



Photocatalytic degradation of environmentally hazardous textile dye azure B in the presence of solar light using Nano BiOCl

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Abstract

This paper studies the environmental application of AOPs in treating dye wastewater. The azure B dye has been chosen as a pollutant. Photocatalytic degradation of azure B by nanoBiOCl was studied under solar light. BiOCl was prepared by a simple method and characterized by XRD and SEM. XRD pattern suggested that the synthesized nano BiOCl was highly pure and crystalline, SEM images depicted the platelike morphology of nanoBiOCl. The average particle size of nanoBiOCl was obtained as 45 nm. The photocatalytic studies have revealed that optimum pH was 8, initial dye concentration was $4.0 \times 10^{-5} \text{ mol L}^{-1}$, catalyst loading was 30 mg/100 ml of dye solution. The optimum concentrations of electron scavengers and salts have also been obtained.

Keywords: AOPs, wastewater remediation, Solar light, BiOCl.

Introduction

Environmental pollution is a continuously growing risk to human health especially in the industrially intense cities. Many health related problems are caused directly or indirectly by environmentally deleterious compounds minamata disease and blue baby syndrome are some of these, many chemicals used for industrial purposes may be carcinogenic too, textile dyes are also the class of compounds which have high perils to disturb our ecosystem in many ways. The most alarmed environmental pollution is wastewater pollution. It is prime necessity to keep our environment clean and healthy and many researchers are actively working for exploring some eco-friendly cleansing methods¹. Although water is the vital element for normal ongoing of life, during these days, clean water is not easily accessible in many regions of the world. Now a day's textile dyes have become unavoidable part of normal human life². Man-made dyes are widely used for many purposes such as textile and paper industries due to their productivity and diversity of colours³. The effluent from manufacturing industries generates non aesthetic pollution and has therefore received increasing attention⁴. However so many methods have been used previously for water remediation like adsorption on activated carbon and reverse osmosis, but each of them have some drawbacks⁵.

Recently photocatalysis has been emerged as a brilliant technique for treating dyes, pesticides, pharmaceutical waste waters and so many organic and inorganic pollutants present in air and water. Wastewater purification is a very important application of this process, apart from this it is also helpful in plant protection, sterilization of instruments in hospitals, this

may be employs to clean pathology apparatus. Photocatalytic degradation is the green techniques, cost effective and converts toxic pollutants into environmentally non-hazardous compounds⁶.

The present work is devoted to the study of azure B dye as a pollutant for photocatalysis and testing the photocatalytic activity of nano BiOCl. BiOCl can be efficiently applied for the treatment of a variety of pollutants. The photocatalytic capability of nano BiOCl can be exhaustively used for environmental decontamination. In this work dye wastewater has been treated under naturally abundant solar light to make the process inexpensive and easy to handle. The advanced oxidation processes with BiOCl using solar light may be proved as a competent technique for environmental significance.

Methodology

Synthesis of Nano BiOCl: All the chemicals were A. R. grade and used as received. Nano BiOCl has been synthesized in laboratory, for the synthesis proper amount of L-Lysine, BiCl_3 , HNO_3 and aqueous ammonia have been used⁷.

Measurement of Photocatalytic activity: All the dye solutions were prepared using double distilled water. To determine adsorption of dye on catalyst surface, experiments were first performed in dark. For solar experiments 100 ml dye solutions were taken in a double walled beaker placed at magnetic stirrer with water circulation to maintain temperature and control evaporation, a known amount of catalyst was added to this solution and illuminated in solar radiation of optimistic intensity. To observe absorbance, Spectrophotometer 166 of

Systonics was used, for measuring light intensity a Lux meter (Lutron LX-101) was used. pH of the solution was adjusted using pH meter. pH was adjusted by either NaOH and H₂SO₄.

