In the Name of God

Razi University

Faculty of Chemistry
Department of Applied Chemistry

M.Sc.Thesis

Title of the Thesis:

Application of advanced oxidation process treating Tire Cord production plant's industrial wastewater

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By:
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March 2013

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March 2013

Acknowledgement

There are several people that I would like to acknowledge, without their aid and support I would not have succeeded in preparing this thesis.

Firstly, I would like to thank my supervisor Dr. Zinatizadeh for his constant encouragement, constructive guidance and helpful suggestions during the course of this research work. I also would like to thank my adviser, Dr. Akia.

Acknowledgements are also extended to my friends in the department of chemistry at Razi University.

Also, I would like to send my deepest thanks to my family for giving me a great life, being my main pillars of strength and moral support through my lengthy education. A special thanks goes to my husband for his love and support.

March 2013
M. Habibi

Abstract

In this study, advanced oxidation processes applied for the treatment of Tire Cord Industrial wastewater (TCW). For this purpose, two advanced oxidation processes including $UV/O_3/H_2O_2$ process and photocatalytic oxidation (TiO_2) process. In part one ($UV/O_3/H_2O_2$ process), in order to investigate the effects of influential variables on the process performance, four independent factors involving two numerical factors, initial H_2O_2 concentration and initial pH, and two categorical factors, ozonation and UV irradiation were selected. The process was modeled and analyzed using response surface methodology (RSM). The region of exploration for the process was taken as the area enclosed by initial H_2O_2 concentration (0-20 mM) and initial pH (3-11) boundaries. For two categorical factors (ozonation and UV irradiation), the experiments were performed at two levels (with and without application of each factor). The response surface methodology (RSM) used in the present study was a general factorial design. In order to analyze the process, two dependent parameters (TCOD removal and BOD_5/COD ratio) as the process responses were studied. Initial H_2O_2 concentration showed a reverse impact on the responses; an increasing effect at low concentration (0-10 m mol/l) and a decreeing effect at higher concentration (10-20 m mol/l). While for initial pH; a decreasing effect on the process responses was found except at the conditions with the lowest and highest levels of H_2O_2concentration which showed no effect. The maximum and minimum process responses were obtained at H_2O_2 concentration 10 and 20 mmol/l and initial pH 3 and 11, respectively. As a result, $O_3/UV/H_2O_2$ system showed better performance with 32 % for TCOD removal and 0.41 for BOD_5/COD ratio. The O_3/H_2O_2 process (with 25 % for TCOD removal and 0.37 for BOD_5/COD ratio) showed to be a bit more effective in comparison with UV/H_2O_2 system (22% for TCOD removal and 0.32 for BOD_5/COD ratio).

The photocatalytic oxidation (TiO_2) process was also analyzed and modeled with three numerical independent factors i.e. initial COD concentration, initial pH and reaction time

using RSM. The region of exploration for the process was taken as the area enclosed by initial COD concentration (200-500 mg/l), initial pH (3-11) and reaction time (20-240 min) boundaries. The RSM used in this stage was a central composite face-centered design (CCFD). As a result, initial COD concentration showed a reverse impact on the TCOD removal efficiency; an increasing effect at low concentration (200-350 mg/l) and a decreeing effect at higher amount of concentration (350-500 mg/l). The reaction time showed a slight increasing effect on the response. Maximum TCOD removal efficiency was modeled to be 38 % at COD_{in} of 350 mg/l and reaction time 240 min. COD_{in} concentration had a reverse impact on the specific COD removal rate (SRR) which was similar trends as obtained for TCOD removal and initial pH did not show significant effect on the response. Maximum SRR was found to be 870 mg $COD_{removed}$/g cat.h at reaction time of 20 min and COD_{in} 350 mg/l. The remarkable decrease in the SRR value by increasing in the reaction time from 20 to 130 min was probably because of an inhibition resulting from poisoning of the photocatalyst surface. Maximum BOD_5/COD ratio was found to be about 0.50 in COD_{in} and initial pH of 350 mg/l and 11, respectively. The trend of changes in the ratio was match with the results obtained for TCOD removal efficiency. COD_{in} have not impact on the final pH and initial pH have a mild reverse effect on the final pH so that an increasing effect at the range of (3-7) and a decreeing effect at the range of (7-11). Maximum and minimum of final pH to be 9.7 and 5.4 that was found in the initial pH_s 11 and 3 respectively. The photocatalytic process induced by O_3 and O_3/H_2O_2 showed TCOD removal efficiencies of 41.1 and 49.7% after 240 min. BOD_5/COD ratio was also determined to be 0.3 and 0.4 respectively for the conditions with O_3 and O_3/H_2O_2. Photocatalytic process with regular periodic regeneration could achieve 49 % TCOD removal efficiency in the condition when the catalyst was regenerated by periodic ozonation against 41% for regeneration by aeration. BOD_5/COD ratio was also improved to values of 0.4 and 0.7 with regenerated by periodic aeration and ozonation, respectively.

