Synergetic decolorization of azo dyes using ultrasounds, photocatalysis and photo-fenton reaction

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ABSTRACT

In the present work, ultrasound irradiation, photocatalysis with TiO_2, Fenton/Photo-Fenton reaction, and the combination of those techniques were investigated for the decolorization of industrial dyes in order to study their synergy. Three azo dyes were selected from the weaving industry. Their degradation was examined via UV illumination, Fenton and Photo-Fenton reaction as well as ultrasound irradiation at low (20 kHz) and high frequencies (860 kHz). In these experiments, we investigated the simultaneous action of the ultrasound and UV irradiation by varying parameters like the duration of photocatalysis and ultrasound irradiation frequency. At the same time, US power, temperature, amount of TiO_2 photocatalyst and amount of Fenton reagent remained constant. Due to their diverse structure, each azo dye showed different degradation levels using different combinations of the above-mentioned Advanced Oxidation Processes (AOPs). The Photo-Fenton reagent is more effective with US 20 kHz and US 860 kHz for the azo dyes originated from the weaving industry at pH = 3 as compared to pH = 6.8. The combination of the Photo-Fenton reaction with 860 kHz ultrasound irradiation for the same dye gave an 80% conversion at the same time. Experiments have shown a high activity during the first two hours. After that threshold, the reaction rate is decreased. PT-IR and TOC measurements prove the decolorization due to the destruction of the chromophore groups but not complete mineralization of the dyes.

1. Introduction

In recent years, pollution-related problems have attracted much attention from several research groups. Organic pollutants, like CFCs, PCBs and PAHs are among the most harmful substances for the environment\textsuperscript{[1]}. One of the main sources comes from wastewater containing dyes. Biotechnological methods are not efficient enough against non-biodegradable substances or need long treatment times and microorganisms, which are sensitive to environmental parameters and conditions\textsuperscript{[2,3]}. Azo dyes are widely used in industry, accounting for nearly 70% of the world’s dye production\textsuperscript{[4,5]}. Production reaches 70,000tn/y and a large percentage of those dyes escape in the environment, causing various problems regarding both human health and soil contamination\textsuperscript{[6,7]}. Azo dyes are not toxic, but many of their decomposition products have high toxicity\textsuperscript{[8,9]}. During the disintegration of the azo dyes, amines particularly toxic are released\textsuperscript{[10]}. Clothing industries demand durable dyes that can withstand discoloration due to daily use. Since they are highly durable and due to their degradation products harmful to the environment, water contaminated from organic pollutants needs to be properly processed\textsuperscript{[11]}. Complete oxidation can be achieved via different Advanced Oxidation Processes (AOPs)\textsuperscript{[12]}. Some of their advantages include environmentally friendly reagents, drastic sludge reduction in sewage treatment plants and the utilization of solar radiation\textsuperscript{[13,14]}. They can be used for the pre-treatment of wastewater, which facilitates the subsequent biological treatment, due to the production of biodegradable products, but also in many cases due to the decrease of sewage toxicity. However, the use of relatively expensive reagents, high cost of light sources (UV irradiation) and the possibility of forming unknown intermediates more toxic than the parent compounds lead to optimization requirements to reduce cost, and improve safety parameters. Currently, advanced oxidation processes are employed by utilizing ozone, H_2O_2, Fenton reagent\textsuperscript{[10]}, oxidizing agents and catalysts\textsuperscript{[3]}, hydrodynamic cavitation\textsuperscript{[15]}, and ultraviolet (UV) light\textsuperscript{[16–18]}. Photocatalysis via UV illumination has attracted considerable

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attention over the past years, with TiO$_2$ being one of the most widely studied, due to its non-toxicity, low cost and strong oxidizing abilities. One important disadvantage is its large bandgap of 3.2 eV (anatase) [19]. However, it remains a good semiconductor photocatalyst for investigating the elementary steps and charge/energy transfer processes of photocatalysis, which can be very beneficial for the characterization of new photocatalytic processes and the development of new photocatalysts. In the last two decades, TiO$_2$ heterogeneous photocatalysis has expanded very quickly, having undergone various energy and environmental issues, such as direct solar H$_2$O splitting into H$_2$ and O$_2$ as well as the decomposition of pollutants in air and H$_2$O at low concentrations [20]. Its photocatalytic properties are derived from the formation of photogenerated charge carriers (hole and electron) which occurs upon the absorption of UV light corresponding to the bandgap. The photogenerated holes in the valence band diffuse to the TiO$_2$ surface and react with adsorbed water molecules, forming hydroxyl radicals (‘OH) [21,22,23,24,25].

