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RESEARCH ARTICLE

Photo Catalytic Removal of Paraquat Dichloride Herbicide in Aqueous Solutions by Using TiO_2 Nanoparticle

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Abstract

In this work treatment of paraquat dichloride herbicide **in** wastewater using TiO_2 nanoparticle as catalyst has been investigated. Different parameters also investigated such as the effect of catalyst loading, the influence of initial dye concentration, and the effect of intensity of light in order to reach to the optimum operational conditions in which the best treated of paraquat dichloride herpicide**.** The highest removal efficiency of paraquat dichloride herbicide **was** indicated at 0.17 gm/100cm^3 mass of aluminum oxide and 100 ppm of paraquat dichloride herbicide**.** photocatalytic degradation of paraquat dichloride herbicide **was** favorable in the 7.33 mW/cm^2 light intensity. The percentage efficiency of removal paraquat dichloride herbicide equal 94. 77 %.

Keywords: *TiO_2 nanoparticle, Paraquat dichloride herbicide, Photoefficiency.*

Introduction

Paraquat dichloride herbicide has been represent one of the essential source of pollution in the world due to increased use of insecticides in agricultural fields to combat farm pests. A large number of researchers around the world have increased their interest in treating these pesticides before disposing them to water sources [1]. The scientists are using different methods for treated the Paraquat dichloride herbicide. Aadvanced oxidation processes (AOPs) have been used for removal many pollutants such as Paraquat dichloride herbicide**,** Azo dye. Aops starting with generation of hydroxyl radical to oxidize organic pollutants [2, 4].

In this work heterogeneous has been employed for the removal a wide range of environmental contaminants.The mechanism of AOPs include the exposure of metal oxide particle with energy equal or greater than band gap the electrons promote from the valance band to conduction band to created photo electrons leaving positive holes in valance band.

Paraquat dichloride herbicide and other pollutants react with high active species super oxide and hydroxyl radicals on the surface of the TiO_2 nanoparticle. Photoelectrons in the conduction band react with adsorbed oxygen producing the highly reactive superoxide radical ion. The positive hole in the valance band reacts with adsorbed water to producing hydroxyl radical then react with pollutants [5,6] Paraquat ($C1_2H_{14}Cl_{12}N_2$) 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 nonselective, killing green plant tissue on contact. It is also toxic to human beings and animals. The effect of paraquat on human includes burns to the mouth, acute respiratory distress, loss of appetite, abdominal pain, thirst, nausea.

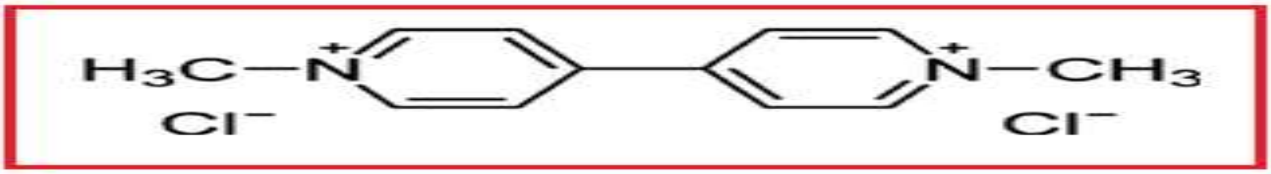

Figure 1: Structure of Paraquat dichloride herbicide

Paraquat dichloride, commonly referred to as "paraquat," is one of the most widely used herbicides; Paraquat is used to control weeds in many agricultural and non-agricultural use sites. It is also used as a defoliant on crops, like cotton, prior to harvest [7].

Materials & Methods

Experimental Section

Materials

The Titanium dioxide (TiO_2) nanoparticle was obtained from sigma-Aldrich. Sodium hydroxide (NaOH): Supplied by Fluka AG. Hydrochloric acid (HCl): Supplied by Fluka AG. Paraquat dichloride herbicide **was** purchased from Hilla market .All chemicals were used without further purification.

