

Solar light assisted photocatalytic degradation of hazardous and highly water soluble pesticide Methomyl using Flower like nano BiOCl

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Abstract—Flower like nano bismuth oxy chloride (BiOCl) was successfully synthesized by a simple hydrolytic method using Bi (NO₃)₃·5H₂O as Bi source material at room temperature. The 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 methomyl under solar light irradiation. The results showed that pesticide molecules could be efficiently degraded over BiOCl under solar light irradiation.

Keywords—BiOCl, Flowerlike, Pesticide, photocatalysis, methomyl, solar light

I. INTRODUCTION

Methomyl, C₅H₁₀O₂N₂S, S-methyl N-[(methylcarbamoyl)oxy] thioacetimidate is a broad spectrum insecticide which belongs to the carbamate family of pesticides. Methomyl is a very toxic and hazardous compound because of its high solubility in water (57.9 g/L at 25 °C) [1]. It can easily cause contamination of both ground and surface water resources [2]. Some work already has been done on degradation studies of methomyl using TiO₂ photocatalysis [2], [3], [4], [5] [6], [7], [8], [9], ZnO photocatalysis [6], [9], Fenton, Photo-Fenton system [2], [6], [10], [11], [12], [13]. A. Zapata et al used commercially available formulation Metomur (20%, w/v, methomyl) for degradation study using Photo-Fenton system [14].

Excessive uses of pesticides are introduced into the environmental system through crops disinfection, industrial pesticide cleaning, misuse and lack of understanding of their ecological effects. Therefore, they become major pollutants due to their extensive use [15]. Hence more effective, lower-cost, robust methods to disinfect and decontaminate waters from source to point-of-use are needed, without further stressing the environment or endangering human health by the treatment itself. Conventional methods of water disinfection and decontamination can address many of these problems. However, these treatment methods are often chemically, energetically and operationally intensive, focused on large systems, and thus require considerable infusion of capital, engineering expertise and infrastructure,

all of which precludes their use in much of the world. Furthermore, intensive chemical treatments such as those involving ammonia, chlorine compounds, hydrochloric acid, sodium hydroxide, ozone, permanganate, alum and ferric salts, coagulation and filtration aids, antiscalants, corrosion control chemicals, and ion exchange resins and regenerates and residuals resulting from treatment can add to the problems of contamination and salting of freshwater sources [16].

Photocatalytic degradation of pesticides by solar light in the presence of a suitable catalyst may provide a cost-effective remediation of pesticide contaminated water. The technology is attractive as solar energy is an inexpensive, renewable energy source. Furthermore, it can lead to complete mineralization as well, thereby eliminating potential effects associated with toxic intermediates. The present work aims to study the photocatalytic degradation of methomyl using flower like nano BiOCl as the photocatalyst in presence of solar radiation. This is the first attempt to degrade any carbamate pesticide using BiOCl and solar light.

II. METHODOLOGY

Chemicals:

All major chemicals were of reagent grade or higher purity (99%). Methomyl pesticide was purchased from Sigma Aldrich (Methomyl PESTANAL). The pesticide was used as such without further purification. The reagent Bi

(NO₃)₃.5H₂O was purchased from AR Merck and HCl was obtained from Merck. Deionised / double distilled water was used throughout this study.

Synthesis of Nanoparticles:

BiOCl samples were prepared by hydrolysing Bi(NO₃)₃.5H₂O at room temperature. Bi(NO₃)₃.5H₂O (9.7g) was dissolved in 70mL of de-ionized water and stirred at room temperature for 1 h to form the precursor BiONO₃. 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 [17].

Characterization methods:

X-ray diffraction patterns (XRD) of the prepared samples were recorded on a PANalytical Empyrean PC equipped with Cu K α radiation (40 kV, 20 mA). The surface morphology of the samples was observed using High Resolution Field Emission Scanning Electron Microscope (HR FESEM). HR FESEM is from Zeiss, model name ULTRA Plus.

