Improved electrolysis of colloid-polluted wastes using ultrasounds and electrocoagulation

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Abstract

In this work, a new strategy for the treatment of wastes polluted with micelles is evaluated. It consists on the concentration of the pollutant by electrocoagulation, the pre-treatment of the concentrated sludge with US and the later application of an electrolytic oxidation. As it is well-known that the electrolytic treatment of diluted solutions generally fits well a first-order kinetic, this concentration is expected to lead to a more efficient process. This approach has been studied using oxyfluorfen polluted wastes. Electrocoagulation has been carried out for the concentration of a wastewater containing oxyfluorfen reducing its volume from 50.00 to 1.39 L. Once obtained the small volume of concentrated liquid waste, several treatments have been applied such as Ultrasonic irradiation or heat followed by electrooxidation. Results show that application of US has a very positive influence on the performance, in particular LF-US. Application time is also an important parameter and heating has a negative effect on results because iron hydroxide flocs compress and seal the pollutant inside making more difficult their destruction by the direct and indirect oxidation reactions.

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24 **Keywords**

25 Ultrasound; diamond electrode; electrocoagulation; concentration techniques;
26 electrolysis.

27

28 **Highlights**

- 29 • Electrocoagulation and US application is a good pretreatment for electrolysis
- 30 • Application of US lead to a higher availability of the pollutants entrapped in
- 31 flocs
- 32 • US application time affects not only to release but to floc structure
- 33 • LF-US are more effective than HF-US as pre-treatment

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39 **1. Introduction**

40 Many chlorinated hydrocarbons have been used as pesticides. In the environment, these
41 chemicals may become into hazardous pollutants, being characterized by a very high
42 persistence. In the past, they were successfully used to control plagues and even
43 illnesses as important as malaria and typhus, but now, many of them are forbidden in
44 most of the advanced countries [1] because of their hazardousness. However, their use
45 in developing countries in which they are not banned, and their remaining effects in
46 those countries in which they were used in the past, makes this removal a priority [2, 3].

47 The contamination of water sources with organochlorine compounds represents a
48 serious problem because of their specific characteristics, such as high lipophilicity,
49 bioaccumulation, long life and potential of long-range transport. There are many types
50 of organochlorine compounds and they can end up into the natural water bodies in many
51 ways. An accidental spill, an unappropriated use, storage or transportation method or
52 even a bad management of wastewater from a pesticide factory can cause a
53 contamination event. In this context, the degradation of organics still represents a
54 challenge because is very complicated to achieve a cost-effective removal down to
55 levels below legal limits. This is why nowadays many studies are approaching not only
56 single but also assisted or combined technologies. Thus, different biological treatment
57 approaches were evaluated for the treatment of these wastewaters [4-10]. For instance,
58 Sousa et al. (2010) used a combination of technologies based on biodegradation with
59 activated sludge followed by pine bark adsorption treatment for lindane and heptachlor
60 removal from liquid wastes [11]. In general, these technologies present the inconvenient
61 of long operation times and that the acclimation of an adequate biological culture can be
62 problematic.

Electrochemically assisted technologies seem to offer a better alternative due to the high reactivity that can promote the anodic materials, especially those based in the use of diamond coatings [12]. Despite diamond coatings are known to be expensive, in particular because they are not commercialize at large scales, their very high efficiency make them suitable for many applications and even competitive with regard to well-known AOPs like ozonation or Fenton, as it was demonstrated in a previous work in which a comparison of the three technologies was carried out for a large variety of wastewaters and operation conditions [13]. From that work, many attempts are being made in order to improve even more the efficiency of the electrolysis, and hence to reduce costs, trying to extend the primary reaction zone from the nearness of the electrode to the bulk. In this context, electrochemical photo and sono-assisted technologies have also been successfully used for the removal of organic compounds from wastewater [14]. Thus, it is well known that the ultrasound irradiation, leads to the formation, growth and disintegration of small bubbles that concentrate the acoustic energy into tiny reaction zones, leading to extreme conditions in a short time, allowing the formation of radicals, as indicated in the equation 1 [15], where))) stands for the ultrasonic irradiation.

