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A REVIEW ON COMPARATIVE STUDY OF HETROCYCLIC COMPOUND (PYRIDINIUM DICHROMATE AND PYRAZOPHOS) ON BASIS OF PHOTOCATALYTIC DEGRADATION.

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Abstract: The present content deliberates the use of photocatalytic method for degradation of heterocyclic and non-heterocyclic contaminants. UV light has been used as radiation sources to activate the photocatalysts. A comparative study of the photocatalytic activity of ZnO, ZnS and CdS has been carried out. Heterocyclic compounds i) Pyridinium dichromate (ii) Pyrazophos.

Key words: heterocyclic,UV light

I. Introduction

1.1. Environmental pollution

The atmosphere of earth has a paper-thin layer of gas which contains life-giving oxygen and allows the efficient cooling of the planet that protects the planet from harmful cosmic and ultraviolet radiations. Many organic and inorganic pollutants such as chemical water, agrochemicals and many more that causes detrimental effects on the environment. Environmental pollution can be demonstrated as an unwanted transformation in chemical, biological and physical characteristics of air, water and land that may or will harmfully affect human life, industrial progress, living conditions and cultural assets. It is often divided in to pollution of water supplies, the atmosphere, and the soil [1].

1.2. Water pollution

The surge in the worldwide adulteration of freshwater systems with industrial, agricultural and domestic waste chemicals is a key environmental problem. Since drinking water is becoming rarer, study into the decontamination of the impure and polluted water has risen significantly because of large amount of pollutants present in it, such as; inorganic, organic pollutants and heavy metals and many more.

Heterocyclic compounds - Pyrazophos, Pyridinium dichromate are the most commonly used and detected pesticides in water [2, 3].

1.3. Materials

The materials were obtained from reputed sources and were used as received without any purification: Zinc Sulfide (ZnS), Zinc oxide (ZnO), Cadmium Sulfide (CdS), Hydrogen peroxide (H2O2) solution (30%), sodium hydroxide (NaOH) and hydrochloric acid were was purchased from Merck. Organic solvents like; methanol, ethanol, CCl4, CHCl3 were purchased from Loba chemie. Pyridinium dichromate was ordered from Sigma-Aldrich. Pyrazophos,

The structures and chemical formulas of heterocyclic compounds used for photocatalytic degradation study using ZnS as semiconductor have been demonstrated below (Figure 1 and 2).

1.3.1.1. **Details of Heterocyclic compounds used for the study** [1-4].

Name	: Cornforth reagent
IUPAC name	: Pyridinium Dichromate
Chemical formula	: $C_{10}H_{12}N_2Cr_2O_7$
Molecular weight	: 376.2 gm/mole

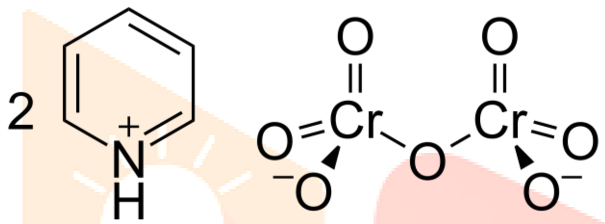

Figure 1. Structure of **Pyridinium dichromate**

Name	: Pyrazophos
IUPAC name	: Ethyl 2-[(diethoxyphosphorothioyl) oxy]-5-methylpyrazolo[1,5-a]pyrimidine-6-carboxylate
Chemical formula	: $C_{14}H_{20}N_3O_5PS$
Molecular weight	: 373.36 gm/mole

