ISSN: 2454-1907
DOI: 10.29121/ijetmr.v4.i12.2017.595

IJETMR
International Journal of Engineering Technologies and Management Research
A Knowledge Repository

EFFECT OF OPERATIONAL PARAMETER ON PHOTOCATALYTIC DEGRADATION OF OXAMYL PESTICIDE

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Abstract:
Flower like bismuth oxy chloride (BiOCl) was successfully synthesized by a simple hydrolytic method at room temperature. The precursor and as-prepared samples were characterized by X-ray diffraction (XRD), High Resolution Field Emission Scanning Electron Microscope (HR FESEM). The results indicated that the as-prepared BiOCl sample is self-assembled hierarchically with nano sheets. The photocatalytic activity of BiOCl was tested on the degradation of the Oxamyl (OM) under solar light irradiation. The results showed that pesticide molecules could be efficiently degraded over BiOCl under solar light irradiation. All the experiment were carried out in the following reaction condition, [OM] = 10^{-4} mol dm^{-3}, BiOCl NPs= 40mg/50ml, pH= 6.3. Effect of operational parameter such as concentration of H_2O_2, $K_2S_2O_8$, $FeCl_3$, Fenton's reagent (Fe^{3+}/H_2O_2) and N_2, O_2 purging on the photocatalytic degradation was observed.

Keywords: *Biocl; Flowerlike; Pesticide; Photocatalysis; Oxamyl; Solar Light.*

Cite This Article: Brijesh Pare, Satish Piplode, and Vaishali Joshi. (2017). "EFFECT OF OPERATIONAL PARAMETER ON PHOTOCATALYTIC DEGRADATION OF OXAMYL PESTICIDE." *International Journal of Engineering Technologies and Management Research*, 4(12: SE), 74-84. DOI: 10.29121/ijetmr.v4.i12.2017.595.

1. Introduction

Oxamyl is a carbamate insecticide/acaricide/nematicide that controls a broad spectrum of insects, mites, ticks, and roundworms. It may work both through systemic distributions in the target pest and on contact. Oxamyl is used on field crops, vegetables, fruits, and ornamental plants and may be applied directly onto plants or the soil surface. Oxamyl is a highly toxic compound in EPA toxicity class I. Oxamyl is extremely toxic to humans whether ingested, inhaled, or contact with the skin [1]. Agricultural wastewater, contaminated with such toxic pesticides, pollutes surface and groundwater through different ways. These types of pollution are very dangerous for eco system. Therefore, removals of such toxic pesticides are very essential to save the ecosystem.

Various methods are available to treat the waste water among this Advance Oxidation Processes (AOPs) are top on the class because it leads complete mineralization of pollutants. The main objective of this research has been the investigation of procedure for the removal of Oxamyl (OM) from polluted waters by using a photocatalysis process involving solar irradiation and

flower like nano BiOCl catalysis and to study the effect of the different experimental variables of this process such as H_2O_2, $K_2S_2O_8$, $FeCl_3$, Fenton's reagent (Fe^{3+}/H_2O_2) and N_2, O_2 purging etc. All the experiment carried out at same reaction conditions; pH=6.2, [OM]= 1 x 10^{-4} mol dm^{-3}, catalyst amount= 40mg/50ml.

2. Materials and Methods

2.1. Chemicals

All major chemicals were of reagent grade or higher purity (99%). Oxamyl pesticide was purchased from Sigma Aldrich (Oxamyl PESTANAL). The pesticide was used as such without further purification. The reagent Bi $(NO_3)_3$ **.**$5H_2O$ was purchased from AR Merck and HCl was obtained from Merck. Deionised / double distilled water was used throughout this study.

2.2. Synthesis of Nanoparticles

BiOCl samples were prepared by hydrolysing Bi $(NO_3)_3$. $5H_2O$ at room temperature. Bi $(NO_3)_3.5H_2O$ (9.7g) was dissolved in 70 mL of de-ionized water and stirred at room temperature for 1 h to form the precursor $BiONO_3$. Then, 40 mL of HCl (1mol/L) was added drop wise to the solution for 60 min and the white precipitates formed were subjected to centrifugal separation and washed several times with deionized water and ethanol until the pH of the system became neutral. The resulting solid was dried at room temperature [2].

