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Treatment Of Methylated Chloro Phenols Using Uv Mediated Oxidation Processes

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Abstract- In this study, decomposition of two methylated chloro phenols - 4chloro3methylphenol (4C3MP) and 2chloro5methyl phenol (2C5MP) are investigated using various UV mediated oxidation processes- Fenton, UV/H_2O_2, UV/Fenton and UV/TiO.. Among all the processes, Fenton accelerated with UV is observed to be efficient in decreasing the COD with a maximum removal rate of 98.5% for 4C3MP and 95.2% for 2C5MP. First order equations were used in evaluating the Kinetic constants. Photo mediated Fenton process is observed to have maximum kinetic constants of 5.1×10^{-3} for 2C5MP and 8.3×10^{-3} for 4C-3MP. Among the two chloro substituted cresols, decomposition of 4C3MP is observed to be higher than 2C5MP i.e., 95.2% for 4CMP and 86% for 2C5MP.

Key words: *Compound reduction, substitution, deactivating, oxidation & kinetic constants.*

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1. Introduction

With industrialization and urbanization, large number of chemical industries sprouted worldwide. These industries consume huge amounts of water for production purpose and at the same time release wastewater at an alarming rate. Since the treatment cost of these wastewaters was high compared to production cost, these industries started releasing wastewaters in to the nearby water bodies. Many of these wastewaters contain non-biodegradable compounds of significant concern. Among them, cresols constitute a significant fraction of hazardous waste especially the methylated chloro phenols because of their chronic effects at 12 mg/L. The two model compounds of the present study 4-chloro and 2-chloro methyl phenols (4C3MP & 2C5MP), pose significant health threat when discharged into the environment due their carcinogenic and refractory nature.

4C3MP is used as a stabilizing agent in paint, textile, and cosmetic industry. It is also a chemical intermediate in the manufacture of some pesticides. 4C3MP is toxic to aquatic flora and fauna and can become persistent in some species of fish. 2C5MP is widely used in pharmaceutical industry. Effluents generated from these industries contain excess of methylated chloro phenols.

Many traditional treatments are available for the removal of such non-biodegradable compounds like adsorption or by membrane filtration [1]. However, some of these methods are either too expensive or involve only transfer of pollutants from one phase to another phase without complete removal. Under such conditions, Photo mediated Oxidation process seem to be an alternative for the treatment of methylated chloro phenols. These methods involve reaction of hydroxyl radical (*OH), with refractory compounds converting them to less toxic compounds. Many AOPs result from the combination of UV radiation with oxidants, like H_2O_2, catalyst like TiO_2 and Fenton reagent.

There have been some studies on the decomposition of 4C3MP using pressurized hot water/supercritical oxidation [2] and temperature activated fenton decomposition and 2C5MP using sonication , but no studies have been carried out using UV mediated oxidation processes. Hence, the main objective of this paper is to estimate the potential of photo mediated oxidation processes such as photo mediated catalytic oxidation (UV/TiO_2), photo mediated chemical oxidation (UV/H_2O_2), fenton, and photo mediated fenton oxidation (UV/H_2O_2–Fe) in degrading the methylated chloro phenols. For a greater efficiency of the treatment processes, operational factors such as pH, initial strength of peroxide, initial strength of iron and catalyst dosage effect are all monitored. Further, tentative degradative pathway of the two model compounds is also proposed.

2. Materials & methods

2.1. Chemicals

Analytical grade 4C3MP & 2C5MP were purchased from Sigma Aldrich. P-25 TiO_2 powder, a gift from Degussa Corporation (Pune, India) contains 80% anatase. Analytical grade chemicals like Ferrous Sulphate, Sulphuric acid, Sodium hydroxide are all procured from Merck while H_2O_2 solution is from Lobachem. For the entire study, Glass distilled water is being used.

2.2. Reactor set-up

A 1.0L cylindrical photo reactor with diameter 12cm and height 13.3cm is used for all the experiments. A quartz tube encases the whole reactor to prevent contact with the solution flowing between the inner and the external wall of the quartz tube. The reactor has provision of inlets and outlets for reactants and withdrawing samples along with ports for temperature measurement. A Teflon painted magnetic mixing bar is placed at the bottom for homogenous mixing of compounds. A 16W mercury vapor lamp is the source of UV light (λmax at 270nm) which is placed in the center and immersed in the phenolic solution. The samples are collected with an air tight syringe at regular intervals (Figure 1).

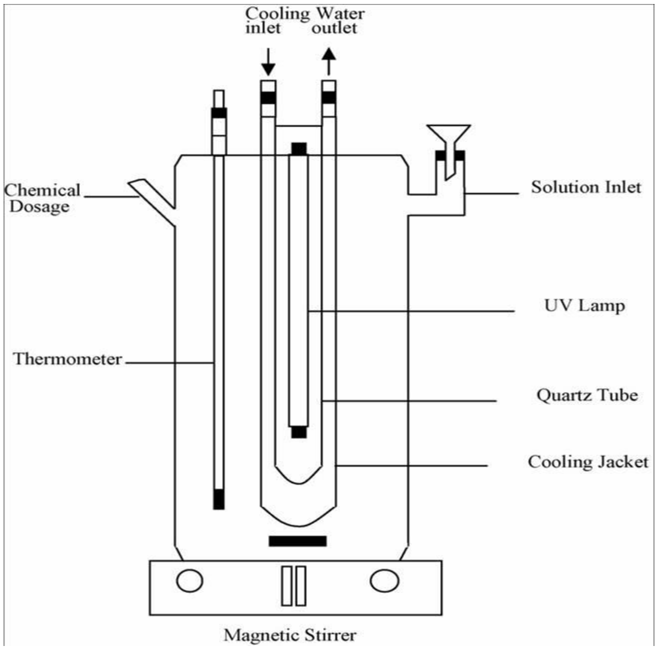

Figure 1 Photo Reactor with 16W UV lamp

2.3 Experimental procedure

Stock solution of methylated chloro phenols with a shelf life 1 week are prepared by dissolving them in methanol solution. Prior to experiments, all the dilutions from stock solution and other standards stored in dark are brought to room temperature. To validate the treatment process and check for any loss on volatilization, control samples are run for every experiment. pH studies are done by adjusting the pH with H_2SO_4 or NaOH (0.1 N /1.0N).

