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Electrochemical advanced oxidation of cosmetics waste water using IrO_2/Ti-modified electrode

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ABSTRACT

Hazardous chemicals of households or industrial drainage of cosmetics materials may be discharged into effluents of water causing high threat to human health. So, unconventional methods are necessary to be applied to remove or even reduce hazardous contaminants concentration. Advanced oxidation process is successfully applied for removal of refractory organic materials. In this study, IrO_2/Ti-modified electrode was prepared and used as anode into an electrolytic cell to increase the oxidation power of the harmful organic materials. It was designed and roughened to have a high surface area for amelioration of electric potential and high efficiency of organic materials degradation. Graphite rod was used as cathode and DC current was applied between both electrodes through the solution of cosmetics wastewater. Ferrous ions were added for the generation of a very powerful oxidizing agent hydroxyl radical ($^{\cdot}OH$) in the solution. Effect of ferrous ions concentrations, sodium chloride concentrations, and pH values were studied and COD was measured to evaluate the optimum conditions of removal efficiency. The results revealed that the addition of 1 g/l Fe^{2+} ions improved the removal efficiency to 98% at pH 3.

Keywords: Cosmetics; Wastewater; Advanced oxidation; Electrochemical; Modified electrode

1. Introduction

Most cosmetics and pharmaceuticals are hazardous materials and the majorities are carcinogenic or contain impurities that cause cancer. These materials include coal tar colors, glycol ethers, parabens, phenylenediamine, diethanolamine (DEA), phthalates, paracetamol, and chlorophene. Also, natural and synthetic cosmetics contain wetting agents like DEA or triethanolamine, both of them are not carcinogenic, but if they exist with some cosmetics products contain nitrites contaminants, they can cause a chemical reaction leading to the formation of highly carcinogenic nitrosamines [1].

In the last three decades, a large variety of advanced oxidation processes, such as chemical [2], photochemical [3], and electro-chemical methods [4–6] have been developed to remove hazardous materials from municipal water. Based on the use of very strong oxidizing agent such as hydroxyl radical ($^{\cdot}OH$) generated *in situ* of the reaction medium. These methods are applied when conventional oxidation techniques become insufficient, because pollutants are refractory

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to oxidize in aqueous medium or partially oxidized, yielding reaction products even with greater toxicity than that of starting pollutants [7,8]. In contrast, hydroxyl radicals generated by electrochemical advanced oxidation are able to non-selectively degradation of most organic and organometallic contaminants in wastewater until their complete mineralization and conversion into CO_2, H_2O, and inorganic ions. The hydroxyl radical is considered as an electrophile due to a deficit of one electron in its valence orbit, so the most common reactions of hydroxyl radicals are electrophilic substitution in aromatic compounds and addition to alkenes (hydroxylation) [9]. Other chemical reactions involving hydroxyl radicals include hydrogen abstraction forming an organic free radical and water (dehydrogenation) [10].

Hydroxyl radical is one of the most reactive chemical species, where relative oxidation power 2.06 is higher than both atomic oxygen 1.78 and hydrogen peroxide 1.31 [11]. Optimal pH range for the application of Fenton process was determined to be from pH 3 to 6, where high pH values will result into inhibition of the Fenton reaction, since the Fe^{2+} ions will be oxidized and form colloidal Fe^{3+} ions. Likewise, a very low pH values <1.5 would result into the decomposition of H_2O_2 into oxygen and water without forming hydroxyl radicals [12].

Electrochemical methods are clean and effective techniques for direct and indirect oxidation [13]. In anodic oxidation these radicals are formed by water oxidation on high O_2-overvoltage anode [14,15]. While, in electro-Fenton method, the generated H_2O_2 at the cathode reacts with Fe^{2+} found in the medium, leading to the formation of hydroxyl radicals by Fenton's reaction [16–18].

Some workers declared that the presence of metal ions such as Fe^{2+}, Ce^{3+}, or Mn^{2+} usually called mediators are oxidized on the anode from a stable low valence state to reactive high valence state, which in turn attack organic pollutants directly and may also produce hydroxyl free radical that promote destruction of organic pollutants [19,20]. Hydroxyl radicals (${}^{\bullet}OH$) are short-lived reactive oxygen species with a high-oxidation potential that can rapidly destroy many refractory organic contaminants [21].

