Preparation and photocatalytic activity of Mn-BiOCl catalyst

REPORT SUBMITTED TO
LOVELY PROFESSIONAL UNIVERSITY
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FOR THE AWARD OF DEGREE OF
M.Sc. (Honors) Chemistry
UNDER THE GUIDANCE OF

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(2017)

CERTIFICATE BY GUIDE

This is to certify that this report for Dissertation-II is a bonafide work done by Indervir Singh Chander in partial fulfillment of the requirement for the Degree of Master of Science (Chemistry).

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Acknowledgement

“It is not possible to prepare a project report without the assistance and encouragement of the other people. This one is certainly no exception”.

On the very outset of this report, I would like to extend my sincere and heartfelt obligation toward all the personages who helped me in the Endeavour without their active guidance, help, cooperation and encouragement, I would not have made headway in the project.

My profound gratitude and deep regards to my guide Dr. Bhawna Sarwan for her exemplary guidance, monitoring and constant encouragement throughout the course of this report. The blessing, help and guidance given by her time to time shall carry me a long way in the journey of life on which I am about to embark.

I extend my gratitude to Lovely Professional University for giving me this opportunity.

My acknowledgement also goes to my department and to my Head of School Dr. Ramesh Chand Thakur, thanks for providing a wonderful environment and opportunity to do this project. Lastly, much gratitude to my parents whose valuable ideas, encouragements, and prayers give me strength and fruitful results in my life.

Thanking you
Indervir Singh Chander
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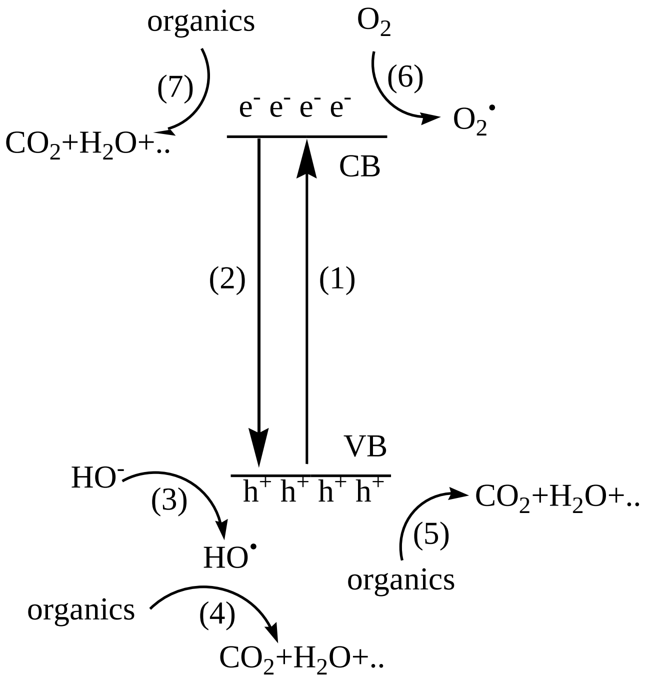
Contents

1. Introduction

Water is the most important part for every species present on earth as it used in many ways by humans and helps in circulating nutrients in biosphere. But the condition of water is becoming worse now days. Industries are contributing as the major source of water pollution. Chemicals secreted from industries are mostly non biodegradable and affect the marine habitat. Chemicals can block the water surface and does not allow sunlight to go down. Dye is such harmful chemical. Major sources of dye are textile industries, paper industry and leather industry. Dyes are generally insoluble in water and cannot be degraded easily. To get rid of this problem, scientist used Advanced oxidation processes (AOPs). AOPs works on the in-situ production of hydroxyl radicals (•OH). These ions can be generated by oxidants (ozone, hydrogen peroxide) or by energy sources (UV light, visible light) or by catalyst (TiO_2, ZnO) [1]. For generation of radical, photocatalytic oxidation is an easy process. Catalyst in presence of energy source can excite its electron to conduction band there by creating hole in the valence band. ZnO, TiO_2, WO_3, VO_4 can be used as catalyst for photocatalysis but they have some drawbacks. BiOCl is another catalyst in the list [2]. Previously it was used for pearly pigment, cosmetics of no toxicity etc. Various experiments shown that it can degrade dyes in UV light as well in visible light. It is having a band gap of 3.46 eV [3]. It can degrade dyes like RhB, Methyl orange, and Methyl Red etc. Photocatalytic activity can also be increased by preparing nano particles or by doping it with metals. Metals like Mn [4], Zn [5], Cu [6], Eu [7] has been taken for doping with BiOCl. The major benefit of doping is that the recombination process decreases as metal form new energy level between conduction band and valence band. Doped nano crystal provides large surface area for absorption and reaction to take place. Metals can alter the band gap by changing the size of the catalyst. Doping BiOCl with Mn increased its photocatalytic activity. Author found that Malachite green was completely degraded by doped BiOCl in 120 min where as undoped Catalyst took 180 mins. Decrease in band gap allows catalyst to work in visible region. Concentration of metal in doping plays important role. There is limit for doping of a catalyst. Doping increases photocatalytic activity but when limit is crossed, photocatalytic activity starts decreasing. Excess metal ions can occupy the surface of catalyst and block the absorption of light, reduces excitation of electrons.

