

# Decolorization of indigo carmine dye by spark discharge in water

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**Abstract**—When a spark discharge takes place in water, apart from reactive radical formation, additional effects take place, such as strong ultraviolet radiation (independent of the solution conductivity) and shock wave formation. The amount of published literature on spark discharge in water is very limited, therefore the goal of the present study was to determine the decolorization efficiency of indigo carmine dye in the spark discharge as a function of discharge energy. Also, a basic study on the effect of UV light on indigo carmine dye removal and hydrogen peroxide decomposition was undertaken. An effect of additives, such as hydrogen peroxide and sodium persulfate, was also studied. The results have shown that an increase in the discharge capacitance leads to a decrease in the dye decolorization time. Hydrogen peroxide, produced by a discharge, is decomposed by the UV light and is mainly responsible for the decolorization. Adding very low concentrations of commercial hydrogen peroxide to the dye solution makes spark discharge in water a “pseudo” H<sub>2</sub>O<sub>2</sub>-UV technology. At 4700pF and with a dye concentration of 20mg/L ( $4.29 \times 10^{-5}$  M), complete decolorization can be achieved in only 2 minutes, which makes the spark discharge in water a competitive technology to the conventional H<sub>2</sub>O<sub>2</sub>-UV process.

**Keywords**— spark discharge, hydrogen peroxide, sodium persulfate, UV light

## I. INTRODUCTION

Liquid-phase, high-voltage, electrical discharge reactors, a type of advanced oxidation technology, have been developed for a variety of environmental applications, such as wastewater and drinking water treatment [1]. Advanced oxidation technologies (AOT), including, for example, ozonization [2], UV photolysis [3], photo-catalysis [4] and electron beams [5], are considered to be promising methods for pollutant destruction because of the high reactivity and non-selectivity of the hydroxyl radical, the primary oxidant formed in these systems. Pulsed electrical discharges produce corona or corona-like streamers in the liquid phase that initiate a variety of physical and chemical processes, such as ultraviolet radiation, shock waves and formation of chemically active species [6,7]. Emission spectroscopy measurements have shown that the primary species created by the water discharge are hydroxyl, hydroperoxyl, oxygen and hydrogen radicals [8]. Direct chemical measurements revealed the presence of hydrogen peroxide and molecular hydrogen and oxygen [9,10].

When a spark discharge takes place in water, apart from reactive radical formation, additional effects take place such as strong ultraviolet radiation (independent of the solution conductivity) and shock wave formation. It has been shown that, in pulsed electrical discharge in water, the UV light can have a strong effect on the bulk liquid but only if the conductivity of the solution is high enough [11].

Robinson et al. [12] studied the effect of the plasma column length on UV radiation. They found that UV radiation is the main form of energy dissipated from the

electric discharge in water. Under certain conditions, 36% of the total energy transferred to plasma can be converted to radiation.

Sun et al. [8] investigated the characteristics of the spark discharge in water using a needle-plate electrode configuration. They also identified OH, H and O radicals as the major short-lived species and hydrogen peroxide as a molecular species. Furthermore, it was found that, for both streamer and spark discharge, the hydroxyl radicals are mainly formed inside the channel, whereas additional hydroxyl radicals exist around the channel in the spark discharge mode due to the hydrogen peroxide decomposition by the UV light.

The literature concerning the contaminants degradation in a spark discharge is very limited and it is mostly focused on the phenol type molecules. Sun et al. [13] studied the degradation of phenol in pulsed streamer discharge mode and in spark mode. They found that the phenol removal efficiency was higher for the spark discharge than for the streamer corona discharge and was greatly enhanced when hydrogen peroxide was added into the solution. Sugiarto and Sato [14] conducted a similar study, again using phenol as a model compound. They compared the phenol degradation efficiency between spark and streamer discharge and found that the best results were obtained when these two discharge models were used in combination (streamer with sparking). Again, the addition of a small amount of hydrogen peroxide led to enhanced phenol removal.

Indigo carmine, together with the indigo, is the most representative indigoid dye, and it is widely used in the textile industry for cotton cloths and other denim products. The decolorization of the indigo carmine dye was investigated by various advanced oxidation technologies, such as Fenton reagent [15], electrochemical oxidation [16] and photo-assisted oxidation [17].

The present study seeks to determine the decolorization efficiency of the indigo carmine dye in the

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spark discharge as a function of discharge energy. Also, a basic study on the effect of the UV light on the indigo carmine dye removal and hydrogen peroxide decomposition is undertaken. Oxidation of indigo carmine dye with the sodium persulfate is also studied.

## II. EXPERIMENTAL

The chemicals used in this study include indigo carmine, hydrogen peroxide and sodium persulfate (all obtained from Fisher Scientific Inc., Japan). All chemicals were used as received from the manufacturer. Tungsten wire (Nilaco, Japan) and stainless steel plate (Nilaco, Japan) were used as received from the manufacturers.