The present study was focused on the preparation of a high surface area modified electrode IrO_2/Ti employed as anode in the electrolytic cell, where at high O_2 over potential, strongly oxidant hydroxyl radical was formed by electro-Fenton reaction. The process can be successfully accomplished to get rid of real cosmetics wastewater by addition of ferrous ions and control of acidic medium. Effects of Fe^{2+} concentration, NaCl concentration, and pH value on the removal efficiency were also studied by measuring COD value.

2. Experimental

2.1. Chemicals

The real wastewater of cosmetics industry contains the main raw materials such as the following ingredients: polydimethylsiloxane (PDMS), D-panthenol, stearic acid, cetyl alcohol, glyceryl monostearate, amphezol K, iso propyl myristate, ollyl alcohol, tween 60, dimethicon 350, vitamin E acetate, methyl paraben, propyl paraben, EDTA disodium, glycerine, perfumes, D-panthenol, tri-ethanol amin, talc powder, and iron oxide dyes (yellow, red and blue). Some types of cosmetics ingredients structure are shown in Fig. 1.

Most of these ingredients are refractory organic compounds and they are difficult to destroy. Cosmetics wastewater was used itself as electrolytic solution into the electrolytic cell. Ferrous sulfate and sodium chloride were added according to the required dose. A dropwise of prepared sulfuric acid (15%) and sodium hydroxide (10%) were added for the adjustment of pH value in acidic medium and alkaline medium, respectively.

2.2. Apparatus

Electrochemical treatment was carried out into a glass cell 15 cm × 7 cm × 8 cm. Both IrO_2/Ti-modified electrode and graphite electrode were fixed at both sides of the cell. A rectifier GW Laboratory DC power supply GPR-3030 was used as a source of DC electric

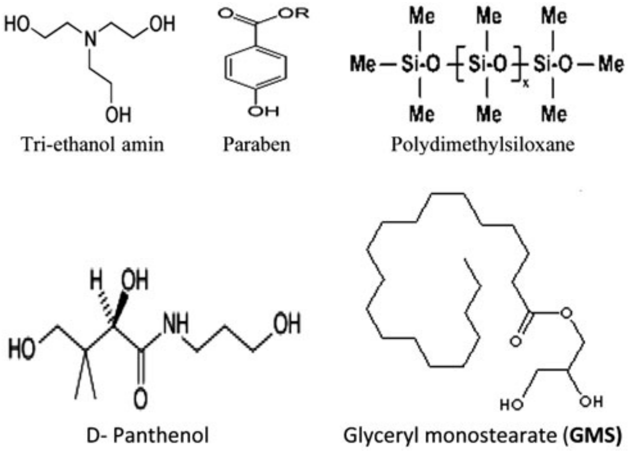


Fig. 1. Chemical composition of some types of organic compounds contained in cosmetic wastewater.

current. The connection between terminals of DC power supply and both electrodes was accomplished by electric cables. Jenway-3505 pH meter was used for the measurement of pH value of the solution before electrochemical treatment and a magnetic stirrer (PMC-Barnstead/Thermolyne, USA) was used for agitation of the solution.

2.3. Preparation of IrO_2/Ti-modified electrode

2.3.1. Etching and polishing

Expanded titanium sheet of 100 mm × 50 mm × 1 mm in dimension was immersed in 0.5 M HF solution for 5 min for removal of titanium oxide, and then rinsed with deionized water. To guarantee the anchor effect for the electro catalysts by surface roughening of the electrode, the expanded titanium was immersed in 10–12 M H_2SO_4 at 80˚C until hydrogen evolution was ceased or decreased due to the coverage of the surface with titanium sulfate. The use of further concentrated sulfuric acid resulted in lower roughness of the surface due to the dissolution of titanium sulfate covered layer. After etching was accomplished, titanium sulfate on the expanded titanium surface was removed by washing by flowing tap water for about 60 min.

