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# ULTRASOUND INDUCED FENTON/PERSULPHATE/$H_2O_2$/ZNO PROMOTED ADVANCED OXIDATION PROCESS FOR THE MINERALIZATION OF INDIGO CARMINE POLLUTANT IN WATER

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**ABSTRACT** Indigo carmine (IC), widely used in textile industry, food colorings, medical diagnostics etc. is a major dye pollutant of water. Ultrasonic (US) degradation of IC in water under different conditions is investigated. The effect of US frequency (200, 350 , 620 and 1000 kHz) and power (20, 40, 60 and 80W) on the degradation profile is evaluated. Optimum degradation is obtained at 350 kHz and 80W in the acidic medium. Combination with $Fe^{2+}$, $H_2O_2$, peroxydisulphate and ZnO enhances the sonodegradation efficiency significantly. The influence of salts/ anions likely to be present in water on the sonolytic degradation varies from inhibition to 'no effect'. Major intermediates formed during the degradation of the dye are identified using LC/MS technique. Eventually the degradation leads to complete mineralization as confirmed by the absence of chemical oxygen demand (COD). Optimum parameters for the mineralization are identified experimentally and appropriate reaction mechanisms are proposed.

**KEYWORDS :** Sonolysis; Indigo Carmine, Mineralization; Water purification

## 1.INTRODUCTION

Development of efficient, economical and environment-friendly technologies for water purification is a high priority area today. Of the many types of industries, textile industry is one of the leading polluters of water/water bodies in terms of toxicity, color and organic load. The absolute removal of dyes and related harmful byproducts from the aquatic environment is a great technological challenge even though the removal of color is not that difficult. Some of the common methods for the treatment of dye-bearing wastewater include coagulation/ flocculation, activated carbon adsorption and membrane treatment. However, they fail to degrade the organic chemicals and simply transfer them from one medium to another. Removal of the last traces of toxic pollutant dye by converting them into harmless products is essential to make the water reusable [1]. Advanced Oxidation Processes (AOPs) have high potential in this respect. This methodology is based on the insitu production of highly oxidizing hydroxyl radicals ($^{\cdot}OH$), which can react nonselectively with most of the organic compounds. The commonly used AOPs include photolysis/photocatalysis, UV/$H_2O_2$, Fenton treatment, photo Fenton, sonolysis, sonocatalysis etc. [2-7]. Among these, sonolysis is one of the most versatile techniques which is widely investigated for wastewater treatment due to the major advantages of safety, cleanliness and energy efficiency. Several reports are available on the sonolytic degradation of chlorinated organic compounds, phenolic compounds, organic dyes, pesticides, endocrine disrupting compounds, perfluorinated chemicals, pharmaceuticals and microcystins [7-12].

Three types of reactions involved in sonolysis are pyrolysis, reaction of $^{\cdot}OH$ and $^{\cdot}H$ and supercritical water oxidation [13,14]. Ultrasound can produce $^{\cdot}OH$ and $H^{\cdot}$ by acoustic cavitation (reaction 1). Generally hydrophobic and volatile compounds undergo degradation via pyrolysis in the interface region. Supercritical water oxidation process provides an additional route for the degradation. The radical generation in sonolysis and subsequent reactions are shown in reactions (2) - (5) [13-15].

$$H_2O + ))) \rightarrow {}^{\cdot}H + {}^{\cdot}OH \tag{1}$$

$${}^{\cdot}H + O_2 \rightarrow HO_2^{\cdot} \rightarrow {}^{\cdot}OH + \tfrac{1}{2}O_2 \tag{2}$$

$$2\,{}^{\cdot}OH \rightarrow H_2O_2 \tag{3}$$

$$2HO_2^{\cdot} \rightarrow H_2O + O_2 \tag{4}$$

$${}^{\cdot}H + H_2O_2 \rightarrow {}^{\cdot}OH + H_2O \tag{5}$$

Indigo Carmine (IC), (5.5'–indigo disulfonic acid disodium salt) is a dark blue dye mainly used in the textile industry for the dyeing of polyester fibers and denim (blue jeans) [16]. In the field of medical diagnostics it is administered intravascularly in a variety of applications such as; to locate urethral orifices, to endoscopically examine gastric cancer and to adjust the position of a catheter in the chemotherapy of hepatic and oral maxillofacial tumours [17,18]. It can also help to target biopsies even better since the homogeneously stained or unstained areas can be correlated with intraepithelial neoplasia. It is also a pH indicator. IC is also used as dye in food and cosmetics industry.

The dye is highly toxic, carcinogenic and has the potential to cause permanent injury to eyes. It can also lead to reproductive and developmental disorders as well as neuron and acute toxicity. Other health effects include possible tumors at the site of application, cardiovascular and respiratory effects and gastrointestinal irritation [18].

Several processes have been suggested for removal of IC and other dyes from wastewater including adsorption, microwave, photochemical and electrochemical methods [19-24]. In the present study, investigation of the sonochemical degradation of the pollutant dye IC is carried out. The effect of various operational parameters such as frequency of US, power density, pH, presence of various additives such as $Fe^{2+}$, $H_2O_2$, $S_2O_8^{2-}$ and anions/salts on the efficiency of degradation is investigated. The chemical structure of IC is shown in figure 1.