All the experiments are performed in batch mode with varying concentrations of H_2O_2 and Fe^{+2} (10:1) in Fenton and photo mediated Fenton, while 1:1 ratio is maintained for experiments with UV/H_2O_2. In UV/TiO_2 experiments, TiO_2 dosage ranging from 0.1g – 0.5g is varied at an interval of 0.1g. The reaction mixture is introduced in to the photo reactor after homogenization for 15min by magnetic agitation. After collection at regular intervals, the samples are centrifuged and sepearted through 0.25µm syringe filters (mdi, India type SY25NN). The seperated samples are submerged with Na_2SO_3 (10%) solution to stop further oxidation process after the treatment and stored in dark for further analysis.

2.4 Analytical procedure

The decomposition of methylated chloro phenols is evaluated with UV-Vis Spectrophotometer (Systronics-1272 wavelength 234 nm).

COD experiments were performed according to STANDARD METHODS of examination of H_2O and wastewater (1989), 21st edition**.** Systronics pH meter is used for measuring the pH. All the samples were diluted with 1:1 ratio for analysis.

3. Results and discussion

The present section deals with the results obtained in different oxidation methods in degrading methylated chloro phenols. The performance of these methods is evaluated in terms of decomposition of methylated chloro phenols and also reduction in COD.

3.1 UV Photolysis

3.1.1 Initial pH Optimization

Figure 2 & 3 represents the effect of pH in UV photolysis on the decomposition of 2C5MP & 4C3MP. At 250ppm of 2C5MP & 4C3MP, the experiments are performed at pH ranging from of 3 to 11. The decomposition of methylated chloro phenols are significantly affected by initial pH values which directly influences $^{\bullet}$OH radical generation. A 36 % of 2C5MP decomposition is observed at pH 3 which then decreased gradually at increased pH. It decreased to 17.9 % and 14% at pH 7 and 11. At a pH of 3, 59% decomposition is achieved in case of 4C3MP similar to previous studies. The decomposition decreased at higher pH (pH>3) to 26%.

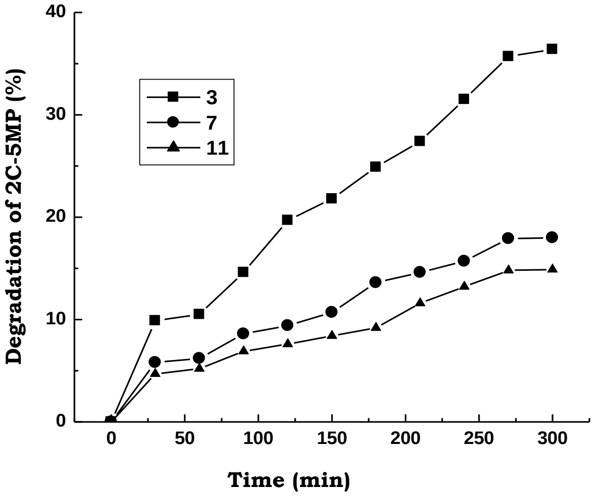

Figure 2 Initial pH Optimization of 2C5MP in UV photolysis

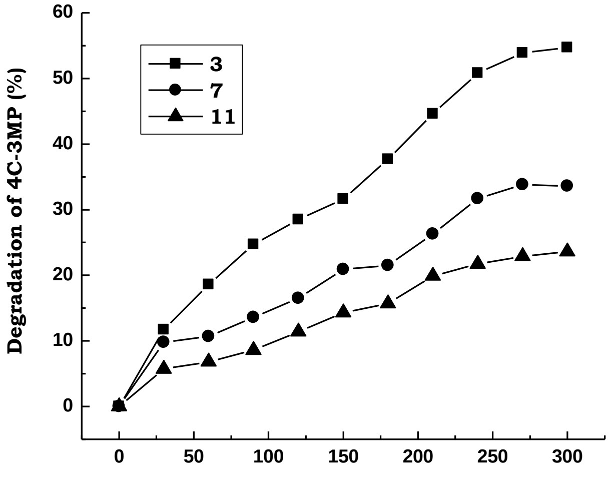

Figure 3 Initial pH Optimization of 4C3MP in UV photolysis

3.1.2 Initial strength Optimizaion

The optimization of initial strength of 2C5MP & 4C3MP in photo mediated experiments is studied with in a range of 50–750ppm at fixed pH of 3. It is observed from figure 4 and 5 that 64% of 2C5MP and 76% of 4C3MP decomposition is achieved with an initial strength of 100ppm of both the compounds. At higher concentrations, the decomposition decreased significantly (17.9% for 2C5MP and 18.6% for 4C3MP). Hence, in all further experiments, 100ppm of methylated chloro phenols is used as the optimum compound concentration.