2.3.2. IrO_2 coating

The expanded titanium was coated with IrO_2 as an intermediate layer, it is required to prevent the formation of insulating titanium oxide between the electro catalytic active substances and the titanium substrate during electrolysis at high current densities for a long time. After drying of sulfuric acid-etched titanium, the IrO_2 coating was carried out as follows: 0.1 M chloroiridic acid butanol solution was coated on the expanded titanium substrate and the specimen was dried at 80˚C for 10 min, then baked at 450˚C for 10 min, and cooled at room temperature. This procedure was repeated three times so as to form a 0.001–0.015 g/cm^2 IrO_2 layer on the titanium substrate. This specimen was finally baked at 450˚C for 1 h, and then cooled at room temperature.

2.4. Experimental procedure

A sample 100 ml of real cosmetics wastewater (COD 7,000 mg/l) was decanted into glass cell, where, both working electrode (IrO_2/Ti-modified electrode) and graphite counter electrode were connected to positive and negative terminals of GW Lab DC power supply as shown in Fig. 2. Ferrous sulfate and sodium chloride were added with continuous agitation until complete dissolution. After complete oxidation of organic materials by using different concentrations and pH, the solution was poured into a settling beaker, and then it was filtered using a suitable filter paper to separate sludge. The sludge was taken to a furnace for drying at 105˚C for 30 min. It was investigated by X-ray diffraction, and the solution was analyzed by COD measurements.

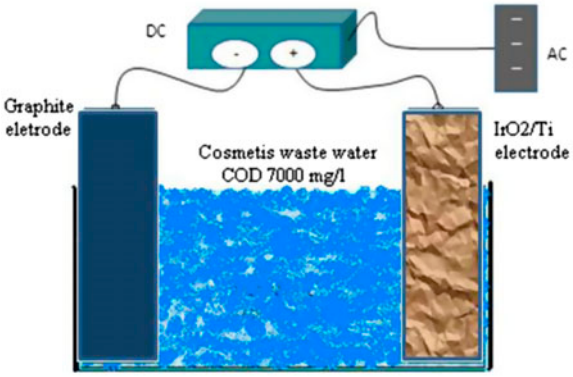


Fig. 2. Electrochemical set up for wastewater treatment.

2.5. COD measurements

The solution was decanted into a settling beaker after electrochemical treatment, and then filtered to separate the precipitated sludge by a filter paper. Clear filtrate sample was diluted to 30 times by addition of distilled water. A sample 2.5 ml was taken to a glass testtube (HACH), where two reagents of potassium dichromate (1.5 ml) and sulfuric acid (3.5 ml) were added. The sample was digested into COD reactor (HACH, USA) for 2 h at 150˚C, cooled for 30 min, and measured by COD meter to detect the removal efficiency of organic materials.

2.6. X-ray diffraction

X'Pert Pro. PANalyltical with monochromator kV = 45 kV, MA = 40 m Holland was used for the analysis of the sludge formed and settled down, which indicate the composition of different material removed as sludge.

3. Results and discussion

3.1. Effect of Fe^{2+} on the removal efficiency

Ferrous ions are essential for the degradation of refractory organic compounds, where the presence of Fe^{2+} ions and hydroxyl groups can support the formation of highly oxidant hydroxyl free radicals. They are strong oxidants in the solution, where highly environmental dangerous long chains organic compounds were broken and converted to environmental friendly small entities of organic compounds and liberation of CO_2, NO_2, or SO_2 gases. As shown in Fig. 3, the addition of small amount of ferrous ions (0.5 g/l) to the solution of cosmetics wastewater reduces COD value from 7,000 to less than 900 mg/l by electrochemical treatment.

The variation of initial pH value of wastewater has obviously influenced the removal efficiency, where at low concentration of Fe^{2+} added to the solution, low removal efficiency was obtained at high pH 9, where the higher COD value $\leqslant$1,500 mg/l was achieved. While, the higher removal efficiency and the lower COD value $\leqslant$500 mg/l was achieved at pH 3.

