



Research Article

Degradation of monocrotophos pesticides using the advanced oxidation method

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Monocrotophos is one of the highly hazardous organophosphate pesticides that is widely used and easily available in India even which had been banned also by WHO. So, in this paper a comparative study is carried out with the degradation of monocrotophos under the treatment of photocatalysis and sonophotocatalysis. The experiments were performed in the immersion well reactor in which UV light was used for degradation purpose and TiO₂ was used in suspended condition as catalysis. The process is optimized and varying on the different parameters like catalyst concentration, operating pH, H₂O₂ concentration., initial pollutant concentration. in photocatalytic experiment. In the photocatalytic experiment sufficient degradation was found under the optimized catalyst during the setup of 2 hours and further synergic effect was noticed between ultrasound and ultraviolet irradiation in the presence of TiO₂. Combined effect of ultrasonic and photocatalytic treatment shown synergic result rather than individual treatment of ultrasound and irradiations with optimized parameters. The complete degradation of recalcitrant organic pollutants increase the chances for the reuse of waste water. Because secondary waste materials are not generated, there is no need to dispose of materials.

Keywords: Pesticides, photocatalysis, sonophotocatalysis, advanced oxidation, synergic effect.

INTRODUCTION

Different type of synthetic pesticides are mostly used worldwide for the agricultural activities and increasing the yield. These pesticides are categorized into various groups such as, insecticides, micro-biocides, fungicides, herbicides etc. But over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species including non target species, air, water, bottom sediments, and food (Miller GT, 2004). In the recent studies, Punjab (India) demonstrated most shocking and dangerous effects of pesticide exposure, mutated DNA has been found in blood samples of farmers in some areas. Children in these areas are suffering from "mental development disorders" by pesticide exposure. Even other states like Gujarat,

Maharashtra, Haryana, Andhra Pradesh and Tamil Nadu are also suffering for the same.

Many organophosphate insecticides (esters of phosphoric acid) such as monocrotophos, parathion, malathion, methylparathion are well known for their bioaccumulation and neurotoxic properties, because they act on the enzyme acetyl cholinesterase. Organophosphate pesticides irreversibly

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inactivate acetylcholinesterase, which is essential to nerve function in insects, humans, and many other animals. So they have full potential for neurotoxicity (Randhawa et al., 2011).

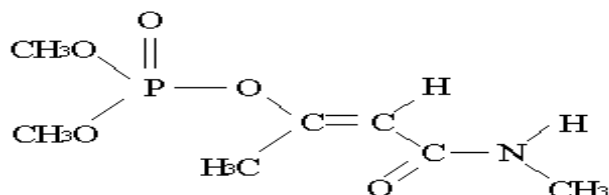
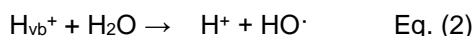
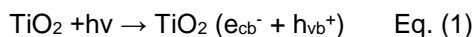


Figure1. Structure of monocrotophos

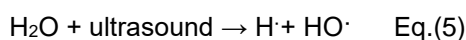
Monocrotophos is one of the highly hazardous organophosphate insecticides that is widely used and easily available in India. The structure of monocrotophos is showing in figure 1. It is acutely toxic to birds and humans, and widespread bird kills, especially of Swainson's Hawks (Bai, et al., (1977). Monocrotophos can be absorbed through injection, inhalation and skin contact. When inhaled, it affects the respiratory system. Many organophosphate pesticides are not completely degrade during conventional treatment technology due to low biodegradability. Field survey shows that due to incomplete mineralization, some amount of pesticides are released in aquatic environment and mix up into ground water and used as a source of drinking water. Many advanced technologies have been developed by researchers for pesticides containing waste water degradation such as, microbial degradation technology, membrane bio filtration. But in the microbial degradation technology (Fang et al., 2004), a special kind of microorganism could be used to for the degradation of an objective pesticide. But in microbial technology the cultivation and purification is very time consuming, and costly method (Yua et al., 2007). So, there is a critical need to set up the emerging alternative technologies that can deal with highly concentrated and toxic non-biodegradable pesticides. Recently, considerable interest has been shown by researchers towards the degradation of pesticides by advanced oxidation process such as photocatalysis, sonolysis, sonophotocatalysis, photofenton. These techniques are basically very eco-friendly and time efficient technology and the most basic advantage of these techniques is complete destruction of any toxic compounds nontoxic ending products and it can be easily carried out at room temperature and atmospheric pressure. Basic principle behind of this technology is the production of OH radical which has high