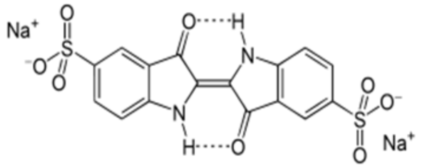


**Fig. 1. Chemical structure of Indigo Carmine**

## 2. MATERIALS AND METHODS

### *2.1. Materials*

IC (>99.6%) and ZnO (>99.5%) used in the study are from Sigma Aldrich India. $H_2O_2$ (30.0% w/v) and $K_2S_2O_8$ (PDS, AnalaR-99%) from Qualigen (India) were used as such without further purification. Various other chemicals used were also of AnalaR grade or equivalent, unless indicated otherwise.

### *2.2. Sonolysis*

Sonication of the reaction system was carried out in a jacketed glass reactor of 500 ml capacity. Ultrasound (US) of different frequencies was generated using an L3 ELAC Nautic ultrasound generator powered by an allied signal R/F generator (T& C power conversion, model AG1006). The variable frequencies used were 200, 350, 620, and 1000 kHz. The power applied varied from 20 to 80W. The temperature was maintained at 25±1°C by circulating cooling water from a thermostat. Typical reactor assembly is shown in figure 2. The disappearance of the dye is followed by using UV/Vis spectrophotometry at a wavelength of 609 nm. The intermediates were detected using LC/MS (Waters Xevo G2 Q-TOF).

### *2.3. Analysis of chemical oxygen demand (COD)*

Open reflux method is used to determine COD of the samples [25]. The sample (50 ml) was pipetted out into a refluxing flask. $HgSO_4$ (1g) was added along with several glass beads. Sulphuric acid reagent (5.5g $Ag_2SO_4$ in 543mL Conc.$H_2SO_4$) was added (5 ml) slowly with mixing to dissolve $HgSO_4$. The sample was cooled while mixing to avoid the possible loss of volatile materials. $K_2Cr_2O_7$ solution (0.05 N, 25 ml) was also added and mixed well. Remaining (70mL) sulfuric acid reagent was added through the open end of the condenser. The whole mixture was refluxed for two hours and cooled thereafter to room temperature. The mixture was diluted to 150mL and the excess $K_2Cr_2O_7$ was titrated against 0.05N Ferrous Ammonium Sulfate (FAS) solution using Ferroin as the indicator. The end point was sharp change in color from blue green to reddish brown. A blank was also carried out under identical conditions using the reagents and distilled water in place of the sample.

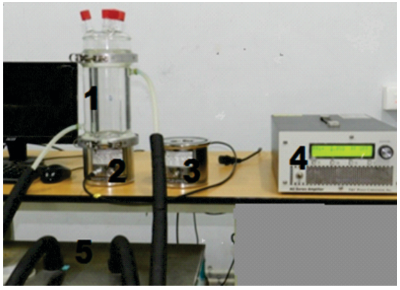


**Fig.2. Sonoreaction assembly, 1: Glass reactor, 2, 3: Variable frequency generators, 4: Power supply unit, 5: Thermostat**

COD is calculated using the following equation:

COD (as mg $O_2$/L) = (A-B) × M × 8000 / mL sample (6) where;

A = mL FAS used for blank
B = mL FAS used for sample
M = Molarity of FAS
8000 = milliequivalent weight of oxygen × 1000mL/L

## 3.RESULTS AND DISCUSSION

Preliminary experiments have shown that irradiation by US (sonolysis) is a viable method for the degradation of traces of Indigo Carmine dye pollutant in water. Hence the process and the influence of various reaction parameters on its efficiency are investigated in detail.

### *3.1. Effect of frequency of US*

The effect of frequency of US on the degradation of IC is measured by performing experiments at four different frequencies, i.e. 200, 350, 620 and 1000 kHz keeping the power constant (80W). The degradation pattern is given in figure 3.

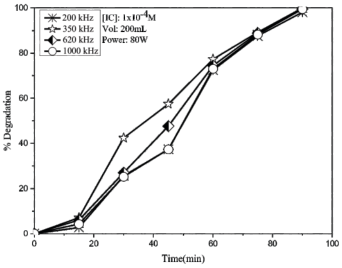


**Fig. 3: Effect of US frequency on the sonochemical degradation of IC**

The rate of degradation does not have any direct correlation with the frequency and is the highest at 350 kHz. The degradation is less at both the lower frequency (200 kHz) and the higher frequency (1000 kHz). Hence simple increase in the frequency does not guarantee increased sonodegradation of the pollutant. A distinct difference in the degradation with frequency was observed only during the early stage of sonolysis (upto 60 minutes). Later on, the degradation efficiency was comparable (>80%) The optimum frequency for the degradation of IC is therefore taken as 350 kHz.