In this work we will prepare the Mn-BiOCl photocatalyst by using hydrolysis method. To examine its photocatalytic activity, methylene blue will be used as a dye contaminant.

Mechanism of Hydroxyl radical generation



BiOCl + *hv* (UV) → BiOCl (e^- +h^+) (1)

e^- + h^+ → *hv'* (recombination) (2)

h^+ + OH^- → $HO^\bullet$ (3)

$HO^\bullet$ → organics → intermediates → CO_2 + H_2O + …. (4)

h^+ + organics → intermediates → CO_2 + H_2O + …. (5)

e^- + O_2 → $O_2^\bullet$ (6)

$O_2^\bullet$ + organics → intermediates → CO_2 + H_2O + …. (7)

When light energy is irradiated on the catalyst, electrons from its valence band gets excited to conduction band, leaving behind hole. Hole can degrade organic molecule into small compounds, process called mineralization. Holes convert hydroxyl ions into hydroxyl radicals. Hydroxyl radicals also help in mineralization [8].

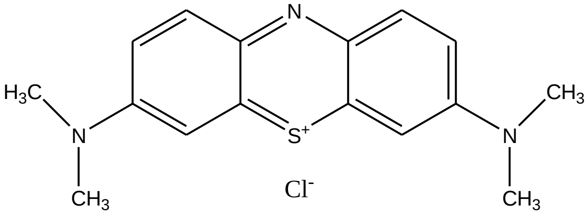
2. Dyes as a contaminant

A dye is a colored substance having affinity toward substrate on which it is applied. Dyes are applied to fabric, paper, plastic, leather in liquid form. A dye consists of chromophore which imparts color to it. Chromophores are the pi electrons in conjugation. Aryl ring is common in most of the dyes.

Type of Dye	Class	Example of Dye
Mordant dye	Anthraquinone Dye	Alizarin
Azo dye	Azo Dye	Trypan Blue
Acid dye	Nitroso Dye	Napthol Green B
Basic dye	Triarylmethane Dye	Crystal Violet
Vat dye	Safranin Dye	Indanthrone

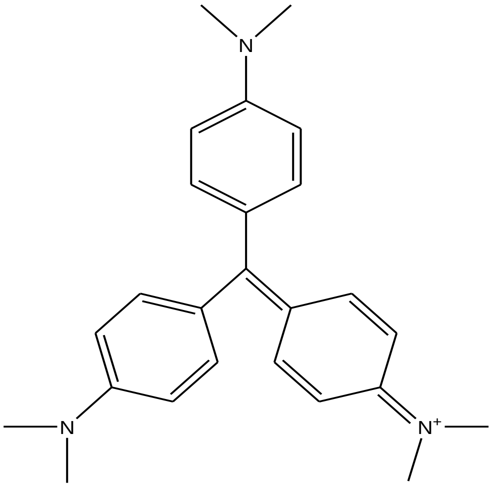
Based on the chemical classification, dyes are according to their chromophores,

Phenothiazine is an organic compound belonging to thiazine class of hetrocyclic compound in which Nitrogen and sulfur is present. One of their derivatives is methylene blue. Methylene blue is basically used for treating methemoglobinemia. Maximum absorption by MB is shown at 670 nm.



