International Journal of Chemical and Biomolecular Science
Vol. 4, No. 4, 2018, pp. 69-80
http://www.aiscience.org/journal/ijcbs
ISSN: 2381-7372 (Print); ISSN: 2381-7380 (Online)

Treatment Technologies for Wastewater from Cosmetic Industry - A Review

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Abstract

The increasing need for a green and eco-friendly environment necessitates a search for treatment processes to mitigate the environmental degradation attendant upon the discharge of wastewater from Cosmetic industries. The proliferation of Cosmetic industries as a means to fulfil the insatiable need of man for personal beautification necessitate this review since their effluent is inevitably discharged into the environment. This present review is aimed at the understanding composition of wastewater from different cosmetic industries for the purpose of proffering a suitable treatment technology. The review highlights the composition of various cosmetic industries, their environmental impacts as well as a myriad of treatment technologies and their optimum operating conditions.

Keywords

Treatment Technologies, Wastewater, Cosmetic Industry

Received: November 23, 2018 / Accepted: December 14, 2018 / Published online: January 16, 2019

1. Introduction

The role of the cosmetic industry in daily human activities cannot be over-emphasized. They have varying functions on applications to the human external body (epidermis, hair system, nails, lips, and external genital organs) which includes Cleaning, Perfuming, and changing appearance as well as maintaining an outlook of the body [1]. Cosmetics can be classified as personal care products which includes fragrances, sunscreen, ultraviolet filters and are employed for the medical treatment of humans in order to enhance their standard of living [2-4]. A few years ago, cosmetics products as well as other personal care products that do not fall within cosmetic regulation (disinfectants, insect repellants, dietary supplements), have raised significant concerns as being of the emerging environmental pollutants because of their effects on the aquatic environment; their ecological and environmental impact. They are sometimes termed to be environmentally persistent, bioactive, and potentially to bio-accumulate [5]. Ostensibly, most of the substances are released in large quantities into the environment dominated by flora and fauna daily through discharge of their wastewater.

Over the years, Cosmetic wastewater has been characterized with contain very high Chemical Oxygen Demand (COD) (> 100000 mg/l), BOD5, Total organic carbon levels, High concentrations of petroleum ether extract, Organic nitrogen, Organic phosphorus, suspended solids, fats and oils, and detergents [6-8]. Most of the dominant contaminants in cosmetic wastewater are scarcely biodegradable and this

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applies not only to surfactants and dyes that are well known but also to fragrances and sunscreen UV light, which are incorporated into their production. They are non-polar and difficult for biological degradation by micro-organisms [6].

Cosmetics wastewater poses a lot of threat to the environment with ecological effects being the most highly pronounced which is as a result of their large external applications such as washing, showering, and bathing thus introduced into the environment unaltered [8-9]. Also, huge amounts of surfactants are released into aquatic and terrestrial environment daily. The upshot is toxicity of plants and animals species which invariably has negative impacts on human health [10]

Several researchers have worked on the characterization of cosmetic wastewater in order to elucidate their composition and impacts on the surrounding environment. Apfel [11] reported that effluents from leather and cosmetic industries deteriorate the quality of groundwater. The result showed that standard parameters investigated were above the permissible limits. Ritter [12] investigated that wastewater from a cosmetic industry poses threat to the environment on discharge without treatment. The results of the findings showed that the effluents contain pollution indicator parameters such as EC, PH, BOD, PO43−, and turbidity are higher than the tolerance limits recommended by the World Health Organization. The microbial study showed the presence of *P. aeruginosa* and *S. aureus* in the effluents. The findings of this study proved that the effluents can be a potential public and environmental health hazard. Melo et al. [8] further probed the toxicity of cosmetic wastewater by conducting an aquatic toxicity bioassay for eco-toxicological characterization by using *C similis*, *C. dubia*, and *P. subcapitata* as an organism at different conditions. The results revealed that the wastewater from the cosmetics company presented high toxicity to all test organisms. The presence of high concentration of COD and BOD above the critical values lay down by international and national regulatory bodies is considered unacceptable in receiving water bodies. This is because they lead to eutrophication and various health impacts in humans and animals [13-15].

Cosmetics is ubiquitous in water bodies and this is a growing concern as it has a long-term environmental and human health effects on exposure to chemicals which are the main constituents of the products [16-18]. In the aquatic environments, cosmetics can lead to bioaccumulation in fish and other water living creatures with a potential to trigger various unexpected interference on them. For instance, chronic exposure to estrogenic pollutants in water can result in the enlargement of fish livers and they can impact negatively on the reproduction systems as well as trigger histo-pathological changes in zebra-fish [19-20]. Notably, they exhibit adverse cumulative effects on terrestrial and aquatic ecosystems [21]. These toxic chemicals are released into aquatic environments through wastewater from sewage treatment plants before they reach the receiving soil, surface water, sediment, and groundwater [2]. This has been reported by different authors in different parts of the world and includes the UK, the US, Italy and accumulate in aquatic environments [23-25]. Some authors in South China, Europe and other regions of the world have also reported this [28-30].

Indubitably, cosmetic wastewater needs to be subjected to intensive treatment before discharge into the environment in order to safeguard the health of both flora and fauna that are widely distributed in the environment. Based on the available literature on treatment of cosmetic wastewater, this review gives an overview of the various treatment technologies that have been adopted to treat cosmetic wastewater in order to achieve zero pollution in compliance with international standards for release of industrial effluents into the environment.

2. Treatment Technologies of Cosmetic Wastewater

The proliferation of cosmetic products which resulted from the ever-increasing demands of human being necessitates the discharge of some pollutants which is characterized by high levels of COD, suspended solids, fats and oils, and detergents into the aquatic body. Thus, its discharge is inevitable but the rate of environmental degradation can be reduced or apprehended by the adoption of various economic and sustainable treatment technologies. Hence, research into more efficient, eco-friendly and economical effluent treatment technologies so as to degrade the complex molecules into simpler ones is crucial to mitigate the polluted water body [11-13]. The various treatment technologies employed for the treatment of this wastewater ranges from conventional biological techniques to physicochemical methods. The latter in most cases is used as a pretreatment stage before the adoption of conventional biological techniques [13].

In this review, various physicochemical and Advanced Oxidation Processes (AOP) treatment technologies for cosmetic effluent will be understudied for economical and efficient ways of mitigating the environmental impact of this effluent.

2.1. Physico-Chemical Technology for Cosmetic Wastewater Treatment

Coagulation

Coagulation is a process in water and wastewater remediation in which coagulants such as ferric chloride, ferric sulfate etc. are added to wastewater in order to micellize the colloidal materials and cause the small particles to aggregate into larger settleable particles [14]. The mechanisms of operation are based on neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate [15]. One of the characteristics of wastewater treatment by coagulation is the removal of suspended solids and organic matters [14].

This process makes use of coagulants among which alum, iron salts, and lime are the commonest and their primary function is to aggregate colloidal particulates into larger particles which can ultimately be removed by sedimentation or floatation [16-17].

