AMERICAN UNIVERSITY OF BEIRUT

EFFICACY OF MULTIVARIATE PROCESS SEQUENCES IN TREATING TANNERY WASTEWATER

by
ABEER SAMIR HAMZEH

A thesis
submitted in partial fulfillment of the requirements
for the degree of Master of Science in Environmental Sciences
to the Interfaculty Graduate Environmental Sciences Program
(Environmental Technology)
of the Faculty of Engineering and Architecture
at the American University of Beirut

Beirut, Lebanon
March 2012

AMERICAN UNIVERSITY OF BEIRUT

EFFICACY OF MULTIVARIATE PROCESS SEQUENCES IN TREATING TANNERY WASTEWATER

by

ABEER SAMIR HAMZEH

Approved by:

Dr. George Ayoub, Professor Civil and Environmental Engineering	Advisor
Dr.Mahmoud Al-Hindi, Assistant Professor Mechanical Engineering	Member of Committee
Dr.Houssam El Rassy, Associate Professor Chemistry	Member of Committee

Date of thesis defense: March 1st, 2012

AMERICAN UNIVERSITY OF BEIRUT

THESIS RELEASE FORM

I, Abeer Samir Hamzeh

☐ authorize the American University of Beirut to supply copies of my thesis to libraries or individuals upon request.

☐ do not authorize the American University of Beirut to supply copies of my thesis to libraries or individuals for a period of two years starting with the date of the thesis defense.

_____
Signature

_____
Date

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to Dr. George Ayoub, my advisor, for his knowledge, patience, guidance and assistance during my studies. I would also like to express my appreciation to Dr Mahmoud Al-Hindi for showing interest in the topic and for his encouragement and valuable input who lead to the improvement of this study. My deepest gratitude also goes to Dr. Houssam EL-Rassy for his technical advice and service as committee member.

I would furthermore like to express my gratitude to Dr. Lucy for her special contribution on the academic and personal levels. My appreciations are also extended to Mr. Joseph Daoud for his help at EERC and Zakeya Deeb for her moral support.

To Mirna and Sara, thank you for your encouragement and your timely assistance in my experimental work. I would also like to thank my friends and colleagues for their support: Khaled S, Rassil, Dana, Nada, Maya and Rana.

I remain grateful to all my family members, especially my Mom, who provided me with all the support throughout my studies. Finally, I am thankful to my fiancé for his help, understanding and unconditional love.

AN ABSTRACT OF THE THESIS OF

Abeer Samir Hamzeh for Master of Science in Environmental Sciences
Major: Environmental Technology

Title: Efficacy of Multivariate Process Sequences in Treating Tannery Wastewater

The increase in water consumption, for both industrial and domestic purposes, is exacerbating water shortages throughout the world. Water is increasingly perceived as a limited resource of environmental and economic values. Accordingly, it becomes crucial to introduce techniques to purify industrial effluents and to recycle process water.

Leather tanning is considered amongst the most "environmentally unfriendly" industrial activities with major pollution impacts on water bodies. This industry uses large quantities of water; it requires about 30–40 L of water per kilogram of hide and in turn, it produces large quantities of liquid effluents. It is also recognized as a serious environmental threat all over the world especially in developing countries where, as a matter of common practice, the effluents are discharged from the leather processing units to surface water bodies and on land without undergoing any treatment. This practice leads to the pollution of surface water and consequently to the ground water and the infiltration of dissolved chemicals into the surrounding soil rendering the soil unfit for cultivation.

Tannery wastewater has a strong color and is heavily polluted; it contains high organic (COD, BOD) and inorganic loadings (ammonia, sulfide, chloride), dissolved and suspended solids and specific pollutants such as vegetable and/or synthetic tannins, sulfonated oils, chromium, arsenic and surfactants.

The objective of this study was to apply a series of treatment processes separately and in combination to determine their efficiencies on pollutant removals from the generated wastewater collected from the largest operating tannery in Lebanon. The aim was to establish a treatment train that can effectively and optimally reduce the concentration of pollutants to environmentally acceptable levels or for further treatment techniques. Simplicity and cost effectiveness were targeted in the selection of the processes.

A total of 25 samples were collected and analyzed for the following parameters: TSS, TDS, COD, conductivity, pH, apparent color, turbidity, total phosphorous, total nitrogen, BOD_5, sulfide, arsenic and chromium. The experimental study comprised coagulation/ flocculation, oxidation (through ozone or Fenton reaction) and adsorption treatment techniques.

This study showed that the sequence consisting of Jar test using liquid bittern as coagulant followed by ozone oxidation and then adsorption onto AC recorded the highest removal efficiencies: 80% for TSS, 89% for apparent color, 92% for turbidity, 61% for COD, 55% for BOD_5, 91% for TP, 60% for TN, 99% for Cr and 94 % for As. Though Fenton oxidation needs to be optimized, it showed promising removal efficiencies.

CONTENTS

ILLUSTRATIONS

TABLES

ABBREVIATIONS

AC	Activated carbon
AF	Anaerobic filter
As	Arsenic
AOP	Advanced oxidation process
ASP	Activated sludge process
ATT	Advanced treatment techniques
BOD_5	Biochemical oxygen demand
COD	Chemical oxygen demand
Cr	Chromium
Cr_2O_3	Chromium oxide
CEPT	Chemically enhanced primary treatment
EC	Electro-coagulation
EF	Electro-Fenton
FeS	Iron sulfide
HRT	Hydraulic retention time
MLVSS	Mixed liquor volatile suspended solids
O_3	Ozone
SBR	Sequencing batch reactor
TDS	Total dissolved solids
TSS	Total suspended solids
TN	Total nitrogen
TP	Total phosphorous

To my Dad

CHAPTER 1

INTRODUCTION

The increase in water consumption, for both industrial and domestic purposes, is exacerbating water shortages throughout the world. The discharge, on a daily basis, of two million tons of industrial /chemicals, agricultural and human wastes to receiving waters (United Nations World Water Development Report, 2003), is on the other hand, leading to a rapid increase in pollution of water bodies.

Water is increasingly perceived as a limited resource of environmental and economic values. Accordingly, the UN policy on sustainable development, established in 1992 by Agenda 21 and the Rio Declaration on Environment and Development, is based on the synergy between socio-economic development and environmental protection in order to reach sustainable development. Hence, expanding the activities aimed at improving the integrated management of the available resources makes a significant contribution towards achieving the objectives of Agenda 21 and the Rio Declaration. With industrial and socio-economic growth, the demand for water has greatly increased resulting in the generation of large amounts of wastewater so that clean water is becoming a scarce resource. Accordingly, it becomes crucial to introduce techniques to purify industrial effluents and to recycle process water.

Leather tanning is considered amongst the most "environmentally unfriendly" industrial activities with major pollution impacts on water bodies to the extent that some authorities consider tannery wastewater as one of the ten most harmful threats to the environment (Aber et al., 2010). It has been reported that the total global quantity of

bovine hides, sheep, goat and pigskins generated yearly amounts to nearly 8×10^6 t as wet salted weight. The tanning industry worldwide used 4×10^6 t of chemicals and produced over 3×10^8 t of wastewater and about 8×10^6 t of solid waste and dewatered sludge (Şengil et al., 2009).

Tannery operations consist of transforming the raw hides, a highly putrescible material, into leather, a stable product with a significant commercial value (Suresh et al., 2001). Raw hides undergo a sequence of mechanical and chemical processes to obtain its final leather form. This conversion takes place in an aqueous medium where acids, alkalis, chromium salts, tannins, solvents, auxiliaries, surfactants, tanning agents (natural or synthetic), sulfonated oils and salts are mixed together (Vidal et al., 2004; Suresh et al., 2001). This industry uses large quantities of water; it requires about 30–40 L of water per kilogram of hide (Rodrigues et al., 2008). In turn, it produces large quantities of liquid effluents (Bódalo et al., 2005). Tannery wastewater has a strong color and is heavily polluted; it contains high organic (COD, BOD) and inorganic loadings (ammonia, sulfide, chloride), dissolved and suspended solids and specific pollutants such as vegetable and/or synthetic tannins, sulfonated oils, chromium, arsenic and surfactants (Szpyrkowicz et al., 1995; Rajalo et al., 1996). These substances are derived from the hides and skins themselves and from the addition of reagents during the processing of these materials (Schrank et al., 2005; Song et al., 2004; Naumczyk et al., 2005; Şengil et al., 2009). The effluent has a broadly fluctuating pH and high temperatures (Aber et al., 2010).

Tannery effluent varies from one plant to another based on its size, the quantity of final leather products, the kind of tanning, the types of chemicals used, the production processes and the treatment technologies adopted for the removal of

aforementioned pollutants (Table1.1). Furthermore, it is reported that variations under the same manufacturing conditions may occur due to the quality of the raw hides/skins processed (Kurt et al., 2007).

Based on their specific characteristics, tannery wastewaters are treated using appropriate technologies which may be physical and/or chemical and/or biological. Since most pollutants in tannery wastewaters appear to be either in particulate form or associated with particulates, physico-chemical treatment remains to be the most commonly used process in addition to other techniques such as ozonation, reverse osmosis, ion exchange and activated carbon adsorption (Song et al., 2004; Tiravanti et al.,1997; Szpyrkowicz et al.,2005; Tahir et al.,2007; Arvanitoyannis et al., 1989).

Recent literature related to tannery wastewater treatment techniques reports that many processes have been investigated. Of these processes, chemical treatment including coagulation/ flocculation through the application of alum or ferric chloride as coagulants has shown reasonable removals in terms of TSS, Cr, COD and turbidity, however, with additional sludge formation (Song et al., 2004). Despite the good removals achieved when colloidal particles are flocculated by the application of alum and ferric chloride, some studies indicate that with, the use of ferric chloride as a coagulant, a blackish color develops once it comes in contact with the tannery wastewater and this was attributed to the formation of soluble FeS generated by iron complexes of tannin-like materials present in the wastewater (Ryu et al., 2007; Ates et al., 1997; Haydar and Aziz 2009).

Table 1.1 Physico-chemical characteristics of tannery wastewater derived from different studies

Parameter	Koteswari et al., 2003	Leta et al., 2004	Szpyrkowicz et al., 2005	Ganesh et al., 2006	Feng et al., 2007	Deepali et al., 2009	Apaydin et al., 2009	Haydar et al., 2009
pH	-	10.72	7.7	7.08	7-8.5	4.74	7.4	7.5-9.6
TDS (mg/L)	15152	6810	-	-	-	33231.39	-	4466-14572
TSS (mg/L)	2005	-	-	2820	-	9485.22	2690	568-2132
COD (mg/L)	8000	11153.67	2426	4800	2400-2600	38166.66	3700	1760-3320
BOD (mg/L)	930	2906	-	-	850-950	1500	1470	390-1320
Ammonical nitrogen (mg/L)	-	162.15	335	128	200-230	-	180	-
Chromium (mg/L)	11.2	32.87	29.3	99	-	-	-	22.9-122.4
Sulfide (mg/L)	228	507.5	286	-	100-120	-	440	-

Electro-oxidation of organic compounds using different types of anodes has also been tested in treating tannery wastewater leading to COD reductions of about 50% (Sundarapandiyan et al., 2010; Vlyssides and Israilides 1997). Although biological treatment methods are generally cheap and simple, their application to tannery wastewater treatment may result in some difficulties, mainly due to the presence of inhibiting and/or biorecalcitrant compounds, like high molecular weight proteins. It has been reported that refractory pollutants caused by textile industries cannot easily be degraded by traditional biological process and remain in the effluent (Vidal et al. 2004; Kim et al. 2002). Since the effluent is presumed to be very resistant to microbial degradation, a combined process of biological treatment and chemical oxidation is commonly used in order to meet water quality standards (Bae et al., 2004).

For the aforementioned reasons, tanning industry is recognized as a serious environmental threat all over the world especially in developing countries where, as a matter of common practice, the effluents are discharged from the leather processing units to surface water bodies and on land without undergoing any treatment (Scholz et al., 2003; More et al., 2001). This practice leads to the pollution of surface water and consequently to the ground water and the infiltration of dissolved chemicals into the surrounding soil rendering the soil unfit for cultivation (Herawati et al., 2000; Ma et al., 2003; Tariq et al., 2005).

In this study, collected wastewater from a local tannery was characterized in terms of the following parameters: TSS, apparent color, turbidity, BOD_5, COD, TN, TP, Cr and As. A series of treatment processes applied separately and in combination were investigated to determine their efficiencies on pollutant removal from the generated wastewater. Chemical treatment through coagulation/ flocculation using bittern as

coagulant was compared to removals achieved with other coagulants such as alum and ferric chloride. The contribution in reduction of pollutants through oxidation processes using ozone and Fenton reaction, and adsorption by granular activated carbon was also investigated. The aim is to establish a treatment train that can effectively and optimally reduce the concentration of pollutants in tannery wastewater to environmentally acceptable levels or for further treatment techniques. In doing so, simplicity and cost effectiveness are targeted in the selection of processes that will minimize the serious risk to the ecosystem and human health in the event that wastewater is left to be discharged untreated.

CHAPTER 2

LITERATURE REVIEW

Tannery wastewater is known to be one of the most toxic industrial effluents. To convert a raw hide into a finished leather product, the procedure involves a complex series of mechanical and chemical processes where a variety of chemicals are integrated into the manufacturing matrix as depicted in figure 2.1. The resulting effluent is normally laden with a variety of pollutants that require removal so as to render the wastewater fit for discharge with minimal impact on the environment. Many studies have been conducted with the objective of alleviating the serious problem of discharge of tannery waste effluents.

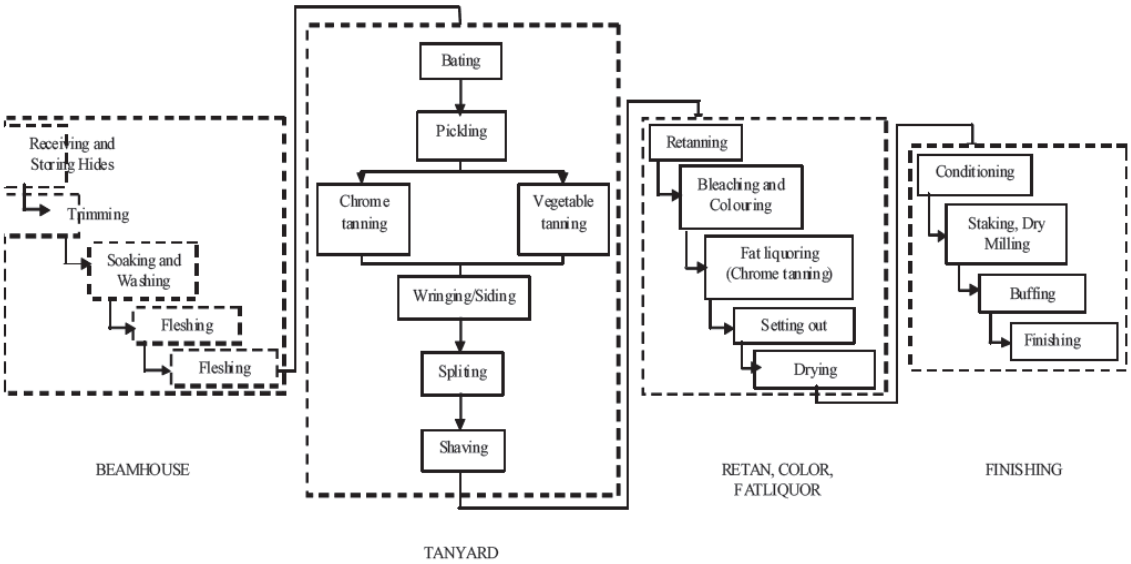


Figure 2.1 General flow diagram for leather process steps (Rameshraja et al., 2011)

Elsheikh et al. (2009) reported that tanneries emit three types of wastewater

1. Unhairing and liming wastewater
2. Tanning wastewater
3. Retanning, dyeing and fat liquoring wastewater (Figure 2.2)

During the first stage belonging to beamhouse processes, raw hides and skins are cleaned and prepared for further processing; the hair, the epidermis and the flesh layers are separated from the hide (Vidal et al., 2004; Konrad et al., 2002; Cooman et al., 2003; Rivela et al., 2004). The skin is further rehydrated and globular proteins are removed at relatively high pH values. Pickling is also performed at this stage. The corresponding wastewater is highly loaded with sulfide and lime (leading to relatively high pH values) and in some cases arsenic is also present. The stage that follows involves the addition of synthetic/vegetable tanning agents in an acidic medium (pH ranging between 2.5 to 3.5) as well as washing, trimming and shaving. At this stage the bulk of the chromium is applied. The last stage includes retanning and wet finishing where the tanned hides are given their final features from added colors to bleached appearance (Barredo-Damas et al., 2010). The effluents resulting from the three stages are combined to form the final tannery effluent, a wastewater laden with a complex array of impurities that require treatment.

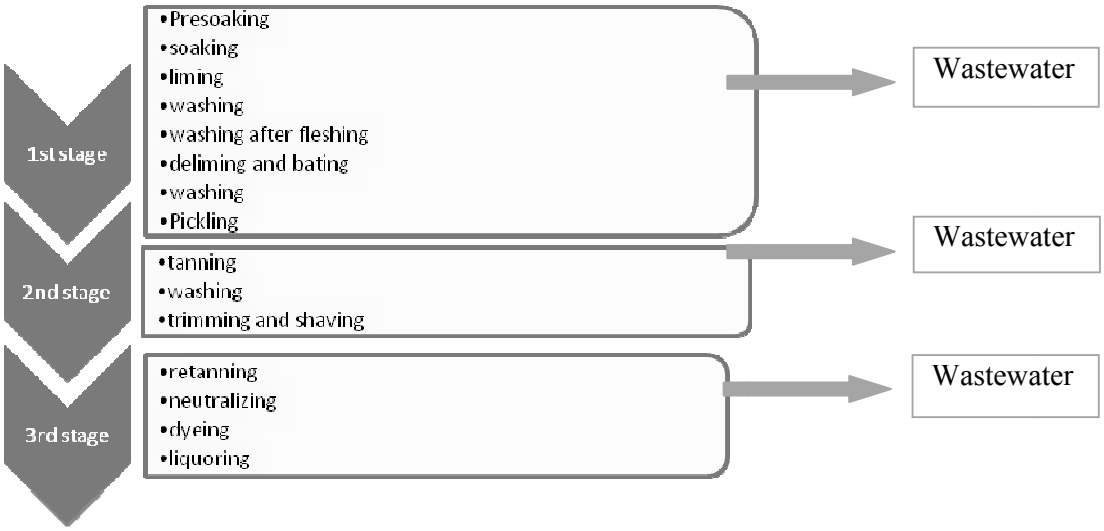


Figure 2.2 Sources of generated tannery effluent (Ros et al., 1998)

Among all the processes, tanning is the fundamental stage which confers to the final product (leather) its stability and essential features. The function of chromium salts in tanning processes is to form a protective layer in order to prevent the penetration of water inside the leather pores avoiding putrefaction. In order to obtain good quality leather, it is necessary to use 2 to 2.5% Cr_2O_3 relative to the mass of the skin (Rao et al., 2002). Chromium is the most employed substance during leather tanning because it presents the most appropriate product quality characteristics to cost ratio. Moreover, chrome tannin provides a great stability and light color to the resulting leather at relatively low costs; it is also distinguished by its processing speed (Fahim et al., 2006). However, in the chromium tanning process, the leather takes up only 60–80% of applied chromium, and the rest is usually discharged into the sewage system. In liquid tanning wastes, chromium ion occurs principally in its trivalent form Cr^{3+}. It is well known that the hexavalent form Cr(VI) is 500 times more toxic than the trivalent form but Cr(III) and Cr(VI) are easily interconvertible especially in alkaline medium and higher

temperatures (Fahim et al., 2006; Kowalski et al., 1994; Covarrubias et al., 2005; GilPavas et al., 2011).

Tanneries generate high strength wastewaters which vary widely in quality depending on the process technology adopted. In fact, the characteristics of tannery wastewater depend on the size of the tannery, the chemicals used in each process, the amount of water used and the type of the final product to be produced (Durai et al., 2011). Deepali et al. (2009) concluded in their comparative study, concerning the physico-chemical properties of tannery effluent discharged from tannery industry, that this effluent is highly contaminated with fluctuating pH and high temperatures and notoriously exceeding the values prescribed by the Standards of Environmental Protection Act. Therefore, treating tannery wastewater to meet discharge standards prior to disposal is a major challenge.

Treatment of tannery wastewater is carried out by physical or chemical or biological or combination of these methods. The performance of a given treatment process depends on the effluent composition while the selection of the appropriate process depends on the quality and requirements of the effluent, cost and environmental capabilities (Costa et al., 2009).

Novotny et al. (1989) and Eckenfelder (1989) reported that tannery wastewater cannot be discharged into public sewers without pretreatment, which should include screening and sedimentation supported by chemical coagulants. Song et al. (2000) proved that plain settling can greatly reduce the cost of discharging the effluent. They reported removal efficiency of 41.5% for COD, of 83.2% for chromium and of 76.1% for SS after three hours of plain settling. Tannery wastewater is typically characterized by deep color content; however, its toxicity is not limited to the aesthetic nature of

receiving streams, but mainly to the aquatic life. Therefore, considerable work has been carried out in the removal of color from tanning industry and adsorption seems to offer the best prospects and moreover, activated carbon is the most popular adsorbent even though it is expensive (Kadirvelu et al., 2000).

Physico-chemical processes are commonly used as pretreatment to or refining steps for biologically treated wastewater, or are used to treat a specific pollutant. Coagulation/flocculation is widely used in removing a wide range of impurities. The most commonly used coagulants are aluminum and iron-based salts. However, there is a discrepancy in affirming the best coagulant to be used. This can be referred to the fact that tanneries generate complexes that are widely varying depending on the process technology used. For instance, Song et al. (2004) reported that ferric chloride was a more efficient coagulant than alum in removing COD (30-37%), SS (38-46%) and color (86%). However, Haydar and Aziz (2009) reported that alum was the most suitable in reducing turbidity, TSS, COD and Cr with 98.7-99.8%, 94.3-97.1%, 53.3-60.9% and 98.9-99.7% respectively. They tested the efficiency removals achieved in treating tannery effluent with various metal salts; alum, ferric chloride and ferric sulfate. Ferric chloride and ferric sulfate generated blackish color when used as coagulant.