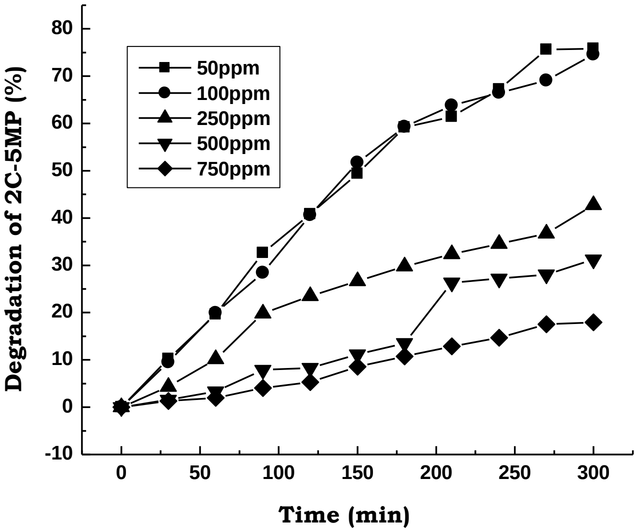

Figure 4 Initial 2C5MP strength optimization in UV photolysis

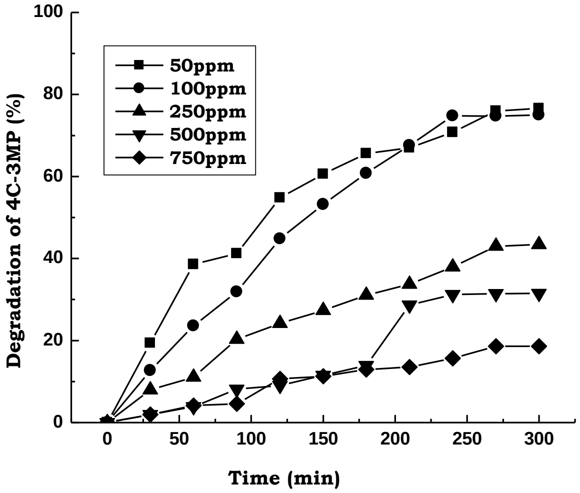

Figure 5 Initial 4C3MP strength optimization in UV photolysis

3.2 UV/H_2O_2 process

3.2.1 Initial H_2O_2 strength Optimization

The peroxide effect on 2C5MP & 4C3MP decomposition is observed by differing the strength of H_2O_2 from 50–500ppm (Figure 6 & 7). At 100ppm of initial peroxide, 48% of 2C5MP decomposition is observed with gradual decrease in the decomposition at higher concentration. The decomposition rate is observed to be high initially (from 50 to 100ppm) which might be due to the generation of more hydroxyl radicals at high peroxide strength. However, 2C5MP decomposition rate slowed down when H_2O_2 strength increased above 100ppm

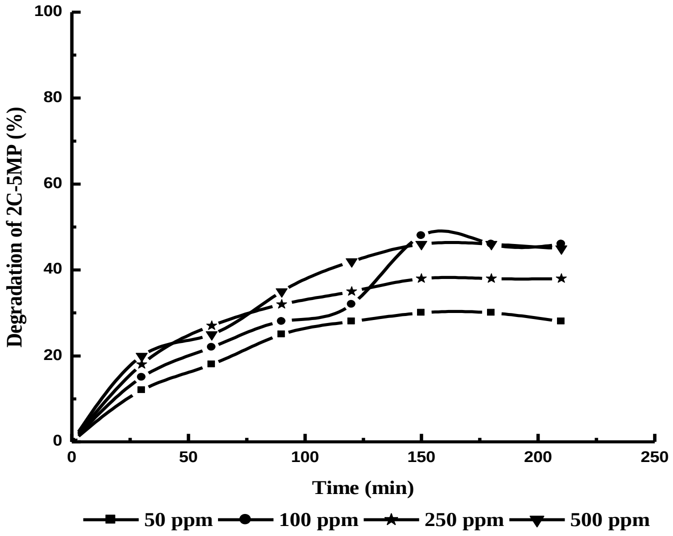

Figure 6 Initial H_2O_2 strength optimization on the decomposition of 2C5MP in UV/H_2O_2 system

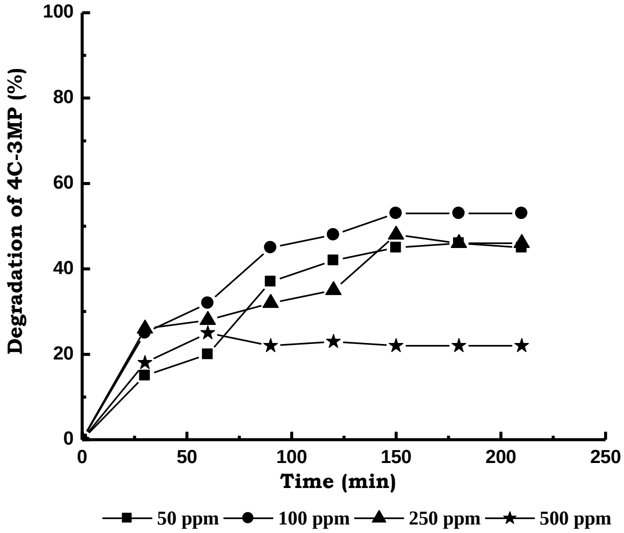

Figure 7 Initial H_2O_2 strength optimization on the decomposition of 4C3MP in UV/H_2O_2 system

As the peroxide strength is increased from 50-100ppm, the decomposition of 4C3MP also increased and it reached to a maximum of 53% at 100ppm of peroxide within 150min. But above this strength (>100ppm), 4C3MP decomposition decreased significantly [3] which might be due to the cleaning effect of $^{\bullet}OH$ radicals at high peroxide strength. Therefore, in further studies 100ppm of peroxide is taken as optimum.