2.3. Characterization Methods

X-ray diffraction patterns (XRD) of the prepared samples were recorded on a PANalytical Empyrean PC equipped with Cu Kα radiation (40kV, 20mA). The surface morphology of the samples was observed using High resolution field emission scanning electron microscope (HR FESEM). The HR FESEM is from Zeiss, model name ULTRA Plus.

2.4. Measurement of Photocatalytic Activity

Pesticide solution was freshly prepared by dissolving in double distilled/deionized water. Prior to light experiments, dark (adsorption) experiments were carried out to know the extent of adsorption of the pesticide on the catalyst. For solar experiments, pesticide solution of 50 mL was taken in double walled vessel with known amount of the catalyst. The solution was illuminated under bright solar light. At specific time intervals, an aliquot (3 ml) of the mixture was withdrawn and centrifuged for 2 minutes at the rate of 3500 rpm to remove the flower like BiOCl particles. A PC based double beam spectrophotometer 2202 of Systronics has been used for measuring absorbance at different time intervals. The intensity of light was measured by a Lux meter (Lutron LX-101). The pH and conductivity of the solution was constantly been monitored using a pH meter and conductivity meter. pH was adjusted by the addition of either NaOH or H_2SO_4.

The efficiency of photocatalytic process was calculated as:

$$\% \text{ efficincy} = \frac{C_o - C}{C_o} \text{x } 100$$

Where C_o is the initial absorbance and C is the absorbance at different time intervals of photocatalytic process.

3. Results and Discussions

3.1. Structural Studies

Fig1 shows the XRD patterns of the Flower like BiOCl sample. The hydrolysis prepared BiOCl was well crystallized. No other diffraction peaks were detected, indicating the high purity of BiOCl. The intense and sharp diffraction peaks suggested that the as synthesized product was well- crystallized. For the BiOCl, the (101), (102), (001) and (110) diffraction peaks are sharper and stronger, while other peaks are relatively weak. This means that BiOCl should favour to grow along the all the three x, y and z axis [3].

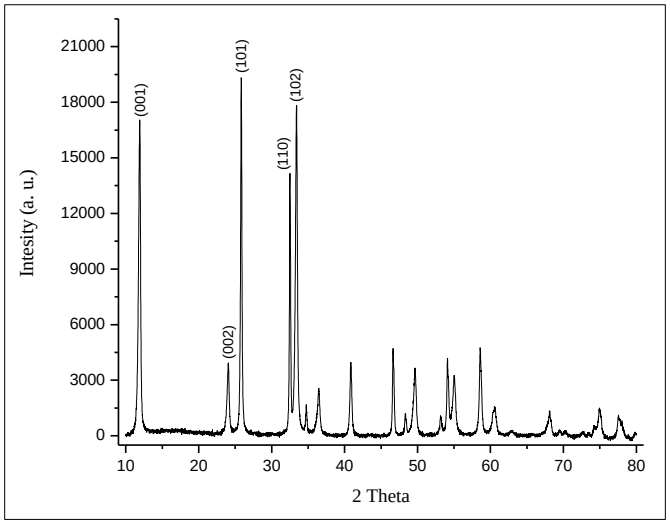

Figure 1: XRD pattern of flower like nano BiOCl

From the x-ray patterns the broadening of the diffraction peaks of the nanoparticles is obvious which is characteristic of nanosized by applying Debye- scherrer formula.

$$D = \frac{0.9\lambda}{\beta COS\theta}$$

Where D is the mean particle size, λ is the wavelength of incident X-ray (1.5406 ˚A), θ is the degree of the diffraction peak, and β is the full width at half maximum (FWHM) of the XRD peak appearing at the diffraction angle θ. The broadening of the absorption spectrum could be due to the quantum confinement of the nanoparticles. The mean calculated crystallite size of the BiOCl nanoparticles shows that the synthesized nanoparticle is 45 nm.

Fig. 2 shows the HR FESEM image of the Flower like nano BiOCl. It can be clearly seen that the BiOCl particles having Flower like structure. The size of the flower is about 4-6 micrometer.

