

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**

Supervisor:

Dr. A.A.L. Zinatizadeh

Advisor:

Dr. M. Akia

By:

Maryam Habibi

March 2013



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**

By:
Maryam Habibi

Evaluated and approved by thesis committee: as.....

Supervisor:Dr. A. A. L. Zinatizadeh

Advisor:Dr. M. Akia.....

External Examiner: Dr. P. Mohammadi

Internal Examiner:Dr. M. Ahmadi.....

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/O₃/H₂O₂ process and photocatalytic oxidation (TiO₂) process. In part one (UV/O₃/H₂O₂ process), in order to investigate the effects of influential variables on the process performance, four independent factors involving two numerical factors, initial H₂O₂ 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 H₂O₂ 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 BOD₅/COD ratio) as the process responses were studied. Initial H₂O₂ concentration showed a reverse impact on the responses; an increasing effect at low concentration (0-10 m mol/l) and a decreasing 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 H₂O₂ concentration which showed no effect. The maximum and minimum process responses were obtained at H₂O₂ concentration 10 and 20 mmol/l and initial pH 3 and 11, respectively. As a result, O₃/UV/H₂O₂ system showed better performance with 32 % for TCOD removal and 0.41 for BOD₅/COD ratio. The O₃/H₂O₂ process (with 25 % for TCOD removal and 0.37 for BOD₅/COD ratio) showed to be a bit more effective in comparison with UV/H₂O₂ system (22% for TCOD removal and 0.32 for BOD₅/COD ratio).

The photocatalytic oxidation (TiO₂) 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 decreasing 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 decreasing 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 pHs 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. BOD₅/COD ratio was also improved to values of 0.4 and 0.7 with regenerated by periodic aeration and ozonation, respectively.

Table of Contents

ContentPage

Chapter 1: Introduction

1.1 Industrial wastewater	2
1.2 Characteristics of wastewater	3
1.2.1 Physical characteristics	3
1.2.2 Chemical characteristics	4
1.3 The Tire Cord plant wastewater	5
1.4 Needs for treatment industrial wastewaters	7
1.5 Environmental regulations of effluent discharge	8
1.6 Problem statement	9
1.7 Research objectives	10
1.8 Scope of study	11
1.9 Organization of the thesis	12

Chapter 2: Literature review

2.1 Introduction	14
2.2 Advanced oxidation process	14
2.2.1 Ozone and ultraviolet radiation (O_3/UV)	15
2.2.2 Hydrogen Peroxide and ultraviolet radiation (H_2O_2/UV)	16
2.2.3 Ozonation with hydrogen peroxide (O_3/H_2O_2)	17
2.2.4 Ozone, hydrogen peroxide and ultraviolet radiation ($O_3/H_2O_2/UV$)	17
2.2.5 Photo-Fenton ($Fe^{2+}/H_2O_2/UV$)	20
2.2.6 Catalytic ozonation	20
2.3 Photocatalytic reaction	21
2.3.1 Mechanism of Photocatalytic reaction	22
2.3.2 Effects of important variables on performance of the photo catalytic oxidation	23
2.3.2.1 Light intensity distribution	24
2.3.2.2 Effect of dissolved oxygen	25
2.3.2.3 Effect of feed flow rate	25
2.3.2.4 Effect of contaminant concentration	26
2.3.2.5 Effect of TiO_2 load	26
2.3.2.6 Effect of light wavelength	27
2.3.2.7 Effect of irradiation time	27
2.3.2.8 Effect of hydrogen peroxide	27
2.3.2.9 Effect of air flow rate	28
2.3.2.10 Effect of temperature	29

2.3.2.11 Effect of pH	29
2.3.3 Summary of application different photocatalytic reactors	30
2.4. Process modeling and optimization	33
2.4.1 Response surface methodology (RSM)	33
2.4.1.1 Central Composite Design (CCD)	34
2.4.1.2 Graphical presentation of the model equation and determination of optimal operating condition	37

