

## **Co<sub>3</sub>O<sub>4</sub> mediated microwave catalysis: A new innovative advanced oxidation process (AOP) for the removal of dye pollutants from water**

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**Abstract:** *MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> are identified as two highly MW active catalysts for the degradation and eventual mineralization of trace amounts of the toxic pollutant dye IC in water. The degradation is much faster compared to identical conventional heating conditions suggesting that the MW effect is not just thermal. 'Specific effects' and 'athermal effects' of MW also contribute to the degradation of the pollutant. The effect of pH on the degradation is only marginal over a wide range of 4-10, thereby proving the ability of MW to modify the pH effect in many cases. Addition of H<sub>2</sub>O<sub>2</sub> has limited influence on the MW-assisted degradation at lower concentration range while it has a positive enhancing effect at higher concentrations. Another oxidant persulphate enhances the MW/Co<sub>3</sub>O<sub>4</sub> degradation. Natural water contaminants like salts/anions also do not affect the degradation significantly. The microwave radiation may not be affecting the surface characteristics of the oxides as in the case of other AOPs even though the lattice oxygen removed from the catalyst plays significant role in the degradation. This lattice oxygen vacancy is later replenished by dissolved oxygen taking MnO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> to its respective original composition.*

**Key words:** *Microwave; Cobalt oxide; Manganese dioxide; Indigo carmine, Hydrogen peroxide,*

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### **I. Introduction**

In recent years, microwave (MW) radiation based processes are extensively investigated for a variety of applications such as inorganic and organic synthesis, polymerization, food sterilization, environmental remediation, waste treatment etc. [1- 4]. Specific advantages of MW include; capability for molecular level heating, increased selectivity of reaction, lowering of activation energy, decreased reaction times and ease of control. MW, individually as well as in combination with other energy sources, has been increasingly investigated as an advanced oxidation process (AOP) for wastewater treatment [5--8]. Combination of MW with oxidants such as H<sub>2</sub>O<sub>2</sub> and persulphate (PS:S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) has been reported to be efficient for the mineralization of many recalcitrant organic compounds such as dyes, phenolic compounds, pesticides and sulphonated aromatic compounds, which are non-degradable by conventional methods [6]. The heterogeneous processes occurring at solid/solid, solid/liquid, solid/gas or liquid/gas interfaces in MW assisted catalytic reactions can be beneficially tailored for environmental remediation of toxic and hazardous materials.

Being a low energy radiation with  $E = 1.6 \times 10^{-3} \text{eV}$ , MW alone may not be able to degrade and mineralize many pollutants. Horikoshi and Serpone [9] demonstrated that MW irradiation can accelerate the photocatalytic degradation of RhB in presence of UV/TiO<sub>2</sub>. Combination of MW with photocatalysis/H<sub>2</sub>O<sub>2</sub> has been reported in the case of oxidation of ethylene over TiO<sub>2</sub>/ZrO<sub>2</sub> [10], oxidative decomposition of aqueous phenol by UV/H<sub>2</sub>O<sub>2</sub> [5] and carbofuran degradation by H<sub>2</sub>O<sub>2</sub> process [6].

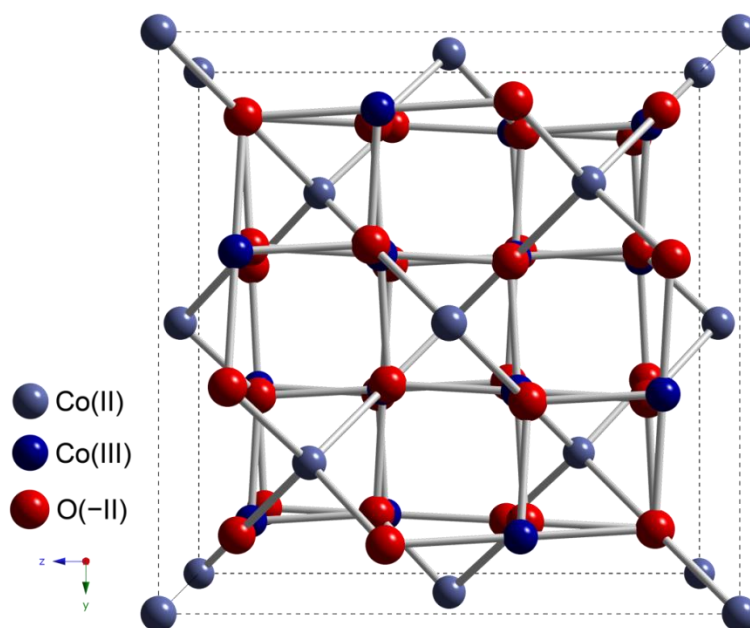
Most of the organic compounds do not absorb electromagnetic energy in the S-band (4-8 GHz) of the MW which is a major limitation for its application in AOPs. This needs to be overcome if MW based reactions are to be used as AOPs. One possible option is the identification of appropriate materials that can absorb considerable amount of MW and then transfer the energy to the reactants [11-13]. In addition to the widely recognized thermal role, MW could also induce organization of the irradiated medium through what is known as 'athermal', 'nonthermal' or "specific" effect of electromagnetic radiation [14,15]. In this context the dielectric constant of the material which

determines its ability to be polarized by an electric field is important [15]. Interaction of MW with dipolar molecules or ionic species results in rapid heating [16]. However, the response of various materials to MW is diverse. Certain materials such as copper reflect MW while some other materials such as S is transparent to MW. Water can absorb MW strongly which makes aqueous pollutants amenable to catalytic degradation by MW. Being an electromagnetic radiation, MW has both electric field and magnetic field component. The electric field component is responsible for the dielectric heating which is caused by dipolar polarization mechanism as well as conduction mechanism. Under the dipolar polarization mechanism, heat is generated in polar molecules. When exposed to oscillating electromagnetic field of matching frequency, polar molecules tend to align themselves in phase with the field. However, the intermolecular forces resist the alignment. This results in random motion of particles which generate heat [17]. The dipolar polarization can generate heat either by interaction between polar solvent molecules such as water or by interaction between polar solute molecules. MW radiation has the appropriate frequency (0.3-30 GHz) to oscillate polar molecules and lead to adequate inter-particle interaction resulting in heating the solution. Hence MW is ideal for simple heating of polar solutions. At the same time, the energy in a MW photon is very low, i.e. of the order of 0.037 kcal/mol which is very low compared to the energy needed to break a molecular bond (80-120 kcal/mol). Hence, in most cases, MW irradiation leaves the structure of the molecule unaffected.

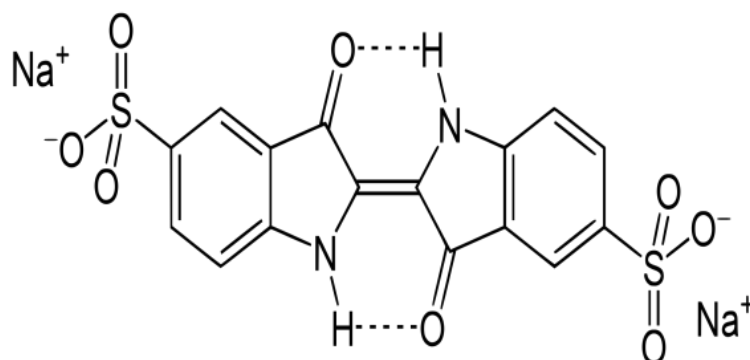
Under the conduction mechanism of MW heating, the electric current generated by oscillation of electrons or ions during MW irradiation faces internal resistance leading to heating of the semiconductor. Hence it is not very useful in the case of materials with very high conductivity, since most of the MW energy that is incident on them is reflected. Hence MW will be especially effective for the degradation of polar solutes. When the substrate is not sufficiently polar, a polar solvent like water can assist in absorbing the MW radiation and heating the medium. This has prompted us to investigate the MW energy as a source of activation for the degradation and mineralization of chemical pollutants in water.