oxidation potential and mainly it's nonselective property. This OH radical can easily react with the toxic compound due to its high potential capability and changed into nontoxic ending products. In the recent years, a conflict interest is growing in sonochemical degradation of pesticides (Chowdhury et al., 2009). Sonolysis process involved using ultra sound waves which leads to production of OH radicals due to cavity formations.

In cavitation phenomena, bubbles are formed on the surface in liquid and due to rapid growth and collapsing of bubbles cavity is formed (Madhavan et al., 2010) and which leads to formation of supercritical condition (1200°C,800atm). But single sonolysis process is not enough for the degradation of any kind of hazardous compound. If sonolysis process includes with other established techniques, it can be alternative emerging technology in order to achieve complete degradation and mineralization. So, the combination of photocatalytic and sonolytic can be a new emerging technique for the degradation of target compound. In photocatalysis degradation of pesticides over TiO₂ has been widely used in the recent days because TiO₂ is photostable, less expensive, non-toxic, and very less gap is found between the valance band and conduction band (Legrini et al., 1993). So, electron can easily jump from valance band to conduction band and hole (H⁺) formation occurs on the side of valance band and OH ion reacts with the valance band and generates the OH radicals .The photo generated electron reacts with O₂ molecule and superoxide ion (O₂⁻) species (Emad et al., 2010). This superoxide ion species is further responsible to react with the H₂O molecule and generate OH radicals and sometimes, manually addition of H₂O₂ produces more OH radicals. (Eq. 1-4)



If two modes of irradiance (UV and US) are jointly used, then more number OH radicals would be produced .



It also enhances the mass transfer organics between liquid phase and solid phase. So, more absorption would be occurring on the surface of catalyst.

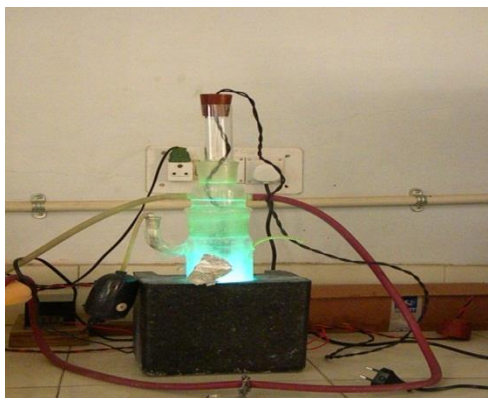


Figure 2. Immersion well reactor

The fast and foremost objective is to study the degradation of commercially available monocrotophos pesticides by sonophotocatalysis under the optimized condition such as, TiO_2 concentration, pH, Oxidant concentration (H_2O_2), Initial pesticides concentration etc.

MATERIALS, METHODS AND EXPERIMENTAL SETUP

Reagents and Samples

Chemicals used in the experiments are Commercially available monocrotophos (37% V/V), TiO_2 (Degussa P-25 and which have BET surface area $50\text{m}^2\text{g}^{-1}$), H_2O_2 (30% V/v), SnCl_2 , Ammonium molybdate (for phosphate estimation), COD reagents were also used for determining the mineralization. Distilled water used for making the solution of sample throughout the process at the conductivity of $25\text{ }^\circ\text{C}/\mu\text{S}\cdot\text{cm}^{-1}$. Commercial monocrotophos pesticides is purchased directly from market. H_2SO_4 (0.1N) and NaOH (0.1N) were used for adjusting the pH in the sample.