The concentration of hydrogen peroxide was determined colorimetrically using the reaction of hydrogen peroxide with titanium ions [18]. Absorbance of the yellow peroxotitanium (IV) complex was measured at  $\lambda=410\text{nm}$  (spectrophotometer Shimadzu UV- 1200). The decolorization of the indigo carmine dye was followed by measuring absorbance at 610nm.

When sodium persulfate was used as electrolyte, three different concentrations were used; 0.42mM (conductivity =  $40\mu\text{S/cm}$ ), 2.10mM (conductivity =  $210\mu\text{S/cm}$ ) and 4.2mM (conductivity =  $440\mu\text{S/cm}$ ).

A power supply for generating high-voltage, pulsed electrical discharges of positive polarity is used. The pulse-forming network consists of variable-voltage kV DC source (company), storage capacitor (2350pF, 4700pF or 9400pF) and a rotating spark gap with pulse repetition frequency of 250 Hz. Current passing through the network is first limited through a current limiting resistor ( $\text{k}\Omega$ ). A diode that positively rectifies the AC current is followed by a capacitor that stores the charge. Next in the circuit is a spark gap and it is connected through electrodes to the capacitor on one side and the reactor on the other side. When the spark gap aligns, the charge stored in the capacitors is discharged across the gap and sent into the reactor. All experiments were conducted with fixed applied voltages of 12 kV. Voltage waveforms were recorded with a Tektronix TDS 1012B fast digital storage oscilloscope.

A 500mL plexyglass reactor with point-to-plane geometry was used. The treated solution volume was 100mL. It was assumed that such small reaction volume did not require additional mixing apart from convection so no external mixing was used. Experiments with and without the dye were performed from deionized (DI) water (conductivity  $<2\mu\text{S/cm}$ ) without addition of any salt. The point high-voltage needle electrode was made from tungsten wire (diameter=0.6mm) and the planar ground electrode was made from stainless steel. Both electrodes were immersed in a water solution and separated by a distance of several mm (see section 3.1 later for details). The point electrode was electrically connected to the output from the spark gap and the stainless steel ground electrode was attached to a ground.

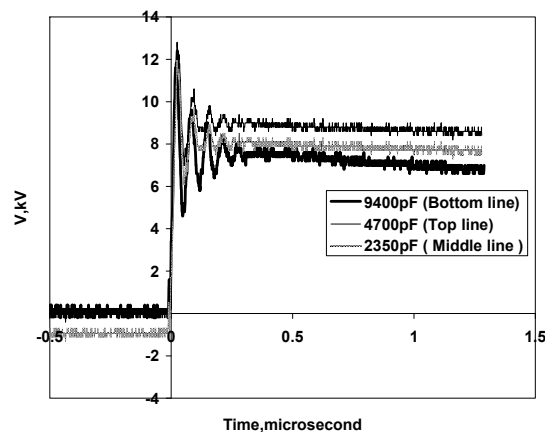


Fig. 1. Voltage waveforms at three different discharge capacitances

All the experiments were repeated at least twice with a reproducibility of less than 10%.

## III. RESULTS AND DISCUSSION

### A. Visual Appearance of the Discharge

The experiments presented in this study were investigated at three different discharge capacitances; 2350pF, 4700pF and 9400pF. The experiments were performed in deionized water with a solution conductivity of less than  $1\mu\text{S/cm}$ . The discharge initiation was different and specific for each capacitance, although all three cases were conducted with the same applied voltage of 12kV.

At 2350pF, if the distance between electrodes were more than 2mm, the spark discharge would not take place. There was no transition from streamer to spark mode but rather a few discontinuous spark channels were instantaneously formed every minute. These channels were not very bright and looked relatively weak in intensity. At 4700pF the distance needed to be set to around 3-4mm for the spark discharge to start. In this case a spark channel in the form of a bright luminous circle emerging from the anode tip was observed. If the same distance was kept between anode and cathode and the capacitance was increased to 9400pF, the spark (luminous circle) became so bright and intense that it drilled a hole through the ground electrode. Therefore, when the discharge capacitance was fixed at 9400pF, the minimum distance between the electrodes had to be around 6mm. At that distance, distinct spark channels were formed and they appeared more frequently than at 4700pF. Although no streamer discharge was formed in any of these three cases, for the 9400pF capacitance it was observed that the tip of the tungsten needle turned red every time before spark occurred. Figure 1 shows the typical voltage waveforms for all three discharge capacitances.