The Fenton reagent is a mixture of hydrogen peroxide and divalent iron salts (Fe$^{2+}$/H$_2$O$_2$), which is an efficient oxidant for a wide variety of organic compounds. During the degradation of hydrogen peroxide catalyzed by iron salts OH$^-$ radicals are formed [26,27,28].

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \quad (R1)$$

A disadvantage of the method, however, is the fact, that the oxidative activity of the Fe$^{2+}$/H$_2$O$_2$ system is significantly reduced when the divalent iron has become trivalent. The result of this is the consumption of significant quantities of the above reagents, as well as the creation of large quantities of mud from precipitation of iron. The effectiveness and efficiency of the previous method can be increased significantly if the trivalent iron is converted back to divalent with radiation of light (UV/VIS). The result of illumination is more beneficial due to the additional creation of OH$^-$ [29,30,31,32].

$$\text{Fe}^{3+} + \text{H}_2\text{O} + \text{hv} (\lambda < 450 \, \text{nm}) \rightarrow \text{Fe}^{2+} + \text{OH}^- + \text{H}^+ \quad (R2)$$

The main factors that influence the results of the oxidation process through Photo-Fenton reagent are pH, temperature, the concentration of iron, and the concentration of H$_2$O$_2$. Researches have suggested values around 3.0 as the optimum pH and it has been reported that the most effective pH value for Fenton and Photo-Fenton processes is in general close to 3.0 [33,34]. Reasons for this are higher amounts of photodecomposable Fe(III)-hydroxy complexes according to reaction R2, the absence of iron precipitation [35] as well as the absence of OH$^-$ scavengers like carbonate and bicarbonate species [36] and no H$_2$O$_2$ decomposition as typical for basic solutions, where H$_2$O$_2$ is unstable and can react to O$_2$ and H$_2$O before OH radicals are formed [37].

Combinations of Fenton reaction and photocatalysis (Photo-Fenton) have been reported by many groups [16–18]. Further, combinations of ultrasounds with photocatalysis (photo-sono) [15], ultrasounds and Fenton reaction (sono-Fenton) as well as all three techniques (sono-Photo-Fenton) [38].

Another interesting approach is the use of ultrasounds, which promise high reaction rates and short treatment times [39,40]. Sonocatalysis is a fast-developing branch of chemistry, which takes advantage of the ultrasound power. This technique is based on the effect of the acoustic cavitation, which can be described as the sequential formation, growth and collapse of bubbles in a so-called hot spot. This results in extreme local heating, high pressures and very short lifetimes. More specifically, these hot spots have temperatures of more than 5000 °C, pressures of 1000 atm and heating/cooling rates of ca. 10$^{10}$ K/s [41,42]. Such conditions have been proven favorable to nonmaterial synthesis in terms of shorter reaction times, smaller particle sizes and phase-selectivity [43]. Ultrasounds can break down the structure of the organic compound by either creating new non-toxic molecules or facilitating their oxidation by other processes. Additionally, they can be applied along with most AOPs, by contributing to additional production of OH radicals, which benefit the oxidation process.

In the present work, advanced oxidation processes like sonocatalysis, photocatalysis and Fenton reaction were used separately and combined to investigate their synergy for the decolorization of industry dyes.

## 2. Experimental section

The reagents in all experiments were used as received without further purification. More specifically, titanium dioxide (Degussa P25, Sigma-Aldrich) and FeSO$_4$·7H$_2$O (alfa Aesar 98%), H$_2$O$_2$, sodium acetate, acetic acid were used as catalytic precursors for the decomposition of azo dyes.

Dermacid Red (CAS: 6406–56–0), Dermacid Black RVE (CAS: 99576–15–5) and Dermacid Brown (CAS: 8011–86–7) were acquired from the leather industry.

