

Significant Enhancement in the Efficiency of the Fenton Process by Solar, Electrolytic and Sonolytic Activation for the Mineralization of Indigo Carmine Dye Pollutant in Water

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ABSTRACT: Advanced Oxidation Processes (AOPs) are projected as relatively cleaner technologies for environmental remediation, in particular for water pollution abatement. One of the major sources of industrial water pollution is the textile industry due to the use of large quantity of water and various toxic and hazardous chemicals at different stages of the operation. Fenton process is a simple, cheaper and convenient method for the degradation and mineralization of many recalcitrant chemical pollutants in water. In this paper, the Fenton process is investigated as a potential tool for the degradation and eventual mineralization of a textile dye, Indigo carmine (IC) in water. The efficiency of the process is accelerated by activation sources such as light, ultrasound and electrochemical energy. Relevant reaction parameters such as ratio of the components Fe^{2+} and H_2O_2 of the Fenton reagent, concentration of the reagent, pH, concentration of the dye, natural contaminants in water, kinetics, volume of the reaction system, oxidants etc. are identified and optimized. The optimized ratio of Fenton reagent is 1:3 ($Fe^{2+}:H_2O_2$) at the optimum pH~4.5. Periodic replenishment of the components, especially H_2O_2 , is essential to achieve mineralization. Complete mineralization of the dye was observed after nine hours of treatment and was confirmed by the COD elimination. Various reaction intermediates formed during the degradation process are identified by LC/MS method. Probable mechanism of the degradation process is also proposed.

KEYWORDS: Advanced Oxidation Process; Fenton Reaction; Solar Fenton; ElectroFenton, Sono Fenton; Indigo Carmine

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I. INTRODUCTION

The textile industry consumes enormous amounts of water during dyeing and finishing operations. Typical medium-scale textile factories produce approximately 1000 m³ of wastewater per day. It is estimated that around 30% of the applied dyes remain unfixed and are discharged in the effluent. Dye-bearing wastewaters are toxic for the environment since dyes are stable compounds and may be carcinogenic. The presence of dyes in water is also undesirable; because even a small amount of these coloring agents is highly visible, and may be toxic to the aquatic environment [1-4]. Conventional biological treatment processes are often less successful because most dyes are practically not biodegradable.

Advanced Oxidation Processes (AOPs) have been widely investigated in recent years as viable, environment-friendly and economical techniques for the removal of toxic and hazardous pollutants such as dyes, pesticides, phenols etc. and the reduction of several heavy metals from water. The techniques include photocatalysis, sonocatalysis, electrocatalysis, wet air oxidation, Fenton process, photofenton process and their combinations which are primarily based on the formation of highly reactive ·OH radicals [6 -12]. According to the reactive phase, AOPs are classified into homogeneous and heterogeneous types. Examples of homogeneous type AOPs include Fenton based processes such as classic Fenton ($H_2O_2 + Fe^{2+}$), Fenton like processes ($Fe^{2+} + H_2O_2 + metal^{n+}$), sono-, photo- and electro-Fenton processes based on O_3 , H_2O_2 , O_3 -UV, H_2O_2 -UV and O_3 - H_2O_2 -UV etc. All processes involving suspended catalysts belong to the category of heterogeneous AOPs. However these processes have gained only limited acceptance so far, as viable and effective methods for the large-scale decontamination of wastewater due to complexity of the process, cost, operational constraints etc.

In this contest, the simple inexpensive classic Fenton process and its variations become important [13]. The hydroxyl radicals produced insitu in the Fenton process are nonselective in degrading organic pollutants [14]. Fenton's reagent is particularly promising due to its low cost, low toxicity of the reagents (Fe(II) and H_2O_2), and the simplicity of the technology. Several studies have shown that the Fenton's process is effective for the degradation of a number of organic compounds [15-17]. In the present study, the possibility of application of Fenton process under various conditions for the removal of the toxic recalcitrant dye Indigo carmine(IC) from water is examined.

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). Indigo Carmine is also used as dye in food and cosmetics industry. Several processes have been suggested for the removal of IC and other dyes from wastewater. These include adsorption, photochemical and electrochemical methods. However no systematic studies have been reported on the application of Fenton process for the removal of last traces of IC from water and make it reusable. The gap is addressed in this study. The structure of Indigo carmine is shown in figure 1.

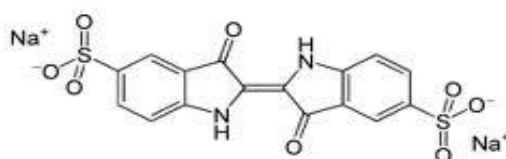


Fig.1. structure of Indigo Carmine

II. MATERIALS AND METHODS

II.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 $FeSO_4 \cdot 7H_2O$ (FS) from Qualigen (India) were used as such without further purification. Various other chemicals used were also of AnalaR grade or equivalent, unless indicated otherwise.

II.2. Degradation/Mineralization Experiments

In a typical experiment, the dye solution of required concentration is mixed with appropriate combinations of $FeSO_4$ (FS) and H_2O_2 in a 250 ml closed beaker. The reaction mixture is continuously stirred by using a magnetic stirrer. The reaction volume is maintained at 50 ml, unless indicated otherwise. The degradation is monitored by analyzing the IC remaining in the system by using UV-VIS spectrophotometry at 609 nm. H_2O_2 is analysed by standard iodometry. The reaction intermediates and products were identified by using Agilent 6460 Triple quad LC-MS.

In the case of solar degradation, the experiments in presence of sunlight were performed in a jacketed pyrex reactor. The dye solution (50 ml) together with the Fenton reagent and/or other additives was taken in the inner compartment and cooling water from a thermostat ($29 \pm 1^\circ C$) was circulated through the outer jacket. The experiments were performed by placing the system at the roof top of our laboratory at Kochi, Kerala, India ($9^\circ 57' 51'' N$, $76^\circ 16' 59'' E$) during sunny days in February-May, September-December 2017 and 2018. The suspension/solution was stirred frequently to ensure uniform mixing. Samples were drawn periodically, filtered through $0.45 \mu m$ filter in the case of suspensions and analyzed for the remaining dye concentration. Solutions/suspension kept under identical conditions in the dark was used as the reference in each case to eliminate the contribution from adsorption and dark reaction, if any, towards the reduction in the dye concentration.

Sonolytic degradation of IC under different experimental conditions is investigated using ultrasound (US) of frequency in the range 200 kHz - 1 MHz and power in the range of 20-80W, as the source of energy. The degradation profile was evaluated as in the case of photolysis. Electrochemical experiments were done using bismuth oxide doped titanium dioxide (BiO_2/TiO_2) coated on titanium plate as the anode and carbon felt cathode in presence of sodium sulfate supporting electrolyte. The experiments were conducted under static anodic potential of 3.4V.

II.3. Analysis of Chemical Oxygen Demand (COD)

Open reflux method was used to determine the COD of the samples [18]. 50mL of the sample was pipetted out into a refluxing flask. $HgSO_4$ (1g) was added to this along with several glass beads. Five (5) mL of sulfuric acid reagent (5.5g Ag_2SO_4 in 543mL Conc. H_2SO_4) was added 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 (25 mL, 0.05N) 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. It was then diluted to 150mL and the excess $K_2Cr_2O_7$ was titrated against 0.05N Ferrous Ammonium Sulphate

(FAS) solution using ferroin as the indicator. The end point was sharp change in color from blue green to reddish brown. A blank experiment was also carried out under identical conditions using the reagents and distilled water in place of the sample.

COD is calculated using the following equation:

COD as mg O₂/L = (A-B) × M × 8000/Volume of the sample, where

A = mL FAS used for blank

B = mL FAS used for sample

M = Molarity of FAS

8000 = Milliequivalent weight of oxygen × 1000mL/L

III. RESULTS AND DISCUSSIONS

III.1. Optimization of Fe²⁺/H₂O₂ ratio

Preliminary experiments have shown that IC can be decolorized by Fenton reagent at room temperature. The degradation/decolorization is practically negligible in presence of the individual components (Fe²⁺ or H₂O₂). The efficiency of the Fenton process for the degradation of any organics depends on the relative concentration of the reagent components FeSO₄ (FS) and H₂O₂. Hence detailed investigations were made for optimizing the ratio of these critical components for the degradation of IC in water. The concentration of IC is kept constant at 1×10⁻⁴M. The % degradation of IC at varying ratios of FS and H₂O₂ at different times of reaction is evaluated. The results are plotted in figure 2.