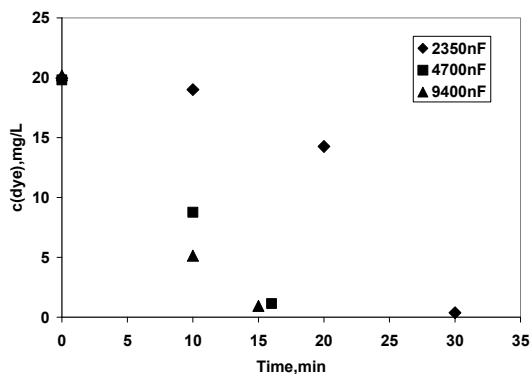


Fig. 2. Indigo carmine decolorization at 12kV and three different capacitances

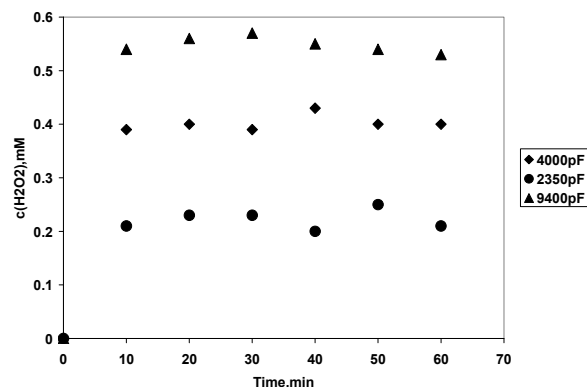


Fig. 3. Hydrogen peroxide formation at three different capacitances

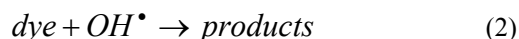
### B. Experimental Results

Figure 2 shows the decolorization efficiency of the 20mg/L indigo carmine dye at 12 kV and three different capacitances. It is clear from Figure 2 that at low discharge capacitance (2350pF) approximately 30 minutes is needed for a complete decolorization of the dye. An increase in capacitance leads to a decrease in the decolorization time. The complete decolorization takes 17 minutes at 4700pF and 15 minutes at 9400pF. Studies have shown that with higher energy input there are more active radicals formed which then react with the pollutant in the bulk and cause faster degradation (decolorization) [8].

At the energy input corresponding to the discharge capacitance of 4700pF, a certain concentration of hydroxyl radicals decolorize the dye. At 9400pF, the total amount of the hydroxyl radical produced should be much higher compared to 4700pF and the dye should be decolorized much faster. Figure 2 shows that approximately same time is needed for the dye to be decolorized at 4700pF and 9400pF although the extent of decolorization is higher after 10 minutes at 9400pF. The concentration of the hydrogen peroxide and hydroxyl radicals produced at 9400pF is higher than the one produced at 4700pF therefore in the beginning (first 10 minutes), the dye decolorization proceeds faster at 9400pF. At that point in time the dye concentration was reduced from 20mg/L to 5mg/L (at 9400pF) and to 9mg/L (4700pF). At such low concentration of dye it is possible that in order to reach a complete decolorization not to high concentration of OH radicals is needed. In that case, both values of energy input (4700 and 9400pF) can provide that amount of OH radicals in the similar time frame so complete decolorization is reached in additional 5minutes for 9400pF and additional 7 minutes for 4700pF.

It is clear from Figure 2 that at 2350pF decolorization proceeds very slowly in the first 10 minutes. As it is going to be discussed later, this is probably caused by a low rate of hydrogen peroxide (hydroxyl radicals) production and destruction at this value of discharge energy.

As it was mentioned in the introduction section, spark discharge in water generates UV light, which can be involved directly in the degradation of the molecules or indirectly via hydroxyl radicals generation. The direct way involves the reaction between UV light and a light absorbing molecule (direct photolysis), whereas the indirect way of utilizing UV light is achieved by initially adding hydrogen peroxide into the solution where following reactions take place:



therefore providing an extra source of hydroxyl radicals.

Before discussing the effect of hydrogen peroxide addition on the dye removal, the results in Figure 3 show the hydrogen peroxide formation without dye in the solution in the spark discharge in water at three different capacitances at 12kV. From this figure it can be observed that, for all three capacitances, after the first ten minutes the rate of hydrogen peroxide destruction becomes greater than the rate of production, leading to the formation of the plateau. This shape of the curves is not in agreement with Zhang et al. [19], who measured a more or less linear rate of hydrogen peroxide production in the spark discharge in water at 19kV and discharge capacitance 4700pF. It is possible that no mixing of the solution contributed to the shape of curves presented in Figure 3. Lack of forced convection resulted in the formation and immediate destruction of hydrogen peroxide right in the spark area, therefore no increase in hydrogen peroxide concentration with time was measured in the bulk.

Table 1 shows the calculated rates of hydrogen peroxide formation (calculated for the first ten minutes) for all three capacitances. It can be seen that, with respect to energy per pulse, the calculated results are in agreement with the results obtained by Zhang et al. [19 エラー! ブックマークが定義されていません。].