All experiments using the Fenton reagent, have been studied at pH = 3 and some of them repeated at pH = 6.8 (supplementary material) in order to find out if the performance is better at pH = 3 as reported in the literature [33,34]. Thus, two different solutions were prepared, when using the Fenton reagent. The first solution consisted of 0.05 M Acetic acid and 8-10$^{-5}$ M sodium acetate leading to a pH of 3. The second solution consisted of 0.12 M H$_2$O$_2$ and 1.8-10$^{-8}$ M Fe cations ions in deionized water leading to a solution with pH = 6.8. The quantities used for each experiment are given in Table 1. Different volumes are due to the different reaction vessels in each apparatus and different concentrations are guaranteeing repeatability in the UV–Vis measurements.

For the experiments of 20 kHz a sonicator tip immersed in the solution was used, whereas at 860 kHz a vessel was mounted on the sonicator who was closing the open bottom of the vessel.

TiO$_2$ photocatalytic experiments were conducted under no UV light irradiation (dark experiments) to verify whether the decolorization is the result of the absorption of the dye on the TiO$_2$ catalyst or chemical reactions due to UV light and the combination of UV light and ultrasounds.

Fenton reagent was tested as a catalyst for the decolorization of azo dyes in two sets of experiments. The first set involved the mixing of Fenton reagent with the azo dyes, while in the second test the pH was set at the value of 3 and dissolving the azo dye directly into the buffer so...
wavelength range with a peak at 380 nm. The glass vessel, permeable to UV light, was put into the photoreactor and kept with continuous cooling water circulation at 25 °C. The quantity of the TiO$_2$ catalyst used in every experiment in which UVA light was applied was 40 mg/L and all the prepared dye solutions were water-based. Overall, the experiment sets are depicted in Table 2 with the respective parameters whereas concentrations of azo dyes were kept at 67 mg/L for Dermacid Black and Dermacid Brown and at 25 mg/L for Dermacid Red.

FT-IR experiments were conducted in a properly calibrated JASCO 4200 model with a wavelength range of 4000–400 cm$^{-1}$ and a resolution of 4 cm$^{-1}$. The preparation of the samples involved a first step of mixing 100 µl of liquid samples with KBr powder and left to dry at 110 °C for 12 h. The second step involved the formation of 13 mm uniaxially pressed "colored" KBr pellets at 10 tn in a GRASEBY Specac uniaxial press.

For the Total Organic Carbon (TOC) values, liquid samples were taken and measured in a properly calibrated SHIMADZU TNM-L (ROHS) instrument.

### 3. Results & discussion

The azo dye properties of absorbing both in UV, due to benzene rings, and visible spectrum, due to the chromophore group (-N = N-), makes UV–Vis spectroscopy a simple and rapid analysis technique. A typical compositional structure of each azo dye is depicted in Fig. 1.

Generally, considering the decolorization of the solution and the -N = N- binding energy in the above structures, the combination of the techniques described in Table 2 must act disruptively to the dissociation of these bonds. From the molecular types above (Fig. 1), the larger molecule (Dermacid Black) contains more -N = N- bonds compared to the other two azo dyes. Fig. 2–Fig. 4 depict the results from all the

![Fig. 1. Typical structures of the azo dyes used.](image)

![Fig. 2. Decolorization of Dermacid Red with different methods.](image)

![Fig. 3. Decolorization of Dermacid Black with different methods.](image)

![Fig. 4. Decolorization of Dermacid Brown with different methods.](image)
methods applied with TiO$_2$ and Fenton reagent with pH = 3. In Table 3, the maximum degradation [%] value is recorded for each azo dye for all the applied methods. In Fig. 5 to Fig. 8 the results from all Fenton including processes are presented with pH adjusted to the value of 6.8 for comparison reasons.

According to the results presented in Fig. 2 to Fig. 4, the use of TiO$_2$, either under UV or under both UV and sonochemical treatment, resulted in degradations of max. 24% for Dermacid Black, 25% for Dermacid Brown and up to 40% in the case of Dermacid Red. In Fig. 3 and Fig. 4 it is obvious that the ultrasound frequency plays an important role as with TiO$_2$ the low-frequency US reduces, whereas the high-frequency US increases the decolorization percentage of Dermacid Black and Dermacid Brown. For Dermacid Red on the other hand the use of ultrasounds along with TiO$_2$ is beneficial independent of the frequency. In comparison with Fenton reagent, TiO$_2$ seemed not to favor the decolorization of the specific azo dye even after 180 min in the cases of Brown and Black azo dyes.