The presence of acidic medium supports the formation of highly adsorption Fe^{2+} ions for a long time into the solution without oxidation to the colloidal non adsorption Fe^{3+} ions. Also, during electrochemical oxidation in acidic medium, hydrogen peroxide can be produced by two electron reduction of oxygen at appropriate cathodic potential on graphite electrode [22].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

Also, COD values were highly decreased by increasing the concentration of Fe^{2+} to 2 g/l, where COD was decreased to 800 and 100 mg/l at pH values 9 and 3, respectively. This indicates that the addition of 0.5 g/l of Fe^{2+} ions at pH 3 was the best economical conditions for the removal of cosmetic organic compounds through low-cost consumption of Fe^{2+} ions. The lowest removal efficiency was observed at very high pH 9 and it was not suitable for oxidation of organic compounds due to the presence of excess OH^- groups into the solution which accelerate the oxidation of Fe^{2+} to Fe^{3+} without complete oxidation of organic compounds. While, in the case of pH 3, highly oxidants $^{\cdot}OH$ free radicals can be formed due to the presence of Fe^{2+} ions.

3.2. Effect of Fe^{2+} on the current intensity

Generally, at a constant electric potential of 20 V, electric current was continuously increased by addition of Fe^{2+} ions at constant concentration of NaCl 0.1 g/l and at different pH values.

It was observed that without addition of Fe^{2+} ions, a low value of current 0.16 A was obtained at different pH values, as shown in Fig. 4, while it was improved to 0.30 A by addition of 0.5 g/l of Fe^{2+} at different pH values.

By continuous addition of Fe^{2+} ions, the concentration increased to 1 g/l and the current was increased and varied according to pH value. In acidic medium of pH 3, a high electric current was obtained due to the presence of high concentration of H^+ ions. After the increase of Fe^{2+} ions concentration, electric current was continuously increased, and the ionic mobility into the solution was increased to overcome the solution resistance.

3.3. Effect of time on the removal efficiency

Adequate time is required for total performance of oxidation reactions in the solution, where most harmful organic materials are completely destroyed into small safe materials. These reactions can be

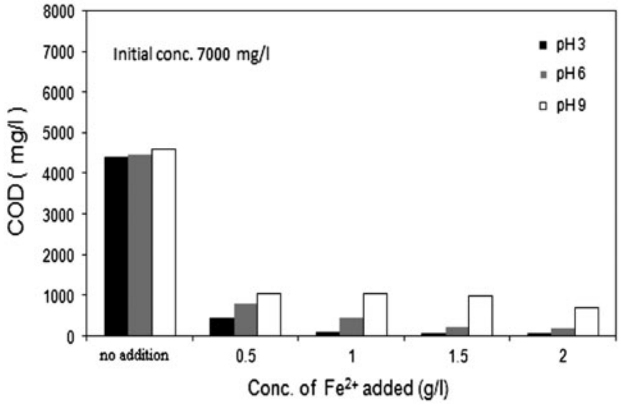


Fig. 3. Effect of concentration of Fe^{2+} on COD value of wastewater of cosmetics drain at constant 20 V, 0.1 g/l NaCl and 20 min.

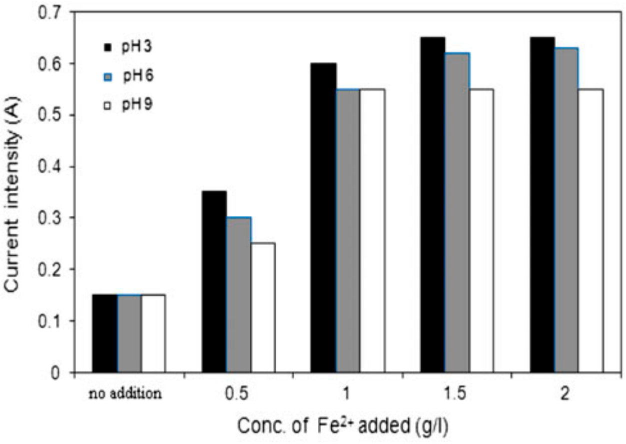


Fig. 4. Effect of concentration of Fe^{2+} on the current intensity during electrochemical treatment at constant conc. of NaCl 0.1 g/l and time 20 min.

accelerated by applying a high current 0.8 A to obtain the lowest COD value, while enough time is required by applying low current 0.2 A to obtain the lowest COD value.

As shown in Fig. 5, the increase of duration time of the electrochemical treatment of cosmetics wastewater led to the progress in the waste organic material removal.

