

Solar and UV based Photo Degradation Studies on Paraquat using Homogeneous and Heterogeneous Photocatalyst

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Abstract— Photocatalytic degradation of paraquat was performed on wastewater by various photodegradation techniques via Solar, Solar/TiO₂, Solar/H₂O₂, UV, UV/TiO₂ and UV/H₂O₂ processes. Studies were also performed to optimize the operating parameters such as pH, initial concentration, catalyst dosage and contact time on photocatalytic degradation of paraquat. It was found that the UV/H₂O₂ photo catalytic process was more effective than any other methods studied for degradation of the paraquat. The maximum degradation of paraquat was 95.27% at 300 minutes for initial pH 7, initial paraquat concentration of 10mg/l and H₂O₂ dosage of 2g/l. The kinetic constant (k) for UV/H₂O₂ was found to 8.26 times greater than solar process and 7.28 times greater than the UV process. The order of reaction rate constant was UV/ H₂O₂ > UV/TiO₂ > Solar/H₂O₂ > Solar/TiO₂ > UV > Solar.

Keyword: Paraquat, Herbicide, Solar, UV, H₂O₂, TiO₂

1. INTRODUCTION

Agriculture plays a dominant role in Indian economy and more than 80% of population depends on it. About 30 percent of the potential food production is said to be lost in India due to insect pest, plant pathogens, weeds, rodents, birds and hence the usage of pesticides has become absolutely essential.

Most of the pesticides have very long half-life times in the soil and are known to elicit their adverse effects by natural hormones in the body and it has been postulated that their long term, low- dose exposure are increasingly linked to the human health effects such as immune suppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer (Crisp et al 1998; Hurley et al 1998).

2. PARAQUAT

Paraquat (C₁₂H₁₄Cl₂N₂) is one of the most widely used herbicides to control weeds. The pyridine is coupled with sodium in anhydrous ammonia to give 4, 4' – bipyridine, which is then methylated with chloromethane to give the desired compound. It is quick – acting and non-selective, killing green plant tissue on contact. It is also toxic to human beings and animals. The effect of paraquat on human include burns to the mouth, acute respiratory distress, loss of appetite, abdominal pain, thirst, nausea,

vomiting, diarrhea, giddiness, headache, fever, muscle pain, lethargy, shortness of breath and rapid heartbeat. The Central Pollution Control Board has prescribed effluent standard of paraquat in pesticide industrial effluent as 23 mg/l (CPCB, 2006). However World Health Organisation (WHO) has recommended the maximum concentration of paraquat in drinking water as 10 µg/L. Though paraquat was banned in many countries especially in European countries, it is widely used in agriculture and industries for control of weeds in India.

Generally, pesticide industries in India have adopted two schemes for treatment of wastewater (COINDS 2006) evaporation and detoxification followed by biological treatment. They have also adopted certain physical and chemical treatment methods like flocculation, precipitation, adsorption on granular activated carbon, air stripping and reverse osmosis. But these methods could transfer pollutants from one phase to another one, but not destroy them.

Photocatalytic degradation of various pesticides have been reported by many researchers such as Diuron by Xe lamp/TiO₂ (Bamba *et al.*, 2008), 2, 4 Dichlorophenoxyacetic acid by UV/TiO₂ (Lu and Chen, 1997), Atrazine, Simazine, Trietazine, Prometon and Prometryn by UV/TiO₂ (Pelizzeti *et al.*, 1990), Carbendazim by UV/TiO₂ (Saïen and Khezrianjoo, 2008), Thiram by UV/TiO₂ (Haque and Munner, 2005), Cartap Hydrochloride(synthetic pesticide) by UV/TiO₂ (Choi *et al.*, 2004), Phosalone by UV/TiO₂ and UV/TiO₂/H₂O₂ (Dhaneshwar *et al.*, 2004), Carbofuran by UV/TiO₂ (Mahalakshmi *et al.*, 2007), 3,4 dichloro propionamide by UV/TiO₂ (Pathirana and Maithreepala, 1997), 2, 4 Dichlorophenoxyacetic acid by UV/ZnO (Sanchez *et al.*, 1996), carabaryl by UV/TiO₂ (Kuo *et al.*, 2008).

In this study, photocatalytic degradation of paraquat by Solar, UV, Solar/TiO₂, UV/TiO₂, Solar Fenton, Solar/H₂O₂ and UV/H₂O₂ processes were conducted. Also the effect of operating variables such as initial concentration of paraquat, dose of catalysts, pH of pesticide solution was studied.