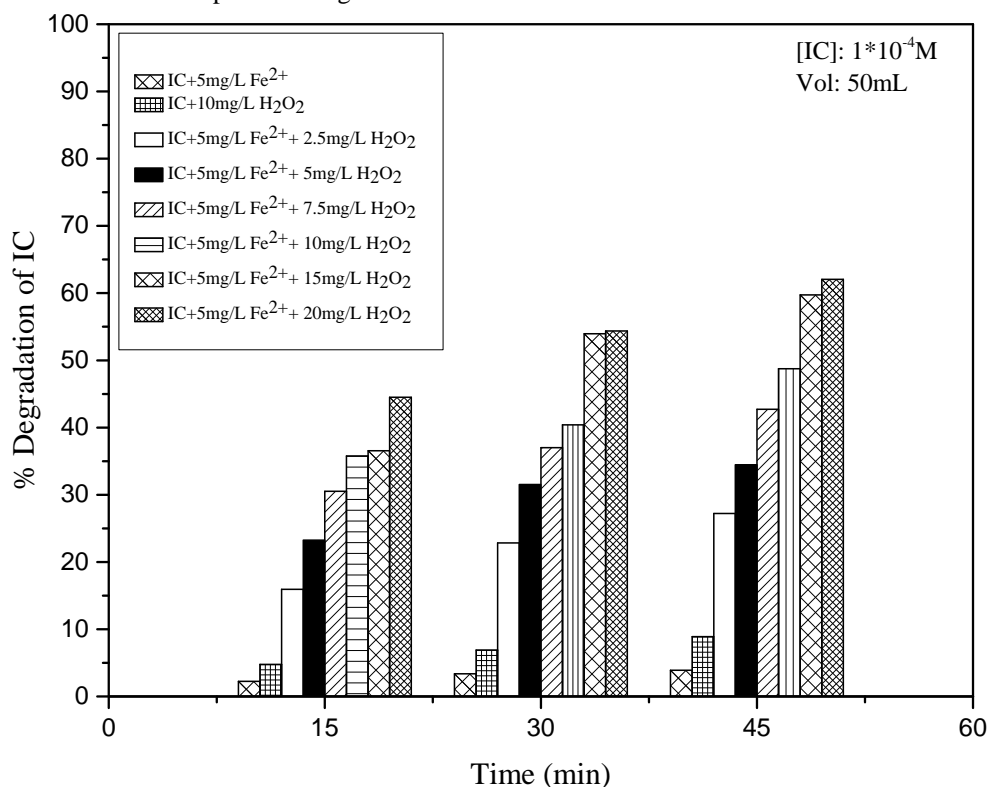


Fig.2: Optimization of Fe²⁺/H₂O₂ ratio for the degradation of IC

As seen from the figure the optimum ratio of Fe²⁺/H₂O₂ under the reaction condition is 5:15. Further increase in H₂O₂ dosage leads to stabilization of the degradation. The actual quantity of Fenton reagent in the ratio of Fe²⁺/H₂O₂= 5:15 (1:3) is further optimized as follows:

III.2. Effect of concentration of Fenton reagent on the degradation of IC

The effect of quantity of the Fenton reagent at the optimized ratio of 1:3 on the decolorization of IC is evaluated and the results are presented in figure 3. The degradation of IC increases with increase in the concentration of Fenton reagent. Eventually the degradation is stabilized (at Fe²⁺:H₂O₂ = 10:30) probably because the concentration of the dye has become relatively less for the effective utilization of the higher availability of FR. However, this optimized quantity depends on other reaction and reactor parameters and may vary under another set of conditions. Hence every time when the reaction conditions are changed, the optimum also needs to be reworked.

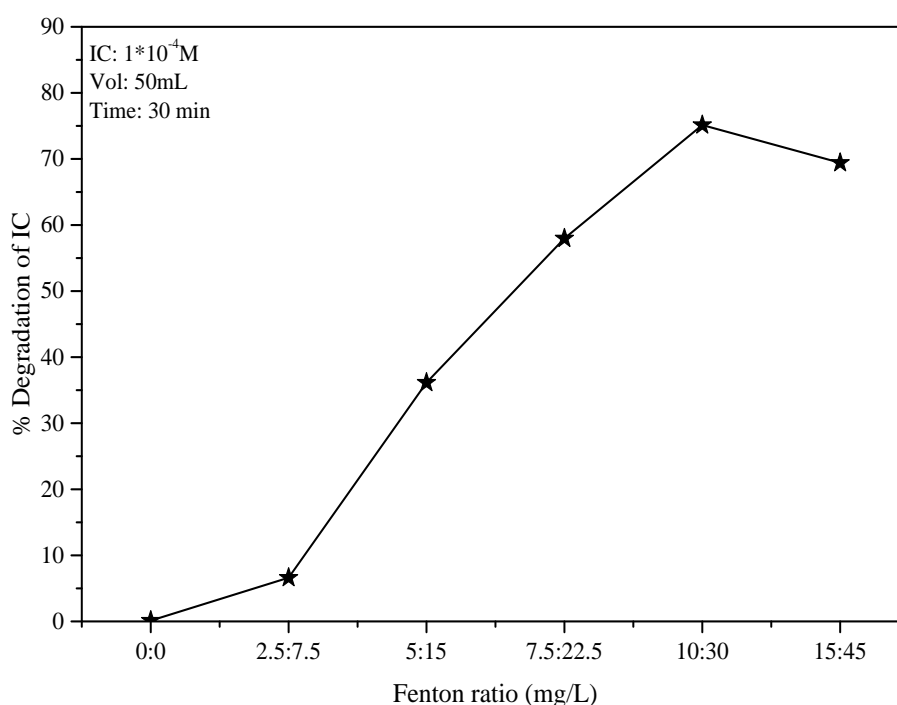


Fig.3: Effect of concentration of Fenton reagent on the rate of degradation of IC

The degradation of IC at different times, using the optimized ratio of the Fenton reagent (1:3) and the quantity [10:30mg/L (Fe^{2+} : H_2O_2)] is studied keeping the concentration of IC constant. The results are shown in figure 4. It is observed that the degradation of IC progresses steadily with time. However, the rate of increase in percentage degradation and consequently the rate of reaction decrease with time, probably because of decrease in the concentration of available IC. Eventually the degradation/decolorization reaches 100%, indicating that the intermediates formed during the degradation does not significantly retard the interaction between the Fenton reagent and IC. This shows that the Fenton process is efficient for the complete decolorization of IC in water. The decreasing rate of decolorization with time indicates that the relative concentration of IC and FR at any point in time of reaction influences the rate of degradation. This is further verified from the effect of initial concentration of IC on its degradation, keeping other parameters constant.

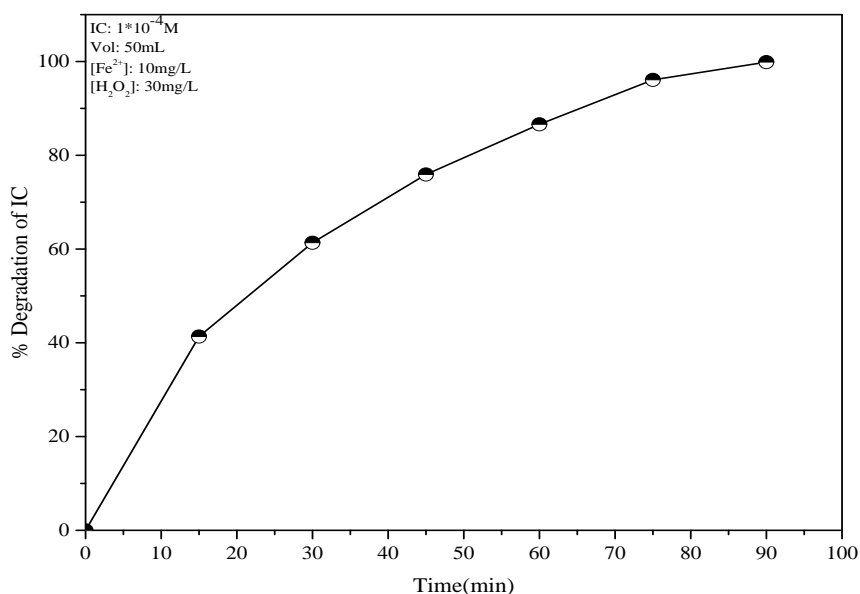


Fig.4: Effect of time on the efficiency of Fenton degradation of IC

III.3. Effect of initial concentration of IC on the Fenton degradation

The effect of concentration of IC on the % degradation is presented in figure 5. The % degradation decreases slowly with increase in concentration of IC. However, the rate of degradation increases steadily with increase in the concentration (Inset of Fig. 5). Beyond a particular optimum concentration ($1 \times 10^{-4} \text{M}$), the rate of degradation slows down. This may be because the concentration of the Fenton reagent is not adequate enough to interact with the higher number of IC molecules available in the system and increase the rate of reaction. Based on these data, $1 \times 10^{-4} \text{M}$ solution of IC is chosen as the optimum for further investigations.