It should be mentioned that the curve shape for the hydrogen peroxide formation presented in Figure 3 corresponds to the shape of the curve for the hydrogen

peroxide production when  $H_2O_2$  is decomposed by UV hydrogen peroxide are reduced after 30 minutes of

TABLE 1  
Rate of hydrogen peroxide formation in the spark discharge ( $V=12kV$ )

Capacitance,pF	Energy per pulse,J ( $E_p=(1/2)*C*V^2$ )	Rate of formation, Ms-1, this work	Rate of formation,Ms-1 Zhang et al.[19]
2350	0.264	$3.5*10^{-7}$	
4700	0.529	$6.5*10^{-7}$	
4700	0.852	-	$8.5*10^{-7}$
9400	1.058	$9*10^{-7}$	

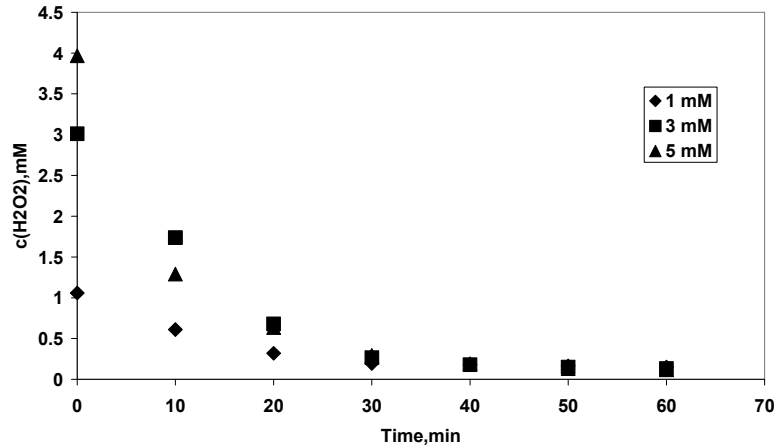
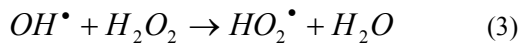


Fig. 4. Decomposition of different initial concentrations of hydrogen peroxide in the spark discharge in water ( $c=4700pF$ )

light. Lukes [11] measured the rate of formation of hydrogen peroxide in the pulsed streamer electrical discharge in water at high solution conductivities ( $500\mu S$ ) where the effect of UV light is of great importance. Actually, he found that with an increase in solution conductivity there is an exponential increase in the radiant power of the UV light. He also found that when hydrogen peroxide is decomposed by UV light, after 15 minutes the rate of decomposition becomes greater than the rate of production and the same plateau as in Figure 3 is formed.

Hydrogen peroxide can be decomposed by the hydroxyl radical attack according to the following reaction:



If there is a source of UV light, an additional reaction (reaction (1)) takes place, which increases the rate of reaction (3) due to the extra hydroxyl radical concentration formed [14].

In order to verify the degradation mechanism of hydrogen peroxide in the solution, experiments with initially present hydrogen peroxide in the solution were performed. For that purpose, a capacitance of  $4700pF$  was chosen. Figure 4 shows the degradation of three different initial concentrations of hydrogen peroxide placed in the reactor at the beginning of the experiment. It can be seen that all three initial concentrations of

experiment to approximately the same value of  $0.17mM$ . If that value is compared to the maximum concentration value of the hydrogen peroxide shown in Figure 3 for the capacitance of  $4700pF$ , it can be seen that they are almost the same. The decomposition of hydrogen peroxide follows a first order kinetics in the first 20 minutes for all three concentrations.

When methanol is present in the solution, an additional reaction takes place:



which disables the occurrence of reaction (3).

Figure 5 shows the degradation of  $3mM H_2O_2$  when  $1mL$  ( $25mM$ ) of methanol is placed in the reactor at the beginning of the experiment. Methanol is a well known radical scavenger and it is assumed that at this concentration, all the hydroxyl radicals react with the methanol rather than with hydrogen peroxide. This assumption can be justified by the following simple calculation. The rates of reaction (3) can be written as:

$$r_{OH-H_2O_2} = k_{OH-H_2O_2} \cdot c(OH) \cdot c(H_2O_2) \quad (5)$$

and that of reaction (4) as:

$$r_{OH-CH_3OH} = k_{OH-CH_3OH} \cdot c(OH) \cdot c(CH_3OH) \quad (6)$$

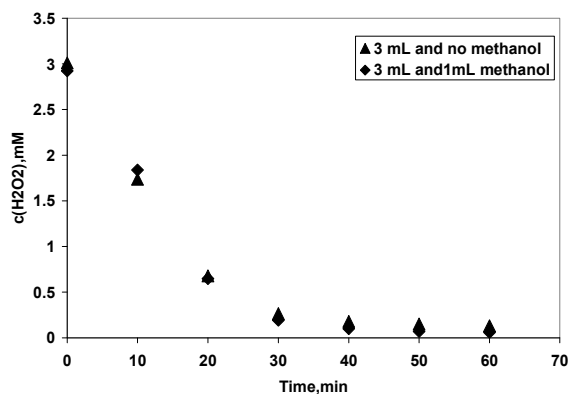


Fig. 5. Degradation of hydrogen peroxide with and without presence of methanol ( $c=4700\text{pF}$ )