3. EXPERIMENTAL METHODOLOGY

Experimental setup of UV Photocatalytic reactor

An annular reactor with an effective volume of 500ml was used and 15W mercury lamp (Sankyodenki 7B made in Japan; supplied by Heber Scientific- India) with wavelength of 352nm was used as UV light source, placed in a double walled immersion well of quartz. The reactor has an inlet and two outlets, one at the top for collecting the excess wastewater and another at the bottom for collection of treated sample. The whole reactor is mounted on a magnetic stirrer to ensure complete homogeneity of the reacting solution.

The reactor was wrapped with aluminium foil to prevent the UV ray into the working area. A tube was inserted at one side of the quartz cylinder and connected to the bottom of a glass condenser through the peristaltic pump. The other end of the condenser was connected to another side of the quartz cylinder through another tube. The condenser was cooled by a cooler (Model – LAUDA WK 1400; made in Germany) in order to prevent the excess heat generated and the reaction temperature was maintained as 21^oC.

The solar photolytic studies were conducted in batch mode in 2 L glass tray containing 500 ml of paraquat solution.

4. RESULTS AND DISCUSSION

Dark Adsorption

10mg/l of paraquat with 1g/l of TiO₂ was kept in dark environment without any stray light. At the end of 24 hrs of contact time, about 10.15% decrease was observed due to adsorption of paraquat on the surface of catalyst. It absorbance is measured at 600nm in UV-Visible Spectrophotometer SPEKOL 1200 (Analytic Jena, Germany) against a standard reference solution.

Effect of pH on photodegradation of paraquat by Treatment Alternatives

The pH of solution affects the adsorption and dissociation of the pollutant on catalyst surface (Lea and Adesina 2001). Hence, degradation studies were conducted in the pH range of 5 – 9 by maintaining other parameters, concentration of paraquat (50mg/l), contact time of 180 minutes, dosage of TiO₂ 1 g/L and that of H₂O₂ as 2 g/L. The solar degradation studies were conducted during 11 a.m to 2.00 p.m and the results are shown in Fig. 2.

The direct photolysis by solar and UV methods did not have any significant effect on paraquat removal. In solar /TiO₂ and UV/TiO₂ method, the paraquat removal was increased with initial pH attained the maximum removal at pH 7 and decreased with further increase in the initial pH.

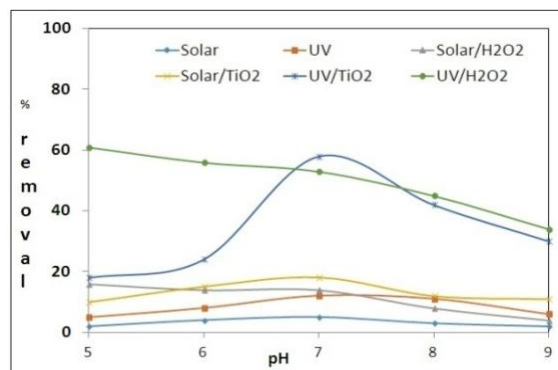


Figure.2. Effect of pH on Photodegradation of Paraquat

The maximum removal efficiency obtained at pH 7 was 17.94% and 57.77% by solar/TiO₂ and UV/TiO₂ methods respectively. The dependence of the degradation rate of paraquat with pH is the consequence of pH changes in the adsorption of paraquat on the surface of TiO₂.

However, the degradation efficiency decreased with increase in the pH from 5 to 9, when H₂O₂ was the photocatalyst for solar and UV processes. The maximum removal of paraquat by solar/H₂O₂ and UV/H₂O₂ was 16.33% and 61.27% respectively at pH 5. H₂O₂ could stay stable at high pH probably because it solvates a proton to form an oxonium ion (H₃O₂⁺). The oxonium ion makes H₂O₂ electrophilic to enhance its stability and reduce the reactivity. Further no hydroxyl radical will be produced if H₂O₂ was not decomposed and so lower degradation was observed at higher pH. Besides, H₂O₂ is also unstable in basic solution and may decompose to give oxygen and water and lose its oxidation ability. Also, the oxidation potential of hydroxyl radical is known to decrease with increasing pH (Eisenhauer 1964) which also reduces degradation.

