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Degradation of Indigo Carmine Using Advanced Oxidation Processes: Synergy Effects and Toxicological Study

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Abstract

The physicochemical degradation of Indigo Carmine (IC) dye in aqueous solution was performed using single and combined Advanced Oxidation Processes (AOP's). Photocatalysis (TiO_2-UV), Ozonation (O_3) and Sonolysis (SN) were tested either in a standalone methodology or by combination of two simultaneous AOP's. The dye conversion was followed by both measurements: 1) color removal determined by UV-VIS spectrometry and 2) organic and inorganic load determined by the chemical oxygen demand (COD). A complete and quick color disappearance of model water waste has been obtained by using combination of non-irradiated AOP's, namely, O_3/SN, which contrasts to the combination of irradiated photocatalysis with O_3 or sonolysis. Color removal with simultaneous TiO_2-UV/SN reached 77% while TiO_2-UV/O_3 reached 96% at similar reaction time. On the other hand, the standalone O_3 yielded the highest color removal (94.4%) in 32 minutes whereas SN reached only 39.2% in 4 hours. The standalone light irradiated TiO_2-UV reached 93.3% color removal in one hour of reaction time. These results indicated that non-irradiated (SN and O_3) enhance synergistic effects that provoke structural changes in dye molecule without reaching total degradation. This is evidenced from FTIR of residuals from reaction mixture in which it has been observed the presence of organic molecules such as aromatics, sulfonic and amines refractory compounds that are mechanistically possible to be found during IC degradation. Also, toxicity tests (MicroTox® Technique) were performed using commercially available bacteria culture before and after IC degradation for each AOP and their combination. Reduction of aqueous dye concentration decreased the level of toxicity of the treated water which is the main target of the AOP's but the presence of the remaining recalcitrant compounds have also toxic effect.

1. Introduction

Textile industry plays an important role the same for domestic as for worldwide economy since many years [1] [2]. Relevance of this industry relies on the overwhelming use of water especially for clothes dyeing such as denim. For instance, 170 l of water are needed for dyeing 1 kg of jeans denim, which dramatically increases the water pollution.

Indigo Carmine (IC) is the most common chemical dye for this process, which is considered as a refractory molecule (Figure 1) since it is required a rather strong chemical treatment for its elimination from the water waste. The presence of this dye in residuals causes notorious change of water color and smell even in very low concentration. Moreover, if some of this water reaches natural streams it can be toxic for aquatic living entities due to the formation of toxic compounds such as aromatic amines [3] [4]. Emergent water treatments for elimination of organic compounds are the Advanced Oxidation Processes (AOP's) that requires rather soft conditions to convert dye molecule to simple products, which are much less toxic. Within these processes, room temperature and atmospheric pressure can be used because the reactive radical (OH•) is produced at these conditions. Also, smooth operating conditions lead to reduce by-products that might be difficult to eliminate as well as to avoid organic mud formation [5]-[10].

Several reports show an increasing interest in studying simultaneous AOP's that reduce different pollutant from water waste by synergic effect. In fact, this is a result of coupling two or more processes efficiency in one stage treatment of contaminated water. AOP's consist of a wide group of technologies that have been used with success in water and wastewater treatment over the last decades and involve direct Ozonation, ozone and/or H_2O_2 in combination with UV, Fenton, photo-Fenton, semiconductor photocatalysis, electrolysis, sonolysis or ultrasound irradiation, wet air oxidation and even biological treatment, among others [11]-[13].

In the present work, the AOP's were used either in a simple or combined treatment of an aqueous solution of IC that represented the textile water waste. Ozone (O_3), sonolysis (SN) and photocatalysis (TiO$_2$-UV) were tested in a separated or combined way to reduce or eliminate the dye concentration under similar operating conditions. A
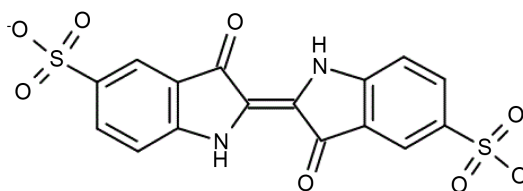

Figure 1. IC molecule structure.

