



## COMPARATIVE DEGRADATION OF PARAQUAT HERBICIDES IN THE PRESENCE/ABSENCE OF ZnO SEMI-CONDUCTOR USING UV ILLUMINATION

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**ABSTRACT** The importance of herbicides towards agricultural production is paramount. Most of these herbicides turn to be toxic to plant and contaminate soil and water which produces poor-quality and unsuitable for ecological health. Water purification through photocatalysis is the most important requirement due to increase health, environment and energy conservation concerns. Nanomaterials are reported to have enhanced surface and particular changes in their biological, physical and chemical properties. This properties makes them gain attention in environmental chemistry. Many scientific methods have been developed to breakdown organic contaminants in water, ZnO nanoparticle is a promising material in terms of nanostructuring and photocatalysis. Recently, the extraordinary properties of ZnO photocatalysis makes it attract more attention in photocatalysis. The heterogeneous catalytic structure through ZnO semiconductors have the capacity to work efficiently and effectively for waste

water treatment. In this present work, Paraquat herbicide was degraded without and with catalyst using UV-Light illumination with time variation. The result obtained showed that the photodegradation efficiency of paraquat without and with ZnO semiconductor after 60 min was found to be 17.8% and 51.6% respectively. After 120 min interval, the efficiency increases to 33.45% and 71.8% respectively. This indicate that ZnO semiconductor has the potentials of degrading paraquat more effectively and less time consuming compared to its degradation in the absence of catalyst.

**Keywords:** Degradation, Catalyst, Paraquat and Semiconductor

## INTRODUCTION

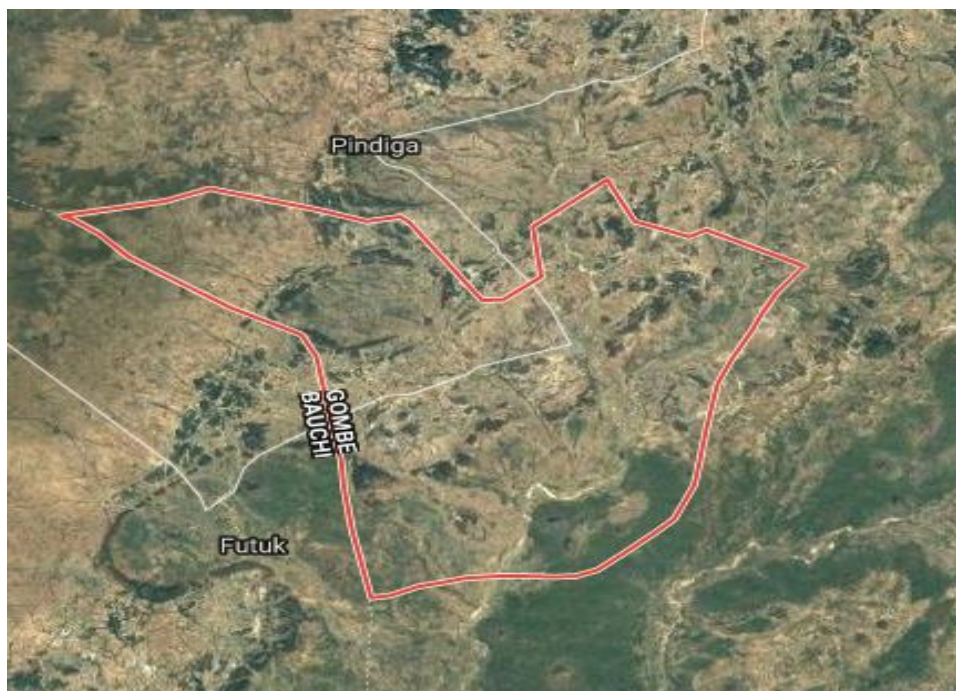
The demand for good quality water by both human and animals (aquatic organism included) have continued to increase with increasing world population and industrial activities. Industrial activities have generated a significant number of pollutants which threat both surface and groundwater (Aguilaret *al*, 2011). Many polluting substance such as industrial waste and effluent are highly toxic, The wastewater released from industries contains highly hazardous and coloured pigments (Azad *et al*, 2017). Nowadays, medical prescription includes a wide range of therapeutic agents, such as analgesics, antibiotics, anticonceptives, antidepressants, anti-coagulants (Kolpin *et al*, 2002). The use and disposal of these substances are not regulated by any current environmental legislation, as it is considered that medicines have a low level of toxicity. (Aguilaret *al* 2011). However, most pharmaceutical and agricultural compounds are dangerous and even lethal for bacteria that degrade organic matter (Wang *et al*,2008).