Where  $k_{OH-H_2O_2}$  ( $=2.7 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$ ) and  $k_{OH-CH_3OH}$  ( $=9.7 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) represent the reaction rate constants between OH radical and hydrogen peroxide and OH radical and methanol, respectively. If the concentration of hydroxyl radicals ( $c(OH)$ ) is taken to be constant and  $c(CH_3OH)=25\text{mM}$  and  $c(H_2O_2)=3\text{mM}$ , then the reaction rates of reactions (5) and (6) can be rewritten as:

$$r_{OH-H_2O_2} = 2.7 \cdot 10^7 \cdot c(OH) \cdot 3 \cdot 10^{-3} = 8.1 \cdot 10^4 \cdot c(OH) \quad \text{Ms}^{-1} \quad (7)$$

$$r_{OH-CH_3OH} = 9.7 \cdot 10^8 \cdot c(OH) \cdot 25 \cdot 10^{-3} = 2.4 \cdot 10^7 \cdot c(OH) \quad \text{Ms}^{-1} \quad (8)$$

The comparison of the values of the rate expression (7) and (8) show that the reaction of hydroxyl radicals with the methanol is much faster than the reaction of hydroxyl radicals with the hydrogen peroxide. So, if the concentration of methanol is high enough in the solution, it is ensured that the hydroxyl radicals will react with methanol rather than with hydrogen peroxide.

It is clear from Figure 5 that there is no difference in the  $H_2O_2$  degradation, with or without methanol, therefore, this result indicates that this concentration of hydrogen peroxide is decomposed by UV light and not by OH radical attack. The experiments with other concentrations (up to 7mM) of hydrogen peroxide also showed no difference in the degradation when methanol is present or absent in the reactor (data not shown).

From these results the following can be concluded. Spark discharge in water generates hydrogen peroxide. When a certain high concentration is reached, the hydrogen peroxide decomposes by the direct reaction with UV light. Any initial concentration of hydrogen peroxide placed in the reactor is decomposed to the value that is determined by the rate of production.

(a) *An effect of hydrogen peroxide on the indigo carmine decolorization experimental results*

It has already been shown that in a spark discharge in water, placing of small concentrations of hydrogen peroxide in the reactor at the beginning of the experiment leads to greater phenol removal [14,19]. Figure 6 shows the effect of the different initial concentrations of hydrogen peroxide on the decolorization efficiency of

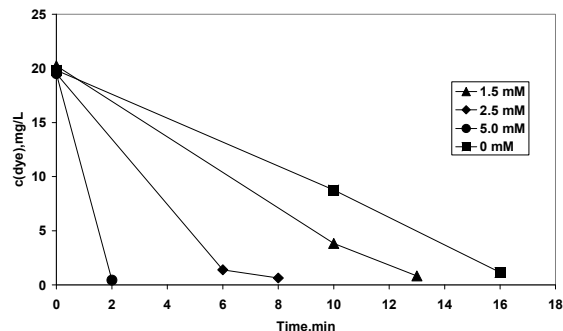


Fig. 6. An effect of different initial concentrations of hydrogen peroxide on the 20mg/L indigo carmine decolorization ( $4700\text{pF}$ )

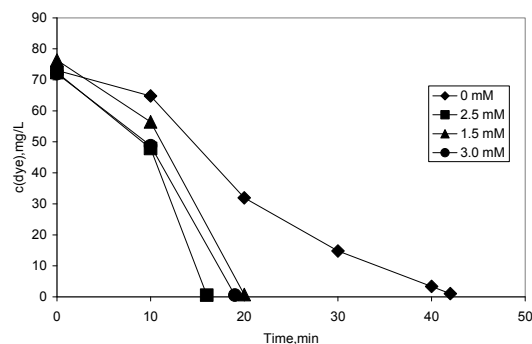


Fig. 7. An effect of different initial concentrations of hydrogen peroxide on the 75 mg/L indigo carmine decolorization ( $4700\text{pF}$ ).

20mg/L indigo carmine. It is clear that when the optimum concentration of hydrogen peroxide is used, the decolorization time of 20mg/L of dye can be reduced up to 2 minutes. Figure 7 shows the effect of the added  $H_2O_2$  on the decolorization efficiency of 75 mg/L. Again, it can be seen that with the optimum hydrogen peroxide concentration the decolorization time can be reduced to approximately 8 minutes.