Chapter 3: Material and Methods

3.1 Chemicals and reagents	40
3.2 Overall experimental flowchart	40
3.3 Experimental setups	42
3.3.1 Set up of UV/O ₃ /H ₂ O ₂ process	42
3.3.2 Set up of Photocatalysis process	44
3.4 TiO ₂ -coated quartz tubes	45
3.4.1 Coating procedure	45
3.4.2 Characterization of TiO ₂ coated on quartz tubes	46
-Atomic force microscope (AFM)	46
-N ₂ adsorption/desorption isotherms (BET)	46
-Scanning electron microscopy (SEM)	46
3.5 Characteristics of Tire Cord plant wastewater	49
3.6 Experimental design	49
3.6.1 UV/O ₃ /H ₂ O ₂ process	50
3.6.2 Photocatalytic process	51
3.7 Analytical procedure	53
3.7.1 Water quality parameters measurements	53
3.7.2 Determination of chemical oxygen demand (COD)	53
-Removing the interference effect of dissolved ozone in COD test	53
-Removing the interference effect of hydrogen peroxide in COD test	54
3.7.3 Determination of biological oxygen demand (BOD)	54
3.7.4 Measurements of ozone	54
3.7.5 Measurement of organic compounds	55

Chapter 4: Results and Discussion

Part One: Process analysis and modeling of the advanced oxidation process

4.1.1 Statistical analysis	60
4.1.2 Process Performance	62
4.1.2.1 TCOD removal	62
4.1.2.2 BOD ₅ /COD ratio	72

Part Two: Process analysis and modeling of the photocatalytic oxidation

4.2.1 Statistical analysis	78
4.2.2 Process Performance	82
4.2.2.1 TCOD removal	82
4.2.2.2 Specific removal rate (SRR)	90
4.2.2.3 BOD ₅ /COD ratio	92
4.2.2.4 Final pH	95
4.2.3 Photocatalyst induced by O ₃ and O ₃ /H ₂ O ₂	96
4.2.4 Photocatalytic process with regular periodic regeneration	97

Chapter 5: Conclusions

Conclusions	100
-------------	-----

Chapter 6: References

References	103
------------	-----

List of Figures

Figures	Page
Fig. 1-1 Discharge of industrial wastewater to eco-system	3
Fig. 1-2 Fractionation of physical characteristics of wastewater	3
Fig. 1-3 Fractionation of chemical characteristics of wastewater	4
Fig. 1-4 Fractionation of COD in Wastewater	4
Fig. 1-5 Flow diagram of the Tire Cord industrial plant	6
Fig. 2-1 Oxidation process advisable according to COD of water.(WAO, wet air oxidation.SCWAO, supercritical wet air oxidation)	18
Fig. 2-2 Presentation of Photocatalytic mechanism	22
Fig. 2-3 Three types of central composite designs for two factors, from left to right: Rotatable,Face-centered, Inscribed (Montgomery, 1991)	35
Fig. 2-4 Central composite faced-centered design with three variables	37
Fig. 3-1 Flowchart of overall experiments	41
Fig. 3-2 Schematic diagram of the laboratory-scale advanced oxidation system	42
Fig. 3-3 Laboratory-scale advanced oxidation experimental set-up used in this study	43
Fig. 3-4 (a) Cylindrical composition of the quartz tubes, (b) position of those surrounded the UVlamp	44
Fig. 3-5 Laboratory-scale experimental set-up of photocatalytic reactor (PCR)	45
Fig. 3-6 (a) SEM, (b) AFM, and (c) BET images of nano TiO ₂ coated on quartz tube	48
Fig. 3-7 Process responses measured or calculated in this study	49
Fig. 4-1 The fate of COD content	57
Fig. 4-2 Predicted vs. actual values plots for (a) TCOD removal, (b) BOD ₅ /COD ratio	61
Fig. 4-3 Response surface for TCOD removal in; (a) with (b) without ozonation and UV irradiation	63
Fig. 4-4 Response surface for TCOD removal (a) without ozonation and with UV irradiation (b) with ozonation and without UV irradiation	64
Fig. 4-5 Interactive effects of DC (UV irradiation-ozonation) on TCOD removal at different pH and H ₂ O ₂ concentration	65
Fig. 4-6 Interactive effects variable AB (initial pH-H ₂ O ₂ concentration) on TCOD removal different conditions of ozonation and UV irradiation	66
Fig. 4-7 Performance of different AOPs treating TCW	67
Fig. 4-8 Changes in COD/COD ₀ versus reaction time at (a) H ₂ O ₂ alone, (b) H ₂ O ₂ /UV, (C) H ₂ O ₂ /O ₃ and (d) H ₂ O ₂ /O ₃ /UV	68
Fig. 4-9 GC-MS analysis of raw TCW	70
Fig. 4-10 GC-MS analysis of organic contaminants in the oxidized TCW by (a) H ₂ O ₂ /O ₃ at pH 9 and (b)H ₂ O ₂ at pH 5	71
Fig. 4-11 Response surface for BOD ₅ /COD ratio at (a) with (b) without of ozone and UV	74