kinetic reaction model was assumed by means of a simple formalism taking into account the complete set of experiments. The reaction performance was followed by determining the dye concentration using UV-VIS spectrometry and by measuring the amount of organic and inorganic load (chemical demand of oxygen). At the last but not the least, toxicity of reaction residuum was evaluated using a commercially available bio-test (MicroTox®) based on reduction of bio-luminesce of aquatic bacteria *Vibrio fischeri*. The principle of this bio-test is the effect that contaminants in water or earth have over living sea bacteria called Vibrio fischeri [14] [15]. Changes in bacteria concentration is sensed by means of natural bio-luminesce that is measured using a special detector. Reduction in bio-luminesce depends on the amount of toxic compounds present in streams. The common expression used for toxicity is the concentration of toxic compound that causes 50% reduction of the initial bio-luminesce, namely, EC50.

2. Methodology

2.1. Materials and Reagents

All the experiments were performed using commercially available chemical reagent, except for ozone that was generated *in-situ*. The indigo carmine disodium disulfonate salt (3,3'-dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt, Aldrich) was dissolved in purified (ion-free) water at the same concentration (50 ppm) for the complete set of experiments. The catalyst TiO_2 used for the catalytic tests was supplied by Sigma-Aldrich Chemie GmbH (USA).

2.2. Experimental Procedures

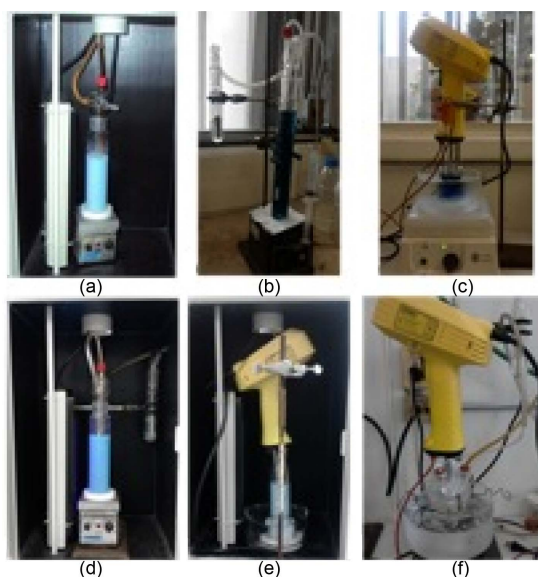The experimental set-up currently used is depicted in Figure 2. The operating conditions

Figure 2. Experimental set-up for oxidation of IC dye. standalone photocatalysis (a), ozonation (b), sonolysis (c). simultaneous photocatalysis/ozonation (d), photocatalysis/sonolysis (e), and ozonation/sonolysis (f).

were set at room temperature and atmospheric pressure. The range of pH was determined by the reaction itself without further external adjustment. The experiments were performed three times for all the operating conditions screening, in order to evaluate the data reproducibility. The following treatments Ozonation (O_3), Photocatalysis (TiO_2-UV) and Sonolysis (SN) were applied standalone, or in combination of irradiated/non-irradiated processes (Photocatalysis-Ozonation (TiO_2-UV/O_3) and Photocatalysis-Sonolysis (TiO_2-UV/SN)) and those of non-irradiated processes (Ozonation/Sonolysis (O_3/SN)) to IC aqueous solution (the model textile wastewater). Color removal by UV-VIS spectrometry and inorganic and organic load by Chemical Oxygen Demand (COD) for all samples was measured. The procedure of this organic load determination was based on complete mineralization through the severe oxidation of organic compounds using a chromic mixture [16] [17]. Finally, residuum of every experiment was dried to obtain solid to perform FTIR analysis. Moreover, a 5 mL residuum of each experiment was kept to perform toxicity test, as it has been describe in previous section.

2.2.1. Photocatalytic Treatment (TiO_2-UV)

The catalytic reactor was a quartz cell that was treated in a UV chamber that was provided of a dual 254/365 nm UV lamp (Cole-Parmer, 8n watts, 115 V/60 Hz and 0.16 A), see Figure 2(a). The amount of catalyst (TiO_2) was evaluated by UV-VIS spectrometry within the range of 10 - 30 mg (difference of 5 mg among experiments) using 10 mL of dye aqueous solution. Reaction mixture was violently stirred during 10 minutes and centrifuged to separate the catalyst. The amount of the catalyst was set in 30 mg from preliminary results and for the subsequent experiments. It is necessary to stress that the experimental set-up was isolated with black paper to avoid influence of external light that could affect the reaction performance. The performance of our experimental conditions were compared to those literature reported by means of two runs at 254 nm and 365 nm [18]. Noteworthy, the best performance of catalytic reaction was obtained using the 365 nm wavelength and the results are currently reported. Reaction time was set at 60 minutes taking samples every 10 minutes. The total volume of dye solution was 200 mL in every experiment.

