

Degradation of Corn Oil Wastes by Fenton Reaction and Under Mildly Basic Media in the Presence of Oxidants Assisted with Sun Light

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Abstract: The degradation of water soluble corn oil wastes was carried out by Fenton reaction and also under mildly basic media in the presence of oxidants, such as hydrogen peroxide and persulfate, assisted with solar light. The degradation efficiency was obtained by analysis of chemical oxygen demand, carbon dioxide and gas chromatography. Over 90% of both chemical oxygen demand abatement and carbon dioxide recovery was accomplished by Fenton reaction. The presence of oxidants during the photodegradation resulted in high chemical oxygen demand abatement of the oil waste with the disappearance of the majority of the initial fatty acids present in the oil waste before treatment.

Key words: photodegradation, hydrogen peroxide, persulfate

INTRODUCTION

The oil and grease discharge from kitchens, restaurants and the industry of commercial food preparation into the sanitary wastewater generates musty odor in sewerage systems. Potential vegetable oil spills can also occur and pollute the soil and water^[1]. Oil and grease (total), also known as fats, form a film on the water surface, stick onto pipes and walls and consequently block strainers and filters increasing the amount of scum in the treatment plants. Fats are not easily decomposed by bacteria and can interfere with the activated sludge process in the transfer of oxygen from the liquid to the interior of living cells^[2,3]. Waste traps are typically installed before the raw wastewater is introduced into sanitary sewers to collect and retain the fat, oil and grease. Usually the lipid materials are removed from the wastewater trap by pumping or skimming. However, part of these materials passes to the sewerage systems. The conventional methods employed for the removal of oil derivatives (i.e., combustion, extraction, biological methods) have several drawbacks, such as low efficiency, long time of the process, secondary pollution of environment and high costs. Another treatment method reported to be a good alternative is the electrocoagulation process^[4].

The aim of this work was to study the degradation of corn oil wastes by means of Fenton reagent and also

under mildly basic media in the presence of oxidants, such as hydrogen peroxide and persulfate, assisted with solar irradiation as alternative treatment processes.

MATERIALS AND METHODS

Chemicals: All solutions were prepared with distilled water (provided by Baxter México) using potassium hydroxide, sulfuric acid, ammonium persulfate, hydrogen peroxide, dichloromethane, iron sulfate and commercial vegetable corn oil (100% pure, Maceite®). All chemicals were analytical grade, used as received without further purification and purchased from Sigma-Aldrich.

Procedure: Emulsions were freshly prepared by weighting 1.867 g of corn oil mixed with 100 mL of basic distilled water (pH 12.5) with centrifuge stirring at 500 rpm during 3 h. Fenton reaction was carried out using different volumes of emulsion to prepare the working lipid aqueous solutions (LS) inside the oil concentration range of 52.2 mg L⁻¹ to 787 mg L⁻¹ at pH 3 in the presence of 1 mM Fe(II) in a total volume of 80 mL. The working solutions employed during the photodegradation in the presence of oxidants, were prepared by diluting 5 mL of emulsion in 50 mL of distilled water. A series of degradation experiments were performed employing glass batch reactors of a

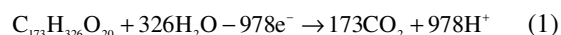
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total volume of 200 mL. Two glass reactors were withdrawn simultaneously at different time intervals to perform analyses of Chemical Oxygen Demand (COD), using the total volume of the oxidized LS of one reactor and Gas Chromatography (GC), using the other one. The COD was analyzed using standard method and standard tubes^[5] inside the range of 0-150 mg L⁻¹ COD. Prior the analyses of COD, the oxidized LS were subjected to extraction with dichloromethane (DCM) to collect the remaining oil from the LS that was not oxidized during treatment. DCM was subsequently evaporated and the dry oxidized LS came back into solution by the addition of 50 mL of basic distilled water (pH 12.5) with centrifuge stirring at 500 rpm during 3 h. GC analyses were carried out using a capillary GC with flame ionization detection for lipid analysis (Carbowax 20M column, Hewlett 5890 Packard Series II). The total volume of each oxidized sample was subjected to esterification prior to GC analysis.

The carbon dioxide evolved during Fenton degradation of the working solution was determined by volumetric titration^[6,7] following the procedure reported elsewhere^[8]. The working LS employed to measure the CO₂ evolution during Fenton degradation were prepared inside the oil concentration range of 590 to 787 mg L⁻¹ at pH 3 in the presence of 1 mM Fe(II) using a total reaction volume of 80 mL.