The size of the bubble (resonance size), number of bubbles formed, life time of the acoustic bubble in the multibubble field and the intensity of collapse are the important factors in sonolytic degradation which in turn depend on the ultrasonic frequency and power [26]. The resonant size of the bubbles decreases with increase in the frequency [27], i.e., the size of the bubble will be in the order 200 kHz > 350 kHz > 620 kHz > 1 MHz. At lower frequency, the bubble pulsation occurs slowly and the life time of the cavitating bubble will be more. Thus, chances of recombination of the reactive $^{\cdot}$OH in the interface get enhanced. At higher frequency, the size of the cavity is reduced. However the availability of reaction site and the number of cavitational events become higher and consequently more $^{\cdot}$OH radicals are generated resulting in faster reaction. The cavitation bubbles become more dispersed and more accessible for the reacting species which also result in enhanced degradation of the substrate [28]. The life time of an acoustic bubble in a multibubble field, which may vary with the applied frequency, is another important factor in sonolytic degradation of organics. Sunartio et al. [29] reported that the life time of a cavitating bubble increases with decreasing frequency, i.e. in the present case, maximum lifetime is at 200 kHz and the least at 1 MHz. Chowdhuri and Vijayaraghavan [15] compared the sonolytic effects at two different frequencies of 200 and 350 kHz and concluded that the life time of the bubble in the acoustic field is comparable at the two frequencies though the relative life time of the cavitating bubble is more at 200 kHz. However the number of cavitations is higher at 350 kHz thereby generating more hydroxyl radical. Consequently degradation of IC is enhanced when frequency is increased from 200 to 350 kHz. But with further increase in the frequency, the relative life time of the bubble becomes lower and therefore the collapse of the bubble will be less violent. This results in decreased formation of $^{\cdot}$OH. This is the likely reason for the lower efficiency of degradation at higher frequencies of 620 and 1000 kHz

### *3.2. Effect of power*

The effect of power of US on the degradation of IC is monitored by varying the power (20W, 40W, 60W and 80W) at a fixed frequency of 350 kHz. The results are shown in figure 4. After the initial induction period, efficiency of degradation increases with increase in power, with maximum degradation at 80W. Acoustic intensity dissipated into the solution is directly related to the applied power [30]. At the appropriate power, the bubble growth starts and reaches the resonant size. This is followed by collapse of the bubbles and subsequent formation of $^{\cdot}$OH.

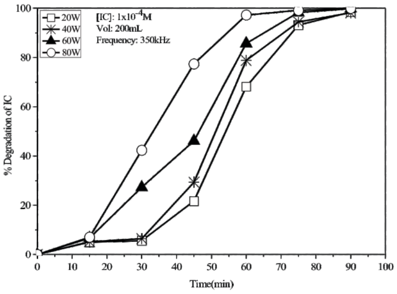


**Fig.4: Effect of US power on the sonolytic degradation of IC**

The hike in power can also enhance the negative pressure exerted by ultrasound. As a result, the bubble expands more in the rarefaction stage and the cavity reaches the resonance size instantly. Consequently pyrolysis and $^{\cdot}$OH formation reaction takes place at accelerated rate [31]. In any case, in the current study, the degradation of IC is completed even at the lower power of US and the net time taken for complete degradation is only marginally less at higher power even though the degradation is more dependent on sono power in the early stages of the reaction.

### *3.3. Effect of Concentration of IC*

The effect of concentration of IC on its sonodegradation is investigated at the optimized frequency (350 kHz) and power (80W) of US. The percentage degradation decreases with increase in concentration (figure 5). However more appropriate measure of the efficiency is the rate of degradation. The rate of degradation of IC at different concentrations is plotted in the inset of figure 5. The rate increases with increase in concentration of IC, reaches an optimum at 1x10$^{-4}$M and decreases thereafter. Accordingly, 1x10$^{-4}$M of IC is chosen as the optimum concentration for further studies.

The degradation of pollutants in water under sonolysis involves their interaction with $^{\cdot}OH$ radicals formed insitu as shown in reactions (1) – (5). However most of the $^{\cdot}OH$ will recombine and produce $H_2O_2$ inside the cavitation bubble and at the gas-liquid interface as shown in reaction (3). $H_2O_2$ is detected in the present system also. It is also possible that the pollutant molecule inside or in the neighborhood of a disintegrating bubble can get thermally degraded due to the supercritical conditions of high local temperature and pressure [13,32].