Photo catalytic Experiments

The photo catalytic degradation of Paraquat dichloride herbicide **has** been investigated in glass photoreactor, which consists of the cylindrical annular – type reactor consisted of two parts. The first part was an outside thimble; running water was passed through the thimble to cool the reaction solution. Owing to the continued cooling, the temperature of the reaction solution was maintained at room temperature. The second part was an inside thimble and the reaction solution (100 cm^3) was put in the reaction chamber. The removal of Paraquat dichloride herbicide was conducted under 125W low-mercury lamp.

All experiments of removal processes of dye have been performed by mixing 0.17 gm / 100 cm^3 of the catalyst with 100 ppm of the dye solution. In order to ensure adsorption equilibrium between surface of catalyst and dye, the suspension solution was kept under stirring in the dark for 30 min.

The solution of dye was bubbled with air (10cm^3/min) during the irradiation. 2 cm^3 of suspension reaction mixture was withdrawn every 10 min, and then centrifuged at 4000rps to remove any residual aluminum oxide particles. All samples taken was analysed at maximum absorption band by UV-vis spectrophotometer.

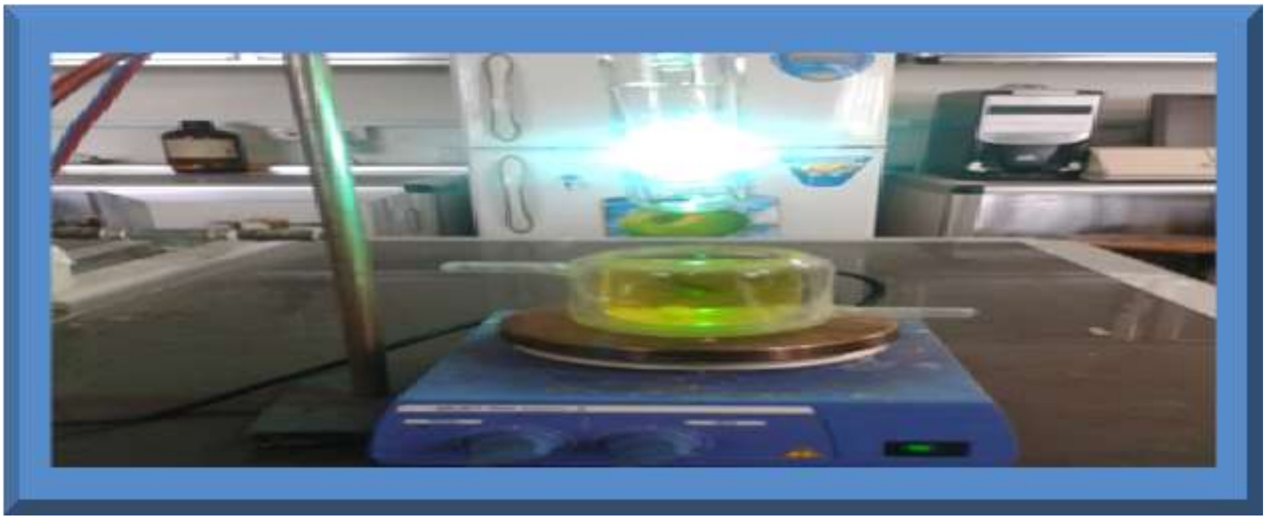

Figure 2: Main parts of the photo catalytic cell used in removal of paraquat dichloride herbicide

Results and Discussion

The Effect of TiO_2 Nanoparticle Loaded Masses on the Photocatalytic Degradation of Paraquat Dichloride Herbicide

Loaded masses of TiO_2 nanoparticle was first parameter has been investigated at range (0.06 - 0.70 gm/100 cm^3), to reach optimum degradation efficiency.The optimum conditions in which these experiments has been done include 100 ppm Paraquat dichloride herbicide, 10cm^3/min flow rate of an air bubble ,at room temperature 298 K .