Rodriguez et al. [20] studied the decolorization of indigo carmine dye by the  $H_2O_2$ -UV advanced oxidation technology. Their experimental results show that the decolorization of  $9 \cdot 10^{-5} \text{ M}$  indigo carmine dye is achieved in 10 minutes by applying a polychromatic UV radiation dose of 29.21 W/L and in the presence of 1mM hydrogen peroxide. They proposed  $H_2O_2$ -UV advanced oxidation as an option to conventional treatment of indigo dye solution-chemical and photochemical oxidation. Table 2 compares the results from [17] with the results obtained in this study. It is clear that with the spark discharge in water the concentration of 75mg/L ( $1.61 \cdot 10^{-4} \text{ M}$ ) of indigo carmine dye, which is almost two times more the concentration used in the  $H_2O_2$ -UV study, can be decolorized in only 17 minutes, which makes spark discharge in water a competitive technology to the  $H_2O_2$ -UV process.

In order to study the direct effect of UV light on the decolorization of the indigo carmine dye, sets of different experiments were performed. Figure 8 shows the decolorization efficiency of the indigo carmine dye at three different experimental conditions. In the experiment with the foil, the aluminum foil was wrapped

TABLE 2  
Comparison of the decolorization time of indigo dye between spark discharge in water and H<sub>2</sub>O<sub>2</sub>-UV process

Technology	Dye concentration [M]	c(H <sub>2</sub> O <sub>2</sub> ) added [mM]	Decolorization time [min]
Spark discharge in water (c=4700pF), This work	4.29*10 <sup>-4</sup> (20mg/L)	0	16
	4.29*10 <sup>-4</sup> (20mg/L)	5	2
	1.61*10 <sup>-4</sup> (75mg/L)	0	43
	1.61*10 <sup>-4</sup> (75mg/L)	2.5	17
H <sub>2</sub> O <sub>2</sub> -UV [20]	9*10 <sup>-5</sup>	0	>40
	9*10 <sup>-5</sup>	1	10

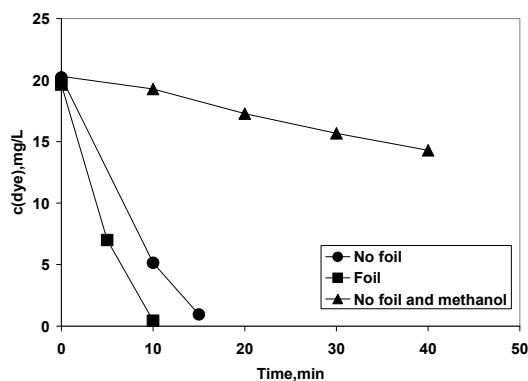


Fig. 8. Decolorization of indigo carmine with and without methanol (4700pF)

around the reactor thereby preventing any loss of UV radiation formed by the discharge. In the experiment with the methanol (also known as the hydroxyl radical scavenger), 1mL of methanol alcohol was added to the dye solution in order to estimate the degree of decolorization caused by the direct UV light photolysis. In all three experiments, sparking at 12 kV (4700 pF) was used as a discharge mode. It is clear from the same figure that without hydroxyl radicals attack (triangles), a very low percentage of dye is degraded therefore excluding direct UV photolysis as the decolorization pathway.

On the other hand, if the reactor is wrapped with aluminum foil (squares), the dye decolorization proceeds much faster, indicating that UV light is involved in the degradation process. Most probably, the UV light reacts with the hydrogen peroxide and forms extra hydroxyl radicals which then, in turn, decolorize the dye. The direct UV light photolysis follows a zero order kinetics with the rate constant  $k=4.04 \cdot 10^{-9} \text{M}^{-1} \text{s}^{-1}$ . The rate constant for the total decolorization (UV light and hydroxyl radical) of the indigo carmine dye is  $k=4.15 \cdot 10^{-8} \text{M}^{-1} \text{s}^{-1}$ , which indicates that 10% of this rate constant goes for the direct UV light photolysis.

Figure 9 shows the effect of the different initial concentrations of hydrogen peroxide on the decolorization efficiency of 20mg/L indigo carmine at 9400pF. Again, it is clear that when an optimum concentration of hydrogen peroxide is used, the decolorization time of 20mg/L of dye can be reduced up to 1 minute. If the concentration of hydrogen peroxide is too high then the hydroxyl radicals that are formed by the

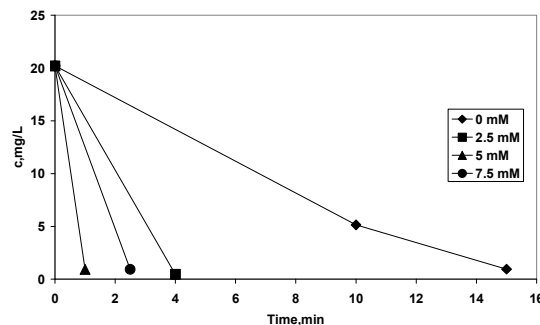


Fig. 9. An effect of different initial concentrations of hydrogen peroxide on the 20mg/L indigo carmine decolorization (9700pF)

hydrogen peroxide decomposition react with the hydrogen peroxide rather than with the dye. This can be seen in Figure 9 when 7.5mM hydrogen peroxide is used. In that case the decolorization is slightly inhibited compared to the experiments where only 5mM hydrogen peroxide was placed.