Sonochemical degradation has been successfully used in the treatment of wastewater polluted with different pollutants such as the endocrine disrupting organochlorine pesticide dicofol [16]. In turn, sono-electrocoagulation showed its efficiency in the removal of organic dyes [17] and sono-electrofenton for the treatment of wastewater polluted with lindane [15]. Another interesting application of ultrasonic waves and hydrogen peroxide was studied by Kida et al, 2018 for the removal of a mixture of pesticides from wastewater [18].

88 However, all these studies have been conducted on "diluted" synthetic or real
89 wastewater. This might be a drawback because a low concentrated wastewater may
90 produce surplus oxidant species and side reactions leading to inefficiencies in the
91 application of AOPs. This is particularly relevant in electrochemical processes, for
92 which a concentration stage has demonstrated to help to increase the efficiency by folds
93 because kinetic typically fits well a first order model. For these models, the same
94 decrease percentage in the pollutant concentration needs for the same applied charge
95 regardless of the initial concentration. That is, a 99% removal of pollutant always needs
96 the same electric charge being the same for the removal of 100 down to 1 ppm than for
97 the removal of 1 ppm down to 0.01 ppm. Thus, the importance of the existence of a
98 concentration step in wastewater treatment has been proved in several previous works of
99 our group. Polar ionic organochlorine compounds have been successfully removed from
100 wastewaters combining electrodialysis and electrooxidation [19, 20]. For the non-ionic
101 colloids compounds, electrocoagulation followed by electrooxidation resulted into a
102 very efficient treatment option [21]. Depending on the characteristics of the target
103 pollutant the following treatment of this concentrated stream will be chosen. For soluble
104 non-ionic, combination of adsorption and electrochemical treatment has also shown
105 very interesting results [21].

106 Taking into account the above-mentioned findings, this work aims to upgrade the whole
107 electrocoagulation-electrolysis treatment process (suited for the treatment of wastes
108 polluted with micelles because it attains their concentration previously to the oxidation)
109 with the application of US. As these are the first trials to check the viability of the
110 technology, synthetic waters polluted with oxyfluorfen, free of natural dissolved organic
111 matter (DOM) will be treated by a combined electrocoagulation-ultrasound-electrolysis
112 process. The first electrocoagulation stage reduces significantly the volume of the
113 effluent and increase the concentration of the target pollutant, so the highly efficient

anode material Boron Doped Diamond was selected to optimize the use of energy and assure a proper degree of treatment. It is worth to take into account the remarkable increases in efficiency reached with the use of this material as compared with the use of other cheaper materials like MMO anodes [22], even more because of the more outstanding formation of oxidants from the salts contained in the wastewater, which are easily activated by irradiation [23]. The oxidation step will be preceded by the optimization of the concentration step by electrocoagulation and the integration of intermediate treatment step (with US), which will increase the global removal efficiency. As it was proved that the pollutant remains trapped in the iron hydroxyl flocs generated in electrocoagulation, ultrasonic irradiation will be applied to crack the conglomeration and release the pollutant in order to be attacked by the oxidant species dosed or produced electrochemically. In this way, it is possible to reduce the time, cost and space needed for the entire treatment process.

2. Materials and methods

Barre® (oxyfluorfen 24%, solvent naphtha (petroleum) > 25%, cyclohexanone < 15%), the model pollutant of this study was provided by a local store. Sodium sulfate 100%, hydrochloric acid 37%, H₂O₂ 33% and sulphuric acid 96% were provided by Panreac and the synthetic wastewater was carefully prepared using ultra-pure miliQ water. Acetonitrile provided by Sigma Aldrich was used for the L-L extraction.

2.1. Experimental

The experimentation began with the concentration by electrocoagulation of a synthetic wastewater containing 100 mg dm⁻³ oxyfluorfen and 3000 mg dm⁻³ Na₂SO₄, as previously used in the research in which the present work is based [21]. The reaction took place in a homemade electrochemical cell equipped with an iron plate as sacrificial anode and a stainless steel plate as cathode with an electrodic area of 100 cm² and 1 cm

electrode gap. The current density applied was $j = 50 \text{ Am}^{-2}$ and the treatment lasted 40 min.