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 an open glass reactor (100mm x 50mm crystallizing dish) with known amount of the catalyst. The solution was illuminated under bright solar light. Deionized/ double distilled water was added periodically to avoid concentration changes due to evaporation. 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 H₂SO₄.

The efficiency of photocatalytic process was calculated as:

$$\% \text{ efficiency} = (C_0 - C) / C_0 \times 100$$

where C₀ is the initial absorbance and C is the absorbance at different time intervals of photocatalytic process.

III. RESULTS AND DISCUSSION

Structural studies:

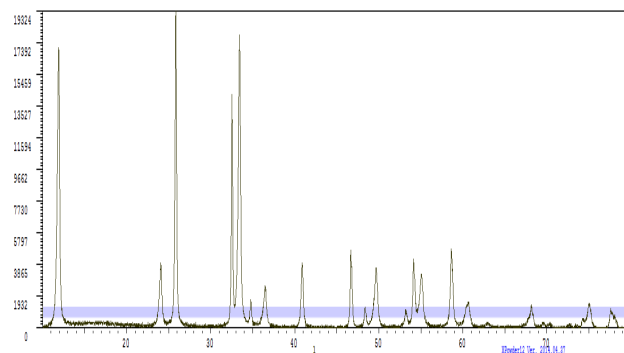


Fig. 1 XRD pattern of flower like nano BiOCl

Fig. 1 shows the XRD pattern of flowerlike nano BiOCl. 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 [18].

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.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the mean particle size, λ is the wavelength of incident X-ray (1.5406 Å), 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.



Fig 2 HR FESEM image flower like nano BiOCl

Photocatalytic Activity:

The photocatalytic activities of flower like nano BiOCl was evaluated through the degradation of 10^{-4} mol dm⁻³ methomyl (MM) in water. To know the photolysis of MM in solar and visible light an experiment carried out and also know the adsorption efficiency of flower like nano BiOCl catalyst a dark reaction only with BiOCl carried out along with photocatalysis in the presence of solar and visible light. Fig. 3 shows the results of the experiment. Results had drawn between C/C_0 versus time where C is the absorbance at a particular time and C_0 is the initial absorbance. The results showed that degradation of MM solution very low under visible light and solar light in the absence of BiOCl and also adsorption of pesticide on BiOCl surface was low. BiOCl was unable to initiate the pesticide degradation in dark. Light source induce the photocatalysis process. Degradation of MM in presence of visible light and BiOCl not shows the favourable results. Photocatalysis using solar light shows the promising results because both UV and visible lights are present in solar light. Thus it can be assumed that UV light is responsible to initiate the photocatalysis reaction. Because BiOCl is wide band gap semiconductor materials and absorbs only UV light and cannot degrade MM pesticide in visible light theoretically. The results concluded that the photocatalytic degradation of MM using solar light is the favourable method to mineralise the pesticide solution and combination of UV and visible light is responsible to induce the process.

Photocatalysis process depends on experimental condition. To know the effect of operational parameter various experiment such as pH, catalyst amount, pesticide concentration, oxidant (H₂O₂), K₂S₂O₈ concentration, FeCl₃ concentration along with other catalysts and stability of catalyst carried out.

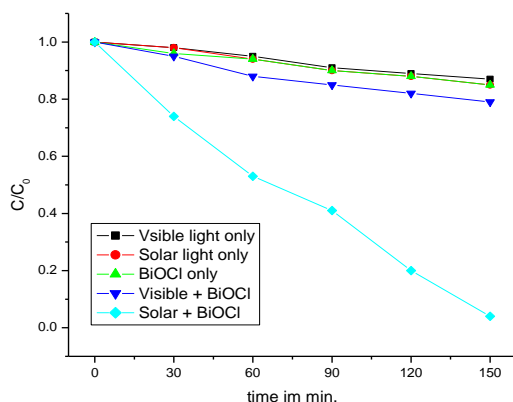


Fig. 3 Degradation study of MM using different system

Experimental condition: [MM] = 10^{-4} mol dm⁻³, BiOCl NPs= 40mg/50ml, pH= 6.3

1. Effect of pH:

pH is one of the most important parameters for the photocatalytic processes. The effect of pH on activity of BiOCl was studied. As it can be seen from Fig. 4 when the pH of the solution, containing pesticide and BiOCl is varied from 2.2 to 12.3, the photocatalytic degradation efficiency reached a maximum at pH 6.3 followed by a decrease of kinetic rate constant in the pH range 6.3 to 12.3. This behaviour can be explained by the surface charge of BiOCl as a function of pH and attack of hydroxyl radical [19].