3.2.2 Initial pH Optimization in UV Peroxide system

In UV mediated peroxide system (UV/H_2O_2), initial pH was varied from 3-11 to study 2C5MP & 4C3MP degradation. It is found that at pH of 7, 48% of 2C5MP (Figure 8) and 55% of 4C3MP (Figure 9) decomposition is achieved. At lower pH (<7), the decomposition was less effective while at high pH (>7) only 10–15% decomposition is observed.

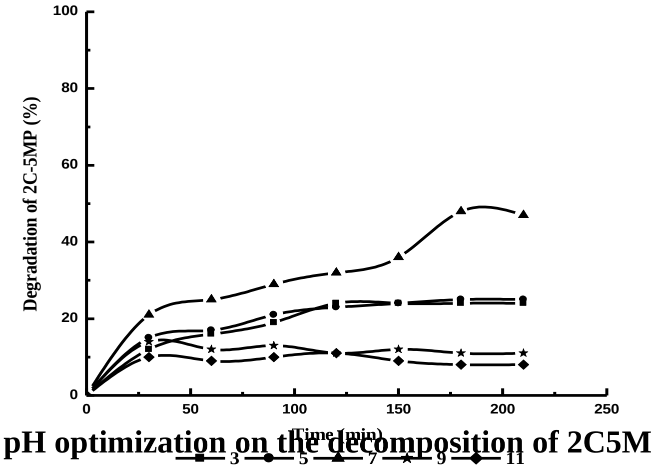

Figure 8 Initial pH optimization on the decomposition of 2C5MP in UV/H_2O_2 system

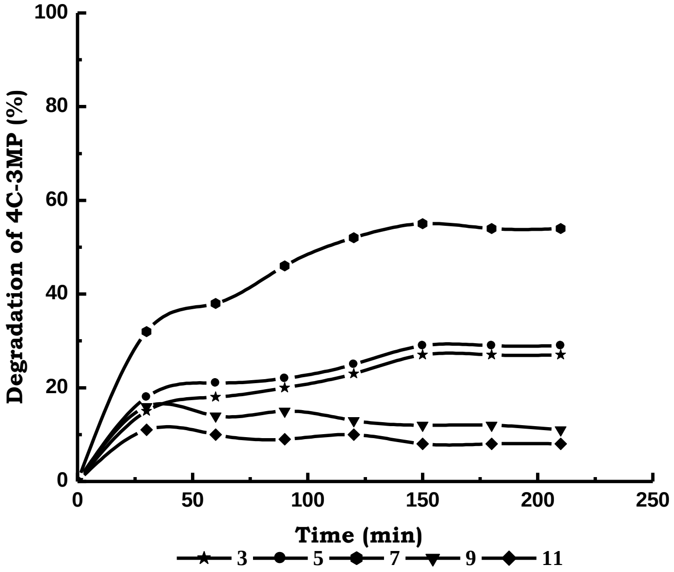

Figure 9 Initial pH optimization on the decomposition of 4C3MP in UV/H_2O_2 system

3.3 Fenton & Photo Fenton process

3.3.1 Initial Fe^{+2} strength Optimization

To find out the effect of Fe^{2+} ion on 2C5MP & 4C3MP decomposition in Fenton and UV mediated Fenton, iron strength was varied at pH 3 from 10 to 50ppm (Figures 10 & 11). The decomposition of 2C5MP was observed to be less than 60% at 10ppm iron strength and it increased gradually due to excess generation of $^{\bullet}$OH radicals [4]. Within 150min, 86% decomposition is observed in photo mediated Fenton while 73% is achieved in Fenton at 20ppm of Fe^{+2}.z

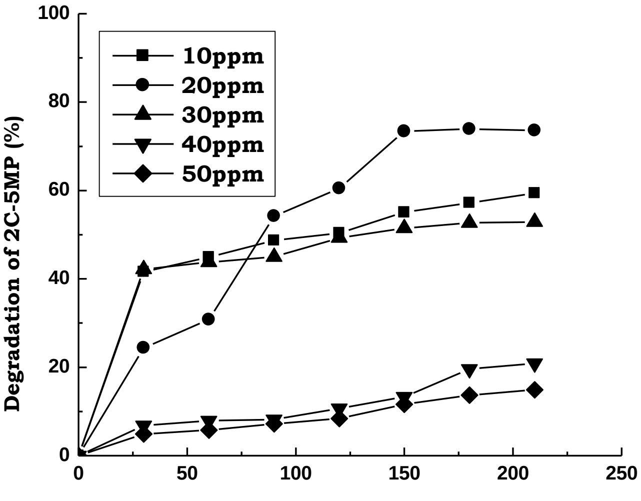

Figure 10 Initial Fe^{+2} strength optimization on the decomposition of 2C5MP in Fenton's oxidation