The concentration is performed in several batches. After the sedimentation, 2 phases are obtained: a liquid phase free of pollutants and a concentrated solid phase, which has entrapped the pollutant. After each batch the installation setup was submitted to a cleaning process with HCl 4 % in order to remove the remaining iron hydroxide from the electrode surface and pipeline. The final solid phase is divided into equal parts, about 0.175 L, and various pretreatment techniques are tested during an established time – 15 minutes. The experimental setup is schematically represented in the Figure SM 1 from the supplementary material of the study.

The proposed techniques for this study are: low frequency ultrasonic irradiation- 75 khZ, high frequency ultrasonic irradiation – 1 MhZ, heat - 90°C and a blank – no pretreatment. The ultrasonic probes are introduced into the concentrated liquid waste in order to achieve a proper and homogeneous procedure.

For the low frequency ultrasonic irradiation, it was used an ultrasonic processor UP200S provided by Hielscher. Meanwhile, for the low frequency ultrasonic irradiation it was used an EPOCH 650 Ultrasonic Flaw Detector and equipped with a 1 MhZ ultrasonic probe provided by Olympus. In addition, it was decided to test the effect of heat in order to check the efficiency of the ultrasonic irradiation [24].

After the pretreatment, a sample of 0.015 L is taken in order to test the chemical oxidation by hydrogen peroxide process (ChOx) and its effect on the system. The remaining volume was treated by electro-oxidation. The ChOx process consists of the addition of hydrogen peroxide to the mixture after suitable pH adjustment. To determine the dose of hydrogen peroxide needed to lower a pollutant load of a polluted stream, the type and concentration of contaminants contained in the stream should be

considered. All theoretical calculations should take into account the stoichiometry of the reaction and the actual dose should be slightly higher [25]. For this particularly case, it was decided to add a concentration of 3000 ppm.

Taking into account the small volume of the liquid waste, for the electrooxidation it was used a small homemade electrochemical cell equipped with a BDD anode and a stainless steel plate as cathode. The anodic area was 28 cm² with 1 cm electrode gap. The current density applied was 172.57 Am⁻² and 60 minutes operation time in discontinuous mode. Samples of 2 mL were taken every 10 minutes during the experiment, counted as homogeneous and diluted 1:10. It must be mentioned that during the electro-oxidation process the formation of foam was observed. When the test was finished, the mixture was let to set down to form 3 phases: solid, liquid and foam. The volumes of each phase were measured, sampled and analyzed.

The concentration of oxyfluorfen was measured by high performance liquid chromatography (HPLC). It uses analytical column Phenomenex Gemini 5 µm C18 with a mixture of acetonitrile/water (70:30 (v/v)) as mobile phase at 0.3 mL min⁻¹. The detection wavelength of 220 nm was selected, and the temperature of the oven was maintained at 25°C. 20 µL was injected, and the oxyfluorfen detection limit was 0.2 mg dm⁻³. Prior to each analysis, all samples were filtered with 0.22 µm nylon filters Scharlau provided by Scharlab. The pH and conductivity were measured using a CRISON pH25+ and CRISON CM35+ device. The total iron concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) with a detection limit < 1.5 ppb. After each experiment the installation setup was cleaned using H₂SO₄ 20 % in order to remove all impurities and rinsed with miliQ water to remove all traces of acid.

Taking into account that the liquid waste treated in this work is very complex, and the pollutant is transferred from one phase to another, it is very important to assure an

accurate calculation of the mass balance. Because of that, pollutant is shown not in concentration but in amount units.