Nanomaterials are reported to have enhanced surface and particular changes in their biological, physical and chemical properties. This properties makes them gain attention in environmental chemistry. Many scientific methods have been developed to breakdown organic contaminants in water, ZnO nanoparticle is a promising material in terms of nanostructuring and photocatalysis. Recently, the extraordinary

properties of ZnO photocatalysis makes it attract more attention in photocatalysis. The heterogeneous catalytic structure through ZnO semiconductors have the capacity to work efficiently and effectively for waste water treatment. (Hapeman-Somich, 1991) reported that different pesticides can be degraded by photochemical and microbiological processes. However, the articles did not report the complete degradation of paraquat. The environmental fate of pollutants depends a lot on their mobility in soils and their tendency to intrude into other environmental compartments such as air and water (Navarro et al, 2009)

Paraquat is the most highly acutely toxic herbicide to be marketed over the last 60 years. Yet it is one of the most widely used herbicides in the world, and in most countries where it is registered it can be used without restriction. It is used on more than 100 crops in about 100 countries. Paraquat is highly acutely toxic and enters the body mainly by swallowing, or through damaged skin, but may also be inhaled. Thousands of deaths have occurred from ingestion (often suicide) or dermal exposure (mainly occupational) to paraquat. Paraquat is corrosive to the skin and once the skin is damaged it is easily absorbed into the body.

## **STUDY AREA**



**Fig 1. Map showing the study location**

## **MATERIALS AND METHOD**

### **Sampling**

200g of paraquat dichloride produced by Nanjing Biochemical Company Limited China was obtained from a local market in Kashere, Gombe State and pure ZnO was obtained from Chemistry laboratory of Gombe State University

### **CALIBRATION OF STANDARD**

From the stock solution of paraquat, desired concentration of standard solution was prepared by serial dilution. Calibration was performed with different standard concentration (10, 20, 30, 40 and 50) ppm, the absorbance of each sample was obtained. 20 ppm was used for the whole experiment as it was found to have the highest absorbance (Fernandes et al, 2017)

## **PREPARATION OF STANDARD SOLUTION**

Portion of paraquat (20 ppm) was weighed using measuring cylinder and transferred into a volumetric flask, deionized water was added to make a solution. The beaker was wrapped with aluminum foil to avoid penetration of light. The wavelength was analyzed using absorbance spectrophotometer and recorded. (Sorolla et al, 2012)

## **PREPARATION OF ZnO SOL GEL**

Propan-2-ol was used in dissolving 0.4 g Zinc acetate at 50-60<sup>0</sup>C. The solution was stirred thoroughly. Using the same temperature, propan-2-ol was again used to dissolve 10 mg of Sodium hydroxide (NaOH) and the solution was stirred continuously. The two solutions were then mixed together in an ice bath. After continuous stirring, the solution is then kept in a water bath for 1 hr to cool. ( Rusmidah et al., 2008)

## **PHOTOCATALYTIC DEGRADATION OF PARAQUAT IN THE ABSENT OF CATALYST.**

20ppm solution of paraquat was prepared and stirred gently to have a homogeneous mixture. Some portion of the solution was transferred to a beaker and wrapped with aluminum foil to avoid light penetration, and placed on a magnetic stirrer; UV bulb was inserted into the solution. The absorbance of the solution was recorded at each time interval (10, 20, 30, 40, 50, 60, 80, 100 and 120) minutes (Ghaida et al, 2018)