Experimental setup and Procedure:

The procedure follows in batch process. Immersion well reactor was used for the photocatalysis which is a batch reactor. This reactor is made up of glass and structured in cylindrical shape. This cylindrical photoreactor was also provided with the circulation of cold water for maintaining the temperature. Medium pressure mercury lamp (125 watt) was used as a source of the UV light at the wavelength of 254nm and aeration was also provided for dual purpose, mixing and aeration. Most important benefit of this reactor is that solution is fully surrounded by mercury light. All of the experimental studies were carried out at normal atmospheric pressure and temperature.

Initially, stock solution concentration of monocrotophos was 200 ppm. 200 ml of aqueous solution is added every time in photoreactor for degradation and TiO_2 is added in reactor at different concentration and sometimes strong oxidant (H_2O_2) is also added in reactor for generating the more amount of OH radicals.

Sonochemical experiment is performed in sonicator bath at the frequency of 33KHz. which is also a batch reactor. Transducer is placed at the bottom surface of sonicator (Madhavan et al., 2010). Complete setup of sonophotocatalysis, immersion well reactor with cooling water jacket and mercury lamp is placed on the surface of sonicator.

Analytic method

UV-Vis spectrophotometer was used for degradation of monocrotophos. In one quartz cuvette sample was placed and in other distilled water as a blank for auto zero and scanned the sample between the range of 200 and 600nm. During the initial scanning of monocrotophos maximum absorbance came at 297nm. Decrease in absorbance of irradiated sample indicates the degradation of pesticides. Calibration curve is generated on different concentration (In ppm.) of monocrotophos because with the using to slope of calibration curve it is easy to determine of the concentration of irradiated sample after the any particular time period. One of the degradation analysis method of monocrotophos was determined by removal of PO_4^{3-} ions concentration through the degradation of monocrotophos. Percentage removal of phosphate ions indicates the degradation of pesticides. The determination of PO_4^{3-} ions is performed with ammonium molybdenum (Shifu et al., 2005). COD test was also performed for the determining the mineralization of monocrotophos.

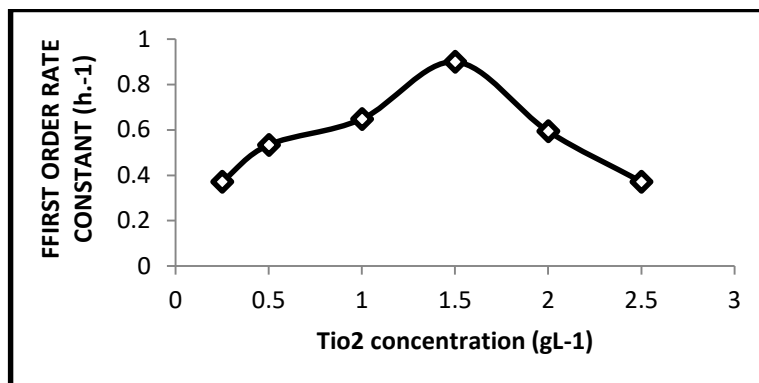


Figure 3. Effect of TiO₂ degussa P25 on 200 PPM Monocrotophos at pH 5

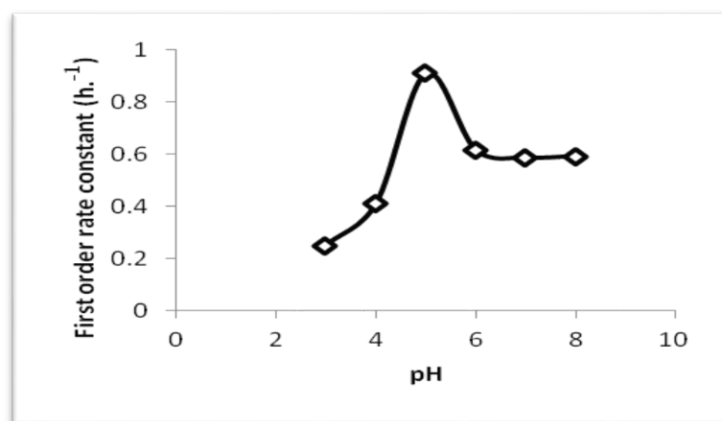


Figure 4. Effect of pH on 200 PPM monocrotophos at TiO₂ concentration of 1.5gm/l

RESULTS AND DISCUSSION

Photocatalytic degradation of monocrotophos under UV radiation:

Photolysis process mainly occurs when any substance absorbs the light. Monocrotophos pesticide (initial concentration 250ppm and natural pH 5) is kept surrounding by the mercury lamp for photocatalysis degradation. Monocrotophos could be degraded >95% in around irradiation period of 5 Hours. Many of intermediates formed when C=C bond is decomposed by OH radicals. So, it leads to generate many phosphorus and nitrogen containing organic compound and further these organic compounds were attacked by OH radicals (due to its nonselective property), phosphates and nitrate ions released (Hua et al., 1995) .

Photocatalytic degradation of monocrotophos under UV irradiation were also studied under the many optimizing

condition such as TiO₂ concentration and effect of pH, effect of H₂O₂, effect of initial concentration, removal of phosphate ions concentration and also mineralization studies .

Effects of TiO₂ Concentration

The effect of catalyst loading on the monocrotophos is studied in the range between 0.5 gL⁻¹ to 2.5gL⁻¹ at its natural pH. The running hour of setup was around of 4 to 5. First of all, rate constant is obtained and plot the graph between time(min.) and lnC₀/C. Initially the reaction rate was constant which follows first order increase with the increasing of catalyst concentration upto 1.5mg/L, as shown in Figure 3. After that rate of constant starts decreasing. Increase of rate constant with the increasing of catalyst loading indicates, light can easily penetrate through the catalyst particles and absorbed by the catalyst surface. The catalyst concentration above optimum level depends on various factors such as reactor

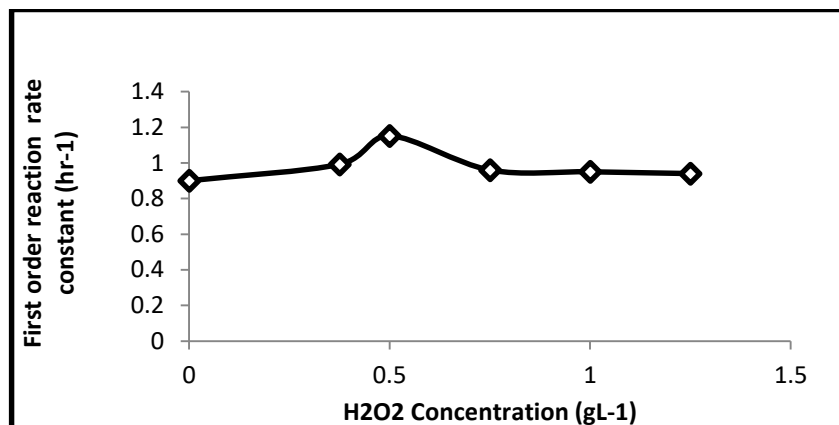


Figure 5. Effect of H₂O₂ on 200 PPM Monocrotophos at TiO₂ concentration of 1.5gm/l ,pH 5