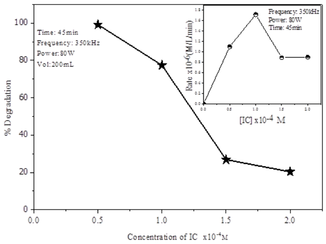


**Fig.5: Effect of concentration of IC on its sonochemical degradation**

The initial degradation of the dye will be dependent on the relative concentration of dye molecules at the interface of the cavitation bubble and the $^{\cdot}OH$ radicals. IC is a low volatile compound and its relative concentration at the cavitation-bubble interface will be less. Consequently, the sonochemical degradation also will be slower. The rate determining step is the generation of $^{\cdot}OH$ either from water or the deprotonation of insitu formed $H_2O_2$ or both under sonolysis. At lower dye concentration, the $^{\cdot}OH$ radicals have lesser number of dye molecules to interact with and the rate of degradation is slower. The degradation takes place primarily in the bulk of the solution where the $^{\cdot}OH$ radical concentration is low because only a small part of the radicals generated at the bubble surface can diffuse into the bulk. With increase in concentration of IC, the frequency of interaction between the substrate and the $^{\cdot}OH$ is more and the rate of degradation increases steadily until the optimum is reached. Beyond the optimum concentration, the rate of $^{\cdot}OH$ radical generation and/or its diffusion into the bulk may not be adequate to interact with correspondingly more of the pollutant molecules and the rate slows down and even decreases. At higher concentration of the dye, the penetration of US into the system and consequently the generation of $^{\cdot}OH$ are inhibited. This also leads to decrease in the degradation. Moreover, as the reaction proceeds, more and more intermediates are formed which will compete with IC for the $^{\cdot}OH$ radicals resulting in further decrease in the rate. Similarly, the concentration of the dye molecules inside the bubble and the bubble-solution interface also will be relatively less in comparison to its overall concentration. This also results in apparent decrease in the rate of degradation at higher concentration. Hence optimization of the concentration of the dye in water is important for achieving efficient and economical decontamination of the polluted water.

### *3.4. Effect of pH*

The pH of the reaction medium is known to have strong influence on all AOPs including US-induced degradation of organic pollutants. Therefore the effect of pH on the sonochemical degradation of IC was studied. The results are shown in figure 6. It is observed that the degradation is more efficient in the acidic region than in the alkaline region. At lower pH, the formation of hydrogen peroxide by the recombination of hydroxyl radicals will be less [33]. Therefore, the number of hydroxyl radical available for the reaction with IC in the liquid region is more. Similarly, the number of reaction sites will increase at this pH due to the increased bubble repulsion caused by the accumulation of hydronium ion in the interface region [34]. This also enhances the degradation at lower pH.

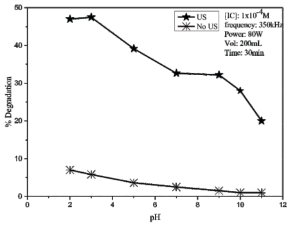


**Fig.6: Effect of pH on the sonochemical degradation of IC**

### *3.5. Effect of power density*

The effect of power density (power/volume) of US on the sonodegradation of IC was studied by taking different volumes of the reaction solution keeping the power applied constant at 80W. By increasing the US power density from 0.16 to 0.8 W/mL (volume decreasing from 500 to 100 mL), the degradation increases steeply initially and slowly thereafter, to level off eventually (figure 7). This implies that the relative volume of the reactants and the applied US power have to be optimized in order to achieve efficient sonodegradation.

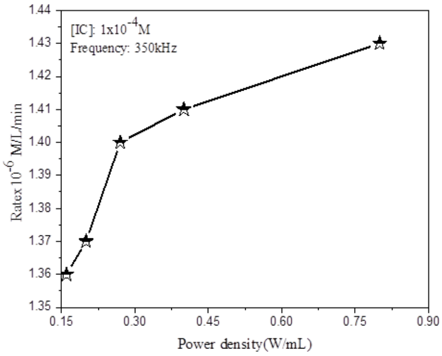


**Fig 7: Effect of US power density on the sonodegradation of IC**

### *3.6. Formation of $H_2O_2$*

The formation of $H_2O_2$ during the sonochemical degradation of organics by recombination of insitu formed $^{\cdot}OH$ has been reported earlier [34]. In the present study also, $H_2O_2$ is formed in the system and its concentration at different times of sonication is measured after the decolorisation. The concentration could not be measured precisely when the system is colored. The results are plotted in figure 8. It is seen that even after the decolourisation, the concentration of $H_2O_2$ is increasing showing that formation as well as the recombination of $^{\cdot}OH$ radicals is continuing. These free radicals interact further with the intermediates formed on decolorization. Eventually, the intermediates also get fully degraded and the system is mineralized completely.

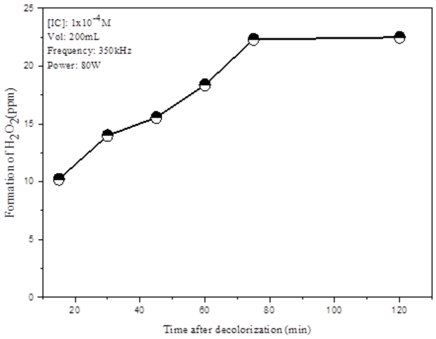


**Fig.8: Formation of $H_2O_2$ during the sonochemical degradation of IC**

Under US irradiation, the $O_2$ present in the solution would be split into reactive $^{\cdot}O$ radicals (reaction 7) which interact with $H_2O$ molecules and form reactive $^{\cdot}OH$ and $H_2O_2$ (reaction 8,9) The 'hot spot effect' of US irradiation in water will also enhance the formation of $^{\cdot}OH$ due to the pyrolysis of water molecules as in reaction (10). This as well as reaction (11) and (12) will also result in the formation of more reactive oxygen species (ROS) such as $^{\cdot}OH$, $HO_2^{\cdot}$ and $H_2O_2$ which will facilitate the degradation and mineralization of the substrate IC (reaction 13).