Effect of Initial Concentration of Paraquat on Photodegradation by Treatment Alternatives

In order to study the effectiveness of photo catalysis with increasing the pollutant concentration, experiments were conducted with synthetic wastewater containing paraquat at concentration ranging from 10 to 50mg/l. For photo catalysis, the initial concentration of pollutants usually was not higher than 100mg/l, beyond this value negative effect of high concentration would occur and photocatalytic efficiency would decrease. The initial pH was maintained as the actual pH for photolysis and TiO₂ photocatalytic studies and 5 for H₂O₂ catalytic study. The results obtained for the effect of initial concentration on paraquat is represented in Fig. 3

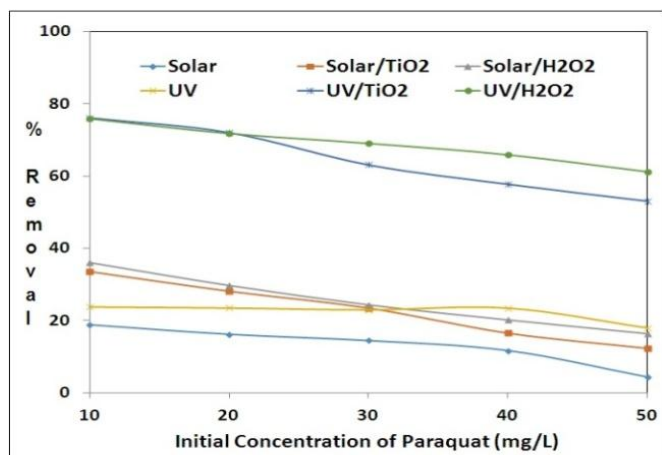


Figure 3. Effect of Initial Concentration

From the Figure it was observed that the degradation efficiency decreased when there is increase in initial concentration of paraquat. The maximum degradation of paraquat observed at initial concentration of 10mg/l at 180 minute was 18.83%, 33.62%, 36.14%, 23.79%, 76.21% and 75.81% by Solar, UV, Solar/TiO₂, solar/H₂O₂, UV/TiO₂ and UV/H₂O₂ respectively. Similarly, maximum degradation of paraquat observed at initial concentration of 50mg/l at 180 minute was 4.37%, 12.24%, 16.33%, 17.85%, 57.77% and 61.27% by Solar, UV, Solar/TiO₂, solar/H₂O₂, UV/TiO₂ and UV/H₂O₂ respectively. Since illumination time and amount of catalyst are constant, the radicals formed on the catalysts remain constant. Hence, the relative number of hydroxyl radical species attacking the pesticide molecules decreased with increase of pesticide concentration (Mengyue et al 1995).

Effect of TiO₂ dosage on paraquat degradation by Solar/TiO₂ and UV/TiO₂ Methods

The catalyst concentration required for particular pollutant is to be optimized as the excess catalyst may reduce the amount of photo energy being transferred in the medium due to opacity offered by the catalyst particles. Therefore, experiments were performed with the TiO₂ dosage ranging from 0.5 – 2.5g/l by maintaining pH 7, Concentration of paraquat as 10mg/l and contact time of 180 minutes. The results obtained are given in the figure 4.

It was observed that the degradation efficiency increased till 1 g/L of TiO₂ and then decreased. The maximum degradation of paraquat obtained with 1 g/L of TiO₂ was 36.13% and 76.21% for solar/TiO₂ and UV/TiO₂ methods respectively.

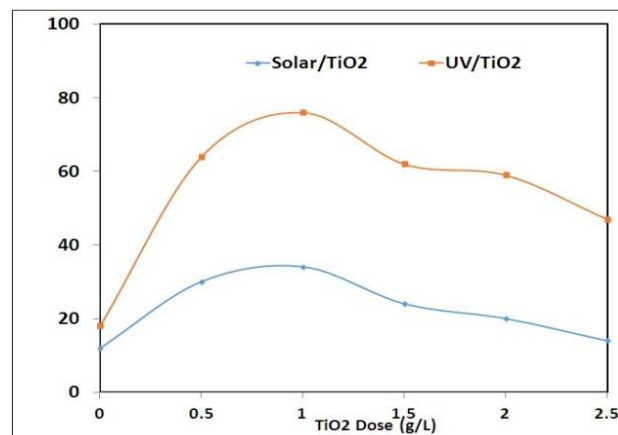


Figure 4. Effect of TiO₂ Dosage

Increase in catalyst dosage above the optimum level resulted in decrease in light penetration and deactivation of activated molecules due to collision with the ground state molecules (Shankar et al 2004).

Effect of H₂O₂ dosage on paraquat degradation by Solar/H₂O₂ and UV/H₂O₂

Similarly, experiments were performed by varying the dosage of H₂O₂ from 0.5 to 2.5g/l by maintaining other parameters pH 5, concentration of paraquat 10mg/l and contact time of 180 minutes. The results obtained for the effect of H₂O₂ dosage on paraquat is given in the Figure 5.