Effect of pH variations: [MM] = 10^{-4} mol dm⁻³, BiOCl NPs= 40mg/50ml

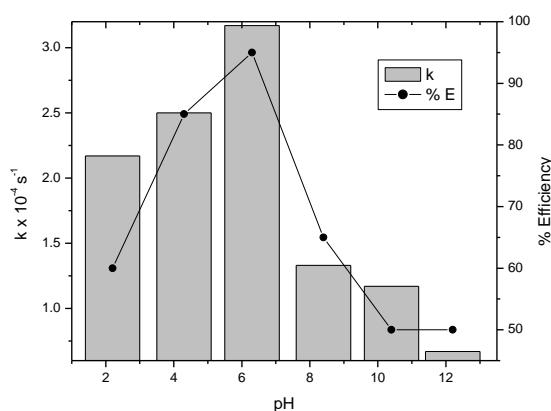


Fig. 4 Effect of pH on photocatalytic degradation of MM

2. Effect of Catalyst Loading:

In order to avoid excess catalyst and ensure total absorption of efficient photons optimum catalyst concentration has to be determined. Thus the effect of photocatalyst weight on the photodegradation of the pesticide was studied in the range of 20 mg/50ml to 70 mg/50ml and results are plotted in Figure. The graph shows that as the concentration of catalyst increased from 20mg/50ml to 40mg/50ml, the degradation rate constant increased from 1.67×10^{-4} s⁻¹ to 3.17×10^{-4} s⁻¹ but on increasing the catalyst concentration up to 70mg/50ml, the rate constant decreased to 1.5×10^{-4} s⁻¹ respectively. The optimum weight of catalyst loading was found to be 40mg/50ml. The increased degradation rate that follows the increase in the catalyst weight can be attributed to the fact that the total active surface area increases with increasing catalyst weight, thus accelerating the process. The decrease in efficiency may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of BiOCl particles. Additionally, in the case of high catalyst loads, we observed agglomeration and sedimentation of BiOCl which makes a significant fraction of catalyst to be inaccessible to either absorbing the pesticide or absorbing the radiation, with

consequent decrease in active sites available to the catalytic reaction [20].

Effect of catalyst loading: $[MM] = 10^{-4} \text{ mol dm}^{-3}$, $\text{pH} = 6.3$