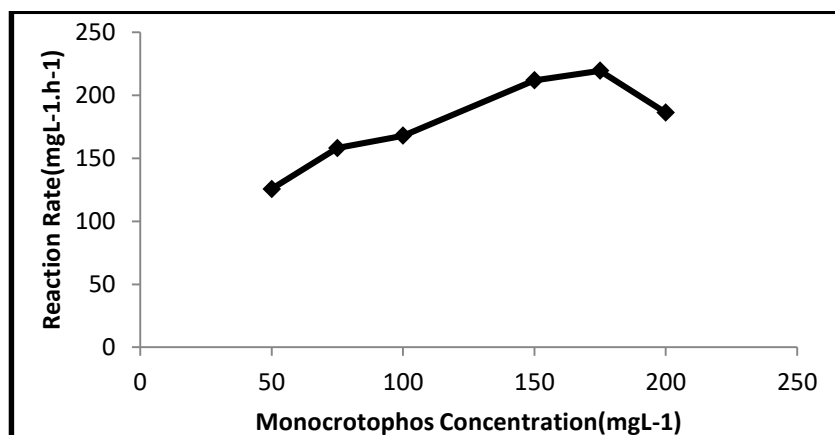


Figure 6. Effects of MCP initial concentration on the photocatalysis degradation at optimum concentration of TiO₂ and pH.

reactor geometry, exposed area of catalyst, light intensity (Matos J. et al., (2010) So, at higher concentration of catalyst loading solution becomes turbid and starts to agglomerated which hindered in the penetration of light .So photocatalytic activity may decreases due to the hinderation of light and reducing of surface area.

Effect of pH

The effect of pH on monocrotophos was studied in the range of between 3 to 8 at optimum concentration of TiO₂ (1.5gm/l), as shown in figure 4. Initially, pH was adjusted by NaOH, H₂SO₄ (0.1N) and rest of parameters were same. Best degradation was achieved at its natural pH 5. It means monocrotophos appears with best degradation in slightly acidic medium. From pH 3 to pH 4 drastically it increased. But in basic medium rate remains constant

suddenly drop down and unchanged. Basic reasons behind the changing the rate constant with the pH are:

- 1) Surface charge of catalyst, absorption and deabsorption of catalyst and it's anionic nature with appoint of zero charge between 5.6 and 6.4 (Abella et al., 2009).
- 2) Some of intermediates are also formed during the decomposition of the pesticides (Abella et al., 2007)

On the surface of TiO₂, titanol (TiO₂.OH) is present, which is amphoteric in nature. In acidic medium H⁺ ions are absorbed on the surface of TiO₂. So, the photo generated electron reacts with the adsorbed H⁺ ion and form H_{ads}[•] but at the higher side of pH the catalyst surface has negative charge found due to its significant fraction of catalyst as TiO₂⁻. So, degradation rate starts to decrease at the higher side of pH. It was also observed during the experiment, pH starts to drop down due to formation of

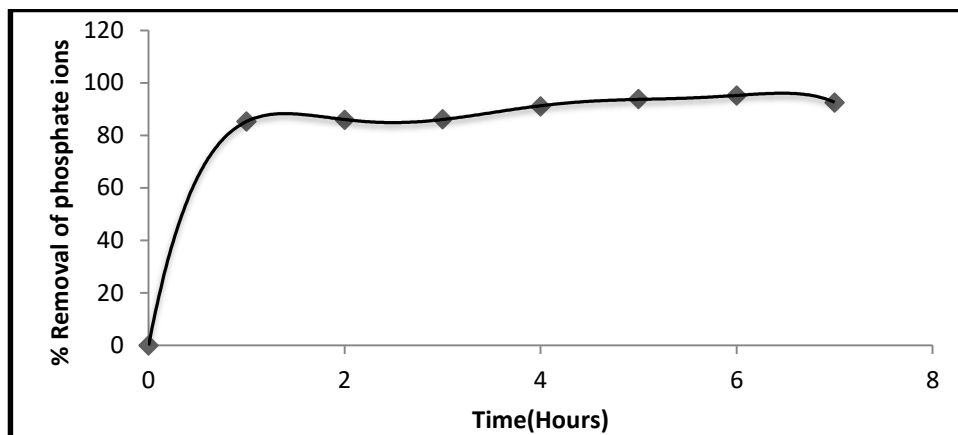


Figure 7. Measurement of removed phosphate ion concentration with the time at its optimum condition of catalyst ,pH, oxidant concentration