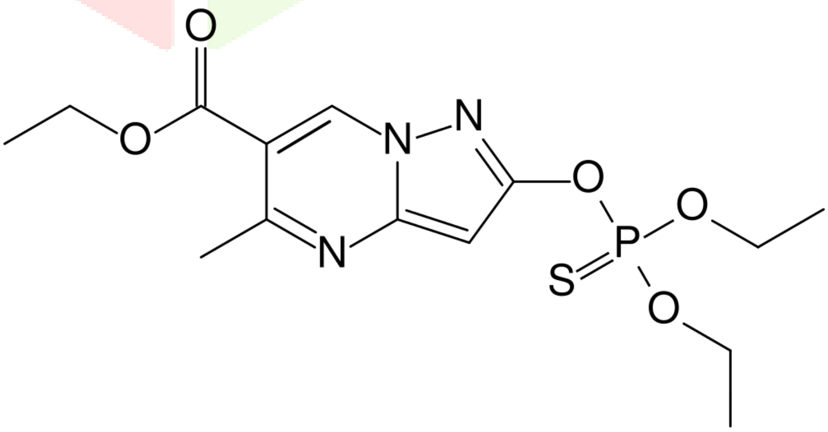

Figure 2. Structure of **Pyrazophos**

II. Comparative study of typical run of Heterocyclic compounds (Pyridinium dichromate and Pyrazophos.)

The photocatalytic degradation of all four compounds has been studied using ZnS as Semiconductor under UV radiation. The kinetic study was carried out at different ʎmax 372, 295, 382, 357 nm for Pyridinium dichromate, Pyrazophos.

The comparative typical run of all four successful experiment have been shown in table 1. The data suggest that after 90 min the absorbance of pyridinium dichromate and Pyrazophos was almost half, while the and had half absorbance after 120 min, compared to initial absorbance (figure 1). This indicates that degradation was occurred in a single step reaction. The rate constant of all four compounds was determined using the expression, k=2.303× slope the equation for the first order reaction.

Table-1. Comparative study of typical run of Heterocyclic compounds

TIME MIN.	PYRIDINIUM DICHROMATE		PYRAZOPHOS	
	ABS	2 + log ABS	ABS	2 + log ABS
00	0.270	1.431	0.282	1.521
30	0.175	1.243	0.179	1.253
60	0.153	1.184	0.161	1.194
90	0.133	1.123	0.139	1.131
120	0.111	1.045	0.121	1.085
150	0.091	0.959	0.095	0.971
180	0.081	0.908	0.086	0.919
210	0.070	0.845	0.065	0.855
240	0.060	0.778	0.059	0.770

III. Comparative study: Effect of different concentration on photocatalytic degradation using ZnS and UV light

The comparative data of effect of various concentration of pyridinium dichromate, pyrazophos, and concentration on the rate of photocatalytic degradation has been mentioned in table 2. Based on comparative data, we have observed that the rate of photocatalytic degradation of two compounds was good with initial 0.3 ×10-4 M. has shown degradation at initial concentration compared while other one compounds have near about degradation rate. It has been observed that rate of degradation was good at 0.5 ×10-4 M concentration. But after certain amount (0.5 ×10-4 M concentration) the rate of degradation was decreases with increase in concentration. So the 0.5 ×10-4 M concentration of all found compounds was easily degraded using optimal condition (figure 2). [6,10,13]