2.2.2. Ozonation (O_3)

The ozone Residual Device was used in this series of experiments. Two volumetric oxygen flows (0.25 and 0.30 liter per minute) and three voltages (0.75, 2 and 3 kV) were tested for ozone production. The reactor was provided of a gas inlet and purge to avoid pressure increases in the system since an accumulation of gas could occur (see Figure 2(b)). Reaction times were set at 6, 12 and 32 minutes for testing with following parameters 0.25 LPM-3 kV, 0.3 LPM-2 kV and 0.3 LPM-0.75 kV, respectively. Sampling was taken every 2 minutes for the first two reaction conditions and every 4 minutes for the latter one.

2.2.3. Sonolysis (SN)

Glass reactor was used for this series of experiments. An ultrasound bath Hielscher UP

200 Ht was used with frequency setting at 26 kHz, 240 V-60 Hz and 200 Watts of power. The experiments were performed using 100% ultrasound width, see **Figure 2(c)**. Unlike the other two oxidation processes, ultrasound tests were longer and sampling were performed every 40 minutes. Temperature in these experiments was controlled externally by means of ice bath to avoid loss of water and error in dye concentration.

2.2.4. Photocatalysis/Sonolysis (TiO₂-UV/SN)

The experimental set-up for these experiments was that used for single TiO$_2$-UV as it has been described. For the sake of comparison, the operating conditions were set in the same range as that used for single AOP's (see **Figure 2(e)**). Experiments were performed using UV-light radiation (only 365 nm wavelength experiment is currently reported) with simultaneous ultrasound treatment. Experimental test was followed during 140 minutes taking samples every 20 minutes.

2.2.5. Photocatalysis/Ozonation (TiO₂-UV/O₃)

The quartz reactor described for photocatalytic section was used for current experiments. Operating conditions were similar to the previous sections but using volumetric ozone flow set in 0.3 liter per minute and 0.75 kV (see **Figure 2(d)**). Once again, only the results obtained at 365 nm wavelength are currently reported. Due to the high reaction rate, the reaction time was set to 16 minutes taking samples every 2 minutes.

2.2.6. Ozonation/Sonolysis (O₃/SN)

The glass reactor described for sonolysis section was used for the current experiments. Also, volumetric flow of 0.3 liter per minute and 0.75 kV were set for ozone production (see **Figure 2(f)**). Also, the high reaction rate under these conditions led to establish 6 minutes as the final reaction time with samples taken every minute.

2.3. Characterization

The chemical oxygen demand (COD) was measured by sample digestion and spectrophotometric quantification at 442 nm, using a DR/2400 portable spectrophotometer (HACH Company, Loveland CO USA 80539) after filtrating spin dry the samples. Color removal was measured by a colorimetric method based on an UV/Vis scan using a Cole-Parmer UV-VIS Spectrometer in a quartz cuvette. Toxicity was determined for every experiment by using MicroTox® technique. These essays are normally used to verify the level of toxic compounds concentration in water or solid waste after treatment. As we explained above, the principle of this bio-test is follows the changes in bacteria concentration by natural bio-luminesce that is measured using a special detector. Reduction in bio-luminesce depends on the amount of toxic compounds present in streams [14] [15].

3. Results and Discussion

3.1. Relationship of Dye Concentration to Spectrometric Response

The wavelength of visible light was 400 - 800 nm while UV region was 200 - 400 nm.

Spectrum of a conventional 50 ppm IC concentration is depicted in **Figure 3**. Quartz cell was used for this analysis. It is worth mentioning that glass cell showed certain interference in sample absorbance at the UV region. According to the UV-VIS spectrum, it can be observed that peaks correspond to structural characteristics of IC. Although it is obvious, it is important to mention that the original blue color of the IC solution has a maximum signal at 610 nm that corresponds to visible region. Also, the three peaks observed at the UV region correspond to structural features of organic molecule. Peak at 290 nm is related to amino group. Signal at 250 nm is attributed to the carbonyl group while that at 205 nm corresponds to resonance of the aromatic ring.