Since there is a consensus about the large sludge volume obtained with the application of metal salts, Haydar and Aziz (2009) presented an attempt to replace the latter with cationic polymers as alternatives. They showed that, at optimum dose of the suitable polymer and for pre-settled effluent, the percentage removals for turbidity, TSS, COD, and chromium were in the range of 94-96%, 69-83%, 25-29%, and 96-97% respectively. Moreover, the produced sludge was reported to be 60% less than that obtained when alum is used as coagulant. Haydar and Aziz (2009) investigated the

performance of cationic and anionic polymers as coagulant aids with alum as coagulant. The combination of cationic polymer with alum resulted in effluent turbidity removal of 97%, TSS removal of 93.5%, total COD of 36.2% and chromium removal of 98.4% versus turbidity removal of 99.7%, TSS removal of 96.3%, TCOD of 48.3% and Cr removal of 99.7% when anionic polymer is added to Alum. They achieved removal efficiencies of 64.3 %, 52.5%, 81.1%, 94.6%, and 98.5% for COD, BOD_5, SS, Cr and S^{2-} respectively using aluminum sulfate and anionic polyelectrolyte.

Conventional biological processes are based on the biodegradation, carried out by microorganisms, of organic matter resulting in additional biomass and carbon dioxide under aerobic conditions and a biogas under anaerobic conditions (Ryu et al., 2007a). Anaerobic biodegradation, though a slower process that is accompanied by unpleasant odors when compared to aerobic treatment, exhibits better performance in treating high strength tannery effluent (Duray et al., 2011). Moreover, anaerobic treatment is more preferable because it is less energy intensive (Durai et al., 2011; Mannucci A., 2010). However, both processes are employed in treating tannery wastewaters.

Lin et al. (1996) demonstrated that conventional aerobic biological processes such as activated sludge are unable to treat textile effluent. They reported that sludge bulking occurs when dyes, present in the effluent, come in contact with the microorganisms used in the process. Ates et al. (1997) showed in their study that only 20% of the total COD is biodegradable and that tannery effluents have a very low BOD_5/COD ratio. All these findings demonstrate that the biodegradability of the wastewater is low. However, the application of the activated sludge process (ASP) operated at a MLVSS concentration of 3500mg/L and aeration time of 12hrs to settled

tannery effluent resulted in 90% and 80% removal efficiencies for BOD and COD respectively. Application of conventional activated sludge treatment to physico-chemically pretreated wastewater recorded BOD_5 values of less than 25mg/L at volumetric loading of less than 2 g BOD_5/L/day, however nitrogen and sulfates concentrations remained high in the effluent (Roš M.et al., 1998). They also showed that the application of conventional activated sludge treatment to a mechanically pretreated wastewater is efficient when a long retention time (several days) is adopted. This combination results in BOD_5 removals ranging between 88% and 97%. The treatment of mechanically pretreated wastewater in a combined anaerobic-anoxic-aerobic reactor registered reductions in BOD_5 >99%, COD>93% and total N> 95% under conditions of long retention time in the reactor. Song et al. (2001) reported that conventional aerobic treatment carried out on supernatants from a coagulation process is effective but the volume of the sludge formed is about 5 times more than that from anaerobic treatment. Many researchers studied the treatment efficiency of the ASP and reported BOD_5 removals ranging between 90% and 97% for aerated and settled tannery effluents (Jawahar et al., 1998; Murugesan et al., 1994; Eckenfelder et al., 2002; Tare et al., 2003).

Anaerobic treatment processes do not require oxygen, produce biogas during the degradation of organic compounds and generate less sludge (Vijayaraghavan et al.,1997). Anaerobic treatments are mainly performed by anaerobic filter (AF) and upflow anaerobic sludge blanket (UASB) reactors (Mannucci et al., 2010). Reported data show that the removal of organic matter in anaerobic processes highly depends on (1) organic load rate, (2) hydraulic retention time (HRT), (3) inlet sulfate concentration, (4) operating temperature and (5) filling material (Mannucci et al., 2010). Rajasimman

et al., (2007) studied the effect of variations in organic loading rates on the achieved COD and BOD_5 removals. They reported COD and BOD_5 removal efficiencies ranging between 46-85% and 65-93% respectively for organic loadings ranging between 5-12 $Kg/m^3/d$. They also reported gas production varying between 2-15 L for the given organic load.

Literature review shows that biological processes are often considered inadequate in treating tannery effluents due the presence of toxic and recalcitrant compounds namely sodium sulphide, used in the dehairing stage, and chromium, used in the tanning stage (Tunay et al., 1994), and to deficiencies in nutrient elements essential for bacterial activity (Song et al., 2001; Chiesa et al., 1985).

Treatments of tannery wastewater that is normally highly loaded with organic and inorganic impurities have been effected thorough both conventional and advanced treatment processes, however, biological processes have not proved to be effective in reducing total dissolved solids (TDS). Advanced treatment techniques (ATT) include membrane separation processes, advanced oxidation processes (AOPs) and membrane bioreactors (Pophali et al., 2011). Amongst ATPs, the membrane separation processes are implemented to ensure complete removal of organic matter and dissolved solids so as to render the treated effluent suitable for reuse. Membrane technology comprises microfiltration, ultrafiltration, nanofiltration, and reverses osmosis. However, the major drawback of this technology is rapid scaling and fouling of membranes resulting in a reduction in flux rate and performance of the system. This is due to the organic pollutants present in tannery wastewater. De Gisi et al. (2009) tested on a pilot scale the removal efficiencies achieved by a combined system consisting of a conventional activated sludge process being a pre-treatment phase and a subsequent reverse osmosis

system. The reported removals included COD: 97.4%, ammonia and nitrate: 96.1% and 98.5% respectively, chloride: 98.8% and sulphate: 99.8%.

AOPs are gaining increased interest in light of the failure of conventional biological and chemical treatment processes in treating toxic and non-biodegradable materials present in tannery effluent (Schrank et al., 2005). They aim at mineralizing contaminant materials. Oxidation is mainly performed by ozone, hydrogen peroxide, Fenton, oxygen and air (Rameshraja et al., 2011; Song et al., 2001). Almost all AOPs are based on the generation of the strong and non selective hydroxyl radicals. Among these, ozone (O_3), being a powerful oxidant, has been extensively used in process industries. Many researchers published the improvements achieved in removing pollutants by integrating an ozonation stage to pre-existing conventional processes. Lopez et al. (1999) reported the efficiency of ozone in improving the biotreatability of recalcitrant effluents; their results indicated that during ozonation, COD decreases by about 50% however BOD_5 increases. They also reported that ozonation is distinguished by its no sludge generation and efficacy in improving the performance of a subsequent biological process.

Preethi et al. (2009) examined the potential of ozone for both color removal and organic reduction. They reported that the achievable COD removals varied between 20-70% depending on the initial COD effluent concentration. They also found that color removal efficiencies varied between 30-90% for the same aforementioned reason. Dogruel et al. (2004) investigated the impact of ozonation before, during and after biological treatment. They measured the reduction in COD for preliminary ozonated raw tannery sample to be in a range of 4 -10%. The highest COD removal efficiencies achieved were 21-34% when ozone was applied during the phase where it is not

competing with the biological treatment in removing biodegradable organic compounds (Jochimsen et al., 1997).

Di Iaconi et al. (2004) treated real tannery wastewater effluent by an integrated process combining a biological process to chemical oxidation using ozone in a sequencing batch biofilm reactor. They reported high efficiency removals of 97%, 98% and 99.9% for COD, ammonia and suspended solids respectively. The ozonation of a secondary treated tannery effluent resulted in color reduction of 76.5%, 84.3%, and 98% at pH values of 3, 7 and 12 respectively (Srinivasan et al., 2011). Also, a removal range of 33.9-34.9% was obtained for COD at pH 12and 3 respectively. Moreover, a maximum COD removal of 64% was registered in a sequential batch reactor (SBR) treating ozonated primary treated tannery effluent. Di Iaconi et al. (2009) reported the efficiency of treating tannery effluent by combining a sequencing batch biofilter granular reactor to an ozonation unit. This integrated system emitted an effluent that meets discharge limits for COD and surfactants and reduced the sludge production by 30 times.

Utset et al. (2000) tested the Fenton reaction, a cheap and easy to handle method, in wastewater treatment. Bae el al. (2004) showed in their study that the Fenton reaction involves two mechanisms; coagulation by ferric ion and oxidation by the OH radical. Moreover, Kang et al. (2002) concluded that in Fenton reaction, color removal was achieved by Fenton oxidation while COD removal was achieved by ferric coagulation. They determined ratios of H_2O_2/Fe^{2+} to be 5.6 for maximal color removal and 1.2 for maximal COD removal. Schrank et al. (2005) concluded in their study that the concentration of H_2O_2 and Fe^{2+} affects removal efficiencies; they also reported on a complete mineralization of COD and BOD_5. Dantas et al. (2003) evaluated the

efficiency of Fenton and Photo-Fenton processes in treating tannery effluent. They reported a decrease of 90% of organic matter in 4hrs. The Fenton process showed COD removal of 83% when1g/L of ferrous ions and 15g/L of H_2O_2 were added in a 3-hr reaction. The electro-Fenton process and electrochemical oxidation process were studied by Kurt et al (2007). They reported a 60-70% reduction in COD within 10 min. Mandal et al. (2010) reported the removal efficiencies achieved at a pH value of 3.5 and 30°C at 30 min reaction for COD, BOD_5, sulfide, total chromium and color to be 69%, 72%, 88%, 5% and 100% respectively. Blanco et al. (2012) compared the application of Fenton reaction and a combination of Fenton reaction and activated sludge and reported a maximal removal of 64% for TOC for the individual process and 92% for the combined process. Due to the fact that tanneries generate a wide range of pollutants, the optimization on pH, Fe^{2+} and H_2O_2 concentrations is critical in reaching maximal removal efficiencies.

Due to the instability of the quality of the raw tannery wastewater, many researchers tested the performance of various combinations of biological, physical and chemical treatment methods. The application of a combined process of physical or chemical with biological process to treat tannery wastewater would give satisfactory results compared to individual treatment processes. Song et al. (2001) investigated the coupling of coagulation with aluminum sulphate and ferric chloride coagulants to anaerobic digestion. The sole treatment with aluminum sulfate or ferric chloride as coagulants at pH 7.5 and an optimum dose of 800mg/L reduced COD, SS, chromium and color up to 32-36%, 64-69%, 77-99%, 85-86% respectively. Further treatment of the supernatant by anaerobic digestion revealed improvements in removal efficiencies

where additional removals of 62-64%, 12-19%, 20-31% and >95% for COD, SS, chromium and sulphide respectively.

Electrochemical methods for the treatment of wastewater attracted great attention after finding it to be effective in treating dyes/textile wastewater (Kim et al., 2002). Szpyrkowicz et al. (2005) carried out a study on electrochemical oxidation of tannery wastewater in an electrochemical reactor equipped with anodes based on noble metals and metal oxides from which they concluded that the rate of pollutant removal is significantly influenced by the type of anode material and electrochemical parameters. Electro-coagulation globally results in OH^- formation, as a consequence of the increase in pH during the operation. The EC process uses continuous current in order to form flocs of metal hydroxides by the electro-coagulation of soluble anodes. At the same time, gaseous H_2 is formed on the cathode, which helps the flotation of particles to the solution surface. Finally, the colloidal materials are agglomerated and removed by flotation or decantation (GilPavas et al., 2011). Feng et al., (2007) studied the electro-coagulation of tannery wastewater with soluble electrodes (mild steel electrodes and aluminum electrodes) at low cell current (< 1 A). The achieved removal efficiencies for COD, ammonia, total organic carbon, sulfide and color were 68%, 43%, 55%, 97% and 84% respectively. They reported that the type of electrode material used in the treatment process affects the removal of sulfides and color where mild steel electrodes removed over 90% of sulfide but produced typical black color precipitate versus aluminum electrode which resulted in better removals in terms of color but the maximum sulfide removal achieved was 12%.

Babu el al. (2007) and Zaroual et al. (2005) also studied the application of electro-coagulation to wastewater using sacrificial electrodes, iron as anode and

aluminum as cathode; they reported the removals of COD, BOD_5, TDS, Cr to be 40%, 28%, 43% and 60% respectively. They determined that power consumption and current density were the factors dictating the optimal conditions; the increase in flow rate and current density significantly increase the reduction of COD, BOD_5, TDS and chromium. Zongo et al. (2011) reported that the treatment performance depends on current density, time of treatment, metal concentration and loaded charge. They concluded that there are values beyond which no improvement is added and that the best registered removals achieved are 93-99% for color and 45-75% for COD. Murugananthan et al. (2004) studied the efficiency of electro-coagulation by testing the performance of soluble anodes of iron and aluminum and insoluble anode of titanium. Consumable anodes like iron or aluminum are advantageous to stable electrodes like titanium due to their ability in removing sulfur species (sulfide, sulfite and sulfate) and suspended solids. Sundarapandiyan et al. (2010) used graphite electrode for the electro-oxidation of tannery wastewater. They reported COD removals of 57.57%-59.73% at pH values of 3 and 5 respectively.

Apaydin et al. (2009) tested the efficiency of two electrochemical treatment processes in treating tannery wastewater; electro-coagulation (EC) and electro-Fenton (EF). They reported that the removal efficiency of the pollutants in the EF process was 10% higher than achieved the EC process accompanied by 20% reduction in energy consumption. However, Elsheikh et al. (2009) showed that electrode activity in an electro-coagulation process decreases due to the formation of a polymeric film on the surface; hence, the application of a physico-chemical pretreatment would be more efficient.

Naumczyk et al. (2005) investigated the electro-coagulation and coagulation with $FeCl_3$ followed by advanced oxidation processes. They reported that electro-coagulation resulted in slightly better removal than coagulation with 93-94% versus 85-88% reduction in COD. The combination of advanced oxidation process consisting of Fenton reaction to electrochemical treatment was investigated by Kurt et al. (2007). The best results achieved by this method were 70% for COD removal at pH 3 and 60% at pH 7.

Traditional methods for dealing with textile wastewater consist of various combinations of biological, physical and chemical treatment methods. In this context, Kim et al. (2002) studied the performance of a pilot scale plant combined process composed of biological pretreatment (fluidized biofilm), chemical coagulation ($FeCl_3.6H_2O$ at pH 6) and electrochemical oxidation (25mM NaCl of electrolyte concentration, 2.1mA/cm^2 current density and 0.7L/min as flow rate). They reported an overall removal of 95.4% and 98.5% for COD and color respectively. Di Iaconi et al. (2002) investigated the performance of an integrated process based on combining discontinuous biological degradation occurring in a sequencing batch biofilm reactor with chemical oxidation, performed by ozone. They reported that this integrated process is characterized by a low solids production, with average removal efficiencies of 97%, 98% and 99.9% for COD, NH_4-N and TSS respectively. Moreover, Vidal et al. (2004) applied a combined oxidative and biological treatment, using Fenton's reagent and an aerobic activated sludge treatment. Removal efficiencies of organic matter from raw unhairing wastewater reach up to 95%. Also**,** Ryu et al. (2007b) evaluated the performance of a biological treatment process consisting of an activated sludge system in treating tannery effluent following seawater flocculation. The overall removal for

COD was 75% at optimum conditions when pH was adjusted to 7 and PO_4-P was added according to the balanced ratio of COD to N to P as 100:5:1. The removal efficiencies by seawater of TSS, COD, TKN, NH_4^+-N, T-P and Cr^{6+} were higher than those achieved by ferric salt when seawater coagulation was used as coagulant.

De Gisi et al. (2009) carried out a study on the combination of a conventional activated sludge as pre-treatment process followed by a physico-chemical process (using a polymer as coagulant) and a pilot scale reverse osmosis unit. They obtained satisfactory results in terms of wastewater reuse criteria in the tannery production cycle. Raghu et al. (2007) concluded that the application of chemical or electrochemical techniques followed by ion exchange system was effective in removing COD, color, conductivity, alkalinity and total dissolved solids. Chemical coagulation showed a maximum COD reduction of 81.3% while electro-coagulation, using iron and aluminum electrodes, showed a maximum reduction of 92.31% at current 0.25A/dm^2 with energy consumption 19.29KWh/kg of COD and 80% at current 1A/dm^2 with energy consumption 130.095KWh/kg of COD for the electrodes respectively.

Every tannery wastewater is unique in quality depending on the process technology and chemicals added, therefore, the selection of the appropriate treatment process presents a major challenge. Each treatment process should be validated experimentally prior to be applied to any effluent. In this study, separate and combined conventional treatment techniques are investigated. Knowing that chemical treatment systems can accommodate variable input loads and flows as well as intermittent and complex discharges, coagulation/flocculation using bittern as coagulant was performed in this research. The obtained results were compared to the performance of alum and ferric chloride as coagulants. And since chemical oxidation is recommended to meet

stringent effluent limitations especially for wastewaters with high COD and color levels, ozonation and Fenton reaction were tested prior and after coagulation. A finishing step consisting of adsorption through activated carbon was coupled to the whole process. It should be noted that the reviewed literature did not show similar studies where comparable wastewater characteristics and treatment sequences were investigated.

CHAPTER 3

MATERIALS AND METHODS

3.1 Wastewater

The current research involved sampling and analyzing wastewater effluent generated from the largest operating tannery in Lebanon over an average period of two years. The tannery is located at Wadi Shahrour, in Mount Lebanon. This tanning factory is fully equipped to transform raw hides into leather. The collected effluent used in this study had undergone a primary mechanical treatment consisting of a consecutive passage through a medium screen followed by a micro-screen (Figure 3.1& Figure 3.2).

Figure 3.1 Medium-sized screen

Figure 3.2 Micro-screen

A total of 25 samples were collected and analyzed for the following parameters: TSS, TDS, COD, conductivity, pH, apparent color, turbidity, total phosphorous, total nitrogen, BOD_5, sulfide, arsenic and chromium. Table 3.1 depicts the characteristics of raw wastewater monitored over the two years and the stated Environmental Limit Values. All of the samples were collected at 10:00-11:00 AM while one sample was collected throughout a working day (from 8:00AM-5:00PM) then mixed all together and reported to characterize the tannery wastewater.

Table 3.1 Characteristics of the tannery wastewater and standards for discharge in a body of water

Parameter	Unit	Range	mean± standard deviation	ELV for existing facilities
pH		5.42-11.33	8.26± 1.95	6-9
TDS	mg/L	3710-9580	5922±1770	-
Conductivity	µs/cm @ 25°C	7420-19140	11830±355	-
TSS (mg/L)	mg/L	490-4995	2193±1417.25	60
Apparent color	mg/L Pt-Co	4175-33500	17018±9323	-
Turbidity	NTU	355-5800	1856±1544	-
Total phosphorous (P)	mg/L	4-20.5	8.68±4.24	10
Total phosphorous $(PO4)^{3-}$	mg/L	12.5-63	26.56±12.52	-
Total nitrogen	mg/L	180-665	322±138.6	30
Sulfides	mg/L	0.443-2.09	0.51±0.06	1
COD	mg/L	1990-8460	4311±1818	125
BOD_5	mg/L	490-2226	1072±497	25
Cr	mg/L	35.42-761.22	306±254	2
As	mg/L	0.004-6.87	1.21±1.83	0.1

Prior to sampling, the appropriate gallons are rinsed two to three times with the effluent collected from the disposal drain. A volume of 20 to 40 liters was collected for each batch and transported immediately to the lab to avoid any possible deterioration in the effluent quality (Figure 3.3). Once the pH and the temperature are recorded, the

remaining sample is prepared for further tests and analyses. Sample preparation methods include raising/lowering the pH, filtration, digestion and/or oxidation.

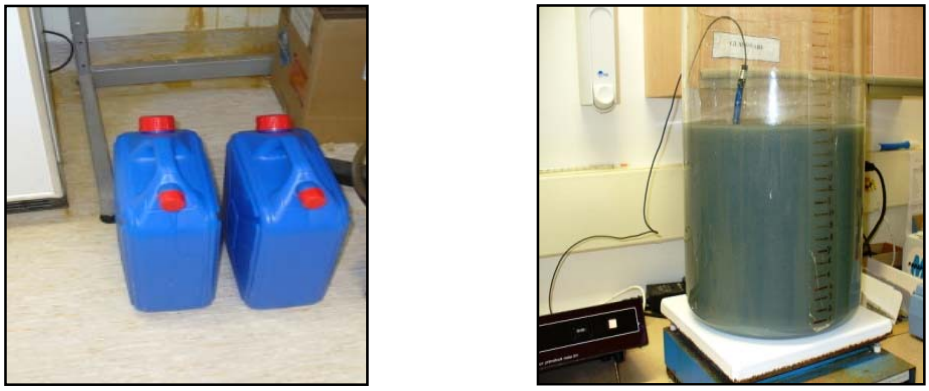


Figure 3.3 Sample of collected wastewater

3.2 Coagulant used

The coagulant, bittern, was obtained from the solar evaporation of seawater from an initial volume and density of 125 L and 1.027 kg/L, respectively, to a final volume and density of approximately 1.3 L and 1.2705 kg/L. The seawater was collected from the Eastern Mediterranean Sea from the beach facing the American University of Beirut (AUB) campus. The evaporation process was carried out using an array of metallic pans installed on the roof of Raymond Ghosson Building (RGB) and in accordance with the criteria and critical density indices reported by (Ayoub et al., 2001). In the course of the solar evaporation process, deposition of calcium salts ($CaCO_3$ and $CaSO_4$) took place in the first pan. Crystallization and settling out of large portions of the NaCl present in the seawater occurred in the second pan, thus ending the evaporation process.

The produced magnesium-rich liquid bittern was collected and stored in a 1.5-L polyethylene container at room temperature to be used later as the source for the magnesium hydroxide coagulant.