3. Results and discussions

3.1 Concentration of oxyfluorfen: effects of US application

The volatility and solubility of the pollutant need to be considered for an optimum selection of the treatment technology to be applied for the removal of wastes polluted with chlorinated pesticides. [16]. In particular, oxyfluorfen is a synthetic compound that presents at 20 °C a water solubility of 0.116 mg L⁻¹ and a vapor pressure of 0.026 mPa [26]. Its low solubility is the key for its efficient removal by electrocoagulation. Thus, from the viewpoint of pollution there are two types of pollutants related to oxyfluorfen in the commercial product used and, consequently, in the aqueous effluents produced with its use: oxyfluorfen emulsified in micelles and the oxyfluorfen dissolved in the water matrix. Because of the low solubility, the first is the primary species contained in aqueous wastes and, in turn, because of the nature of the surfactant typically used in the formulation of the commercial products, oxyfluorfen molecules stabilized within the surfactant micelles will form an aggregate with a negatively-charged surface. The coagulation of these micelles with iron was described in a previous work [21] according to the typical mechanisms of the electrochemically assisted coagulation [27]. In this work, we have used what it was considered the optimum condition for this process and results of seven electrocoagulation tests in terms of phase separation are shown in Figure 1.

Figure 1. Concentration assays using electrocoagulation – 7.1 dm³ wastewater per test.

Dark blue - raw wastewater; light blue –treated wastewater; brown - concentrate waste

As it can be seen, the electrocoagulation concentration step is able to reduce the volume of the wastewater down to 2.78% the initial volume and concentrate the pollutant by more than 1 log-unit, what initially can be expected to be an advantage for an efficient oxidation process, regardless of the technology applied, because all AOP are more efficient when treating highly-concentrated wastes. Moreover, the conductivity of the obtained concentrated stream, an essential parameter in any electrochemical process, is around 5 mS cm⁻¹ facilitating the further removal reactions.

The concentrated phase contains iron hydroxide and oxyfluorfen micelles. Initially, these micelles are not fully available for a later oxidation stage (because they are hidden in the structure of the floc) and it would be desirable to separate partially micelles from the flocs. One possibility is to acidify the concentrated phase, although it would require the addition of a strongly acidic solution [21]. This treatment concept has been evaluated in another work of our group but it is not the best approach from the environmental point of view, because of the huge amounts of acid needed, which lead to a low sustainable technique. Because of that, in this work, the application of high-frequency (HF) and low-frequency (LF) ultrasounds (US) is going to be evaluated. The mechanical energy applied with these waves is expected to have an influence on the

structure of the flocs allowing the release of the micelles (at least partially). In addition, as these processes also lead to a heating of the waste, a thermic treatment was also studied for the sake of comparison. Results obtained during the application of these three techniques to the flocs obtained in the electrocoagulation tests carried out are shown in Figure 2.

In part a, it can be seen that additional compaction of the flocs is obtained with the application of US with respect to the obtained in an equivalent settling time with the non-processed sludge. These changes of the structure of the flocs are also seen with the application of heat and, comparing the typology of the US, they are more important for low frequency US than for high frequency waves.

In part b, where the continuous line stands for the initial concentration, it can be seen that the final value of oxyfluorfen measured in the mixture is lower than the initial value. Because all test were made open air, this difference can be explained by the evaporation, which increases with the heating of the liquid mixture. In addition, what is more relevant is the higher presence of oxyfluorfen in the liquid phase in the LF-US test, which indicates the breakage of the floc and the release of micelles when the liquid undergoes the application of this type of mechanical energy. This is not observed in the other cases. In fact, in the case of the preheating treatment the floc seems to be more compact and difficult to be attacked, and an important concentration of the micelles remain in the flocs, even after adding very large amounts of acids to produce its release. Temperature does not affect oxyfluorfen, which can only be degraded at temperatures over 331°C. Taking this into account there is not a surprise the fact that by applying heat no degradation occur [26].

Figure 2. Influence of the pretreatment applied on the a) compaction of the iron hydroxide flocs: black column – solid phase; grey – liquid phase. Initial volume of sample 0.175 dm³. b) liberation of oxyfluorfen from the solid phase represented as millimoles in: * - liquid phase; ■ - solid phase; ○ - mixed sample.