The linear response of the dye concentration (ppm) to maximal UV-VIS absorbance is confirmed according to **Figure 4**. Samples of known IC concentration were prepared for the spectrometric calibration curve. The range of dye concentration was from 0 to
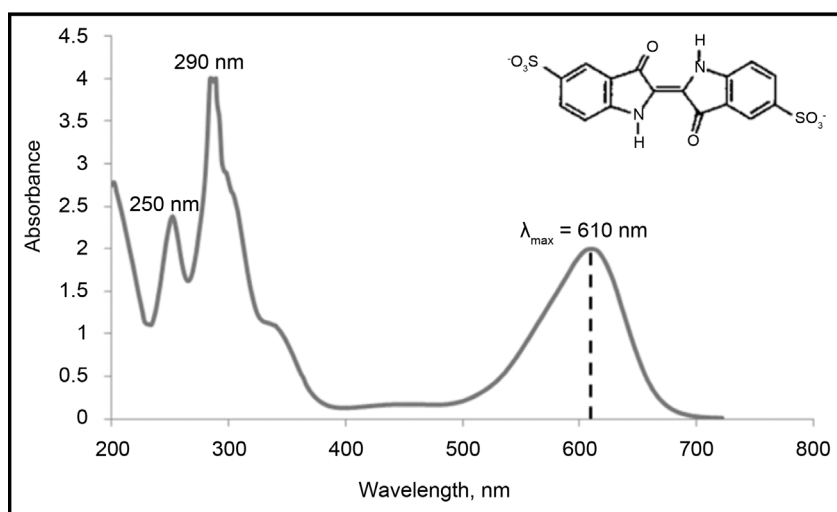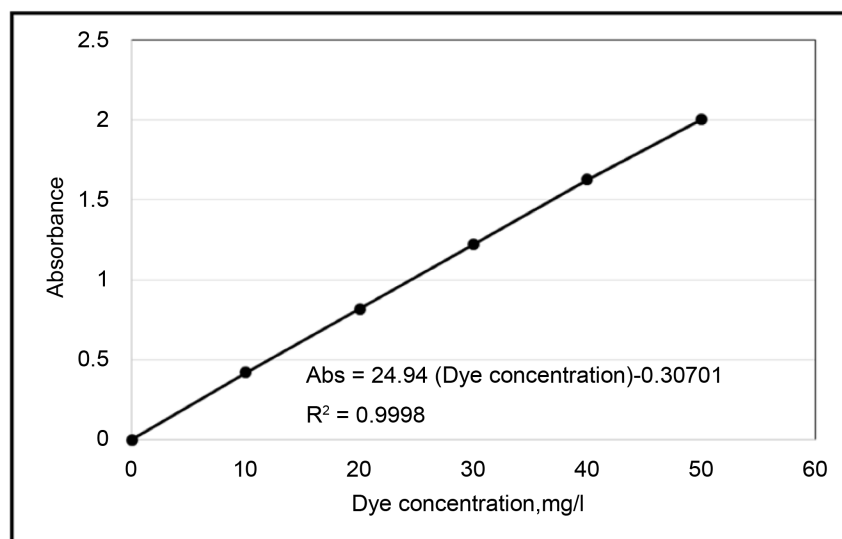

Figure 3. UV-Vis spectrum of IC.

Figure 4. Calibration curve of IC at $\lambda = 610$ nm.

50 ppm since the latter was the initial IC aqueous concentration.

3.2. Chemical Oxidation Using Standalone Processes

Figure 5(a) shows the behavior of color disappearance as a function of time for the standalone oxidation process. The color removal occurs faster in the presence of O_3 than TiO_2-UV irradiated catalytic and SN treatment. This indicates that treatment with O_3 enhances the rate of oxidation almost twice that of TiO_2-UV and 17 times that from SN.