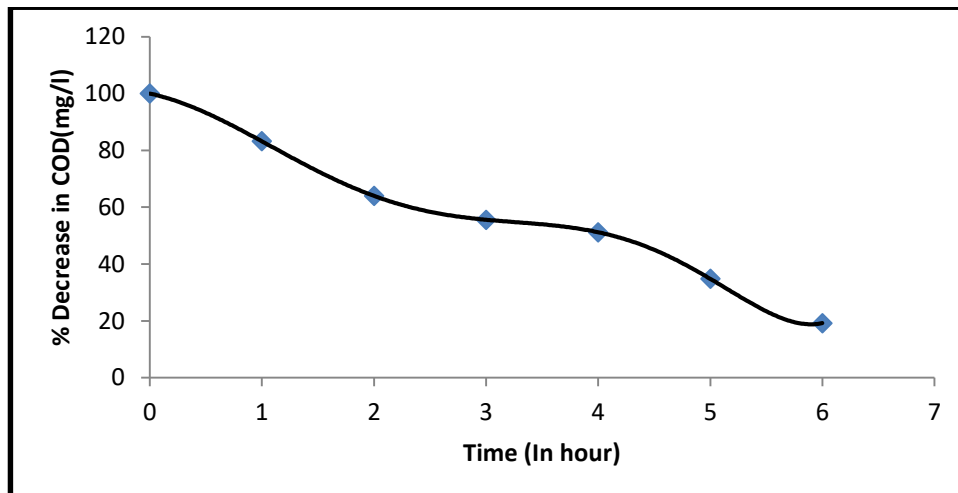


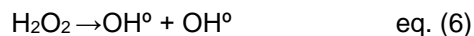
Figure 8. Study of mineralization (% Decrease in COD with the time at its optimum condition of catalyst, pH, oxidant)

some acidic intermediates after the degradation (Avasaralaa et al., 2011).

Effect of Strong Oxidant (H₂O₂)

The effect of H₂O₂ on the degradation of monocrotophos was studied between the range of 0.25 ml to 2.5ml at the optimum TiO₂ concentration and pH 5. The running hour of setup was around of 2 to 5 hr. which depends on the effect of H₂O₂ on monocrotophos, as shown in Figure 5. Hydrogen peroxide is a clear liquid, slightly more viscous than water. Main reason of the study of H₂O₂ on the degradation of monocrotophos, it's having strong oxidant capability. So, during the breaking of bond it releases OH radicals (Eq. 6) which enhances the degradation rate of monocrotophos within less period of

time. As (figure 5) indicates that first order reaction rate was achieved higher at 0.5ml H₂O₂ concentration in less period of time in comparison to optimum TiO₂ and pH reaction rate.



But, after the increasing of H₂O₂ concentration above it's optimum level, reaction rate constant starts to decrease and then remain constant. No further degradation occurs because at the higher concentration of H₂O₂, more OH radical ions would be releasing and after some time, they will be started to recombine. So, after a certain period of time, number of OH radicals would be reduced and degradation rate decreases.