$O_2 \rightarrow 2\,^{\cdot}O$ (7)
$O + H_2O \rightarrow 2\,^{\cdot}OH$ (8)
$^{\cdot}OH + ^{\cdot}OH \rightarrow H_2O_2$ (9)
$H_2O \quad + >>> \rightarrow \quad H^{\cdot} + ^{\cdot}OH$ (10)
$H^{\cdot} + O_2 \rightarrow O + ^{\cdot}OH$ (11)
$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$ (12)
$IC + ROS\ (^{\cdot}OH,\ HO_2^{\cdot},\ H_2O_2\ \text{etc.}) \rightarrow\rightarrow \text{Intermediates} \rightarrow\rightarrow \text{Mineralization}\ (CO_2, H_2O)$ (13)

### *3.7. Effect of hydrogen peroxide*

Since $H_2O_2$, a powerful oxidant, is formed insitu during the sonolytic process, it is quite possible that the rate of degradation of IC is enhanced by its increasing presence in the system. The effect of $H_2O_2$

on the degradation of IC is investigated by initially adding different concentrations of $H_2O_2$ (10-50 mg/L) under standardized sonoconditions. The results are shown in figure 9.

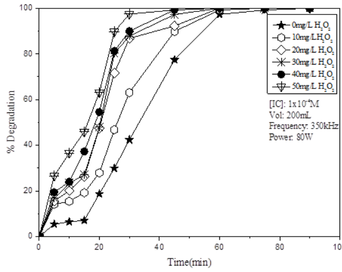


**Fig.9: Effect of $H_2O_2$ on the sonochemical degradation of IC**

The degradation is enhanced in the presence of $H_2O_2$. Control experiments in the presence of $H_2O_2$ without sonication showed no significant degradation within the time frame of experiments. The degradation increases with increase in the concentration of $H_2O_2$. At lower concentration, there is an induction period, which is probably due to the slower generation of $^{\cdot}OH$ radicals. However, eventually the rate is enhanced at all concentrations. Complete (100%) degradation is achieved in about 25 min. with 50mg/L of added $H_2O_2$, while it takes approximately 60 minutes at lower concentrations. The enhancement can be attributed to the additional $^{\cdot}OH$ formed during the sonication by the pyrolysis of hydrogen peroxide as in reaction (14) [35, 36].

$H_2O_2 \rightarrow 2^{\cdot}OH$ (14)

However the $^{\cdot}OH$ can also act as a scavenger of $H_2O_2$ thereby reducing the net concentration of $H_2O_2$ as follows:
$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO_2^{\cdot}$ (15)

The detrimental effect of $H_2O_2$ at higher concentration [37-39] on the AOP degradation of organics is not quite evident here. However the enhancement in degradation with increase in $H_2O_2$ concentration slows down at higher concentration indicating that the scavenging of $^{\cdot}OH$ by $H_2O_2$ is also taking place in parallel. The enhancement by added $H_2O_2$ can be explained in two possible ways: i) $H_2O_2$ molecules that enter the cavitation bubbles during sonication are broken into OH radicals, which enter the solution, interact with and degrade the IC. ii) The $H_2O_2$ oxidizes IC directly. However the higher rate of enhancement is not sustained later on. This can be explained as follows: In the beginning, added $H_2O_2$ decomposes faster in presence of US producing maximum OH radicals which can degrade IC. However, the decomposition of $H_2O_2$ to water and oxygen ($H_2O_2 \rightarrow H_2O + O_2$) also occurs in parallel which restricts the continued availability of the oxidizing species for IC degradation. Further, even in those experiments without externally added $H_2O_2$, the $H_2O_2$ formed in-situ will be accelerating the reaction rate. Hence the effect of initially added $H_2O_2$ is not that prominent in the later stages of the reaction.

### *3.8 Effect of $Fe^{2+}$*

The insitu formation of $H_2O_2$ in the reaction system opens up the possibility of enhancing the degradation significantly, by introducing $Fe^{2+}$ to the system and promoting a Fenton like reaction. This will initiate a combination AOP, i.e. SonoFenton and its associated additive or even synergistic effect. In order to verify this possibility, the effect of added $Fe^{2+}$ on the degradation of IC is investigated. $FeSO_4$ is added to the dye solution prior to sonication by keeping the frequency and power constant at 350 kHz and 80W respectively. All reaction parameters are kept the same as those in the case of regular sonolysis. In order to maintain the ideal Fenton condition [40,41], the initial pH of the solution was maintained at 4-5. The results are compared with those under simple sonolysis as well as comparable Fenton conditions and are shown in figure 10. The sonodegradation increases in the presence of $Fe^{2+}$. The percentage degradation of IC after 15 min of sonication in presence of 50 mg/L $Fe^{2+}$ is 99%. During this period, the degradation under simple Fenton is 40% while it is only 5% under simple sonolysis.