The time consumed for the removal of these materials is highly influenced by the electric current applied, where at high-applied current 0.8 A, the lowest COD 1,000 mg/l was obtained after 10 min, while at low-applied current 0.2 A, the lowest COD 950 mg/l was obtained after 20 min.

At constant electric potential, the increase of Fe^{2+} ions enhanced the removal efficiency in the solution of cosmetic wastewater. Fig. 6 depicts that the removal efficiency was improved by continuous addition of Fe^{2+}, where COD value was reduced to 1,400 mg/l by addition of low concentration of Fe^{2+} ions 0.5 g/l at constant potential 20 V, NaCl 0.1 g/l and pH 6. At the same conditions, COD was continuously reduced to 960 mg/l by increasing of Fe^{2+} concentration to 2 g/l. This indicates the necessity to add Fe^{2+} to produce more amounts of free radicals which reinforce the oxidation of organic compounds, as the following reactions:

$$Fe(OH)_2 \rightarrow Fe(OH)_3 + e^-$$

$$OH^- + e^- \rightarrow {}^{\cdot}OH$$

Hydroxyl radicals then react with organic compounds by three types of reactions: hydrogen atom abstraction, electrophilic addition on double bond, and electron transfer [23].

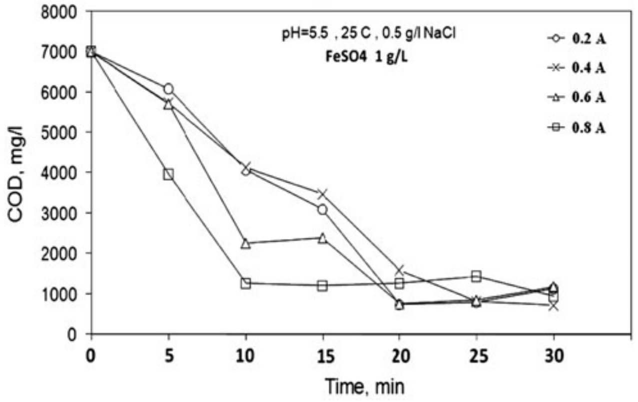


Fig. 5. Effect of time on the removal efficiency during electrochemical treatment at constant conc. of Fe^{2+} 1 g/l and NaCl 0.1 g/l.

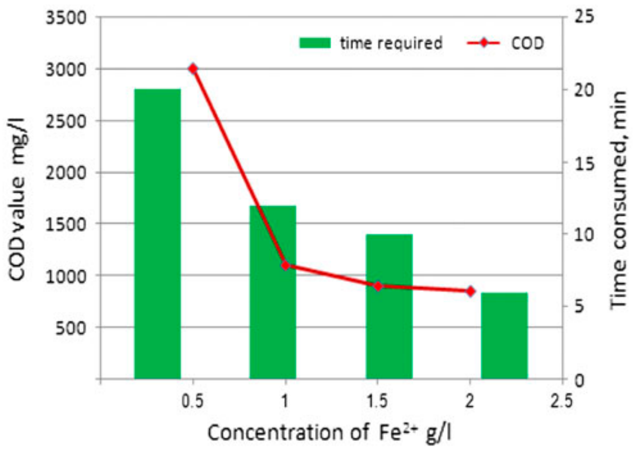


Fig. 6. Effect of concentration of Fe^{2+} on COD value and time consumption at 0.1 g/l NaCl, 20 V and pH 3.

$$RH + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}R$$

$$PhX + {}^{\cdot}OH \rightarrow PhXOH^{\cdot}$$

$$RX + {}^{\cdot}OH \rightarrow RX^{\cdot+} + OH^-$$

On the other hand, as the concentration of Fe^{2+} ions increased the electric current was increased. Accordingly, the time required for destruction of organic materials was decreased at constant potential 20 V.

Without addition of Fe^{2+} ions, the time consumption was higher than 20 min due to low electric current at constant NaCl concentration 0.1 g/l. While time was decreased gradually from 20 to 12 min by continuous addition of Fe^{2+} to 1 g/l. The excess addition of Fe^{2+} more than 1 g/l revealed a continuous decrease of time due to continuous increase of current by addition of Fe^{2+} concentration more than 1 g/l.