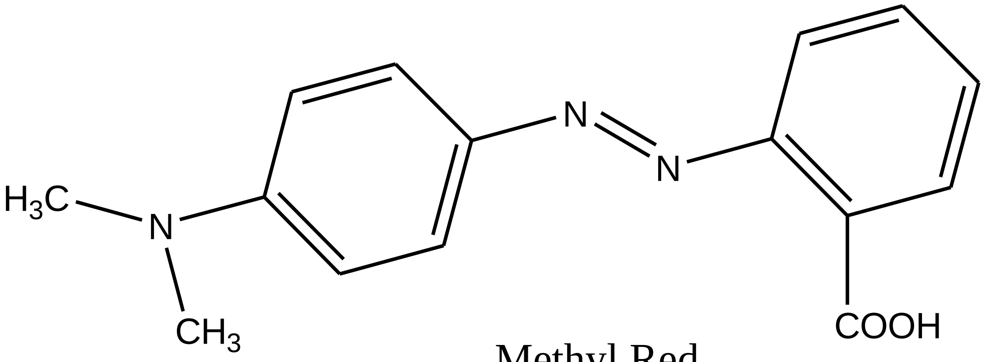
Methylene Blue

Dyes which contain Triarylmethane as their backbone are called **Triarylmethane** Dyes. These types of dyes have intense color. Dyes in this class varies according to the substitution on the aryl group like if dimethlamino group is present at *p*-position than it is methyl violet dye, and if primary or secondary group are there than it is fuchsine dye. Some of the important dyes are crystal violet, malachite green, cresol red, phenol red etc.



Crystal Violet

Dyes which contain R-N=N-R' in their chemical structure, belongs to **Azo dye** class. In most of the cases R is aryl group. Azo dyes are mostly used in textile industry, leather industry and in some foods. Due to π-delocalization, it gives various colors like oranges, reds and yellows. Examples of Azo dye are Methyl red, Methyl orange, Trypan Blue etc.



Methyl Red

For our work, we have selected methylene blue as dye contaminant and will be mineralized using doped BiOCl.

3. Preparation of Mn-doped BiOCl

Mn-doped BiOCl particles will be prepared by using hydrolysis method by taking different concentration of Mn as a dopant. The prepared samples will be characterized by XRD, SEM, TEM and UV-vis sperctroscopy to study their structural, morphological and optical properties respectively.

4. Proposed methodology during tenure of work

The photocatalytic reaction will be carried out in a batch reactor with dimension of 7.5 cm × 6 cm (height ×diameter) provided with a water circulation arrangement in order to maintain temperature between 25-30 ^{0}C. Slurry will be placed inside the reactor and stirred magnetically with simultaneous exposure to light by placing the photoreacter under visible light source. At specific time interval, sample will be withdrawn and centrifuged to remove photocatalyst particles in order to assess rate of decolourization and degradation photometrically using Vis. Spectrophotometer. The pH will be constantly monitored using a pH meter. The pH of the reaction mixture will be adjusted by adding a dilute solution of H_2SO_4 or NaOH.

5. Review of the work:

1. Chemical Structure of BiOCl

Electronic structure of BiOCl was firstly studied by **K L Zhang et al** using a density functional method (TB-LMTO) [9]. They showed that it consist of 6s and 6p valence state for Bi, 2s and 2p state for O, 3s and 3p state of Cl. The calculated electronic structure of BiOCl confirms that it has an indirect band-gap of 3.46 eV, and the Cl 3p and Bi 6p states dominate the highest occupied molecular orbitals (HOMO) and the lowest unoccupied orbital (LUMO), respectively. The photocatalytic activity was studied over Methyl orange degradation and comparison was made with TiO_2. MO was completely photo degraded by BiOCl in 10 min but 5% remained in solution when treated with TiO_2.

Later, **Huang et al** [10] studied electronic structure by plane wave pseudopotential method. With Bi 5d state, the indirect band was found to be 2.80 eV, whereas in absence of Bi 5d state band gap was 2.59 eV. Different Bismuth Oxyhalides (BiOCl, BiOBr and BiOI) gave band gaps of 2.80, 2.36 and 1.75 eV respectively.

The crystal structure of BiOCl was studied by **K. G. Keramidas et. al** [11] which demonstrate that the structure belongs to the tetragonal space group *P4/nmm* and the cell constants, obtained by a least-squares calculation from direct 0-value measurements on the diffractometer, are ***a*** = 3.8870(5) and **c** = 7.3540(5). Each Bi atom is eight-coordinated by four O atoms at distances of 2.316 Ä and four Cl atoms at distances of 3.059 Ä in the form of an asymmetric decahedron. Crystal has 2 BiOCl molecules in a unit cell. Therefore, this compound has a complex structure with 18 valance electrons per unit cell.