In comparing the type of US applied, when high frequency ultrasonic energy is applied, it can be observed that the liberation of oxyfluorfen is also achieved but in lower extension, as compared to the results obtained by applying low frequency ultrasonic waves. This means that there is an important influence of the type of US applied and that LF (which are associated more to mechanical changes rather than to the formation of radicals) seems to be more effective for this application.

Anyway, this pre-treatment is used for improving the performance of a later oxidation stage and its success has to be related to the enhancement in a later oxidation stage. Because of that, the effluents of the previous tests were submitted to different oxidation technologies in order to evaluate the effect of the changes produced in the mixture during the pretreatments on the availability of the micelles for being oxidized and, hence, on efficiency of these oxidation processes.

3.2. Performance of ChOx process

In order to evaluate if the changes undergone by the sludge may affect to the efficiency of the removal, the oxidation with hydrogen peroxide was proposed, because of its simplicity and because of the huge amounts of iron contained in the sludge (that in electrocoagulation is produced as iron (II) species, although in the later oxidation is primary present as iron (III), so it cannot be considered as an optimized Fenton process). To test this process, the pH was adjusted to 3 and hydrogen peroxide was added with an over-stoichiometric ratio of 1.1:1 (mg H₂O₂/ mg oxyfluorfen). Figure 3 presents the variation of the concentration of oxyfluorfen in the mixed sample after 30 minutes of ChOx reaction.

Figure 3. Influence of the pretreatment on the degradation efficiency of ChOx process: white column – before H₂O₂; black column – after H₂O₂

As seen, the effects of the hydrogen peroxide addition are more important in the case of the sludge pretreated with LF-US, although the total removal obtained is not very high in any of the cases evaluated. No differences are found in comparing the non-pretreated sample with that pretreated with HF-US. Results are even worse for the system pretreated with heat, indicating again the floc-compacting effects previously described. These results are in agreement with those shown before regarding the release of micelles and indicate that the energy applied with the LF-US has a very positive effect

on the treatment efficiency, allowing to improve the removal by more than 4 times. Regarding the low efficiency of the ChOx processes in the removal of oxyfluorfen, the effects of the hydrogen peroxide and ultrasonic irradiation on the removal of a similar organochlorine compound have been evaluated in other works [15, 18, 28] showing similar low values. Thus, the addition of hydrogen peroxide can lead to additional oxidative degradation pathways while acting as a radical promotor. However, it can also act as a scavenger if the concentration is beyond the optimum level. Although +3 is the oxidation state of the primary iron species contained in the sludge, the product of the electrocoagulation is iron (II) cation. This means that an important amount of iron (II) species can be present during the ChOx process inside the flocs and that in a certain way, this process can be considered as a Fenton process. The H_2O_2 reaction, as presented in Eq (2), is predominant in the bulk solution phase where the reaction between the pollutant and active radicals follows the removal of $\text{OH}\cdot$ rather than at bubble interfacial region where the recombination of active radicals along with thermal decomposition govern [29, 30].

On the other hand, an excessive addition of hydrogen peroxide can lower the efficiency of degradation. This is due to the formation of radicals with a significantly lower oxidant potential than hydroxyl radicals generated by the reaction of hydroxyl radicals with hydrogen peroxide as detailed in the Eq (3- 6) [31].

3.3. Performance of electrochemical oxidation

The results obtained in the test with the ChOx process have informed about the good prospective of using LF-US to pre-treat sludge containing micelles of oxyfluorfen before the application of an oxidation technology. However, this process was not as suitable as the electrochemical oxidation for the treatment of sludge, because in this later treatment many oxidation mechanisms are combined which help to avoid the flanks observed in the ChOx technology. In Figure 4, it can be seen the evolution of the concentration of oxyfluorfen during the electrolytic experiments for each of the pretreatment performed to the sludge. During the tests an important production of foam was observed, which can be explained in terms of the surfactants contained in the sludge.