Earlier studies have shown that  $MnO_2$  which has dielectric constant of  $\sim 10000$  is excellent as a MW catalyst for the degradation organic pollutants in water [8,18].  $MnO_2$  has very good coupling with MW radiation, has excellent porosity, semiconductivity and mixed-valent properties which make it a probable MW catalyst for the degradation of a variety of pollutants. Another semiconductor shown to have comparable physical characteristics is  $Co_3O_4$  [18].  $Co_3O_4$  is a magnetic p-type semiconductor with wide application in solid state sensors, electro chromic devices, heterogeneous catalysis etc.  $Co_3O_4$  can be prepared in different nanostructures such as nanotubes, nano rods, nano fibres, hollow nanostructures etc and offers the potential for wide variety of applications. Considering these, the application of  $Co_3O_4$  as an MW catalyst for the degradation of one of the widely used special application dye, i.e. Indigo carmine (IC) is examined in the current study. Typical spinel structure of  $Co_3O_4$  is given in Figure.1

Indigo Carmine (3,3'-dioxo-1,3,1',3'-tetrahydro-[2,2']-bi-indolylidene-5,5'-disulphonic acid disodium salt) is an important industrial dye used for dyeing of clothes and also for medical diagnostic purposes. It can also help more precise target biopsies since the homogeneously stained or unstained areas can be correlated with intraepithelial neoplasia [19]. The chemical structure of IC is as in Figure 2.



**Figure 1.** Spinel structure of  $\text{Co}_3\text{O}_4$



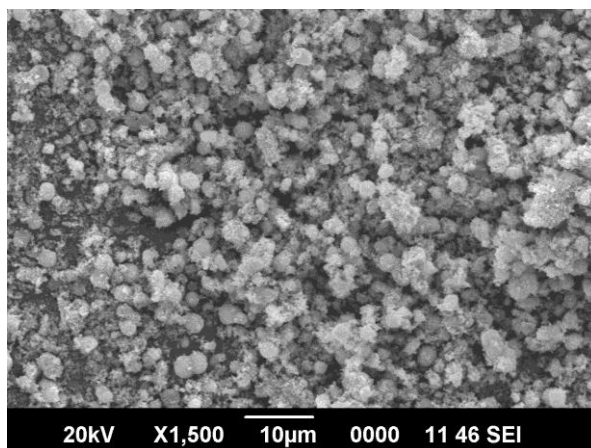
**Figure 2.** Structure of Indigo Carmine

IC is highly toxic, carcinogenic and has the potential to cause permanent injury to eyes. It can also lead to reproductive, developmental, neuro and acute toxicity. Other health effects include possible tumors at the site of application, cardiovascular and respiratory effects and gastrointestinal irritation [20]. Extensive application of the dye will naturally lead to environmental contamination through different routes, in particular water. Many investigations aimed at the removal of the dye from water have been reported [21-25]. Most of these are based on Advanced Oxidation Processes (AOP), especially photocatalysis.

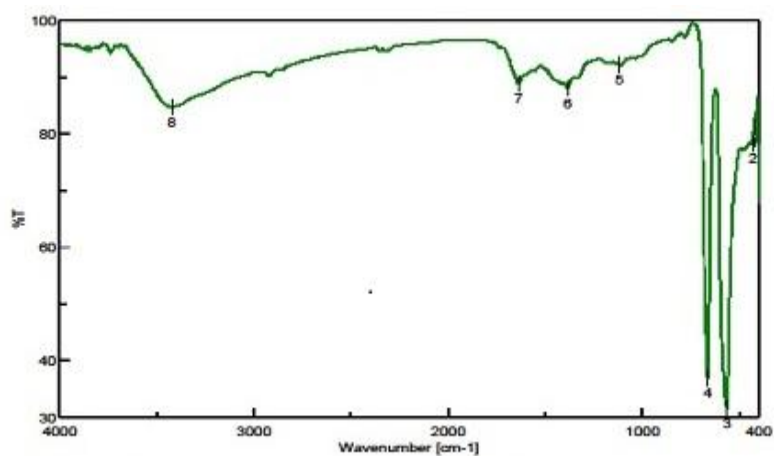
In the present study we are reporting the results of our investigations on the application of Microwave catalysis with  $\text{Co}_3\text{O}_4$  as the catalyst for the removal of IC in small concentrations from water. The efficacy of the MW based technique is evaluated by examining the degradation of IC under various reaction conditions and identifying the optimum parameters. The results are compared with those under identical conditions in presence of  $\text{MnO}_2$ .

## II. Materials and Methods

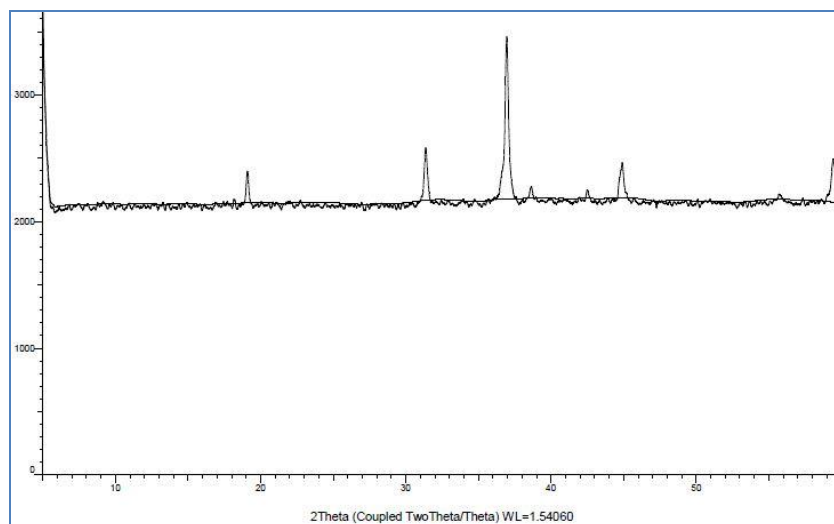
MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> used in the study were supplied by Merck India Limited. The particles were approximately spherical and nonporous with > 99% purity. The surface area of both MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> as determined by the BET method is ~31 m<sup>2</sup>/g. Typical SEM image (recorded by using JEOL Model JSM-6390 LV) is shown in Figure 3A. Typical FT-IR spectrum (recorded by FT-IR Jasspo 4100 type A) and XRD pattern (recorded by Bruker D2 Phaser, applying monochromatized Cu K<sub>α</sub> radiation) are shown in Fig 3B and C respectively.



**Figure 3A.** SEM image of Co<sub>3</sub>O<sub>4</sub>



**Figure 3B** FT-IR Spectrum of Co<sub>3</sub>O<sub>4</sub>



**Figure 3C** XRD pattern of Co<sub>3</sub>O<sub>4</sub>

The particle size was analysed using Malvern Mastersizer 3000. The average particle size of MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> was 3.2 and 4.7 μm respectively. The pore volume of both was ~0.05cm<sup>3</sup>/g.

Indigo carmine (AnalaR Extra Pure Grade > 99.5% purity) from Sisco Research Laboratories Pvt. Ltd (India) was used as such without further purification. Doubly distilled water was used in all the experiments. All other chemicals were of AnalaR Grade or equivalent.

Adsorption studies were performed as follows [26]:

A fixed amount (0.1 g) of the catalyst was added to 100 ml of IC solution in a 250 ml reaction flask and the pH was adjusted as required. The suspension was agitated continuously at constant temperature of 29 ± 1<sup>o</sup>C for 2 hrs to achieve equilibrium. The suspension was then kept undisturbed for 2 hr and was then centrifuged at 3000 rpm for 10 min. After centrifugation the concentration of IC in the supernatant was determined colorimetrically. Keeping the suspension overnight before centrifuging did not make any significant difference indicating that the 2 hr period is adequate to complete the adsorption.

The adsorbate uptake was calculated from the relation

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where C<sub>0</sub> is the initial adsorbate concentration (mg/L), C<sub>e</sub> is the equilibrium adsorbate concentration in solution (mg/L), V is the volume of the solution in liter, W is the mass of the adsorbent in gram and q<sub>e</sub> is the amount adsorbed in mg per gram of the adsorbent.