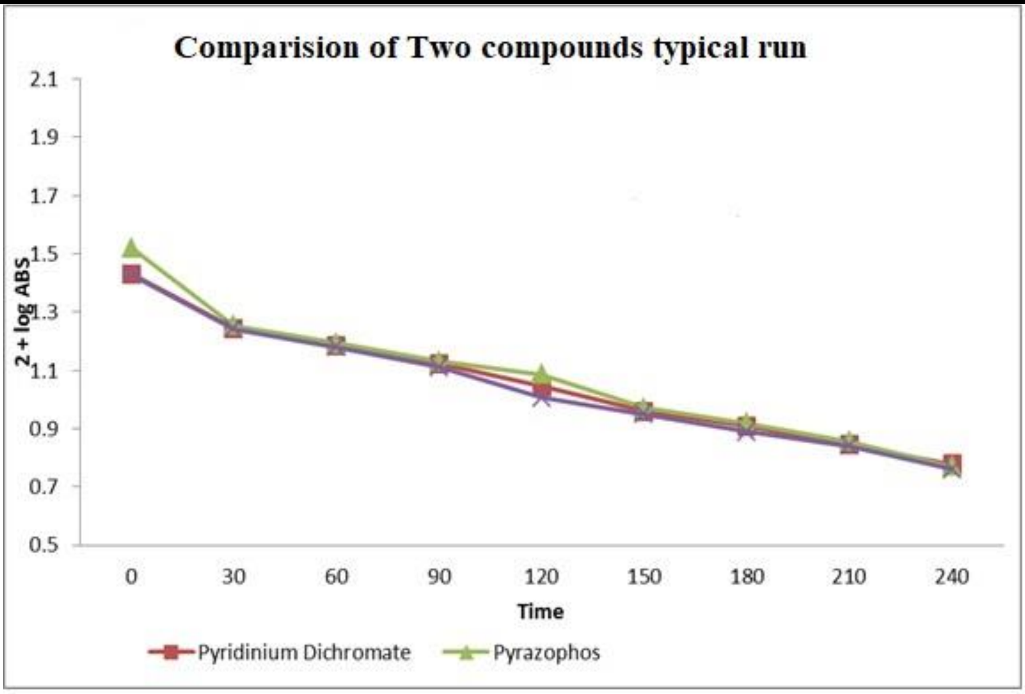

Figure 1. Comparision of two compounds typical run [9]

IV. Comparative study: Effect of amount (semiconductor) on photocatalytic degradation using ZnS and UV light

The amount of semiconductor has much more effect on photocatalytic degradation rate of heterocyclic molecules. Because of this reason different amounts of semiconductor were used in the current study. The comparative data on effect of amount of semiconductor for photocatalytic degradation using ZnS and UV light are cited in Table 2. We have observed that the initial rate of photocatalytic degradation of all four compounds was between 4 to 5.9 K (min-1 × 10-3). Which was then increases as the amount of photocatalyst increases up to 250 mg but after reaching a certain amount (300 mg) it decreased. The rate of degradation reaction, using 200 mg of semiconductor, for pyridinium dichromate and pyrazophos was 6.2 and 6.1, respectively (figure 47). The addition of extra ZnS around 250 mg seems to cover the whole surface area and therefore, an addition of photocatalyst more than 250 mg does not effectively increase the degradation rate. The optimum degradation rate for all compounds was obtained at 200 mg of semiconductor.

Table 2. Effect of amount of semiconductor

Amount of photocatalyst (mg)	Pyridinium Dichromate	Pyrazophos
	K ($min^{-1} \times 10^{-3}$)	
100	4.00	4.00
150	5.01	5.01
200	6.20	6.10
250	6.20	6.20
300	6.70	6.10
350	6.30	6.00

(Concentration = 0.5×10^{-4} M, Light Intensity = 3.69 $mWcm^{-2}$, Temperature = 301 K)