## **PHOTOCATALYTIC DEGRADATION OF PARAQUAT IN THE PRESENCE OF CATALYST**

20ppm of paraquat solution was prepared and stirred gently to have a homogeneous mixture. Some portion of the solution was transferred into a beaker and wrapped with aluminum foil to avoid light penetration and placed on a magnetic stirrer, 0.4g of catalyst (ZnO) was added to the solution and UV bulb was inserted into the solution. Some portion of the solution was pipette at regular time interval of

(10, 20, 30, 40, 50, 60, 80,100 and 120)minutes and filtered. The absorbance of the solution was recorded.

(Ghaida et al, 2018)

## RESULT AND DISCUSSION

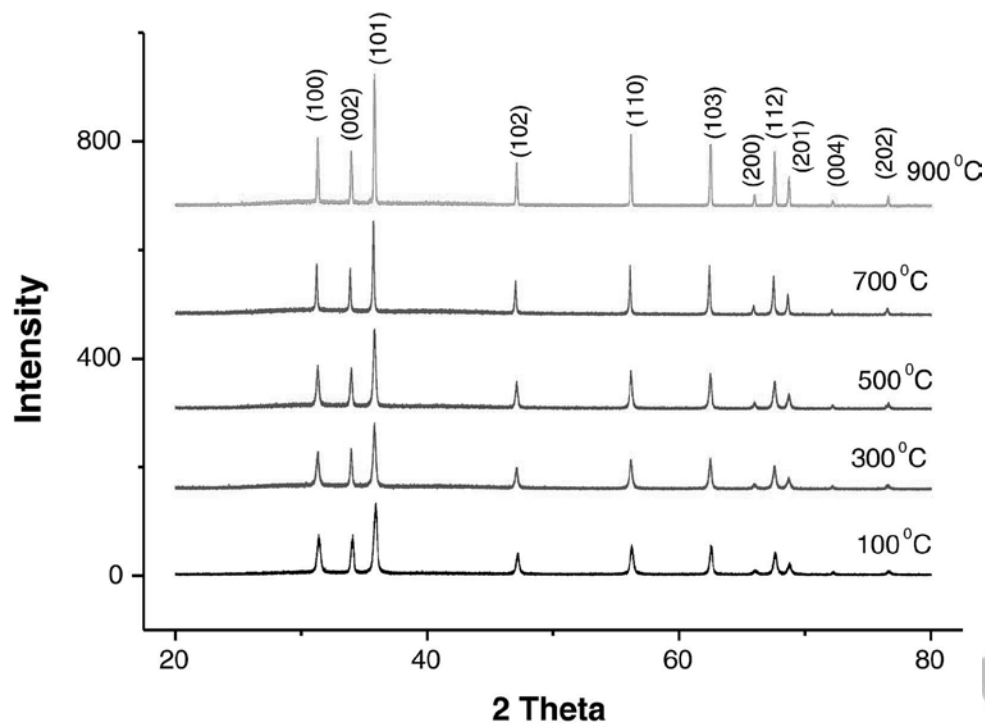


Figure 1: XRD pattern of prepared ZnO nanoparticles.

The presence of the broad lines of the peak shows that the material consist of particles which in nano scale range. From figure 1, the full-width at half-maximum, position and the intensity of the peak can be determined. The diffracted peaks which are seen at  $31.83^\circ$ ,  $34.52^\circ$ ,  $36.33^\circ$ ,  $47.63^\circ$ ,  $56.71^\circ$ ,  $62.96^\circ$ ,  $68.13^\circ$ ,  $69.18^\circ$  have been acutely indexed as hexagopal wurtzite phase of ZnO. (Khoshhesab et al, 2011). It has a lattice constant  $a = b = 0.324$  nm and  $c = 0.521$  nm. (JCPDS,1977). It also prove that the synthesized nano-powder does not contain impurities, this is because it does not have any characteristic XRD peaks apart from ZnO peaks.