The MW experiments were performed using simple pyrex glass reactor and aqueous solutions of IC of the desired concentration. The temperature was monitored using digital pyrometer. In the case of experiments with added catalysts, specified quantity of the catalyst was suspended in the dye solution and kept as suspension by periodic mechanical mixing. A microwave oven of 2450 MHz frequency and variable power upto 500 W was used in the experiments. The reactor was placed on the turn-table in the microwave oven as is done usually. Upto eight reactors could be placed in the oven at a time. As and when required, an in-house designed jacketed reactor with provision for circulating water was used for specific experiments. Experiments were initiated by supplying the desired power to the system. The reaction temperature was normally kept at 35 ± 2<sup>o</sup>C and controlled by regulating coolant water flow/switching off the MW oven periodically. For experiments with extra additives appropriate quantity of the additive solution/suspension/solid in water was introduced into the IC

solution such that the net concentration of respective components will be as desired. Periodically samples were drawn, centrifuged in the case of experiments with catalysts to remove the suspended materials and analysed for IC using Spectrophotometry at 608 nm. Whenever required,  $H_2O_2$  concentration is determined by standard iodometry. Conventional Heating (CH) experiments were conducted in a water bath instead of the microwave oven under otherwise identical conditions. Room Temperature (RT) experiments are done by simply keeping the reaction system under exactly identical conditions but without CH or MW irradiation. The removal efficiency (%) was calculated by applying the following equation

$$\text{Removal efficiency} = [(C_0 - C) / C_0] \times 100 \quad (2)$$

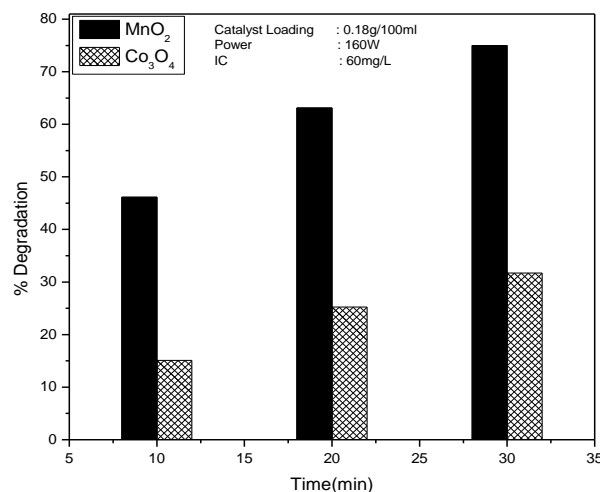
Where  $C_0$  is the initial IC content and  $C$  is the content retained in solution at any point in time.

### III. Results and Discussion

$MnO_2$  was characterized and its identity was confirmed as reported earlier [18]. Characterization by similar techniques confirmed the identity of  $Co_3O_4$  also. The physicochemical parameters as measured are provided in section 2. SEM image (Figure 3A) shows generally uniform shaped particles with porous structure and smooth surface. FTIR spectrum (Figure 3B) reveals characteristic absorption peaks for metal-oxygen bonding. The peaks around 430 and 564  $cm^{-1}$  may be originating from the stretching vibrations of the metal-oxygen bond characteristic of spinel metal oxide [28]. The band at 564  $cm^{-1}$  may be associated with the  $OB_3$  vibration in the spinel lattice where B denotes  $Co^{3+}$  in an octahedral hole. The band at 662  $cm^{-1}$  can be attributed to the  $ABO_3$  vibration where A denotes the  $Co^{2+}$  in a tetrahedral hole. The data shows that the presence of small amounts of oxides of Co other than the  $Co_3O_4$  cannot be ruled out.

The XRD pattern (Figure 3C) showed typical diffraction peaks characteristic of  $Co_3O_4$  as compared with literature. The position of the characteristic peaks at 2Theta (degree) of 59, 56, 45, 39, 37, 31 and 18 and their relative intensity are in good agreement with the literature data [27] from which it is inferred that the material has good crystalline structure. All the diffraction peaks are distinct and can be indexed to pure cubic phase of  $Co_3O_4$ . No peaks from other phases are detected indicating that the oxide has high purity.

Comparison of  $Co_3O_4$  with  $MnO_2$ , which has been proven to be one of the most efficient MW catalysts for the decontamination of water from chemical pollutants [8,18] shows that the former is also MW active, the efficiency being ~ 50% of the latter. See Figure 4.



**Figure 4.** Comparative efficiency of  $MnO_2$  and  $Co_3O_4$  for the degradation of IC.

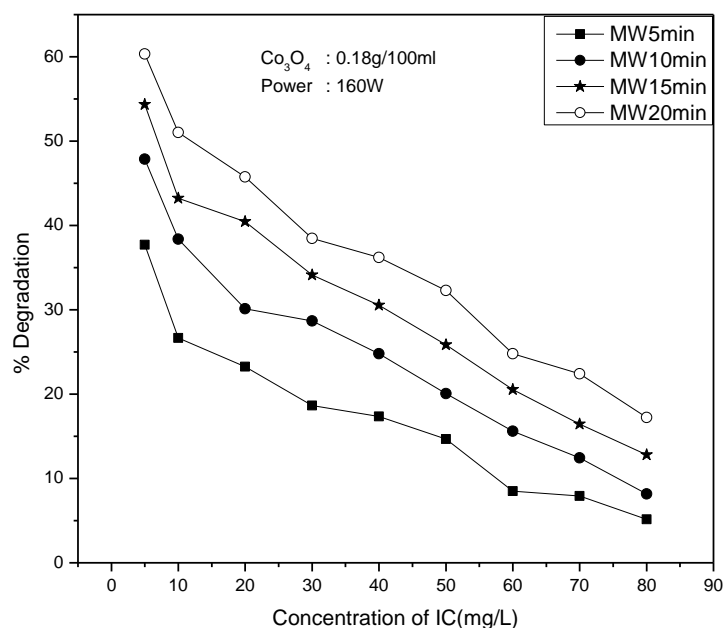
Exploratory experiments showed that conventional heating (CH) under identical conditions resulted in ~ 10% decrease in the concentration of the dye as against ~35% under MW. The removal of the dye under CH conditions does not increase with time and remains stable throughout the period of experiment. The decrease in the concentration of the dye at room temperature (RT) of  $29\pm 2^{\circ}\text{C}$  is also ~10%. This shows that the decrease is due to simple adsorption and it may be presumed that conventional heating in presence of  $\text{Co}_3\text{O}_4$  (CH/ $\text{Co}_3\text{O}_4$ ) does not degrade the dye appreciably. Adsorption measurements at various concentrations at various times of contact also show decrease in concentration in the same range. This clearly demonstrates that the role of MW in the degradation of IC in presence of  $\text{Co}_3\text{O}_4$  is not simply thermal. Hence the  $\text{Co}_3\text{O}_4$  catalysed MW (MW/ $\text{Co}_3\text{O}_4$ ) degradation of IC is investigated in detail in order to identify optimum reaction parameters, including the influence of externally added components and the main intermediates/products. Wherever relevant, the results are compared with those in presence of  $\text{MnO}_2$

### **3.1. Effect of $\text{Co}_3\text{O}_4$ dosage**

Investigations on the effect of  $\text{Co}_3\text{O}_4$  dosage on the degradation of IC shows that the degradation increases steadily with increase in loading and reaches an optimum at 1.8 g/L. At higher loadings there will be more number of adsorption sites and hence better adsorption of the dye. This will lead to more effective MW activation on the dye molecule and consequent degradation. However, at very high loadings in the same reactor, the catalyst particles may get aggregated causing relative decrease in the number of available active surface sites accessible per gram of the catalyst. The particles cannot be fully and effectively suspended beyond a particular loading in a particular reactor which also leads to suboptimal penetration of radiation. Hence the degradation levels off or even decreases at higher loadings. However, the optimum catalyst loading is applicable under well defined experimental conditions only as it will depend on not only the physicochemical characteristics of the reaction medium, but also on the size, shape and geometry of the reaction assembly. Hence, for each reactor configuration the optimization has to be made separately. Since the optimum loading of  $\text{Co}_3\text{O}_4$  under MW is 1.8g/L, all further experiments were carried out with this dosage. The optimum dosage under identical conditions is same, i.e. 1.8g/L, in the case of  $\text{MnO}_2$  also.

### **3.2. Effect of concentration of IC**

The efficiency of most AOP processes for the degradation of water pollutants depends on the concentration of the substrate. This parameter is examined in detail. The % degradation of IC at various concentrations (5-80 mg/L), under otherwise identical conditions in MW/ $\text{Co}_3\text{O}_4$  systems is shown in figure 5.