Several factors such as coagulant type, a dose of coagulant, optimum pH and dose and type of coagulant aid are responsible for the removal efficiency of this process. $Ca(OH)_2$ as a coagulant aid not only facilitate coagulation but also regulate the pH of the medium [18].

In wastewater remediation, coagulation processes are majorly used for the removal of colloidal material with potentials to impart color and turbidity [14]. It is also used as a pretreatment prior to biological treatment in order to enhance the biodegradability of the wastewater during the biological treatment. The hybridization of coagulation and precipitation processes has found major usability in the treatment of wastewater to separate suspended and/or fatty particles [20]. The pros of this treatment technology over other physicochemical processes is its cost-effectiveness as well as low energy consumption [21].

1. Operating conditions

An intensive study on pieces of literature relating to the application of coagulation to wastewater treatment was carried out and the following optimum operating conditions was observed. In this process, the operating variables that ensure optimal working conditions are pH, type and dose of coagulant and type and dose of coagulant aids.

Effect of pH

The pH of the medium to a large extent determines the form of the coagulant in the sewage tank [20]. The Fe-species present in the medium at pH of 4.6 and 8.23 when Ferric chloride and $Ca(OH)_2$ were used as coagulant and coagulant aids respectively to treat a wastewater from a personal care products industry are $Fe(OH)^{2+}$ and $Fe(OH)_3$ respectively and this ultimately determine the mechanism of removal [21]. He observed neutralization of negatively charged particles when $Fe(OH)^{2+}$ was in solution while $Fe(OH)_3$, a hydrophobic substance, works by adsorption of particulate contaminants in particulate through surface interactions. Amuda and Amoo [22], operated optimum pH of 9 when ferric chloride is used to treat beverage industry effluent. It is of note to monitor the pH because the higher dosage of the coagulant which increases the concentration of metallic ion have high tendency to reduce the removal efficiency of this process due to the reduction in the pH value [22].

Effect of Coagulant Dosage

The optimum dose of a coagulant is the value above which there is no massive difference in the increase of removal efficiency with a further addition of coagulant [19]. At a higher dose of the coagulants, there is an attended substantial increase in the removal efficiency as measured by the removal rate of COD, TSS, and TP. However, at a particular concentration of the coagulant above the limit, the removal rate of COD, TSS and TP decreases with an increase in the dosage of coagulant. This may be due to the re-suspension of solids at that concentration [23]. Furthermore, the addition of the coagulant far beyond the limit will have no effect on the removal efficiency and this can be attributed to the accumulation of positive charges on the particles surface thereby re-dispersing the particles.

Effect of coagulant aids

Coagulant aids such as polyelectrolytes facilitate the treatment of water and wastewater and may also be used as a primary coagulant for the same purpose [25]. Polyelectrolytes in most cases are advantageous over chemical coagulants because they are easy to handle and are easily biodegradable [26]. The removal efficiency of COD, TSS and TP serve as the benchmark to measure the optimal dose of coagulant aids [14]. It was observed that the simultaneous increase of both the coagulant and coagulant aid below the optimal dosage improves the removal efficiency of the of COD, TSS, and TP. However, further addition of the coagulant aid above the optimum dosage result into a gradual decrease in the removal of TSS due to the re-suspension of particles at higher doses of the coagulant aid (Polyelectrolyte, calcium hydroxide, etc.) [14]. This is contrary with respect to the removal rate of COD as an excess dose of the coagulant aid flocs formation. As a result of the suspension of a greater number of flocs, the removal of a larger amount of organic matter which is a measure of COD will be enhanced due to the availability of larger surface area on which adsorption of the organic matter took place [22].

Effect of residual metallic ion content

The concentration of the residual metallic ion content in treated effluent after the coagulation/flocculation process is one of the ways to measure the correct coagulant dose to be used [27-28]. Amuda and Amoo [22] observed that when 250 and2000 mg /L alum doses were used for treatment, the total amount of Al^{3+} present is 9.8 and 10.1 mg Al3+/1 L in wastewater. It was observed that the higher dose of the coagulant decreases the residual metal ion concentration in the supernatant. Amuda and Amoo [22] reported that higher dose of ferric chloride increased supersaturation of Fe $(OH)_3$ when Ca $(OH)_2$ was used as a coagulant aid. Hence, increased nucleation rate of Fe $(OH)_3$ consequently removed the iron in solution more effectively by being adsorbed by the precipitate.

Table 1. Overview of earlier studies on coagulation/flocculation.

S/N	REFERENCES	EXPERIMENTAL CONDITONS	IMPORTANT FINDINGS
1.	El-gohary et al., 2009	A Phipps & Bird standard jar-test unit Model 7790-400 and the sample placed under a state of rapid stirring (267 rpm) while the coagulant was added slowly to the solution under stirring for 60 s. Operating pH varied in the range of 4.6-8.23. 600 mg/l of the coagulant ($FeCl_3$) was aided by 300-500 mg/l lime Ca $(OH)_2$.	At this operating condition, the% removal rate for COD_{total}, COD_{sol}, COD_{part}, BOD_{5total}, TSS (105 °C), VSS (550 °C) Total-P, Oil and grease and BOD_5/COD ratio are 75.8±9.7, 62.9±14.8, 95.4±1.8, 78.0±15.8, 96±3, 92±4.7, 60.2±40, 75.8±3.3 and 15.2 respectively. Coagulation under this operating condition is ineffective in the removal of BOD_5/COD ratio (15.2%).
2.	El-gohary et al., 2009	A Phipps & Bird standard jar-test unit Model 7790-400 and the sample placed under a state of rapid stirring (267 rpm) while the coagulant was added slowly to the solution under stirring for 60 s. Operating pH is 6.9. 700mg/l of the coagulant (Alum) was aided by 120-200 mg/l lime (Ca $(OH)_2$.	At this operating condition, the% removal rate for COD_{total}, COD_{sol}., COD_{part}, BOD_{5total}, TSS (105 °C), VSS (550 °C) Total-P, Oil and grease and BOD_5/COD ratio are 76.7±9.9, 68.0±10.6, 89.4±8.9, 74.1±19.3, 93.6±4.7, 87.0±5.6, 88.1±3.2 and 76.2±1.9. It was observed that the chemistry of removal is adsorption and neutralization of charge.
3.	Aloui et al., 2009	3.0 g/l of alum (coagulant) was aided by 1 g/ l lime Ca $(OH)_2$with an operating pH of 7.	The removal rate of Anionic surfactant, COD and BOD_5 are53.3, 37.3 and 51.2% respectively. The mechanism of removal at this operating condition is sweep-floc coagulation by embellishing the aluminum hydroxide precipitate (Gregory and Duan, 2001).
4.	El-gohary et al., 2009	A Phipps & Bird standard jar-test unit Model 7790-400 and the sample placed under a state of rapid stirring (267 rpm) while the coagulant was added slowly to the solution under stirring for 60 s. The Operating pH is 9.1. 800 mg/l of ferrous Sulfate was aided by 260 mg/l lime (Ca $(OH)_2$.	At this operating condition, the% removal rate for COD_{total}, COD_{sol}., COD_{part}, BOD_{5total}, TSS (105 °C), VSS (550 °C) Total-P, Oil and grease and BOD_5/COD ratio are 77.5±9.6, 65.6±15.3, 95.7±2.6, 78.7±15.6, 94.3±3.3, 89.4±8.1 and 82.2±7.4, 76.4±3.1 respectively. This coagulant is only effective in an alkali medium.
5.	Bogacki et al., 2011	Waste water from Cosmetic industry in Poland were refrigerated to 4°C and was allowed to settle for 30 min in order to remove easily settleable solids. The optimum pH used is 9.0 with 900 mg/l of $FeCl_3$ as the coagulant.	The% removal efficiency of COD was 66.4%. He also observed an absolute (100%) removal of colour and turbidity at this operating condition. The remediating efficiency of coagulation was attributed to a large amount of suspensions as well as the presence of large amounts of polycyclic musks (aromatic compounds). It is of note to state that the predominant form of iron in wastewater at that pH is Fe (OH)3.