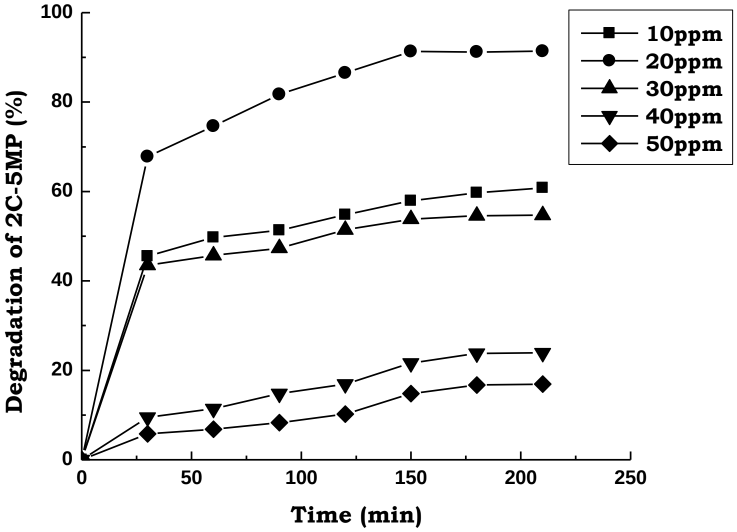

Figure 11 Initial Fe^{+2} strength optimization on the decomposition of 2C5MP in Photo mediated Fenton's oxidation

With an increase in the dosage of iron, significant decomposition of 4C3MP is observed (Figures 12 & 13). In Fenton procedure, adding of Fe^{+2} from 10-20ppm enhanced the degradation of 4C-3MP and attained to. An increase of 79.5% decomposition of 4C3MP is observed with the increase in dosage of iron from 10-20ppm, which is due to rapid formation of hydroxyl radicals catalyzed by ferrous ion. Photo mediated Fenton reaction increased the decomposition of 4C3MP leading to a rapid decomposition compared to Fenton process [34]. In Photo mediated Fenton process, 95% decomposition is observed at 20ppm of iron strength with in 150min (Figure 13). However, an increased iron strength (>20ppm) did not increase the decomposition which might be due to side reactions of hydroxyl radical with iron ions.

$$Fe^{+2} + {}^{\bullet}OH \longrightarrow Fe^{+3} + OH$$

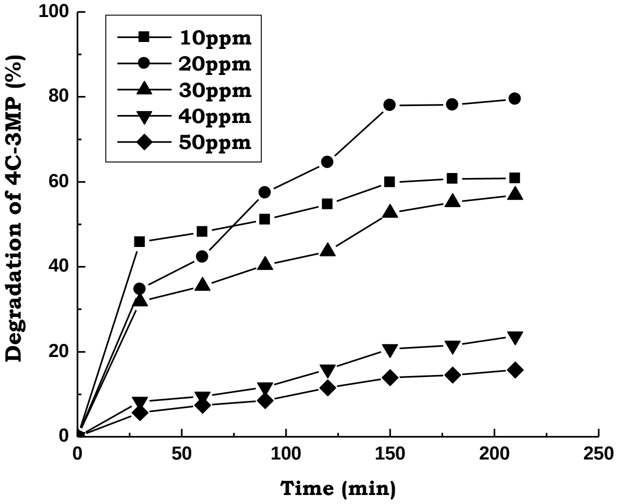

Figure 12 Initial Fe^{+2} strength optimization on the decomposition of 4C3MP in Fenton's oxidation

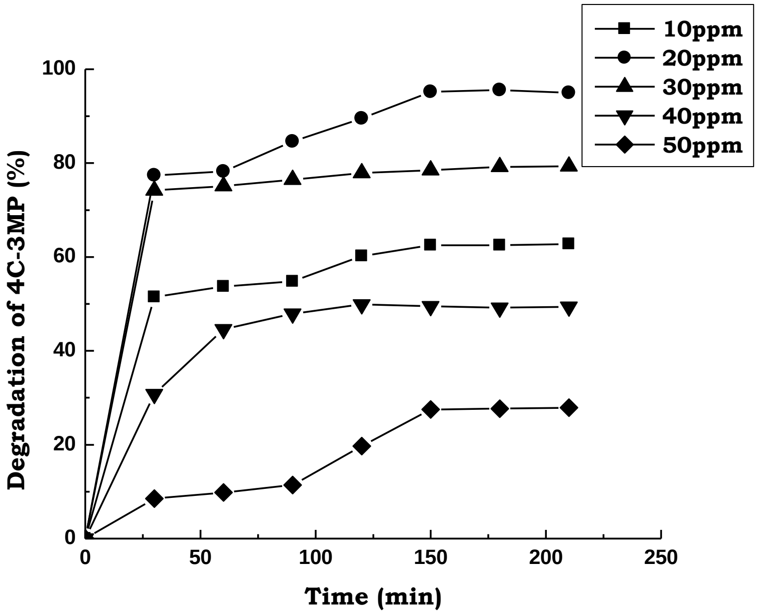

Figure 13 Initial Fe^{+2} strength optimization on the decomposition of 4C3MP in Photo Fenton's oxidation

3.4 Photo mediated decomposition using TiO_2 as catalyst

3.4.1 Initial pH Optimization

To study the pH effect with 0.2g of TiO_2 on 2C5MP & 4C3MP degradation, experiments are conducted by varying the pH from 3-11. It is observed that the decomposition of the compounds was high at neutral pH compared to basic and acidic pH. Basic medium with pH values >7.0 enhance carbonate ion formation, which scavenge hydroxyl ion generation that are responsible for oxidation reaction.

At pH 7, 58% and 70% decomposition of 2C5MP and 4C3MP respectively is observed within 180min (Figure 14 & 15). TiO_2 is amphoteric in nature with a point zero charge around pH 6-7 [5] and hence oxidation reaction is found to be effective at this pH.