Table 3.2 Physico-chemical characteristics of the liquid bittern produced

Parameter	**Measured value**
pH	6.67
Specific gravity	1.27
TDS (mg/L)	$342x10^3$
Conductivity (ms)	108.6
Ca^{2+} (mg/L)	0
Mg^{2+} (mg/L)	$53.6x10^3$
Cl^- (mg/L)	$222.5x10^3$
SO_4^{2-} (mg/L)	$46.3x10^3$

The concentration of Mg^{2+} in the bittern, available for the formation of $Mg(OH)_2$, amounted to 53600 mg/L. The use of bittern as a coagulant required raising the pH of the wastewater to levels of around 11.3 being the optimal pH around which $Mg(OH)_2$ will operate most effectively (Haydar and Aziz 2009; Ayoub et al. 1999). The pH was raised using a stock solution of lime [$Ca(OH)_2$], which by itself induces settling and which was prepared by dissolving 5 g of CaO powder supplied by PDH Limited, Poole, England in 100 mL of distilled water.

Aluminum sulfate and ferric chloride used in the comparative evaluation with bittern were laboratory grade $Al_2(SO_4)_3.18H_2O$ supplied by MERCK and $FeCl_3$, Iron III chloride anhydrous supplied by BDH Laboratory Supplies.

3.3 Adsorbent

The adsorbent used is commercial coconut-shell-based granular activated carbon, AquaSorb CS supplied by Jacobi Carbons AB, Sweden, with the following characteristics: Iodine number: 1050 mg/g; BET surface area: 1100m^2/g; total pore volume: 0.62 cm^3/g; and apparent density: 510 kg/m^3. The AC was packed in columns consisting of acrylic plastic tubes (Figure 3.4).

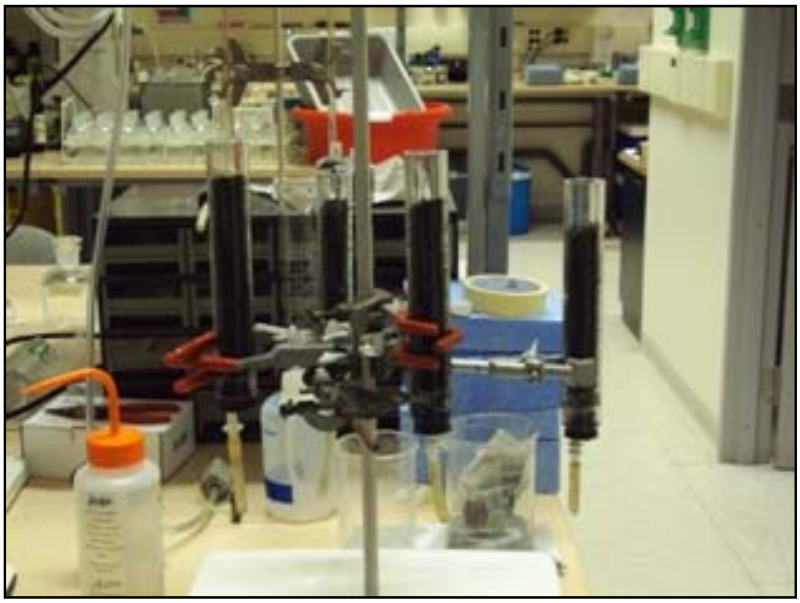


Figure 3.4 AC packed in acrylic plastic tubes

3.4 Oxidation processes

3.4.1 Ozonation

Ozone is well known to be a powerful oxidant that has been extensively used in various industries at various levels to remove the organic and inorganic content present in the wastewater through a single step without generating an extra sludge (Preethi et al., 2009; Pophali et al., 2011). The ozone generating equipment system used in this research involves a “Corona Discharge Ozone Generator Microzone 300” supplied by

Clear Water Tech,LLC, California, USA, that generates 300 mg/hr of ozone gas and is equipped with a variable supply control. The air supply to the generator was done using an air pump model AC-9902 supplying air at a value of 3.5L/min at a pressure of 0.012Mpa and as supplied by Resun, Shenzhen, China**.** A diffuser stone coupled to the generator through a plastic hose was used to deliver the ozone to the tested sample. A batch of 25-30L of raw wastewater was used as the main feed to the individual test performed after oxidation for a period of 1:30-2:00 hrs with ozone at a feed rate of 300mg/hr (Figure 3.5). All experiments were conducted at room temperature (25±1 °C) and at the original pH of the effluent.

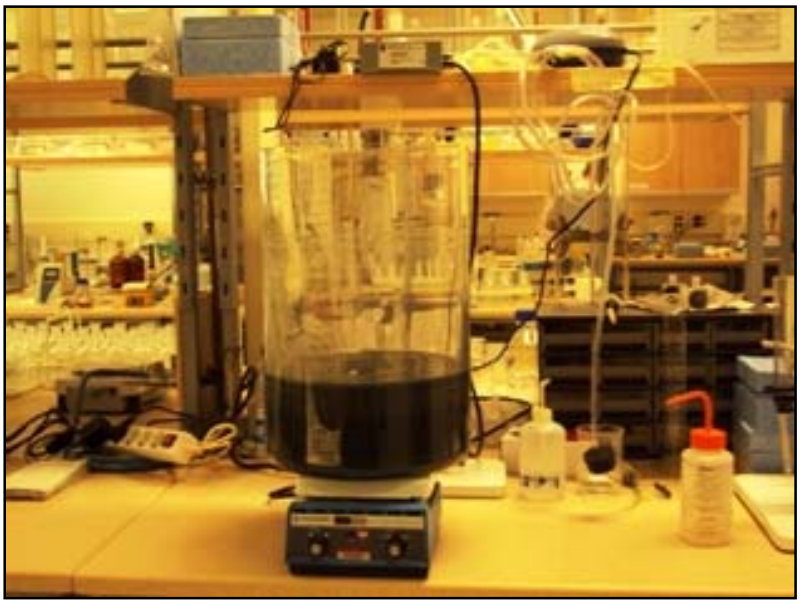


Figure 3.5 Ozone generator

3.4.2 Fenton Reaction

The Fenton process is considered to be one of the most efficient AOPs. It is based on an electron transfer between H_2O_2 at 30% concentration and a catalyst, most commonly used is Fe^{2+} (from ferrous sulfate heptahydrate) as depicted in the following equations:

$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + {}^{\cdot H}O_2 + H^+$

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH$

$H_2O_2 + OH^{\cdot} \rightarrow H_2O + {}^{\cdot}O_2H$

${}^{\cdot}O_2H \leftrightarrow {}^{\cdot}O_2^- + H^+$

$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^-$

${}^{\cdot}O_2H + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2$

${}^{\cdot}O_2H + Fe^{2+} \rightarrow Fe^{3+} + HO_2^-$

$Fe^{3+} + {}^{\cdot}O_2^- \rightarrow Fe^{2+} + O_2$

$Fe^{2+} + {}^{\cdot}O_2^- \rightarrow Fe^{3+} + H_2O_2$

${}^{\cdot}O_2H + {}^{\cdot}O_2^- \rightarrow O_2 + H_2O_2$

$PCP + {}^{\cdot}OH \rightarrow$ by-products (1)

by-products (1)$+ {}^{\cdot}OH \rightarrow$ byproducts (2) (Zimbron.A et al., 2009)

The Fenton reactions were carried out over a period of 2 h in jars of 2000 mL capacity. The reaction mixture inside the reactor, consisting of 2000 mL of tannery effluent at pH 3.5, was continuously stirred. The H_2O_2/Fe^{2+} and H_2O_2/COD ratios adopted were 9 and 4, respectively as recommended by Vidal et al. (2004).

3.5 Experimental Setup

The experimental study comprised a series of tests in which coagulation/

flocculation, oxidation (through ozone or Fenton reaction) and adsorption were conducted individually or in combination under controlled laboratory conditions using a standard six-jar test apparatus (model 300) obtained from Phipps and Bird, Inc, Richmond, Virginia (Figure 3.6). As for adsorption, several dimensional acrylic plastic columns of 25mm inner diameter were used to receive jar test supernatants from each of the jars that underwent coagulation/flocculation/settling. Also, the effect in variation of the total AC bed height was also investigated by allowing the flow of 200 mL of the adsorbate solution which was obtained after the jar test showing the highest removal in terms of TSS (Figure 3.7). Table 3.3 presents the depth of the tested AC beds, the corresponding loading rates and the dry mass of required AC.

Table 3.3 Depth and dry mass of the tested AC beds

Depth of AC bed (cm)	**10cm**	**15cm**	**20cm**	**35cm**	**40cm**	**45cm**
Dry mass of AC (g)	25	40	49	91	105	117
Loading rate ($WWcm^3/ACcm^3$)	4.08	2.72	2.04	1.16	1.02	0.91

Before starting the experimental part, the bed in use was rinsed by deionized water up through the column and the first 10 mL of the filtered samples were discarded to avoid any residual impurity in the AC.

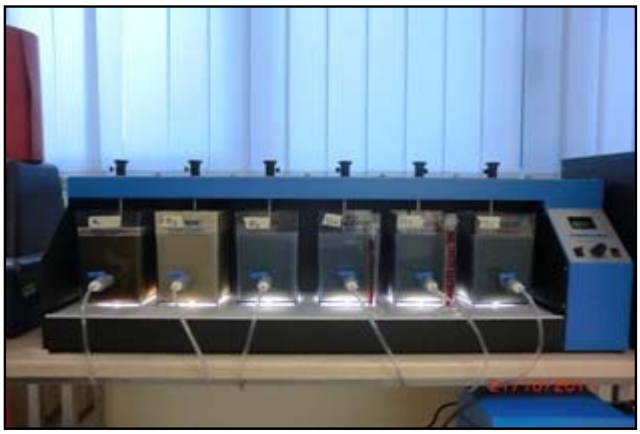


Figure 3.6 Jar test apparatus

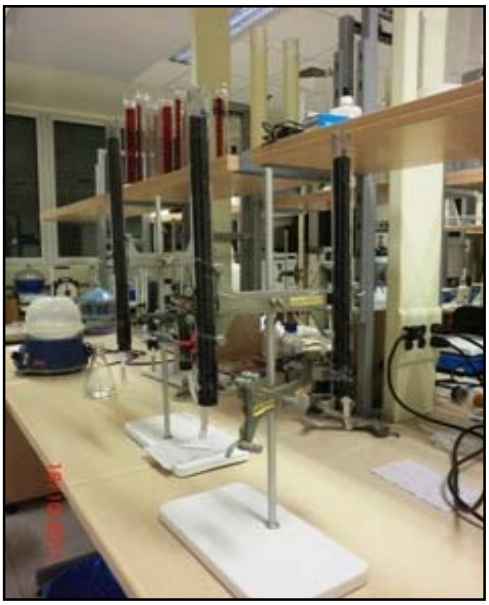


Figure 3.7 AC columns

3.6 Testing Procedure

Twenty five sets of experiments were conducted in which an average of quintuplicate was performed for each test. All of the tests underwent coagulation/ flocculation and/or oxidation as well as adsorption treatment. A separate set was conducted for comparison on the coagulation treatability of the wastewater using $Al_2(SO_4)_3$, $FeCl_3$, and bittern. Only two parameters were evaluated for the latter set, namely, TSS and BOD. In this set pH adjustments were made to arrive at the optimal pH for the different coagulants, where the pH was raised from a value of 7.3 to 7.5 using lime for both alum and ferric chloride. For the jar experiments, aliquots of 1.0 L of the tannery wastewater were transferred in succession to the six jars where the first jar was used as a control and the other five jars were alkalized using $Ca(OH)_2$ to a pH of 11.3±0.1. Bittern doses of 5, 10, 15, 20 and 25 mL/L were added respectively. The jar test was then conducted by operating the stirrers for flash mixing at a G of 135 s^{-1} for one minute. The speed of the stirrers was then reduced to impart a G of 23 s^{-1} for 20

min to allow flocculation to take place. The multiple stirrers were then stopped for a 30-minute quiescent settling period, followed by carefully decanting 500 mL of clarified supernatant from each of the six jars to be used for the measurement of the selected parameters and to carry out the adsorption tests. The adsorption test was conducted by passing 200 to 250 mL of the settled effluent through the column packed with granular activated carbon and the effluent collected for re-measurement of the selected parameters. Oxidation with Fe^{2+} and H_2O_2 were carried out using a standard jar test apparatus. The oxidation experiments were conducted in 2000 mL jars. All single and combined sequences were tested and all tests were conducted at a temperature of 25±1 °C as illustrated in the table 3.4

Table 3.4 Tested sequences

Tested sequences	**Experimental conditions**			
Sequence No.1: **Jar test** Aim: compare efficiency removals using Alum, Ferric chloride and bittern	Jar test No.1 -Raw sample (control) -Beaker1 (raw sample undergoing jar test) -Beaker 2 (raw with adjusted pH to 7.5 undergoing jar test) Beaker 3, 4, 5 and 6 (raw with adjusted pH to 7.5 with different Alum doses)	Jar test No.2 -Raw sample (control) -Beaker1 (raw sample undergoing jar test) -Beaker 2 (raw with adjusted pH to 7.5 undergoing jar test) Beaker 3, 4, 5 and 6 (raw with adjusted pH to 7.5 with different ferric chloride doses)	Jar test No.3 -Raw sample (control) -Beaker1 (raw sample undergoing jar test) -Beaker 2 (raw with adjusted pH to 11.3 undergoing jar test) Beaker 3, 4, 5 and 6 (raw with adjusted pH to 11.3 with different bittern doses)	Tested parameters: BOD_5 TSS
Sequence No.2 **Jar test→ AC adsorption** Aims: 1-evaluate the efficacy of bittern as a coagulant 2- evaluate the removal efficiencies achieved when chemical treatment (jar test) and adsorption (AC) are combined	1st stage: -Equalization of the tannery wastewater in 50L beaker capacity using a magnetic stirrer -aliquot of 1liter was transferred without any further treatment (Raw) - aliquot of 2 liters was transferred to undergo jar test (Beaker 1)	2nd stage: -The remaining tannery wastewater underwent pH raise to 11.3±0.1. Aliquots of 2 liters are then transferred to beakers to undergo jar test (Beaker2, 3, 4, 5 and 6) Beaker 2, 3, 4 , 5 and 6 contain alkalized wastewater with different bittern doses	3rd stage: -Once the jar test is performed, raw sample and supernatants from beaker 1-6 were subjected to adsorption through granular AC columns - Each sample was allowed to pass by a different column in order to avoid clogging and/or release of adsorbate from the carbon bed.	Tested parameters Raw sample, supernatants from jar test and samples after carbon adsorption were characterized for the following parameters: TSS, TDS, conductivity, pH, apparent color, turbidity, COD, BOD5, TN, TP, Cr and As
Sequence No.3 **Ozonation→ Jar test→AC** Aims: 1- test for removal efficiencies when tannery wastewater was ozonated. 2-evaluate the removal efficiencies achieved when tannery wastewater was oxidized (with ozone) then underwent jar test and finally subjected to carbon adsorption	1st stage: -Equalization of the tannery wastewater in 50L beaker capacity using a magnetic stirrer -aliquot of 1liter was transferred without any further treatment (Raw) - remaining sample was oxidated with ozone for 1:30-2:00hrs, then aiquot of 1L from the oxidized sample was removed (Raw oxi)	2nd stage: -Aliquot of 2 liters was removed and referred to as Beaker 1. - remaining sample was alkalized to ph=11.3 - aliquots of 2 liters were transferred after ozonation to the jar test (Beaker2, 3, 4, 5 and 6), then different doses of bittern were added	3rd stage: -after the jar test, raw, raw oxi, beaker 1-6 were subjected to carbon adsorption	Tested parameters Raw sample, oxidized raw, supernatants from jar test and samples after carbon adsorption were characterized for the following parameters: TSS, TDS, conductivity, pH, apparent color, turbidity, COD, BOD5, TN, TP, sulfides, Cr and As

<table>
<tr>
<td>Sequence No.4
Jar test→ ozonation→ AC
Aims: 1- test for removal efficiencies when ozonation is performed after Jar test
2-evaluate the removal efficiencies achieved when tannery wastewater was chemically treated (Jar test) then oxidized and finally subjected to carbon adsorption</td>
<td>1st stage:
-Equalization of the tannery wastewater in 50L beaker capacity using a magnetic stirrer
-aliquot of 1liter was transferred without any further treatment (Raw)
-aliquot of 2 liters was transferred to jar test (beaker 1)
- remaining sample was alkalized to pH=11.3
-aliquots of 2 liters, once alkalized, were subjected to jar test. Different doses of bittern were tested.</td>
<td>2nd stage
-after coagulation/ flocculation/settling, supernatants were oxidized individually.</td>
<td>3rd stage
once underwent jar test followed by ozonation, raw, B1-B6 were subjected to carbon adsorption</td>
<td>Tested parameters
Raw sample, supernatants from jar test and samples after carbon adsorption were characterized for the following parameters: TSS, TDS, conductivity, pH, apparent color, turbidity, COD, BOD5, TN, TP, Cr and As</td>
</tr>
<tr>
<td rowspan="2">Sequence No.5
a-Fenton reaction→ jar test→AC
b-Jar test→Fenton reaction→ AC

Aim: 1- to test, on the same tannery wastewater sample, the efficiency to Fenton reaction before and after the jar test.</td>
<td rowspan="2">1st stage:
-Equalization of the tannery wastewater in 50L beaker capacity using a magnetic stirrer
-Aliquot of 1 L was transferred, without any further treatment (Raw)</td>
<td colspan="2">Tested Matrices</td>
<td>Tested parameters</td>
</tr>
<tr>
<td colspan="2">1-Raw+ pH(3-3.5) +H_2O_2+ settling
2-Raw+ pH (3-3.5)+ H_2O_2+$FeSO_4$ + settling
3-Beaker with optimum dose of bittern
4-Ozone oxidation+ jar test with optimum dose of bittern
5-Raw + pH(3-3.5)+ H_2O_2 then pH raised till 11.3+ addition of optimum dose of bittern
6-Raw + pH(3-3.5)+ H_2O_2+ $FeSO_4$ then pH raised till 11.3+ addition of optimum dose of bittern
7-jar test with optimum dose then ozone oxidation
8-jar test with optimum dose then Fenton reaction</td>
<td>TSS, TDS, conductivity, pH, apparent color, turbidity, COD, BOD5, TN, TP, Cr and As</td>
</tr>
</table>

3.7 Analytical Procedure

The influent and effluent quality parameters including pH, turbidity, TSS, TDS, apparent color, conductivity, COD, BOD5, total phosphorus, total nitrogen, sulfide, chromium, and arsenic were determined according to Standard Methods (APHA/AWWA/WEF, 2005) using methods as shown in Table 3.5.

Table 3.5 List of analyzed parameters and adopted analytical procedures

Parameter	Type of Analysis	Analytical Instrument	Reference Method
pH	Electrometric	ORION RESEARCH Microprocessor pH/ millivolt meter 811, USA	SM 4500-H^+ B
Turbidity	Nephelometric	MONITEK NEPHELOMETER Model 21, USA	SM 2130B
TSS	Gravimetric	Fisher Scientific Model 655G / Voyager OHAUS V12146	SM 2540D
TDS	Electrometric	Cole Parmer Model# 19820-10, USA	SM 2510B
Apparent color	Colorimetric, Pt-Co	HACH DR/2010 Portable Datalogging Spectrophotometer, USA	SM 2120C
Conductivity	Electrometric	Cole Parmer Model# 19820-10, USA	SM 2510B
COD	Colorimetric	HACH DR/2010 Portable Datalogging Spectrophotometer / HACH heating COD Reactor,USA	SM 5220D
BOD_5	Membrane electrode	WTW Oxi 538, Germany	SM 5210B
Total Phosphorous	Persulfate digestion/ Colorimetric	HACH DR/2010 Portable Datalogging Spectrophotometer / HACH heating COD Reactor,USA	SM 4500-P-B(5),E
Total Nitrogen	Colorimetric/ Persulfate digestion	HACH DR/2010 Portable Datalogging Spectrophotometer / HACH heating COD Reactor,USA	HACH N° 10072
Chromium	AAS-flame	THERMO ELECTRON CORPORATION M-SERIES, USA	SM flame 3111
Arsenic	AAS-GF	THERMO ELECTRON CORPORATION GF 95 Graphite Furnace	SM GF 3113

CHAPTER 4

RESULTS AND DISCUSSION

As mentioned earlier, the tannery industry is classified among the industries with the highest water requirements. The restricted availability of water, rising costs of wastewater discharge and stringent discharge regulations make it necessary to introduce treatment techniques to purify tannery effluents in order to recycle process water or at least to reduce its loaded impurities. The performance of coagulation/ flocculation, using different types of coagulants, combined with an advanced oxidation process performed by ozone or Fenton reaction is presented in this section. Also, the added efficiency of adsorption treatment onto activated carbon was investigated and reported herein.

4.1 Wastewater Characterization

The results of the wastewater characterization as well as the National effluent concentration standards to be complied with before discharge in a body of water (MoE, 2001) are presented in Table 3.1. As expected, the composition of the raw wastewater may be classified as strong. It is highly loaded with organic matter and has strong color, turbidity, arsenic and chromium contents which by far exceed the stated environmental limits. As mentioned previously, its composition varied continuously depending on the type of hides/skins being processed, the added chemicals and the tanning process adopted. The BOD_5/COD ratio was determined to be $0.248 \pm 8 \times 10^{-3}$ indicating a wastewater of low biodegradability (Ahn et al., 1999). It is established that the optimum ratio of COD: N: P for a biological treatment should be 100:5:1 (Tchobanoglous et al.,

1991). However, as noted from the table 3.1 a ratio of 100:30:0.8 reflects a high nitrogen content and a deficient phosphorous value.

4.2 Jar tests

4.2.1. Comparison of alum, ferric chloride and bittern as coagulants

Coagulation/flocculation is the most suitable process for removing suspended particles from wastewater and consequently enhances the effectiveness of subsequent treatment processes. Since aluminum and ferric salts are reported to be the most commonly used coagulants in treating industrial wastewater, it was deemed necessary to test their performance in treating the wastewater of the tannery under study. Upon the addition of ferric chloride, a blackish color was developed (Figure 4.1). This reaction was attributed to the formation of FeS (Haydar et al., 2009). By visual comparison with alum-coagulated samples (Figure 4.2) bittern was found to surpass both ferric chloride and alum (Figure 4.3). Numerically, almost equal removal efficiencies were attained for TSS and BOD_5 when using the three coagulants (Figure 4.4a & 4.4b). Maximal recorded removals ranged between 94 and 100% for TSS and 40% for BOD_5.