III.4. Effect of pH on the Fenton degradation of IC

The pH is a very important and critical parameter in the efficiency of the Fenton's process. Change in pH of the solution, results in variation in the concentration of Fe^{2+} and consequently the rate of production of $\bullet\text{OH}$ radicals which are responsible for oxidation of IC [19]. The influence of pH on the decolorization of IC was investigated by keeping all other parameters constant and the result is presented in figure 6. The results show that Fenton process is favored only in the acidic pH range especially upto pH~ 5. Above pH 5, the generation of $\bullet\text{OH}$ decreases sharply due to the formation of Fe^{3+} ions which tend to precipitate in the form $\text{Fe}(\text{OH})_3$ as in reaction (1).



This reaction is favored at higher pH [20]. Therefore, the initial pH value has to be in the acidic range (<5) to generate the maximum amount of $\bullet\text{OH}$ radicals and thus to oxidize the organic compounds.

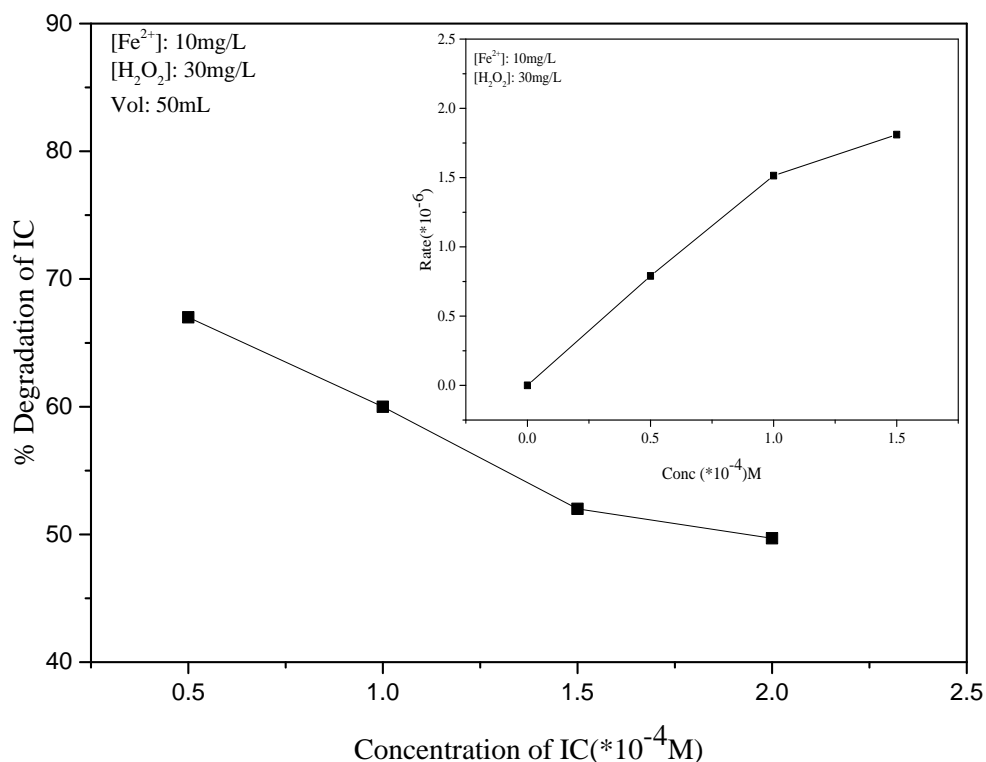


Fig.5: Effect of initial concentration of IC on its Fenton degradation [Inset: Concentration Vs Rate plot]

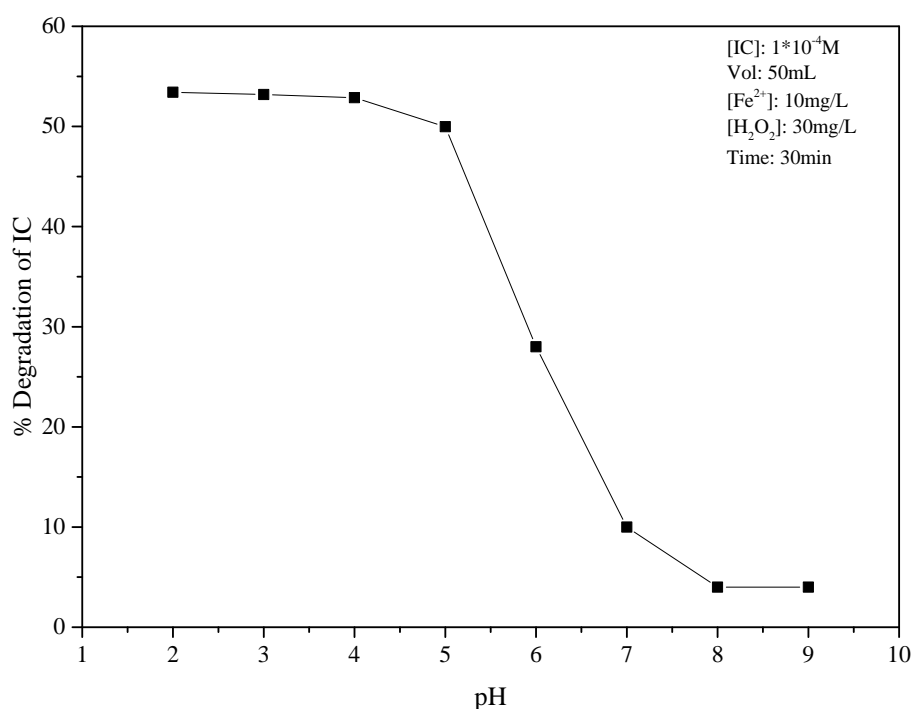


Fig.6: Effect of pH on the Fenton degradation of IC

III.5. Effect of Persulfate on the Fenton degradation of IC

Persulfates ($S_2O_8^{2-}$) are proven to be strong oxidants in AOPs due to the insitu formation of highly reactive $SO_4^{\cdot-}$ radical anions. Hence the probability of enhancing the efficiency of the Fenton process by the addition of persulfate (PS) is tested at various concentrations and the results are presented in figure 7.

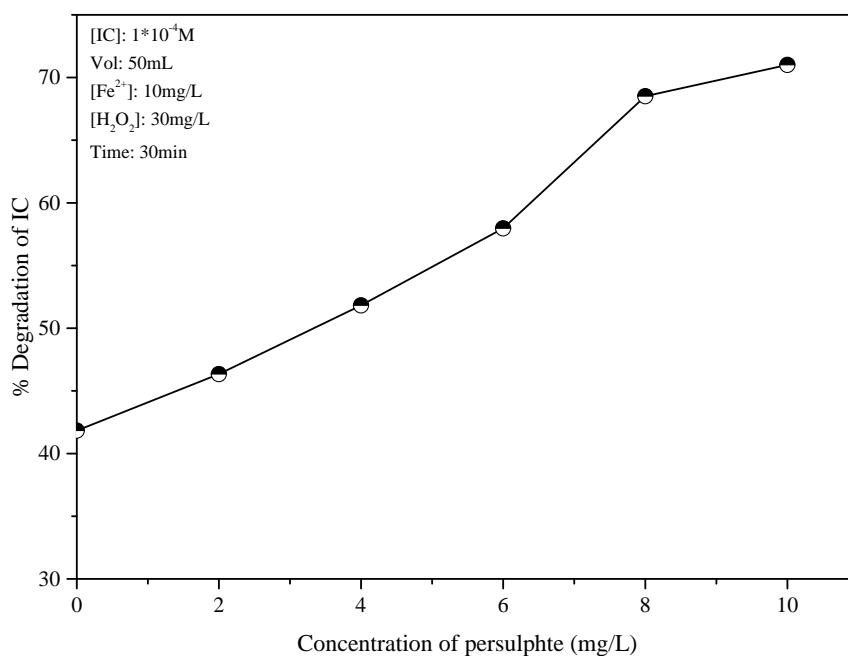
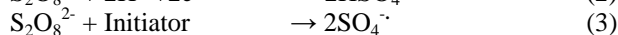
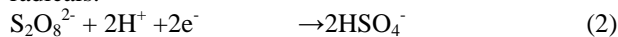


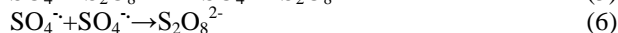
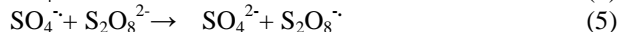
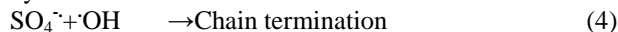
Fig.7: Effect of persulfate at various concentrations on the Fenton degradation of IC

The results show that persulfates enhance the Fenton reaction (FR)- induced degradation of IC moderately. Persulfate anion is the most powerful oxidant of the peroxygen family of compounds and one of the strongest oxidants used in environmental remediation. In addition to its direct oxidation capability, persulfates

can be induced to form highly reactive sulfate radicals, which are also powerful oxidants as the hydroxyl radicals.