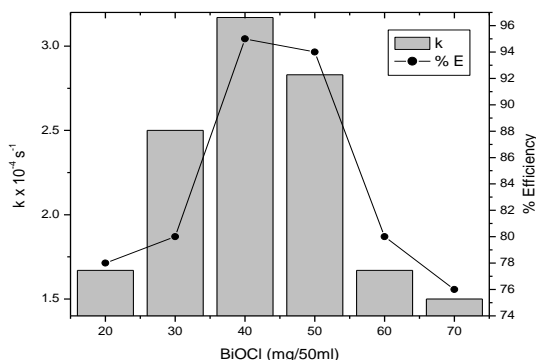


Fig. 5 Effect of catalyst loading on photocatalytic degradation of MM

3. Effect of pesticide concentration:

Effect of pesticide concentration was also studied by taking different concentrations of pesticide from $0.6 \times 10^{-4} \text{ mol dm}^{-3}$ to $2.6 \times 10^{-4} \text{ mol dm}^{-3}$. The results are shown in Fig. 6. It was observed that the rate of photocatalytic degradation increased with increasing concentration of the pesticides upto $10^{-4} \text{ mol dm}^{-3}$. This might be attributed to the fact that as the concentration of pesticides increased, more pesticide molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate. On further increase in pesticide concentration, the equilibrium adsorption of pesticide on catalyst surface active sites increases, which hinders the competitive adsorption of OH^- on the same sites, which means a lower formation rate of $\bullet \text{OH}$ radicals. The increase in pesticide concentration also decreases the path length of photons entering the pesticide solution. At high pesticide concentration, a significant amount of UV and visible light may be absorbed by the pesticide molecules rather than the catalyst and this may also reduce the catalytic efficiency. Consequently, the degradation rate decreased to $0.16 \times 10^{-4} \text{ s}^{-1}$ as the pesticide concentration increased upto $2.6 \times 10^{-4} \text{ mol dm}^{-3}$ [21].

Effect of pesticide concentration: $\text{BiOCl NPs} = 40 \text{ mg/50ml}$, $\text{pH} = 6.3$

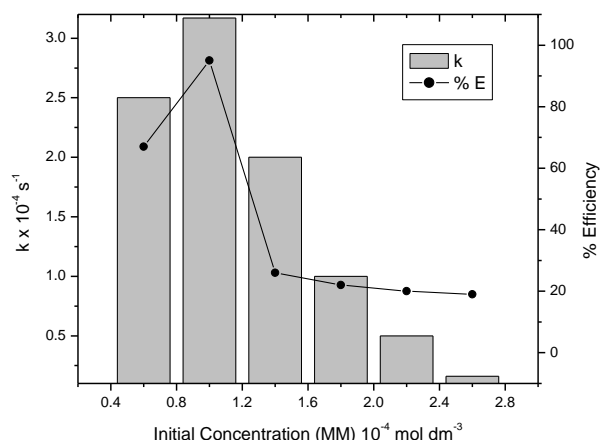
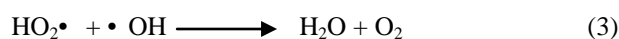
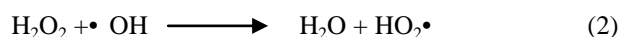


Fig. 6 Effect of initial concentration of MM on photocatalytic degradation of MM

4. Effect of H_2O_2 :

Fig. 7 shows the relationship between rate constant for the degradation of methomyl and initial concentration of H_2O_2 . The results indicate that the degradation of methomyl was increased by increasing the concentration of H_2O_2 . This can be explained by the effect of the additionally produced hydroxyl radicals. With increasing H_2O_2 concentration from $2 \times 10^{-6} \text{ mol dm}^{-3}$ to $4 \times 10^{-6} \text{ mol dm}^{-3}$, the rate constant increases but above this range the improvement was not obvious. This may be due to recombination of hydroxyl radicals and also hydroxyl radicals reaction with H_2O_2 , contributing to the $\bullet \text{OH}$ scavenging capacity (Eqs. (2)– (4)) [22].



Effect of H_2O_2 : $[MM] = 10^{-4} \text{ mol dm}^{-3}$, $\text{BiOCl NPs} = 40 \text{ mg/50ml}$, $\text{pH} = 6.3$