The results have been noted in Figure 3. When the amount of loaded masses of TiO_2 nanoparticle increases the number of active sites available for the generation of highly reactive radicals increased, there for the removal of dye increased until reach to 0.17 gm/ 100 cm^3 which represent optimum value in which the best removal of Paraquat dichloride herbicide .

Above the optimum value of catalyst the removal of Paraquat dichloride herbicide decreases due to the decrease of light penetration and increase of light scattering. The interception of the light by the suspension solution, in such case a part of catalyst surface area decreased slightly or approaches constantly [8-13].

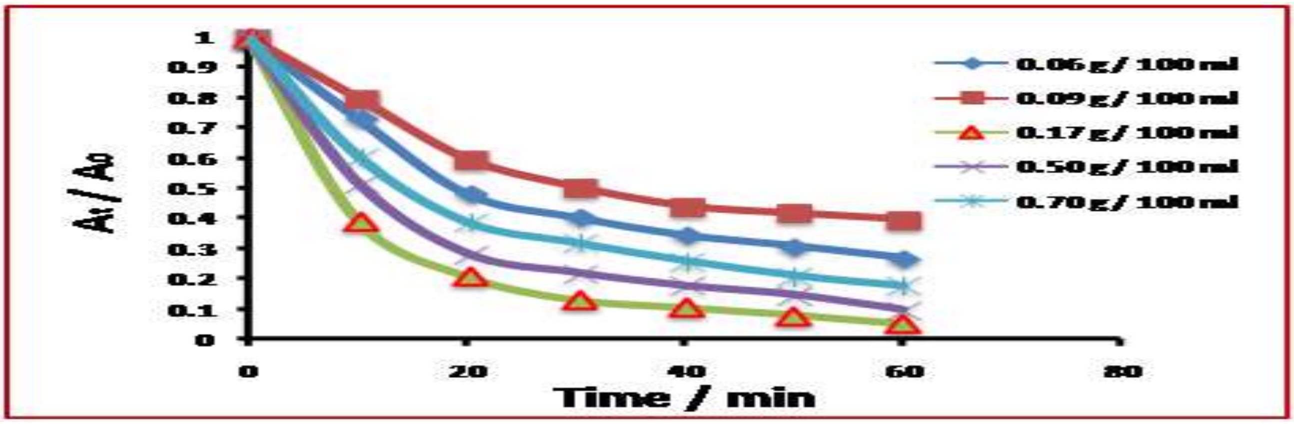

Figure 3: Effect of loading mass on removal of Paraquat dichloride herbicide using UV radiation, initial condition: 100 ppm Paraquat dichloride herbicide

The Effect of Initial Concentration of Paraquat Dichloride Herbicide on Removal Processes

The removal of Paraquat dichloride herbicide **has** been conducted by using different initial Paraquat dichloride herbicide concentration in the range (100 - 500 ppm).

These experiments was performed at range (0.17gm / 100 cm^3) ,the suspension solution was irradiated with 7.33 mW/cm^2 intensity of light, flow rate of air bubble 10 cm^3/ min, at room temperature and 0.17 gm/100 cm^3 of TiO_2 nanoparticle as acatalst .

As illustrated in Figure4. the removal of Paraquat dichloride herbicide decreases with increased the initial concentration of Paraquat dichloride herbicide because the number of active site of TiO_2 nanoparticle catalyst doesn't change, so when the concentration of Paraquat dichloride herbicide increases and cover all active sites that can cause reduced generation of an electron-hole pair which subsequently reduces the removal of Paraquat dichloride herbicide .

The optimum concentration of dye was 100 ppm the greatest removal of Paraquat dichloride herbicide because the Paraquat dichloride herbicide **was** cover the largest area of the TiO_2 nanoparticle particles, therefore absorbed maximum exciting photons to generate higher concentration of the activated catalyst [14,15].

