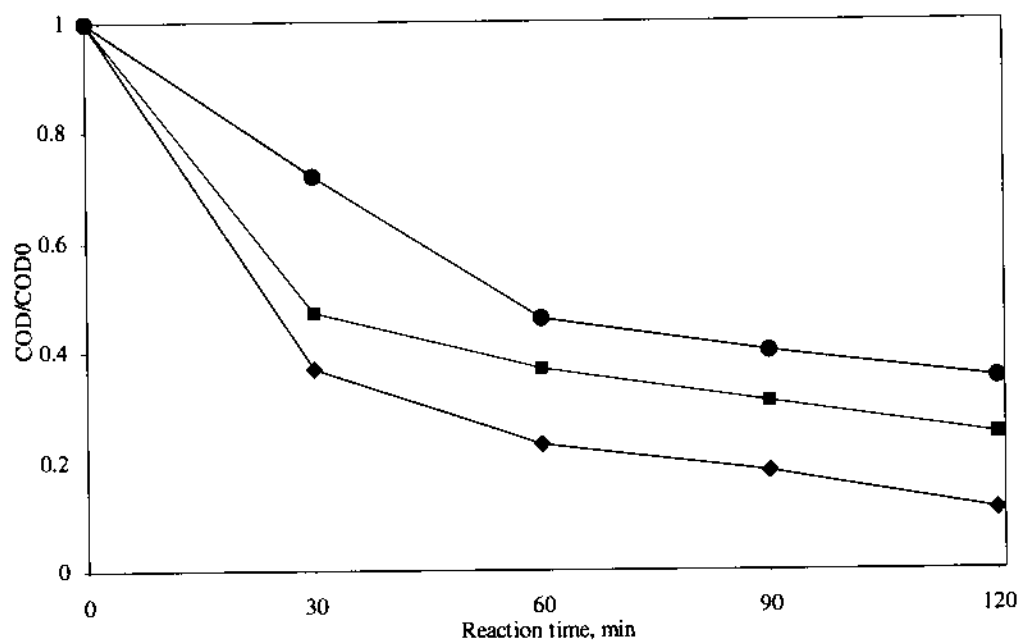
A higher temperature gives a greater removal of TOC (Figure 4.1) and COD (Figure 4.2) and turbidity during the WAO of paint wastewater. For instance, the uncatalysed WAO resulted in almost 63%, 75% and 85% TOC removals after 120 min of oxidation at 180°C, 200°C and 220°C respectively. 65%, 75% and 89% COD removals at 180°C, 200°C and 220°C respectively and 72%, 80% and 94% turbidity reductions were achieved after 120 min of oxidation at 180°C, 200°C and 220°C respectively.

TOC and COD were not completely destroyed at the conditions studied, indicating that there were organics that are refractory to further oxidation. Thus, there is always proportionally more residual TOC than COD, indicating that there was more partial oxidation (to residual organics) than total oxidation to CO<sub>2</sub>.

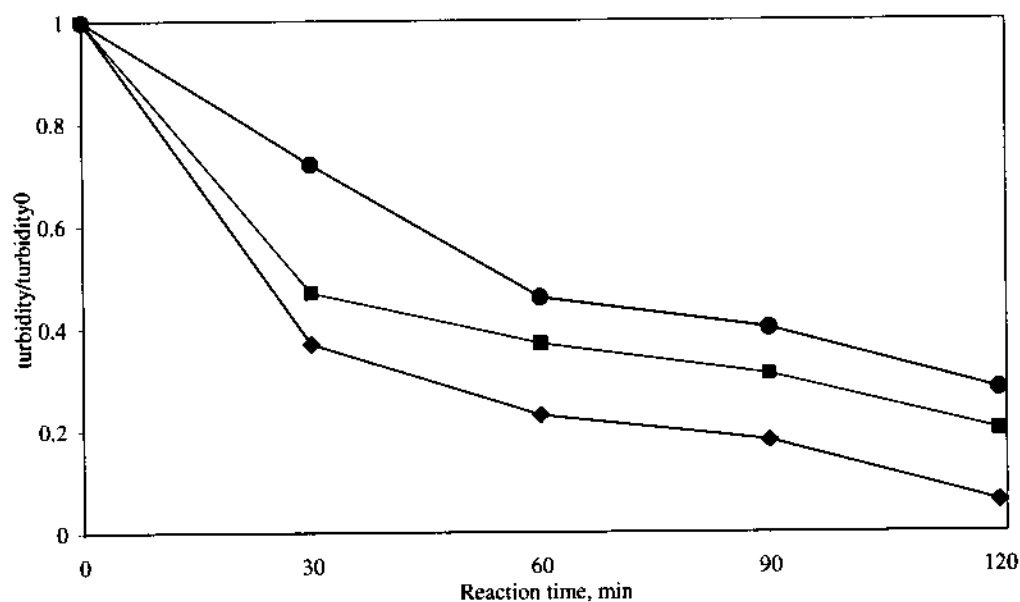
These results are therefore consistent with those of Mantzavinos et al. (Mantzavinos et al. 2000(b)) and Patterson et al. (Patterson et al. 2001) for oxidations of anionic surfactant where they indicated that there was more partial oxidation than total oxidation to CO<sub>2</sub>. Mantzavinos et al. (Mantzavinos et al. 2001) found that only about 20% and 35% TOC decrease was recorded after 40 and 200 min of uncatalysed oxidation at 200°C respectively, while the COD decrease was 32% and 50% respectively. They also found that even after 390 min of oxidation, not all of the organic compounds present in the reaction mixture were completely oxidised since only 51% and 58% TOC and COD decrease respectively, was recorded. Patterson et al. (Patterson et al. 2001) studied the effect of temperature on the uncatalysed WAO of LAS at temperatures between 180°C and 240°C. They found TOC and COD were not completely destroyed, indicating that refractory organics were present. They observed that even at 240°C and pressure of 4.85 MPa, the COD removal was about 70%. Thus it can be said that there was more partial oxidation than total oxidation to CO<sub>2</sub>.