RESULTS AND DISCUSSION

Table 1 shows the chemical names and composition of the fatty acids present in Maceite® corn oil^[9]. Its sticky nature and composition make difficult its degradation. In order to oxidize the fatty acids present in the LS, it is necessary to withdraw several electrons from each fatty acid. The composition of the fatty acids is formed basically by atoms of carbon (C), oxygen (O) and hydrogen (H). The condensed formula of the LS can be obtained by the sum of the corresponding atoms of all the fatty acids as C₁₇₃H₃₂₆O₂₀. In order to mineralize the fatty acids, a total of 978 electrons would be necessary to withdraw from the LS, as shown by Eq. 1.



Equation (1) shows that the degradation of the fatty acids generates protons making acidic the solution. Figure 1, shows the pH behavior during the photodegradation of the LS under different experimental conditions. It is observed that in the absence of oxidant (■), the pH remains practically constant after a reaction period of 2 h with a slow pH decrease afterwards. The presence of oxidants (●, ▲) increases the photolytic degradation of the LS demonstrated by the generation of a rapid pH change in the first minutes of reaction. In order to prevent the emulsion to come apart and the oil adhered on the reactor wall due to pH decrease during photodegradation, the pH was maintained over 6 by adding small KOH pellets to the reactors. Emulsions can be broken by acidification, the addition of alum or iron salts (high concentration), or the use of emulsion-breaking polymers^[10]. The arrow, in Fig. 1, shows the time when the pH was increased and kept between the pH values of 9 to 11 for the photodegradation of the working solutions in the presence of oxidants.

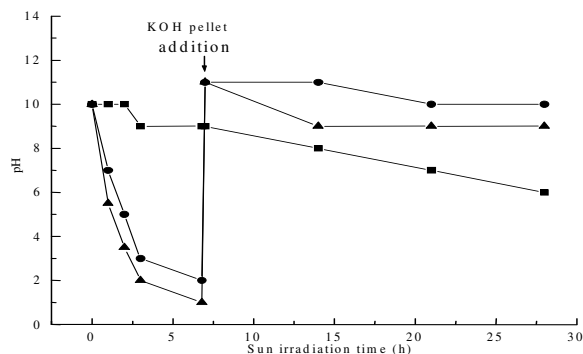
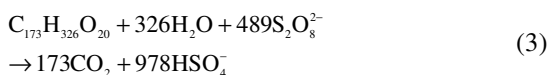
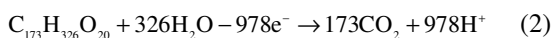


Fig. 1: Graph showing the pH change as a function of sun irradiation time for the degradation of a lipid aqueous solution initially containing 1.867 g L⁻¹ C₁₇₃H₃₂₆O₂₀ by photolysis: (■) in the absence of oxidants, (●) with 0.334 M H₂O₂ and (▲) with 0.334 M S₂O₈²⁻

Table 1: Chemical names and composition of the fatty acids present in the corn oil (Maceite®)

Common Name	Scientific Name	%	Chemical Formula
Myristic Acid	Tetradecanoic acid	0.04	CH ₃ (CH ₂) ₁₂ COOH
Palmitic Acid	Hexadecanoic acid	11.00	CH ₃ (CH ₂) ₁₄ COOH
Margaric acid	Heptadecanoic acid	0.09	CH ₃ (CH ₂) ₁₅ COOH
Stearic Acid	Octadecanoic acid	1.76	CH ₃ (CH ₂) ₁₆ COOH
Arachidic Acid	Eicosanoic acid	0.51	CH ₃ (CH ₂) ₁₈ COOH
Palmitoleic Acid	9-Hexadecenoic acid	0.26	CH ₃ (CH ₂) ₅ C=C(CH ₂) ₇ COOH
Oleic Acid	9-Octadecenoic acid	29.39	CH ₃ (CH ₂) ₇ C=C(CH ₂) ₇ COOH
Linoleic Acid	9,12-Octadecadienoic acid	55.66	CH ₃ (CH ₂) ₄ C=CCH ₂ C=C(CH ₂) ₇ COOH
Alpha-Linolenic Acid (ALA)	9,12,15-Octadecatrienoic acid	1.25	CH ₃ CH ₂ C=CCH ₂ C=CCH ₂ C=C(CH ₂) ₇ COOH

The reactions that take place between the fatty acids and the oxidants are shown in Eq. 2 and 3, one mole of fatty acids requires 489 moles of hydrogen peroxide and 489 moles of persulfate ions respectively.