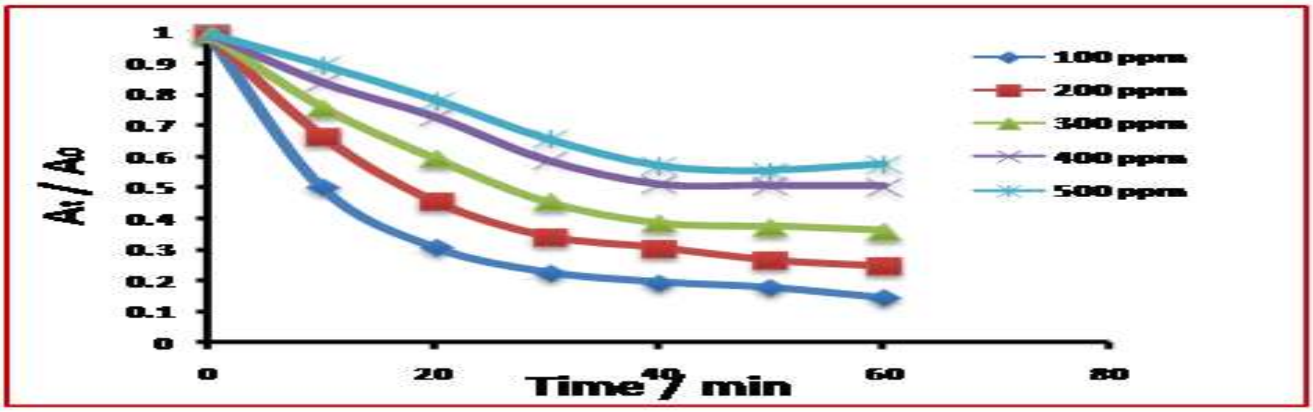

Figure 4: Effect of Paraquat dichloride herbicide concentration on removal process under UV irradiation, initial condition: amount of TiO_2 nanoparticle = 0.17 gm / 100 cm^3

Effect of PH Parameter on Photo Catalytic Degradation of Paraquat Dichloride Herbicide

The effect of initial PH range (3 - 9) on the photo degradation of Paraquat dichloride herbicide has been tested .

The pH of the aqueous solution was adjusted using 0. 1 N HCl and 0.1N NaOH. A series of experiments has been performed under the optimum condition, 0.17 gm /100cm^3 titanium dioxide nanoparticles, 100 ppm of Paraquat dichloride herbicide, 10 cm^3/min flow rate of air bubble, and irradiated with7.33 mW/cm^2.

The effect of PH includes two steps, firstly hydroxylated the surface of titanium dioxide nanoparticles (Ti-OH) in aqueous solution. The second step reacting the hydroxide surface (Ti -OH) with acidic medium (low PH) absorb protons to become positively charged and with an alkaline medium (high PH) lose protons to become negatively charged as shown in equation below[16] .

$Ti\text{-}OH + H^+ \rightarrow TiOH_2+$ acidic medium **(1)**

$Ti\text{-}OH + OH^- \rightarrow TiO^- + H_2O$ alkaline medium **(2)**

Figure 5 shown that the photo degradation efficiency of Paraquat dichloride herbicide increased with increasing pH until reach PH = 6.7(the zero point charge of titanium dioxide =6.3) [17, 18] in which photo catalytic efficiency equal 93.71 % due to produce the hydroxyl radical which is generated from oxidizing hydroxyl ions, on the other hand increases absorption of Paraquat dichloride herbicide on the surface of titanium dioxide nanoparticles.

Above the zero point charge of titanium dioxide nanoparticles in alkaline medium, photo catalytic degradation of Paraquat dichloride herbicide has been gradually decreasing due to reducing the Paraquat dichloride herbicide absorbed on the negative charge surface of titanium dioxide Nanoparticles.