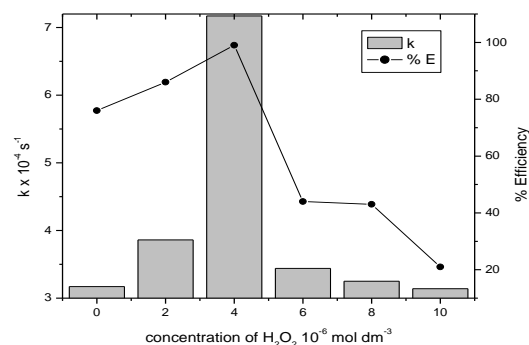


Fig. 7 Effect of H_2O_2 on photocatalytic degradation of MM

5. Effect of $K_2S_2O_8$:

$K_2S_2O_8$ can trap the photogenerated conduction band electron resulting in the formation of sulphate ion ($SO_4^{\cdot-}$), a strong oxidizing agent which can participate in degradation process. The decrease in rate constant above optimum concentration is due to the adsorption of sulphate ions formed during the reaction on surface of catalyst deactivating a section of photocatalyst (Fig. 4.8) [23]. Amount of sulphate ion ($SO_4^{\cdot-}$) is one of the main parameters to influence photocatalytic processes. In this study, to obtain the optimal initial sulphate ion ($SO_4^{\cdot-}$) concentration, the investigation was carried out in the range of (2×10^{-6} to 10^{-5} mol dm^{-3}). The results are shown in Fig. 4.8. It can be seen that degradation rate of methomyl distinctly increased with the increasing amount of sulphate ion ($SO_4^{\cdot-}$). So, Degradation process addition of sulphate ion ($SO_4^{\cdot-}$) at 4×10^{-6} mol dm^{-3} increases rate constant of reaction from $3.17 \times 10^{-4} s^{-1}$ to $3.75 \times 10^{-4} s^{-1}$. The rate constant of methomyl began to decrease when the concentration of sulphate ion ($SO_4^{\cdot-}$) was higher than 4×10^{-6} mol dm^{-3} .

Effect of $K_2S_2O_8$: [MM] = 10^{-4} mol dm^{-3} , BiOCl NPs= 40mg/50ml, pH= 6.3

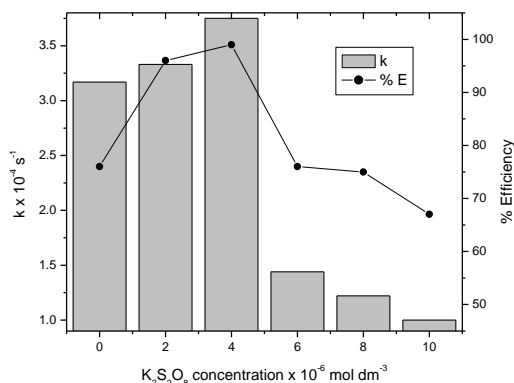


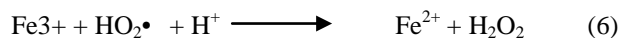
Fig. 8 Effect of $K_2S_2O_8$ on photocatalytic degradation of MM

6. Effect of $FeCl_3$:

Amount of ferrous ion is one of the main parameters to influence the photocatalytic processes. In this study, to obtain the optimal initial Fe^{3+} concentration, the investigation was carried out in the range of (2×10^{-6} to 10^{-5} mol dm^{-3}). The results are shown in Fig. 4.9. It can be seen that degradation rate of methomyl distinctly increased with the increasing amount of Fe^{3+} . So, Degradation process addition of Fe^{3+} at 2×10^{-6} mol dm^{-3} increases rate constant of reaction from $3.17 \times 10^{-4} s^{-1}$ to $3.83 \times 10^{-4} s^{-1}$. The rate constant of methomyl began to decrease when the concentration of Fe^{3+} was higher than 2×10^{-6} mol dm^{-3} .

Ferric ion (Fe^{3+}) known to behave as an electron scavenger (Eq. (5)) thus preventing the recombination of electron hole

pairs. Under the experimental conditions the following reactions become significant.



When $FeCl_3$ concentration was in excess of 4.0×10^{-6} mol dm^{-3} the degradation rate constant values decreased gradually due to the deposition of Fe^{3+} ions on the BiOCl particles. Active sites of the BiOCl got covered with Fe^{3+} ions [24].