**Figure 5.** Percentage degradation Vs Concentration of IC at different time intervals.

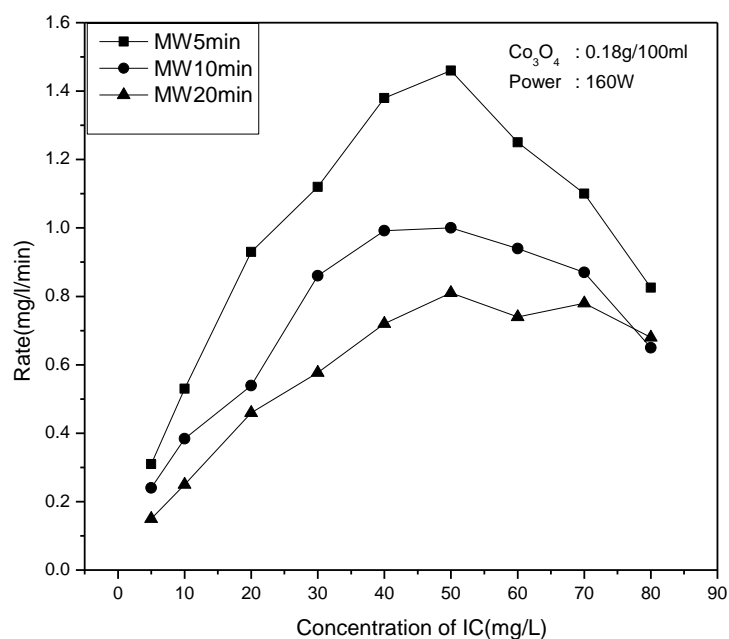
As expected, the percentage degradation decreases with increases in concentration. However, the rate of degradation increases with increase in concentration and reaches an optimum at 40-50 mg/L of IC. Above this concentration, the rate decreases, the decreasing trend being very steep in the case of initial rate in the first five minutes. The trend remains more or less the same after different durations of irradiation. The rates of degradation as a function of concentration at various times of irradiation is computed and shown in figure 6. The rate decreases with time at all concentrations possibly due to relative decrease in the concentration of substrate and competition from various reaction intermediates for catalyst sites. Variation in the chemistry of the reaction system with time may affect the efficiency of MW to penetrate and thus the ability to activate adequate number of surface sites.

The effect of concentration of IC on the kinetics of the degradation is similar to most of the AOP systems which follow variable kinetics, with pseudo first order at lower concentrations and eventually zero order at higher concentrations.

### 3.3. Effect of MW power

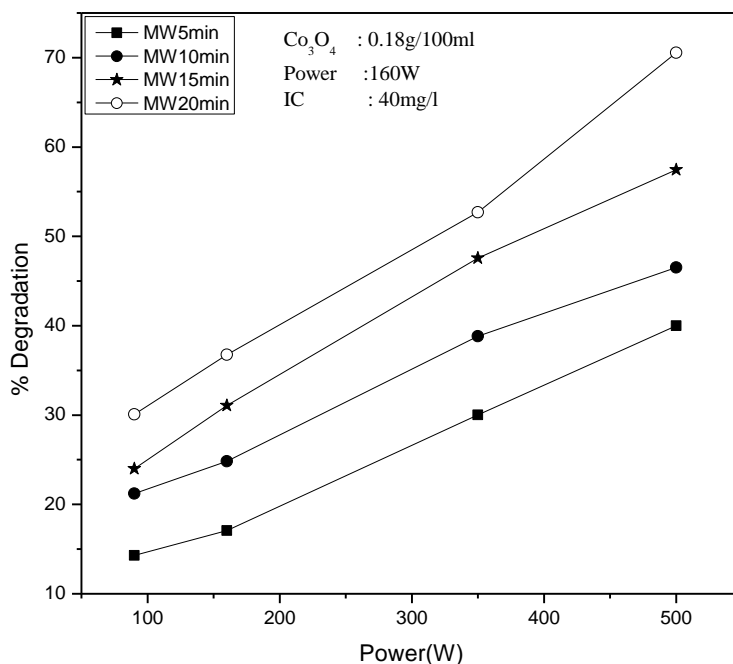
Power of MW is reported to influence the processes driven by MW. Earlier studies from our laboratory showed that the MW initiated degradation of organic pollutants in water is enhanced





**Figure 6.** Rate of degradation of IC at various concentrations.

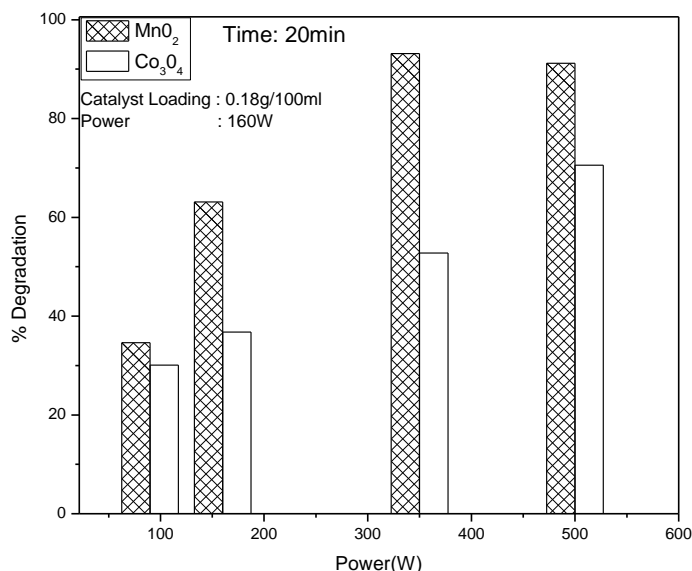
by increase in power [18,29]. This possibility is tested with  $\text{Co}_3\text{O}_4$  catalyst and the results are shown in Figure. 7A.



**Figure 7A.** Effect of MW power on the degradation of IC.

When the power increased ~ 4 times from 90W to 350 W, keeping all other parameters constant, the degradation in 10 minutes almost doubled from ~ 22% to ~ 40 %. The enhancement effected in 20 minutes by increase in power from 90 to 500W was ~ 2.5 times, i.e. from ~ 30% to ~ 70 %. However, at higher MW power, the rate of heating is quite faster leading to over-volatilizing of

water during the reaction. In order to avoid this, all further experiments were carried out at 160W and in most cases, for two durations of 10 and 20 minutes. Under these conditions, the rate of degradation is proceeding at reasonable rates and can be followed more correctly and consistently. Comparison of the effect of MW power on  $\text{Co}_3\text{O}_4$  and  $\text{MnO}_2$  for the degradation of IC shows that the trend is identical, even though the latter is more efficient. Also, in the case of  $\text{MnO}_2$ , the degradation stabilises at higher power at ~ 90% in 20 minutes while it continues to increase with power throughout in the case of  $\text{Co}_3\text{O}_4$  (Figure 7B).



**Figure 7B.** Comparative effect of MW power on  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$  induced degradation of IC.

The increase in MW power is known to increase the rate of heating leading to faster attainment of higher temperature, especially in the case of  $\text{Co}_3\text{O}_4$ . Hence the degradation at higher power can be partially attributed to this. This is evident from the steeper increase in degradation when the power is increased from 350 to 500 MW. Since this steep rise is not observed in the initial stages, it can be attributed to the difference in the effect of temperature on various intermediates formed and accumulated in the system during the degradation of the pollutant. Also the effect is different in the case of  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$ . Similar results have been reported earlier by Horikoshi et al [13] and Vidya Lekshmi et al [18].

The formation of a number of reaction intermediates during the degradation of IC in similar MW systems has been confirmed by LC/MS studies. Some of the intermediates are listed in Table 1.