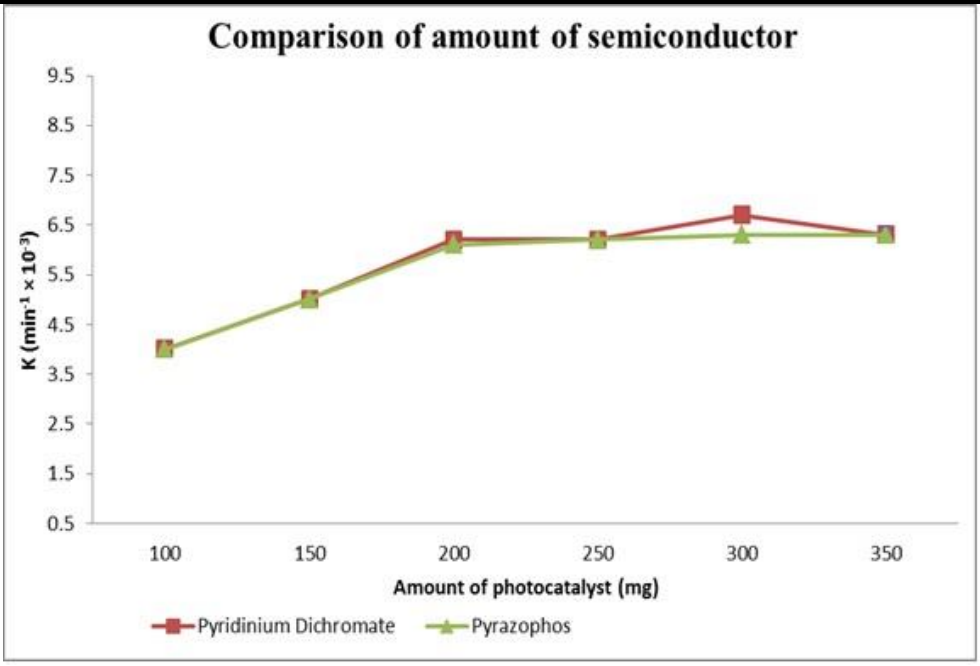

Figure 2. Effect of amount of semiconductors: Pyridinium dichromate and Pyrazophos [6]

V. Comparative study: Effect of light intensity on photocatalytic degradation using ZnS and UV light

To observe the effect of light intensity on the rate of photocatalytic degradation of pyridinium dichromate and pyrazophos (heterocyclic) solution, the different distance between source of light and exposed surface area have been kept. The comparative data these experiments using various distances are reported in table 3. For this study, we have used five different intensities of lights 2.06, 3.06, 3.69, 3.85 and 4.77. It has been found that the rate of photocatalytic degradation increased with increasing light intensity up to 3.69, it is fact that as light intensity increases, electron striking over unit area of semiconductor increases and hence the reaction rate has to increase.

Table 3. Effect of light intensity [13]

Light intensity ($mWcm^{-2}$)	**Pyridinium Dichromate**	**Pyrazophos**
	K ($min^{-1} \times 10^{-3}$)	
2.06	2.0	1.9
3.06	3.2	3.5
3.69	6.2	6.1
3.85	9.0	8.5
4.77	10.0	10.0

(Concentration = 0.5×10^{-4} M, Zinc Sulphide = 0.2 gm, Temperature = 301 K)

VI. Comparative study: Effect of pH on photocatalytic degradation using ZnS and UV light

The pH of solution has noticeable impact on the rate of photocatalytic degradation of all four compounds. The effect of pH on the reaction rate was investigated between pH range 2.0 to 9.0 and the results are depicted in table 4. The comparative data indicates that rate of photocatalytic degradation of pyridinium dichromate was increases with increasing pH up to 5.2 after that; there was sudden fall in degradation rate after this pH. The degradation rate of pyridinium dichromate was 6.2, at pH 5.2. In case of pyrazophos the rate of degradation was 6.1 at 7.0 pH. In all cases, the reaction rate was moderately decreased with increase in pH. It happens may be due to generation of dissimilar species at different pH value.

Table 4. Effect of pH [5]

pH	Pyridinium Dichromate	Pyrazophos
	K ($min^{-1} \times 10^{-3}$)	
2.0	2.90	3.11
3.0	4.47	3.70
4.0	5.18	4.27
5.2	6.20	5.10
6.0	2.63	5.89
7.0	4.50	6.10
8.0	5.90	2.83
9.0	5.9	4.20

(Concentration= 0.5×10^{-4} M, Zinc Sulphide = 0.2 gm, Light Intensity = 3.69 $mWcm^{-2}$, Temperature = 301 K)

VII. Comparative study: Effect of band gap in photocatalytic degradation using ZnS and UV light

The semiconductor has separated whole and electron pair that carry out photocatalytic reaction hence, band gap energy plays an important role in photocatalysis. The effect of band gap in photocatalytic degradation of all four compounds was studied with help of semiconductors having different band gap energy such as; ZnO, ZnS and CdS. The comparative studies of experiments (figure 3) are reported in table 5, which indicated that Zinc sulphide (3.8 eV), has highest rate constant compared to other semiconductor. The other semiconductors were not even able to start the degradation reaction.