2.2. Oxidation Treatment Technology for Cosmetic Wastewater

The bureaucratic regulations operational in the discharge of industrial effluent necessitates the implementation of new treatment technologies for a more efficacious treatment of a myriad of wastewaters. Several oxidation technologies such as Hydrothermal Oxidation Technology (HOT) e.g. catalytic wet peroxide-oxidation, Advanced Oxidation Processes (AOP) e.g. Fenton oxidation and Chemical Oxidation Technology (COT) e.g. ozonation have been reported as reliable strategies to mitigate toxicity and increase the biodegradability of cosmetics effluent [13, 29, 30, 31]. For the case of this study, emphasis will be laid on the AOPs.

2.2.1. Catalytic Wet Air Oxidation

Catalytic wet peroxide oxidation (CWPO) process is based on the oxidation of organic pollutants by hydrogen peroxide in the presence of a metal-bearing solid catalyst [29]. The CWPO process initially adapted the classical Fenton's reagent to treat highly phenolic organic compounds with the removal efficiencies (up to 95%) under mild conditions using hydrogen peroxide and a homogeneous Fe^{2+} catalyst [32].

In spite of the efficiency of the homogeneous Fe2+ catalyst in the elimination of organic pollutants, this process has drawbacks in the narrow range of pH (Usually around 3.0) and difficulties in the recovery of the catalyst which may lead to secondary pollution [33]. This inadequacies encountered in the usage of CWPO can be overcome by the use of a heterogeneous catalyst. Thus, a great number of materials containing iron, copper and aluminum supported on oxides, clays, zeolite and polymers as active catalysts have been proposed to exhibit the advantages of heterogeneous catalysis thereby exuding a relatively higher oxidation efficiency as well as a lower sensitivity to pH compared with homogeneous catalysis at the same operating conditions [32-33]. The heterogeneous catalytic wet hydrogen peroxide oxidation (CWHPO) is advantageous over the classical homogeneous Fenton-like process in the following ways: (i) Improvement of the catalytic activity; (ii) the lack of secondary pollutant due to the iron-containing sludge; (iii) the widening of the pH range and the possibility of re-usage of catalyst in successive cycles [34-35].

The choice of solid catalyst to use for the process among other factors cannot be overemphasized as this goes a long way to determine the efficiency of this treatment technology. It was observed that some organic pollutants have the propensity to deactivate the catalyst as well as leach out the catalytically active elements [34, 37]. Several studies carried out with clay-based catalysts immobilized with Fe hydroxo complexes or mixed with (Al–Cu) complexes have proven the efficiency of mixed pillared clays in the total oxidation organic compounds in water with the use of hydrogen peroxide as the oxidant [36-37]

One of the advantages of the process is the allowance it provides for the operation to be carried out in an ambient condition and at a lower cost [38].

1. Operating conditions

Effect of the solid support

The choice of solid catalyst determines to a large extent the remediating effectiveness of this process as it dictates the mechanism of reaction for removal. CWPO depletes pollutants either by adsorption on a solid support or by total or partial mineralization of organic matter by the generated hydroxyl radicals [39]. The mineralization of organic matter depends on the oxidant generated and this is absolutely dependent on the interaction between the solid catalyst.

Bautista et al. [29] observed that the decomposition of H_2O_2 was produced in two competing ways when Fe catalyst immobilized activated carbon was used to remediate effluents from the cosmetics industry. He suggested that the decomposition of H_2O_2 gives rise to HO• and HOO• radicals by the action of Fe while the Activated Carbon (AC) surface promotes the decomposition into H_2O_2 into O_2 which is not reactive at the operating temperature.

However, decomposition into O_2 by the action of AC is probably depending on the organic pollutant in question [40]. In the case of phenol oxidation, it works contrariwise since phenol is adsorbed onto the activated carbon in a much higher amount than the organic pollutant in the cosmetic effluent thereby clogging the carbon surface which inhibits the decomposition of H_2O_2 into O_2. Consequently, Fe supported on activated carbon has been successfully used for phenol oxidation but have reduced efficiency for cosmetic effluent due to the decomposition of H_2O_2 into O_2 [40].

Also, in the case of Fe/ γ-Al_2O_3, the adsorption of organic matter on the surface of the Al_2SO_3 is negligible but yet proved to be more effective than the Fe/AC for the treatment of these cosmetic wastewaters by CWPO [41]. This is due to the non-production of O_2 in spite of the interaction of H_2O_2 with the surface of alumina but rather only the Fe catalyst decomposes H_2O_2 into HO• and HOO• due to the inertness of alumina with H_2O_2 [42]. Summarily, the interaction between H_2O_2 and the solid support in the presence of the organic matter should be considered when choosing a solid support for the catalyst.

Effect of the immobilized metal load.

The metal content of the catalyst used in CWPO process plays a very important role in the decomposition of H_2O_2 into its radicals for the mineralization of the organic matter present in the pollutant [30]. Increasing the metal load of the catalyst will lead to an increase in the removal efficiency of the process provided that the concentration of the metal doesn't exceed the acceptable limit. Thus, any concentration above the limit will lead to a decrease in the degradation efficiency. Bautista et al. [29] in the remediation of effluents from cosmetic industry using CWPO observed a decrease in COD (83.5–75.5%) and TOC (55.9 - 52.0%) when the Fe supported on alumina increased from 4% of optimum dosage to 8%.

Effect of calcination temperature

The mineralization of organic matters in the wastewater also depends on the calcination temperature of the catalyst during catalyst build-up. The increase in calcination temperature of the catalyst results in the reduction of COD and TOC removal [41]. This reduction in the efficiency is as a result of the decrease in the content of the metal (e.g. Fe_2O_3) nanoparticles due to the high calcination temperature and this ultimately leads to a decrease in the decomposition of H_2O_2 into HO• and HOO• radicals [43].

Bautista et al. [29] showed a higher content of α- Fe_2O_3 nanoparticles in the catalyst calcined at a lower temperature (33% at 300°C and 26% at 450°C) respectively.

Effect of operating temperature

The effect of the operating temperature largely determines the rate of decomposition of H_2O_2 as well as the conversion of COD and TOC [28]. An increase in temperature enhances the decomposition into HO• and HOO• radicals thereby leading to higher COD and TOC abatement. On the contrary, high reaction temperatures promote thermal degradation of H_2O_2 into O_2 (a weak oxidant) and this ultimately reduces the remediating efficiency of CWPO process [39].