Figure 10 compares the rate constant for the dye decolorization and rate constant for the hydrogen peroxide formation as a function of the pulse energy. It is clear that with an increase in the pulse energy a decolorization rate constant is almost reaching a plateau indicating that any further increase in the pulse energy will not have a significant effect on the dye decolorization efficiency. The hydrogen peroxide data follows a similar trend.

It was already shown that UV light has a significant effect on the indigo carmine decolorization and that the dye removal proceeds via hydroxyl radical attack. These hydroxyl radicals could be formed directly from water and react with the dye or they could be formed via hydrogen peroxide decomposition and then react with the dye. Measurements dealing with the quantification of the hydroxyl radicals in the pulsed electrical discharge in water [21] have shown that only 5% of the total amount of OH radicals diffuses into bulk to react with the molecules. Sun et al. [8] found that around the spark channel in water there is a layer of hydroxyl radicals which does not exist in the streamer discharge. They concluded that these additional hydroxyl radicals are formed by the hydrogen peroxide decomposition.

Based on this observation, one can assume that hydrogen peroxide decomposition is mainly responsible for the dye removal. The rate constant for the hydrogen peroxide formation is increasing with the pulse energy

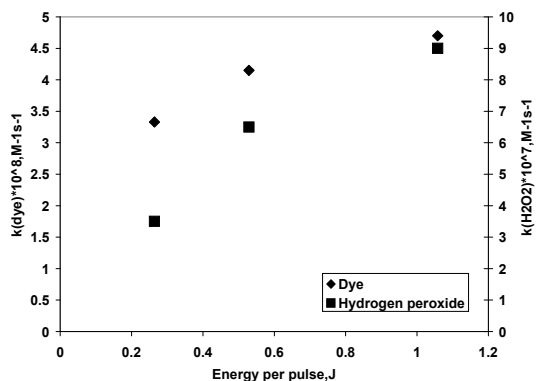


Fig. 10. Comparison of the rate constant of dye decolorization (20mg.L) and hydrogen peroxide formation as a function of the pulse energy

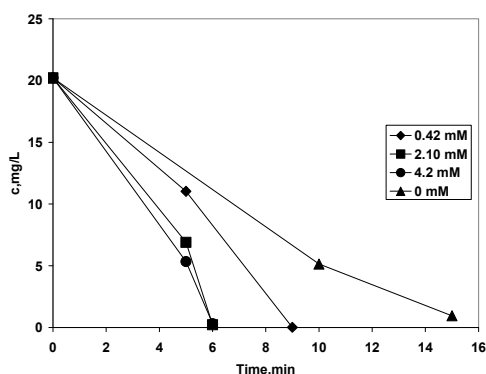


Fig. 11. An effect of sodium persulfate addition on the indigo carmine decolorization (4700 pF)

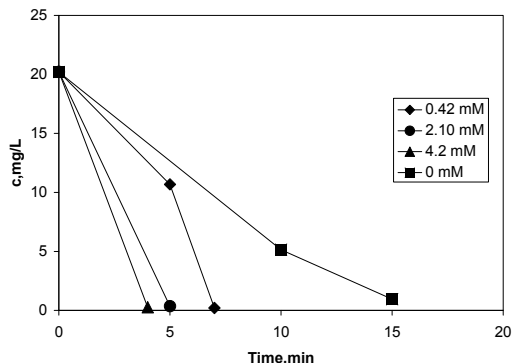
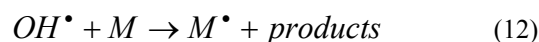
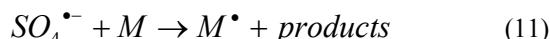
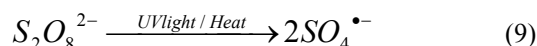


Fig. 12. An effect of sodium persulfate addition on the indigo carmine decolorization (9400 pF)

but there is not a big difference between rate of formation at 0.529J and 1.058 J, therefore there is no big difference between dye removal at these two values. On the other hand, the rate constant for the dye decomposition at 0.264J is determined as a slope (see Figure 2) after 10 minutes because at that initial time there was no decolorization. This is most probably due to the fact that in the first ten minutes there is not enough hydrogen peroxide formed for the dye decolorization to take place and also at such small pulse energy it was experimentally observed that the intensity of the UV light was very weak. Also, the low intensity of the UV light could lead to the lower rate of the hydrogen peroxide decomposition.