Figure 2: HR FESEM image of flower like nano BiOCl

3.2. Photocatalytic Activity

3.2.1. Effect of H_2O_2

Hydroxyl radicals play an important role in the photocatlytic degradation of pesticides. Studies showed that H_2O_2 could enhance the formation of hydroxyl radicals as well as inhibit the electron/hole (e^-/h^+) pair recombination. Therefore the photocatalytic degradation of oxamyl pesticide has been conducted at different concentration of H_2O_2 as shown in Fig. 3. The results indicated that the rate of degradation of OM increased with increasing concentration up to 4.0×10^{-6} mol dm^{-3} of H_2O_2 above this concentration, degradation efficiency was found to be decreased. This is because hydrogen peroxide could have inhibited the electron-hole recombination by accepting photogenerated electron from the conduction band of semiconductor and promoted charge separation and also form HO• radicals [4] according to Eqs. (1), (2).

$$H_2O_2 + O_2^{\bullet -} \longrightarrow {}^{\bullet}OH + HO^- + O_2 \quad (1)$$

$$e^-_{CB} + H_2O_2 \longrightarrow {}^{\bullet}OH + OH^- \quad (2)$$

When H_2O_2 was present in excess it might act as hole or $^{\bullet}OH$ scavenger having detrimental effect on photocatalytic degradation. This suggests the need for to know optimum concentration of the H_2O_2 for the maximum efficiency.

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet} \quad (3)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad (4)$$

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \quad (5)$$

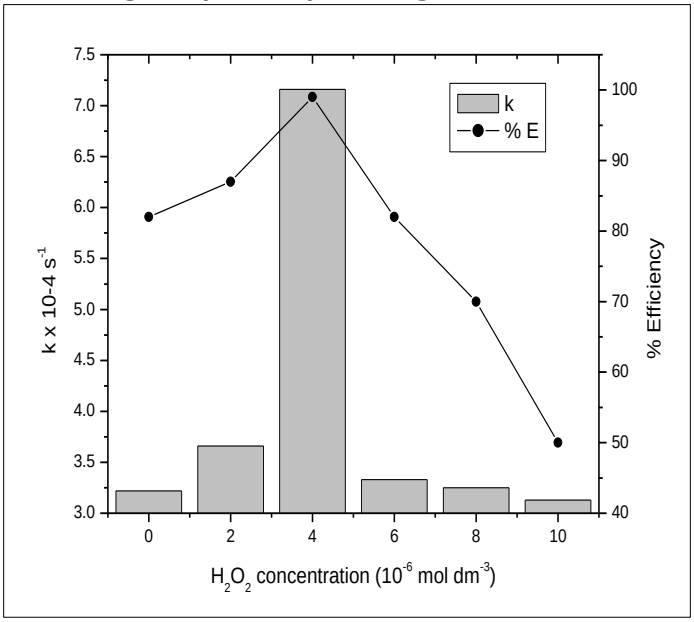

Figure 3: Effect of H_2O_2 on photocatalytic degradation of OM

3.2.2. Effect of $K_2S_2O_8$

Amount of sulphate ion ($SO_4^{-\bullet}$) is one of the main parameters to influence photocatalytic processes. In this study, to obtain the optimal initial sulphate ion ($SO_4^{-\bullet}$) concentration, the investigation was carried out in the range of 2 x 10^{-6} to 1 x 10^{-5} mol dm^{-3}. The results are shown in Fig. 4. It can be seen that degradation rate of Oxamyl distinctly increased with the increasing amount of sulphate ion ($SO_4^{-\bullet}$).