**TABLE 1** Intermediates formed during the MW-catalytic degradation of IC

Sl No	1	2	3	4	5
	m/z 201	m/z 217	m/z 245	m/z 227	m/z 233
Structure proposed					

Determination of the chemical oxygen demand (COD) at various intervals showed that it decreased gradually, thus indicating slow mineralization. The intermediates formed in stage 1 are getting degraded further to form a series of organic acids such as acetic acid (AceA), tartaric acid(TA), malic acid(MA), oxalic acid(OA), acrylic acid(AcrA) etc [21]. Of these, oxalic acid and acetic acid were identified as two stable final products in the present case. Preliminary studies showed that these two acids do not inhibit the degradation of IC. Actually they enhance the degradation of MW/ Co<sub>3</sub>O<sub>4</sub>/IC probably due to the enhanced MW heating efficiency of the system in their presence. Accumulation of intermediates such as OA, AceA, nitrobenzene, MA etc is already reported in AOP systems with IC [21,30]. The effect of MW may be relatively more on these intermediates than the IC. MW which is a kind of electromagnetic wave, with very small wavelength causes about 2.45 billion times of vibrations /translations/rotations of water molecules [31]. These kind of molecular movements can contribute to increasing the temperature and increasing the rate of degradation, the rates being different for different molecules.

It is also possible, as in the case of MW/MnO<sub>2</sub>/IC system, that the organic acids enhance the adsorption of IC on the catalyst resulting in more efficient MW access to the substrate molecules. Preliminary investigations on the adsorption under various conditions show that the adsorption of IC is not affected much by the organic acid intermediates. In some instances, the adsorption is moderately enhanced. This rare possibility of ‘assisted adsorption’ needs to be subjected to further investigation.

### 3.4. Effect of pH

The effect of pH on the degradation of IC in presence of MW/Co<sub>3</sub>O<sub>4</sub> and RT/Co<sub>3</sub>O<sub>4</sub> under otherwise identical conditions is shown in figure 8.

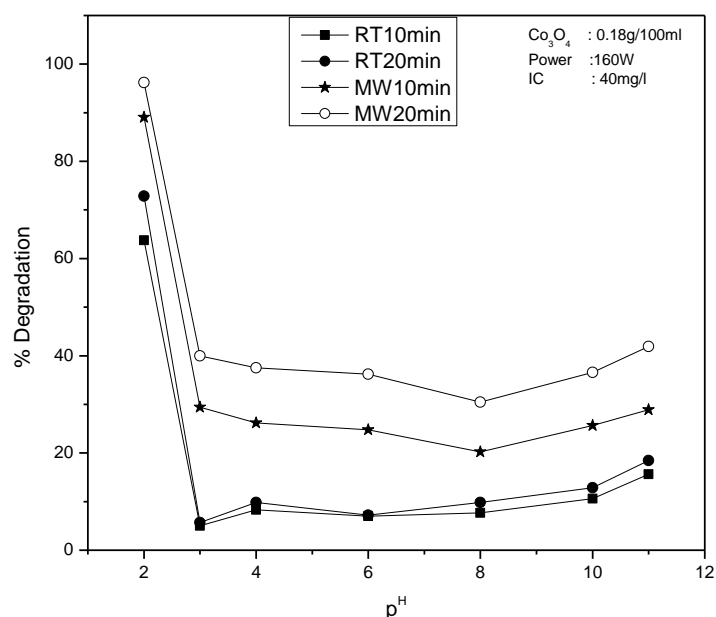


Figure 8. Effect of  $p^H$  on the degradation of IC.

At all pH, the degradation is more under MW, compared to room temperature suggesting that the variation is not simply the effect of pH. The degradation remains more or less steady in the pH range of 4-10 at the respective values in both cases. The degradation is very high at  $pH < 3$ . The drastic increase in degradation occurring below  $pH 3$  cannot be explained based on the point of zero charge (PZC) of  $\sim 7.3$  of  $Co_3O_4$  as is done in the case of AOPs involving semiconductors. Below the PZC the surface is positively charged and hence its oxidizing ability can be sharply enhanced. IC is a dianionic dye in aqueous solution and it can keep the dianionic configuration in the pH range 3-11 [24]. This implies that there will be strong electrostatic interaction between the positive catalyst surface and the dianions at lower pH which can lead to strong surface-substrate interaction and subsequent reaction. However in the current instance, the degradation remains the same from pH 3-10, with slight increase from pH 8 onwards. However, under MW, the typical zeta potential curve may not be evident as under normal photo or thermal activation processes and the zeta potential may remain positive over a wider range [32]. Hence a simple correlation between the PZC based surface charge on the catalyst and the surface-substrate interaction derived processes may not be precise in the presence of MW. The distortion of pH effect on chemical reactions by MW and other AOP processes has been reported earlier too [33]. The alleviation of pH dependence of  $MnO_2$  assisted degradation of Methylene blue in presence of MW also has been reported [34]. The high degradation under extreme pH of  $< 2$  even without MW irradiation shows that it is partly due to pH induced degradation/transformation of the dye. However, MW plays its own accelerating role, as in the case of many MW initiated processes, once the reaction is initiated. The dramatic increase in the degradation of IC at around pH 2 has been reported during the photocatalytic oxidation of the dye on Mn supported  $TiO_2$  also [24]. Since the IC keeps its anionic configuration upto around pH 11, the anionic as well as the neutral species of the hydrophilic IC can access the positively charged surface or at least come closer to it leading to interactions and subsequent reactions. At higher pH, when there are more OH ions present in the system, formation of more reactive  $\cdot OH$  radicals is possible and they can interact with the IC in close proximity to the surface or in the bulk causing the degradation.

Heterogeneous degradation of many organics is known to be initiated with the formation of precursor complex between the substrates and surface bound metal atom [35], in this case Co. Electrons are transferred from the organic compound to the surface bound Co on the  $\text{Co}_3\text{O}_4$  surface. This results in the oxidative degradation of the pollutant and concurrent reduction of Co to low-valent state. Thus  $\text{Co}_3\text{O}_4$  can also play the role of an oxidant. Dissolved  $\text{O}_2$  in solution can oxidise the Co(II) to Co(IV) again. Normally at solution  $\text{pH} > \text{PZC}$  when the surface is negatively charged, the re-adsorption of free Co(II) ions in solution back onto  $\text{Co}_3\text{O}_4$  surface can take place and this is responsible for the catalytic oxidation. In the current instance, at the natural pH of 5.6 of the reaction system,  $\text{Co}_3\text{O}_4/\text{MW}$  is ~6-8 times more efficient than  $\text{Co}_3\text{O}_4/\text{RT}$ . Comparative effect of pH on the MW degradation of IC in presence of  $\text{Co}_3\text{O}_4$  and  $\text{MnO}_2$  is shown in Fig 9.

The pH effect remains comparable in both cases. The relatively higher efficiency of  $\text{MnO}_2$  over  $\text{Co}_3\text{O}_4$  is also retained throughout. The identical pH effect in presence of two different oxides indicates that MW plays an important role in modifying the pH effect irrespective of the nature of the catalyst. However, the pH effect may be even more complex and needs to be investigated in detail.

### 3.5. Effect of added $\text{H}_2\text{O}_2$

Addition of oxidants such as  $\text{H}_2\text{O}_2$  and persulphate is known to enhance the rate of degradation of many organic pollutants by AOP techniques. The mechanism of enhancement involves the generation of highly reactive  $\cdot\text{OH}$  and other radicals capable of interacting with and degrading the pollutants. Hence the effect of addition of  $\text{H}_2\text{O}_2$  which can form OH radicals under MW irradiation on the degradation of IC is examined.