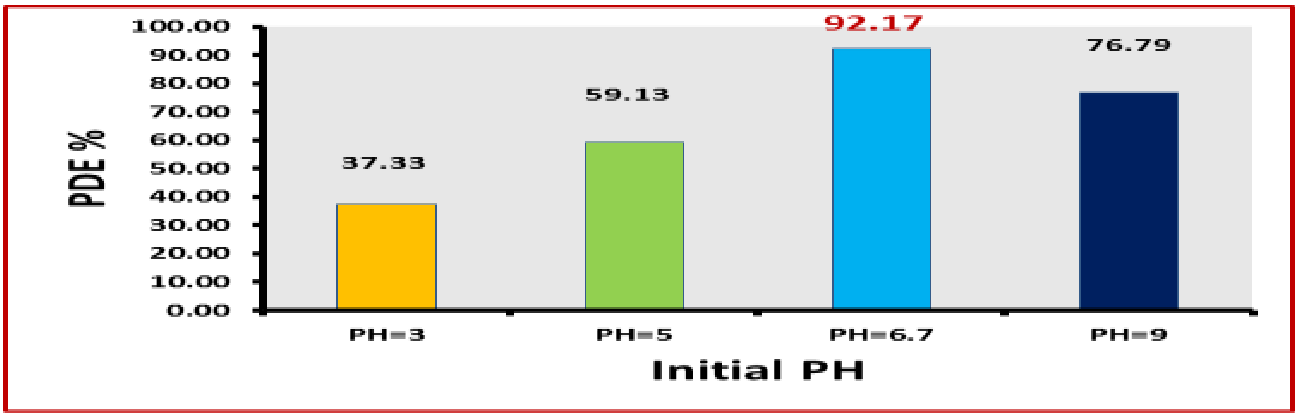

Figure 5: Photo catalytic degradation of Paraquat dichloride herbicide at variation initial pH using UV radiation, initial Paraquat dichloride herbicide concentrations = 100 ppm, amount of photo catalyst titanium dioxide nanoparticles = 0.17 gm / 100 cm^3

The Effect of Light Intensity on Removal of Paraquat Dichloride Herbicide Using TiO_2 nanoparticle

Light intensity was last parameter investigated in this project, include performed series experiments for study the removal of Paraquat dichloride herbicide **at** range (1.22-7.33) mW/cm^2.

The rate of removal Paraquat dichloride herbicide was conducted at 0.17 gm/cm^3 loaded mass of TiO_2 nanoparticle with 100 ppm of Paraquat dichloride herbicide, 10cm^3/min flow rate of an air bubble at room temperature .As shown in Figure 6. The increasing of light intensity lead to increased the removal Paraquat dichloride herbicide from waste water because increased electron–hole formation which was required for the electron transfer from the valence band to the conduction band of catalyst[19,20].

The optimum value of light intensity 7.33 mW/cm^2 in which the high removal of Paraquat dichloride herbicide and the removal efficiency equal to 94.77 % as shown in Figure 7.