Table 1 summarized the experimental kinetic results of IC degradation as well as the final dye conversion not only for standalone processes but also for their combination. The pH was measured at the end of each experiment and it was rather similar for all cases (4.5 - 5.7). It is well known that the actual oxidation species are those free oxygen-based radicals ($\bullet OH$, $HO_2\bullet$, and $O_2^-\bullet$) [10], which are generated in situ from water, O_3 and O_2 and promoted by light irradiation. These species play important role in different reactions towards a complete mineralization of organic molecules. It is relevant, hence, to provide these reactant species to the system to be able decompose as much as possible the dye molecule to low-molecular weight compounds (e.g., small aldehydes, carboxylic acids or small inorganic compounds), CO_2, and H_2O, without significant
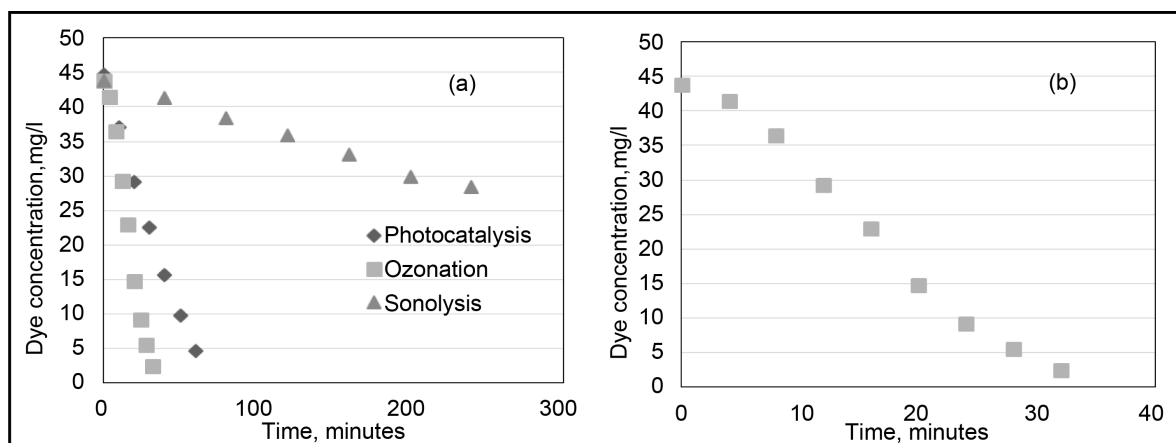

Figure 5. Color removal of indigo carmine aqueous solution using standalone oxidation processes (a) and a closed-up to the ozonation curve (b).

Table 1. Experimental kinetic results of IC degradation with different AOPs.

AOP	Calculated averaged reaction rate, $\times 10^{-6}$, mol l^{-1} min^{-1}	Dye removal, %
TiO_2-UV	1.6	89.7
O_3	2.5	94.5
SN	0.2	39.2
TiO_2-UV/SN	0.5	77.4
TiO_2-UV/O_3	4.8	89.5
O_3/SN	17.8	100.0

production of pollutant secondary solids. Discussion relies in the mass transport limitations of both dye and oxidizing molecules, which are present in this type of process. One can control and avoid these limitations by using high-speed stirring and heat. For our results, it is can be evidenced some diffusion limitation for ozonation from the initial reaction rate but it reaches steady state condition quite soon. It can be assumed that a pseudo-equilibrium of ozone dissolution and reactant species formation is reached within the first 5 minutes of treatment, see **Figure 5(b)**. Once these species are generated the subsequent oxidation reaction takes place very fast until almost complete color removal is obtained (94.5% final dye removal). Color removal concerns only elimination of the chromophore group in the dye molecule but the complete mineralization of the molecule is not assured only by the type of process. This is evidenced from the results of the total organic load analyses and the toxicity determination of the residuum from the reaction.

Table 2 shows the percentage of organic load by chemical oxygen demand (COD). The results indicate the amount of remaining organic molecules susceptible to be mineralized. The lower the values of organic load the more complete the dye oxidation due to the treatment. The O_3 yielded the lower remaining organic load of the set of standalone processes within a rather short time. According to results, SN is not that effective as expected for both color removal and organic molecules degradation. This indicates that the oxidizing species are scarcely formed by SN treatment, which means that activation of these molecules is an energy demanding process.