(b) An effect of sodium persulfate on the indigo carmine decolorization

It is well known that the decomposition of sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) leads to the formation of highly oxidative sulfate radical anions. The standard reduction potential of the sulfate radical is around 2.01 V while the hydroxyl radical potential is 2.80 V [22]. The decomposition of sodium persulfate can be initiated by either elevated temperatures ( $>40^\circ\text{C}$ ) or UV light according to the following simplified scheme:



Sulfate radical anion can attack the molecule (in this case indigo carmine dye) directly (reaction 11), indirectly via OH radical formation (reaction 10) or by both mechanisms (reactions 11 and 6). Figures 11 and 12 show an effect of sodium persulfate addition on the indigo carmine decolorization efficiency at 4700pF and 9400pF, respectively. It can be seen that at both capacitances an addition of persulfate ions led to the decrease in the decolorization time of the dye the same as in the case of added hydrogen peroxide. Adding more than 0.05g per 100mL of solution volume didn't have any greater effect on the decolorization time. This is probably due to the limited rate conversion of the persulfate ions to the sulfate radical anions.

Compared to the hydrogen peroxide oxidation, at 4700pF faster decolorization is achieved by the use of hydrogen peroxide and at 9400pF, a slightly lower concentration of persulfate ions is needed to achieve a similar decolorization time.

In these experiments it is assumed that the sodium persulfate is mainly decomposed by the UV light emitted from the spark channel although it could be partially decomposed by the heat in the thin layer surrounding the channel [23]. Assuming that the temperature around the spark channel is independent of the solution conductivity and knowing that the radiant power of the plasma channel is exponentially increasing with an increase in the solution conductivity, one can conclude that with an increase in persulfate ion concentration there is an increase in solution conductivity leading to the higher light intensity and faster persulfate conversion to sulfate radical anion.

Figure 13 shows the corresponding waveforms for the two different persulfate ion concentrations in the solution. The waveforms are shown only for the 9400 pF (at 4700pF similar waveform pattern is observed) and

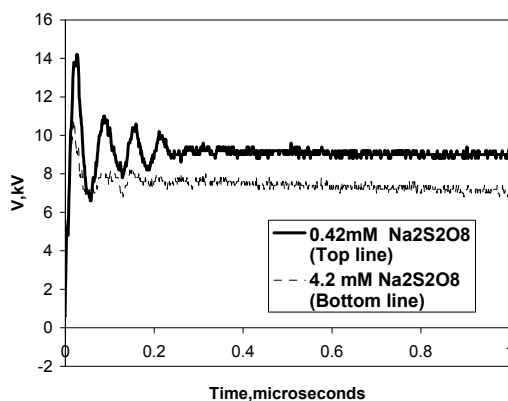


Fig. 13. Pulse waveforms for the two different persulfate ion concentrations in the solution (9400pF)

expanded to show the early pulse rise time. It was observed experimentally that with an increase in the salt content there was a difficulty in achieving a spark. Also from Figure 13 it is visible that the pulse waveform for 4.2mM persulfate solution has a lower peak amplitude than, for example, 0.42mM persulfate solution. It is assumed that due to increased conductivity current flows prior to the sparking, resulting in lower peak voltages.

#### IV. CONCLUSION

The decolorization of the indigo carmine dye at three different discharge capacitances in a spark discharge was investigated. The best decolorization time of 15 minutes was achieved at the highest (9400pF) capacitance for the 20mg/L of the initial dye concentration although not very different decolorization time is achieved at the lower capacitance of 4700pF. At the lowest capacitance (2350pF) 30 minutes is required for the same dye concentration to be decolorized. Spark discharge in water produces hydrogen peroxide but the rate of its decomposition is higher than the rate of formation. It has been shown that the hydrogen peroxide is decomposed by the UV light and not by a hydroxyl radical attack. Adding commercial hydrogen peroxide at the beginning of the experiment to the indigo carmine solution leads to a decrease in the decolorization time. At 4700pF and the dye concentration of 20mg/L ( $4.29 \times 10^{-5}$  M), the complete decolorization can be achieved in only 2 minutes. Comparing this result ( $4.29 \times 10^{-5}$  M dye decolorized in 2 minutes) to a conventional  $H_2O_2$ -UV study ( $9 \times 10^{-5}$  M dye decolorized in 10 minutes) it can be concluded that the spark discharge in water is a competitive technology to the  $H_2O_2$ -UV process.

By comparing the rate constants for the dye decolorization and rate constant for the hydrogen peroxide formation as a function of the pulse energy, it was observed that with an increase in the pulse energy a decolorization rate constant is almost reaching a plateau indicating that any further increase in the pulse energy will not have a significant effect on the dye

decolorization efficiency. The hydrogen peroxide rate formation constant followed a similar trend again indicating its effect on the dye removal. Finally, an effect of the persulfate ions on the indigo carmine dye was also studied.

It was observed that an addition of persulfate ions leads to the decrease in the decolorization time of the dye, the same as in the case of added hydrogen peroxide. Compared to the hydrogen peroxide oxidation, at 4700pF faster decolorization is achieved by the use of hydrogen peroxide and at 9400pF, a slightly lower concentration of persulfate ions than hydrogen peroxide is needed to achieve a similar decolorization time.

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