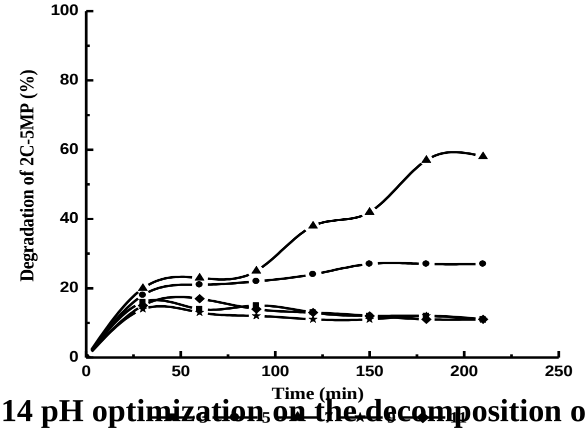

Figure 14 pH optimization on the decomposition of 2C5MP in UV/TiO_2 system

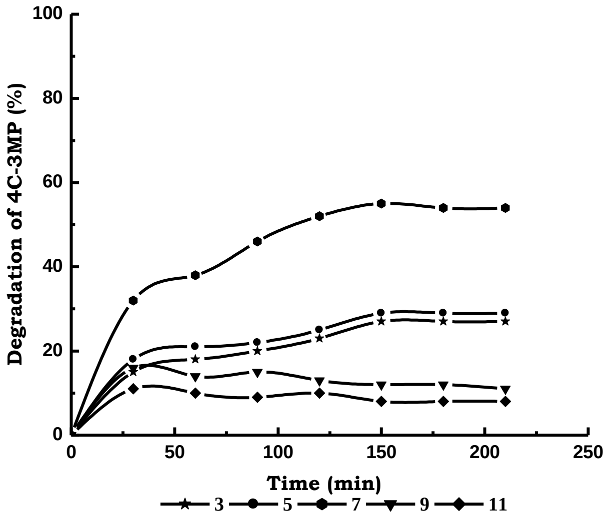

Figure 15 pH optimization on the decomposition of 4C-3MP in UV/TiO_2 system

3.4.2 TiO_2 dosage Optimization

TiO_2 dosage variation (0.1, 0.2, 0.3, 0.4 and 1.0 g) is studied for 2C5MP & 4C3MP at neutral pH (Figure 16 & Figure 17). At 0.3g of dosage of TiO_2 and within 180min 72% and 75% decomposition of 2C5MP & 4C3MP is achieved. The high reaction efficiency at this dosage may be due to increased active sites for oxidation process.

When the dosage of the catalyst was increased above 0.3g, the reaction efficiency decreased due to loss of interaction between photons and catalyst. While at low catalyst dosage, the efficiency decreased due to non-availability of active sites for oxidation process to occur.

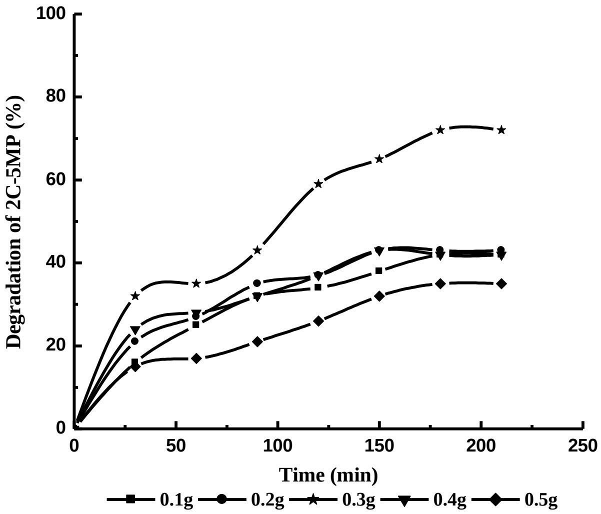

Figure 16 TiO_2 dosage optimization on the decomposition of 2C5MP in UV/TiO_2 system

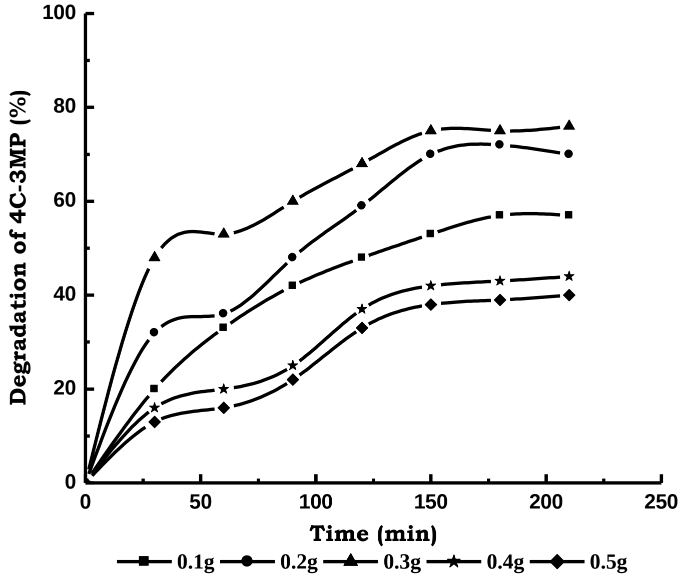

Figure 17 Effect of TiO_2 dosage on the decomposition of 4C-3MP in UV/TiO_2 system

3.5 Comparative study of various treatment systems

3.5.1 COD reduction

The decomposition of 2C5MP & 4C3MP with advanced treatment systems is evaluated using reduction in COD and compound. In COD reduction experiments of 2C5MP (figure 18), it was observed that 20.1% reduction in COD could be achieved with UV alone but very slowly. The COD reduction is found to increase (38%) when peroxide is added to the system with increased free radical formation. In Fenton process, COD reduction increased to 58.7%. The COD reduction rate increased to 85% when the catalyst TiO_2 is used along with UV. The optimum COD decrease of 95.2% is achieved with photo mediated Fenton process.