Results of toxicity for the standalone AOP's are related to the degree of bioluminescence observed using the Microtox® biotest. After the 15 minutes treatment of the *Vibrio fischeri* bacteria culture with residuum of every experiment, the bio-luminiscence was measured and the result was compared to the blank test that is the 100% bio-luminiscence value obtained with bacteria alone. According to the results, the products obtained during dye oxidation (intermediates or final mineralization products) show toxic effect for the bacteria. Apparently, the product obtained in SN shows no toxic effect; since the response reached 100%, see **Table 2**. So far, it is difficult to know what the reason is for this result since we still have no clues of the chemical structure of any product in each experiment. In this concern, FTIR analyses might help

Table 2. Organic load of dye degradation by standalone and combined AOP's.

AOP	Time, min	Organic load by COD, (%)	Toxicity test, % biochemiluminiscence[a]
Indigo Carmine, (blank test)[2]	0.0	100.0	100.0[b]
TiO_2-UV	60.0	35.3	51.0
O_3	32.0	17.9	70.0
SN	240.0	80.3	100.0
TiO_2-UV/SN	140.0	25.6	53.0
TiO_2-UV/O_3	16.0	24.2	60.0
O_3/SN	6.0	26.7	74.0

[a]Measured after 15 minutes treatment of *Vibrio fischeri* bacteria biotest with residuum of each oxidation process.
[b]Blank test means that only bacteria is present in the biotest.

to elucidate the type of functional groups that can relate a chemical structure of oxidation products.

The FTIR spectra of IC dye reagent and the reaction product from each process are depicted in Figure 6. Since the signals obtained from FTIR spectroscopy are caused by substance-specific vibration modes of the molecular structure, they can readily be attributed to functional groups as it is shown in Table 3. There are some similarities among the spectra of the reference dye and those from the residuum of each reaction product.

The FTIR spectra of untreated IC dye showed the specific peaks in fingerprint region (1500 - 500 cm^{-1}) for the orto-para-disubstituted benzene rings, which is supporting to the peak at 1613 cm^{-1} for the C = C stretching of the benzene ring. A characteristic peak in the range 1100 - 1000 cm^{-1} is related to the S = O stretch band with the most significant absorbance peak being at 1030 cm^{-1} and another one in the range 740 - 690 cm^{-1} for the C-S stretching vibrations due to sulfur containing functional groups. The observed bands in the region of 3300 - 3500 cm^{-1} are due to the O-H stretching that can be attributed to water remains. The band assigned to carbonyl bond can also be observed at ~1660 cm^{-1}.

For all the synthesized samples from experiments, the whole set of bands of the molecular skeletal vibrations were shifted, broadened and reduced after oxidation treatment. This result together with those of color removal and toxicity indicate that partial or complete dye molecule degradation has occurred. Perhaps the formation of sulfonates, carbonates, formates, acetates, propionates, benzoates, etc., suggest that the products were undergoing irreversible chemical changes, probably due to concomitant degradation and autoxidation reactions of the products formed during the reductive dye degradation. These results suggest that AOP's easily react with chromophore group but further degradation of intermediates that contain phenyl groups becomes more difficult which leads to toxic and recalcitrant compounds formation. Nevertheless, these intermediate compounds are rather less toxic than IC molecule [10].

3.3. Chemical Oxidation Using Combined Oxidation Processes: Synergy Effects

The actual combination of oxidation processes lead to better and more promising experimental results. The trend in color removal is depicted in Figure 7 for the combined AOP's.