3.4. Effect of NaCl concentration

The addition of salts such as NaCl played an important role for the increase of ionic strength and electric conductivity through the solution. Hence, electric current was increased leading to the enhancement of removal efficiency. At constant Fe^{2+} concentration of 0.5 g/l and time 20 min, low removal efficiency was observed without addition of NaCl, where COD

5,490 mg/l and current 0.09 A were measured, as shown in Fig. 7. The increase of NaCl concentration led to the improvement of the removal efficiency, where the measured COD value was reduced from 7,000 to 2,120 mg/l as the current increased from 0.09 to 0.18 A.

Moreover, the electric dissociation of NaCl gives the advantage of the oxidants formation such as Cl_2, OCl^-, and ClO_3, which support the oxidation of organic materials. Salt addition to the electrolytic solution can enhance the ionic transfer and overcome the resistance against electric current, this indicates the advantage of salt addition for the increase of $Fe(OH)_2$ formed in acidic medium, which play an important role for organic pollutant degradation by copolymerization and coagulation. The removal efficiency of cosmetics organic compounds from wastewater was also improved by indirect oxidation of organic materials; this takes place through the chlorine generation and hydrolysis according to the following reactions:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2 \rightarrow HOCl + Cl^- + H^+$$

$$HOCl \rightarrow OCl^- + H^+$$

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2HCl$$

The electrolytic solution is composed of chlorine, hypochlorous acid, hypochlorite as well as a small amount of O_2 evolved at high-current density [24,25].

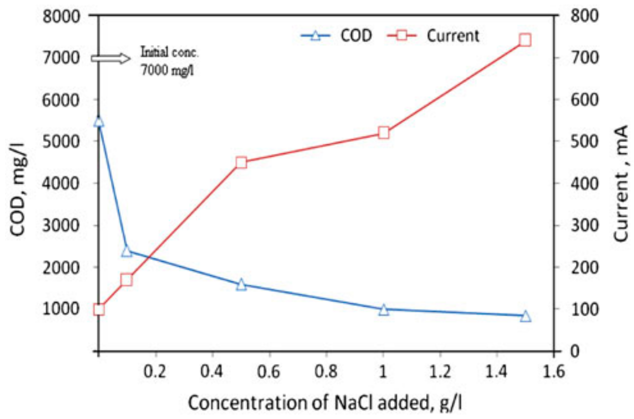


Fig. 7. Effect of NaCl added on the current intensity during electrochemical treatment at constant Fe^{2+} conc. 0.5 g/l, 20 V, pH 3 and time 20 min.

Accordingly, the advantage of NaCl addition was also extended to improve the removal efficiency in a low time and consequently, the economic cost and energy consumption was reduced.

Also, the auto generation of Cl_2 gas into the solution of wastewater can be exploited in the disinfection purposes, if the wastewater contains bacteria and bio-contamination cannot be tolerated.

3.5. *Sludge characterization by X-ray diffraction*

Finally, the solution was filtered and analyzed by COD measurements, where it revealed that the COD value was reduced to less that 150 mg/l, the variation of wastewater characteristics after electrochemical treatment is shown in Table 1.

The sludge formed after electrochemical oxidation of cosmetics wastewater was analyzed by XRD, where the chart revealed the presence of peaks of different forms of iron oxides, such as Fe_2O_3 and Fe_3O_4 as shown in Fig. 8. This indicates the removal of iron of both iron oxide dyes (yellow, red, and blue) and ferrous ions added. Other obvious peaks of silicon oxide also appeared, indicating the removal of polydimethylsiloxane found in cosmetics wastewater.

Table 1
Characteristics of wastewater before and after electrochemical treatment

Variable	Before EAO	After EAO
COD	7,000 mg/l	150 mg/l
pH	4	7.2
Colour	Yellowish brown	Clear
Turbidity	500 NTU	75 NTU