2. BiOCl Nanoparticles

Bulk BiOCl with large grain sizes, however, have some disadvantages such as small specific surface areas, long migration distances for the photo excited electron–hole pairs and an increase in the recombination of the electron–hole pairs, which adversely affect photocatalytic activities. Hence preparation of nanostructured BiOCl photocatalyst doubtless deserves to be taken into account in future research. Many researchers prepared different structures of BiOCl to increase the photocatalytic activity of catalyst like nanowires [12], nanoflower [13], nanospheres [14]. **Sujuan Wu** and co-workers prepared bismuth oxychloride (BiOCl) nanowire arrays by Anodic

Aluminum Oxide (AAO) template assisted sol-gel method [12]. In this study, AAO templates behave as substrate along with controlling the size of nanostructure. SEM images of as prepared sample show that nanowires of 100 nm diameter and length 2- 6 µm, assembled in the pores of AAO templates, were formed. Nanowire formation provides large surface area for the degradation to take place; it can alter the band gap. Nanowires in this method degraded the Rh B dye in the presence of UV light by 32 % from initial concentration. The band was found to be 3.4 eV. After this successful results of BiOCl nanowire, in same year **Sujuan Wu et al** synthesized nano structures on Anodic Aluminium Oxide (AAO) templates via sol-gel combined with the vacuum-air extraction method [15]. They found that concentration has great effect over the morphology of the nano structure. The flakes are almost vertically aligned on the surface, but at lower sol concentration, nanowire arrays are aligned along the channels. BiOCl flake films are also prepared on the glass substrate, and the flakes were horizontally oriented on the surface. Photocatalytic activity was examined with degradation of Rh B dye by BiOCl flakes on glass and BiOCl flakes on AAO. BiOCl flakes on glass degraded only ~3% of dye where as BiOCl flakes on AAO template removed ~42% of initial dye concentration. So the comparison study shows that the vertically aligned flakes exhibited higher photocatalytic activity that flake like film.

Song et al. reported the synthesis of nanostructured flowerlike BiOCl using pyridine as a solvent [13]. Different compositions of pyridine and water was taken this the following process. Compositions affect the size of nano flowers. FESEM (Field emission scanning electron microscope) images shows that in pure water the size of nano flower was 200 nm, which is much more than the size in mixed composition of pyridine and water. Size gradually increased as we increased the ratio of pyridine. It took 8 min to degrade the MO dye under UV light. This shows its excellent photocatalytic activity and is higher than P25 catalyst and 2 min are saved.

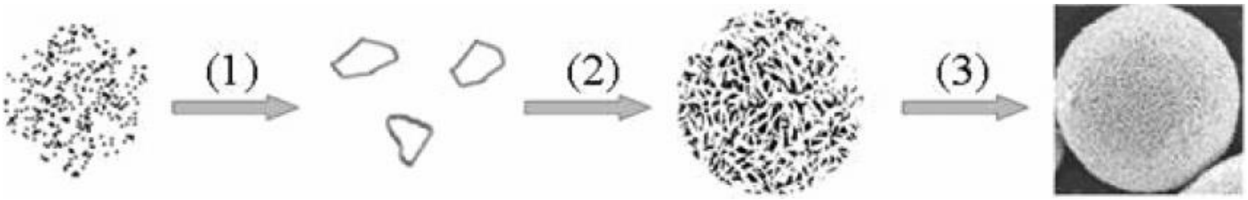
Nanoflowers of BiOCl are another candidate for photocatalysis as they exhibit special morphology and large surface area**. Cao S et al.** fabricated flower like hierarchical structure by a template free method and Bi film was mixed in solution of H_2O_2 and HCl [16]. BiOCl nanopetals were formed around the Bi sphere used as substrate, when the substrate was dipped in the solution of H_2O_2 and HCl for 1 min. With the passage of time more petals were formed. FESEM images showed that nanopetals have smooth surface, polycrystalline structure was not there. High concentration of H_2O_2 and HCl lead to high reaction velocity [17]. Later, **Cao and co-workers** improved their work by adding a connecting layer of chromium to get good quality of BiOCl film on silicon substrate. In this work, on silicon substrate they deposited chromium film, about 10nm thick, and Bi film, about 100 nm thick, by electron-beam evaporation. Substrate temperature was kept at 190^{O}C. After this, substrate was dipped in solution of H_2O_2 and HCl and yielded BiOCl film. Photocatalytic activity was evaluated by degrading RhB under visible region and found that at wavelength of 554nm, the absorption value changes by 52% after 8 h's visible light irradiation.