Hence, the balance between the two competing ways of the decomposition of H2O2 into HO• radicals (promoted by Fe) or O_2 (favored at increasing temperature) plays a major role in determining the efficiency of organic matter removal. In addition, increase in temperature below acceptable limit also increases the biodegradability of the effluent [41].

Bautista et al. [29] showed that during the CWPO of cosmetic wastewaters with the Al–4%FeT300 (4% of Fe supported on Al_2SO_3 at a calcination temperature of 300) catalyst, the COD removed per unit H_2O_2 increased from 0.21 to 0.39 when the temperature was raised from 70°C to 85°C which is still in the range of the working temperature of 85°C.

2. Overview of the earlier studies on catalytic wet peroxide oxidation

Few researchers have looked into catalytic wet peroxide oxidation for the treatment of cosmetic wastewater. However, Bautista et al. [29] worked on waste-water samples from a cosmetic industry in Spain with characteristics of COD (4730 and 2300 mg/L) and total organic carbon (TOC) (1220 and 686 mg/L).

The experiment was carried out in batch in 100 mL stoppered glass bottles in a thermostated shaker, which maintains a constant temperature with a stirring velocity equivalent to 200 rpm. The catalyst used was in a powdered form and at 5 g/L Catalysts based on Fe supported on γ-Al_2O_3 calcined at 300°C with 4% Fe content and a working temperature of 85°C was used. The operating pH was 3.0 and the concentration of H2O2 used was 9050 mg/L.

The result of this experiment is a remarkable COD and TOC reduction around 85 and 55.9% respectively. The Fe/α-Al_2O_3 catalyst showed a reasonable stability such that 15% decrease in activity was observed after three successive runs. The Increase of Fe load of the catalyst from 4% (optimum dosage) to 8% decreases the COD (83.5 – 73.5%) and TOC (55.9 – 52.0%) removal [29].

2.2.2. Electrochemical Oxidation

Electrochemical Advanced Oxidation Process (EAOPs) is an amalgam of several processes that use electrochemical techniques to generate strong oxidants. This treatment technology is based on the generation of strong oxidants (hydroxyl radicals (●OH)) electrochemically. The various types of Electrochemical Advanced Oxidation Process are Electrochemical Oxidation (EO), electrocoagulation, electro-flotation, electro-dialysis, electro-Fentonphotoelectro-Fenton etc. [44].

EO has become attractive to environmentalist because of its capacity to completely mineralize highly recalcitrant organic pollutants, such as pharmaceuticals, pesticides, personal care products, and even carboxylic acids [46-50]. Apart from the efficient removal of highly refractory organic compounds, the EO also present several advantages over other AOPs, such as mild operating atmosphere under ambient condition, absence of additional requirement of auxiliary chemicals, non-production of secondary waste streams that require further treatment, could be easily synergized with other water treatment technologies and present affordable capital and operational costs [44, 51, 52]. All these aforementioned characteristics make EO eco-friendly with a small carbon footprint.

In this study, the chemistry and optimum operating conditions of EO or Anodic Oxidation will be thoroughly investigated.

1. Principles of electrochemical oxidation

The mechanism/chemistry of electrochemical oxidation is the redox reactions taking place at anode (e.g. oxidation of pollutants) and cathode (e.g. reduction of heavy metals) to remove pollutants, which have been widely used as a heavy metal remediation solution [53-54]. The reaction mechanism of electrochemical oxidation involves two pathways namely (i) direct electron transfer to the anode surface M and (ii) indirect oxidation [55-57].

In the first pathway, electrons are transferred between the anode surface (M) and the organic pollutants involved. It involves the intermediation of the electrons which oxidizes some highly refractory organic pollutants at defined potentials [56-57]. This process involves four pathways the surface, (iii) direct electrochemical reaction by charge transfer to the pollutant and (iv) desorption and transport of oxidized products to the bulk [53].

The second pathway of indirect oxidation involves electro-generation of highly oxidant species at the electrode surface [58]. These oxidants such as heterogeneous reactive oxygen species (ROS) (from electrolysis of oxidation of water to oxygen), powerful $^\bullet$OH radicals at the anode surface (M ($^\bullet$OH)) (from anodic oxidation of water) by Eq. (1), H_2O_2 oxidant (from dimerization of M ($^\bullet$OH)) by Eq. (2) and Ozone (from water discharge at the anode surface) by Eq. (3) [58].

$$M + H_2O \rightarrow (M\,^\bullet OH) + H^+ + e^- \quad (1)$$

$$2\,(M\,^\bullet OH) \rightarrow 2MO + H_2O_2 \quad (2)$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- \quad (3)$$

In spite of the remediating efficiency of EO, the formation of organo-chlorinated species such as chloramines, trihalomethanes, haloacetonitriles, and haloketones, as a result, the reaction of active chlorine species with different functional groups of organic matter [59-60] is a major drawback of AO. This is because organo-chlorinated products display high toxicity and usually more refractory than parent molecules.

The efficiency of EO depends absolutely on the mass transfer of pollutants from the bulk to the surface of the anode [56]. Hence, the electrocatalytic properties of anode materials play an important role in the removal efficiency of EO technology

[58]. It has been reported that the nature of anode material determines the rate of degradation of organic pollutants. Sometimes partial organics degradation alongside the formation of many recalcitrant species were observed while total organics mineralization alongside the production of few amounts of refractory intermediates were noticed using another anodic material.

2. Optimum operating conditions

pH of the medium

The pH of the medium to a large extent determines the form of the oxidant in the reaction medium. The commonest oxidant generated electrochemically from agents existing in bulk solution such as chloride, sulfate, phosphate, carbonate, and oxygen, respectively are active chlorine species, persulfate, per-phosphate, percarbonate, H_2O_2 etc. [61]. At a pH range of 1-3, the predominant active chlorine species present is Cl_2 while the dominant species present from pH range of 3-8 is HClO and for pH above 8, the predominant species is ClO [62]. The oxidation of organic matter is faster in acidic medium than in alkaline medium because HClO (E^o = 1.49 V/SHE) and Cl2 (E^o = 1.36 V/SHE) exhibit higher redox potentials than ClO− (E^o = 0.89 V/SHE [64]. At a pH higher than 8, the oxygen in the medium is reduced to hydroperoxide ion (HO2−) rather than H_2O_2 in the acidic medium [63].

The nature of the electrode

The efficiency and selectivity of anodic oxidation, as well as the rate of degradation of organic matters, depends strongly on the nature of anodic material [64]. In some cases, organics are partially degraded with the production of many recalcitrant species and in other cases, total mineralization of organic pollutants are observed [44]. Bautista et al. [30] justify the discrepancy in the rate of degradation as the interaction of M ($^\bullet$OH) with the anode surface and the result of this is the existence of two types of anode materials which are called active anode and non-active anode.