Carbon dioxide (CO₂) is a byproduct from the oxidation and mineralization of the fatty acids.

The theoretical oxygen demand (ThOD) of the fatty acids can easily be predicted as the lipid pollutant only contains atoms of C, H and O on its molecule. ThOD^[11] can be calculated from Eq. 4 and 5.



$$ThOD, mgL^{-1} = [(SC_{O_2})(MW_{O_2}) / (MW_{Lipid})](LC) \quad (5)$$

where SC_{O₂} is the stoichiometric coefficient of oxygen, MW_{O₂} is the oxygen molecular weight, MW_{Lipid} is the lipid compound molecular weight and LC is the lipid concentration in the emulsion (mg L⁻¹).

Fenton degradation: Degradation of the fatty acids present in the LS was carried out by Fenton reaction (under mildly acid media). The LS used during Fenton degradation had an initial oil concentration of 52.7 mg L⁻¹ with a COD of 150 mg L⁻¹. The ThOD (151.5 mg L⁻¹) of such solutions was very close to the experimental COD as predicted by Eq. (4). In order to oxidize 52.7 mg L⁻¹ of C₁₇₃H₃₂₆O₂₀ it is required 9.47 mM of H₂O₂ in the Fenton reaction. Different molar relations of [H₂O₂] / [C₁₇₃H₃₂₆O₂₀] were tested to measure the COD decay during Fenton degradation as a function of reaction time. It is observed, on Fig. 2, that a molar relation less than the stoichiometry decreases the COD ~70% while the stoichiometry one, given by Eq. 2, achieves a COD abatement of ~90% from its initial value. However, increasing further the H₂O₂ concentration inhibits degradation achieving lower COD abatement than that obtained for the stoichiometric H₂O₂ concentration. The decrease in the degradation efficiency by increasing the H₂O₂ concentration is because of the scavenging effect^[12]. The scavenging effect can be explained by Eq. 6:

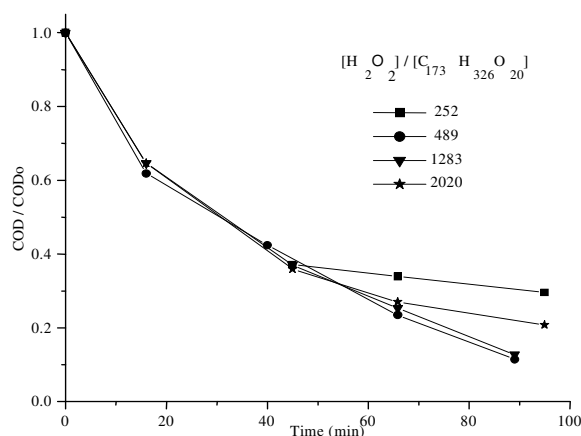


Fig. 2: COD decrease as a function of reaction time by Fenton degradation of a lipid aqueous solution initially containing 52.7 mg L⁻¹ of corn oil using different initial concentrations of H₂O₂ at pH 3 and 1 mM Fe²⁺

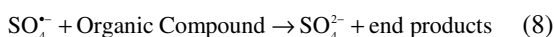
Table 2: Carbon dioxide recovery from the oxidation of the lipid solutions by Fenton reaction

[C ₁₇₃ H ₃₂₆ O ₂₀] initial (mM)	CO ₂ recovery (%)	COD abatement after CO ₂ recovery (%)
0.217	97	91
0.257	95	93
0.289	99	98

When the molar concentration of H₂O₂ is greater than the stoichiometric one, the H₂O₂ reacts with the [•]OH radicals in the aqueous solution; decreasing in this way, the amount of [•]OH radicals available for degrading the organic compounds.

Carbon dioxide evolution: Table 2, shows the CO₂ evolved during the oxidation of the LS by Fenton reaction after 21 h of reaction. The initial concentrations of oil tested and COD decrease after CO₂ measurements are also shown in this table. The initial concentration of the LS was increased approximately by a factor of 10 from those tested for the different molar relations; therefore more time was needed to oxidize the fatty acids present in the LS. Fenton reactions were carried out in the presence of 0.128 M H₂O₂ and 1 mM Fe²⁺. A second addition of 0.064 M H₂O₂ and Fe²⁺ was carried out after the first 12 h of reaction in order to have both: (a) an excess of the oxidant with respect to the stoichiometry reported by Eq. 2 to each test and (b) to ensure that the oxidation was complete. It is observed that over 95 % of CO₂ was evolved on the experimental tests. It is also observed that high COD abatements were achieved, in agreement with the high CO₂ measured.