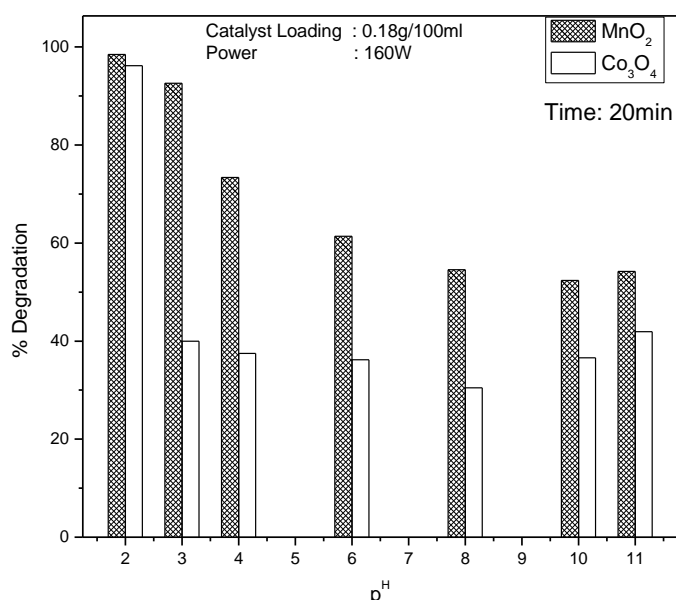
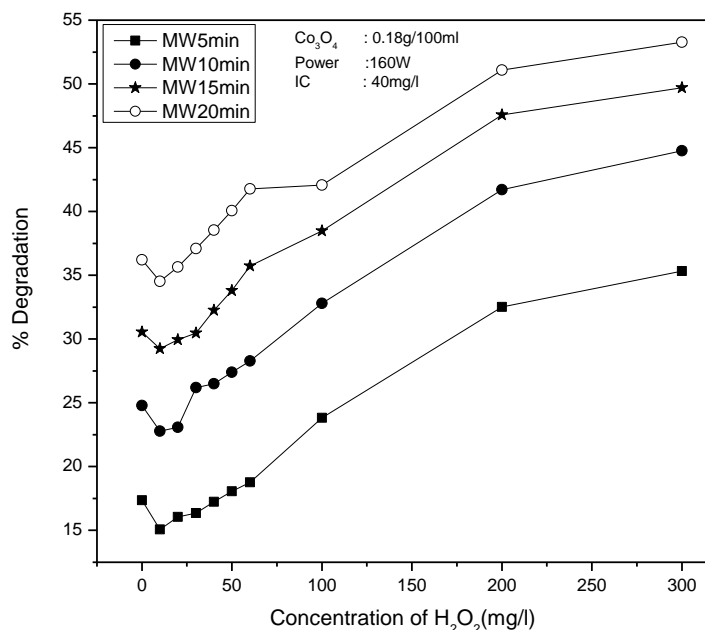


Figure 9. Comparative effect of  $\text{pH}$  in the presence of  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$ .

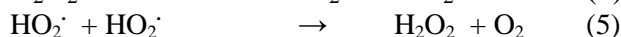
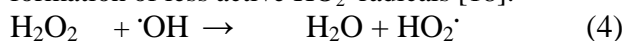


At lower concentrations of  $\text{H}_2\text{O}_2$  (5 mg/L) it acts as an inhibitor of the MW/ $\text{Co}_3\text{O}_4$  degradation of IC as shown in figure 10.

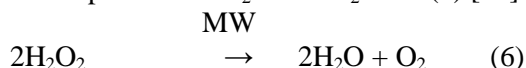


**Figure10.** Effect of added H<sub>2</sub>O<sub>2</sub> on the degradation of IC

The inhibition is attributed to the mutual destruction of H<sub>2</sub>O<sub>2</sub> and ·OH resulting in the formation of less active HO<sub>2</sub>· radicals [18].



Further, in the presence of MW radiation, H<sub>2</sub>O<sub>2</sub> is known to absorb MW energy and undergo decomposition to H<sub>2</sub>O and O<sub>2</sub> as in (6) [10].



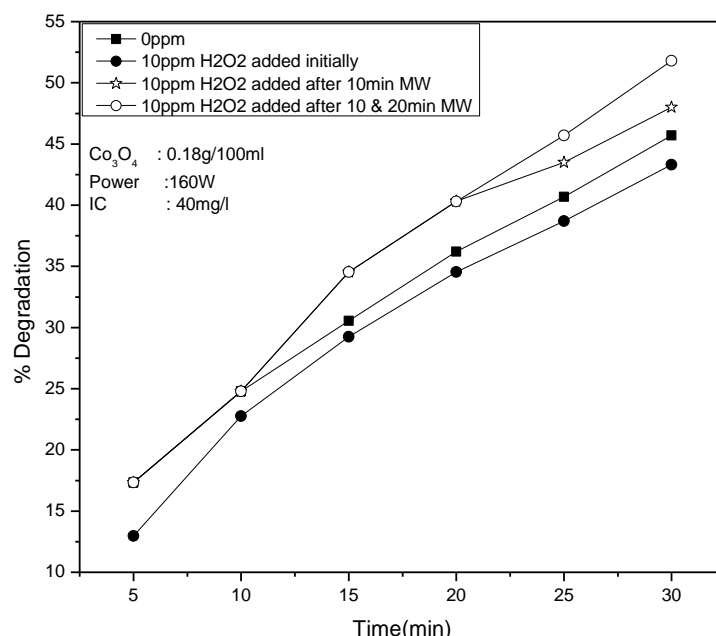
This naturally results in decrease in the MW available for the catalyst and the substrate as well as reduction in the availability of reactive OH radicals which lead to decrease in the degradation of IC. It is also known that H<sub>2</sub>O<sub>2</sub> is formed insitu in the system though its concentration does not increase with time as it undergoes periodic oscillation [31,34]. Similar results are reported in the case of sono, photo and sonophotocatalytic degradation of organic pollutants in water [35,36].

However, at higher concentrations, H<sub>2</sub>O<sub>2</sub> has an enhancing effect. The degradation of IC steadily increases with increase in the concentration of H<sub>2</sub>O<sub>2</sub>. This is understandable since at higher concentrations there will be higher rate of formation and hence sufficient population of ·OH radicals which can compensate for the competitive mutual destruction of ·OH and H<sub>2</sub>O<sub>2</sub>. The trend remains the same under thermal condition as well as at RT/MW conditions showing that the net concentration of H<sub>2</sub>O<sub>2</sub> in the system is critical in deciding its role as an inhibitor or enhancer.

The actual quantity of H<sub>2</sub>O<sub>2</sub> formed in the system is not reproducible in repeated experiments and instances of complete absence of H<sub>2</sub>O<sub>2</sub> are also observed. This inconsistency may be partly due to the strong adsorption and/or decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of oxides such as Co<sub>3</sub>O<sub>4</sub> or MnO<sub>2</sub>. As seen above, H<sub>2</sub>O<sub>2</sub> serves the role of producer and scavenger of ·OH radicals simultaneously. Part of the OH radicals formed from the decomposition of H<sub>2</sub>O<sub>2</sub> will be used for the degradation of IC and the other part will be interacting with H<sub>2</sub>O<sub>2</sub> itself and degrading it. Thus the net concentration of OH radicals available for degrading the dye and/or other reactions will always be fluctuating. This concurrent formation and decomposition of H<sub>2</sub>O<sub>2</sub> as well as various other complex free

radical interactions together with the partial absorption of MW by  $H_2O_2$  result in unpredictability and inconsistency in the effect of concentration of  $H_2O_2$  on the MW/ $Co_3O_4$ /IC reaction.

The complex effect of  $H_2O_2$  is further verified by its in-between addition to the MW/ $Co_3O_4$ /IC reaction in progress. The result is shown in Fig. 11.

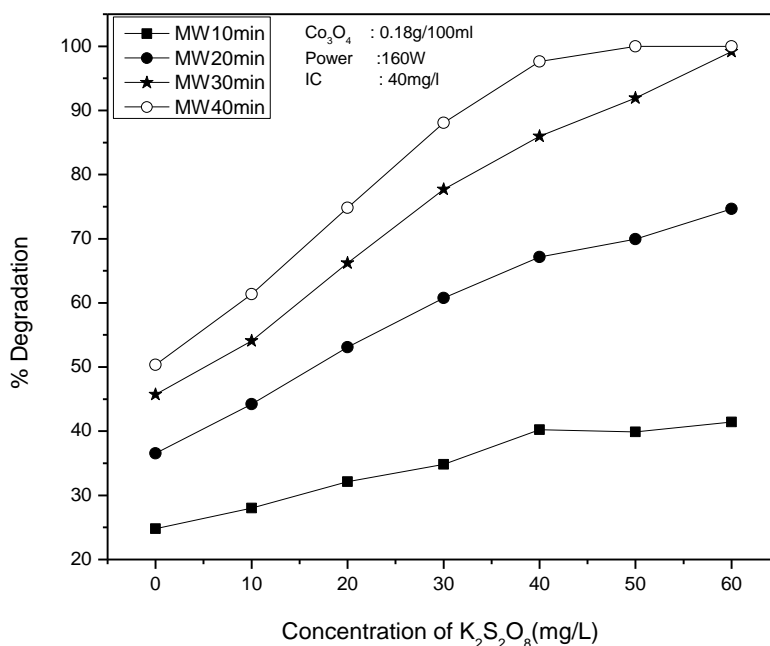


**Figure 11.** Effect of initial & in between addition of  $H_2O_2$  on the degradation of IC.

$H_2O_2$ , at lower concentration of 10 mg/L inhibited the degradation. However after about 10 min of MW irradiation when ~25% of IC has degraded, addition of more  $H_2O_2$  (10 mg/L) into the reaction system enhances the degradation. Further addition of 10 mg/L of  $H_2O_2$  at ~40% degradation enhances the degradation further. Hence it is evident that the effect of  $H_2O_2$  is concentration-dependent and once sufficient concentration of  $H_2O_2$  is available to overcome the insitu detrimental processes by other reactive radicals, as explained earlier, the effect is enhancement.