Combination of AOP's lead to higher conversions and reaction rates which is evidence of the presence of a synergistic effect between treatments. When ozone is present either in TiO$_2$-UV or SN processes, the reaction rate increases significantly, see Table 1. The combination of SN and TiO$_2$-UV, however, is not that good as expected even though the reaction rate is increased three times that obtained with standalone SN. It is worth mentioning that during these experiments, the catalyst was stuck to the reactor walls, which might limit its activity, but allowing the oxidation reaction to take place. The case of O$_3$ is more promising either in the presence of a catalyst or with SN treatment. The O$_3$ treatment enhances SN reaction rate more than 100 times, which indicates
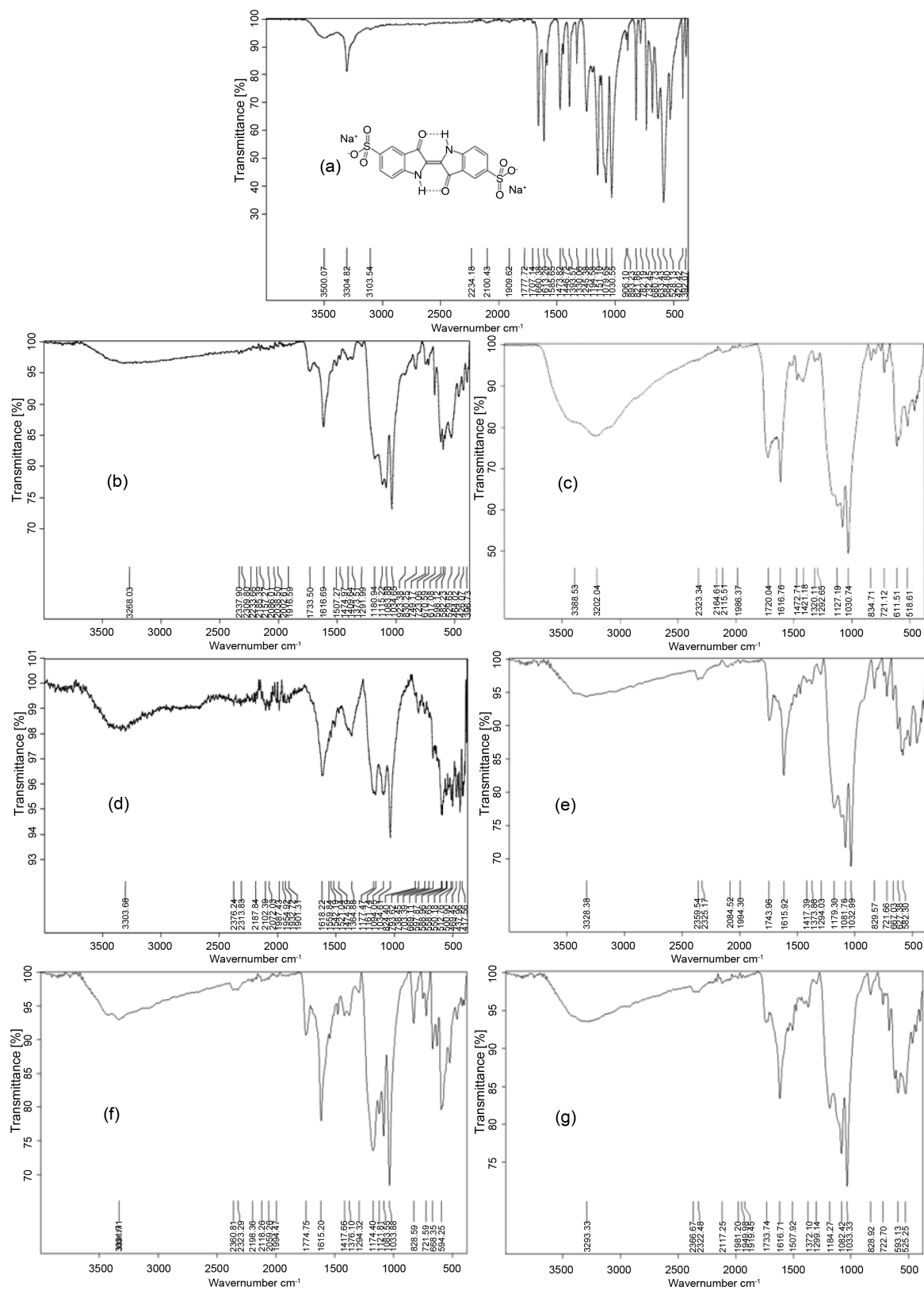
Figure 6. FTIR spectra of IC (a) and reaction product of standalone photocatalysis (b), ozonation (c) and sonolysis (d) as well as combined photocatalysis/ozonation (e), sonolysis/ozonation (f) and sonolysis/photocatalysis (g).

Table 3. FTIR signals and corresponding functional groups (cm^{-1}).