Results and discussion

Structural studies: The XRD pattern of as prepared nano BiOCl sample suggested that nano BiOCl was highly pure and well-crystallized Figure-1. The average particle size of the sample has been calculated by applying Debye-scherrer formula⁸, and it was found to be 45 nm. The SEM image of the as-prepared nano BiOCl showed that it is present in the form of many plates with smooth surface Figure-2.

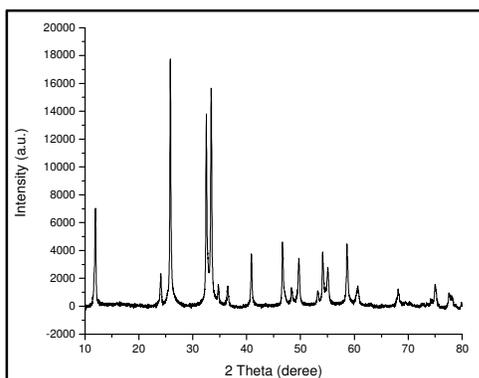


Figure-1: XRD Pattern of Nano BiOCl.

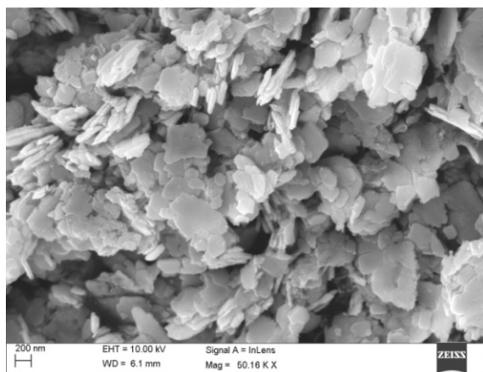


Figure-2: SEM Image of Nano BiOCl.

Photocatalytic Studies: Effect of pH: As pH leads to the generation of OH⁻ radicals, it is the most important operating parameters in photocatalytic aquatic systems. The relative experiments were performed between the pH range 4 to 11 to degrade Azure B wastewater by keeping all the other factors constant. It was found that the pH greatly affects the degradation rate, as pH was increased the degradation of azure B also increased from $2.64 \times 10^{-4} \text{ s}^{-1}$ to $6.60 \times 10^{-4} \text{ s}^{-1}$ due to generation of more OH⁻ ions and at pH 8 most efficient degradation rate was observed. Above pH 8 the rate of degradation was found to be decreased from $3.79 \times 10^{-4} \text{ s}^{-1}$ to $2.22 \times 10^{-4} \text{ s}^{-1}$. A fall in the rate is observed because of repulsion between negatively charged azure B and OH⁻ ions. Results are summarized in Figure-3.

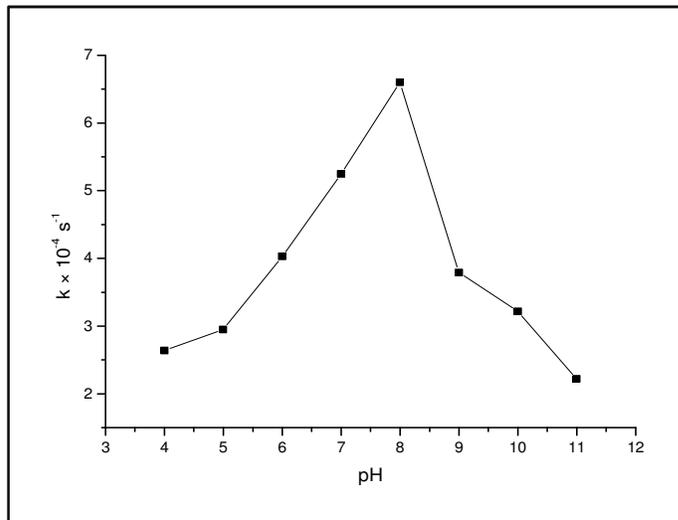


Figure-3: Effect of pH on Photocatalytic degradation of azure B. pH: [Az B]= $4 \times 10^{-5} \text{ mol L}^{-1}$, BiOCl NPs=30mg/100 ml.