**Figure 4.1.** The normalised TOC reduction from WAO treatment of paint wastewater at 20 bars of O<sub>2</sub> pressure, varying temperatures. -●-, 180°C; -■-, 200°C; -◆-, 220°C



**Figure 4.2.** The normalised COD reduction from WAO treatment of paint wastewater at 20 bars of O<sub>2</sub> pressure, varying temperatures. -●-, 180°C; -■-, 200°C; -◆-, 220°C



**Figure 4.3.** The normalised turbidity reduction from WAO treatment of paint wastewater at 20 bars of O<sub>2</sub> pressure, varying temperatures. -●-, 180°C; -■-, 200°C; -◆-, 220°C

#### 4.2.2 Mechanisms of Thermochemical Oxidation of LAS

The mechanism of wet air oxidation of organic compounds is very complex. In many cases the oxidation goes through a very complicated pathway and leads to the formation of many different intermediates. However, it is generally recognised that wet air oxidation of organic pollutants leads to the formation of intermediates, such as short organic acids. For uncatalysed wet air oxidation, the thermal oxidation of aromatic substrates and their transformation to lower molecular weight and organic acids is generally thought to proceed through a free radical chain auto-oxidation process (Arslan and Ferry 2002; Mantzavinos et al. 1996(a); Pintar and Levec 1995). The oxidation consists of three important steps: initiation, propagation and termination.

Equations 4.1 to 4.9 show the possible general reactions involved during the auto-oxidation of aromatic substrates. Initiation involves the formation of alkyl radicals



through a) attack of oxygen on the original molecule (Eq. 4.1) and b) high temperature (Eq. 4.2). As soon as an alkyl radical ( $R^\bullet$ ) is generated, it reacts readily with oxygen to form an alkyl peroxy radical ( $ROO^\bullet$ ) through Eq. 4.5. The main propagation reaction is the hydrogen abstraction by alkyl peroxy radicals from the original molecule to form a hydroperoxide ( $ROOH$ ) and a new alkyl radical (Eq. 4.6). This propagation reaction is usually the rate-determining step for auto-oxidation. In most cases, the termination step occurs by reaction of two alkyl peroxy radicals (Eq. 4.7).

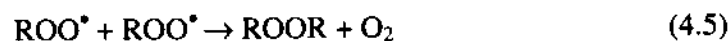
Initiation:



Propagation:



Termination:



Decomposition:



The decomposition of the hydroperoxides (Eq. 4.8) formed through the propagation reaction (Eq. 4.6) leads to the rapid degradation of aromatic substrates during auto-oxidation. The radicals generated through reaction (Eq. 4.7) can further react with the original molecule to form the alkyl radicals (Eq. 4.7 and Eq. 4.8), which again can participate in the propagation step. Further breakdown of the hydroperoxides would lead to the formation of aldehydes and acids (Eq. 4.9).

## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

A greater temperature increases the treatment of paint wastewater: for the 120 min uncatalysed WAO of paint wastewater at 20 bars of oxygen pressure, increasing the temperature from 180°C to 220°C increased the TOC removal from 63% to 85% respectively, increased the COD removal from 52 to 66% respectively and turbidity reduction from 72 to 94% respectively. The rapid oxidation of paint wastewater and their transformation to lower molecular weight fractions and organic acids has been explained as a free radical chain process (Arslan and Ferry 2002; Huang et al. 1993; Mantzavinos 1996(c); Pintar and Levec 1995; Rivas et al. 1998).

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