Moreover, at the surface of an active anode with low O2-overpotentials, the M ($^\bullet$OH) is transformed into a higher state of oxide or superoxide MO as shown in Eq. (4). The interaction of M ($^\bullet$OH) with the anode surface M produces a redox couple (MO/M) which acts as a mediator in the oxidation of organics.

$$M\,(^\bullet OH) \rightarrow MO + H^+ + e^- \qquad (4)$$

On the contrary, in non-active anodes with high O_2-overpotentials, the M ($^\bullet$OH) are weakly physic-sorbed at the surface of the anode and this reacts with the organics thereby mineralizing them. As a law, the higher potential for O2 evolution of the anode material, the weaker is the interaction of M ($^\bullet$OH) with the surface of the anode and the greater the organic pollutant degradation [64]. Summarily, the rate of electrode reactions is a function of the electro-catalytic activity of the anode material [65].

The nature of the organic pollutant

The remediating strength of EO depends on the efficiency of the direct anodic oxidation and indirect oxidation. The effectiveness of indirect oxidation depends on the nature and strength of the oxidant [63]. The oxidants such as active chlorine species, persulfate, per-phosphate and H_2O_2 are electrochemically generated from agents existing in the bulk solution such as chloride, sulfate, phosphate, carbonate, and oxygen, respectively [64]. In other words, the type and the nature of the oxidant electrochemically generated depend absolutely on the nature of organic pollutants. In some cases, salts are externally added in order to generate the desired oxidant.

Active chlorine species are the main oxidizing agents for indirect oxidation employed in wastewater treatment. The oxidation of organic pollutants with active chlorine is based on the direct oxidation of chloride ions at the anode to yield chlorine (Cl_2) as depicted by Equation (5), which diffuses away from the anode to be disproportionate to hypochlorous acid (HClO) and chloride as shown by Equation (6) [64].

$$2Cl^- \rightarrow Cl^2 + 2e^- \qquad (5)$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \qquad (6)$$

3. Overview of the earlier studies on electrochemical oxidation

In spite of the remediating efficiency of electrochemical oxidation, few pieces of research have experimented on its treatment of effluents from cosmetic waste-water industry. Zhang et al. [65] studied cyclic and linear siloxanes in cosmetic wastewater. The wastewater samples were collected in high-density polyethylene bottles from a cosmetic Waste Water Treatment Plant at Beijing, China.

The pollutant detected are Dodecamethylcyclohexasiloxane (D6, $C_{12}H_{36}O_6Si_6$) and linear siloxanes (L5 ($C_{12}H_{36}O_4Si_5$), L6 ($C_{14}H_{42}O_5Si_6$), L7 ($C_{16}H_{48}O_6Si_7$), L8 ($C_{18}H_{54}O_7Si_8$), L9 ($C_{20}H_{60}O_8Si_9$), L10 ($C_{22}H_{66}O_9Si_{10}$), L11 ($C_{24}H_{72}O_{10}Si_{11}$), L12 ($C_{26}H_{78}O_{11}Si_{12}$), L13 ($C_{28}H_{84}O_{12}Si_{13}$), L14 ($C_{30}H_{90}O_{13}Si_{14}$), L15 ($C_{32}H_{96}O_{14}Si_{15}$), L16 ($C_{34}H_{102}O_{15}Si_{16}$), L13 ($C_{28}H_{84}O_{12}Si_{13}$), L14 ($C_{30}H_{90}O_{13}Si_{14}$), L15 ($C_{32}H_{96}O_{14}Si_{15}$), L16 ($C_{34}H_{102}O_{15}Si_{16}$). These pollutants are present at a dominant level. The operating parameters in form of reaction time, current density, electrode plate distance, and electrode plate amounts are 20 min., 20 mA/cm2, 1.0cm and 5 pairs respectively. The anodic and cathodic materials were stainless steel plates.

It was observed that Dodecamethylcyclohexasiloxane (D6) and linear siloxanes (L5 to L16) were remediated in the range of 30.2% to 93.3%. Also, the removal efficiency of siloxane was significantly enhanced with increasing applied current density when the reaction time was increased from 0 to 20 min [65].

2.2.3. Fenton's Oxidation

Fenton's oxidation reaction is a method that uses a mixture of hydrogen peroxide and iron salts (Fe^{2+}) which produces hydroxyl radicals ($OH^{\bullet}$) in an acidic medium at ambient conditions [30]. The chemistry behind this process is the formation of reactive oxidizing species, able to effectively degrade the pollutants of the effluent and it involves pH adjustment, oxidation, neutralization and coagulation [68].

The little or no energy input necessary to activate the Fenton's reagent (H_2O_2 and iron salts (Fe^{2+}) makes this process advantageous over many physicochemical processes [66]. Furthermore, this method produces hydroxyl radicals with a reagent that are not capital intensive and also requires a relatively short time for the completion of the reaction. Hence, Fenton's reaction is often used when a high reduction of COD is of great necessity [67]. This oxidation process has found application in the treatment of sundry industrial wastewaters such as textile, pharmaceutical, paper and pulp, dyes, petroleum, and olive oil industry wastewaters [30]. This method is suitable for the discoloration of colored contaminants/pollutants and removal of odor ingredients with low energy consumption [13]. It also effectively destroys toxic wastes and non-biodegradable compounds in order to render them more suitable for conventional biological treatment [69].

1. Optimum operating conditions

An investigative analysis of the earlier published articles on the application of Fenton oxidation reaction to effluent treatment was carried out and the following optimum operating conditions was observed. In this process, the operating variables that ensure optimal working conditions are pH, temperature, iron, and hydrogen peroxide doses [30]. These factors vary depending on the source and composition of effluent under treatment.

Effect of pH

The pH of the medium to a large extent significantly affects the degradation of pollutants [70]. The optimum pH for different scientist varies between 2 and 4 [71-73]. At a pH lower than 2.5, $(Fe\ (II)\ (H_2O))^{2+}$will be formed thereby reducing the rate of reaction and the end result of this is the production of a lesser quantity of hydroxyl radicals thereby leading to the reduction of the degradation efficiency [74]. At a pH greater than 4, formation of Fe (II) complexes with the buffer occur thereby reducing the rate of decomposition of the pollutants because of the decrease of the unbounded iron species in the solution and ultimately bringing about the cessation of the production of ferrous ion [75]. A significant decrease was observed by Bautista et al. [30] in the efficiency of the process at high and low pH.

Amount of Ferrous Iron

The removal efficiency of the Fenton's process increases with an incremental increase in Fe2+ dose and subsequently decreases as it increases the organic matter of the influent [30, 76]. Also, at a higher Fe^{2+} dose, the scavenging effect is being favored as this will enhance the decomposition of H_2O_2 thereby engendering a rapid generation of hydroxyl radicals and a high concentration of this species in solution [30, 77]. However, as the ferrous ion concentration increases, the residual iron concentration as well the sludge in the effluent increases above the allowable limit, thereby incurring substantial cost for removal [78]. Also the recombination of OH radicals as well as brown turbidity that deterred the absorption of UV light resulted from higher addition of iron salt [79].