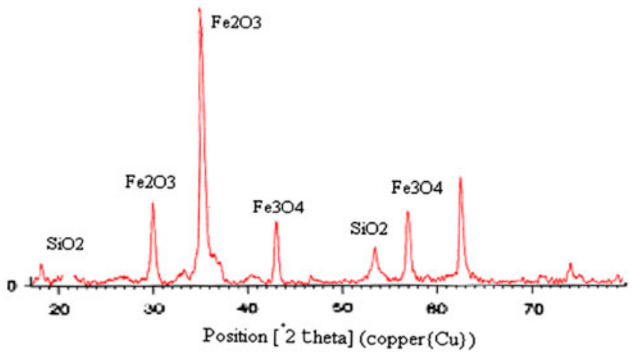
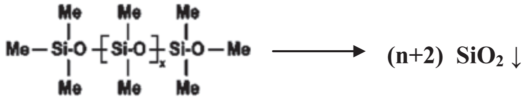

Polydimethylsiloxane (PDMS)

Fig. 8. X-ray diffraction analysis of the sludge formed after EAO treatment of cosmetics wastewater.



$$\mathrm{Me-\underset{Me}{\overset{Me}{Si}}-O-\left[\underset{Me}{\overset{Me}{Si}}-O\right]_x-\underset{Me}{\overset{Me}{Si}}-O-Me} \longrightarrow (n+2)\ \mathrm{SiO_2}\downarrow$$

$$Fe^{2+} + OH^- \rightarrow Fe(OH)_2 \qquad \text{(at anode)}$$

$$Fe(OH)_2 \rightarrow Fe(OH)_3 \downarrow + e^-$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \qquad \text{(at cathode)}$$

So, recalcitrant organic compounds found as a waste into the drain of cosmetics industries can be removed by electrochemical advanced oxidation method, using IrO_2/Ti electrode, where total removal of organic materials was accomplished by catalytic oxidation.

The presence of ferrous ions into the solution of wastewater is very important for the oxidation and degradation of recalcitrant organic compounds, where Fe^{2+} can be oxidized to Fe^{3+} and free electron was liberated to form a strong oxidant hydroxyl radical.

In this process, the degradation and mineralization of 7,000 mg/L of cosmetics wastewater were executed by using high oxygen over potential-modified electrode IrO_2/Ti electrode as anode. IrO_2/Ti electrode showed electrocatalytic oxidation behavior, where a direct oxidation of organic materials occurred.

Simultaneously, indirect electrochemical oxidation also occurred by electro-Fenton process in the presence of Fe^{2+} ions and Cl_2/OCl^- produced during electrolysis in the presence of NaCl.

In the electro-Fenton process, hydrogen peroxide is produced in the required amount from the electrochemical reduction of oxygen. These conditions are essential for the formation of Fenton reagent reactions (Indirect oxidation), where the highly oxidant $^{\cdot}OH$ free radical can be formed according to the following steps: (1)electrochemical reduction of dioxygen into $^{\cdot}O^{-2}$ and formation of H_2O_2 in acidic medium; and (2) reaction of H_2O_2 with Fe^{2+} ions yielding $^{\cdot}OH$ radicals (electro-Fenton reaction) [26]. In these conditions, Fe^{3+} ions are electrochemically reduced to Fe^{2+} ions (electro catalytic system).

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

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

So, both direct and indirect electrochemical oxidations support and accelerate the degradation of highly harmful organic compounds in a short time. A potent oxidants hydroxyl free radicals are formed in that appropriate conditions, which are highly adsorbed onto the organic materials and leads to their decomposition and complete mineralization to less-harmful compounds.

4. Conclusion

Advanced electrochemical oxidation was successfully used for the removal of harmful organic materials of real cosmetic wastewater. High-removal efficiency was achieved by using a high O_2 over potential IrO_2/Ti electrode as anode, where a direct oxidation of organic compounds occurred. Also, indirect oxidation simultaneously occurred by electro-Fenton reaction in the presence of Fe^{2+} and Cl_2/OCl^- reaction in the presence of NaCl. After each oxidation process, COD was measured to indicate the success degradation of persistence compounds, where the refractory organic pollutants were oxidized to less harmful, friendly environmental materials. The addition of Fe^{2+} ions gives the advantage of formation of $^{\cdot}OH$ free radical, which has the ability of oxidation of dissolved and suspended contaminants. More enhancement of removal efficiency was achieved by addition of sodium chloride (0.1 g/l) as a source of chlorine which has a role in the oxidation process by forming HOCl. The applied technique is economically promised where the removal efficiency 89% can be attained by reducing the time required for complete degradation of organic compounds to 5 min.

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