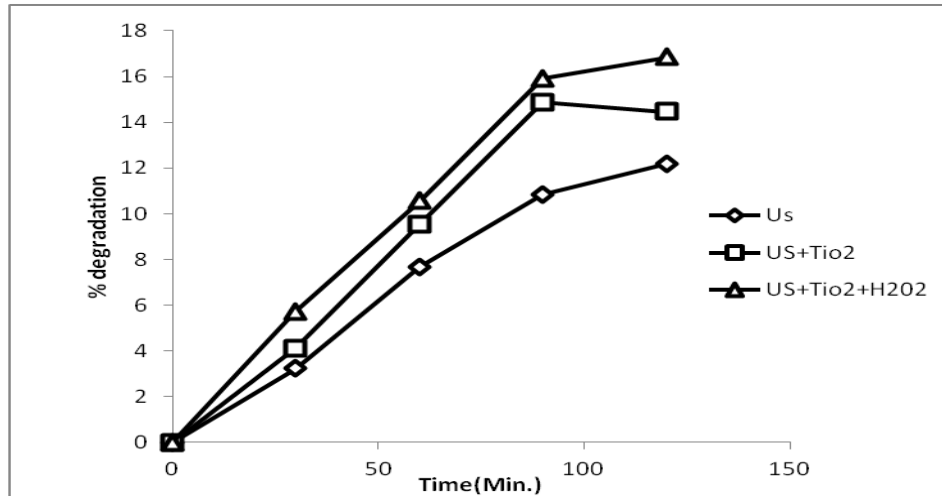


Figure 9. Percentage of Degradation rate due to Sonolytic (US) and Sonocatalytic (US+TiO₂) and Sonocatalytic + oxidant processes (US+TiO₂+H₂O₂)

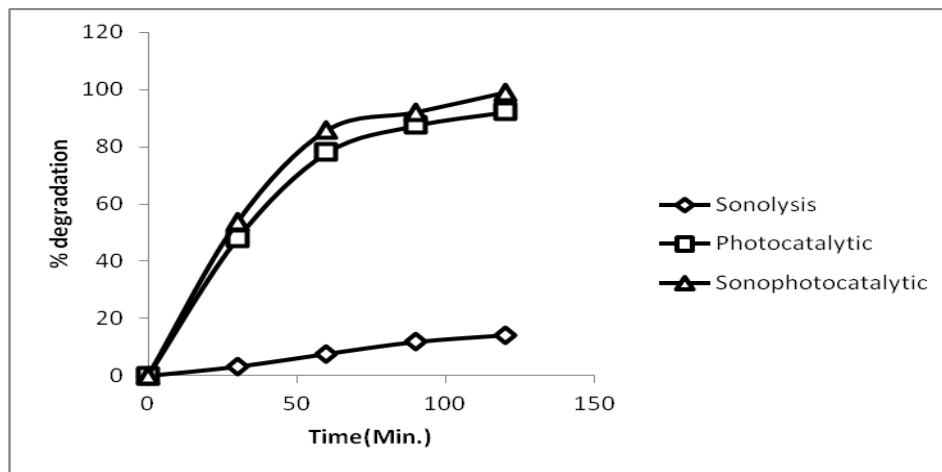


Figure 10. Percentage Degradation rate due to Sonolytic (US) and Photocatalytic(UV+TiO₂) and Sonophotocatalytic(US+UV+TiO₂+H₂O₂)

Effects of Initial concentration of monocrotophos

The effect of initial monocrotophos concentration on photocatalytic degradation was studied in concentration range of 50ppm to 200 ppm, as shown in Figure 6. Initially rate of constants were obtained by plotting the linear graph between time (min.) and $\ln(C_0/C)$ corresponding to different concentration and further which were used to calculate the rate of reaction by the multiplication of rate constant and initially concentration of monocrotophos. According of this figure, rate of reaction is continuously increased with the concentration of monocrotophos upto 175ppm, after that its levels off. Because reaction can easily extent between OH radicals and initial concentration upto 175 ppm, because upto optimum

concentration of substrate, fully active sites of substrate are available for OH radicals but after increasing the concentration of monocrotophos reaction rate drops due to reduction of OH radicals in comparison of compound concentration.

Measurement of Phosphate ions concentration

Measurement of Phosphate ions concentration is studied due to organophosphate category of monocrotophos .In the structure of monocrotophos, PO_4^{2-} group binds one side from carbon double bond and another side from ester group by single bond. So, during the degradation of monocrotophos, single bond can easily break and phosphate group easily releases (Konstantinou et al., 2002).

$$\% \text{ Synergy} = \frac{(K_{US+UV+TiO_2+H_2O_2}) - (K_{UV+TiO_2+H_2O_2} + K_{US+TiO_2+H_2O_2})}{(K_{US+UV+TiO_2+H_2O_2})} \quad \text{eq. (7)}$$

So measurement of removal PO_4^{2-} ion concentration was studied with the time at the optimum condition of catalyst and oxidant as shown in Figure 7. In figure 7, removal of phosphate 95% was found during the running of 6 hour setup and after that it became constant. Ammonium molybdate blue method was used for determination of PO_4^{2-} concentration. In the result, PO_4^{2-} ions concentration increased with the time. So, it shows that monocrotophos is degraded in the UV light.