In the case of Fenton reagent (Fig. 2 to Fig. 4), we observe that adjusting the pH to 3 is increasing the degradation (degree of decolorization) of all azo dyes. At pH = 3 there is an increase of 15% in Dermacid Red (Fig. 2) and a significant rise of 25% in Dermacid Black.
(Fig. 3) as compared to the one with unadjusted pH (Fig. 5 to Fig. 8). In the case of Dermacid Brown, the contribution of Fenton reagent to its decolorization found insignificant though increasing at pH = 3. The maximum degradation percentage for each method applied is depicted in Table 3 for all three azo dyes.

Continuing with the use of Photo-Fenton (Fig. 2 to Fig. 4), all dyes were decolorized more easily, reaching in the case of Dermacid red a remarkable 77% decolorization with Ph-Fenton + US(860) after 120 min. In comparison with pure Fenton reagent, Photo-Fenton (at pH = 3) is more efficient as the maximum decolorization seems to be reached after only 60 min, which is half the time of Photo-Fenton. Decolorization of Dermacid black is increased by 45% in 60 min due to pH adjustment at a value of 3.

The synergistic effect of low (20 kHz) and high (860 kHz) frequency ultrasounds with the above discussed combination of photocatalysis and Fenton reagent are also depicted in Fig. 2 to Fig. 8. On can see, that using the Photo-Fenton technique alongside ultrasounds, both at low (20 kHz) and high (860 kHz) frequency at pH = 6.8 (Fig. 5 to Fig. 8) are lowering the degradation of the azo dyes as compared to the Photo-Fenton combination. On the contrary, using pH = 3 the synergistic combination of ultrasounds, UV and Fenton reagent are reaching the maximum values of the degradation with 90% in the case of Photo-Fenton (pH = 3) + US(20) (Fig. 2 to Fig. 4).

From the presented results, photocatalysis alone is not able to decolorize the dyes Dermacic Red (Fig. 2) and Dermacic Black (Fig. 3), while the combination of UV and ultrasounds acts energetically and increases the decolorization degree. For both dyes, the US frequency in combination with photocatalysis seems not to have any influence. On
On the other hand, using US and Photo-Fenton boosts decolorization. More specifically, for Dermacid Red both frequencies with Photo-Fenton demonstrate a superior decolorization rate and lead to a degradation percentage of 75% after 60 min. After that time, it stopped showing an absorbance peak in the UV–Vis spectrophotometer.

Moreover, in order to verify whether this result is caused by the synergy, an experiment was performed, where UV illumination was applied after the pre-sonication of the solution which led to decolorization of only 32%. By only utilizing ultrasounds, there was no effect on the dye, thus it is not presented on the graph.

Dermacid Black shows similar results in terms of the synergy, compared to the other methods (Fig. 3). The combination US (20 kHz) with Photo-Fenton led to a decolorization percentage of 85%. The deviation between 20 kHz and 860 kHz could be possibly explained by the cavitation size produced by different frequencies, which releases different energy amounts.

We observe that in both dyes (Dermacid Red and Dermacid Black) Photo-Fenton with or without US exhibits a higher decolorization rate in a shorter time as compared to photocatalytic experiments with or without ultrasounds. It turned out that Dermacid Brown is an extremely stable azo dye, as it did not decolorize by applying different degradation methods like US and UV irradiation. It was therefore necessary to use AOP combinations at high intensities in order to obtain satisfactory results (Fig. 4).

The only method combination that was able to decolorize Dermacid Brown is Photo-Fenton at pH = 3 in combination with US (Fig. 4). The most effective US frequency was 860 kHz, which led to a conversion percentage of 74%.

Taking into account the better decolorization performance using two or all three we assume that the increased decolorization is due to the increased production of OH radicals which attach the organic dyes and initiate their decolorization resp. degradation. In Fig. 9 typical reactions are presented on which this assumption is based.

It is generally assumed that the observed decolorization is due to the destruction of the chromophore groups in the azo dyes. FT-IR analysis was conducted at the two methods that maximum degradation/decolorization was observed for the three azo dyes (Fig. 10 to Fig. 15). In general, four major distinguishable peak ranges of wavelength are identified in the FTIR spectra (3600–3400, 1700–1500, 1500–1300, and 1300–1000 cm⁻¹). The first region in 3600–3400 cm⁻¹ is attributed to the vibrations of O–H bands of H₂O molecules [44] that are present in the processes. The region of 1700–1500 cm⁻¹ is attributed to a strong N-O stretching band, while the 1500–1300 cm⁻¹ region is attributed to -N=N- bonds with sharp peaks as reported elsewhere. The last region of 1300–1000 cm⁻¹ depicts the C-O bonds [45,46]. In all FTIR diagrams, the vibrations in the region of 3600–3400 cm⁻¹ is obvious but not meaningful in our case as it can represent not only the OH-groups in the dye molecule but also the increased production of OH radicals from ultrasound-assisted.