Functional group	IC	TiO$_2$-UV	O$_3$	SN	TiO$_2$-UV/O$_3$	TiO$_2$-UV/SN	O$_3$/SN
O-H	3500	-	3388	-	-	-	-
>N-H	3304	3260	3202	3003	3328	3293	3371
>C = O	1660	1733	1730	-	1743	1733	1744
C = C	1613	1616	1616	1618	1615	1616	1616
C-N	1151	1180	1127	1177	1179	1184	1174
S = O	1030	1034	1031	1034	1032	1032	1033
C-S	732	749	721	738	721	722	722
R-O	1245	1291	1292	1161	1294	1299	1294
	1079	1084		1094	1081	1182	1083
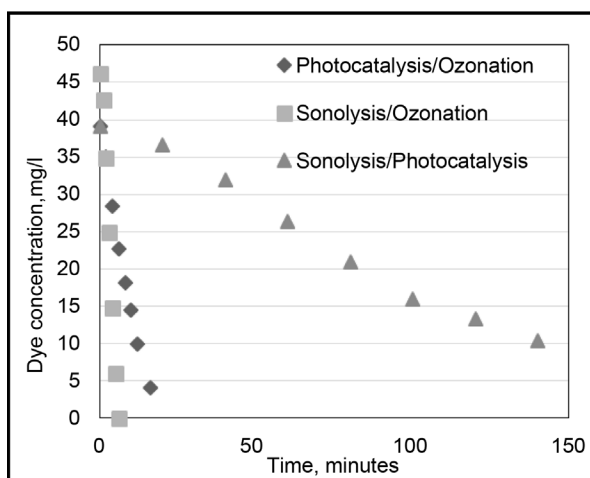
Figure 7. Color removal of aqueous solution of indigo carmine using combined AOP's.

that there must be an activation process on the oxidation species formation, which is promoted by SN. Moreover, O$_3$/SN treatment led to complete color removal in a very short time. It has been mentioned that O$_3$ might be affected by transport limitations since ozone gas has to be dissolved in the aqueous reaction media to produce oxidation agent such as the hydroxyl group. By using SN, it seems that ozone solubility is not affected but the production of hydroxyl oxidation agent formation is enhanced. Importantly, the experimental pH of the O$_3$/SN experiment was the lowest (4.5) of the complete set of experimental series. The combination of TiO$_2$-UV/O$_3$, however, was moderated although the reaction rate was twice that of standalone O$_3$ and three times that of standalone TiO$_2$-UV.

Concerning the remaining organic load of the combined oxidation processes, similar values were obtained regardless the type of processes combination. This is also confirmed by the toxicity assessment since similar results were also observed. Obviously, the removal of the color is not sufficient to assure there is complete mineralization of the IC molecule and this is the case of the current results. There still some refractory

intermediate molecules, which require more severe operate conditions to be fully reacted. In this regard, the best results were obtained, again, for the O_3/SN combination since only 26% of the initial *Vibrio fischeri* culture was affected by the reaction product, which was obtained from the 6 minutes experimental test. These recalcitrant compounds are also evidenced from FTIR spectra depicted in Figure 6.

4. Conclusion

The degradation of IC by advanced oxidation processes presents some similarities and strong differences depending on the type of process. In general, from our current results, standalone AOP process or the combination of these led to similar refractory intermediates regardless the level of conversion. These compounds showed some toxic effect on life organism. The chemical nature of the reaction product was evidenced by means of FTIR spectra that showed the same fingerprint for all cases of AOP's but different from IC spectrum. The FTIR signals for sulfur, nitrogen and oxygen containing groups were observed as well as phenyl groups, which indicated the presence of carboxylates such as formates, acetates or propionates, as well as sulfates and amine or amide functional groups (isatine, for instances). The ozonation was the best process either being used as standalone or in combination with photocatalytic and sonolysis process. The presence of ozone enhanced formation of those oxidant species such as hydroxyl and peroxydril radical ($\bullet OH$, $HO_2 \bullet$, and $O_2^- \bullet$). When ozone was used under ultrasound treatment the best results in conversion and mineralization were obtained (from organic load and toxicity results). This means that ultrasound promotes gas diffusion in the reaction media as well as the formation of the mentioned oxidizing species. The photocatalysis, on the other hand, appeared not to be as effective as it was expected. There was the assumption that SN provokes cavitation phenomena of the catalyst particle that affected its performance during combined TiO_2-UV/SN treatment. Because of this, the catalyst efficiency was limited and synergy between TiO_2-UV/SN as well as TiO_2-UV/O_3 never showed up.

Acknowledgements

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