The synergy index of sonoFenton process in comparison to the additive effect of sono and Fenton process is calculated for this time period, using the relation,
Synergy index $(US + Fenton) = R_{(US+F)} / (R_{US} + R_F)$ (16) where

$R_{(US+F)}$, $R_{US}$ and $R_F$ are the rates of degradation under sonoFenton, sono and Fenton conditions respectively. In this case, the synergy index (SI) is 2.2, suggesting very strong synergy by

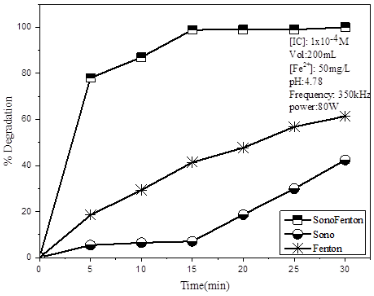


**Fig.10: Effect of added $Fe^{2+}$ on the sonochemical degradation of IC**

combining the two processes, especially in the early stages of reaction. This reconfirms the formation of $H_2O_2$ insitu under sonication which makes the Fenton process possible in presence of added $FeSO_4$. The Fenton process results in the formation of more reactive free radicals such as $^{\cdot}OH$, $HO_2^{\cdot}$ etc. as in reactions (17) – (21). However, with time of reaction, the synergy/additive effect becomes less and less significant (SI decreases to ~1.25 and ~ 1.0 after 25 and 30 min. respectively) probably because the concentration of the dye has become too low to show any significant enhancement in the rate of degradation by the combination process (over the sum of the degradation by respective individual processes).

Various reactions taking place in presence of $Fe^{2+}$ and $H_2O_2$ (Fenton reaction) under US irradiation can be summarized as follows:
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + {}^{\cdot}OH$ (17)
$H_2O_2 + ))) \rightarrow 2\,{}^{\cdot}OH$ (18)
$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO_2^{\cdot}$ (19)
$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+$ (20)
$Fe(OOH)^{2+} + ))) \rightarrow Fe^{2+} + HO_2^{\cdot}$ (21)
$2Fe^{3+} \rightarrow 3Fe^{2+}$ (22)
$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^+ + O_2$ (23)

Thus it is seen that the US induced formation of $^{\cdot}OH$ radicals in aqueous solutions is enhanced in the simultaneous presence of $Fe^{2+}$ and $H_2O_2$. Complex redox reactions also take place leading to the formation of hydroperoxide radicals and reduced $Fe^{2+}$ ions [40] which also results in enhanced degradation of the pollutant.

### *3.9 Effect of persulfate*

The enhancement in the sonochemical degradation of IC in presence of $H_2O_2$ opens up the possibility of using another powerful oxidant persulfate. Accordingly, sonolysis of IC was done in the presence of peroxydisulfate (PDS) as an additive. It is observed that the degradation is faster in the presence of PDS. The sonodegradation of IC is ~ 30% in the absence of PDS while it is ~ 62% in presence of PDS (15 mg/L) in 20 minutes. The results are shown in figure 11. Sonolysis of PDS results in the formation of sulfate radical anion which is a selective oxidant (2.6 V). Oxidative degradation of organic compounds by sulfate radical is well documented [42]. The degradation is increasing with increase in concentration of PDS, in the range 10-25mg/L. The degradation is complete in less than 1 hr. even at the lowest concentration of PDS, i.e., 10mgL. PDS can diffuse to the interfacial region where pyrolysis also produces sulfate radical.

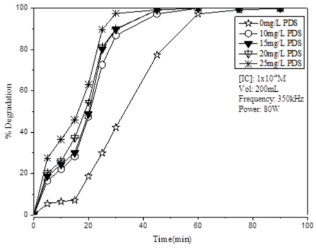


**Fig.11: Effect of PDS on the sonochemical degradation of IC**

Various ROS such as $H_2O_2$, $Ho_2^{\cdot}$, $^{\cdot}OH$ etc. and $SO_4^{\cdot-}$ formed during the irradiation by radical inter conversion reactions interact with IC in the bulk, leading to its degradation into various intermediates and eventual mineralization (reactions 24 – 32) . The results also show that both $H_2O_2$ and PDS have comparable enhancing efficiency. The OH radicals interact more with the $SO_4^{\cdot-}$ resulting in the destruction of both by chain termination (reaction 29). Hence addition of more PDS is necessary to sustain the generation of $SO_4^{\cdot-}$ and consequently the degradation of IC to drive the reaction to completion, especially so at later stages of reaction when the rate becomes slower. However, too much excess of PDS can lead to deactivation of $SO_4^{\cdot-}$ as in reaction (33).