$K_2S_2O_8$ could trap the photogenerated conduction band electron resulting in the formation of sulphate ion ($SO_4^{\bullet-}$) a strong oxidizing agent. In addition it can trap the photogenerated electrons and or generated hydroxile radicals.

$$S_2O_8^{2-} + e^-_{CB} \longrightarrow SO_4^{2-\cdot} + SO_4^{2-} \quad (6)$$

$$SO_4^{\bullet-} + e^-_{(CB)} \longrightarrow SO_4^{2-} \quad (7)$$

$$SO_4^{\bullet-} + H_2O \longrightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \quad (8)$$

$$SO_4^{\bullet-} + OM \longrightarrow SO_4^{2-} + \text{intermediates} \quad (9)$$

$$SO_4^{\bullet-} + \text{intermediates} \longrightarrow \text{mineralization} \quad (10)$$

The decreased in rate of photodegradation above optimal concentration 2.0 × 10^{-6} mol dm^{-3} is due to the adsorption of sulphate ions formed during the reaction on surface of BiOCl deactivating a section of photo-catalyst [5].

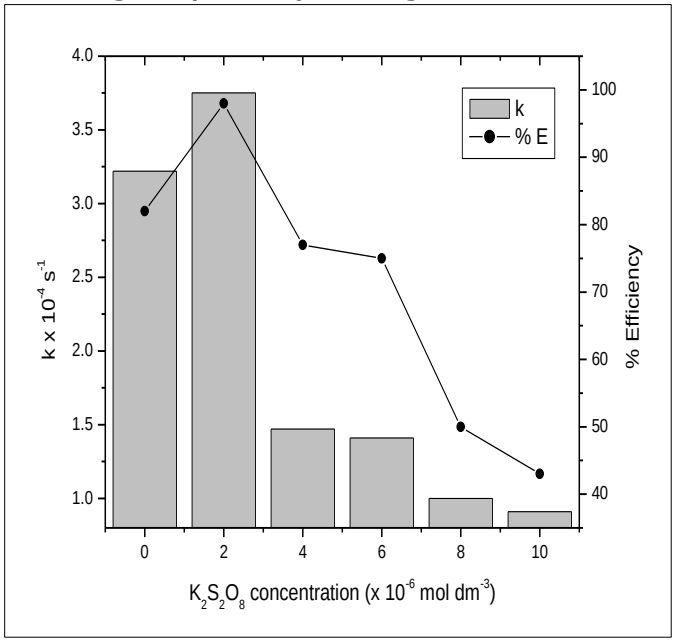

Figure 4: Effect of $K_2S_2O_8$ on photocatalytic degradation of OM

3.2.3. Effect of $FeCl_3$

The effect of $FeCl_3$ on the degradation efficiency has been studied by varying the concentration from 2 x 10^{-6} to 10^{-5} mol dm^{-3}. The rate constant values increased 3.22 x 10^{-4} s^{-1} with the increase in concentration of $FeCl_3$ 2.0 × 10^{-6} mol dm-3. Thereafter, rate constant values decreased to 1.41 x 10^{-4} s^{-1} on further increase in concentration of $FeCl_3$ up to 10 × 10^{-6} mol dm^{-3}. The results have been reported in Fig. 5. Ferric ion (Fe^{3+}) are known to behave as an electron scavenger (Eq. (11)) thus preventing the recombination of electron hole pairs. Under the experimental conditions the following reactions become significant [6].

$$Fe^{3+} + e^-_{CB} \longrightarrow Fe^{2+} \quad (11)$$

$$Fe^{3+} + HO^{\bullet}_2 + H^+ \longrightarrow Fe^{2+} + H_2O_2 \quad (12)$$

$$Fe^{2+} + H_2O_2 + H^+ \longrightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad (13)$$

The mechanism of degradation process can be explained by following equations:

$$OM + h\upsilon_{\text{ visible}} \longrightarrow {}_1OM^* \text{ or } {}_3OM^* \quad (14)$$

$${}_1OM^* \text{ or } {}_3OM^* + BiOCl\ (Fe^{3+}OH^-) \longrightarrow BiOCl\ (Fe^{2+}\ {}^{\bullet}OH) + OM^{+\cdot} \quad (15)$$

$$BiOCl\ (Fe^{2+}\ {}^{\bullet}OH) + H_2O_2 \longrightarrow BiOCl\ (e^-_{CB}) + BiOCl\ (Fe^{3+}\ {}^{\bullet}OH) \quad (16)$$

$$BiOCl\ (e^-_{CB}) + O_2 \longrightarrow O_2^{\bullet -} \longrightarrow HO^{\bullet}_2 \quad (17)$$

$$OM / OM^{+\cdot} + {}^{\bullet}OH / O_2^{\bullet -} / HO^{\bullet}_2 \longrightarrow \text{Degradation products} \quad (18)$$