H_2O_2 Concentration

The degradation efficiency of the process increases with the incremental increase in H_2O_2 concentration up to a limit due to the higher production of hydroxyl radicals and this enhances the rate of TOC conversion [78]. On the contrary, the progressive increase in the dose of H2O2 produces no significant difference and ultimately lead to the decrease in the rate of removal probably due to the auto-decomposition of H_2O_2 to oxygen and water and also recombination of $OH^{\bullet}$ radicals [79]. The residual hydrogen peroxide concentration must not exceed 300 mg/l in order to avoid toxicity which can impair the existence of many micro-organisms and this will affect the overall removal efficiency in a situation where Fenton oxidation is used as a pretreatment to biological treatment [70].

Effect of Temperature

Few studies elucidated the effect of temperature on the efficiency of this oxidation process. The effect of temperature is dependent on the dosage of Fe (II) ion in solution. Lin and Lo [75] reported an operating temperature of 30◦C whereas Rivas et al. [70] operated an optimum temperature in the range of 10 to 40◦C. At a low dosage of Fe^{2+}, increase in temperature in the range of (25–75◦C) positively affect the degrading efficiency (especially in form of TOC conversion) and as the concentration of iron increases, the degrading effect decreases and becomes counterproductive at very high Fe^{2+} dosage [30].

However, the simultaneous increase of the temperature and the Fe^{2+} dose both improve the decomposition of H_2O_2 engenders a rapid generation of hydroxyl radicals which favors the occurrence of $OH^{\bullet}$ consuming reactions rather than oxidation of the organic matter [30].

Table 2. Review of earlier research works on Fenton oxidation.

S/N	REFERENCES	EXPERIMENTAL CONDITONS	IMPORTANT FINDINGS
1.	Bautista et al., 2010	Cosmetics effluent samples were stored at low temperature (4°C) in a dark environment immediately after reception from the cosmetic industry. The oxidation of organic matters were carried out in batch in 100mL stoppered glass bottles placed in a thermostated bath. The operating pH, Fe^{2+} concentration andH2O2 concentration to COD initial weight ratio corresponding to the theoretical stoichiometric value are 3.0, 200 mg/L and 2.12 respectively.	At 25°C TOC conversion was 45% while at 50 °C, 60% conversion was achieved. This is to say TOC conversion increases with temperature, however, it decreases as the Fe^{2+} dose increases and drastically reduce at higher Fe^{2+} loadings.
2.	Bogacki et al., 2013	Cosmetics Wastewater samples were refrigerated at 4°C and the process was conducted in a 1L cylindrical reactor. The operating pH, Fe^{2+} concentration and H_2O_2 concentration are 3.0, 1,000 mg/l and 300 mg/l respectively.	The COD Content of the effluent reduce from 2,888 mg/l to 295mg/l which invariably amounts to 87.7% removal rate. It is noteworthy to state that a deviation of the pH from 3.0 leads to a rapid decrease in the efficiency of the process. Also, the effect of the Fenton Process increases with increasing dosage of the reagents.
3.	Kang and Hwang 2000.	A real effluent with COD of approximately 1500 mg/l was understudied. 2 Litres capacity Fenton reactor operated at constant temperature of 25°C alongside a magnetic stirrer. The operating pH, FeSO4 dosage and hydrogen peroxide concentration are in the range of 2–9, 250–2250 mg/l and 0–1600 mg/l respectively.	The COD remediating efficiency is maximum around an operating pH of 3.5 and reduced drastically above a pH of 6.The higher the $FeSO_4$ dosage, the higher the COD removal rate until a concentration of 500 mg/l, beyond which COD removal remains constant and subsequently decreases.

3. Conclusion

Several processes have been under study so as to tackle the discharge of cosmetic products consisting high levels of COD, suspended solids, fats and oils, and detergents into the aquatic body. This comprises of water bodies rises with the increasing demand for cosmetic products. It is now of great importance to set up a physicochemical wastewater treatment technology which predominantly involves coagulation to increase the particles size of the product increases by agglomeration of the particles into a bigger size. The coagulation method, however, is followed up by certain operating conditions which will enhance the effectiveness of this technology. One of the vital conditions to this process involves the PH which relates the form of the coagulant in the sewage tank. Furthermore, in enhancing the coagulation process, the use of coagulant aid particularly the biodegradable polyelectrolyte at the optimum dosage, which enhances the treatment of the water and the wastewater. In other to measure the efficiency of the coagulant used necessity is placed on the determination of the residual metallic ion content in the treated effluent after the process. The catalytic wet air oxidation process is another viable approach to the treatment of water and wastewater by the oxidation of the pollutant with hydrogen peroxide in the present of metal-bearing catalysts. However, the process is deficient as a result of narrow PH range and its difficulty in the recovery of catalyst used generating secondary pollution. Apart from the Fenton's oxidation reaction which utilizes the mixture of hydrogen peroxide and iron salts to produce hydroxyl radical, electrochemical oxidation involves the generation of strong oxidant. This process has appreciable advantages over the previously discussed process in the aspect of complete mineralization of highly recalcitrant organic pollutants, such as pharmaceuticals, pesticides personal care products and even carboxylic acids other than the efficient removal of highly refractory organic compounds.

References

[1] Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products. Available online: http://eurex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:342:0059:0209:en: PDF (accessed on 15 July 2017).

[2] Kosma, C. I.; Lambropoulou, D. A.; Albanis, T. A. Occurrence, and removal of PCBs in municipal and hospital wastewaters in Greece. J. Hazard. Mater2010, 179 (1–3), 804–817.

[3] Liu, J. L.; Wong, M. H. Pharmaceuticals and personal care products (PPCPs): a review on environmental contamination in China. Environ. Int2013, 59, 208–224.

[4] Muthanna, T. M.; Plósz, B. G. The impact of hospital sewage discharge on the assessment of the environmental risk posed by priority pharmaceuticals: hydrodynamic modeling and measurements. 11th International Conference on Urban Drainage, Edinburgh, Scotland, UK. 2008.

[5] Brausch, J. M.; Rand, G. M. A review of personal care products in the aquatic environment: Environmental concentrations and toxicity. Chemosphere2011, 82, 1518–1532.

[6] Jan Bogacki; Jeremi Naumczyk; Piotr Marcinowski; Małgorzata Kucharski. Treatment of cosmetic wastewater using physicochemical and chemical methods. Chemik2011, 65, 2, 94-97.

[7] Puyol, D.; Monsalvo, V. M.; Mohedano, A. F.; Sanz, J. L.; Rodriguez, J. J. Cosmetic wastewater treatment by upflow anaerobic sludge blanket reactor. Journal of Hazardous Materials2011, 185, 1059–1065.

[8] Melo, E. D; Mounteer, A. H; Henrique, S. L.; Cibele, B. B.; Izabella, M. F. C. Toxicity identification evaluation of cosmetics industry wastewater. Journal of Hazardous Materials 2013, 244– 245, 329– 334.

[9] Ternes, T. A.; Joss, A.; Siegrist, H. Scrutinizing pharmaceuticals and personal care products in wastewater treatment. Environ. Sci. Technol. 2004, 38, 392A–399A.

[10] Jardak, K.; Drogui, P.; Daghrir, R. Surfactants in aquatic and terrestrial environment: Occurrence, behavior, and treatment processes. Environ. Sci. Pollut. Res. 2016, 23, 3195–3216.