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Chapter 1

Introduction

1.1 Industrial wastewater

Industrial wastewater is one of the important pollution sources in the pollution of the water environment. During the last century a huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas. This resulted in serious pollution problems in the water environment and caused negative effects to the eco-system and human’s life. There are many types of industrial wastewater based on different industries and contaminants; each sector produces its own particular combination of pollutants. Like the various characteristics of industrial wastewater, the treatment of industrial wastewater must be designed specifically for the particular type of effluent produced. The amount of wastewater depends on the technical level of process in each industry sector and will be gradually reduced with the improvement of industrial technologies. The increasing rates of industrial wastewater in developing countries are thought to be much higher than those in developed countries. This fact predicts that industrial wastewater pollution, as a mean environment pollution problem, will move from developed countries to developing countries in the early 21st century [1]. Fig. 1-1 shows an untreated industrial wastewater discharge into eco-system.

1.2 Characteristics of wastewater

1.2.1 Physical characteristics

The basically physical characteristics of wastewater are showed in Fig. 1-2. The total solids in a wastewater consist of the insoluble or suspended solids and the soluble compounds dissolved in water. Between 40 and 65 % of the solids in an average wastewater are suspended. Solids may be classified in another way as well: those that are volatilised at a high temperature (600 °C) and those that are not. The former are known as volatile solids, the latter as fixed solids. Usually, volatile solids are organic [2].

1.2.2 Chemical characteristics

The principalchemical characteristics of wastewaterare showed in Fig. 1-3. Over the years, a number of different tests have been developed to determine the organic content of wastewaters. Laboratory methods commonly used today to measure gross amounts of organic matter in wastewater include (1) biochemical oxygen demand (BOD), (2) chemical oxygen demand (COD) and (3) total organic carbon (TOC). Fractionation of COD in wastewater based on biodegradability is shown in Fig. 1-4.

The principal chemical tests include free ammonia, organic nitrogen, nitrites, nitrates, organic phosphorus and inorganic phosphorus [2]. Nitrogen and phosphorus are important because these two nutrients are responsible for the growth of aquatic plants. The excessive accumulation of nutrient (N, P) discharge to surface water can pose serious ecological problems that affect the health of aquatic life and consequently that of human and animals. Therefore, Nutrient removal from wastewater is of vital importance as the discharge standards have been more stringent [3].

1.3 The Tire Cord plant wastewater

In order to produce polyester and polyamide textiles, Tire Cord plant uses the polyester and polyamide as the basic material for production. In this way, several units i.e. spinning, twisting, weaving and finally preparation dip product are used. The flow diagram of the processes of the Tire Cord plant is summarized in the Fig. 1-5.