Various reactions leading to the formation and interactions of $SO_4^{\cdot-}$ are as follows:

$S_2O_8^{2-} + ))) \rightarrow 2SO_4^{\cdot-}$ (24)

$SO_4^{\cdot-} + RH \rightarrow R^{\cdot} + HSO_4^{-}$ (25) Where RH=IC

$So_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + H^{+} + {}^{\cdot}OH$ (26)

$S_2O_8^{2-} + RH \rightarrow SO_4^{\cdot-} + HSO_4^{-} + R^{\cdot}$ (27)

${}^{\cdot}OH + (RH, R^{\cdot}) \rightarrow$ Intermediates $\rightarrow$ products (28)

$SO_4^{\cdot-} + (R^{\cdot}, {}^{\cdot}OH) \rightarrow$ Chain termination (29)

$2SO_4^{\cdot-} \rightarrow S_2O_8^{2-}$ Chain termination (30)

$2\,{}^{\cdot}OH \rightarrow H_2O_2$ Chain termination (31)

$2R^{\cdot} \rightarrow RR$ Chain termination/Further degradation (32)

$SO_4^{\cdot-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\cdot-}$ (33)

### *3.10. Effect of addition of ZnO*

ZnO has been proven to be a good catalyst for the sono and photo degradation of many organic pollutants in water. Hence the effect of ZnO on the sono degradation of IC is tested under standardized condition for sonolysis. The degradation increases moderately in presence of the catalyst (figure 12). With increase in catalyst dosage, the degradation increases slowly reaches an optimum at 0.06g and stabilizes thereafter. The sonodegradation is more in the presence of ZnO compared to that with ultrasound alone. This may be because in presence of ZnO under US irradiation, more hydroxyl radicals are produced which will react with more of the IC molecules and degrade them. ZnO is an efficient catalyst offering surface sites for the adsorption of the substrate leading to enhanced interaction with the surface generated ${}^{\cdot}OH$ radicals. It is known that presence of suspended particles of appropriate size and amounts in water lead to increase in the acoustic noise and rise in the temperature in the irradiated liquid [43,44]. Presence of suspended solids in the liquid can provide more nucleation sites for cavitation bubbles at their surface. This will result in decrease in the cavitation thresholds which is responsible for the increase in the number of bubbles when the liquid is irradiated by US. Increase in the number of cavitation bubbles increases the pyrolysis of water which also leads to increase in the generation of reactive free radicals and degradation of IC under sonication. However, any increase in the catalyst dosage beyond the optimum will only result in the aggregation of particles which will limit the number of catalytically active accessible sites at the surface. Higher dosage of suspended particles will also disturb the transmission of ultrasound in the aqueous medium. Hence there is no further increase in degradation of the pollutant beyond a particular dosage. The sonoluminescence resulting in UV irradiation may also accelerate the reaction through photocatalysis since ZnO is an efficient photocatalyst [27,37,43].

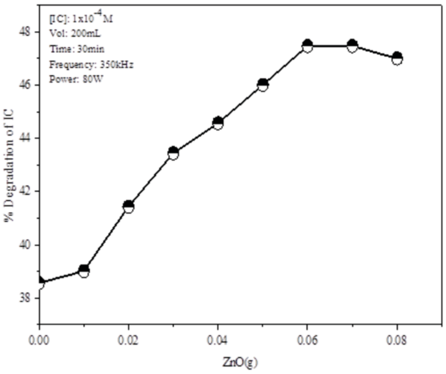


**Fig.12: Effect of ZnO at different dosages on the sonochemical degradation of IC**

### *3.11. Comparative degradation efficiency of IC in presence of additives*

Further to the experiments conducted in presence of various additives individually as above, preliminary studies were made on the efficiency of various combinations for the degradation of IC (in terms of the time taken for complete decolorization). The results are shown in figure 13.

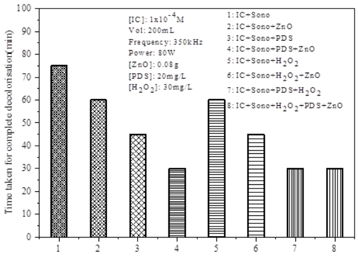


**Fig.13: Comparison of the time taken for complete decolorization of IC in presence of different additives**

Accordingly the most efficient systems for the degradation of IC are: i) sonolysis in presence of ZnO and PDS (US/PDS/ZnO), ii) sonolysis in presence of $H_2O_2$ and PDS (US/PDS/ $H_2O_2$) and iii) sonolysis in presence of PDS,$H_2O_2$ and ZnO (US/PDS/$H_2O_2$/ZnO). Sonolysis in presence of $H_2O_2$ and ZnO (US/$H_2O_2$/ZnO) as well as in presence of PDS (US/PDS) are also efficient, though slightly less than the earlier three systems. The relative efficiency of various systems for the deciolorization is in the order:

(US/PDS/ZnO) $\approx$ (US+PDS+$H_2O_2$+ZnO) $\approx$ (US/PDS/$H_2O_2$) > US/$H_2O_2$/ZnO $\approx$ US/PDS > US/$H_2O_2$ $\approx$ US/ZnO (34)

The relative efficiency of the additives for enhancing the efficiency of degradation of the pollutant may vary with the concentration of the additive which may be attributed to the multiple interactions of various reactive free radicals at different stages of reaction leading to different intermediates [43,44]. However, such variation is not significant in the present case for the decolorization of IC.