With 4C3MP (Figure 19), the COD reduction was found to be highest (98.5%) in photo mediated Fenton reaction. In UV/TiO_2, the COD reduction was observed to be 88.4%. While UV alone could reduce the COD to 25.6%, it was further enhanced to 65.2% when peroxide was added to the system. In Fenton system, COD reduction of 68.5% is observed.

The order of reduction in COD in both cresols is found to be:

UV/Fenton > UV/TiO_2 > Fenton > UV/ H_2O_2 > UV

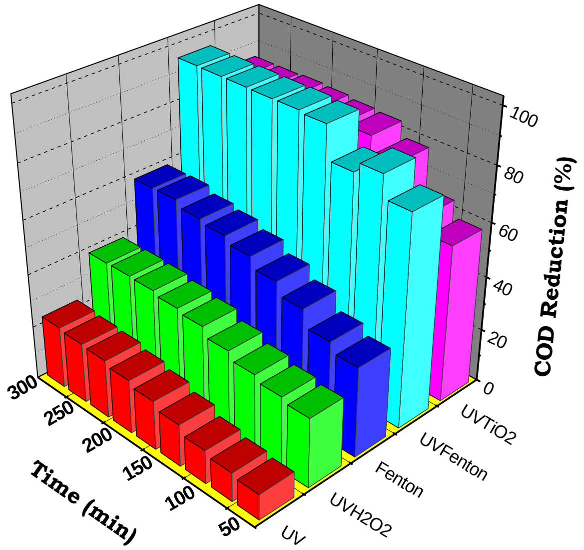

Figure 18 COD Reduction of 2C5MP with different oxidation systems

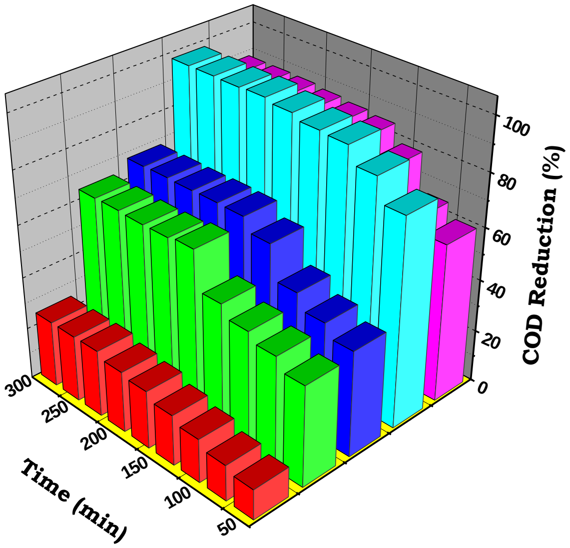

Figure 19 COD Reduction of 4C3MP with different oxidation systems

3.5.2 Compound reduction

UV process is observed to be a very slow method in degrading the compound with 36% of 2C5MP and 58% of 4C3MP. The decomposition of both the compounds is enhanced with 48% and 64.3% decomposition of 2C5MP & 4C3MP when peroxide is added to the system. In Fenton and UV/TiO_2, systems, 73 & 72% decomposition of 2C5MP and 79.5% & 75% decomposition of 4C3MP is observed. Photo mediated Fenton showed high efficiency among all the treatment system with 86% of 2C5MP and 95.2% of 4C3MP degradation.

3.5.3 Decomposition rate

2C5MP & 4C3MP decomposition rates with time for various treatment systems is observed to follow the pseudo first order kinetics (Figure 20 & 21) which is expressed as:

$$\ln C_t / C_0 = -k^* t$$

Where C_0 and C_t represent 2C5MP & 4C3MP strength at times (minutes) 0 and t, while k* represents pseudo first order rate constant.

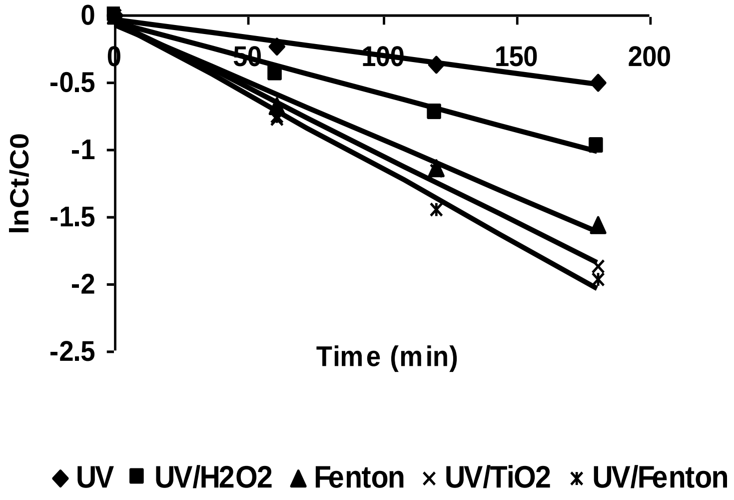

Figure 20 Kinetics showing the decomposition of 2C5MP with various treatment systems