Chen et al. synthesized BiOCl nanoflowers in the presence of nitric acid and L-Lysine [18]. They produced BiOCl nano-flower of band gap 2.87 eV. L-Lysine was used as template in this process. In the absence of L-Lysine, the micro particles were irregularly formed. When L-Lysine was added without HNO_3, it generated micro needles. But, by addition of L-Lysine and HNO_3 together, flower like nanostructures was appeared. This evident that the size of nano particle can be controlled by addition of HNO_3. It controlled the hydrolysis of $BiCl_3$ (Calcination) also. SEM images show that the average size of the flower was found to be 1.5μm. Due to narrow band gap of 2.87 eV, RhB was degraded under visible light and found it far better than TiO_2.

Ping Ye et al [19] also prepared flower like BiOCl by simple template free hydrolytic method. They observed that the flower like structures formed due to self assembly of nanosheets. Initial compound used to start a reaction was $BiONO_3$ was spherical in shape with diameter of 50 nm, as shown by SEM images. After 40 min, flower like nano particles was formed. Photocatalytic activity was evaluated by degradation of RhB and they found it better than TiO_2. It is because of wide band gap, more positive valence band potential. Photo-excited holes have stronger oxidation ability so it works better than TiO_2.

BiOCl nanospheres are the new field of interest as photocatalyst. **Zhang and co-workers** prepared microshpheres by one-pot solvothermal process using ethylene glycol as solvent [14]. In their work they proposed mechanism by which nanospheres can be formed. SEM images shows that the diameter of spheres was 1-3 µm. High resolution SEM images shows that microspheres was made of small nanoplates fused together.

Illustration of Possible Formation Mechanism of Hierarchical BiOCl



(1) Formation of BiOCl nanoparticles and their growth into nanoplates. (2) EG-induced self-assembly of these nanoplates to form loose microspheres. (3) Formation of regular

hierarchical microspheres through a dissolution-recrystallization process of the preformed nanoparticles

Photocatalytic activity was studied by degrading MO under UV and Visible light. Under UV light MO degradation was about 17% which was higher than TiO_2, which degraded only 10%. These nanospheres were active under visible light also. BiOCl degraded 15% of MO in 3 h.

3. Doping in BiOCl:

BiOCl having 3.46 eV band gap it is difficult to increase the separation charge efficiency and to improve its photocatalytic activity. Many steps have been taken, including various hierarchical nanostructures [20], halogen mixing solid solutions [21], crystal facet control and coupling BiOCl with other materials (graphene, oxides, metal, salts). Out of all these, doping it with metals and non-metals has found to be an effective way to improve photocatalytic activity of photocatalyst [22]. When catalyst is doped with metal, it creates new energy level between Conduction Band (CB) and Valence Band (VB). At newly formed energy state excited electron can settle and can go to CB also. So the energy required to excite electron is reduced. In the absence of metal an electron can return back to VB, then photo degradation will not proceed. So metal doping is effective in photo degradation process. There are less chances of electron-hole recombination. This enhances photocatalytic activity of catalyst.

1. **Band gap narrowing**: **G. Chen et al**. [23] doped N in BiOCl, they observed that doping caused replacing of oxygen atoms by nitrogen atom thereby giving narrow band gap than normal BiOCl. Photocatalytic activity of N-BiOCl was found to be higher than normal BiOCl under visible light.
2. **Oxygen vacancies**: **X. Zhang** [24] and other authors found that oxygen vacancies affect the photocatalytic activity of BiOCl. They bind substrates more strongly than the normal oxide sites. The indirect band gap for $BiO_{15/16}Cl$ was found to be 2.76 which is less than experimental data, i.e. 3.43.
3. **Use of strong oxidizing agent: J. Di and co-workers** [6] used H_2O_2, an oxidizing agent, for photocatalytic degradation of Dye. Metal ions like Fe^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+} decomposes H_2O_2 to give hydroxyl ion (•OH). Hydroxyl ions being non-selective oxidant, along with photocatalyst, degrade organic pollutants to CO_2 and H_2O.