Figure 4.1 Tannery effluent treated with $FeCl_3$

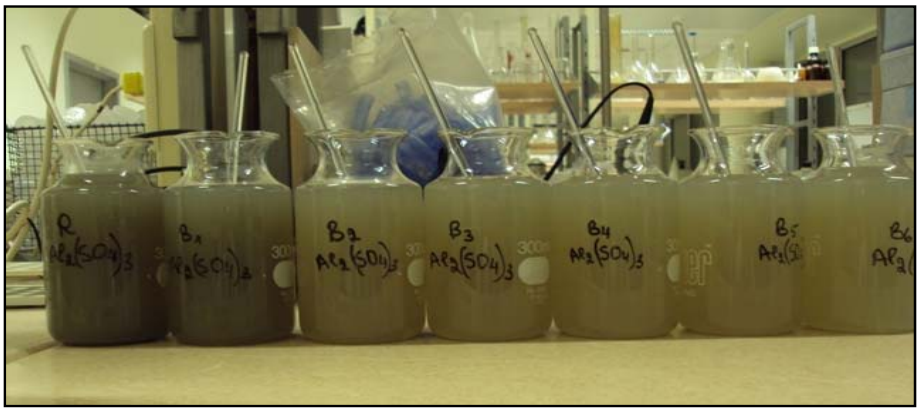


Figure 4.2 Tannery effluent treated with Alum

Figure 4.3 Tannery effluent treated with bittern

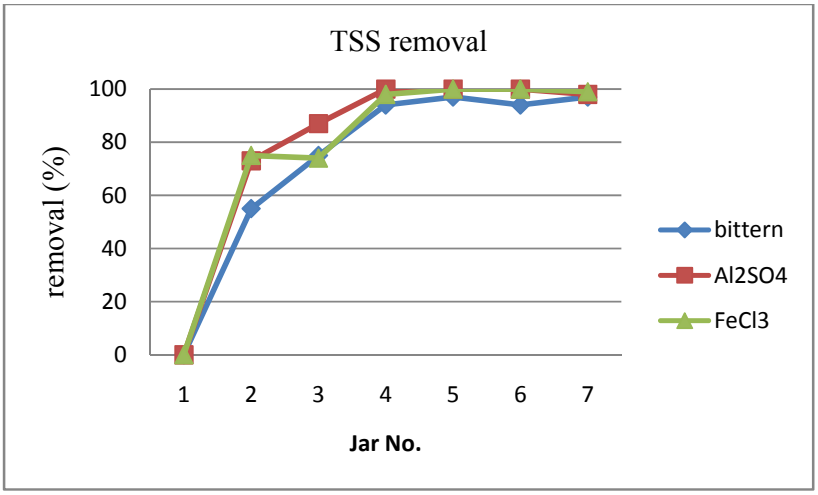


Figure 4.4a TSS removals using different coagulants

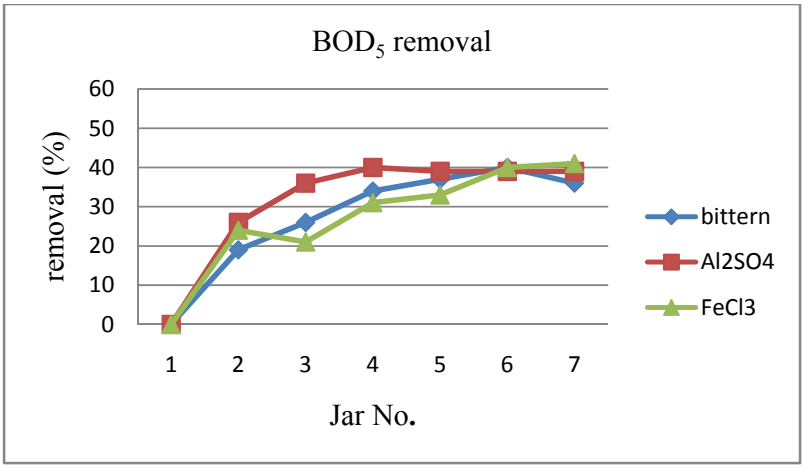


Figure 4.4b BOD_5 removals using different coagulants

4.3 Advanced oxidation processes

AOPs are chemical oxidative treatment technologies that aim at generating the non selective but powerful oxidant OH radical (Gulyas et al., 1997). This process can be used to transform recalcitrant organic impurities to biodegradable compounds.

4.3.1 Ozonation

The sole application of ozonation in treating tannery wastewater did not show any removal efficiency, on the contrary, negative results were obtained for most of the measured parameters except for arsenic in which a reasonable removal of 58.2%±19.92 was recorded (Table 4.1).

Table 4.1 Removal efficiencies for different parameters when ozone oxidation is performed

Parameter	**average ± SD**	**Parameter**	**average ± SD**
TSS	-12% ±27.35	TP	-3.4%±12.3
Apparent color	-1%±12.23	TN	-10.6%±15.63
Turbidity	-12.25%±5.62	Sulfides	5%±0.001
COD	-1.8±7.66	Cr	3.6%±18.8
BOD	-7.8%±15.02	As	58.2%±19.92

4.3.2 Ozonation + AC

The effect of combining ozone oxidation with adsorption onto activated carbon was studied. It was found that parametric removals were enhanced appreciably especially for As where removal efficiency of 77.25% was recorded. The removal percentiles are given in Table 4.2.

Table 4.2 Removal efficiencies for different parameters when ozone oxidation is coupled to AC adsorption

Parameter	Average	Parameter	Average
TSS	60.75%	TP	16.8%
Apparent color	24%	TN	26.2%
Turbidity	44.75%	Sulfides	-
COD	38.80%	Cr	54%
BOD	32%	As	77.25%

4.3.3 Ozonation followed by alkalization

Tannery wastewater was oxidized for 5 min followed by pH adjustment. The increase in pH was performed by adding lime, CaO (5%) as $Ca(OH)_2$ until reaching a value of 11.3±0.1. Removal efficiency measurements were conducted to determine the impact of the combined effect of ozonation and alkalization. As depicted from Table 4.3, very minor improvement is noted as a result of alkalization.

Table 4.3 Removal efficiencies for different parameters when ozone oxidation is coupled to alkalized tannery effluent

Parameter	Removal (%)	Parameter	Removal (%)
TSS	-41%	TP	-3%
Apparent color	8%	TN	6%
Turbidity	-23%	Sulfides	-
COD	1%	Cr	4%
BOD	-9%	As	61%

4.3.4 Ozonated/alkalized sample followed by AC adsorption

The efficiency of adsorbing pollutants of pre-oxidized/alkalized tannery wastewater onto AC was also investigated. In general reduced removal efficiencies were recorded as compared to the combined effect of ozonation/ adsorption. Except for higher removal efficiency for As from 77.25 to 83% all the remaining parameters recorded lower efficiencies. The improvement in As removal is attributed to the fact that arsenic, when oxidized to arsenate, exhibits higher removal efficiencies. A marked reduction is noted for TSS, apparent color and turbidity. This is attributed to the suspended solids introduced by the addition of lime.

Table 4.4 Removal efficiencies for different parameters when ozonated/alkalized effluent is coupled to AC adsorption

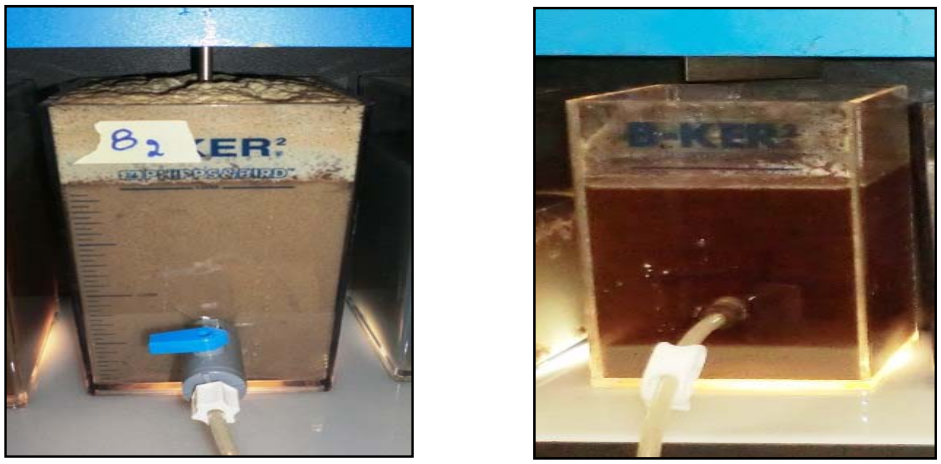
	Removal (%)	**Parameter**	**Removal (%)**
TSS	-28%	TP	16%
Apparent color	16%	TN	39%
Turbidity	21%	Sulfides	-
COD	30%	Cr	17%
BOD	16%	As	83%

The aforementioned test results showed that ozonation followed by adsorption through activated carbon was practically the most efficient in terms of TSS (60.75%), apparent color (24%), turbidity (44.75%), COD (38.8%), BOD_5 (32%) and Cr (54%) removals. It was noticeable that increased removal efficiencies of arsenic were obtained in all scenarios comprising ozone oxidation ranging between 58.2-83%. The obtained results demonstrate the effectiveness of the ozonation treatment in enhancing the biodegradable portion of the solids in the tannery wastewater as BOD_5 slightly increases while COD decreases. Also, low color removals can be related to the lower pH values

under which the activity of adsorption as well as oxidation by ozone is reduced (Srinivasan et al., 2009; Preethi et al., 2009).

4.3.5 Fenton Reaction

Fenton process is an oxidative degradation process in which hydroxyl radicals are the main oxidizing species (Sillanpaa et al., 2001). This process is based on the transfer of electrons between peroxide and a catalyst, mainly a metal ion such as Fe^{2+}, with the reaction taking place under acidic conditions at pH 3-3.5 (Kang and Hwang., 2000). The application of Fenton reaction to tannery effluent after lowering the pH by the addition of H_2SO_4 showed removal efficiencies of 95% ,97% , 84%, 48%, 66% , 62% and 74 for TSS, turbidity, COD, TN, BOD, Cr and As respectively. It should be noted that treated tannery effluent presented minor improvements in its color. Bae et al. (2004) reported that the improvement in the quality of the wastewater effluent is due to a combined factor; the first is through ferric coagulation and the second is a result of the oxidation by the OH radical. A better COD removal with a value of 84% was achieved compared to that presented by Bae et al. (67.7%). However, as noted before, the direct contact of Fe with the wastewater resulted in the formation of a blackish color. The relatively high removals can be attributed to the double role of iron as a coagulant and as a catalyst in the oxidation process (Figure 4.5).



(a) During oxidation (b) After oxidation

Figure 4.5 Application of Fenton reaction to tannery effluent

4.4 Sequences in treating tannery wastewater

Several methods have been developed to treat tannery wastewater. However, because of the complexity of the wastewater, no one single method could successfully be adopted. A combination of these methods was found necessary to achieve proper treatment.

4.4.1 Jar test with bittern + AC

Tannery wastewater was subjected to jar test followed by adsorption onto AC. Table 4.5 summarizes the experimental condition for each jar and the measured parameters were averaged. Graphs representing the variation of the percent removals with variable coagulant concentrations and adsorption are presented in figure 4.6-4.14. It is to be noted that the x-axis denotes Jar numbers ranging from 1 to 7 containing different doses of bittern.

Table 4.5 Experimental conditions (Jar test + AC)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7
Sample	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater
pH adjusted to 11.3±0.1	no	no	yes	yes	yes	yes	yes
Bittern volume, ml	0	0	0	5	10	15	20
Jar test	no	yes	yes	yes	yes	yes	yes

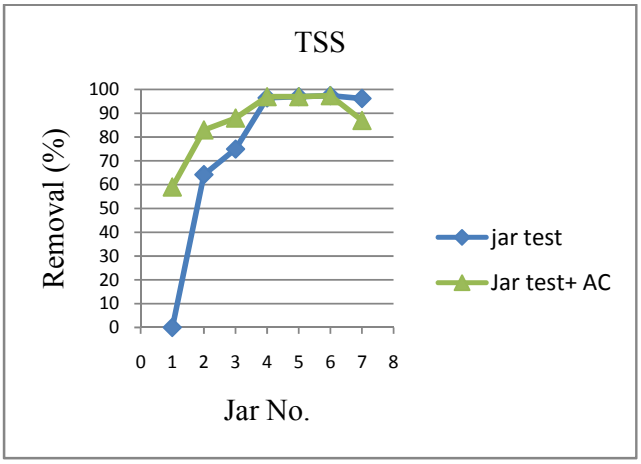


Figure 4.6 TSS removals

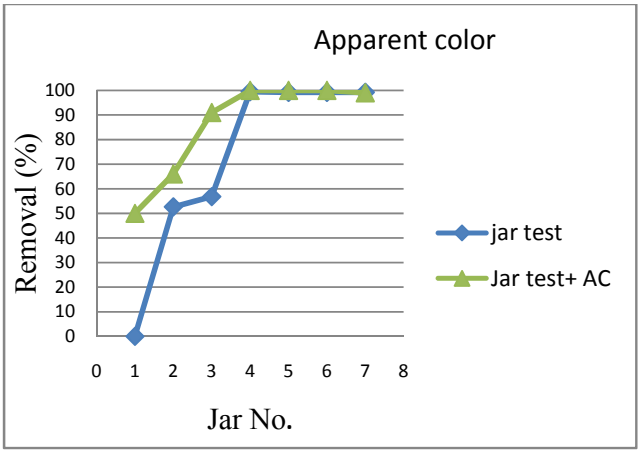


Figure 4.7 Apparent color removals

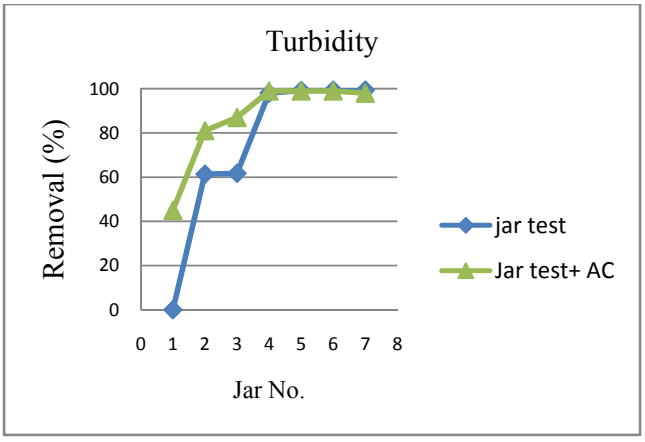


Figure 4.8 Turbidity removals

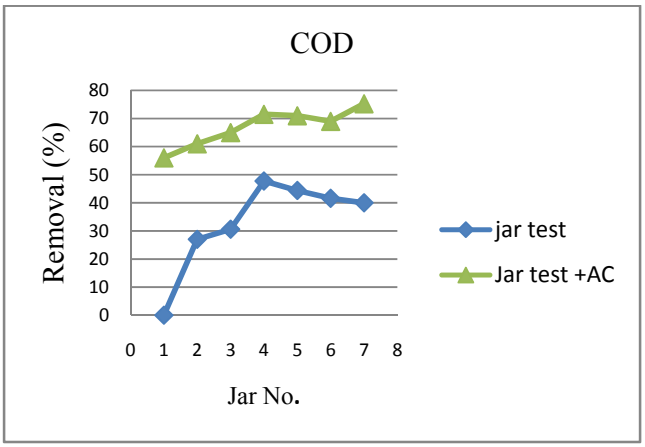


Figure 4.9 COD removals

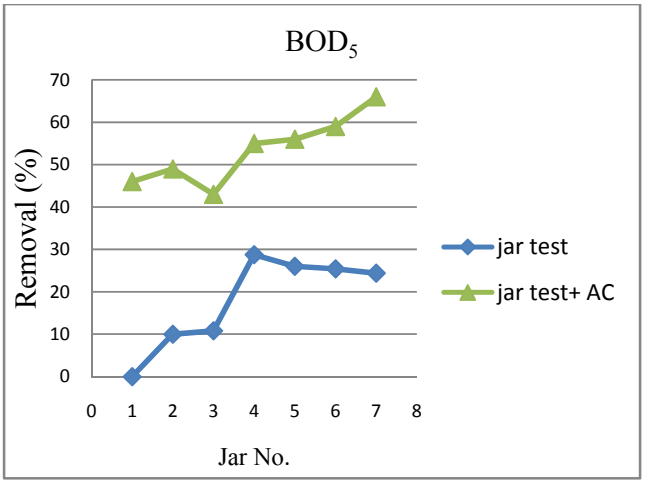


Figure 4.10 BOD_5 removals

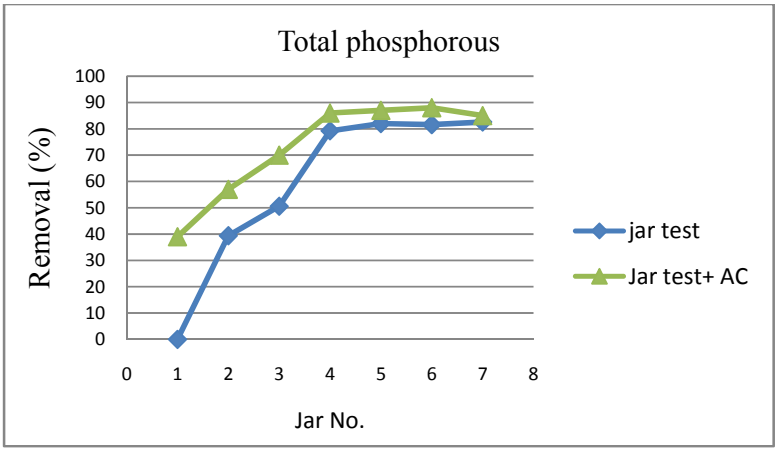


Figure 4.11 Total phosphorous removals

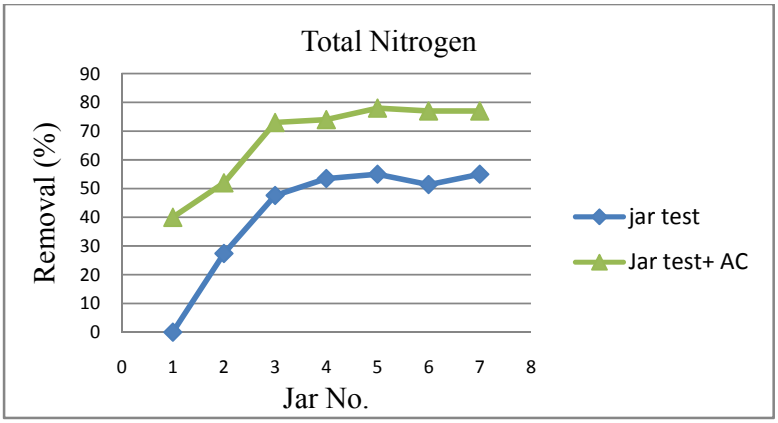


Figure 4.12 Total nitrogen removals

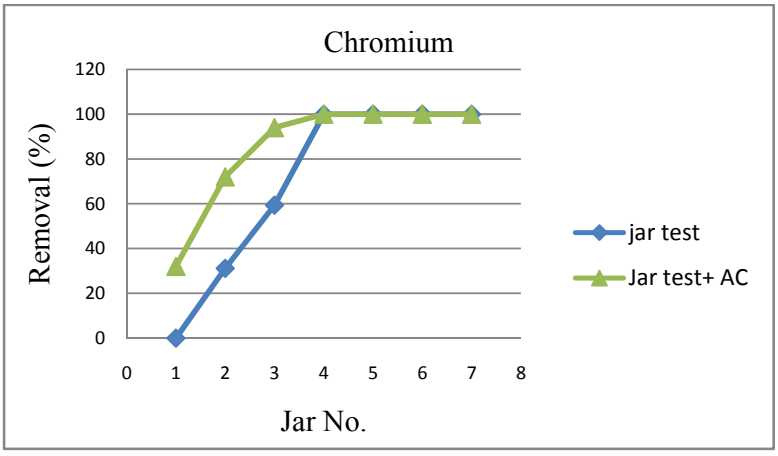


Figure 4.13 Chromium removals

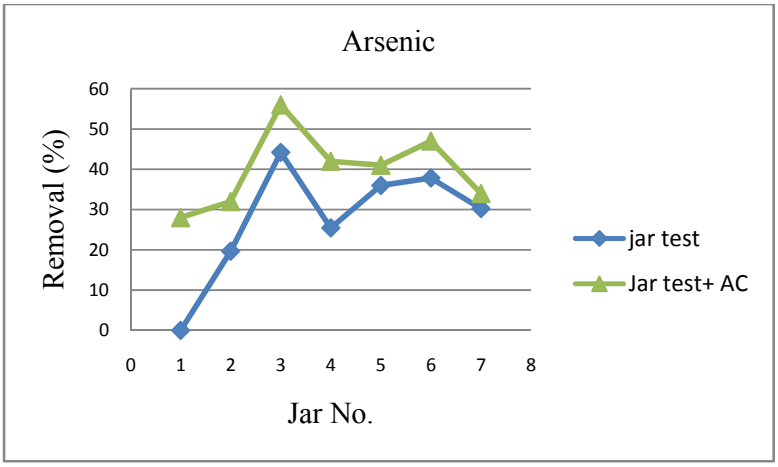


Figure 4.14 Arsenic removals

Since major pollutants in tannery wastewater are in particulate and colloidal forms, chemically enhanced primary treatments are extremely beneficial (Haydar et al., 2009). Highest impurities removals occurred at lowest dose of bittern (5ml/L) when added to alkalized wastewater and underwent jar test (Jar No.4) beyond which there was no further significant improvements. Table 4.6 presents a comparison of the results with previously reported values. Adsorption alone showed to positively impact removals for TSS, apparent color, turbidity and Cr up to Jar No.4. However, no noticeable improvement by adsorption was noted beyond that point, this is attributed to the fact that removals at Jar No.4 and beyond by bittern coagulation achieved removals close to 100%.