[11] G. Apfel, Pollution control and abatement in the cosmetic industry, CTFA Cosmet. J. 4 (1972) 28–32.

[12] U. Ritter, Environmental pollution aspects at plants for cosmetics production, Wachse 115 (1989) 383–386. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions Parag.

[13] R. Gogate*, Aniruddha B. Pandit Chemical Engineering Section, M. U. I. C. T., Matunga, Mumbai 400019, India Accepted 4 April 2003.

[14] O. S. Amuda, A. O. Alade, Coagulation/flocculation process in the treatment of abattoir wastewater, Desalination 196 (2006) 22–31.

[15] J. Duan, J. Gregory, Coagulation by hydrolyzing metal salts, Advances in Colloid and Interface 100–102 (2003) 475–502.

[16] M. Plattes, A. Bertrand, B. Schmitt, J. Sinner, F. Verstraeten, J. Welfring, Removal of tungsten oxyanions from industrial wastewater by precipitation, coagulation and flocculation processes, Journal of Hazardous Materials 148 (2007) 613–615.

[17] G. Li, J. Gregory, Flocculation and sedimentation of high turbidity waters, Water Research 25 (1991) 1137–1143.

[18] F. El-Goharya, A. Tawfika, U. Mahmoud National Research Center, Water Pollution Research Department, 2009. El-Behouth St., Dokki, Cairo, Egypt.

[19] Amuda, A. Alade Department of Pure and Applied Chemistry, Department of Chemical Engineering, LadokeAkintola University of Technology, Ogbomoso, 210001, Received 9 June 2005; accepted 3 October 2005.

[20] P. Jarvis, B. Jefferson, J. Gregory, S. A. Parsons, A review of floc strength and breakage, Water Research 39 (2005) 3121–3137.

[21] I. A. Amoo, O. O. Ajayi, K. O. Ipinmoroti, O. S. Amuda, Performance optimization of coagulants/flocculants in the treatment of effluent from soap/detergent industry, in: S. I. Ahonkhai (Ed.), Proceedings of the 27th International Conference Chemical Society of Nigeria, Mindex Press, Benin City, Nigeria, 2004, pp. 415–420, Nigeria.

[22] O. S. Amuda, I. A. Amoo, Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment, Journal of Hazardous Materials 141 (2007) 778–783.

[23] H. I. Abdel-Shafy, O. Abo-El-Wafa, M. A. Azzam, Chemical treatment of industrial effluent, in: International Conference. Heavy Metals in the Environment, New Orleans, 1987, p. 452.

[24] M. B. Vanotti and P. G. Hunt, Trans. ASAE, 42 (1999) 1833–1840.

[25] K. Zhu, M. Gamal El-Din, A. K. Maawad, and D. Bromley, Environ. Technol., 25 (2004) 1177–1187.

[26] J. Szpak, D. Woods and K. Bouchard, Water Qual. Res, J. Can., 31 (1996) 51–64.

[27] Aguilar, E. Lefebvre, M. Y. Rahni and B. Legube, Environ. Technol., 17 (1996) 381–387.

[28] Bautista P., Mohedano A. F., Casas J. A., Zazo J. A., Rodriguez J. J., (2010), Oxidation of cosmetic wastewaters with H2O2 using a Fe/g-Al2O3 catalyst, Water Science and Technology, 61, 1631-1636.

[29] Bautista P., Mohedano A. F., Gilarranz M. A., Casas J. A., Rodriguez J. J., (2007), Application of Fenton oxidation to cosmetic wastewaters treatment, Journal of Hazardous Materials, 143, 128-134.

[30] Perdigón-Melón J. A., Carbajo J. B., Petre A. L., Rosal R., García-Calvo E., (2010), Coagulation-Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater, Journal of Hazardous Materials, 181, 127-132.

[31] Ovejero, J. L. Sotelo, F. Martinez, L. Gordo, Novel heterogeneous catalysts in the wet peroxide oxidation of phenol, Water Sci. Technol. 44 (2004) 153–160.

[32] W. Najjar, S. Azabou, S. Sayadi, A. Ghorbel, Screening of Fe–BEA catalysts for wet hydrogen peroxide oxidation of crude olive mill wastewater under mild conditions, Appl. Catal. B: Environ. 88 (2009) 299–304.

[33] J. Barrault, M. Abdellaoui, C. Bouchoule, A. Majeste´, J. M. Tatiboue¨ t, A. Louloudi, N. Papayannakos, N. H. Gangas, Catalytic wet peroxide oxidation over mixed (Al–Fe) pillared clays, Appl. Catal. B-Environ. 27 (2000) 225–230.

[34] M. N. Timofeeva, S. Ts. Khankhasaeva, S. V. Badmaeva, A. L. Chuvilin, E. B. Burgina, A. B. Ayupov, V. N. Panchenko, A. V. KIlukova, Appl. Catal. B: Environ. 59 (2005) 243–248.

[35] J. Barrault, C. Bouchoule, K. Echachoui, N. Frini-Srasra, M. Trabelsi, F. Bergaya, Appl. Catal. B: Environ. 15 (1998) 269.

[36] M. Abdellaoui, J. Barrault, C. Bouchoule, N. Frini-Srasra, F. Bergaya, J. Chim. Phys. 96 (1999) 419.

[37] F. Luck, Catal. Today 27 (1996) 195. M. Abdellaoui, Thesis, University of Poitiers, 14 September1999.

[38] Rey, M. Faraldos, J. A. Casas, J. A. Zazo, A. Bahamonde, J. J. Rodriguez, Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: Influence of iron precursor and activated carbon surface, Appl. Catal. B-Environ. 86 (2009) 69–77.

[39] J. A. Zazo, J. A. Casas, A. F. Mohedano, J. J. Rodriguez, Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst, Appl. Catal. B-Environ. 65 (2006) 261–268.

[40] N. Al-Hayek, J. P. Eymery, M. Dore´, Catalytic oxidation of phenols with hydrogen peroxide, Water Res. 19 (1985) 657–666.

[41] N. Al-Hayek, M. Dore´, Oxidation of phenols in water by hydrogen peroxide on alumina supported iron, Water Res. 24 (1990) 973–982.

[42] Cuzzola, M. Bernini, P. Salvadori, A preliminary study on iron species as heterogeneous catalysts for the degradation of linear alkylbenzene sulfonic acids by H2O2, Appl. Catal. B-Environ. 36 (2002) 231–237.

[43] F. C. Moreira, J. Soler, A. Fonseca, I. Saraiva, R. A. R. Boaventura, E. Brillas, V. J. P. Vilar.

[44] Incorporation of electrochemical advanced oxidation processes in multistage treatment system for sanitary landfill leachate, Water Res. 81 (2015) 375-387.

[45] J. R. Domínguez, T. González, P. Palo, J. Sánchez-Martín, M. A. Rodrigo, C. Sáez,

[46] Electrochemical degradation of a real pharmaceutical effluent, Water Air Soil Poll. 233 (2012)2685-2694.