Figure 4. Influence of the pretreatment process on the removal of Oxyfluorfen during electro-oxidation test $j=172 \text{ A m}^{-2}$ (cell voltages between 10 and 12 V): ■ heat 90°C; ▲ 1 MHz ; * 75 kHz; ● blank.

As it can be seen, oxyfluorfen can be successfully removed from sludge, regardless of the pre-treatment used, although this pre-treatment has a great influence on the rate of removal and, hence, on the efficiency of the process. Thus, when no pretreatment is applied, it is achieved a modest removal efficiency of 23% after applying a specific

current charge of 3.2 Ah dm^{-3} . It is a good result, in particular if considering the complexity of the system and that we are dealing with a highly concentrated mixture and that the electric charge applied is low. It indicates that the electrolytic treatment is generating oxidants capable of destroying the micelles more efficiency than the hydrogen peroxide. At this point, it has to be taken into account that the presence of sulphate and other anions in the mixture leads to the formation of strong oxidant species such as persulfates, peroxophosphates or peroxocarbonates. The BDD is very well known for its impressive efficiency in the removal of persistent organic pollutants [12, 32-34].

When ultrasonic irradiation is applied prior electro-oxidation the removal efficiency significantly improves. In the case of LF-US the results improve greatly and this pretreatment provides the best results, with about 90%, meanwhile the high frequency shows a lower removal of about 65%. These are good results because they demonstrate the capability of US to enhance the performance of the electrolysis and open the possibility of designing new more efficient treatments for non-soluble pollution. In addition, these results strengthen the initial theory that the cavitation helps to open the floc and to liberate the pollutant favoring the degradation by means of direct and indirect oxidant reactions. As it was previously mentioned, a heating pretreatment can seal the pollutant into the flocs and hinder its destruction. As it can be seen from the Figure, there is no degradation during the electro-oxidation.

Figure 5 represents the amount of oxyfluorfen (in millimoles) found in each one of the final phases after the electro-oxidation. In this way, the balances are clearer and it can be quantified if the pollutant has been removed or just transferred to another phase.

Figure 5. Influence of the combined processes on the: a) compaction of the solid phase and foam production: black column – solid phase: grey – liquid phase; white – foam. b) oxyfluorfen concentration on each phase of the sample: * - liquid phase; ■ - solid phase; ▲ - foam; ○ – mixed sample

As it can be seen, the speciation reveals the high performance of the combined process. Once again, the best results are obtained when low frequency ultrasonic irradiation is applied as pretreatment achieving the highest reduction in the concentration of the pollutant.

3.4 Optimization of conditions for the combined process

Once established that the pretreatment with low frequency ultrasonic energy allows to attain the best results on the degradation by electro-oxidation, it was decided to study the influence of the LF-US energy dosing time. In this way, the whole process can be optimized in order to obtain the maximum removal efficiency with the minimum energy consumption. For this, tests were conducted at 75 KhZ during 5, 10 and 15 minutes.

In Figure 6 it can be seen the influence of the US application time on the pollutant release represented in mgL⁻¹. As expected, this amount increases with the LF-US application time.

Figure 6. Influence of the irradiation time on the release of oxyfluorfen from the solid phase at 75 kHz

This means that by adjusting the irradiation time to the pollutant concentration from the mixture it is possible to favor the release of the oxyfluorfen micelles from the iron hydroxide flocs allowing their further treatment or reuse. Further details of this release are shown in Figure 7, where it can be appreciated the influence of the irradiation time on the release of oxyfluorfen from the iron hydroxide found in each phase of the mixture represented in millimoles along with their volume. The initial compaction of the sludge (which reverses at longer times) and the higher release of micelles (which informs about floc opening) are observed in the Figure.

a)

b)

Figure 7. Influence of the irradiation time on the: a) compaction of the solid phase: black column – mixture sample; grey- solid phase: white – liquid phase. b) oxyfluorfen concentration on each phase of the mixture: * - liquid phase; ■ - solid phase; ○ – mixed sample

The higher release of oxyfluorfen should be reflected on a better performance of electrolysis. In Figure 8, it can be seen the influence of the pre-treatment time on the removal of the oxyfluorfen during electro-oxidation tests.