Table 4.6 Comparison of results with previous CEPT studies

	Cationic polymers (Haydar & Aziz., 2009)	**Alum (Haydar& Aziz.,2009)**	**Alum/$FeCl_3$ (Song et al., 2004)**	**$FeCl_3$ (Haydar & Aziz., 2009)**	**$FeSO_4$ (Haydar & Aziz., 2009)**	**Al-sulfate+ anionic polyelectrolyte (Ros et al., 1998)**	**Lime+ bittern + AC (Ayoub et al., 2011)**
Turbidity	94-96%	98.7-99.8%	NR	NR	NR	NR	99%
TSS	69-83%	94.3-97.1%	38-46%	70%	70%	81.1%	97%
COD	25-29%	53.3-60.9%	30-37%	40%	40%	64.3%	71%
Cr	96-97%	98.9-99.7%	74-99%	74-99%	74-99%	94.6%	99.7%
BOD5	NR	NR	NR	NR	NR	52.5%	57%
Phosphorous	NR	NR	NR	NR	NR	NR	87%

NR: not reported

4.4.2 Ozonation+ Jar test +AC

Relative low removals of COD and arsenic were the trigger to apply an oxidation phase. It is well known that strong oxidants such as ozone are considerably able to improve the biotreatability of recalcitrant effluents on one side and to oxidize arsenic into arsenate on the other. In fact, arsenic exhibits low removal efficiencies compared to arsenate because of its negative charge in the pH range of 4-10 (Ayoub et al., 2011; Office of Groundwater and drinking Water, 1999). Table 4.7 shows the array of conducted tests while figures 4.15-4.23 depict the removal efficiencies recorded when ozonation and adsorption are coupled to jar test. A second set of jars was used to supplement the first set when tests required more than six jars.

Table 4.7 Experimental conditions (oxidation+ jar test + AC)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7	Jar No.8	Jar No.9
Sample	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater
pH adjusted to 11.3±0.1	no	no	no	yes	yes	yes	yes	yes	yes
Bittern volume, ml	0	0	0	0	5	10	15	20	25
Ozone oxidation	no	yes	yes	yes	yes	yes	yes	yes	yes
Jar test	no	no	yes	yes	yes	yes	yes	yes	yes

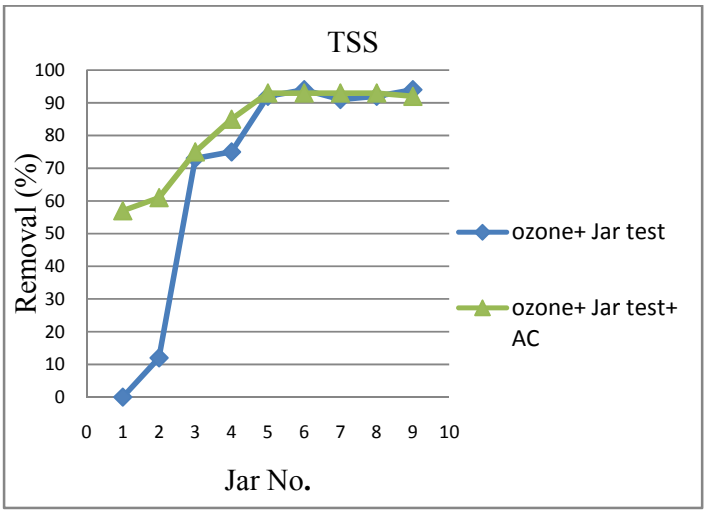


Figure 4.15 TSS removals

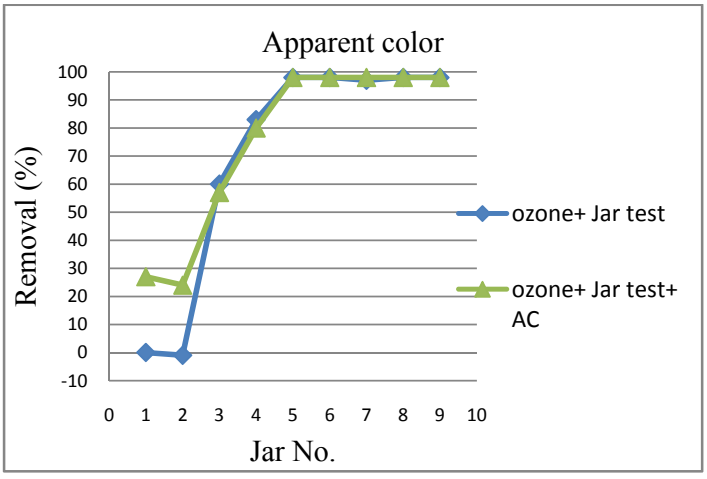


Figure 4.16 Apparent color removals

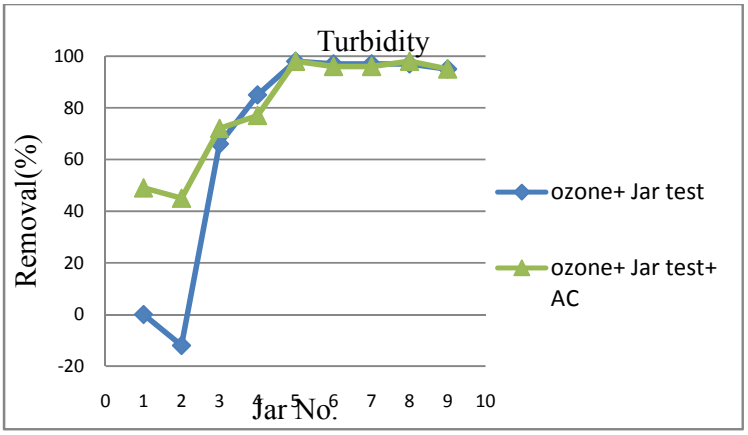


Figure 4.17 Turbidity removals

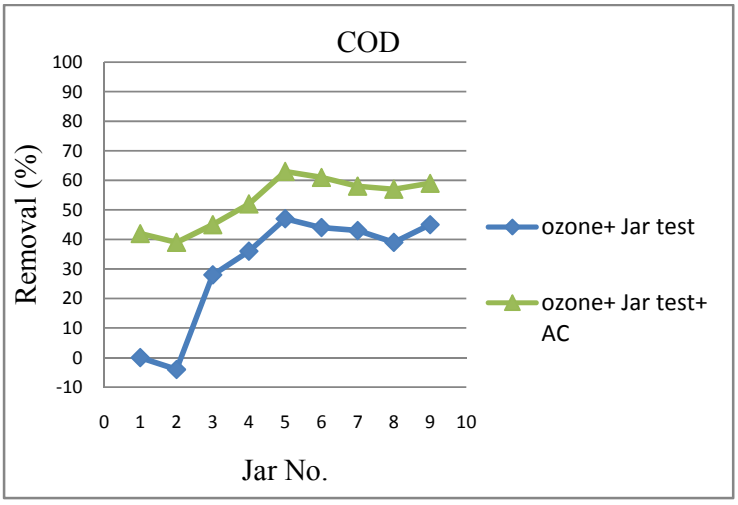


Figure 4.18 COD removals

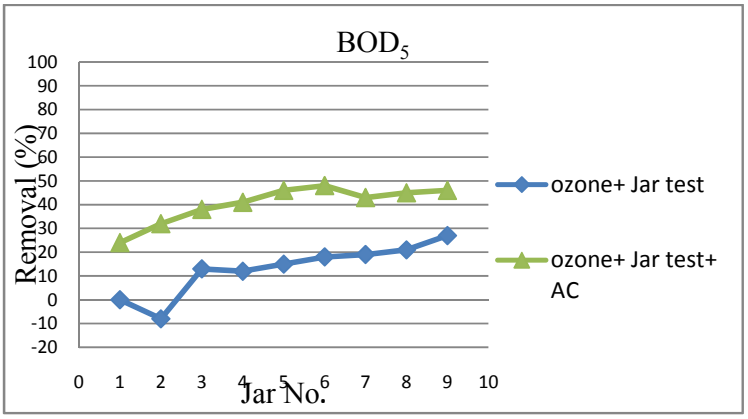


Figure 4.19 BOD_5 removals

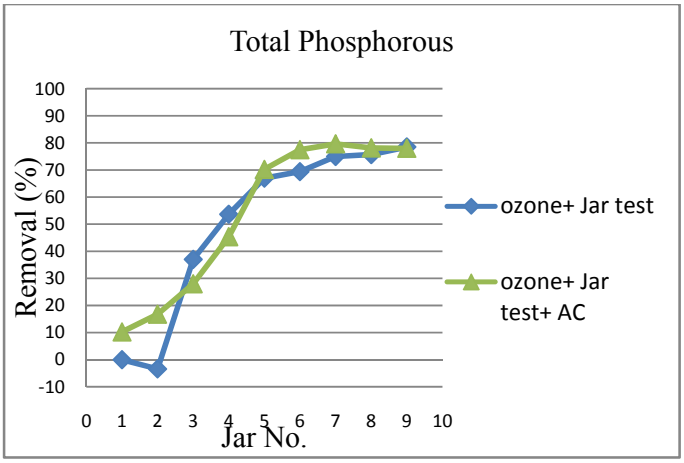


Figure 4.20 Total phosphorous removals

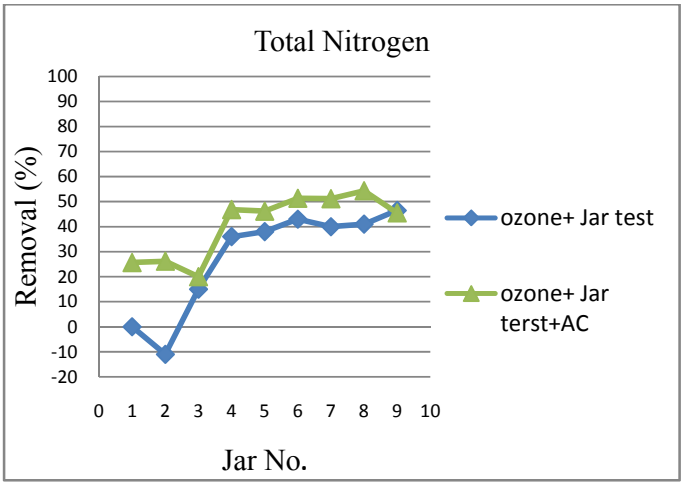


Figure 4.21 Total nitrogen removals

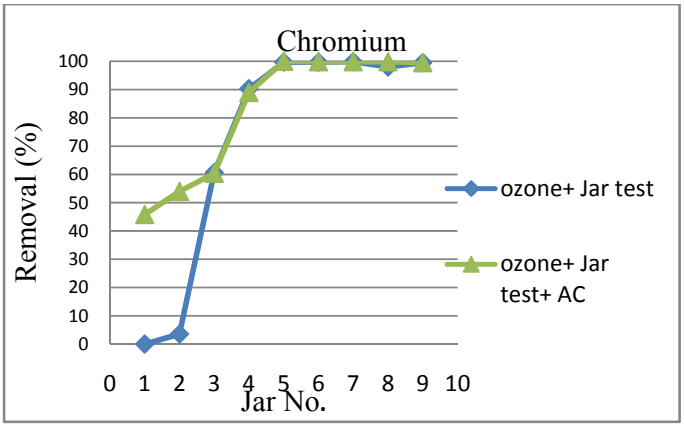


Figure 4.22 Chromium removals

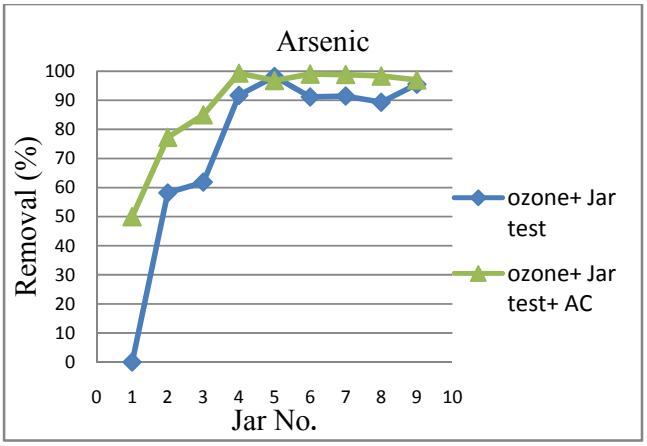


Figure 4.23 Arsenic removals

The maximum TSS (93%), apparent color (98%), turbidity (98%), COD (63%), chromium (100%) and arsenic (99%) reductions are obtained at Jar No.5 which has been oxidized, alkalized to a pH of 11.3 and went through the jar test at a bittern dose of 5mL/L. The maximum removals achieved after the application of ozonation and jar test were improved symmetrically when samples were subjected to AC adorption. A 100% removal was reached for both chromium and arsenic. It should be noted that ozonation of the raw sample showed a removal efficiency of 77.5% for As which is by far greater than the maximal achieved effciciency when jar test was coupled to AC adsorption (42%). This confirms the efficacy of oxidation in removing arsenic. Ozonation had a negative impact on COD, BOD_5, TP and TN removals, this can be attributed to the dissociation of particles that took place during oxidation. However, when adsorption was added to the ozonated wastewater, an added improvement of 30-40% for the afforementioned parameters was noted.

4.4.2.1 Effect of variations in bed depth in the adsorption phase

Originally oxidized tannery wastewater was allowed to undergo the jar test where different doses of bittern were added to the alkalized effluent (pH=11.3). As soon as the coagulation/ flocculation and settling phases ended the supernatants from all of the jars were tested for TSS and apparent color removals. Jar No. 3 in which 5ml/L of bittern was added showed the best removals (99% for both measured parameters). Aliquots of 1L of JarNo.3 were transferred to AC columns of different bed depths (10cm, 15cm, 20cm, 35cm, 40cm, and 45cm). By doing so, tannery wastewater was allowed to pass through different loading rates. The experimental conditions are summarized in table 4.8. In this set of experiments, the x-axis accounts for the different AC bed lengths. The obtained results are presented in table 4.9.

Table 4.8 Experimental conditions for different AC bed depths

	Beaker 3	**10cm**	**15cm**	**20cm**	**35cm**	**40cm**	**45cm**
Sample	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater
pH adjusted to 11.3±0.1	yes	yes	yes	yes	yes	yes	yes
Bittern volume, ml	5	5	5	5	5	5	5
Ozone oxidation	yes	yes	yes	yes	yes	yes	yes
Jar test	yes	yes	yes	yes	yes	yes	yes
AC column length, cm	-	10	15	20	35	40	45

Table 4.9 Removal percentiles for measured parameters according to the different bed depths

		B3	10 cm	15cm	20cm	35cm	40cm	45cm
Ozone oxidation+ Jar test+ AC at different bed depth	**TSS**	95.99%	96.2%	96.62%	97.47%	97.47%	98.1%	98.31%
	Apparent color	99%	99%	99%	100%	100%	100%	100%
	Turbidity	99%	100%	99%	100%	100%	100%	100%
	COD	46%	60%	59%	67%	72%	75%	75%
	BOD_5	25%	40%	41%	51%	48%	30%	35%
	Total phosphorous	75%	83%	76%	97%	84%	82%	85%
	Total nitrogen	46%	63%	68%	69%	66%	75%	79%
	Chromium	99%	100%	100%	100%	100%	100%	100%
	Arsenic	99%	99%	99%	100%	100%	100%	100%