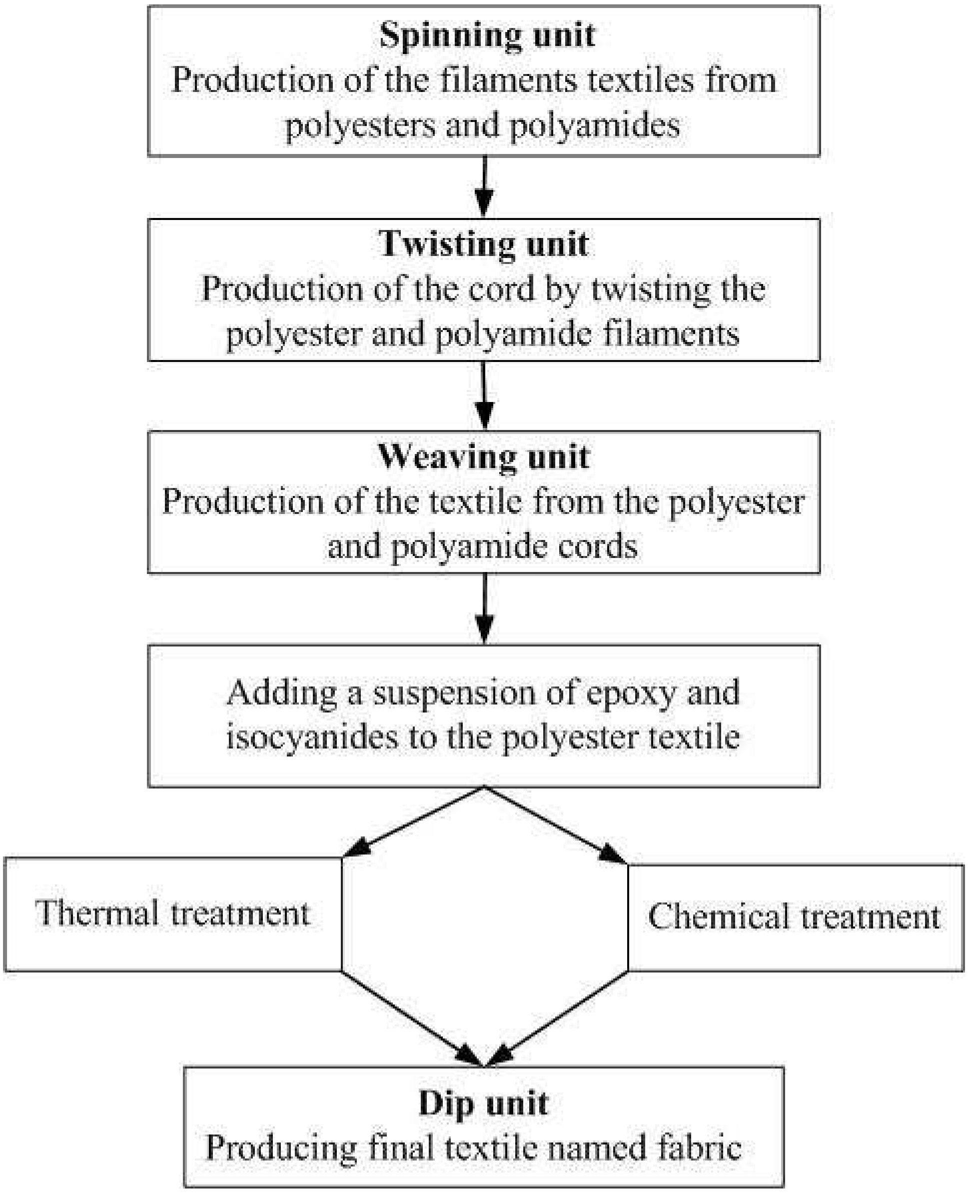

Fig. 1-5. Flow diagram of the Tire Cord industrial plant.

The chemicals content of the TCW produced by the Tire Cord production plant are mainly produced from the dip unit and the list of the chemicals are presented in Table 1-1. From the Table, the compounds are mostly recalcitrant and non biodegradable. It is noted that some of the chemicals, i.e. pyridine compounds, are not even detected in COD test.

Table 1-1.List of chemicals content of TCW.