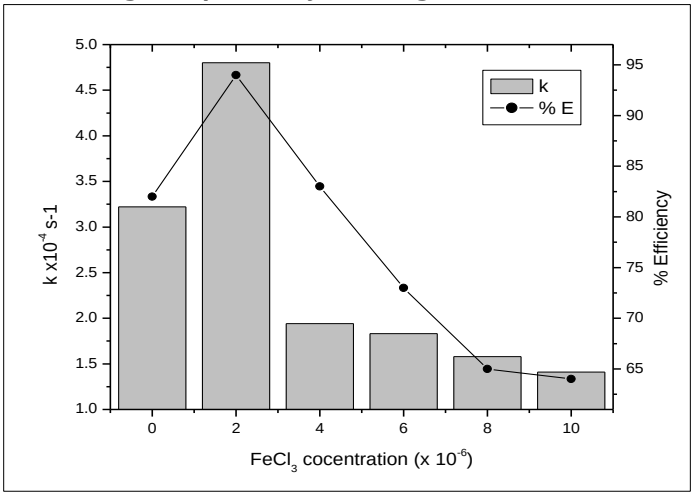

Figure 5: Effect of $FeCl_3$ on photocatalytic degradation of OM

3.2.4. Effect of Fenton's Reagent (Fe^{3+}:H_2O_2)

Homogenous catalysis by Fenton's reagent has been one of the most applied AOPs for its ability to degrade high loadsof organic compounds even in highly saline conditions. In Fenton's process Fe^{3+} or Fe^{2+} and H_2O_2 are used. In the present study $FeCl_3$ is used as Fe^{3+} source. A series of experiments were carried out over a wide range of Fe^{3+}:H_2O_2 ratio at constant Oxamyl concentration of 10^{-4} mol dm^{-3} and at constant pH 6.2 without catalyst and one experiment also carried out with catalyst amount 40 mg/50ml having same experimental condition. The results are reported in Fig. 6. Rate constant had a value of 5.63×10^{-4} s^{-1} on the addition of [Fe^{3+}: H_2O_2] in the molar ratio [1.1.5]. At this ratio the degradation process is very fast because at this ratio more •OH radicals were available to attack the pesticide molecule. With change in ratio Fe^{3+} and H_2O_2 acts as a scavenger of highly reactive •OH free radicals to form hydroperoxyl radicals. These radicals are much less reactive and do not contribute to oxidative degradation of organic substance [7].

Fe^{2+} (aq) + H_2O_2 both react and generate •OH radicals. The mechanism for the Fenton reaction is shown in (Eq. (19)):

$$Fe^{2+}(aq) + H_2O_2 \longrightarrow Fe^{3+}(aq) + OH^- + HO^{\bullet} \quad (19)$$

The Fe^{2+} can be reverted back to Fe^{3+} via different mechanisms:

$$Fe^{3+}(aq) + H_2O_2 \longrightarrow Fe^{2+}(aq) + HO_2^{\bullet} + H^+ \quad (20)$$

$$Fe^{3+}(aq) + HO_2^{\bullet} \longrightarrow Fe^{2+}(aq) + O_2 + H^+ \quad (21)$$

If catalyst used with Fenton's process the process become more effective H_2O_2 might be generated via the BiOCl photocatalysis also participate in the reaction. Many researchers have

reported the addition of H_2O_2 in enhancing both the photo-Fenton and BiOCl photocatalysis reactions. In this case following mechanisms occurred:

$$H_2O_2 + e- \longrightarrow HO^{\bullet} + HO^{-} \quad (22)$$

$$O_2^{\bullet-} + H_2O_2 \longrightarrow O_2 + HO^{\bullet} + HO^{-} \quad (23)$$