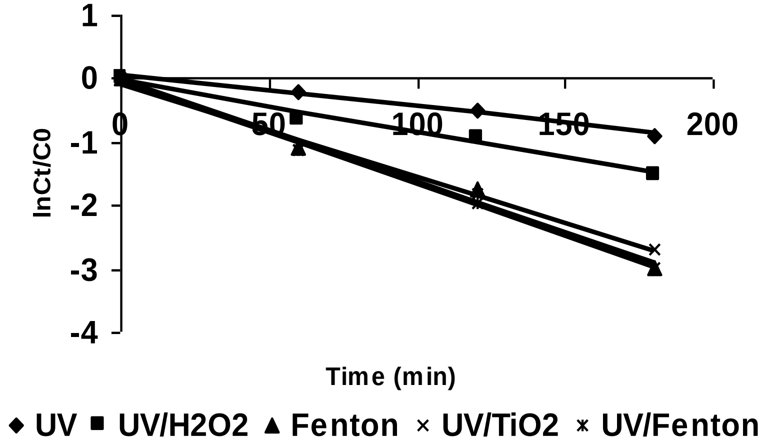

Figure 21 Kinetics showing the decomposition of 4C3MP with various treatment systems

S.No	Oxidants	K (min^{-1})	r^2
1.	UV/Fenton	5.1 × 10^{-3}	0.99
2.	UV/TiO_2	4.2 × 10^{-3}	0.98
3.	Fenton	4.3 × 10^{-3}	0.98
4.	UV/ H_2O_2	2.1 × 10^{-3}	0.98
5.	UV	1.4 × 10^{-3}	0.97

Table 1 2C5MP - rate constants

S.No	Oxidants	K (min^{-1})	r^2
1.	UV/Fenton	8.3 × 10^{-3}	0.99
2.	UV/TiO_2	7.8 × 10^{-3}	0.99
3.	Fenton	6.6 × 10^{-3}	0.98
4.	UV/ H_2O_2	5.6 × 10^{-3}	0.98
5.	UV	4.9 × 10^{-3}	0.98

Table 2 4C3MP – rate constants

Table 1 & 2 shows the rate constants obtained with linear regression analysis confirming the efficiency of photo mediated Fenton oxidation in the decomposition of 2C5MP & 4C3MP. All the treatment processes studied followed pseudo first order equation with highest rate constants of 5.1× 10^{-3} & 8.3×

10^{-3} for 2C5MP & 4C3MP in photo mediated Fenton oxidation. However, a slight deviation from linearity (r^2 =0.97) is observed in UV system attributing to its low efficiency in degrading the cresols.

3.5.4 Degradative pathway

Among the two model compounds studied in the present paper, 4C3MP decomposition is observed to be very fast compared to 2C5MP. The OH group present in both the methylated chloro phenols is highly reactive and directing in electrophilic aromatic replacement of direct hydroxyl charged particle attack on electron rich positions. Since the hydroxyl radical attack is on electron rich chloro group, there is a considerable reduction in the stearic effect on 4C3MP making it more vulnerable to decomposition process. Figure 22 shows the tentative degradative pathway of 4C3MP & 2C5MP.

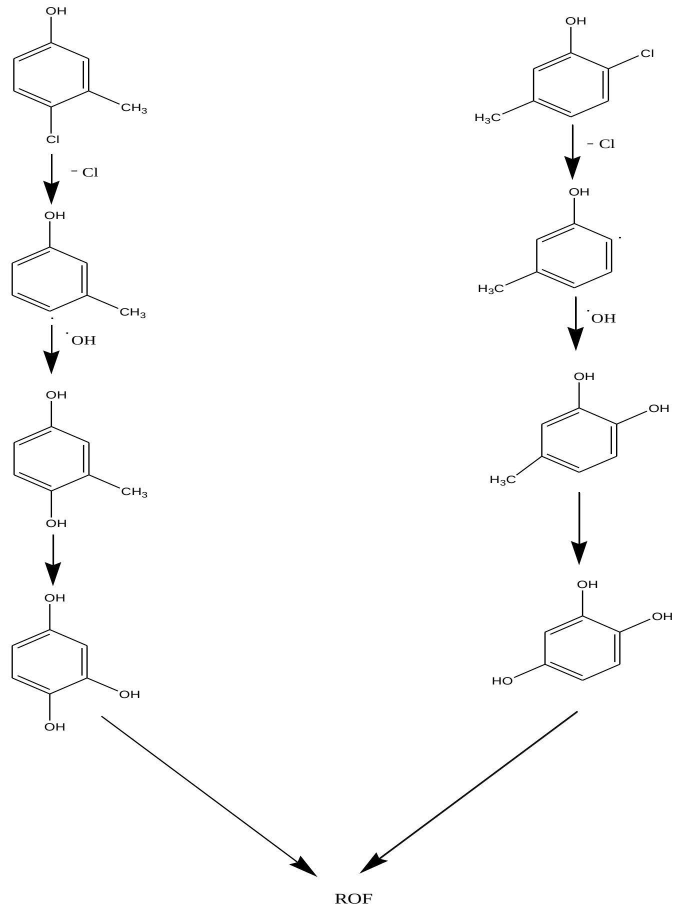

Figure 22 Tentative Degradative pathways of methylated chloro phenols

4. Conclusions

Photo mediated Fenton system is found to be efficient in degrading the cresols compared to other treatment systems.

- UV alone was found to be less efficient in the decomposition of cresols.
- UV peroxide was observed to enhance the treatment system but it required longer reaction time.
- Photo mediated Fenton process was efficient in achieving maximum COD as well as compound reduction.
- This was confirmed by kinetic studies which showed linearity in all the treatment systems except for UV that slightly deviated showing its least efficiency in the decomposition of cresols.
- 4C3MP decomposition is much faster compared to 2C5MP due to the position of active chloro group.

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