### 3.6. Effect of added persulphate

In this context, another oxidant, i.e. persulphate ( $S_2O_8^{2-}$ ) (PS) ( $E^0 = 2.1$  V) is investigated as a potential enhancer of the MW/ $Co_3O_4$  degradation of IC. Specific advantages of PS include high solubility and stability at ambient temperature. Further, the end-product of PS promoted mineralisation is the  $SO_4^{2-}$  ions, which are relatively harmless and considered environment-friendly. However PS as such does not cause any degradation of IC or other organic pollutants and needs a powerful activation source. Hence MW/PS is tested under different conditions for the degradation/mineralization of IC. The degradation is enhanced significantly as shown in Fig.12.

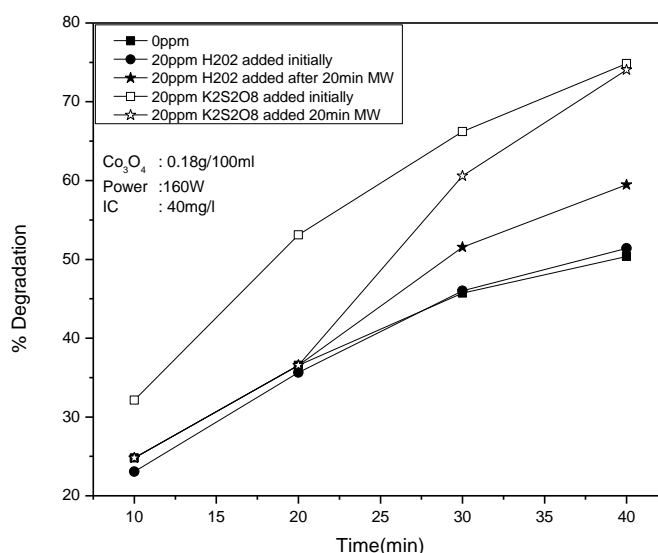


**Figure 12.** Effect added  $K_2S_2O_8$  on the degradation of IC.

The enhancing effect of PS also is concentration-dependent with an optimum concentration in the range of 40-50 mg/L under current reaction conditions. The enhancing role is further verified by in-between addition of PS to the reaction system in which the degradation of IC in progress. The results are plotted in Fig 13.

Addition of PS has a clear distinct enhancing effect. While the normal MW/  $Co_3O_4$  degradation of IC in 40 minutes is ~50%, addition of PS at the 20<sup>th</sup> minute, enhances the same to ~75%. The figure also clearly illustrates the superiority of PS over  $H_2O_2$  as the oxidant. Addition of  $H_2O_2$  in place of PS in the above experiment increases the degradation to ~ 60% only. Our investigations have also revealed that excess PS has no negative effect and hence any unused oxidant can be used for fresh input of IC pollutant which is important from the economic angle. Combination of these two oxidants, i.e.  $H_2O_2$  and PS, widely used in many AOTs, resulted only in slight enhancement of the degradation achieved in presence of PS and the combined effect is less than the additive effect of the two oxidants.

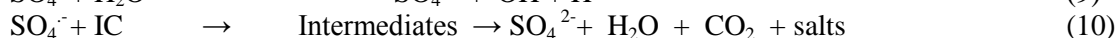
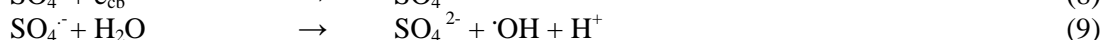
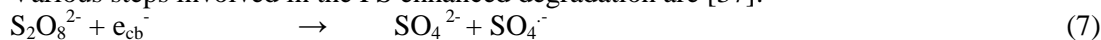




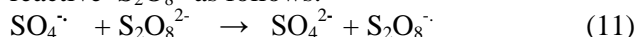
**Figure 13.** Effect of initial & in between addition of  $K_2S_2O_8$  /  $H_2O_2$  on the degradation of IC.

The enhancement in the PS/MW degradation of organics is attributed to the formation of highly reactive  $SO_4^{\cdot-}$  from PS. With increase in concentration of PS more reactive  $SO_4^{\cdot-}$  radicals are formed under thermal or MW. These radicals initiate/propagate a series of chain reactions ultimately resulting in the degradation of IC [30]. Various ROS such as  $H_2O_2$ ,  $HO_2^{\cdot}$ ,  $\cdot OH$  etc formed insitu can also interact with IC leading to its degradation and mineralization. However the formation of  $\cdot OH$  radicals by this route is not very dominant and the degradation is mostly taking place by the interaction with the  $SO_4^{\cdot-}$  radicals.

Various steps involved in the PS enhanced degradation are [37]:



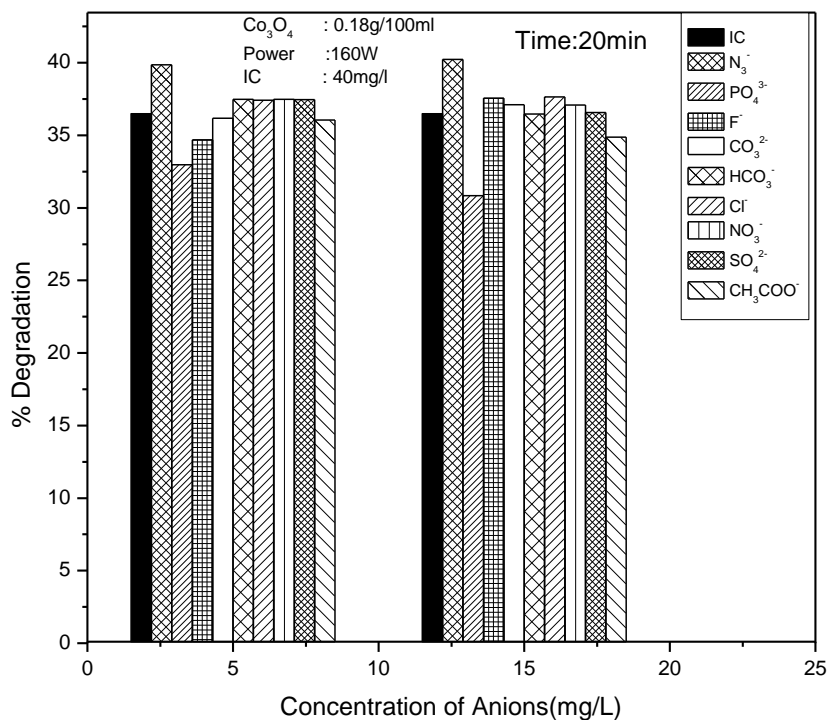
At higher concentrations of PS,  $SO_4^{\cdot-}$  can interact with the former and transform the same to less reactive  $S_2O_8^{\cdot-}$  as follows:



Hence the rate of degradation slows down at higher concentration of PS and with reaction time.

### 3.7. Effect of Anions / Salts

The water used in industries often contains a variety of salts/anions as contaminants. Since it is not economical to decontaminate the water, these salts will form part of the effluent discharge as well. Hence any AOP aimed at mineralizing the toxic/hazardous pollutants in water must consider the effect of these salts on the efficiency of respective processes. Accordingly, the effect of few commonly found anions in water, i.e.  $F^-$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $Cl^-$  on the MW/ $Co_3O_4$  degradation of IC is tested at two different concentrations (5 mg/L and 15 mg/L of the anions after 20 min) and two different reaction times (10 mg/L of the anion after 10min, 30 min). The results are plotted in Fig 14A and B.