Fatty acids degradation by oxidants assisted with solar light: Photodegradation of the fatty acids solution was carried out using persulfate ions ($S_2O_8^{2-}$), hydrogen peroxide and a mix of these two oxidants. Photolysis of $S_2O_8^{2-}$ produces two sulfate radical anions (Eq. (7)), which are strongly oxidizing species ($E^\circ = 2.6V$), generating a very reactive ion $SO_4^{\bullet-}$, able to attack organic compounds by abstraction of a hydrogen atom or addition on unsaturated molecules^[13].



Several degradation tests were carried out employing a LS initially containing $1,866.7 \text{ mg L}^{-1}$ of corn oil. The experiments were performed from 10:00 h to 16:00 h (during the months from May to October) to take advantage of the high incident solar light. The LS has high COD content and its experimental value is $5,341.2 \text{ mg L}^{-1}$. The theoretical oxygen demand ($5,364.6 \text{ mg L}^{-1}$) predicted by Eq. (4) and (5) is very close to the experimental one because the fatty acid molecules have atoms of C, H and O. Figure 3 depicts the experimental COD abatement during photodegradation in the absence and presence of $0.334 \text{ M } S_2O_8^{2-}$ as oxidant in the pH interval of 9 to 11 under solar light; the concentration of the oxidant was that of the stoichiometry (Eq. (3)). COD abatement of $\sim 82\%$ was achieved during the photolytic degradation of the LS assisted with solar light and persulfate while a 31.6% of COD decrease was reached by the sole effect of the sun light. Figures 4 and 5 shows the chromatograms obtained at different irradiation time intervals by the photodegradation of the fatty acids solution in the absence and presence of persulfate oxidant. There are some peaks numbered from 1 through 19 (Fig. 4.a) with the greatest areas in all chromatograms obtained. It is observed, in the chromatograms of figure 4, that the total area of each chromatogram has been modified by the sole action of the sun light at different irradiation time with respect to the initial chromatogram without treatment (Fig. 4.a). The total area of the chromatogram of Fig. 4.b decreased 59% after 3 h of photolysis with the appearance of a new peak marked with an x indicating the formation of a new substance and the disappearance of peaks 8 and 10. It can also be inferred that part of the substances with retention times greater than that of peak 9 were converted into the substances related to peaks 1 to 9. Similar behavior is observed in Fig. 4.c and 4.d with a decrease in the total area of 66% at 14 h

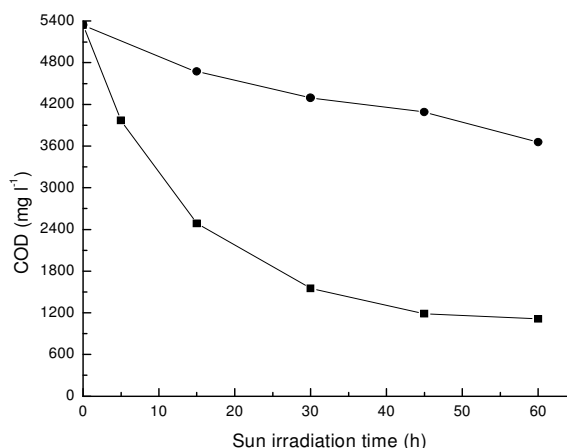


Fig. 3: COD abatement as a function of sun irradiation time for a lipid solution initially containing 1867 mg L^{-1} of corn oil in the (●) absence and (■) presence of $0.334 \text{ M } S_2O_8^{2-}$ as oxidant, both at pH between 9-11