**PHOTOCATALYTIC DEGRADATION OF PARAQUAT IN THE ABSENCE AND PRESENCE OF CATALYST**

**TABLE 1: DEGRADATION OF PARAQUAT IN THE ABSENCE OF CATALYST**

<b>TIME (MIN)</b>	<b>CONCENTRATION (PPM)</b>	<b>%DEGREDEATION</b>	$\frac{C_0}{C_t}$	$\ln \frac{C_0}{C_t}$
10	19.86	0.7	1.007	0.0069
20	19.20	4.0	1.041	0.0402
30	17.54	12.3	1.140	0.1310
40	17.20	14.0	1.162	0.1501
50	16.65	16.7	1.201	0.1831
60	16.43	17.8	1.217	0.1964
80	15.80	21.0	1.265	0.2351
100	14.81	25.9	1.350	0.3001
120	13.31	33.4	1.502	0.4068

**TABLE 2: DEGRADATION OF PARAQUAT IN THE PRESENCE OF CATALYST**

<b>TIME (MIN)</b>	<b>CONCENTRATION (PPM)</b>	<b>%DEGRADATION</b>	$\frac{C_0}{C_t}$	$\ln \frac{C_0}{C_t}$
10	19.28	3.6	1.037	0.3633
20	17.49	12.55	1.143	0.1336
30	14.51	27.45	1.378	0.3206
40	13.54	32.3	1.477	0.3900
50	11.17	44.15	1.790	0.5822
60	9.68	51.6	2.066	0.9038
80	8.10	59.5	2.469	0.9038
100	6.14	69.3	3.257	1.1808
120	5.64	71.8	3.546	1.2658

**DISCUSSION**

**DEGRADATION IN THE ABSENCE OF CATALYST**

The evaluation of the degradation of paraquat under the effect of UV irradiation was carried out with time variation of 10,20 30,40,50,60,80,100 and 120 minutes using maximum absorption spectrum of 190nm and the concentration of 20ppm without the addition of catalyst. Table 1 showed the degradation of paraquat without catalyst with time variation. From the result obtained, we can see that the percentage degradation is slightly increasing with increase in time from 10 minutes(0.7%)to 120minutes(33.45%).



These shows that the degradation of paraquat occur even at the absence of catalyst but the percentage degradation was not large enough which is an indication that with increasing irradiation time, the rate of degradation of paraquat increased due to the formation of OH radicals.

## **DEGRADATION IN THE PRESENCE OF CATALYST**

As with the degradation without the addition of catalyst, the evaluation of the degradation of paraquat was also done with time variation of 10minutes to 120minutes but in this case with the addition of 0.4g optimized ZnO semiconductor on a maximum absorption spectrum of 190nm and a concentration of 20ppm. Table 2 shows the degradation of paraquat in the presence of ZnO semiconductor with time variation which shows that there is large increase in percentage degradation from 10 minutes (3.6%) to 120 minutes (71.8%). Degradation is achieved at 60 minutes (51.6%) which is an indication that the percentage degradation of paraquat in the presence of ZnO semiconductor is more effective and less time consuming compared to its degradation at the absence of catalyst. The amount of UV irradiation absorbed by the semiconductor with time variation result in the speedy degradation paraquat.

## **CONCLUSION**

Based on these results, UV irradiation degraded paraquat in the absence of a semiconductor with lower percentage of 0.7% at 10minutes and 33.45% at 120minutes and overall average of 16.19%, but the degradation is more effective in the presence of a semiconductor with the percentage degradation of 3.6% at 10minutes and 71.8% at 120minutes with the overall average of 41.36%. These showed that paraquat can be degraded under UV irradiation over long time period also ZnO can serve as catalyst to speed the process over time.

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