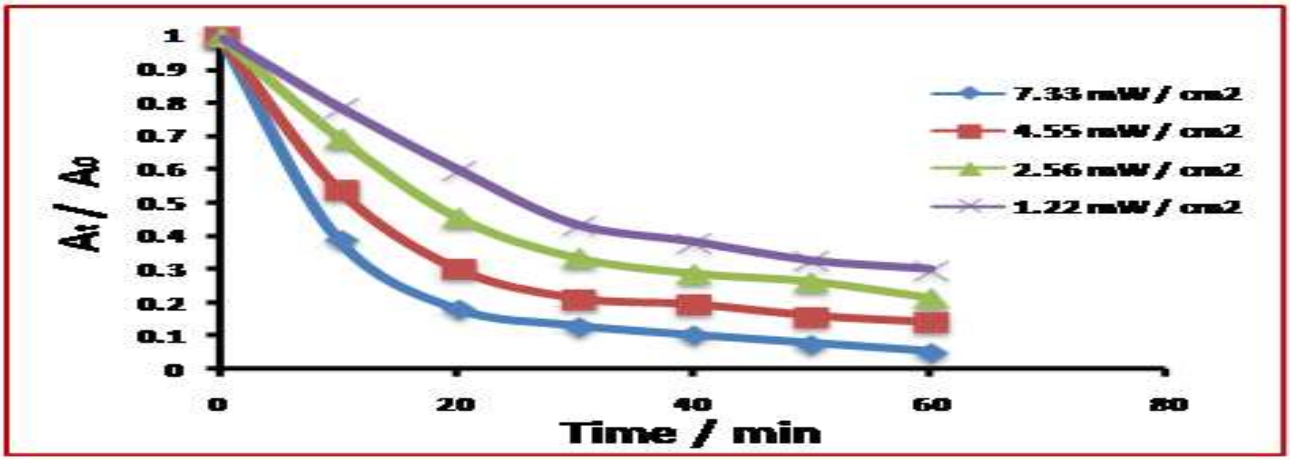

Figure 6: The change of (A_t / A_0)with irradiation time at the different light intensity with 0.17 gm/100cm^3 of TiO_2 nanoparticle, on removal of Paraquat dichloride herbicide

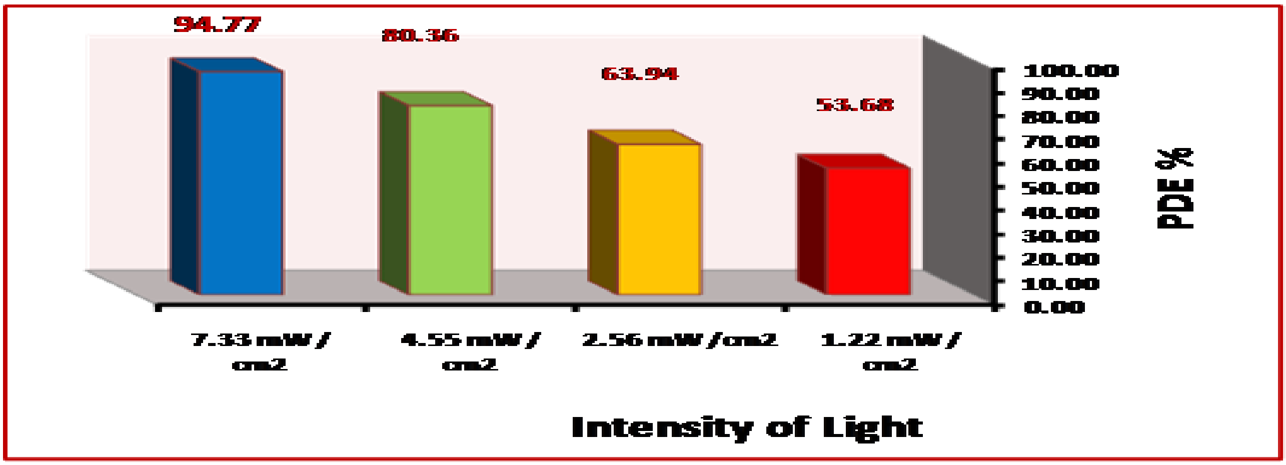

Figure 7: The change percentage of removal Efficiency with irradiation time at different light intensity, initial Paraquat dichloride herbicide concentrations = 100 ppm, the amount of loaded mass of TiO_2 nanoparticle = 0.17 gm / 100 cm^3

Conclusion

The experiments has been carried out in the absence of light and TiO2 nanoparticle no reaction occurs. The photocatalytic degradation of Paraquat dichloride herbicide depended on the amount of catalyst dosage and the optimum value equal 0.17 gm / 100 cm3 of TiO2 nanoparticle with 100 ppm concentration of Paraquat dichloride herbicide as optimum value and light intensity 7.33mW/cm2 and 10 cm3/min bubble of air . Removal processes decrease with increase concentration of Paraquat dichloride herbicide due to the decrease of the concentration OH- adsorbed on the catalyst surface. Removal process of Paraquat dichloride herbicide increases with the increase of light intensity. The percentage efficiency of removal Paraquat dichloride herbicide equals 94.77 % .

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