Mn doping is a way of increasing photocatalytic activity studied by **Brijesh Pare** and co-workers [4]. In this study, Mn-BiOCl was prepared by simple hydrolysis method. The Crystallite size was found to be 39.6 nm for pure crystal and 34.4 nm for Mn-BiOCl. This difference was observed due to replacement of Bi^{3+} ions having radii 0.096 nm by Mn^{2+} ions of radii 0.080 nm. In SEM images, the calculated particle size of doped BiOCl was found in the range of 0.47-5 µm whereas undoped BiOCl have size 1-3 µm. Mn doped BiOCl exhibited absorbance in visible region (400-600 nm) i.e. red shift, whereas pure BiOCl was working under the UV region. By Tauc relation, author calculated band gap of doped and undoped BiOCl to be 2.75 eV and 3.48 eV, respectively. Undoped BiOCl degraded MG dye 64% from its initial concentration under 120 min of irradiation time. Whereas doped degraded dye to 98% in same time.

J. Xia and coworkers prepared Fe/BiOCl porous microspheres by ethylene glycol (EG)-assisted solvothermal method [25]. [Omim]$FeCl_4$, an ionic liquid, acted as a source of Cl and Fe. XRD analysis suggested that Fe^{3+}, having ionic radii 0.79 nm, replaced Bi^{3+} of radii 1.03 nm. This was observed by the characteristic peak of Fe/BiOCl sample. Raman spectroscopy results confirmed that Fe is coordinated with O after replacing Bi atom. Size of doped BiOCl was found to be 1 µm by SEM images. Photocatalytic activity was examined under visible light for RhB and MB in the presence of H_2O_2. In the presence of H_2O_2 only, 7.5% of RhB was degraded in 25 min of irradiation. In the presence of Fe/BiOCl, in 25 min irradiation time, 75 % of RhB was degraded. Pure BiOCl degraded 20.9 % RhB in same time. The increase in photocatalytic activity is possibly due to increase in surface area, as porous microspheres of 1 µm size are formed, which allowed more absorption of incident light. Other can be narrow band gap i.e. 1.85 eV.

J. Di and coworkers synthesized uniform spherical Cu modified BiOCl with higher photocatalytic activities through one-pot solvothermal method, which work under visible light [6]. In this experiment, [Omim]$CuCl_3$, an ionic liquid, was used which is the source of Cu and Cl. $Bi(NO_3).5H_2O$ and EG solution along with ionic liquid were made to mix and yielded doped BiOCl. They prepared different metal-catalyst (Cu/BiOCl) ratios, (1 : 3), (1 : 1), (5 : 1) and (10 : 1). XRD analysis showed that final crystals formed do not contain any impurity. SEM images confirmed that crystals are spherical in shape with diameter of 3-5 µm. (1 : 3) sample degraded 98% MB, (1 : 1) degraded 96%, (5 : 1) degraded 100% MB and (10 : 1) degraded 93% under 75 min irradiation. This indicates that concentration affects the photocatalytic activity. More concentration either can lead to increase of band gap or can destroy the structure also. But as compared to pure BiOCl, it works better. According to proposed mechanism by author, Cu2+ improves the inner charge transfer rate and prevent the recombination of photo-generated electron thereby increases photocatalytic activity.

BiOCl has also been doped with Zn^{2+} by **Wen Ting Li et al** [5]. They doped BiOCl with different molar concentrations of Zn/BiOCl, 0.03, 0.07 and 0.10. XRD pattern indicates that Zn doping does not affect the crystal structure. Zn doped BiOCl had less intense peaks as the Zn content was increased. Author found that it was due to replacement of Zn with Bi in the lattice structure. SEM and TEM images also confirmed that there is no effect of doping on structure. Using DRS results the band gap value was 3.37 eV. They found that the photocatalytic activity has been increased. Doped BiOCl degraded Rhodamine B (RhB) within 8 mins. Results also show the stability and recyclability of catalyst. Photo generated electron hole pair and large surface area enhanced photocatalytic activity of catalyst.

Guihua Chen and co-workers prepared N-doped BiOCl by Ethylenediamine Assisted hydrothermal method [26]. Doped catalyst was prepared simply by mixing Bi $(NO_3)_3.5H_2O$ solution with KCl solution. To adjust the pH to 7, ethylenediamine (EDA) was used for doped product and NaOH was used for pure BiOCl catalyst. Diffuse reflectance spectra (DRS) of N-BiOCl show red shift toward longer wavelength. This concludes that N-BiOCl has capability of degrading RhB in visible region. SEM images shows that flower like structure was formed by self assembly of nanoplates. Absorptive ability of pure BiOCl is more than doped BiOCl but under visible light N-BiOCl degraded RhB better. This was due to formation of localized 1s state in the band gap by Nitrogen.