Both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ have similar oxidation potential ($\cdot\text{OH} = 2.80$, $\text{SO}_4^{\cdot-} = 2.60$) and hence presence of persulfate is expected to enhance the Fenton degradation at least additively. However, the effect of PS on the Fenton process is not quite significant. This may be because the $\text{SO}_4^{\cdot-}$ generated in situ may be getting deactivated by interactions as follows:



Hence it may not be economically viable to use PS in the Fenton process for the decolorization of IC, since it provides no additional advantage.

III.6. Effect of salts/anions on the Fenton degradation of IC

The presence of chemical contaminants such as salts/anions/cations is known to influence the efficiency of AOPs for the mineralization of pollutants in water. Anions are used at different stages of the dyeing process and are hence likely to be present in the effluent water from dye related operations. In this context, the effect of few common anions (Cl^- , CO_3^{2-} , HCO_3^- , PO_4^{3-}) which are likely to be present in many natural water sources on the efficiency of the decolorization of IC by the Fenton process is examined. The results are presented in figure 8.

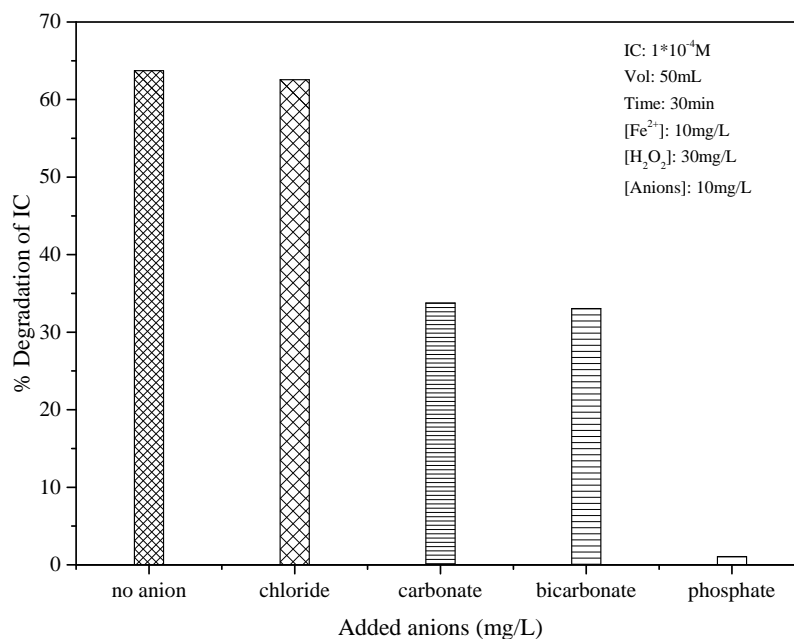
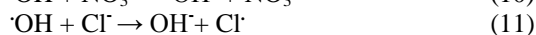
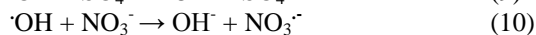
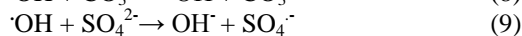
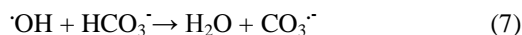


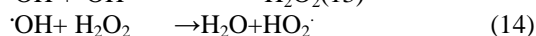
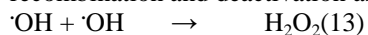
Fig 8: Effect of anions on the Fenton degradation of IC

Anions of the specified concentration are added to the reaction system individually and the Fenton degradation of IC in their presence was compared with the normal system. Results show that chloride has no effect on the degradation while carbonate and bicarbonate are good inhibitors. Phosphate is a strong inhibitor which retards the degradation of IC almost completely.

The main reason for the inhibition by anions may be the scavenging of the reactive $\cdot\text{OH}$ radicals formed in situ during the Fenton reaction resulting in the formation of radical anions as follows [20-22]:



The radical anions formed in the process are also moderately active for the degradation of organics. Their concentration will be increasing steadily in the system, unlike the $\cdot\text{OH}$ radicals which decrease progressively by recombination and deactivation as in reactions (13) and (14).

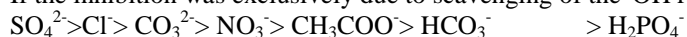


Hence, reasonable rate of degradation will continue even in presence of the $\cdot\text{OH}$ radical-scavenging anions. The scavenging rate constants for the anions are given in table 1.

Table 1: Scavenging rate constants for the anions

Anions	Scavenging rate constants ($\text{mol}^{-1}\text{s}^{-1}$)
NO_3^-	1.4×10^8
Cl^-	4.3×10^9
CO_3^{2-}	3.9×10^8
SO_4^{2-}	1×10^{10}
H_2PO_4^-	2×10^4
CH_3COO^-	7.0×10^7
HCO_3^-	8.5×10^6

If the inhibition was exclusively due to scavenging of the $\cdot\text{OH}$ radicals, it should have been in the order:



Since this sequence is not followed, scavenging of the anions cannot be considered as the main reason for the inhibition. The very strong inhibition in presence of PO_4^{3-} in this homogeneous system is surprising even though anions are known to inhibit many heterogeneous AOPs due to the blocking of the catalytically active surface sites. In this homogeneous system with no suspended catalyst particles this possibility for inhibition is ruled out. In the case of PO_4^{3-} it is possible that the radical anion formed from phosphate is practically not active like other radical anion. It is also possible that the Fe^{2+} of the Fenton reagent will interact with PO_4^{3-} thereby decreasing the amount of the cations needed for the formation of $\cdot\text{OH}$ by the Fenton reaction.

Another reason for the anion effect in the case of Fenton reaction is the variation in pH in presence of the anions. Even mild variation in the pH, especially from the optimum of ~ 4 can affect the Fenton process strongly. The pH of the system with various anions is shown in figure 9.

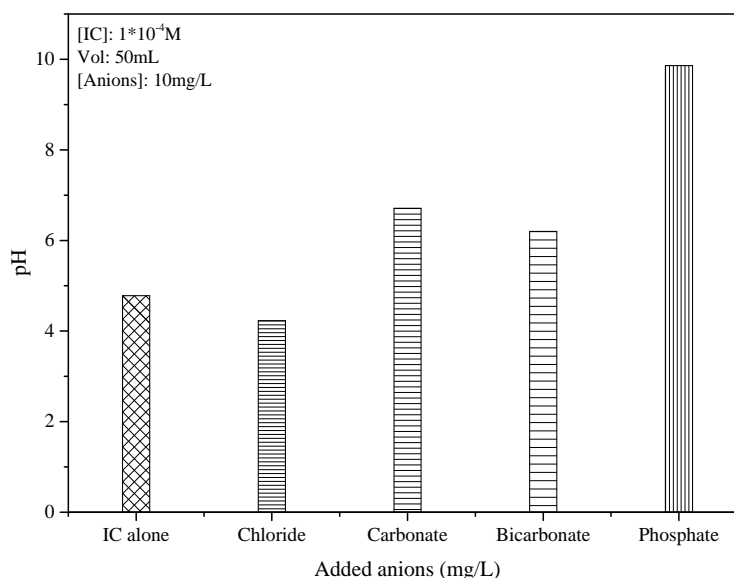


Fig.9: pH of the dye solution in presence of anions

The pH decreases moderately in presence of Cl^- which is a favorable condition for Fenton reaction. As expected in this case the anion has no effect. CO_3^{2-} and HCO_3^- increase the pH of the medium which is unfavorable for the Fenton degradation. Hence the inhibition can be attributed to this. By the same yardstick, the inhibition by PO_4^{3-} also can be explained because the $\text{pH} \sim 9$ in presence of PO_4^{3-} is totally unfavorable for the degradation as seen in figure 6.

III.7. Effect of ZnO on the Fenton degradation of IC

Earlier studies have shown that ZnO and TiO₂ mediated photo, sono and microwave (MW) activated AOPs efficient for the degradation and mineralization of a variety of pollutants[23-25]. Of these two widely investigated semiconductor oxides, ZnO has been proven to be more active for solar energy harvesting due to its better absorption characteristics in the visible range of solar spectrum. In this context, experiments were done to verify whether ZnO can be used beneficially in the Fenton process, either under ambient condition or in presence of powerful activation sources such as sunlight, UV-Vis light or ultrasound. The results are presented in figure 10.