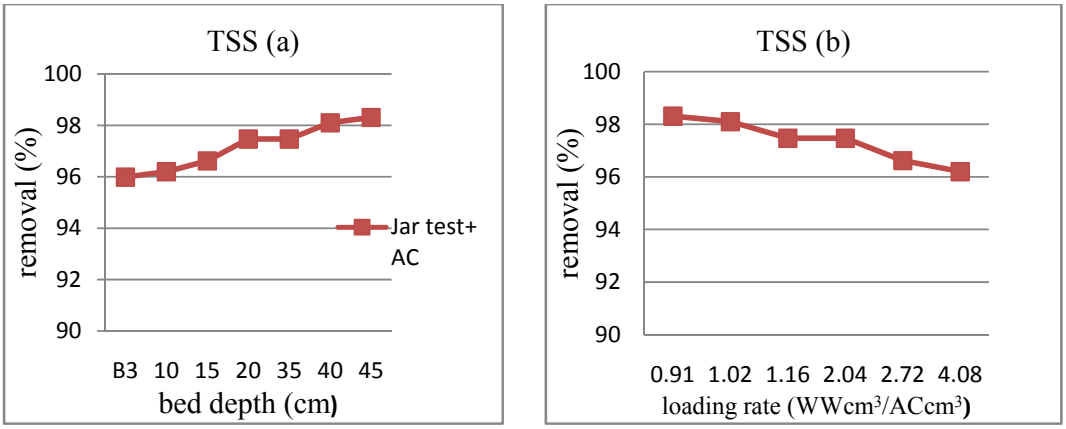


Figure 4.24 TSS removals

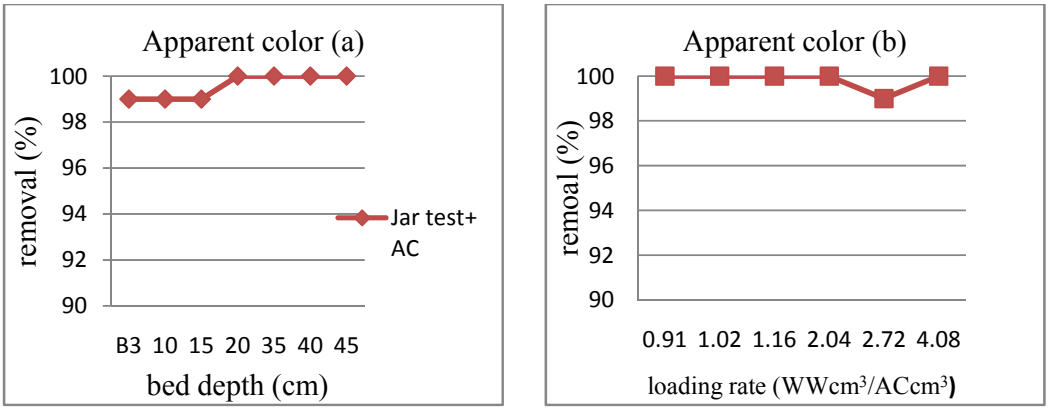


Figure 4.25 Apparent color removals

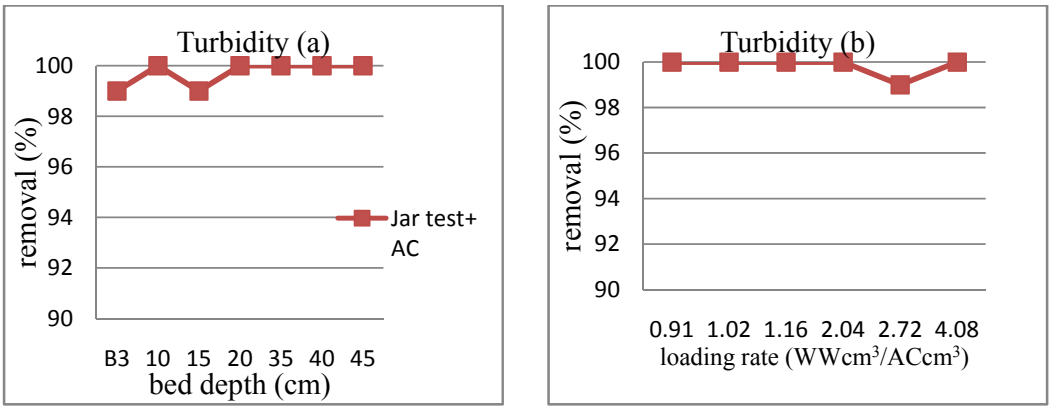


Figure 4.26 Turbidity removals

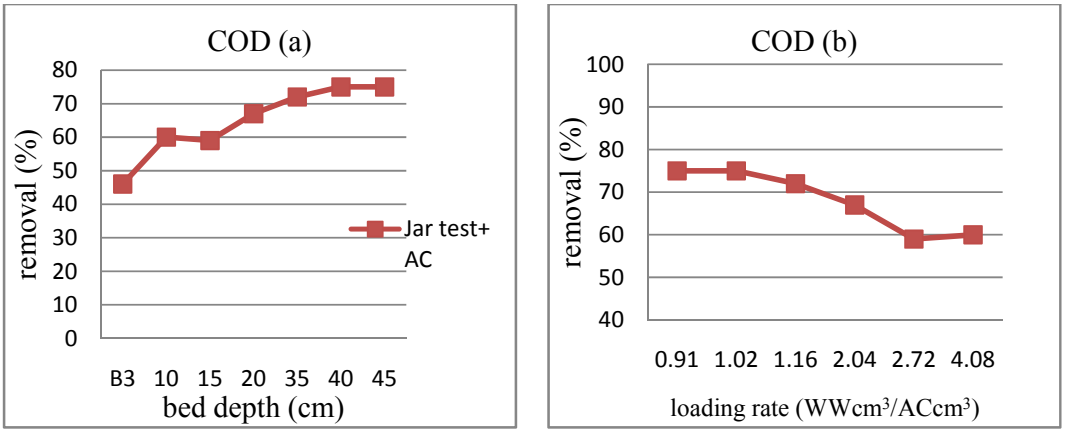


Figure 4.27 COD removals

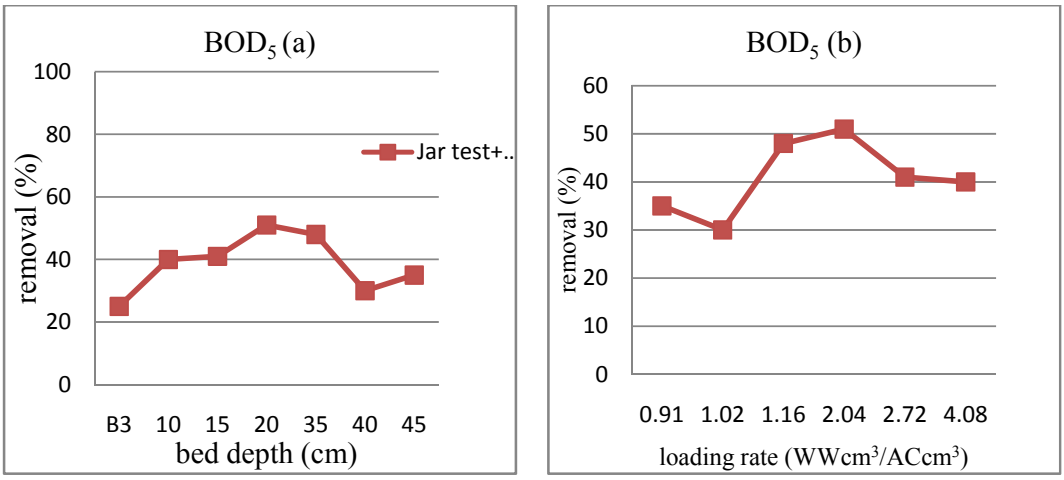


Figure 4.28 BOD_5 removals

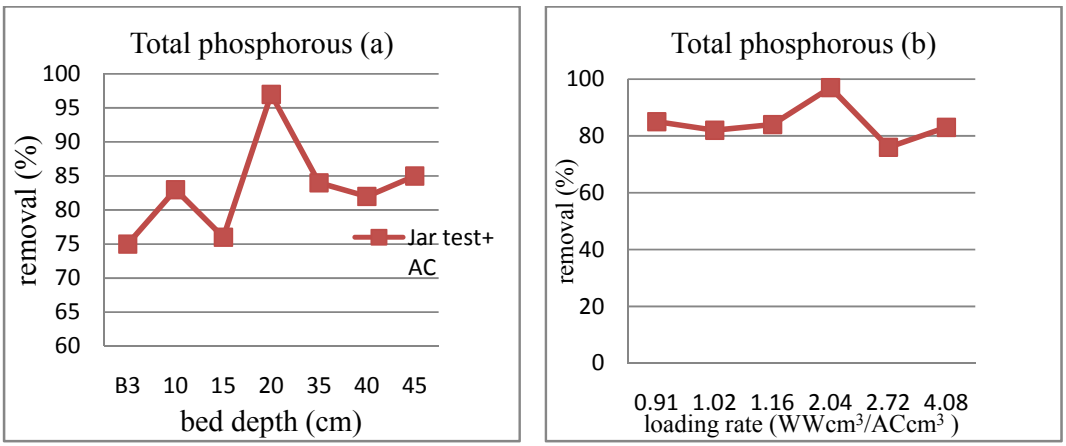


Figure 4.29 Total phosphorous removals

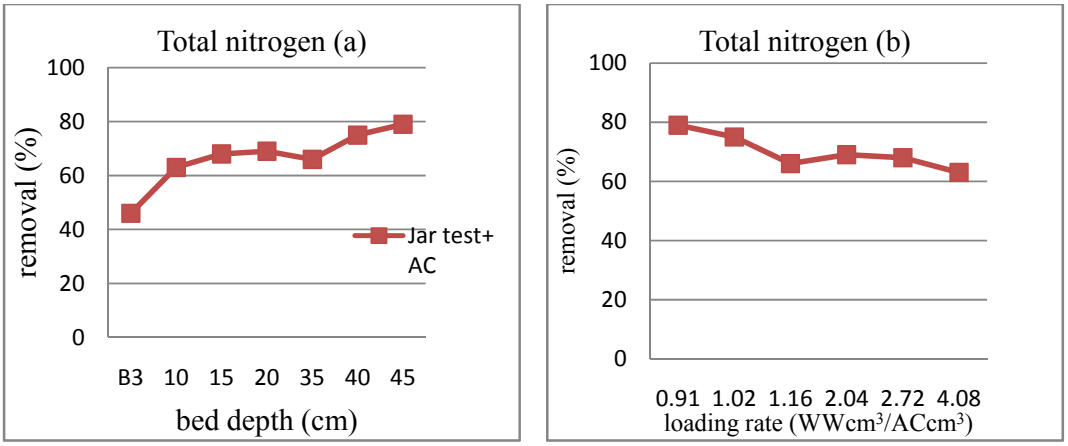


Figure 4.30 Total nitrogen removals

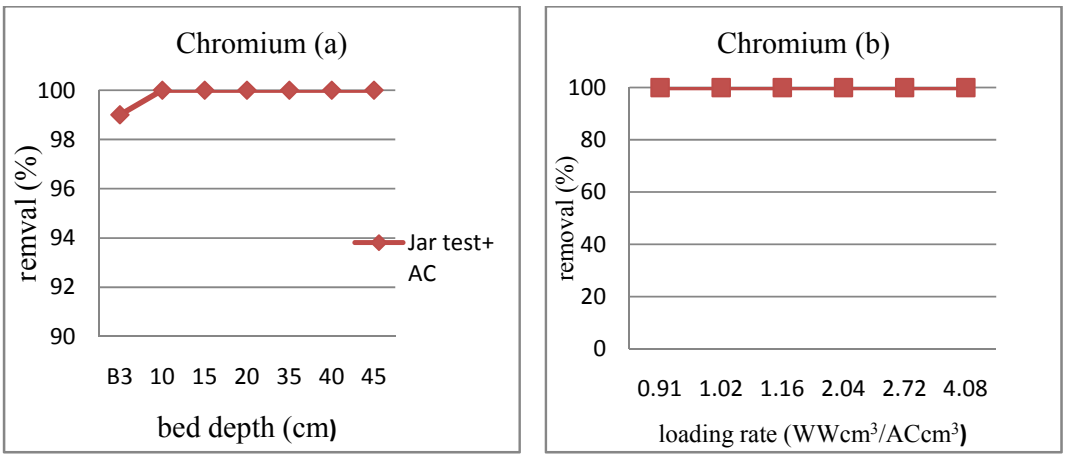


Figure 4.31 Chromium removals

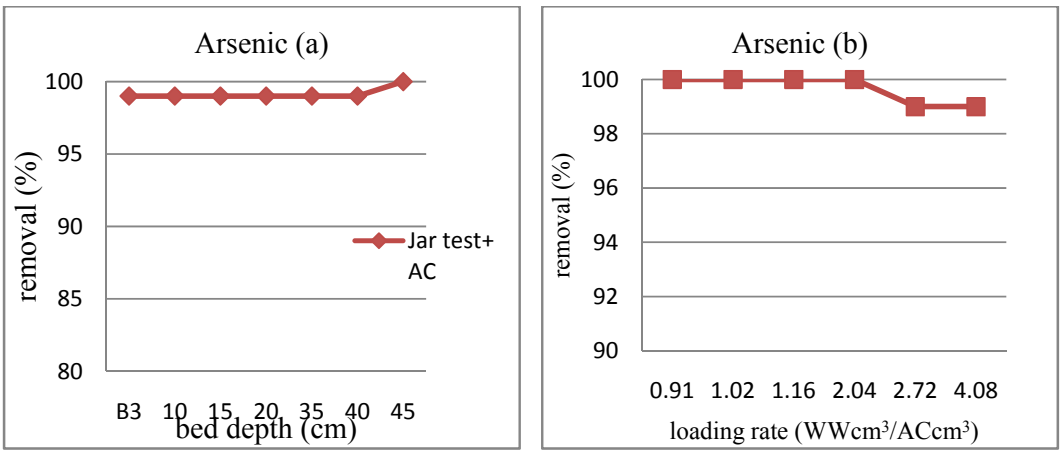


Figure 4.32 Arsenic removals

The variation in the bed depth of the AC affected COD, BOD_5, TP and TN removals. It can be noted that as the retention time increases removal of impurities increases and peaks at a certain loading rate and remain constant at that level. The maximal recorded removal efficiencies of COD, BOD_5, TP and TN are found to be 75%, 51%, 97% and 79% respectively. A 100% removal was achieved for apparent color, turbidity, Cr and AS. The reported improvements for the tested parameters show that as the loading rate decreases, removal efficiency increases. It is to be noted that more pronounced results as to the variation with depth could have been obtained where that the effluent did not undergo oxidation before being applied on the AC bed.

4.4.3 Jar test+ Ozone+ AC

Treatment of tannery wastewater was tested for several scenarios. In this section, the performance was evaluated based on the application of the jar test followed by ozone oxidation. The overall removal is based on the combined effect of the two stages to which adsorption is added using a constant AC bed depth. The reported efficiencies represent the average of 5 readings. The experimental conditions are given in table 4.10 and the removal efficiencies are presented in figure 4.33- 4.41.

Table 4.10 Experimental conditions (Jar test+ Ozonation + AC)

	Jar No.1	**Jar No.2**	**Jar No.3**	**Jar No.4**	**Jar No.5**	**Jar No.6**	**Jar No.7**
Sample	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater	tannery wastewater
pH adjusted to 11.3±0.1	no	no	yes	yes	yes	yes	yes
Bittern volume, ml	0	0	0	5	10	15	20
Jar test	no	yes	yes	yes	yes	yes	yes
Ozone oxidation	no	no	yes	yes	yes	yes	yes