### *3.11 Effect of anions*

Anions/salts likely to be present in most of natural waters are known to influence the efficiency of many AOPs for water purification. In this context, the effect of few such anions i.e., $SO_4^{2-}$, $Cl^-$, $CO_3^{2-}$, $HCO_3^-$, and $PO_4^{3-}$ on the rate of sonolytic degradation of IC is investigated and the results are presented in figure 14. The anions have no effect on the degradation of IC at the concentration studied here except in the case of $PO_4^{3-}$ which is known to be a strong inhibitor of most AOPs. Studies at different concentration ranges of various anions (5-15 mg/L) on the degradation of IC confirm that the concentration effect is negligible at least in this range. This suggests that sonolysis is an efficient source of AOP activation for the removal of IC even from natural water containing dissolved salts. However, at much higher concentration of the anions (which is not natural in most water sources), the possibility of inhibition cannot be ruled out as has been reported in few earlier studies [44].

Since the efficiency of sonolysis for the degradation of IC in water is higher in the presence of additives such as PDS, $H_2O_2$, ZnO and/or their combination, the effect of anions is tested under these conditions as well. In these cases also anions have practically no effect except the inhibition by $PO_4^{3-}$. This implies that the most efficient systems identified earlier, i.e. US/PDS/ZnO, US/PDS/$H_2O_2$/ZnO or US/PDS/$H_2O_2$ can be used for the decontamination of water from IC even in the presence of moderate amount of natural anions.

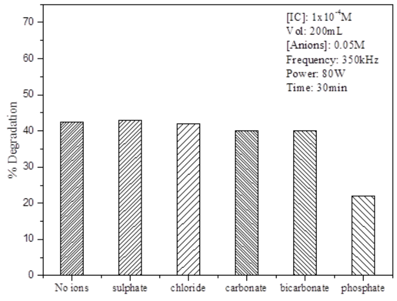


**Fig. 14. Effect of common anions in water on the sonolytic degradation of IC**

### *3.12. Mineralization studies*

The efficiency of any AOP for the decontamination of water depends on its ability to completely mineralize the pollutants into harmless products. The mineralization in this case is tested by measuring the chemical oxygen demand (COD) of the system at different times of sonication. The COD disappears completely in 10 hr. time by simple sonication in the absence of any oxidant or catalyst (figure 15). The time taken for complete mineralization of IC is much less in presence of specific additives, as shown in figure 16.

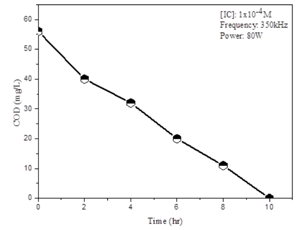


**Fig. 15.: Reduction in COD during sonochemical degradation of IC**

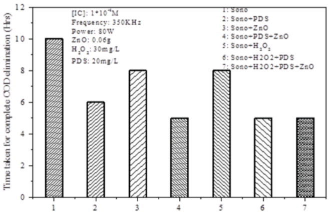


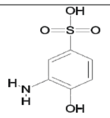
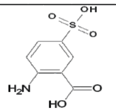
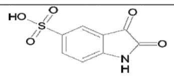
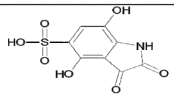
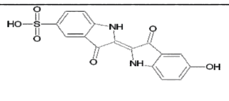
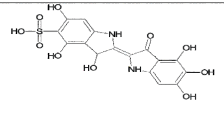
**Fig.16: Comparison of the time taken for complete mineralization of IC under sonolysis in presence of different additives**

The efficiency of mineralization of various systems is in the order:
(US/PDS/ZnO) ≈ (US/PDS/$H_2O_2$) ≈ (US+PDS+$H_2O_2$+ZnO) > US/ PDS > US/$H_2O_2$ ≈
US/ZnO (35)

The mineralization as well as the decolorization follows the same pattern thereby suggesting that the degradation of the intermediates formed during the decolorization is also facilitated by the oxidants.

The longer time taken for mineralization compared to decolorization shows that the former proceeds through the formation of recalcitrant intermediates which take longer time to be irreversibly transformed into harmless $CO_2$, $H_2O_2$ and salts. Various intermediates formed during degradation of IC are analyzed by LC/MS and are shown in Table 1.

**Table 1: Major intermediates identified during the sonodeg radation of IC**

| m/z | Molecular structure |
|---|---|
| 188 |  |
| 216 |  |
| 225 |  |
| 257 |  |
| 357 |  |
| 423 |  |

## 4.CONCLUSION

Ultrasound irradiation at appropriate power and frequency is an efficient mode of activation in advanced oxidation process (AOP) for the decolorization as well as mineralization of Indigo Carmine dye pollutant in water. The mineralization, which is confirmed by measuring the chemical oxygen demand, proceeds through a number of intermediates. These intermediates are identified and characterized by LCMS. Combination of sonolysis with additives such as $Fe^{2+}$, $H_2O_2$, peroxydisulphate and ZnO enhances the efficiency of the process for decolorization as well as mineralization. The presence of salts/anions commonly found in water does not inhibit the degradation or mineralization, except in the case of $PO_4^{3-}$ ions. Hence the sonolytic AOP, under suitably standardized conditions, is a potential technique for the decontamination of water from Indigo Carmine (IC) pollutants even in the case of natural effluents containing moderate amounts of salt contaminants.

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