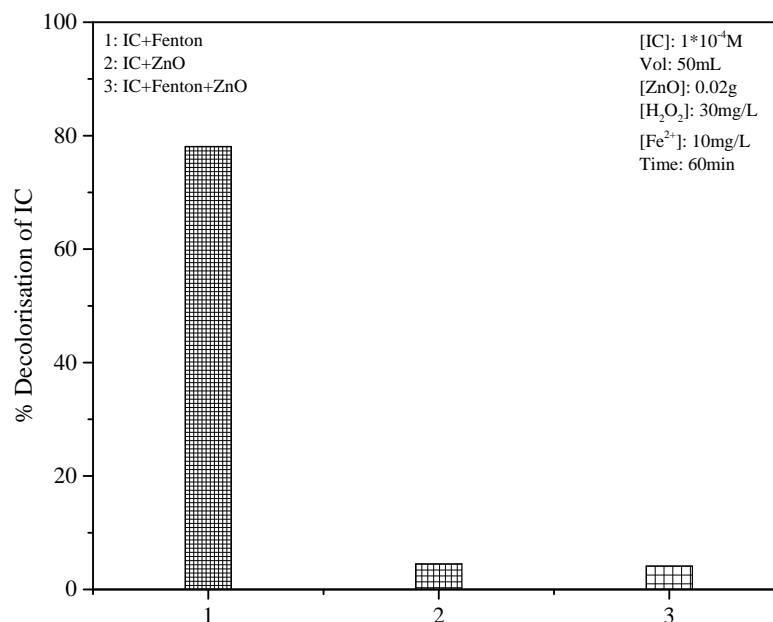


Fig.10: Effect of ZnO on the Fenton degradation of IC

In this heterogeneous system, in the absence of any light irradiation, ZnO inhibits the Fenton degradation of IC almost completely.

The adsorption of H₂O₂ on ZnO and consequent decrease in the concentration of the former as the cause of the inhibition is ruled out since the adsorption has been experimentally observed to be negligible. Hence, the suspended ZnO particles may be inhibiting effective interaction between Fe²⁺ and H₂O₂ thereby reducing the rate of formation of reactive ·OH radicals. The substrate also may get shielded from interaction with the reactive free radicals by the ZnO particles which also may lead to the inhibition. Presence of ZnO also increases the pH of the medium which is another unfavorable factor for the Fenton reaction as stated earlier. The pH of the standard IC-FR system increases from 4.5 to 7.5 in presence of ZnO (figure 11). The effect of pH (Fig. 6) clearly illustrates that the degradation is severely inhibited at pH 7. However, when the pH of the suspension with ZnO is modified to acidic condition of normal Fenton system, i.e. 4.5, the degradation of IC proceeds faster, though the rate is less compared to that of normal Fenton (without ZnO). The result is shown in figure 11 inset. Hence at least one of the main causes for the inhibition by ZnO is its effect on the pH.

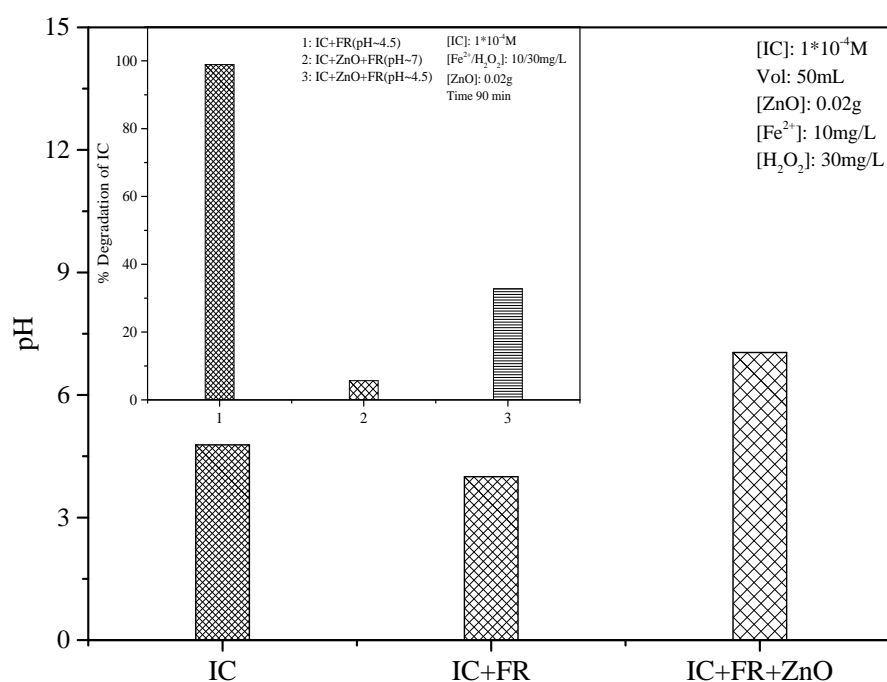


Fig.11: pH of the solution with and without ZnO

[Inset: Effect of ZnO on the Fenton degradation of IC with and without adjusting the pH]

The effect of variation in ZnO dosage on the efficiency of the normal Fenton system is experimentally verified and the results are plotted in figure 12. The degradation of IC decreases with increase in the amount of ZnO and is almost completely inhibited above 0.010g. The effect of varying amounts of ZnO on the pH of the system is shown in the inset of the figure. The data clearly shows that increase in the pH of the system is one of the major causes of the inhibition in presence of ZnO.

The inhibiting effect of ZnO is further verified by adding ZnO in between to the Fenton degradation in progress and observing the effect. It is observed that the degradation which was proceeding smoothly, stopped instantly and stabilized. No further degradation was observed even after long time. The result is shown in figure 13.

III.8. Effect of volume of the reactor

Since Fenton reaction is a relatively simple facile process which proceeds smoothly as long as there is sufficient concentration of the reagents and the substrate, the effect of volume of the reaction system on the rate of degradation of IC is tested under optimized reaction parameters in the same reactor. The results which are shown in figure 14 confirm the expected outcome, i.e. the rate of degradation is maintained as long as the ingredients are available in required quantities. The initial increase in degradation with increase in volume from 25 to 50mL shows that there is an optimum volume at which the Fenton process is more efficient compared to very low volume. This also indicates that the volume of the reaction system is not a constraint for the scaling up of the process at industrial level.