No.	Type of compound	No.	Type of compound
1	Styrene	10	Cyclo undecene,1.methyl
2	Pyridine 2-ethyl	11	7-Heptadecene,17-chloro
3	Pyridine 2-ethenyl	12	Tetradecane
4	Diethyl disulfide	13	Phenol,2,4-bis(1,1-dimethylethyl)
5	Alpha methyl styrene	14	Diphenyl sulfide
6	n-Decane	15	1-monolinoleoylglycerol trimethylsilyl ether
7	Benzene, 1-bromo-3 methyl	16	Heptacosane
8	Naphthalene,decahydro-1,6-dimethyl	17	Resorcinol
9	Naphthalene,decahydro-2,3-dimethyl	18	Formalin

1.4 Needs for treatment of industrial wastewaters

Industry views wastewater treatment as an imposed necessity which it employs when it is compelled to, especially when wastewater’s effect on the receiving watercourse is readily visible or when public approval and claim will be gained for the expenditure and effort.Industry should attempt to treat its wastewater at the lowest cost that will yield a satisfactory effluent for the particular receiving stream, which may necessitate considerable study, research, and pilot investigations. Planning ahead will provide time to make appropriate decisions. Conversely, lack of planning on minimizing wastewater treatment costs may mean that a sudden demand for an immediate solution will cause industry to decide to cease production. To prevent any health hazards caused by discharging wastewater to water streams, the wastewater must be treated before discharge. Such treatment should comply with the terms of the legislation defining the characteristics of the effluent discharging in water streams. The concept of planning and development should be based on the criteria to protect land, water resources, aquatic life in streams and rivers and marine life from pollution and to safeguard public health as a high priority. The environmental inspection on wastewater treatment plants aims to support and strengthen the protection of both the environment and the public health, since the pollution generated from the industrial establishments has a negative impact not only on the environment, but also on the health of the individuals. Therefore, it is noted that most of the procedures that could be implemented by industrial establishments to reduce the negative environmental impacts, will also lead to reducing the effects that present a threat to the health of workers within the plants and the public living in regions affected by the various emissions from the plants.

In this respect, the effectiveness of the inspection on industrial wastewater treatment plants will lead to the protection of the environment and the protection of workers and public health.

1.5 Environmental regulation of effluent discharge

The extremely pollution loading on the water resources from various sources (municipal, industrial, and agricultural) has been led to the more and more strict environmental protocols. The permitting adjustable effluent standards are applied based on the demands of dominant environmental circumstances. The effluent discharge standards usually related to effluent wastewater are presented in Table 1-2.

Table 1-2. Effluent discharge standards for treated wastewater (Iran).

Pollutant		**Discharge to surface water (mg.L^{-1})**	**Discharge to well (mg.L^{-1})**	**Agricultural usages (mg.L^{-1})**
Biological Oxygen Demand	BOD_5	30	30	100
Chemical Oxygen Demand	COD	60	60	200
Dissolved Oxygen	DO	2	-	2
Total Suspended Solids	TSS	40	-	100
Ammonium	NH_4	2.5	1	-
Nitrite	NO_2	10	10	-
Nitrate	NO_3	50	10	-
Phosphate (as P)	PO_4	6	6	-
Total Dissolved Solids	TDS	10	10	-
Turbidity	Turb.	50 (NTU)	-	50 (NTU)
Oil & Grease	O&G	10	10	10
Detergents	ABS	1.5	0.5	0.5
Sulfides	H2S	3	3	3
Sulfites	SO3	1	1	1
Sulfates	SO4	400	400	500

1.6 Problem statement

Due to increasing consciousness about the environment and more severe environmental regulations, treatment of industrial wastewater has been a key aspect of research. The composition of industrial effluents is characterized by diverse in constituents with high concentration level [4]. The complex composition of the industrial wastewater accounts for, in some cases, unpredictable toxicological and ecotoxicological effects [5]. Recalcitrant pollutants are problems associated with industrial wastewaters which are not typically considered in conventional treatment processes design.