Figure 8. Influence of the ultrasonic irradiation time at 75 kHz on the removal of Oxyfluorfen during electro-oxidation tests at 172 A m⁻² (cell voltages between 10 and 12 V): ▲ 0 min; • 5 min; ■ 10 min; * 15 min.

As it can be seen the removal efficiency increases with the irradiation time and current density applied. The behavior of the untreated sample is very similar to the one that has with only 5 minutes of ultrasound irradiation. This means that the degradation is related to the liberation degree and proves once more the stability of the concentrate mixture.

With 10 minutes of ultrasound irradiation it seems that the degradation gets to a stationary state after 40 minutes of electro-oxidation. On the other hand, by increasing the irradiation time to 15 minutes it is possible to achieve a 90 % of removal efficiency.

It is interesting to compare the changes at the two highest times, which indicates that changes in the floc structure needs for longer irradiation periods.

Likewise, as explained earlier, it is very important to represent the concentration of the pollutant from each final phase. For this, Figure 9 presents the influence of the US application time on the oxyfluorfen removal. The concentrations are expressed in millimoles for a better quantification of the pollutant.

Figure 9. Influence of irradiation time on the: a) compaction of the solid phase and foam production: black –solid phase; grey – liquid phase; white – foam. b) oxyfluorfen concentration on each phase of the mixture: * - liquid phase; ■ - solid phase; ▲ - foam; ○ – mixed sample

The electro-oxidation test sustains the fact that by applying an adequate disturbing agent and liberate the pollutant it can be more easily degraded. The longer US application times affect to the amount of pollutant contained in the foam, promoting its oxidation and consequently leading to a much more efficient removal of the pollutant.

3.5 Conceptual model of the combined LF-US / electrolysis process

Because of the enmeshment coagulation mechanisms, after the electrocoagulation, most part of the pollutant is found trapped in the iron hydroxide flocs. This structure presents certain stability allowing to separate the pollutants by sedimentation. By applying an

disturbing agent such ultrasonic energy or heat, the structure can be damaged and the flocs can change their properties [35] as represented in Figure 10.

Figure 10. Schematic representation of the ultrasonic irradiation effect on the iron hydroxyl flocs which contain the oxyfluorfen micelles and they further removal options.

Depending on the treatment applied, the floc may break, open or even compress being able to release the pollutant or seal it better. As it can be seen, when ultrasonic irradiation is applied, the floc opens and release part of the pollutant. Meanwhile, heat does the opposite and produced a more compact floc. These changes in the floc mean that with a proper optimization, the iron hydroxide may be recovered and used in other applications [36-38].

When oxidants are added (or directly produced from the ions contained or released during the degradation of wastewater), they can attack easily the micelles suspended in solution. In addition, they can adsorb onto the flocs and attack the micelles enmeshed into them, although with a lower efficiency. Same mechanisms applied for

electrochemical oxidation, although in this case there are more oxidation mechanisms and this explains the higher efficiency observed with this technology.

4. Conclusions

From this work, the following conclusions are drawn:

- Combination of electrocoagulation, ultrasounds and electrolysis is a feasible technology for the removal of micelles from liquid wastes. This has been demonstrated with an oxyfluorfen polluted waste.
- Application of ultrasounds has a positive effect on the release of pollutant entrapped from flocs formed during electrocoagulation. LF-US shows better performance than HF-US. Heating (which is a side effect of the application of US) has the opposite effect and lead to a more important entrapping of the pollutant inside the flocs
- Performance of the chemical oxidation with hydrogen peroxide and electrolysis is greatly improved with the pre-treatment with US of the flocs. In everycase, electrolysis overcomes results obtained by the addition of hydrogen peroxide.
- US application time is a very important parameter and it does not only influence on the release of the pollutants from the flocs but also on the floc compaction

5. Acknowledgments

The financial support from the Spanish Ministry of Economy, Industry and Competitiveness and European Union through project CTM2016-76197-R (AEI/FEDER, UE) is gratefully acknowledged.

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571