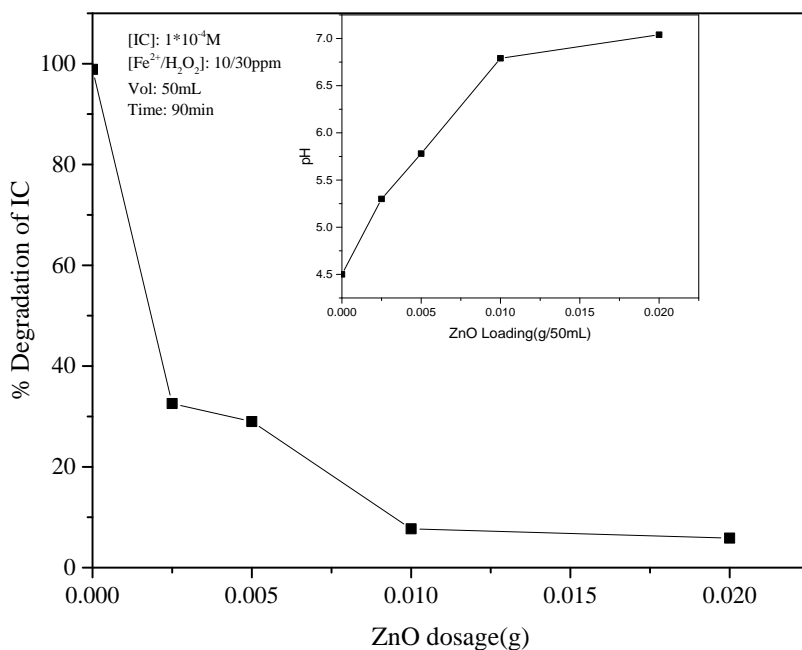


Fig.12: Effect of increasing dosage of ZnO on the Fenton degradation of IC

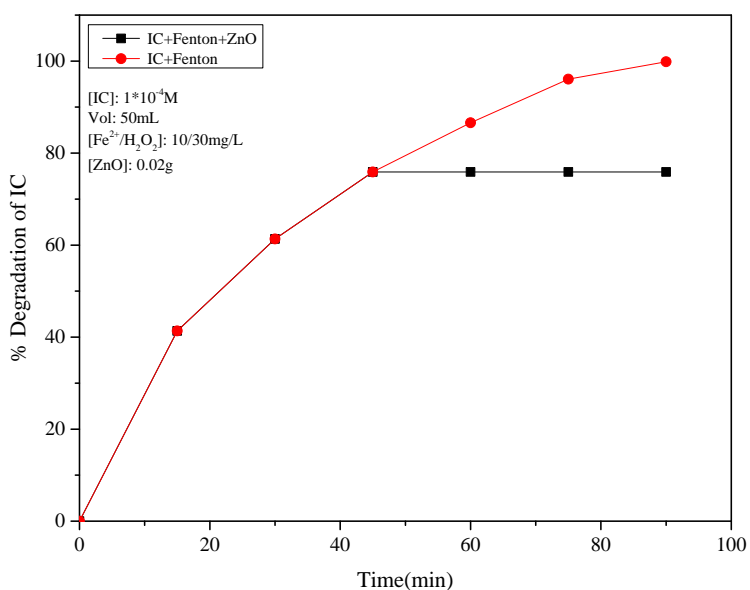


Fig 13: Effect of in between addition of ZnO on the Fenton degradation of IC

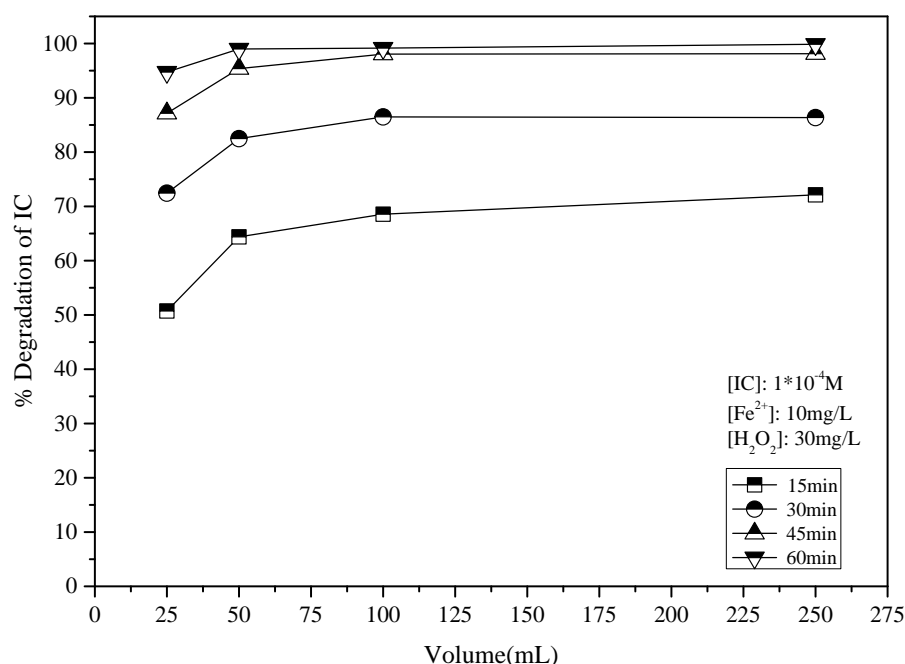


Fig.14: Effect of volume on the Fenton degradation of IC

III.9. Mineralization of IC during Fenton degradation

The efficiency of any water purification technique depends ultimately on its ability for mineralizing the chemical pollutant and bringing down the Chemical Oxygen Demand (COD)/total organic carbon (TOC) to 'nil' or acceptable level. In this context, the COD of the IC/Fenton reaction system is measured at different times of reaction and the results are plotted in figure 15.

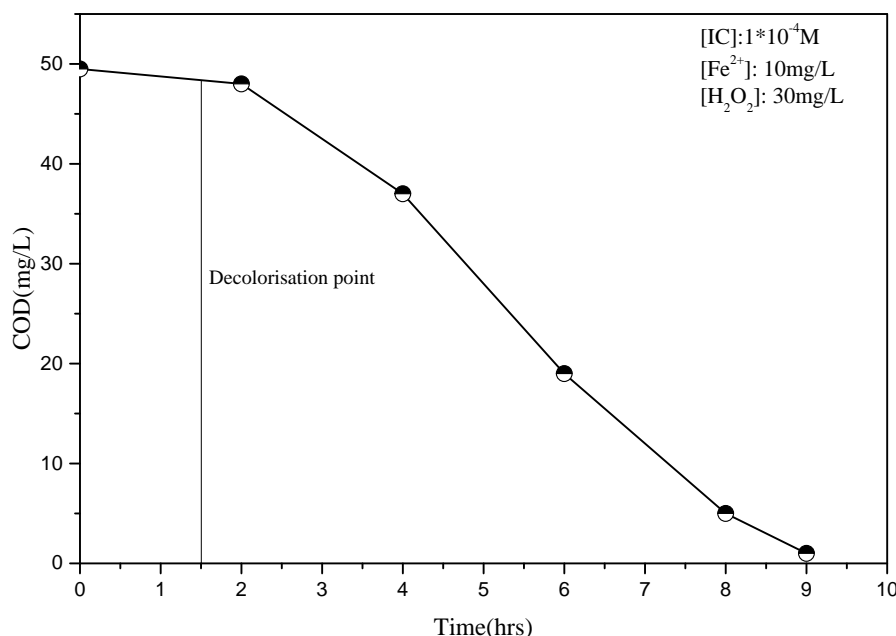


Fig 15: Mineralization of IC during Fenton degradation

As seen in the figure, the COD remains fairly steady till decolorization of IC and decreases steeply thereafter indicating that at least some of the intermediates formed during the decolorization are not stable and get mineralized fast. Continuation of the Fenton reaction results in complete mineralization. Hence it may be confirmed that Fenton process is an efficient inexpensive method for the complete removal of IC pollutant from water. Various intermediates present in the system at 50% degradation are analyzed by LC/MS and the results

are shown in table 2. Eventually these intermediates also get degraded as seen from the complete elimination of COD in 9 hr. of Fenton reaction.

III.10. Activation of Fenton process by external energy sources

The efficiency of Fenton process has been reported to be enhanced by activation using external energy sources[26]. In this context, the application of three sources of energy, i.e., light (photofenton), ultrasound (sonofenton), and electrolysis (electrofenton) on the efficiency of the Fenton process for the degradation of IC is tested and the results are as follows:

III.10.1.Solar Photofenton process

The time taken for complete decolorization of IC in presence of Fenton reagent is reduced from 90 min. to 15min. under solar irradiation. Presence of ZnO in classic Fenton has been proven to decrease the efficiency of the process, primarily due to change in pH (see Section III.7). However, being a good solar photocatalyst, ZnO is likely to enhance the efficiency of Fenton process under sunlight. This possibility is tested under solar Fenton and the results of decolorization of IC are compared with and without ZnO under different conditions (figure 16).The efficiency of decolorization is in the order:

Solar Fenton > Solar photocatalytic Fenton in presence of ZnO (pH adjusted to the regular Fenton pH) > Fenton > ZnO Photocatalysis>photocatalytic Fenton in presence of ZnO (no pH adjustment).

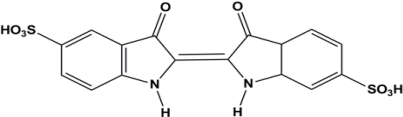
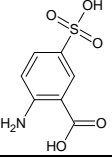
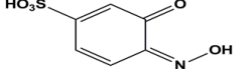
The results clearly demonstrate the superiority of the solar Fenton process for the degradation of IC. The presence of ZnO is unable to accelerate the degradation and overtake the efficiency of the simple photofenton process. This is probably because the extra OH radicals generated by the photocatalytic action of ZnO is not enough to compensate for the ZnO-inhibition in the generation of OH radicals by the interaction of Fe^{2+} and H_2O_2 . Hence it may be presumed that Solar Fenton process is highly efficient for the decontamination of water from traces of IC pollutants.

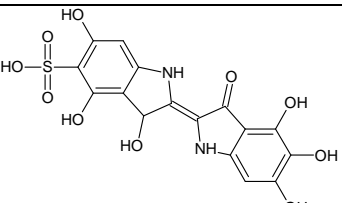
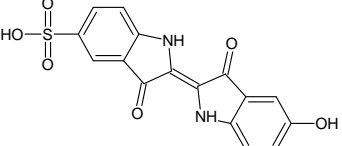
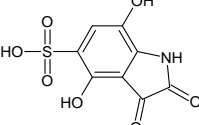
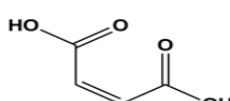
III.10.2. Sonofenton Process

The effect of ultrasound (US) with frequency 350 KHz and power 80W as a source of activation on the Fenton degradation of IC is investigated.Experiments were carried out under the conditions optimized for normal Fenton. The results are shown in figure 17.

The time taken for complete decolorization of IC under sonofenton(30 min.) is much less compared to sono only (75 min.) or Fenton only (90 min.). The results also show that the combined process (sonofenton) is synergistic and is worth investigating in depth.