Table 5. Effect of band gap [8]

Semiconductor used	Band gap	Pyridinium Dichromate	Pyrazophos
		K ($min^{-1} \times 10^{-3}$)	
CdS (200mg)	2.42 eV	0.0	0.0
ZnO (200mg)	3.20 eV	0.0	0.0
ZnS (200mg)	3.80 eV	6.2	6.1

(Concentration = 0.5×10^{-4} M, Light Intensity = 3.69 $mWcm^{-2}$, Temperature = 301 K)

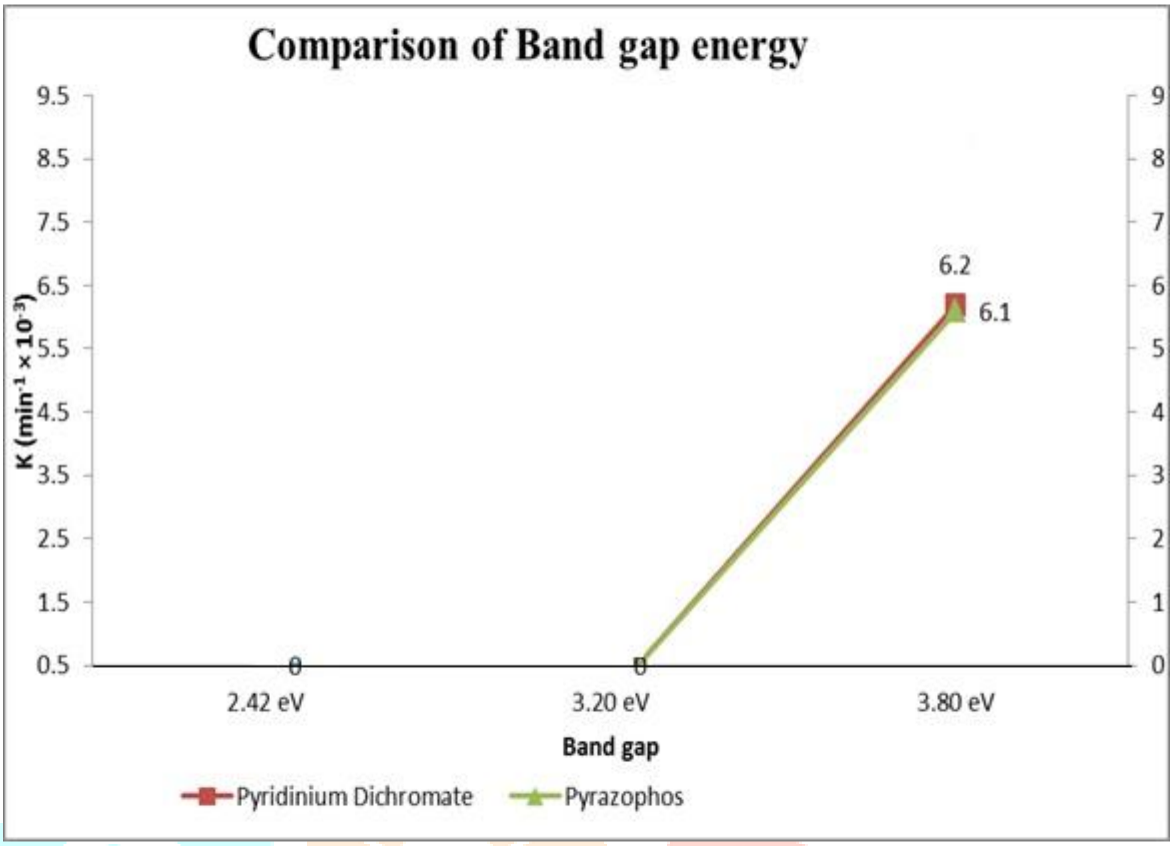

Figure 3. Effect of Band gap energy: Pyridinium dichromate, Pyrazophos [11]

VIII. Comparative study: Effect of radical quencher in photocatalytic degradation using ZnS and UV light

Radical quencher is mainly used to end the photocatalytic degradation reactions. We have used various alcohols for quenching free radicals in this present research. We have used methanol and ethanol to examine the effect of radial quencher. It was observed that addition of methanol; and ethanol as quencher, bring to an end successfully the degradation reaction which was occurred. In all cases; two heterocyclic, the reaction was totally quenched even in minor amount (figure 4). The comparative data are tabulated in Table 06.