Upon irradiation of Fe^{3+}/H_2O_2/BiOCl/OM system with solar light, production of $HO^{\bullet}$ radicals increased involving a very complex mechanism as shown below:

$$OM + h\upsilon_{\text{visible}} \longrightarrow {}_1OM^* \text{ or } {}_3OM^* \quad (24)$$

$${}_1OM^* \text{ or } {}_3OM^* + BiOCl\,(Fe^{3+}OH^-) \longrightarrow BiOCl\,(Fe^{2+}\,{}^{\bullet}OH) + OM^{+\cdot} \quad (25)$$

$$BiOCl\,(Fe^{2+}\,{}^{\bullet}OH) + H_2O_2 \longrightarrow BiOCl\,(Fe^{3+}\,{}^{\bullet}OH) + OH^- + {}^{\bullet}OH \quad (26)$$

$$BiOCl\,(Fe^{2+}\,{}^{\bullet}OH) + H_2O_2 \longrightarrow BiOCl\,(Fe^{3+}\,{}^{\bullet}OH) + HO_2^{\bullet} + H^+ \quad (27)$$

$$BiOCl\,(Fe^{2+}\,{}^{\bullet}OH) \longrightarrow BiOCl\,(Fe^{3+}\,{}^{\bullet}OH) + BiOCl\,(e^-_{CB}) \quad (28)$$

$$BiOCl\,(e^-_{CB}) + O_2 \longrightarrow O_2^{\bullet-} \longrightarrow HO^{\bullet}_2 \quad (29)$$

$$H_2O_2 + O_2^{\bullet-} \longrightarrow OH^- + {}^{\bullet}OH + H^+ \quad (30)$$

$$H_2O_2 + BiOCl\,(e^-_{CB}) \longrightarrow OH^- + {}^{\bullet}OH \quad (31)$$

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O_2 + HO^{\bullet}_2 \quad (32)$$

$$OM / OM^{+\cdot} + {}^{\bullet}OH / O_2^{\bullet-} / HO^{\bullet}_2 \longrightarrow \text{Degradation products} \quad (33)$$

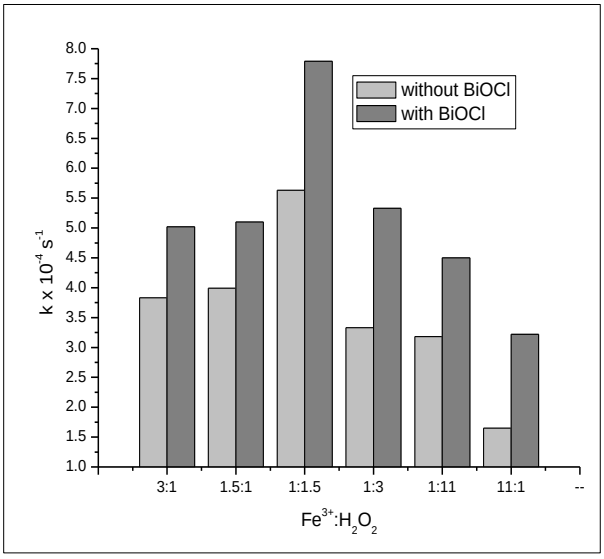

Figure 6: Effect of H_2O_2

3.2.5. Effect of Bubbling of N_2 And O_2

In this parameter the N_2 and O_2 gas purged in the photocatalysis system to know the effect of these gases in photocatalytic degradation of OM under chosen reaction conditions. Two different experiments have been carried out in first experiment N_2 gas purged and in second experiment O_2 gas purged taking same reaction condition. We have observed that dissolved N_2 and O_2 gases play significant role in the degradation of dissolved organic pollutants. The experimental results indicated that the degradation of OM was much higher in the presence of molecular oxygen. [8].