Table 2: Intermediates formed during the Fenton degradation of IC

m/z	Molecular structure
422	
216	
202	
226	
243	

423	
225	
357	
258	
116	

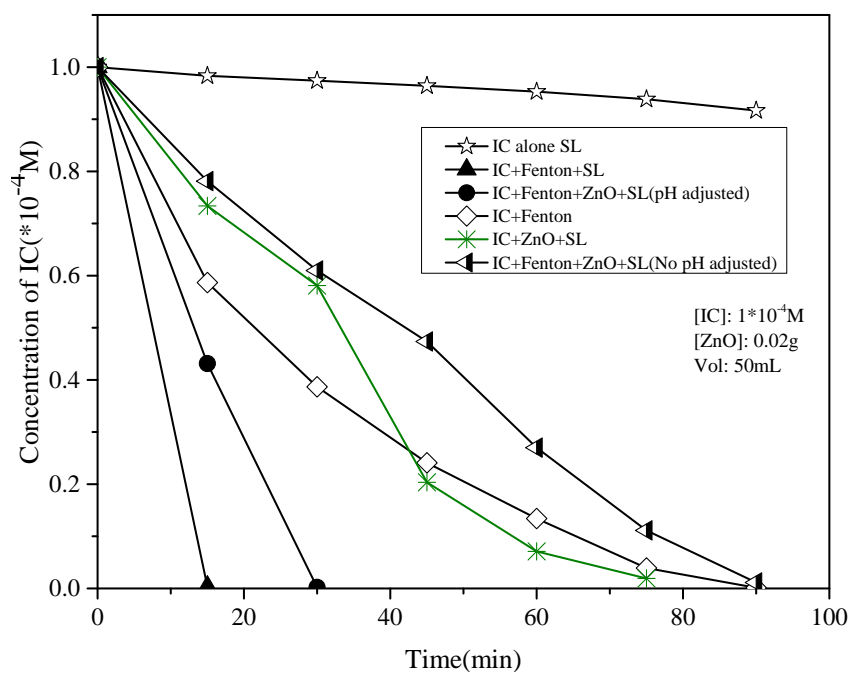


Fig 16: Comparison of different solar photoFenton processes for the degradation of IC

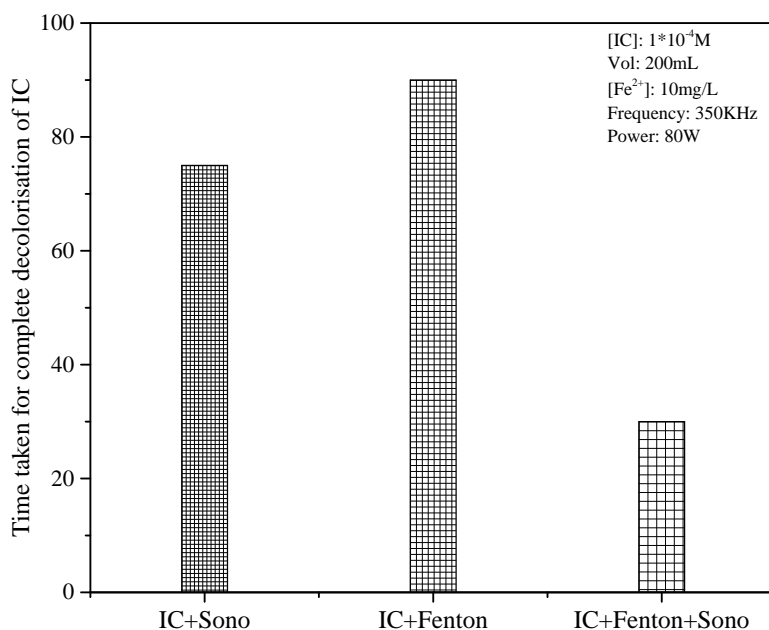
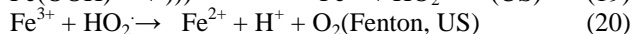
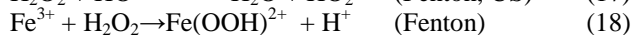
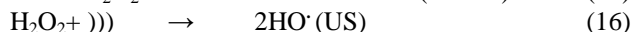
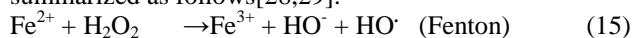
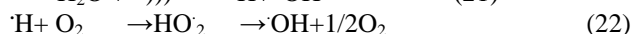
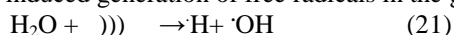


Fig.17: Comparison of Fenton and SonoFenton processes for the degradation of IC

Ultrasound coupled with Fenton's reagent utilizes the advantages of the two methods to generate more $\cdot\text{OH}$ radicals which can effectively enhance the degradation of IC. Also cavitation under US gives additional activation through pyrolysis, which will enhance the degradation. In heterogeneous sono-Fenton process, acoustic cavitation can enhance mass transfer, dispersion, and deaggregation of particles. [27]. The increased formation of reactive $\cdot\text{OH}$ radicals under Fenton, Ultrasound irradiation and the combination process can be summarized as follows [28,29]:



In Fenton process, the propagation of US waves into the media results in two effects, i.e., enhanced interaction of Fe^{2+} with H_2O_2 and enhanced regeneration of Fe^{2+} in the system. This leads to more efficient generation of $\cdot\text{OH}$ radicals and consequently enhanced degradation of the pollutant. This is in addition to the US-induced generation of free radicals in the gas bubble and/or in the bulk of the system as follows:



Various parameters relevant for US-Fenton process such as power and frequency of the US, relative concentration of H_2O_2 and Fe^{2+} , presence of sono active catalyst, effect of cross-contaminants on the efficiency of the process etc. can be further evaluated and optimized for improving the efficiency of the process which is beyond the scope of the current study.

III.10.3. ElectroFenton (EF) Process

Earlier studies have shown that electrochemical process can be a viable AOP for the mineralization of pollutants from water [30-32]. Combination of electrochemical and Fenton process (EF) is another hybrid like photo-Fenton process worth investigating for enhanced efficiency of the Fenton process. Appropriately designed EF process has the advantage of in situ generation of H_2O_2 and Fe^{2+} and can thus avoid the drawbacks of the chemical Fenton process. In the electrochemically assisted Fenton process also, the $\cdot\text{OH}$ is produced via the usual Fenton's reaction. However in this case, Fenton's reagent is electrochemically generated in situ, thus avoiding the use of high quantities of H_2O_2 and iron (II) salt. It was developed and extensively applied over the last two decades [33,34].

In the present study, the electrolytic degradation of IC is combined with the classic Fenton process. Bismuth doped titanium dioxide on titanium anode and carbonfelt cathode in presence of sodium sulfate supporting electrolyte which has been proven to be an efficient electrochemical system for the degradation of IC is chosen for the study. Fe^{2+} is added to the system and together with the insitu formed H_2O_2 a Fenton like system is evolved. The degradation of the dye is faster in the case of electroFenton compared with that of the normal electrolytic or Fenton reaction. The results are shown in figure 18. As in the case of sono-Fenton and photo-Fenton, electro-Fenton process also is synergistic.

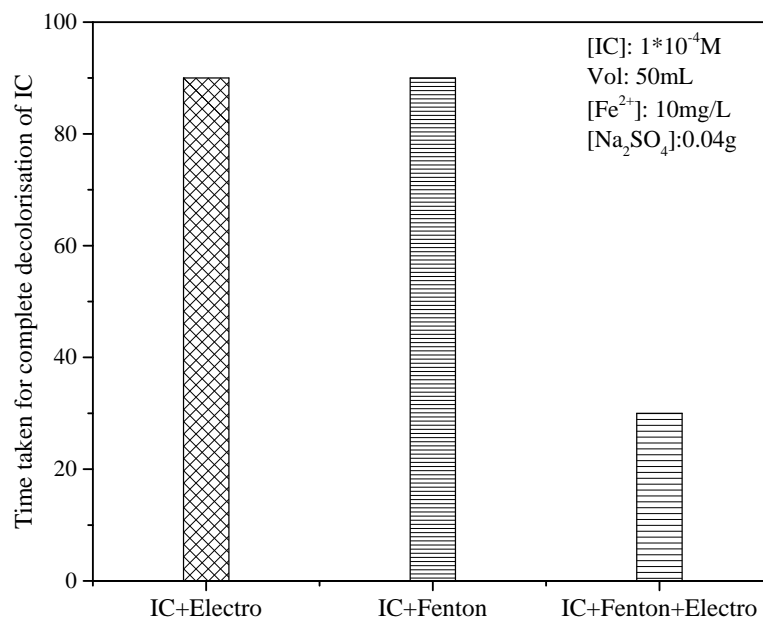


Fig.18: Comparison of Fenton and electro-Fenton process for the degradation of IC

In the electro-Fenton process, pollutants are destroyed by the action of Fenton reagent in the bulk as well as the anodic oxidation at the anode surface. Hence the insitu H_2O_2 production is slower because O_2 solubility in water is low and the current efficiency also is low at lower pH of the Fenton reagent. One way to sustain the efficiency of electro-Fenton process is to continuously add H_2O_2 and Fe^{2+} . However the efficiency of Fe^{2+} regeneration from Fe^{3+} is slow even at optimal current density. Consequently, the rate of degradation will slow down with time. The efficiency of the electro-Fenton process depends on the nature of the electrodes, pH, catalyst concentration, electrolyte, dissolved O_2 level, temperature, current density etc. Detailed investigation on these factors will be important in identifying the optimum conditions. However this is beyond the scope of the current study and is not undertaken here.