Mineralization Studies

Main objective is to determination of mineralization of any hazardous compound with the time is to find out that in how much time any complex compound can be converted in the harmless product. The Mineralization Studies was done by COD analysis method and results are clearly shown in figure 8. The graph (Fig. 8) is plotted between the time and % decrease in COD of compound. Under our experiment method, photocatalysis process can be 80% mineralized of monocrotophos compound at initial concentration of 200 PPM in 6 hours. After 6 hour only 20% COD is remain

Ultrasound irradiation

Ultrasound irradiation is a new process in AOP for water treatment (Figure 9) which further enhances the water treatment by forming cavity on the surface of liquid and ultimately helps to produce OH radicals. Many factors produce effect on the efficiency such as intensity of ultrasound, temperature, complexity of the substrate. Mainly this experiment is performed in the ultrasonic bath or ultrasonic probe. In our experiment, sonolysis process was performed in ultrasonic bath at the frequency of 33kHz. The alone sonolysis process 9 to 10 % degradation could be achieved with in some hour of running setup and further degradation was achieved 14 and 15 % respectively in case of US + TiO_2 and US + $TiO_2 + H_2O_2$.

Sonophotocatalysis Process

Sonophotocatalysis is an emerging treatment process improves the overall efficiency of the AOPs and chemical reaction kinetics. In the sequential experiment of photocatalysis and sonolysis, best results were achieved in the combination of these two technologies (Figure 10). Such combination has more additive effect which leads to enhance the degradation by generating more OH radicals. Sonophotocatalysis degradation of monocrotophos was performed at the optimum condition of photocatalysis and 98% degradation was achieved in 2

hours which was higher than photocatalysis and alone sonolysis.

Synergic effect

When the multiple process are used such as photocatalysis, sonocatalysis, sonophotocatalysis so for finding out the synergistic effect among all experiment, synergic index is used which is based on the rate constants of all experiments (Elena S, 2002). It can be quantified as the normalized difference between the rate constants obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonocatalysis.

If the synergic effect is positive it means combined effect has more valuable in comparison of both individuals treatment.

In our study the rate constant of combined process ($K_{US+UV+TiO_2+H_2O_2}$) is 1.598 hr^{-1} and rate constant of ($K_{UV+TiO_2+H_2O_2}$) is 1.324 hr^{-1} and for $K_{US+TiO_2+H_2O_2}$ is 0.046 hr^{-1} .

Therefore % synergy is **17.52%**.

CONCLUSION AND RECOMMENDATIONS

The quantity of pesticides compound entering the environment each year is reported to be similar to the amount of pharmaceuticals compound used each year. Pesticides compounds are majorly suspicious environmental contaminants as they are biologically active, which obviously is a part of their nature.

Commercial available monocrotophos pesticides has been successfully degraded in the presence of TiO_2 photocatalyst and 94 % degradation was found after only 2 hours in UV light treatment and under the optimum catalyst dose of 1.5 gL^{-1} , pH of 5, oxidant concentration (H_2O_2) of 0.5 gL^{-1} when stock solution concentration was 200 mgL^{-1} .

So, when sonophotocatalyst (combined treatment technology) experiment was performed under the all the optimum condition than 98% degradation was achieved only within 2 hours and 88% mineralization within 6 hours. Because sonophotocatalyst treatment enhances the treatment by releasing the more and more OH radicals and also enhances the mass transfer ratio.

Abbreviation

TiO_2 = Titanium Dioxide
 HO^{\cdot} =Hydroxyl ion
 H^+ =Proton Species

O₂⁻ =Superoxide ion
 HO°= Hydroxyl Radical
 H₂O₂=Hydrogen Peroxide
 O₂=Oxygen molecule species
 UV=Ultraviolet
 US=Ultrasound

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