The mechanism can be explained as follows:

$$O_2 + e^- \longrightarrow O_2^{-\bullet} \quad (34)$$

$$H_2O_2 + BiOCl\ (e^-) \longrightarrow {}^{\bullet}OH + HO \quad (35)$$

$$O_2^{\bullet} + H_2O_2 \longrightarrow {}^{\bullet}OH + HO + O_2 \quad (36)$$

$$O_2^{\bullet} + H^+ \longrightarrow HO_2^{\bullet} \quad (37)$$

$$HO_2^{\bullet} + BiOCl\ (e^-) \longrightarrow HO_2^- \quad (38)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \quad (39)$$

$$2\ HO_2^{\bullet} \longrightarrow O_2 + H_2O_2 \quad (40)$$

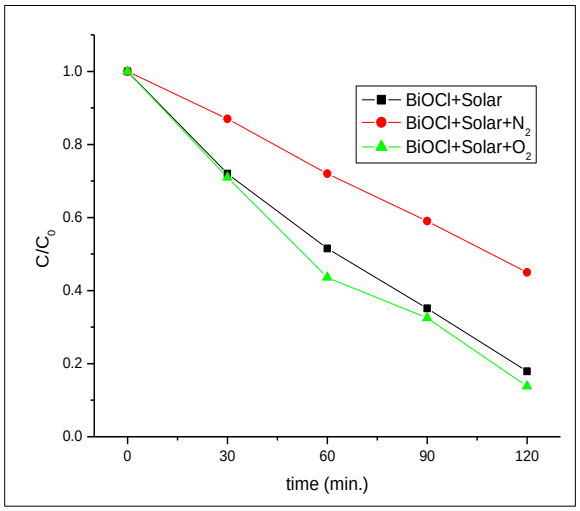

Figure 6: Effect o N_2 and O_2

4. Effect of Other Catalyst

The effects of various photocatalysts such as flowerlike nano BiOCl, nano BiOCl, bulk BiOCl, bulk ZnO, nano ZnO on degradation have been investigated at same condition. The results are shown in Fig. 7 indicated that BiOCl exhibits excellent performance in terms of both adsorption

and degradation of Oxamyl. The highest photocatalytic activity was observed in the presence of flower like BiOCl. The results showed that flower like nano BiOCl was most efficient than other catalyst. The order of activities of the photocatalysts flowerlike nano BiOCl > nano BiOCl > nano ZnO > bulk BiOCl > bulk ZnO. Hierarchical structures could enhance solar light utilization significantly because of the multiple reflections of ultraviolet and visible light within the interior structure of the flower like BiOCl. Such enhancements could generate more of •OH radiclas, electrons and holes and thus that can promote photocatalytic activity in the flower like nano BiOCl sample [9].

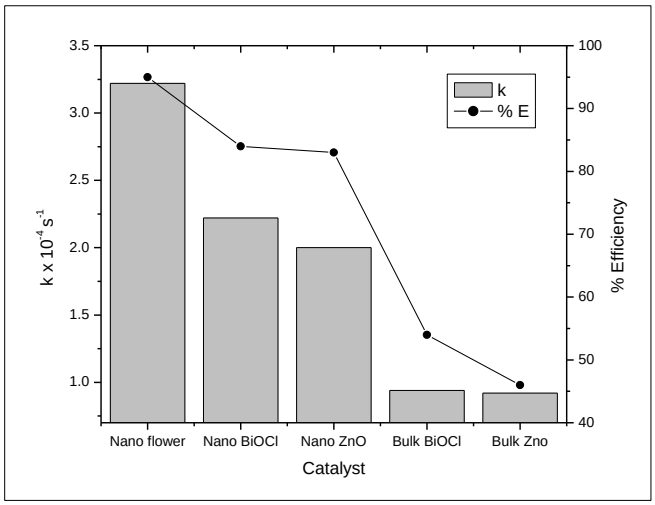

Figure 7: Effect of other catalyst

5. Conclusions and Recommendations

Flower like nano BiOCl synthesized by hydrolysed method. BiOCl shows promising catalytic activity in solar for oxamyl pesticide degradation. Various operational parameters such as H_2O_2, $K_2S_2O_8$, $FeCl_3$, Fenton's reagent (Fe^{3+}/H_2O_2) and N_2, O_2 purging etc. affects the photoctalysis poetesses. Addition of oxidants and electron scavenger enhance the photocatalysis process. Homogenous photocatalysis and combination of heterogeneous and homogenous process also a very good technique to treat the waste water. This research opens new possibilities to provide some insight into nano sized and hierarchical structure semiconductors photocatalysts for degrading organic pollutants and other applications.

Acknowledgements

The authors are grateful to IISER Bhopal for XRD and HR-FESEM analysis.

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