	irradiation.	
Fig. 4-12	Response surface for BOD ₅ /COD ratio at (a) without ozonation and with UV irradiation (b) with ozonation and without UV irradiation	74
Fig. 4-13	COD fractionation for the samples after the treatment process	76
Fig. 4-14	Predicted vs. Actual values plots for (a) TCOD removal, (b) SRR and (c) Final pH, in photocatalytic reactor	81
Fig. 4-15	(a) Response surface, and (b) contour plates for TCOD removal at initial pH 7	85
Fig. 4-16	Response surface plots for TCOD removal efficiency as a function of reaction time and initial pH at (a) COD _{in} =200 mg/l, (b) COD _{in} =350 mg/l, and (c) COD _{in} =500 mg/l	85
Fig. 4-17	Performance of different photocatalytic treating TCW	86
Fig. 4-18	Interactive effects of AC (COD _{in} - initial pH) on TCOD removal at different reaction times	87
Fig. 4-19	Interactive effects of BC(reaction time-initial pH) on TCOD removal at different COD _{in} concentrations	87
Fig. 4-20	Changes in COD/COD ₀ versus reaction time at different COD _{in} concentration (a) 500,(b) 350 and (C) 200 mg/l.	88
Fig. 4-21	GC-MS analysis of organic contaminants in the oxidized TCW by COD _{in} 350mg/l at pH 11	89
Fig. 4-22	Response surface plates for specific removal rate at different reaction times (a) 20 and (b) 130 min	92
Fig. 4-23	BOD ₅ /COD ratio under different conditions studied	93
Fig. 4-24	COD fractionation for the samples after the treatment process	94
Fig. 4-25	(a) Response surface and (b) contour plats for final pH at reaction time 240 min	96
Fig. 4-26	performance of the photocatalytic process induced by O ₃ and O ₃ /H ₂ O ₂	97
Fig. 4-27	Performance of photocatalytic process with regular periodic recovery by aeration and Ozonation	98

List of Tables

Tables		Page
Table 1-1	List of chemicals content of TCW	7
Table 1-2	Effluent discharge standards for treated wastewater (Iran)	9
Table 2-1	Summary of results PCR studies on degradation several dyes	32
Table 3-1	List of chemicals and reagents	40
Table 3-2	Characteristics of Tire Cord production wastewater	49
Table 3-3	Experimental range and levels of the independent variables	50
Table 3-4	Experimental conditions for UV/O ₃ /H ₂ O ₂ process	51
Table 3-5	Experimental range and levels of the independent variables	52
Table 3-6	Experimental conditions for photocatalytic process	52
Table 4-1	ANOVA results for the equations of the Design Expert 6.0.6 for studied responses	61
Table 4-2	Details of GC-MS chromatogram of raw TCW and several treatment processes	72
Table 4-3	Order of experiments number according to operating conditions	75
Table 4-4	ANOVA results for the equations of the Design Expert 6.0.6 for studied responses	80
Table 4-5	Details of GC-MS chromatogram of raw TCW and one treatment process	90
Table 4-6	Order of experiments number according to operating conditions	94

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 principal chemical characteristics of wastewater are shown 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.