Table 6. Effect of radical quencher [8]

Compounds	**λmax**	**Typical run $K\times10^{-1}(min^{-3})$**	**Radical quencher**			
			Methanol	**Methanol (4ml)**	**Ethanol (2 ml)**	**Ethanol (4ml)**
Pyridinium Dichromate (PdC)	372	6.2	0	0	0	0
Pyrazophos (PyP)	295	6.1	0	0	0	0

(Concentration= 0.5×10^{-4} M, Zinc Sulphide = 0.2 gm, Light Intensity = 3.69 $mWcm^{-2}$, Temperature = 301 K)

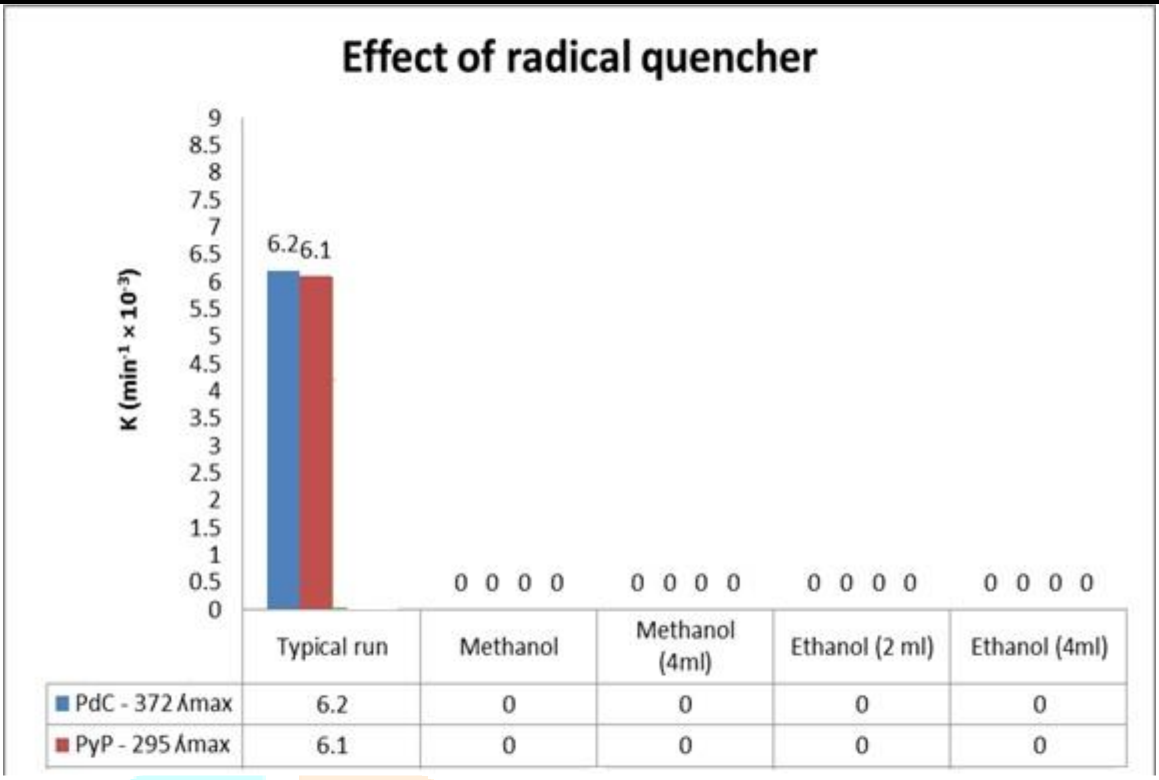

Figure 4. Effect of Quencher: Pyridinium dichromate and Pyrazophos [12][1]

IX. Conclusion

In conclusion, based on comparative study, pyridinium dichromate was degraded around 5.2 and 5.8 pH, while Pyrazophos shows degradation near neutral pH at 6.9, in the presence of ZnS as semiconductor under UV irradiation. Out of two semiconductors ZnS proved to be successful to carry out photocatalytic degradation reaction of all compounds in aqueous and carbon tetra chloride (pyrazophos). All the reactions were found first order kinetic reaction. The reactions were totally stopped by quencher like alcohols.