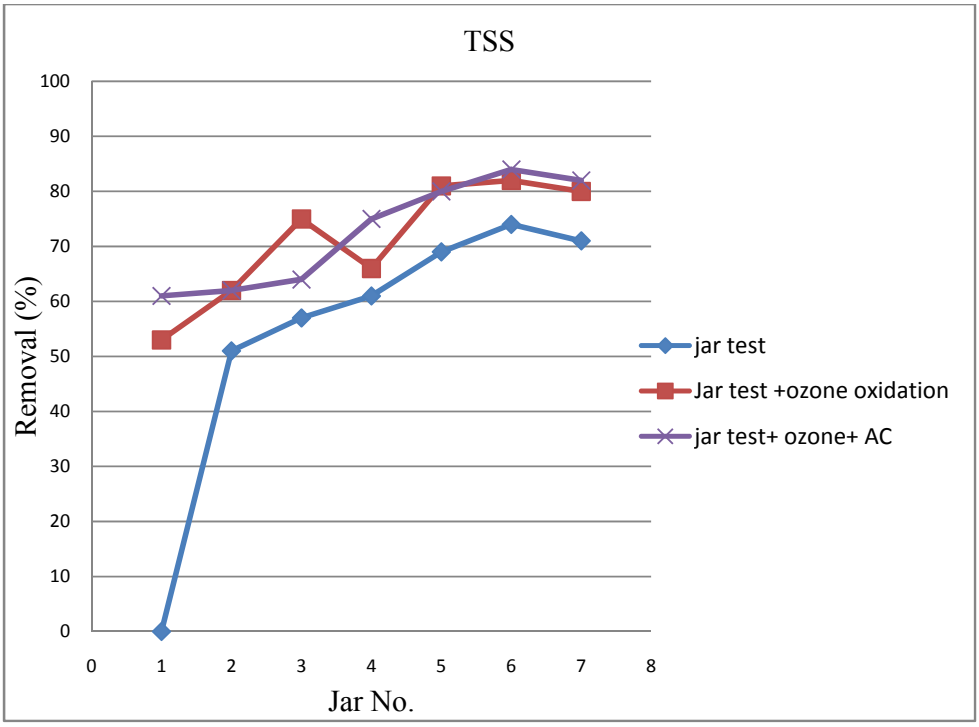


Figure4.33 TSS removals

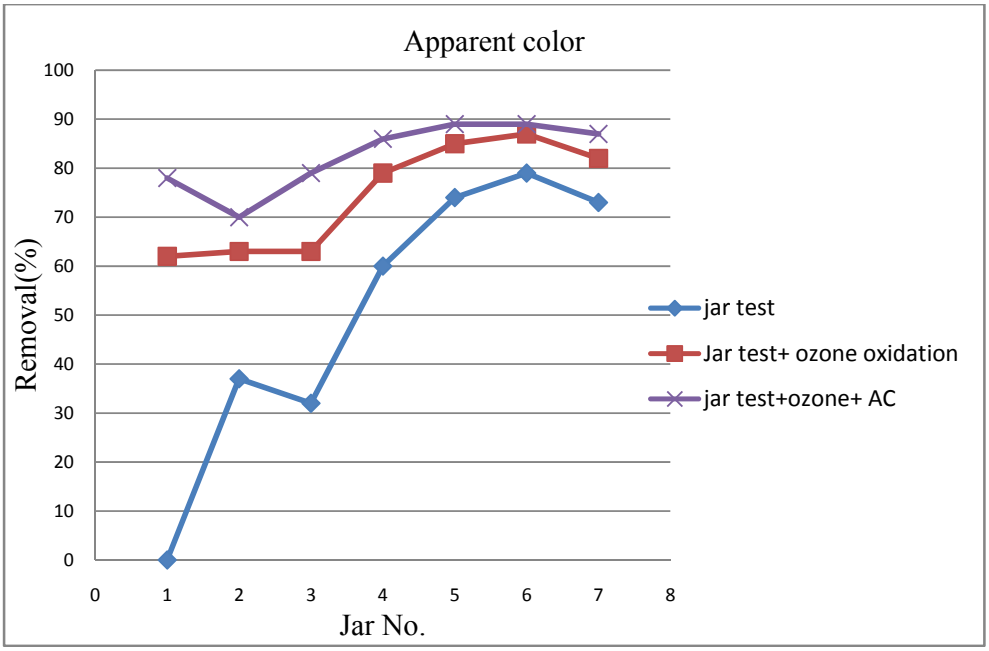


Figure 4.34 Apparent color removals

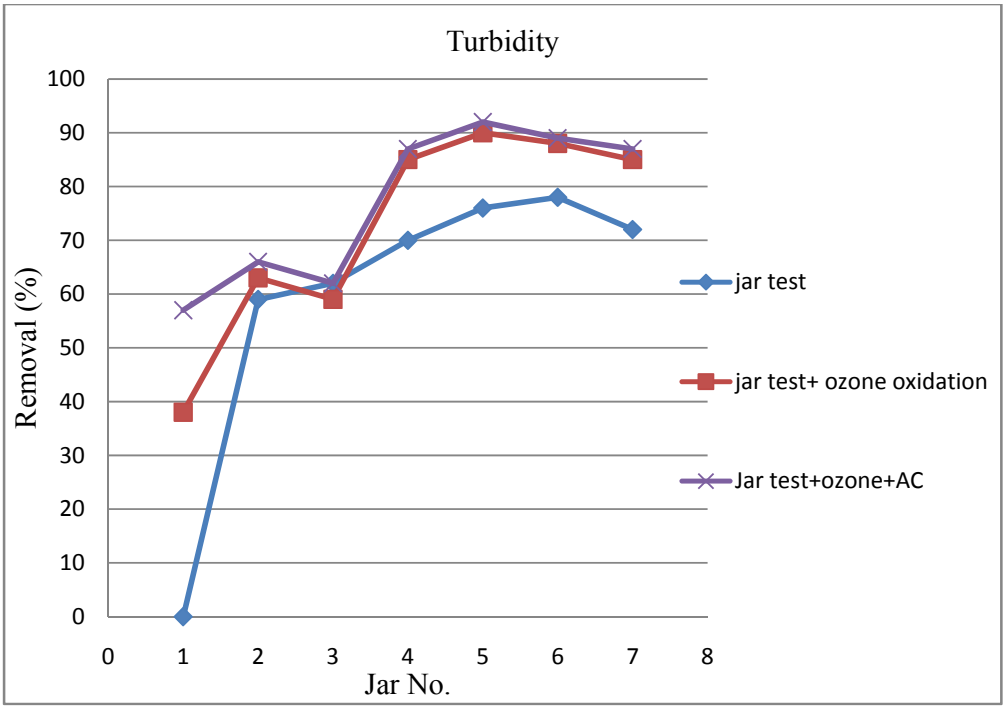


Figure 4.35 Turbidity removals

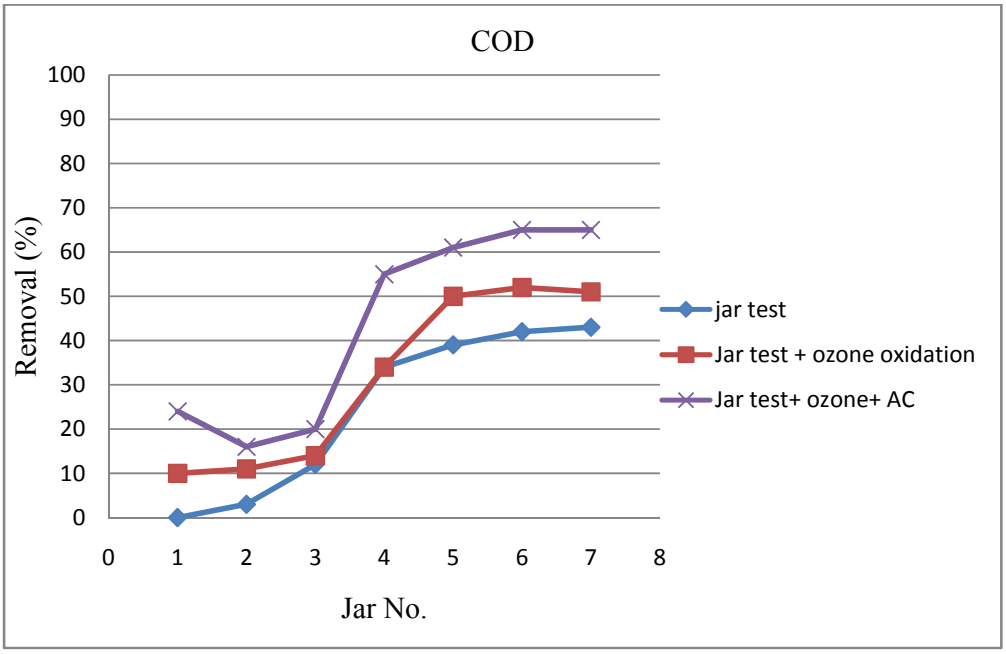


Figure 4.36 COD removals

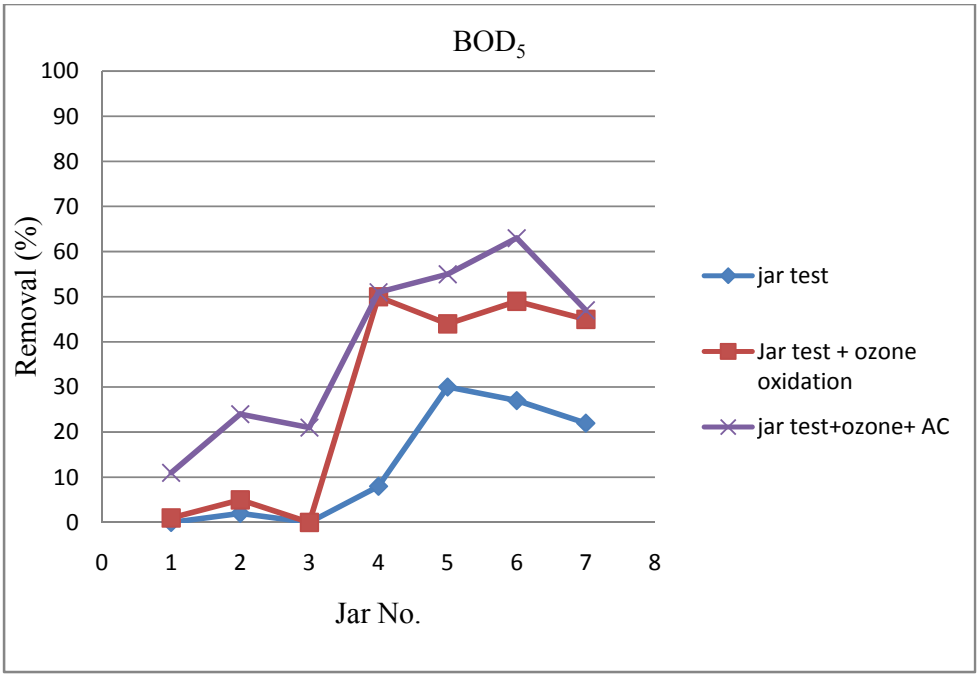


Figure 4.37 BOD_5 removals

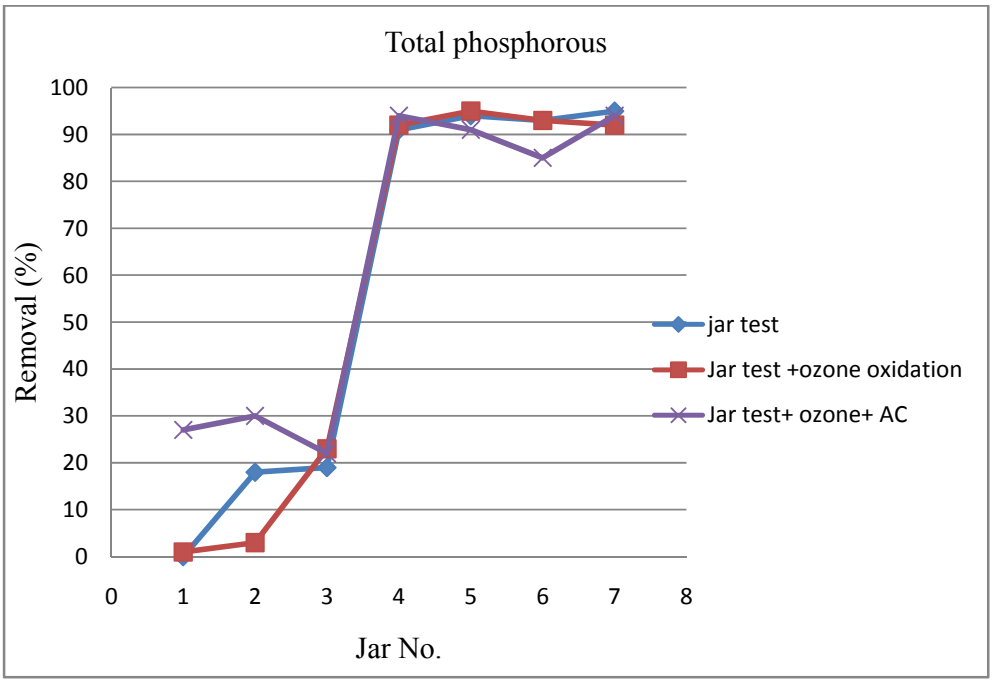


Figure 4.38 Total phosphorous removals

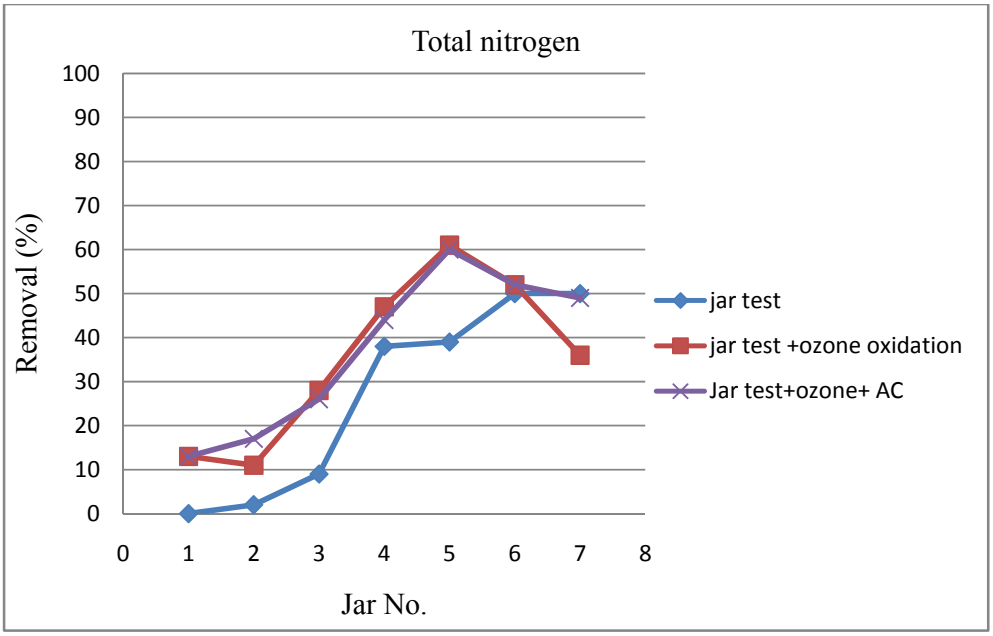


Figure 4.39 Total nitrogen removals

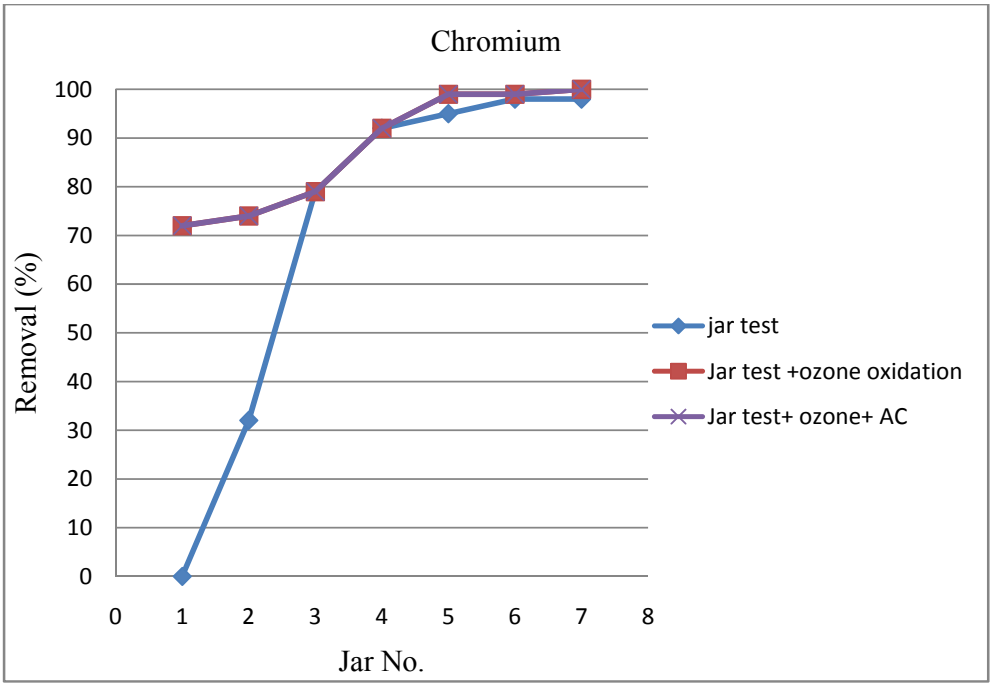


Figure 4.40 Chromium removals

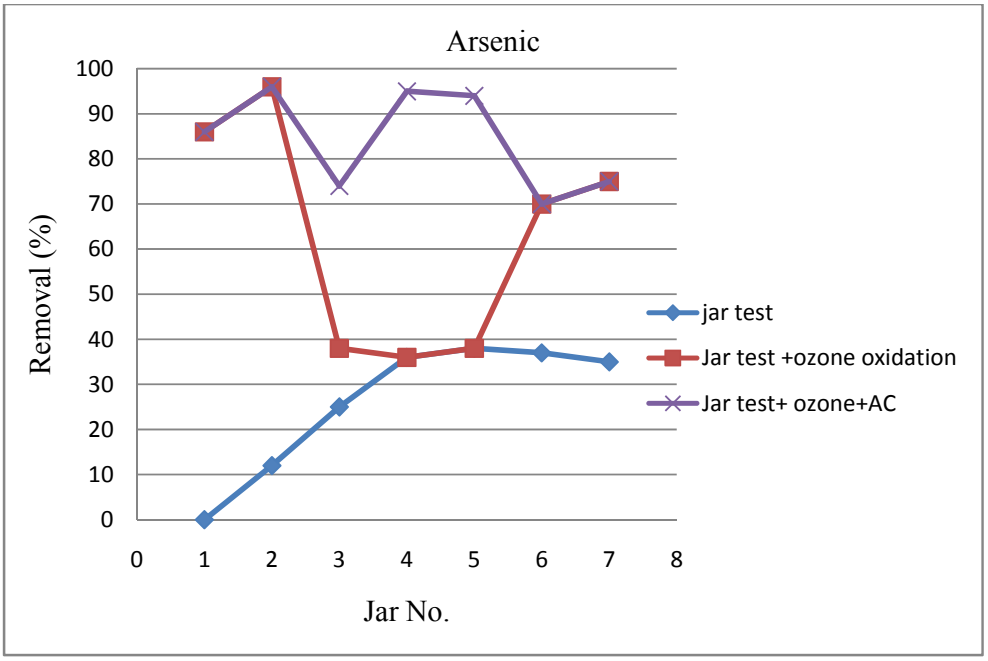


Figure 4.41 Arsenic removals

Maximal removal efficiencies for TSS, apparent color and turbidity were 84%, 89% and 92% respectively. Also, COD, BOD_5, TP and TN removals amounted to 65%, 63%, 94% and 60%. These results are comparable to those achieved when ozonation was prior to jar test. This shows that ozonation does not have to follow a specific order in a treatment sequence. It should be noted that after performing the jar test, maximal removals for TSS, apparent color and turbidity were obtained at Jar No.6, which has been alkalized to a pH value of 11.3 at a bittern dose of 15ml/L. However, once ozonation was applied, Jar No.5 which has been alkalized to a pH value of 11.3 at a bittern dose of 10ml/L registered the highest removals for the same parameters. Hence, oxidation allowed achieving better removals for lower coagulant dosage. Adsorption showed a positive effect in removing the oxidized organic fraction (COD and BOD_5) of the tannery wastewater once the latter has underwent the jar test, while it did not add to the removal of nitrogen and phosphorous. Arsenic removal behavior was fluctuating

and complex as shown in figure 4.41. When performing the coagulation/flocculation treatment, Jars No. 4, 5, 6 and 7 achieved the highest removal averaging to 38%. Upon oxidation, Jars No.1 and 2 showed the highest removals of 86% and 96% respectively. However, oxidation did not show any improvement for Jars No.4 and 5. The erratic behavior noted for As removal could not be explained scientifically.

4.4.4 Selection of optimal process

The best combination of treatment processes depends upon intrinsic advantages and drawbacks that favor or exclude its utilization. The achieved removal efficiencies of the different tested sequences are presented in table 4.11. As depicted in this table, each sequence has improved to some extent the quality of tannery effluent. The application of the jar test with bittern as a coagulant showed the highest removals for TSS, apparent color and turbidity. However, comparable removals are achieved by the three tested sequences in terms of BOD_5, COD and Cr. An oxidative phase is found efficient in reducing arsenic content in tannery wastewater; however, the achieved removal efficiencies did not show a notable difference in placing this phase whether prior or after the jar test. Accordingly, the best sequence in treating tannery effluent having similar physico-chemical characteristics is found to be the application of the jar test followed by ozonation and then adsorption onto granular activated carbon.

Table 4.11 Removal efficiencies for the tested parameters achieved by the different sequences

Parameter	Jar test at 5ml/L bittern + AC	Ozonation + Jar test at 5ml/L bittern + AC	Jar test at 10ml/L bittern + ozonation+ AC
TSS	97%	93%	80%
Apparent color	100%	98%	89%
Turbidity	99%	98%	92%
COD	71.5%	63%	61%
BOD_5	55%	46%	55%
TP	86%	70.25%	91%
TN	74%	46.2%	60%
Cr	100%	100%	99%
As	42%	96.8%	94%

4.4.5 Sequence comparisons

A single batch was performed to assess the removal efficiencies achieved for the measured parameters when the different tested sequences are applied to a tannery wastewater having the same physico-chemical characteristics. Table 4.12 presents the composition of the tannery sample under study as well as the achieved removal efficiencies for each sequence.

Table 4.12 Raw composition and removal efficiencies for the different tested treatment sequences

	Raw	Jar test (bittern)	Ozone oxidation followed by jar test (bittern)	Jar test (bittern) followed by ozone oxidation	Fenton oxidation	Fenton oxidation followed by jar test (bittern)	Jar test followed by Fenton reaction
TSS	1580 (mg/L)	96%	96%	95%	95%	90%	57%
Apparent color	16400 (mg/L)	99%	99%	98%	<0	98%	<0
Turbidity	1850 (mg/L)	99%	99%	99%	97%	99%	97%
COD	4246.7 (mg/L)	49%	57%	59%	84%	59%	81%
BOD5	5.15 (mg/L)	11%	38%	45%	66%	24%	83%
Total phosphorous	312.5 (mg/L)	83%	82%	83%	<0	75%	<0
Total nitrogen	1183.25 (mg/L)	46%	53%	61%	48%	34%	33%
Chromium	761.22 (mg/L)	100%	100%	100%	62%	92%	100%
Arsenic	0.213 (mg/L)	36%	56%	99%	74%	99%	100%

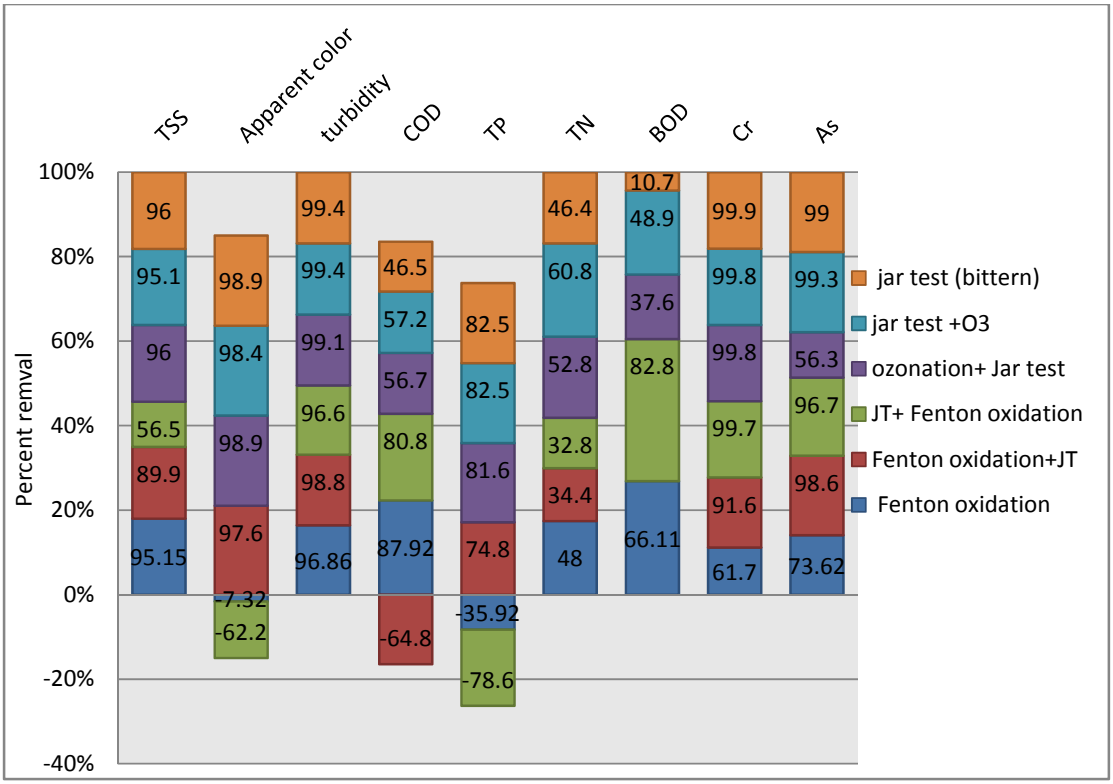


Figure 4.42 Removal efficiencies for the different tested sequences

As depicted in figure 4.42 and presented in table 4.12, there is not a well-defined sequence able to remove all of the impurities at the same maximal level. Coagulation/ flocculation using bittern as coagulant showed promising impurity removals except for the organic fraction where removals of 10.7% and 46.5% are recorded for BOD_5 and COD respectively. Once the jar test is followed by ozonation, improvements in removing the latter parameters are achieved to become 48.9 % and 57.2% respectively. However, when jar test is followed by Fenton oxidation better removals are registered: 82.8% for BOD_5 and 80.8% for COD.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study was conducted to evaluate the impact of different treatment processes on the removal of the different impurities available in tannery wastewater of an existing Tannery located at Wadi Shahrour, and to arrive at the sequence by which these processes are to be applied to obtain optimal treatment results. The study also aimed at evaluating the efficacy of using bittern as coagulant compared to the commonly used coagulants i.e. ferric chloride and aluminum sulphate. The multivariate sequences efficiencies were evaluated based on the removals effected of a set of parameters including TSS, apparent color, turbidity, COD, BOD_5, nitrogen, phosphorus, chromium and arsenic. The main conclusions that can be drawn on the basis of the results obtained under the used experimental conditions are the following:

- The characteristics of tannery wastewater varied widely and complex in its nature, therefore, by no means would pre-treatment using medium screening and micro-screening meet the standards for discharge.

- Practically equal efficiencies were attained in the treatment of tannery wastewater using alum, ferric chloride and bittern. Though competitive in their performance, bittern surpasses the two other coagulants as it is a cheap source of Mg^{2+}.

- Tannery wastewater contained non-biodegradable organic impurities reflected in the low BOD_5/COD ratio, which render the biological treatment inefficient.

- The application of ozone after the jar test showed a slightly better removal for BOD_5 and COD which increased from 46% to 55%.

- The application of AC through different loading rates showed that as the loading rate decreased, impurities removals increased.

- Fenton oxidation enhanced the biodegradability of the investigated wastewater as COD decreased from 4247mg/L to 513mg/L reflecting a removal efficiency of 87.92%. However, ozonation required a subsequent adsorption phase to show a maximal COD removal of 62.27%.

- Fenton oxidation showed promising removals particularly for the organic fraction of the tannery wastewater.

- The jar test coupled to AC adsorption sequence allowed the following removal efficiencies: 99% for TSS, 100% for apparent color, 99% for turbidity, 71.5% for COD, 55% for BOD_5, 86% for TN, 74% for TP, 100% for Cr and 42% for As.

- The sequence consisting of Ozonation-Jar test-AC showed the following removal efficiencies: 93% for TSS, 98% for apparent color, 98% for turbidity, 63% for COD, 46% for BOD_5, 70.25% for TP, 46.2% for TN, 100% for Cr and 96.8% for As.

- The application of Jar test followed by ozonation and AC adsorption showed similar removals to those achieved when ozonation is applied prior to the jar test, however, this sequence allowed to achieve these removals at a lower dose

of the bittern coagulant. Hence, Jar test- Ozonation-AC adsorption sequence is to be applied in order to reach optimal treatment results. The removal efficiencies were 80%, 89%, 92%, 61%, 55%, 91%, 60%, 99%, and 94 % for TSS, apparent color, turbidity, COD, BOD_5, TP, TN, Cr and As respectively.

5.2 Recommendations

Based on the results of this study, the following recommendations are proposed:

- Apply coagulation/flocculation with liquid bittern as coagulant to the existing plant as it was proved to be efficient and cost effective in reducing the strength of the generated effluent before its discharge in the environment.
- Test for the sludge generated after each sequence since further treatment is required for it.
- Optimize on the application of ozone based on the pH and ozone dosage.
- Further tests should be done on the Fenton oxidation as it showed promising removal efficiencies for COD and BOD_5 and arsenic especially that this oxidative technique is more cost-effective than ozone.

APPENDIX

Removal efficiencies for different parameters and the corresponding standard deviations (Jar test)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7
TSS	0%	64.2%±21%	75%±20.5%	96.5%±2%	97%±2.3%	97.4%±2.7%	96.2%±2.1%
Apparent color	0%	52.6%±29.5%	56.8%±42.7%	99.5%±0.6%	99.2%±0.8%	99.2%±0.8%	99.2%±0.8%
Turbidity	0%	61.4%±27%	61.75%±50%	98%±2.7%	99.2%±1.3%	99.4%±0.5%	99.4%±0.9%
COD	0%	27%±20.3%	30.6%±21.3%	47.75%±11%	44.4%±11%	41.6%±11%	40%±14.5%
BOD	0%	10%±14%	10.8%±20%	28.75%±21%	26%±20%	25.4%±13.5%	24.4%±18.6%
TP	0%	39.4%±32.12%	50.6%±32%	79.25%±10%	82%±8.8%	81.6%±8.6%	82.6%±9%
TN	0%	27.4%±21.4%	47.6%±30.6%	53.5%±24%	55%±30%	51.4%±32.5%	55%±18.6%
Cr	0%	32.13%±31%	59.36%±54.5%	99.975%±0.013%	99.986%±0.0089%	99.978%±0.013%	99.966%±0.043%
As	0%	19.66%±33.89%	44.2%±23.38%	25.45%±11.67%	36%±22.81%	37.85%±26.24%	30.25%±36.5%

Removal efficiencies for different parameters and the corresponding standard deviations (Jar test+ AC)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7
TSS	59%±12%	83%±11%	88%±4%	97%±1%	97%±0%	97%±2%	87%±10%
Apparent color	50%±41%	66%±29%	91%±7%	100%±0%	100%±0%	100%±0%	99%±0%
Turbidity	45%±39%	81%±15%	87%±10%	99%±0%	99%±0%	99%±0%	98%±2%
COD	56%±7%	61%±10%	65%±11%	71%±6%	71%±5%	69%±7%	75%±7%
BOD	46%±10%	49%±5%	43%±6%	55%±3%	56%±4%	59%±6%	66%±10%
TP	39%±21%	57%±32%	70%±20%	86%±6%	87%±5%	88%±5%	85%±7%
TN	40%±15%	52%±18%	73%±22%	74%±22%	78%±21%	77%±3%	77%±21%
Cr	32%±33%	72%±23%	94%±6%	100%±0%	100%±0%	100%±0%	100%±0%
As	28%±3%	25%±12%	56%±14%	42%±13%	41%±10%	47%±7%	34%±3%

Removal efficiencies for different parameters and the corresponding standard deviations (Oxidation+ Jar test)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7	Jar No.8	Jar No.9
TSS	0%	12%±25%	73%±6.76%	75%±25.5%	92%±5.32%	94%±4.15%	91%±5.56%	92%±5.25%	94%±3.54%
Apparent color	0%	-1%±30%	60%±19.57%	83%±28.25%	98%±1.6%	98%±1.5%	97%±1.5%	98%±1.1%	98%±1.41%
Turbidity	0%	-12%±23%	66%±19.84%	85%±22.64%	98%±1.14%	97%±3.33%	97%±2.04%	97%±1.87%	95%±6.36%
COD	0%	-4%±15%	28%±12.27%	36%±19.28%	47%±8.08%	44%±6.38%	43%±6.99%	39%±9.44%	45%±4.24%
BOD	0%	-8%±13%	13%±6.99%	12%±8.87%	15%±10.06%	18%±10.42%	19%±9.72%	21%±14.74%	27%±11.31%
TP	0%	-3.4%±23%	37%±20.99%	53.71%±21.82%	67%±8.46%	69.43%±7.48%	75%±7.19%	75.71%±7.04%	78.5%±7.78%
TN	0%	-11%±19%	15%±18.57%	36%±23.47%	38%±15.31%	43%±14.74%	40%±12.6%	41%±14.8%	46.5%±12%
Cr	0%	3.6%±22%	60.67%±21.8	90.29%±18.28%	99.67%±0.52	99.7%±0.5%	99.86%±0.4	98%±0.45%	99.5%±0.71%
As	0%	58.2%±35%	61.8%±44.2%	91.71%±11.2%	98.17%±1.94	91.14%±16.5%	91.4%±17.5	89.33%±22.3%	95.5%±6.36%