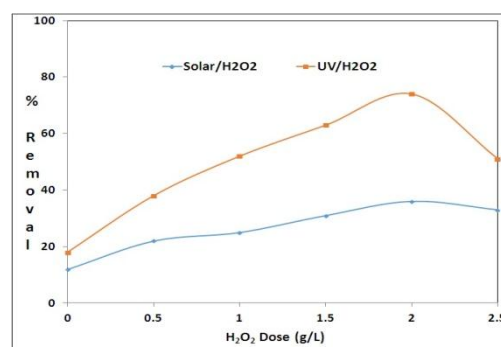


Figure 5. Effect of H₂O₂ on photodegradation of Paraquat

Similar to TiO₂ studies, the degradation increased with dose from 0.5 to 2g/l, and a sharp decrease was observed afterwards. which might be due to the self decomposition of H₂O₂. It may also act as a free radical, thereby decreasing the concentration of hydroxyl radicals and reducing the degradation efficiency (Kang and Hwang 2000). The maximum degradation occurred at 2 g/L of H₂O₂ at 180 minutes was 33 and 74% for Solar/H₂O₂ and UV/H₂O₂ methods respectively.

Effect of inorganic ions by solar photo degradation of paraquat

The experiments were conducted in the optimized condition pH 7, concentration of paraquat 10mg/l and contact time of 180 minutes. The concentration of the Ammonical nitrogen, Nitrite, Nitrate formation by solar photodegradation was only about 10.12mg/l, 11.97mg/l and 9.29mg/l respectively because during the degrading process indicated that the pesticide was decomposed with the evolution of inorganic ions. The concentration of the Ammonical nitrogen, Nitrite, Nitrate formation is only about 17.89mg/l, 24.56mg/l and 13.45 mg/l respectively by solar/TiO₂ process. In case of paraquat, the formation of Nitrate was much lower than the Nitrite possibly because of the sequential oxidation of the amine group on the molecular structure to form nitrate being a slow process. The concentration of the Ammonical nitrogen, Nitrite, Nitrate formation is improved upto 30.12 mg/l, 39.18 mg/l and 30.13 mg/l respectively compared to above two process by solar/H₂O₂ process.

The concentration of the Ammonical nitrogen, Nitrite, Nitrate formation is increased upto 40.39 mg/l, 43.17 mg/l and 34.56 mg/l respectively by UV degradation. It was accounted generally in photocatalytic experiments the presence of chloride ions affects the adsorption step which also absorbs UV light partly and reduces degradation.

The concentration of the Ammonical nitrogen, Nitrite, Nitrate formation is increased upto 60.75 mg/l, 50.16 mg/l and 47.82 mg/l respectively by UV/TiO₂ method. The concentration of the Ammonical nitrogen was increased upto 71.45% whereas nitrate and nitrite formation was decreased to some extent in UV/H₂O₂.

Kinetics of Removal of Paraquat by different Photocatalytic Process

The results with respect to paraquat removal under different photocatalytic methods follow pseudo first order. The plot of ln(C_t / C₀) versus time t gives a straight line passing through the origin, the slope of which is first order rate constant (R). The kinetics of the various photocatalytic processes are depicted in Table 1 and represented in figure 6. The kinetic constant (k) for UV photocatalytic studies were almost double that of solar photocatalytic method.

Table 1 Kinetics of removal of paraquat

Concentration of paraquat	Method of treatment	Linear Regression Equation	K x 10 ⁻³ Min ⁻¹
10mg/l	Solar	ln(C _t /C ₀) = 0.0052t	5.2
	UV	ln(C _t /C ₀) = 0.0059t	5.9
	Solar/TiO ₂	ln(C _t /C ₀) = 0.0094t	9.4
	Solar/ H ₂ O ₂	ln(C _t /C ₀) = 0.0127t	12.7
	UV/ TiO ₂	ln(C _t /C ₀) = 0.015t	15
	UV/ H ₂ O ₂	ln(C _t /C ₀) = 0.023t	23

The order of reaction rate constant was UV/ H₂O₂ > UV/TiO₂ > Solar/H₂O₂ > Solar/TiO₂ > UV > Solar. Thus UV/H₂O₂ was found to be highly effective in degradation of paraquat than any other processes.

5. CONCLUSIONS

The major conclusions drawn from the above study are given below

- The UV/H₂O₂ photocatalytic method is highly effective in degradation of paraquat. UV/H₂O₂ is strongly superior to Solar, UV, Solar/TiO₂, UV/TiO₂ and Solar/H₂O₂ processes in degradation of paraquat.
- The order of reaction rate constant was UV/ H₂O₂ > UV/TiO₂ > Solar/H₂O₂ > Solar/TiO₂ > UV > Solar.
- The kinetic constant (k) for UV/H₂O₂ was found to be 8.26 times greater than solar process and 7.28 times greater than the UV process.

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