X. References

1. Keith, J. A., and Carter, E. A. (2012). Theoretical insights into pyridinium- based photoelectrocatalytic reduction of CO_2. *Journal of the American Chemical Society*, *134*(18), 7580-7583.
2. Ertem, M. Z., Konezny, S. J., Araujo, C. M., and Batista, V. S. (2013). Functional role of pyridinium during aqueous electrochemical reduction of CO_2 on Pt (111). *The journal of physical chemistry letters*, *4*(5), 745-748.
3. Tantis, I., Bousiakou, L., Frontistis, Z., Mantzavinos, D., Konstantinou, I., Antonopoulou, M., and Lianos, P. (2015). Photocatalytic and photoelectrocatalytic degradation of the drug omeprazole on nanocrystalline titania films in alkaline media: Effect of applied electrical bias on degradation and transformation products. *Journal of hazardous materials*, *294*, 57-63.
4. Vinodgopal, K., Bedja, I., and Kamat, P. V. (1996). Nanostructured semiconductor films for photocatalysis. Photoelectrochemical behavior of SnO_2/TiO_2 composite systems and its role in photocatalytic degradation of a textile azo dye. *Chemistry of materials*, *8*(8), 2180-2187.
5. Nagaveni, K., Sivalingam, G., Hegde, M. S., and Madras, G. (2004). Photocatalytic degradation of organic compounds over combustion-synthesized nano-TiO_2. *Environmental science and technology*,

38(5), 1600-1604

6. Li, J., Li, J., Chen, Q., Bai, J., and Zhou, B. (2013). Converting hazardous organics into clean energy using a solar responsive dual photoelectrode photocatalytic fuel cell. *Journal of hazardous materials*, *262*, 304-310.

7. Lianos, P. (2011). Production of electricity and hydrogen by photocatalytic degradation of organic wastes in a photoelectrochemical cell: the concept of the photofuelcell: a review of a re-emerging research field. *Journal of Hazardous Materials*, *185*(2), 575-590.

8. Su, K., Ai, Z., and Zhang, L. (2012). Efficient Visible Light-Driven Photocatalytic Degradation of Pentachlorophenol with Bi_2O_3/TiO_{2}–xBx. *The Journal of Physical Chemistry C*, *116*(32), 17118-17123.

9. Rahman, A., Ching, Y. C., Ching, K. Y., Awanis, N., Chakraborty, A. K., Chuah, C. H., and Liou, N. S. (2015). Surface modification of natural fiber using Bi_2O_3/TiO_2 composite for photocatalytic self- cleaning. *Bio Resources*, *10*(4), 7405-7418.

10. Fedorov, K., Jia, L., Guo, X., and Li, J. (2016). Influence of Sulfation Treatment on Photocatalytic Performance of Mesoporous Bi_2O_3–TiO_2 Composites. *Journal of Nanoscience and Nanotechnology*, *16*(7), 7490-7496.

11. Zhang, R., Wu, H., Lin, D., and Pan, W. (2009). Preparation of Necklace-Structured TiO_2/SnO_2 Hybrid Nano fibers and Their Photocatalytic Activity. *Journal of the American Ceramic Society*, *92*(10), 2463-2466.

12. Zhang, Z., Shao, C., Li, X., Zhang, L., Xue, H., Wang, C., and Liu, Y. (2010). Electrospun nanofibers of ZnO− SnO_2 heterojunction with high photocatalytic activity. *The Journal of Physical Chemistry C*, *114*(17), 7920-7925.

13. R. H. Salvi, L. S. Bhutadiya, J. J. vora, Photocatalytics Study Of Pyrazophos In Presence Of Zinc Sulphide, Ijrar -International Journal of Research and Analytical Reviews (IJRAR), E-ISSN 2348-1269, P- ISSN 2349-5138, Volume.5,Issue 4, Page No pp.598-604