III.10.4. Comparison of different hybrid Fenton processes for the decolorization of IC

Comparison of various types of Fenton processes for the decolorization of IC is shown in figure 19. The combination process is more efficient and synergistic compared to simple Fenton process with the efficiency being in the order;

Photofenton > Electrofenton \approx Sonofenton \approx Photocatalytic (ZnO) fenton (pH adjusted) > Photocatalytic (ZnO) fenton (no pH adjustment) > Fenton

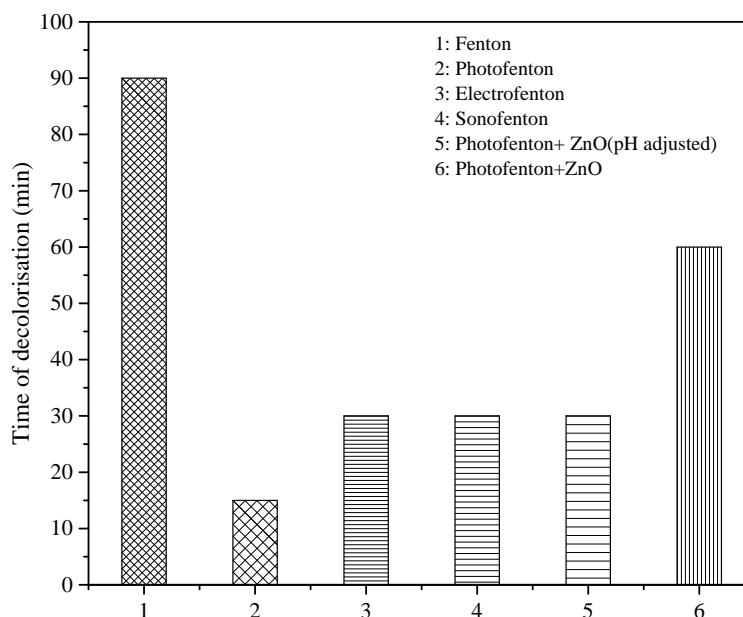


Fig.19: Comparison of different combinations of Fenton process for the decolorisation of IC

Comparative rate and synergy of the combination process over respective individual processes are computed and tabulated in Table 3.

Table 3: Comparative rate of degradation of IC under Fenton and combination Fenton process

Process	Initial rate of degradation ($\times 10^{-7}$ mg/L/min)	Synergy
Fenton	13.7	-
Photolysis	8.7	-
Solar PhotoFenton	33.0	1.47
Sono	2.3	-
SonoFenton	19.0	1.19
Electro	8.3	-
ElectroFenton	23.0	1.06

However, the synergy decreases with time of reaction, possibly because of the formation of intermediates which also compete with the substrate for the reactive free radicals. The results in Fig.19 reveal that solar photo-Fenton is the most efficient process (among those tested here) for the decolorization of IC. Photocatalytic Fenton with ZnO as the catalyst (after adjusting the pH to that of classic Fenton) is only as efficient as electro and sono-Fenton. Presence of ZnO increases the pH of the system which is detrimental to the efficiency of Fenton process as has been discussed earlier. Hence adjustment of the pH to the optimum pH of normal Fenton is important in any combination Fenton process. In any case, presence of a solar photocatalyst such as ZnO may be beneficial for the efficiency of the solar process, which is verified by testing the role of solar photocatalysis in the mineralization of IC (which is verified by COD reduction).

III.10.5. Comparison of the COD reduction using different combinations of Fenton reaction

The efficiency of various Fenton processes for the total mineralization of IC is verified experimentally by reduction in chemical oxygen demand (COD) of the system under respective processes and the results are presented in figure 20.

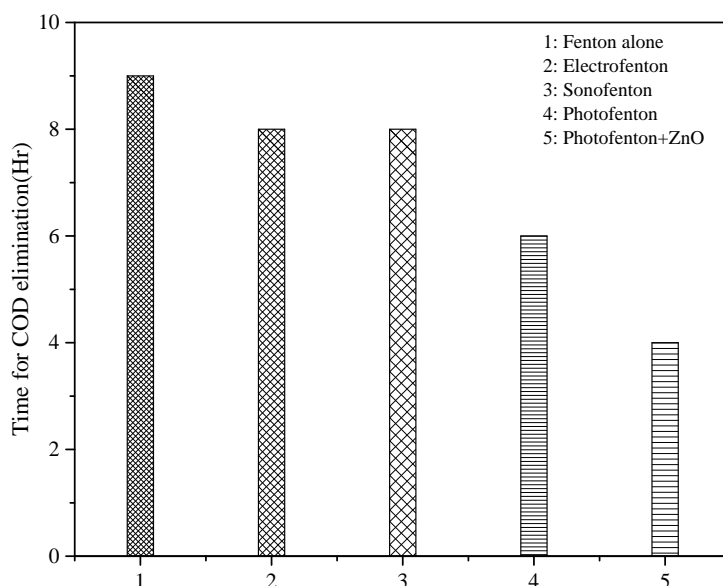


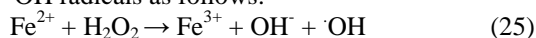
Fig.20: Comparison of the COD reduction using different combinations of Fenton process

Solar photocatalyticfenton with ZnO catalyst is identified as the most efficient process for COD reduction. The comparative efficiency is in the order;

ZnO-solar photocatalyticfenton>Photofenton>Sonofenton \approx Electrofenton> Fenton.

III.11. General Mechanism

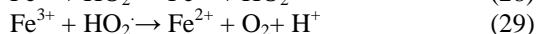
The first step in the Fenton reaction is the oxidation of ferrous to ferric ions and decomposition of H_2O_2 into $\cdot OH$ radicals as follows:



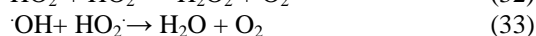
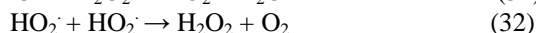
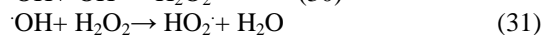
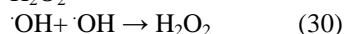
The Fe^{3+} is reduced by excess H_2O_2 to regenerate Fe^{2+} and more free radicals as in reaction (26)



Other possible reactions are:



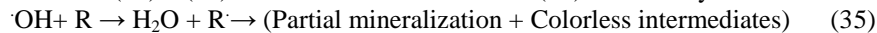
The highly reactive free radicals may get deactivated by self-scavenging, interaction with other radicals and/or H_2O_2



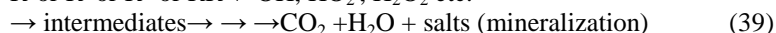
In the absence of any organic substrate to be oxidized, H_2O_2 self-decomposes as in reaction (34).



In presence of organic molecules (R), such as IC in the current instance, the degradation can take place as in reactions (36) – (37) or dimerization occurs as in (38). Eventually mineralization takes place as in (39).



R^{\cdot} or R^- or R^+ or $RR + \cdot OH, HO_2\cdot, H_2O_2$ etc.



Thus at room temperature and pressure itself, a series of reactive free radicals are generated and these can interact with the dye in a variety of ways to produce intermediates and eventually mineralize the pollutant. The decolorization/mineralization is accelerated by external energy sources such as UV light, sunlight, ultrasound, microwave, electrolysis etc. Relevant mechanisms are discussed in respective sections in this paper.

IV. CONCLUSION

Classic Fenton reaction involving use of simple Fe^{2+} salt and H_2O_2 at the optimized ratio under ambient conditions is revisited and used as an effective advanced oxidation technique for the removal of traces of the toxic dye pollutant Indigo Carmine from water. pH is a critical parameter in the process. Many naturally occurring contaminant salts in water adversely affect the mineralization of the dye. The volume of the reactants is not a constraint as long as the necessary ingredients are available in the required ratio. These factors together with the relative simplicity of the process make Fenton reaction a promising candidate for economic and efficient waste water treatment. ZnO which is an efficient photocatalyst in many AOPs inhibit the Fenton degradation in the presence as well as absence of light, probably due to change in pH and the presence of suspended particles which inhibit the interaction between Fe^{2+} and H_2O_2 and thereby the formation of $\cdot\text{OH}$. The degradation is enhanced synergistically by external sources of activation such as sunlight, ultrasound and electrochemical energy. Photocatalytic-Fenton process with ZnO as the catalyst is more efficient than other processes including photo-Fenton for the mineralization of the dye pollutant. Various intermediates formed during the degradation are identified by LC/MS.

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