From the Ph-Fenton + US(20) (Fig. 10) and Ph-Fenton + US(860) (Fig. 11) processes the decolorization is mainly attributed to the breaking of the two major N=N and N=N bonds (Fig. 12) in the region of 1500–1300 cm⁻¹ as these peaks are diminished. The two following regions (1700–1500 cm⁻¹ and 1300–1100 cm⁻¹) are depicting the breaking of N-O and C-O bonds respectively.

From TOC measurements, Dermacid Red exhibited up to 2.6% removal of TOC in the above two processes using Fenton combined with US and UV. This fact implies that its molecular type is broken in the -N=
N- bond (responsible for decolorization) leaving only one NaO₃S-phenyl group for carbon removal. This bond cleavage, evident from the 1300–1100 cm⁻¹ region in FTIR diagrams leads to the high decolorization percentage while the later is not directly related to the TOC removal. The following plausible decolorization mechanism for Dermacid Red is suggested below:

In the case of Dermacid Black the most promising methods for decolorization proved to be Ph-Fenton and Ph-Fenton + US(860). FTIR spectra (Fig. 13 and Fig. 14), respectively, depict the bond vibrations at the same distinguishable peak ranges of wavelength as mentioned above. Especially, in the region of 1500–1300 cm⁻¹, there is a significant change in the transmittance values of the N = N group.

Results from TOC measurements showed a TOC removal of 21% in the process of Ph-Fenton and 22% TOC removal in the process of Ph-Fenton + US(860). This percentage is attributed to the breaking of two -N = N- groups, in comparison to Dermacid Red. From FTIR spectra, these are verified from the diminishing peaks in the region of 1500–1300 cm⁻¹ for -N = N- and in 1300–1100 cm⁻¹ for the NO₂-phenyl and (NH₂)₂-phenyl groups as seen in the suggested possible decolorization mechanism below:

Dermacid Brown decolorization seemed to be most favored also by Ph-Fenton and Ph-Fenton + US(860) methods. The stretching bands for this azo dye are also observed in the region of 1500–1300 cm⁻¹, for Ph-Fenton process (Fig. 16) and Ph-Fenton + US(860) (Fig. 17). A possible similar mechanism of decolorization that leaves NO₂-phenyl and SO₃Na-phenyl groups for enhanced TOC content which is suggested in Fig. 18 which is indirectly verified by the diminishing peaks at the 1300–1100 cm⁻¹ region in the FTIR spectra (Fig. 17).

As all TOC results do not show a substantial reduction of the carbon content, we assume that despite the increased decolorization percentage, the mineralization process with all three dyes is only initiated and needs much more time or harsher conditions in order to increase the percentage of the degradation process.

4. Conclusions

The effective decolorization of azo dyes is possible by the combination of advanced oxidation processes like photocatalysis and Fenton reaction in the presence of ultrasound. The use of specific ultrasound frequencies can effectively break down the azo dyes into smaller molecules, which can be handled easier. Also, ultrasound waves increase the mass transport between the solution phase and the catalyst surface. Experiments have shown substantial decolorization already during the first two hours. After that threshold, the reaction rate is decreased. This time is reduced down to one hour using Photofenton method combination. The synergetic effect between UV and ultrasounds is evident throughout the experiments. On the other hand, it has been found, that not every method combination is able to increase the decolorization degree of the azo dyes. The Photo-Fenton reagent is more effective with US 20 kHz and US 860 kHz for the azo dyes originated from the weaving industry at pH = 3 as compared to pH = 6.8.

We assume that the increased decolorization is due to the synergetic effect of the increased production of aggressive OH radicals, as they are produced in each of the used methods and thus their concentration is higher when using all methods combined.

Since industrial dyes are mixtures of various azo dyes, each one behaves differently, thus they require special treatment and a universal method cannot be defined.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2020.105367.

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