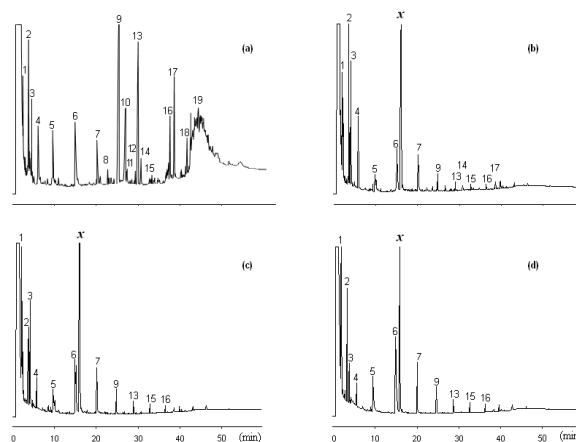


Fig. 4: Chromatograms for a lipid aqueous solution initially containing 1867 mg L^{-1} of corn oil: (a) raw effluent, (b) after photolysis for 3 h, (c) after photolysis for 14 h, (d) after photolysis for 21 h. All at pH between 9-11, under sun light

and 73% at 21 h respectively. The changes of the total area of the chromatograms are both indicative of the fatty acids degradation, in agreement with the 32% COD reduction (Fig. 3) by the sole action of photolysis. Figure 5 shows the chromatograms for the treated LS in the presence of oxidant at different irradiation times. A significant enhancement was achieved after treatment. Figure 5.a presents the chromatogram for the LS after 3 h of photolysis in the presence of persulfate. It is

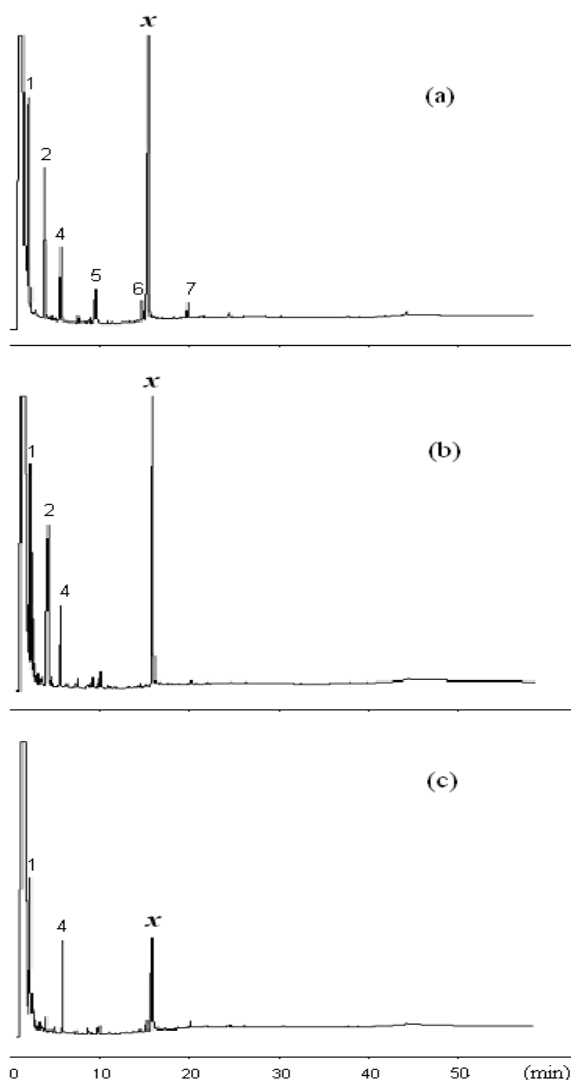


Fig. 5: Chromatograms for the oxidation of a lipid aqueous solution initially containing 1867 mg L^{-1} of corn oil in the presence of $0.334 \text{ M S}_2\text{O}_8^{2-}$: (a) after photolysis for 3 h, (b) after photolysis for 14 h, (c) after photolysis for 21 h. All at pH between 9-11, under sun light

observed a decrease in the area of peaks 2 and 4 to 7 with the disappearance of peaks 3 and 8 to 19. It is also observed that peak 1 slightly increased and a new peak (marked with an x) appeared indicating the formation of a new substance. The number of peaks was reduced to 7, (63% in peak reduction) with a 92% decrease in total area. These results indicate that the substances with retention times greater than that of peak 7 were converted into the substances related to peaks 1 to 7. Figure 5.b shows the chromatogram after 14 h of photolysis with oxidant.