Meichao Gao and coworkers [7] doped BiOCl with Eu^{3+} by simple combustion method. XRD pattern shows that Bi^{3+} ion was replaced by Eu^{3+} ion and small size crystals was obtained. Rough surface crystals of doped BiOCl were formed having width 0.5-2 µm indicated by SEM images. A DRS spectrum shows that when concentration of Eu was increased band gap transition shifts to longer wavelength and its efficiency also increased in UV region. They found that new energy level of Eu is formed between VB and CB instead of modifying it. The doped product showed continuous absorption in UV light region and the band gap also decreased. Photocatalytic activity was observed over degradation of RhB. They have found that photo degradation has been increased, compared with the pure BiOCl, as the Eu^{3+} formed the oxygen vacancies and absorption in UV region. Eu3+ doped BiOCl showed high stability as used for 6 times and its photo degradation ability was not much affected.

Concluding, Simple Hydrolysis method is useful for preparing the doped BiOCl. It does not require any complicated instruments and less time is required for sample preparation. Product formed at last is smaller in size, as compare to pure, and provide large surface are for absorption. Band size was also less than undoped BiOCl making easy excitation of electrons. Within 120 min, dye was completely degraded whereas undoped degraded only half of the dye in same time.

4. **Applications of BiOCl**

Toxic chemicals are increasing at alarming rate day by day in air and water. Various steps are being taken for making clean environment. Photocatalysis is one of the way by which chemicals can be degraded. Metal oxides are candidate for photo degradation. BiOCl is one of the metal oxides. It works under UV light as well as under Visible light. Earlier BiOCl was used for pearly pigment, cosmetic of no toxicity and catalyst. Later many authors found it useful in degradation of dyes and for purification process.

Carlos R. Michel and co-workers prepared BiOCl nanocatalyst and studied its properties for gas sensing. [27]. BiOCl was prepared by surfactant assisted method. TEM images show that particles of irregular shape, size ranging between 180 nm to 700 nm was obtained. For sensing of gas, impedance was observed by forming film of BiOCl on alumina substrate of 600 µm. Impedance of 6.6 kΩ was recorded when CO, of 200 ppm concentration, was introduced at 300°C. Result yielded was same after repeating it many times. Test for CO_2 and O_2 was also performed but the results were not satisfactory.

K. K. Saini along with their workers synthesized BiOCl by soft chemical method route [28]. Bismuth nitrate and KCl was used as precursor for reaction. Morphological analysis done by SEM shows that nanoplate of 5 to 25 nm thickness was obtained. Photodegradation of MB was done under visible light and completely degraded it in 3 hours. Maximum absorption by methylene was shown at 664 nm which corresponds to visible region. Band gap was found to be 3.4 eV, which is large, but it is better as it degraded MB in visible light.

Guisheng Li et al synthesized RhB-BiOCl system and used for the degradation of pollutants like 4-chlorophenol (4-CP) and air pollutant nitric oxide under visible light [29]. $Bi(NO_3)_3$ and NaCl was used for the preparation of photocatalyst. XRD studies shows absence of any impurity in synthesized product. FESEM images shows that microspheres of BiOCl are formed with average size of 3 µm. BiOCl catalyst on irradiation of visible light degraded 90% of RhB after 150 min. Then RhB-BiOCl system was used for the degradation of 4-CP. Author also described mechanism for the degradation of 4-CP. When light strikes RhB it releases electrons and these electrons go to the CB of BiOCl. These electrons react with hydroxyl groups and oxygen to produce oxidative radicals which degrade 4-CP.

6. Objectives of the Research

1. To optimize the reaction conditions for the degradation of dyes under investigation.
2. Investigation of the catalytic efficiency of doped-BiOCl.
3. To envisage most plausible mechanism of photocatalytic reaction.

7. Expected outcome of proposed work

1. Evolution of safe and simple method for the treatment of water containing dyes as pollutant.
2. Optimization of reaction conditions will help to generate a set of conditions under which photocatalytic degradation is effective.
3. Photocatalytic degradation mechanism of dye under consideration will help us to understand the intricate process of degradation and decolorisation for dyes.
4. The results of present work and respective literature survey will help in establishing that the heterogeneous photocatalysis could be employed as a powerful tool for the elimination of dyes under investigation from water.

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