Removal efficiencies for different parameters and the corresponding standard deviations (Oxidation+ Jar test+ AC)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7	Jar No.8	Jar No.9
TSS	57%±7.44%	61%±8%	75%±5.5%	85%±4.79%	93%±3.16%	93%±4.55%	93%±6.78%	93%±4.02%	92%±7.07%
Apparent color	27%±20.61%	24%±	57%±15.65%	80%±33.08%	98%±1.79%	98%±1.75%	98%±1.94%	98%±0.82%	98%±0%
Turbidity	49%±25.29%	45%±21%	72%±12.04%	77%±33.71%	98%±1.26%	96%±4.38%	96%±4.28%	98%±1.3%	95%±4.95%
COD	42%±15.07%	39%±13%	45%±10.08%	52%±14.46%	63%±3.87%	61%±7.12%	58%±8.07%	57%±8.91%	59%±13.44%
BOD	24%±12.94%	32%±14%	38%±10.65%	41%±7.41%	46%±13.01%	48%±10.5%	43%±12.33%	45%±17.06%	46%±6.36%
TP	10.25%±8.42%	17%±10%	28%±9.64%	45.4%±10.7%	70.3%±5.4%	77.5%±6.9	79.67%±5%	78.2%±6.5%	78%±4.24%
TN	25.67%±11.1%	26%±12%	20%±12.71%	46.83%±20%	46%±10.64%	51.3%±8.8	51.2%±9.1%	54.3%±9.2%	45.5%±9.2%
Cr	45.83%±18.3%	54%±13%	60.4%±20.4	89%±18.5%	100%±0%	99.8%±0.4	99.83%±0.4	99.83%±0.4	99.5%±0.7%
As	50%±50.01%	77%±36%	85%±25.5%	99.3%±1.03%	96.8%±5.54	99%±1.26%	98.8%±1.17	98.3%±2%	97%±2.83%

Removal efficiencies for different parameters and the corresponding standard deviations (Jar test+ Oxidation)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7
TSS	53%±15%	62%±20.5%	75%±16%	66%±14%	81%±11%	82%±7%	80%±8%
Apparent color	62%±17%	63%±32%	63%±36%	79%±25%	85%±18%	87%±19%	82%±16%
Turbidity	38%±22%	63%±31%	59%±19%	85%±20%	90%±12%	88%±12.1%	85%±11%
COD	10%±24%	11%±8%	14%±11%	34%±14%	50%±17%	52%±18.4%	51%±20%
BOD	1%±32%	5%±34%	0%±31%	50%±34%	44%±35%	49%±19%	45%±26%
TP	1%±14%	3%±6%	23%±11%	92%±7%	95%±4%	93%±6%	92%±3%
TN	13%±7%	11%±12.75%	28%±18%	47%±9.9%	61%±10%	52%±21%	36%±42%
Cr	72%±21%	74%±21%	79%±18%	92%±6%	99%±5%	99%±1.1%	100%±0%
As	86%±12%	96%± 38%	38%±51%	36%±48%	38%±51%	70%±9%	75%±26%

Removal efficiencies for different parameters and the corresponding standard deviations (Jar test+ Oxidation+ AC)

	Jar No.1	Jar No.2	Jar No.3	Jar No.4	Jar No.5	Jar No.6	Jar No.7
TSS	61%±12%	62%±14%	64%±11%	75%±13%	80%±10%	84%±15%	82%±14%
Apparent color	78%±9%	70%±9%	79%±11%	86%±14%	89%±6%	89%±3%	87%±5%
Turbidity	57%±15%	66%±16%	62%±11%	87%±8.9%	92%±4%	89%±5%	87%±7%
COD	24%±35%	16%±25%	20%±31%	55%±26%	61%±21%	65%±30%	65%±35%
BOD	11%±16%	24%±23%	21%±25%	51%±34%	55%±21%	63%±31%	47%±26%
TP	27%±28%	30%±22%	22%±18%	94%±6%	91%±4%	85%±7%	94%±3.7%
TN	13%±32%	17%±23%	26%±21%	44%±15%	60%±18%	52%±34%	49%±31%
Cr	72%±11%	74%±13%	79%±21%	92%±0.6%	99%±0.7%	99%±0.4%	100%±0.3%
As	86%±21%	96%±11%	74%±25%	95%±3%	94%±3.5%	70%±36%	75%±34%

BIBLIOGRAPHY

Aber, S., D. Salari, and M. R. Parsa.Employing the taguchi method to obtain the optimum conditions of coagulation-flocculation process in tannery wastewater treatment. *Chemical Engineering Journal* 2010,162 (1): 127-34.

American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), Standard methods for the examination of water and wastewater, twenty-first ed, 2005,Washington, D.C.

Apaydin, O., U. Kurt, M. T. Gönüllü. An investigation on the treatment of tannery wastewater by electrocoagulation. *Global Nest Journal* 2009, 11 (4): 546-555.

Arvanitoyannis, I., I. Eleftheriadis, and E. Tsatsaroni. Influence of pH on adsorption of dye-containing effluents with different bentonites. *Chemosphere* 1989,18 (9-10): 1707-11.

Ates, E., Orhon, D., and Tünay, O. Characterization of tannery wastewaters for pretreatment - selected case studies. *Water Science and Technology*, 1997, 36 (2-3):217-223

Ayoub, G. M., M. El-Fadel, A. Acra, and R. Abdallah. Critical density index for the solar production of bittern from seawater. *International Journal of Environmental Studies,* 2001, 58 (1): 85-97.

Ayoub, G. M., F. Merehbi, R. Abdallah, A. Acra, and M. E. El Fadel. Coagulation of alkalinized municipal wastewater using seawater bittern. *Water Environment Research,* 1999, 71 (4): 443-53.

Ayoub, G.M., Hamzeh, A, Semerjian,L. Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption. *Desalination*, 2011, 273: 359–365.

Bae, W., Lee, S. H., and Ko, G. B. Evaluation of predominant reaction mechanisms for the fenton process in textile dyeing wastewater treatment*. Water Science and Technology*, 2004, 49(4): 91-96

Barredo-Damas, S., M. I. Alcaina-Miranda, M. I. Iborra-Clar, and J. A. Mendoza-Roca. Application of nanofiltration/reverse osmosis membranes to textile effluents aiming its reclamation and reuse: Influence of operating conditions. Paper presented at Chemical Engineering Transactions, 2010 (21):1027-1032

Bódalo, A., J. L. Gómez, E. Gómez, A. M. Hidalgo, and A. Alemán. Viability study of different reverse osmosis membranes for application in the tertiary treatment of wastes from the tanning industry. *Desalination*, 2005,180 (1-3): 277-84.

Buljan,J. Salinity within tannery effluents,*World Leather* 2005(18): 18–20.

Chiesa, S. C. and R. L. Irvine. Growth and control of filamentous microbes in activated sludge: An integrated hypothesis. *Water Research* , 1985,19 (4): 471-479.

Cooman, K., M. Gajardo, J. Nieto, C. Bornhardt, and G. Vidal. Tannery wastewater characterization and toxicity effects on daphnia spp. *Environmental Toxicology*, 2003, 18 (1): 45-51.

Costa, C. R. and P. Olivi. Effect of chloride concentration on the electrochemical treatment of a synthetic tannery wastewater. *Electrochimica.Acta* ,2009, 54 (7): 2046-2052.

Covarrubias, C., R. Arriagada, J. Yáñez, R. García, M. Angélica, S. D. Barros, P. Arroyo, and E. F. Sousa-Aguiar. Removal of chromium(III) from tannery effluents, using a system of packed columns of zeolite and activated carbon. *Journal of Chemical Technology and Biotechnology* 2005, 80 (8): 899-908.

De Gisi, S., M. Galasso, and G. De Feo. Treatment of tannery wastewater through the combination of a conventional activated sludge process and reverse osmosis with a plane membrane. *Desalination* 2009,249 (1): 337-342.

Deepali.,K.K.Gangwar., B.D.Joshi Comparative study of physico-chemical properties of effluent from tannery industries. *Indian Journal of Environmental Sciences J*, 2009, 3(2):49-52.

Di Iaconi, C., F. Bonemazzi, A. Lopez, and R. Ramadori. Integration of chemical and biological oxidation in a SBBR for tannery wastewater treatment. *Water science and technology* 2004, 50 (10):107-114.

Di Iaconi, C., A. Lopez, R. Ramadori, A. C. Di Pinto, and R. Passino. Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR). *Water Research* 2002,36 (9): 2205-2214.

Di Iaconi, C., R. Ramadori, and A. Lopez. The effect of ozone on tannery wastewater biological treatment at demonstrative scale. *Bioresource Technology* 2009,100 (23): 6121-6124.

Dogruel, S., E. A. Genceli, F. G. Babuna, and D. Orhon. Ozonation of nonbiodegradable organics in tannery wastewater. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 2004, 39 (7): 1705-1715.

Durai, G. and M. Rajasimman.. Biological treatment of tannery wastewater - A review. *Journal of Environmental Science and Technology* 2011, 4 (1) : 1-17.

Eckenfelder,W.W.Industrial Water Pollution Control.McGraw-Hill.New York. 1989.p.64.

Eckenfelder,W.W. Industrial Water Pollution Control.McGraw-Hill, Singapore, 2002.

Elsheikh, M. A. -. Tannery wastewater pre-treatment. *Water Science and Technology*, 2009, 60 (2):433-440.

Fahim, N. F., B. N. Barsoum, A. E. Eid, and M. S. Khalil. Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste. *Journal of Hazardous Materials* 2006,136 (2): 303-9.

FENG, J. -w, Y. -b SUN, Z. ZHENG, J. -b ZHANG, S. LI, and Y. -c TIAN. Treatment of tannery wastewater by electrocoagulation. *Journal of Environmental Sciences,* 2007, 19 (12): 1409-1415.

Ganesh,R., G. Balaji, R.A Ramanujam. Biodgradation of tannery wastewater using sequencing batch reactor-respirometric assessment. *Bioresour.Technol.,* 2006, 97: 1815-1821

GilPavas, E., I. Dobrosz-Gómez, and M. Á. Gómez-García.The removal of the trivalent chromium from the leather tannery wastewater: The optimization of the electro-coagulation process parameters. *Water Science and Technology*, 2011, 63 (3): 385-94.

Haydar, S., and J. A. Aziz. Characterization and treatability studies of tannery wastewater using chemically enhanced primary treatment (CEPT)-A case study of saddiq leather works. *Journal of Hazardous Materials*, 2009,163 (2-3): 1076-83.

Haydar, S. and J. A. Aziz. Coagulation-flocculation studies of tannery wastewater using combination of alum with cationic and anionic polymers. *Journal of Hazardous Materials*, 2009,168 (2-3): 1035-1040.

Herawati, N., S. Suzuki, K. Hayashi, I. F. Rivai, and H. Koyama.Cadmium, copper, and zinc levels in rice and soil of japan, indonesia, and china by soil type. *Bulletin of Environmental Contamination and Toxicology*, 2000, 64 (1): 33-9.

Jawahar, A.J., M. Chinnsdurai,J.K.S Ponselvan and G.Annadurai. Pollution from tanneries and options for treatment of effluent. *Ind.J.Environ.Protec.*,1998,18:672-672.

Jochimsen, J. C. and M. R. Jekel.Partial oxidation effects during the combined oxidative and biological treatment of separated streams of tannery wastewater. *Water science and technology*, 1997, 35(4): 337-345.

Kadirvelu, K., M. Palanival, R. Kalpana, and S. Rajeswari.Activated carbon from an agricultural by-product, for the treatment of dyeing industry wastewater. *Bioresource Technology* , 2000, 74 (3): 263-265.

Kang,S.F., Liao,C.H., Chen,M.C.Pre-oxidation and coagulation of textile wastewater by the Fenton process. *Chemosphere* , 2002, 46: 923–928.

Kim, T. -H, C. Park, J. Lee, E. -B Shin, and S. Kim.Pilot scale treatment of textile wastewater by combined process (fluidized biofilm process-chemical coagulation-electrochemical oxidation). *Water Research*, 2002, 36 (16): 3979-88.

Konrad, C., K. E. Lorber, R. Méndez, J. Lopez, M. Muñoz, D. Hidalgo, C. Bornhardt, M. Torres, and B. Rivelca.Systematic analysis of material fluxes at tanneries. *Journal of the Society of Leather Technologies and Chemists*, 2002, 86 (1): 18-25.

Koteswari, Y.N, R. Ramanibai. The effect of tannery effluent on the colonization rate of plankets: A microcosm study. *Turk.J.Biol.,* 2003, 27:163-170.

Kowalski, Z.Treatment of chromic tannery wastes. *Journal of Hazardous Materials*, 1994, 37 (1): 137-41.

Kurt, U., O. Apaydin, and M. T. Gonullu.Reduction of COD in wastewater from an organized tannery industrial region by electro-fenton process. *Journal of Hazardous Materials* , 2007, 143 (1-2): 33-40.

Leta,S., F.Assefa,L. Gumaelius, G.Dalhammar. Biological nitrogen and organic matter removal from tannery wastewater in pilot plant operations in Ethiopia. *Applied Microbiol. Biotechnol.*, 2004, 66: 333-339

Lin, S. H. and C. F. Peng.Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge. *Water Research*, 1996, 30 (3): 587-592.

Lopez, A., G. Ricco, R. Ciannarella, A. Rozzi, A. C. Di Pinto, and R. Passino. Textile wastewater reuse: Ozonation of membrane concentrated secondary effluent. *Water science and technology*, 1999 ,40 (4-5): 99-105.

Ma, H., X. Wang,C. Zhang.Cr(III) accumulation and phytoavailability in alkaline soils contaminated by tannery sludge. *Chemical Speciation and Bioavailability*, 2003, 15 (1):15-22.

Mandal,T., Dasguptab, D., Mandala, S., Dattac,S.Treatment of leather industry wastewater by aerobic biological and Fenton oxidation process. *Journal of Hazardous Materials,*2010,180:204–211.

Mannucci, A., G. Munz, G. Mori, and C. Lubello.Anaerobic treatment of vegetable tannery wastewaters: A review. *Desalination* , 2010,264(1-2): 1-8.

More, S. V., S. John, B. Seetarama Rao, B. Unni Nair, and R. Seeta Laxman.Chromium removal and reduction in COD of tannery effluents by actinomycetes. *Indian Journal of Environmental Health*, 2001, 43 (3): 108-13.

Murugesan,V. and R.Elangoan. Biokinetic parameters for activated sludge process treating vegetable tannery waste.*Ind.J.Environ.Protec*.,1994,14: 511-515.

Murugananthan, M., G. Bhaskar Raju, and S. Prabhakar.Removal of sulfide, sulfate and sulfite ions by electro coagulation. *Journal of Hazardous Materials*, 2004, 109 (1-3): 37-44.

Naumczyk, J., and M. Rusiniak. Physicochemical and chemical purification of tannery wastewaters. *Polish Journal of Environmental Studies*, 2005, 14 (6): 789-97.

Novotny, A., Imhoff,K.R., Olthof,M., Krenkel,P.A.Karl Imhoff's Handbook of Urban Drainage and Wastewater Disposal. John Wiley&Sons,New York, 1989.p.260.

Preethi, V., K. S. Parama Kalyani, K. Iyappan, C. Srinivasakannan, N. Balasubramaniam, and N. Vedaraman.Ozonation of tannery effluent for removal of cod and color. *Journal of Hazardous Materials*, 2009, 166 (1): 150-154.

Pophali, G., R,Hedau,S., Gedam,N., Rao,N.N., Nandy,T.Treatment of refractory organics from membrane rejects using ozonation. *Journal of Hazardous Materials,* 2011, 189 (2011):273-277

Raghu, S. and C. Ahmed Basha.Chemical or electrochemical techniques, followed by ion exchange, for recycle of textile dye wastewater. *Journal of Hazardous Materials*, 2007, 149 (2): 324-330.

Raganathan,K., Kabadgi,S.S. Studies on Feasibility of Reverse Osmosis (Membrane) Technology for Treatment of Tannery Wastewater. *Journal of Environmental Protection*, 2011 (2): 37-46.

Rajalo, G., and T. Petrovskaya.Selective electrochemical oxidation of sulphides in tannery wastewater. *Environmental Technology*, 1996, 17 (6): 605-12.

Rao,J.R., Thanikaivelan, P., Nair, B.U.An eco-friendly option for less-chrome and dye-free leather processing: In situ generation of natural colors in leather tanned with Cr-Fe complex. *Clean technologies and Environmental Policy,* 2002 (4):115-121.

Rameshraja, D. and S. Suresh.Treatment of tannery wastewater by various oxidation and combined processes. *International Journal of Environmental Research* 5, 2011 (2): 349-360.

Rivela, B., R. Méndez, C. Bornhardt, and G. Vidal.Towards a cleaner production in developing countries: A case study in a chilean tannery. *Waste Management and Research*, 2004,22 (3): 131-41.

Rodrigues, M. A. S., F. D. R. Amado, J. L. N. Xavier, K. F. Streit, A. M. Bernardes, and J. Z. Ferreira.Application of photoelectrochemical-electrodialysis treatment for the recovery and reuse of water from tannery effluents. *Journal of Cleaner Production*, 2008, 16 (5): 605-11.

Roš, M., and A. Gantar.Possibilities of reduction of recipient loading of tannery wastewater in slovenia. *Water Science and Technology*, 1998, 37 (8): 145-52.

R. Ramesh Babu, N.S. Bhadrinarayana, K.M.Meera Sheriffa Begum, N.Anantharaman. Treatment of tannery wastewater by electrocoagulation. *Journal of the University of Chemical Technology and Metallurgy*, 2007, 42 (2), 201-207.

Ryu, H. -D, S. -I Lee, K. -Y Chung.Chemical oxygen demand removal efficiency of biological treatment process treating tannery wastewater following seawater flocculation. *Environmental Engineering Science*, 2007, 24 (3): 394-9.

Scholz, W., Lucas M, Techno-economic evaluation of membrane filtration for the recovery and reuse of tannery chemicals, *Water Res*.2003, 37: 1859–1867.

Schrank, S. G., H. J. José, R. F. P. M. Moreira,H. Fr Schröder. Applicability of fenton and H2O2/UV reactions in the treatment of tannery wastewaters. *Chemosphere*, 2005, 60 (5): 644-55.

Şengil, I. A., S. Kulaç, M. Özacar.Treatment of tannery liming drum wastewater by electrocoagulation. *Journal of Hazardous Materials*, 2009, 167 (1-3): 940-6.

Song, Z., C. J. Williams,R. G. J. Edyvean.Treatment of tannery wastewater by chemical coagulation. *Desalination*, 2004, 164 (3): 249-59.

Song, Z., C. J. Williams, R. G. J. Edyvean.Coagulation and anaerobic digestion of tannery wastewater. *Process Safety and Environmental Protection*, 2001, 79 (1): 23-28.

Song, Z., C. J. Williams,R. G. J. Edyvean. Sedimentation of tannery wastewater. *Water Research* , 2000, 34(7): 2171-2176.

Srinivasan, S. V., G. P. S. Mary, C. Kalyanaraman, P. S. Sureshkumar, K. Sri Balakameswari, R. Suthanthararajan, and E. Ravindranath. Combined advanced oxidation and biological treatment of tannery effluent. *Clean Technologies and Environmental Policy*, 2011 :1-6.

Sundarapandiyan, S., R. Chandrasekar, B. Ramanaiah, S. Krishnan, and P. Saravanan. Electrochemical oxidation and reuse of tannery saline wastewater. *Journal of Hazardous Materials*, 2010, 180 (1-3): 197-203.

Suresh, V., M. Kanthimathi, P. Thanikaivelan, J. Raghava Rao, and B. Unni Nair.An improved product-process for cleaner chrome tanning in leather processing. *Journal of Cleaner Production*, 2001, 9 (6): 483-91.

Suthanthararajan, R., E. Ravindranath, K. Chitra, B. Umamaheswari, T. Ramesh, and S. Rajamani. Membrane application for recovery and reuse of water from treated tannery wastewater. *Desalination*, 2004, 164 (2): 151-156.

Szpyrkowicz, L., S. N. Kaul, R. N. Neti, and S. Satyanarayan. Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater. *Water Research*, 2005, 39 (8): 1601-13.

Szpyrkowicz, L., J. Naumczyk, and F. Zilio-Grandi. Electrochemical treatment of tannery wastewater using Ti/Pt and T/P/Ir electrodes. *Water Research*, 1995, 29 (2): 517-24.

Tahir, S. S., and R. Naseem. Removal of cr(III) from tannery wastewater by adsorption onto bentonite clay. *Separation and Purification Technology*, 2007, 53 (3): 312-21.

Tare,V., S. Gupta and P.Bose. Case studies on biological treatment of tannery effluents in India.*J.Air Waste Manage.Assoc*., 2003, 53:976-982.

Tariq, S. R., M. H. Shah, N. Shaheen, A. Khalique, S. Manzoor, and M. Jaffar. Multivariate analysis of selected metals in tannery effluents and related soil. *Journal of Hazardous Materials*, 2005, 122 (1-2): 17-22.

Tiravanti, G., Petruzzelli, D., and Passino, R. Pretreatment of tannery wastewaters by an ion exchange process for cr(III) removal and recovery, *Water Science and Technology*,1997, 36 (2-3):197-207.

Tunay, O., D. Orhon, and I. Kabdasli.Pretreatment requirements for leather tanning industry wastewaters. *Water Science and Technology*, 1994, 29 (9:) 121-128.

Vidal, G., Nieto, J., Mansilla, H. D., and Bornhardt, C. Combined oxidative and biological treatment of separated streams of tannery wastewater, Water Science and Technology, 2004, 49 (4): 287-292.

Vijayaraghavan, K. and D. V. S. Murthy. Effect of toxic substances in anaerobic treatment of tannery wastewaters. *Bioprocess Engineering* , 1997, 16 (3): 151-155.

Vlyssides, A. G.,C. J. Israilides.Detoxification of tannery waste liquors with an electrolysis system. *Environmental Pollution*, 1997, 97 (1-2): 147-52.

Zaroual, Z., M. Azzi, N. Saib, Y. Karhat, and M. Zertoubi. Treatment of tannery effluent by an electrocoagulation process. *Journal of the American Leather Chemists Association*, 2005, 100 (1): 16-21.

Zimbron, J.A.,Reardon, K.F. *Water Research,* 2009,43:1831-1840.

Zongo, I., J. Wéthé, B. Merzouk, A. H. Maïga, F. Lapicque, and J. -P Leclerc. Electrocoagulation for the treatment of two textile wastewater and simulated tannery effluents: Energetic study and operating parameters effects on pollutants removal. *European Journal of Scientific Research*, 2011, 62 (2): 216-235.