**Figure 14A.** Effect of anions at different concentrations on the degradation of IC.

As the figures show, the anions have no significant effect on the degradation of IC at different concentrations and different reaction times. Even a strong inhibitor like PO<sub>4</sub><sup>3-</sup> has only little influence in this case. This is an advantage of MW over other activation processes. Many parameters such as pH, presence of contaminants etc which have severe detrimental effect on other AOPs such as sono, photo and electro processes have practically no effect under MW, which is important from the commercial application angle.

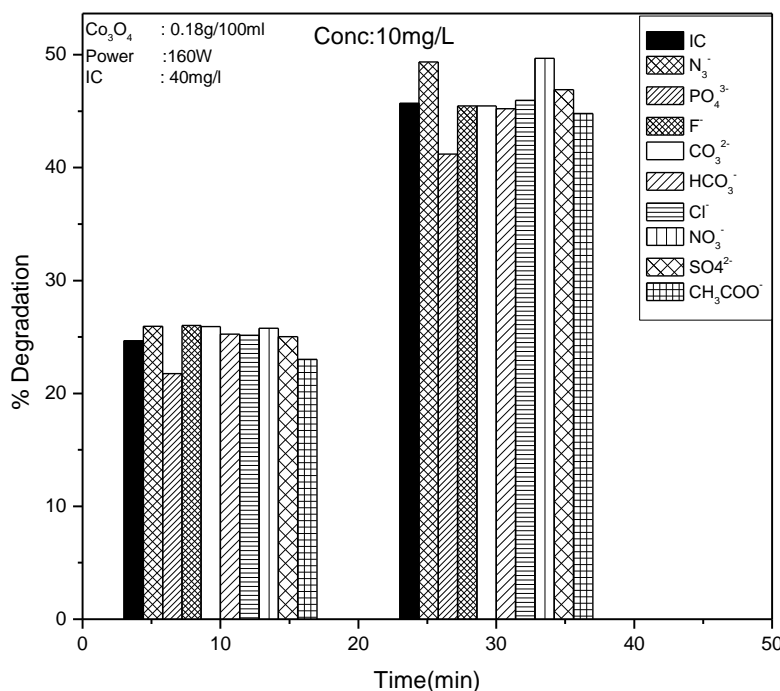


Figure 14B. Effect of anions on the degradation of IC at different times of reaction.

#### IV. General mechanism

MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> are strong MW absorbents which can significantly absorb and transfer MW energy. This could create large number of ‘hot spots’ which could enhance the degradation of molecules [38]. Elevation of temperature provides increments of kinetic energy to the molecules, thereby enhancing the collision rate. However not all collisions will have sufficient energy and orientation to induce reactions leading to degradation or mineralization. An ideal excitation source is one that can favor efficient collision and consequent reaction by modifying the energy distribution of molecule. This kind of ‘anisotropic excitation’ is possible under MW irradiation, which is not the case under conventional heating which causes isotropic excitation and thus inefficient collision [1]. Even under identical temperatures, different reaction rates could be observed under thermal and MW conditions, and this is due to the different distribution of kinetic energies of the molecules. This ‘athermal effect’ induced by materials such as MnO<sub>2</sub> or Co<sub>3</sub>O<sub>4</sub> which can strongly absorb and transfer MW energy, could create large amounts of ‘hot spots’ which can enhance the degradation of molecules [13, 39]. Electrophilic O<sub>2</sub> ions such as O<sub>2</sub><sup>-</sup>, O<sup>-</sup> and O<sup>2-</sup> which are derived from lattice oxygen of MnO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> show high reactivity [40,41] and take part in reactions leading to the degradation of IC. The vacancies of lattice oxygen are later replenished by molecular oxygen dissolved in solution.

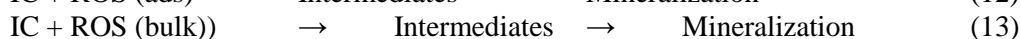
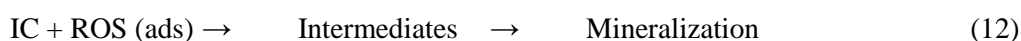
The comparatively higher degradation under MW compared to CH can be attributed to the specific effects of MW in addition to the thermal effects. It is well known that the average bulk temperature of the MW system will be higher than the boiling temperature under normal heating at atmospheric pressure. This is due to the exceedingly faster rate of MW power dissipation throughout the entire bulk resulting in ‘superheating’ of the system [42]. The dielectric MW heating can also reduce the normal ‘wall effects’ which occurs in conventional heating. Hence numerous ‘hot spots’ will be formed which could trigger massive nucleation of seeds throughout the bulk solution. This will result in enhanced interaction and reaction leading to faster degradation of the pollutant.

The enhancement in the presence of catalysts can also be explained based on the specific MW effect of 'selective heating' which is the ability of polar substances with higher dielectric constant to preferentially absorb more MW energy. Oxides such as  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$  with relatively higher dielectric constant will get more heated by MW. When the surface is covered by MW absorbing hydroxyl groups, the formation of reactive species will also be more and this will accelerate consequent reactions leading to ultimate degradation of the pollutant.

Another factor leading to the enhanced degradation in presence of MW is the non-thermal effect, also referred to as athermal effect which is different from the thermal/kinetic/specific effects of MW. This happens when the MW electric field interacts with specific molecules in the reaction system which may not lead to any macroscopic temperature rise, though selective heating is still possible. Thus MW can induce re-orientation of dipolar molecules resulting in changes in the activation energy and/or pre-exponential factor of the Arrhenius equation related to the specific process. Further, formation of polar reaction intermediates or the increase in polarity when the molecules go from ground state to the transition state can result in lowering of activation energy and increased reaction. Determination of the activation energy for the degradation of IC in presence of MW/ $\text{MnO}_2$  showed decrease by about 20%.

The reaction is very slow in presence of MW alone without catalyst, probably because the energy of the MW photons is quite low ( $10^{-5}\text{eV}$ ) compared to chemical bonds. Hence MW alone cannot initiate a degradation reaction while in presence of MW-active catalysts like  $\text{MnO}_2$  or  $\text{Co}_3\text{O}_4$ , it can initiate and accelerate the reaction. The degradation of IC in the presence of MW/ $\text{MnO}_2$  or MW/ $\text{Co}_3\text{O}_4$  is significantly more compared to that in presence of CH/catalyst suggesting that it is not only the simple thermal effect that is responsible for the degradation and eventual mineralization, though its contribution cannot be ruled out.

Various reactive oxygen species (ROS) such as  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2\cdot$ ,  $\cdot\text{OH}$  etc formed from the lattice, surface and dissolved oxygen, as explained earlier can interact with IC leading to its degradation and eventual mineralization as in the case of other AOPs, i.e.



The study clearly shows that  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$  are two efficient MW catalysts for the removal of organic pollutants in trace amounts from water, the former being more efficient than the latter. 'Microwave flash heating' reduces the overall reaction time leading to faster degradation and eventual mineralization.

## V. Conclusion

$\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$  are identified as two highly MW-active catalysts for the degradation and eventual mineralization of trace amounts of the toxic pollutant dye IC in water. The degradation is much faster compared to identical conventional heating conditions suggesting that the MW effect is not just thermal. 'Specific effects' and 'athermal effects' of MW also contribute to the degradation of the pollutant. The effect of pH on the degradation is only marginal over a wide range of 4-10, thereby proving the ability of MW to modify the pH effect in many cases. Addition of  $\text{H}_2\text{O}_2$  also has only moderate influence on the MW-assisted degradation at lower concentration range while it has a positive enhancing effect at higher concentrations. Another oxidant persulphate enhances the MW/ $\text{Co}_3\text{O}_4$  degradation. Natural water contaminants like salts/anions also do not affect the degradation significantly. The microwave radiation may not be affecting the surface characteristics of the oxides as in the case of other AOPs even though the lattice oxygen removed from the catalyst plays significant role in the degradation. This lattice oxygen vacancy is later replenished by dissolved oxygen taking  $\text{MnO}_2/\text{Co}_3\text{O}_4$  to its original composition.

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