Effect of $FeCl_3$: [MM] = 10^{-4} mol dm^{-3} , BiOCl NPs= 40mg/50ml, pH= 6.3

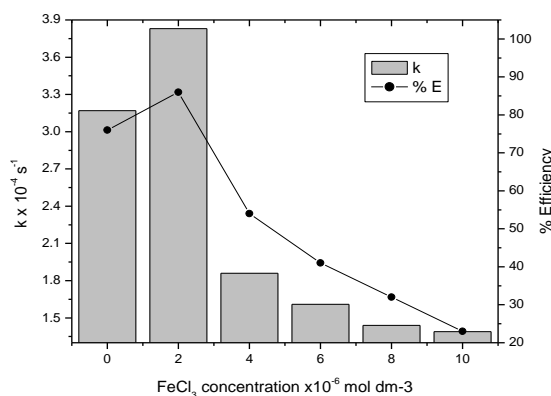


Fig. 9 Effect of $FeCl_3$ on photocatalytic degradation of MM

7. 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 shown in Fig. indicate that BiOCl exhibits excellent performance in terms of both adsorption and degradation of Methomyl. The highest photocatalytic activity was observed in the presence of flower like BiOCl. The results show that flower like nano BiOCl is more 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 light utilization significantly because of the multiple reflections of light within the interior structure of the flower like BiOCl. Such enhancements could generate more of electrons and holes and thus that can promote photocatalytic activity in the flower like nano BiOCl sample [25], [26].

Effect of other catalysts: [MM] = 10^{-4} mol dm^{-3} , Catalyst= 40mg/50ml, pH= 6.3

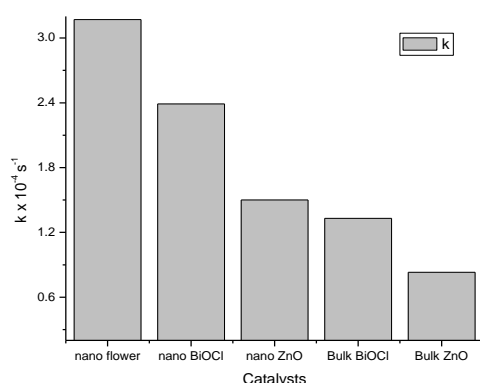


Fig. 10 Effect of other catalyst on photocatalyst degradation of MM

8. Stability test for BiOCl activity:

To assess the stability of the BiOCl in the photocatalytic reaction, BiOCl was re-examined for two more cycles. As shown in Fig. 11, the photocatalytic performance of the as-prepared BiOCl for MM degradation was effectively maintained for 120 minutes of testing. After three cycles of repetition tests for photodegradation of MM, catalyst did not exhibit any significant loss of activity. This experimental result indicated that BiOCl is quite stable and has good photocatalytic performance on degradation of MM [27].

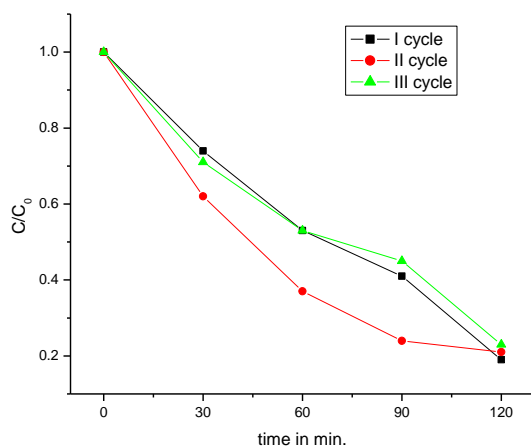


Fig. 11 MM degradation by BiOCl

Experimental Condition: $[MM] = 10^{-4} \text{ mol dm}^{-3}$, BiOCl NPs= 40mg/50ml, pH= 6.3

IV. CONCLUSION AND FUTURE SCOPE

Flower like nano BiOCl synthesized by hydrolysed method. BiOCl shows promising catalytic activity in solar for methomyl pesticide degradation. UV light present in solar light induce the photocatalytic activity of BiOCl. As prepared flower like nano BiOCl exhibit excellent photocatalytic activity to degrade MM in 150 min. under experimental

condition. Size and morphology plays an important role in photocatalytic activity. Hierarchical structures could enhance light utilization significantly because of the multiple reflections of light within the interior structure of the flower like nano BiOCl. Such enhancements could generate more of electrons and holes and thus that can promote photocatalytic activity in the flower like nano BiOCl. This work provides an example of size and shape dependent photocatalytic properties and also opens new possibilities to provide some insight into nano sized and hierarchical structure semiconductors photocatalysts for degrading organic pollutants and other applications.

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