[47] H. Olvera-Vargas, N. Oturan, E. Brillas, D. Buisson, G. Esposito, M. A. Oturan, Electrochemical advanced oxidation for cold incineration of the pharmaceutical ranitidine: Mineralization pathway and toxicity evolution, Chemosphere 177 (2014) 644-651.

[48] C. A. Martínez-Huitle, A. De Battisti, S. Ferro, S. Reyna, M. Cerro-López, M. A. Quiro, Removal of the pesticide methamidophos from aqueous solutions by electrooxidation using Pb/PbO2, Ti/SnO2, and Si/BDD electrodes, Environ. Sci. Technol. 42 (2008) 6929-6935.

[49] N. Oturan, E. D. van Hullebusch, H. Zhang, L. Mazeas, H. Budzinski, K. Le Menach, M. A. Oturan, Occurrence and removal of organic micropollutants in landfill leachates treated by electrochemical advanced oxidation processes, Environ. Sci. Technol. 49 (2015) 12187-12196.

[50] S. Garcia-Segura, E. Brillas, Mineralization of the recalcitrant oxalic and oxamic acids by electrochemical advanced oxidation processes using a boron-doped diamond anode, Water Res. 45 (2011) 2975-2984.

[51] S. Garcia-Segura, E. Brillas, L. Cornejo-Ponce, R. Salazar, Effect of the Fe3+/Cu2+ ratio on the removal of the recalcitrant oxalic and oxamic acids by electro-Fenton and solar photo electro-Fenton, Sol. Energy 124 (2016) 242-253.

[52] P. Grafias, P. Xekoukoulotakis, D. Mantzavinos, E. Diamadopoulos, Pilot treatment of olive pomace leachate by vertical-flow constructed wetland and electrochemical oxidation: An efficient hybrid process, Water Res. 44 (2010) 2773-2780.

[53] S. Garcia-Segura, E. Brillas, Advances in solar photo electro-Fenton: Decolorization and mineralization of the Direct Yellow 4 diazo dye using an autonomous solar pre-pilot plant, Electrochim. Acta 140 (2014) 384-395.

[54] L. Feng, E. D. van Hullebusch, M. A. Rodrigo, G. Esposito, M. A. Oturan, Chem. Eng. J. 228 (2013) 944-964. 69.

[55] C. A. Martínez-Huitle, M. A. Rodrigo, I. Sirés, O. Scialdone, Chem. Rev. 115 (2015) 13362-13407.

[56] E. G. Janzen, Y. Kotake, R. D. Hinton, Free Radical Biol. Med. 12 (1992) 169-173.

[57] E. Brillas, J. A. Garrido, R. M. Rodríguez, C. Arias, P. L. Cabot, F. Centellas, Port. Electrochim. Acta 26 (2008) 15-46.

[58] Y. Deng, J. D. Englehardt, Waste Manage. 27 (2007) 380-388.

[59] Sergi Garcia-Segura a, Joey D. Ocon b, Meng Nan Chong Electrochemical Oxidation Remediation of Real Wastewater Effluents - A review *aLaboratorid'Eletroquímica de Materials i Medi Ambient, Universitat de Barcelona, Barcelona, Spain 2017.

[60] L.-C. Chiang, J.-E. Chang, T.-C. Wen, Water Res. 29 (1995) 671-678.

[61] A. Y. Bagastyo, D. J. Batstone, I. Kristiana, W. Gernjak, C. Joll, J. Radjenovic, Water Res. 46 (2012) 6104-6112.

[62] M. Panizza, G. Cerisola, Chem. Rev. 109 (2009) 6541-6569.

[63] C. Boxall, G. H. Kelsall, Hypochlorite Electrogeneration. 2. Thermodynamics and Kinetic model of the Anode Reaction Layer, Symposium on Electrochemical Engineering and the Environment, Institution of Chemical Engineers, Rugby, United Kingdom, 1992, pp. 59-70.

[64] C. A. Martínez-Huitle, E. Brillas, Appl. Catal. B: Environ. 87 (2009) 105-145.

[65] M. Panizza, G. Cerisola, Chem. Rev. 109 (2009) 6541-6569.

[66] C. Zhang, J. Wang, T. Murakami, A. Fujishima, D. Fu, Z. Gu, J. Electroanal. Chem. 638 (2010) 91-99.

[67] R. J. Bigda, Consider Fenton's chemistry for wastewater treatment, Chem. Eng. Prog. 91 (1995) 62–66.

[68] N. San Sebastian, J. F´ıguls, X. Font, A. Sanchez, Pre-oxidation of an extremely polluted industrial-wastewater by the Fenton's reagent, J. Hazard. Mater. B 101 (2003) 315–322.

[69] Schreiber M. E. Bahr J. M. (2002). Nitrate-enhanced bioremediation of BTEX contaminated groundwater: parameter estimation from natural-gradient tracer experiments. J. Contam. Hydrol. 55:29–56.

[70] Suflita J. M, Caldwell M. E. (2000) Detection of phenol and benzoate as intermediates of anaerobic benzene biodegradation under different terminal electron-accepting conditions, Environ. Sci. Technol. 34:1216–1220.

[71] Sedlak, D. L., Andren, A. W., 1991. Oxidation of chlorobenzene with Fenton's reagent. Environ. Sci. Technol. 25, 777.

[72] F. J. Rivas, F. J. Beltran, O. Gimeno, J. Frades, Treatment of olive oil mill wastewater by Fenton's reagent, J. Agric. Food Chem. 49 (2001) 1873–1880.

[73] B. G. Kwon, D. S. Lee, N. Kang, J. Yoon, Characteristics of p-chlorophenol oxidation by Fenton's reagent, Water Res. 33 (1999) 2110–2118.

[74] N. San Sebastian, J. F´ıguls, X. Font, A. Sanchez, Pre-oxidation of an extremely polluted industrial-wastewater by the Fenton's reagent, J. Hazard. Mater. B 101 (2003) 315–322.

[75] Gallard, H., De Laat, J., Legube, B., 1998. Influence du pH sur la vitssed'oxydation de composes organiques par FeIIy H2O2. Mechanismes reactionnelsetmodelization. New J. Chem. 263.

[76] Lin, S. H., Lo, C. C., 1997. Fenton process for treatment of designing wastewater. Water Res. 31, 2050.

[77] Benitez, F. J., Beltran-Heredia, J., Real, F. J., Acero, J. L., 1999a. Enhancement of the ozonation of wine distillery wastewaters by anaerobic pretreatment. Bioprocess. Eng. 21, 459.

[78] M. Kitts, C. D. Adams, G. T. Daigger, The effect of Fenton's reagent pretreatment on the biodegradability of a nonionic surfactant, Water Res. 33 (1999) 2561–2568.

[79] X. Wang, Y. Song, J. Mai, Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate, Journal of Hazardous Materials 160 (2008) 344–348.

[80] Ebrahiem E. Ebrahiem, Mohammednoor. N. Al-Maghrabi and Ahmed R (2013). Mobarki Chemical Engineering Department, Faculty of Engineering, Jazan University, Saudi Arabia removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology. Faculty of Engineering, King Abdul-Aziz University, Jeddah, Saudi Arabia.