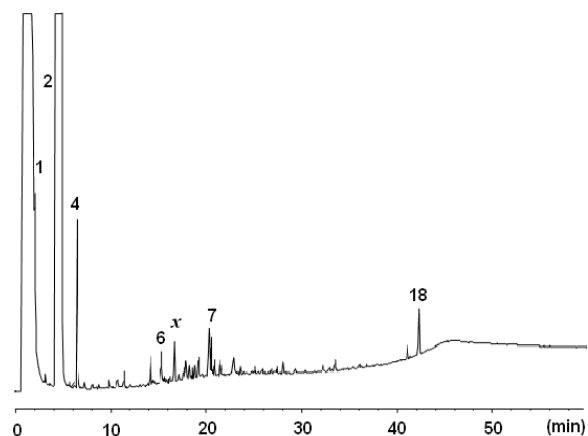


Fig. 6: Chromatogram for the oxidation of a lipid aqueous solution initially containing 1867 mg L^{-1} of corn oil in the presence of $0.334 \text{ M H}_2\text{O}_2$ after photolysis for $\sim 20 \text{ h}$ at pH between 9-11 under solar light

It is observed that only 3 peaks remain and the area of peaks 2 and 4 slightly decreased, the peak x still remains with its area slightly smaller. Finally, figure 5.c presents the chromatogram for 21 h of photolysis with oxidant. There are 3 remaining peaks and the total area of the chromatogram changed significantly with a decrease of 97%. The area of the new peak (x) decreased $\sim 60\%$ in comparison to that on figures 5.a and 5.b and, the area of peak 1 decreased $\sim 30\%$ in comparison with the initial chromatogram (Fig. 4.a). It is also observed that the area of peak 4 is smaller to that without treatment. These results have shown that the substances continued to be transformed into those with smaller retention times (smaller molar weights) with the appearance of a new one which was also degraded with a reduction of its area in $\sim 60\%$. These results are in agreement with the results obtained by the rapid pH changes and COD abatement during photolysis in the presence of persulfate as oxidant, as depicted in Fig. 3.

Figure 6 presents the chromatogram for the oxidation of the LS by photolytic treatment in the presence of $0.334 \text{ M H}_2\text{O}_2$ after $\sim 20 \text{ h}$ of sun irradiation. Three additions of $\sim 0.111 \text{ M}$ of H_2O_2 were carried out to complete the stoichiometry of H_2O_2 concentration along the 20 h reaction time. It is observed that the number of peaks was reduced to 6 with the appearance of two new peaks (a new one that appeared before peak 6 and that marked before with an x) with 58% in peak reduction, as compared with the chromatogram without treatment (Fig. 4. a). The height

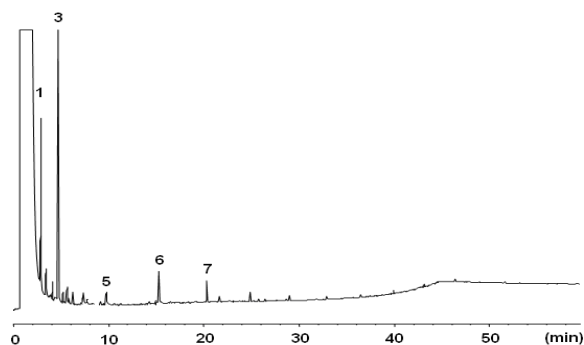


Fig. 7: Chromatogram for the oxidation of a lipid aqueous solution initially containing 1867 mg L^{-1} of corn oil in the presence of $10 \text{ mM S}_2\text{O}_8^{2-}$ and $0.334 \text{ M H}_2\text{O}_2$ after photolysis for $\sim 20 \text{ h}$ at pH between 9-11 under solar light

of peak x was very much decreased in comparison with that in the chromatogram of figure 5.c. However, such peak x , peaks 2, 4, 18 and the other new one that appeared before peak 6 in Fig. 6, disappeared with the initial addition of $10 \text{ mM S}_2\text{O}_8^{2-}$ together with the H_2O_2 as shown in Fig. 7 decreasing the number of peaks to 5 where peaks 1 and 3 still remain. The simultaneous use of the oxidants aided to eliminate the new two substances that appeared during the oxidation. Other peaks also continued to be transformed into those with smaller retention times.

CONCLUSION

It has been shown that corn oil wastes can be degraded by Fenton reagent achieving high yields of carbon dioxide and high abatements of the initial chemical oxygen demand. Cooking oil wastes of high COD can also be degraded by both Fenton and photolysis in the presence of oxidants such as persulfate and hydrogen peroxide with the disappearance of the majority of the fatty acids initially present in the oil wastes before treatment. These two oxidants can be electrochemically generated avoiding the necessity for the addition of chemicals into the effluent to be treated. This work offers a friendly alternative to the biological treatment for the treatment of vegetable oil wastes.

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