Effect of Catalyst Loading: The influence of catalyst concentration on rate of azure B degradation was studied by altering the catalyst concentration in the reaction mixture and keeping the other factors constant. The amount of catalyst was varied from 5 mg to 60 mg/100 ml. With an increase in amount of catalyst from 5 mg to 30 mg/100 ml the rate was found to increase from $4.03 \times 10^{-4} \text{ s}^{-1}$ to $6.60 \times 10^{-4} \text{ s}^{-1}$ because of an increase in the number of active sites available on the catalyst surface. After this, further increase in the weight of photocatalyst from 40 mg to 60 mg/100 ml decreases the rate as $5.33 \times 10^{-4} \text{ s}^{-1}$ to $3.30 \times 10^{-4} \text{ s}^{-1}$. It is because with more catalyst, tendency of agglomeration of photocatalyst increases which leads to the less available surface area of catalyst¹¹. The photodegradation of azure B for different concentration of nano BiOCl is shown in Figure-4.

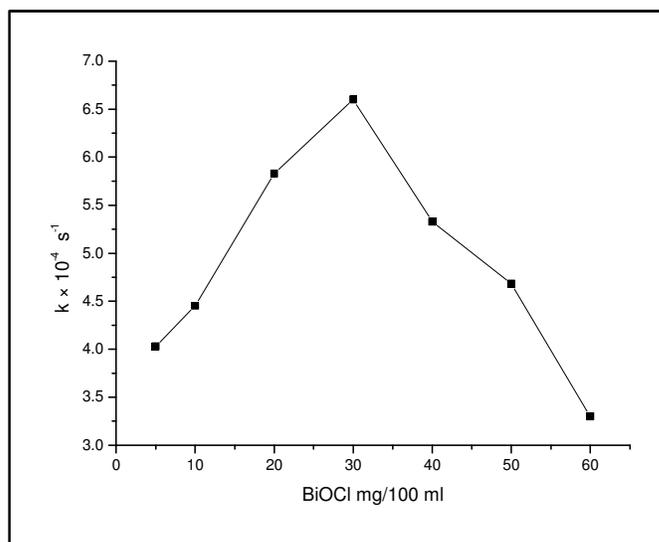


Figure-4: Effect of Catalyst Loading on Photocatalytic Degradation of Azure B. [Az B]= $4 \times 10^{-5} \text{ mol L}^{-1}$, pH=8.

Effect of Initial Dye Concentration: The concentration of dye has been varied from $1.0 \times 10^{-5} \text{ mol L}^{-1}$ to $7.0 \times 10^{-5} \text{ mol L}^{-1}$ and other factors were kept constant. The experimental data shows that an increase in concentration of azure B dye from $1.0 \times 10^{-5} \text{ mol L}^{-1}$ to $4.0 \times 10^{-5} \text{ mol L}^{-1}$ increases the degradation rate constant from $3.41 \times 10^{-4} \text{ S}^{-1}$ to $6.60 \times 10^{-4} \text{ S}^{-1}$. On further increase in dye concentration from $5.0 \times 10^{-5} \text{ mol L}^{-1}$ to $7.0 \times 10^{-5} \text{ mol L}^{-1}$ reduces the degradation rate constant values from $4.95 \times 10^{-4} \text{ S}^{-1}$ to $3.45 \times 10^{-4} \text{ S}^{-1}$. This may be explained as where there rate increases more dyes molecules are offered for reaction and where there rate decreases dye molecules creates an obstacle in the path for light to approach photocatalyst. The graphical results are presented in Figure-5.