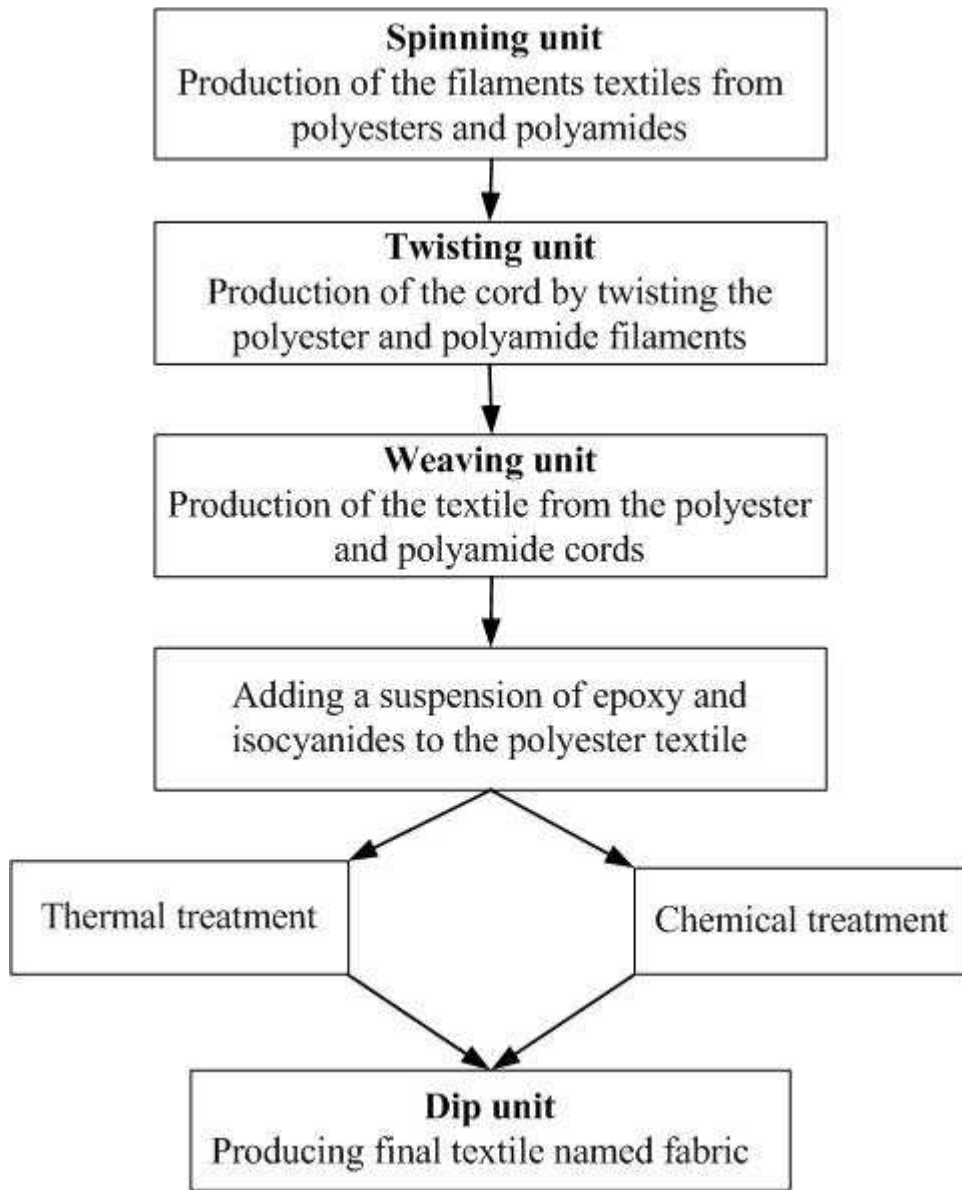


Fig. 1-5.Flow diagram of the Tire Cord industrial plant.

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	H ₂ S	3	3	3
Sulfites	SO ₃	1	1	1
Sulfates	SO ₄	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.