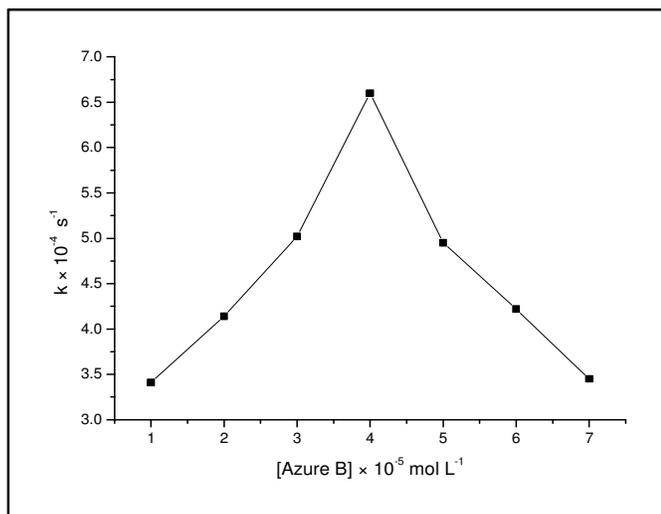


Figure-5: Effect of initial dye concentration. BiOCl NPs=30 mg/100ml, pH=8.

Effect of Oxidants: In the present investigation with the increasing concentration of H_2O_2 from $2.0 \times 10^{-6} \text{ mol L}^{-1}$ to $6.0 \times 10^{-6} \text{ mol L}^{-1}$ the rate constant values increased from $7.59 \times 10^{-4} \text{ S}^{-1}$ to $9.13 \times 10^{-4} \text{ S}^{-1}$, while further increase in concentrations results in decrease in rate of degradation. An increase in rate is due to increase in number of OH^\cdot and rate decreases because of decreasing number of photoholes.

Similar results have obtained in case of another oxidant $\text{K}_2\text{S}_2\text{O}_8$. The degradation rate of azure B was found to be maximal at $6.0 \times 10^{-6} \text{ mol L}^{-1}$ of $\text{K}_2\text{S}_2\text{O}_8$. The addition of persulphate led to form sulphate radical anion ($\text{SO}_4^{\cdot-}$) which is a strong oxidant and lead to chemical change in reaction mixture¹³. The summarized results are presented in Figure-6.

Effect of Varying Salt Concentration: Salts such as NaCl and Na_2CO_3 play an important role in dyeing process and usually comes out along with the sectional wastes in textile industries. The photocatalytic degradation rate decreased with the increases in Cl^- and CO_3^{2-} ions concentration from $2.0 \times 10^{-5} \text{ mol L}^{-1}$ to $12.0 \times 10^{-5} \text{ mol L}^{-1}$. The cause of inhibition is due to the ability

of these ions to act as hydroxyl radical (OH^\cdot) scavengers. Results are summarized in Figure-7.

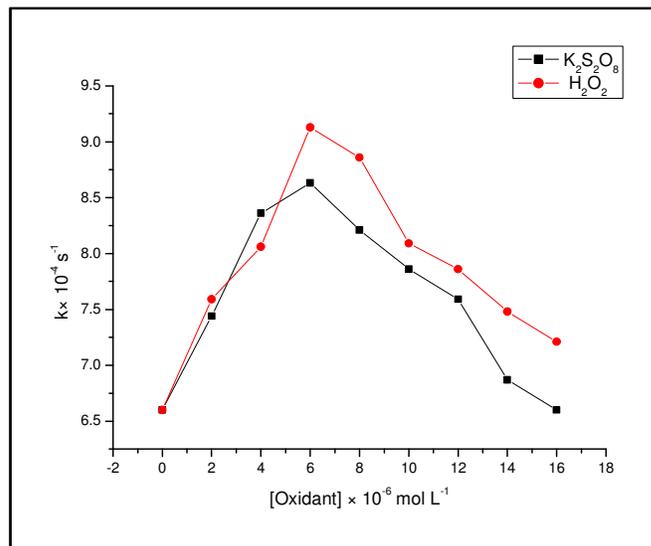


Figure-6: Effect of oxidants on photocatalytic degradation of Azure B. [Az B]= $4 \times 10^{-5} \text{ mol L}^{-1}$, BiOCl NPs=30mg/100ml pH=8.

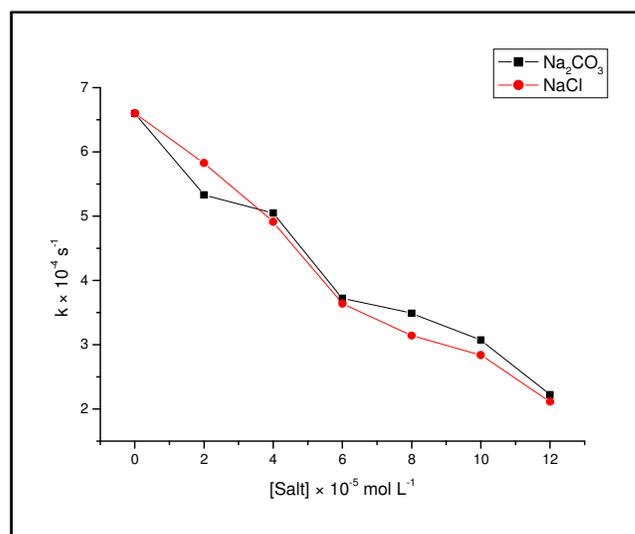


Figure-7: Effect of Varying Salt Concentration on Photocatalytic Degradation of Azure B. [Az B]= $4 \times 10^{-5} \text{ mol L}^{-1}$, BiOCl NPs = 30mg/100 ml

Effect of other photocatalysts: Photocatalytic degradation studies have been done with other photocatalysts as well. The order of photoactivity follows the order: flower like BiOCl > plate like BiOCl > Nano ZnO > Bulk BiOCl > Bulk ZnO. The degradation rate constant for flower-like nano BiOCl, plate-like nano BiOCl, nano ZnO, Bulk BiOCl and bulk ZnO was found to be $7.17 \times 10^{-4} \text{ S}^{-1}$, $6.60 \times 10^{-4} \text{ S}^{-1}$, $5.83 \times 10^{-4} \text{ S}^{-1}$, $4.68 \times 10^{-4} \text{ S}^{-1}$, $4.26 \times 10^{-4} \text{ S}^{-1}$ respectively¹⁴. Results are summarized in Figure-8.

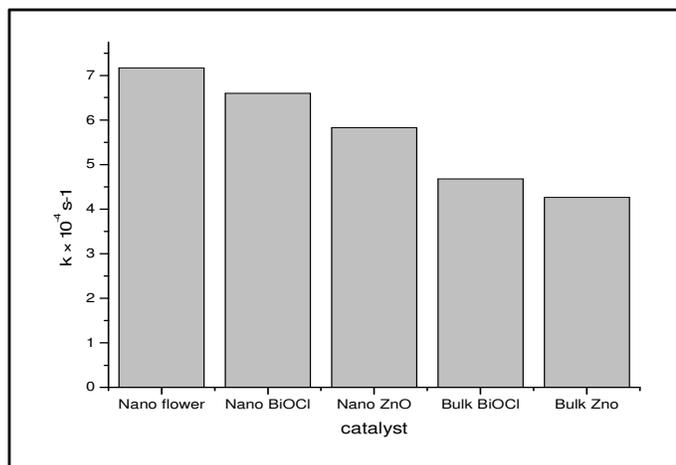


Figure-8: Effect of other catalysts on photocatalytic degradation of Azure B. $[Az B]=4 \times 10^{-5} \text{ mol L}^{-1}$, BiOCl NPs=30 mg/100ml.

Conclusion

The results announced that photocatalytic degradation is an efficient technique for the treatment of textile wastewaters. In this study azure B has been treated efficiently by this method. This study suggests that photocatalytic degradation is an efficient method for environmental treatment, the method can also be used for wastewaters other than textile effluents. BiOCl can be effectively used for wastewater remediation. Using solar light this method become more cost effective.

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