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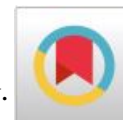
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EFFECT OF OPERATIONAL PARAMETERS ON PHOTOCATALYTIC DEGRADATION OF TOLUIDINE BLUE UTILIZING BiOCl NANOPLATES IN SOLAR LIGHT

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Abstract:

This work is devoted to the study of the effects of various operational parameters such as H_2O_2, $K_2S_2O_8$, NaCl, Na_2CO_3, $FeCl_3$, Fenton's reagent, O_2, N_2 purging, effect of other photocatalysts on the photocatalytic degradation of toluidine blue dye by as synthesized nano BiOCl under solar light in following conditions pH= 11, catalyst loading= 30 mg/100ml and initial dye concentration= 4×10^{-5} mol L^{-1}. Nano BiOCl was prepared by a simple hydrolysis method at room temperature and characterized by X-ray diffraction (XRD) and High Resolution Field Emission Scanning Microscope (HR FESEM). XRD pattern suggested that the synthesized nano BiOCl was highly pure and crystalline, SEM images depicted the platelike morphology of nano BiOCl. The average particle size of nano BiOCl was obtained as 45 nm. It was observed that these operational parameters greatly influenced the rate of photocatalytic degradation. The optimum concentrations of oxidants, salts, $FeCl_3$ and Fenton's reagent for photocatalysis of toluidine blue have also been obtained.

Keywords: *Photocatalysis; operational parameters; wastewater remediation; Solar light; BiOCl nanoplates; XRD; HR FESEM.*

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1. Introduction

Toxic organic wastes from various sectors like sewage, domestic waste, textile, pharmaceutical, and pesticide waste waters are among the greatest challenges to environmentalists. Konstantinou and Albanis stated that textile dyes and other dyestuffs from various industries constitute one of the largest classes of pollutants and represents a threat to environment [1, 2, 3, 4]. Therefore it is necessary to treat such effluents before combining to the fresh water stream because when this huge amount of dyestuffs enter in running water, leads to many ecological and health issues [5]. It is necessary to treat wastewaters from the source itself.

Recently, heterogeneous photocatalysis has attracted immense interest among the environmental scientists for wastewater remediation due to its simplicity, low cost and high degradation efficiency. Photocatalysis involves the adsorption of dye on semiconductor photocatalysts and absorption of radiation by semiconductor particles. The size and shape of semiconductor, and other operational parameters greatly affects the rate of photocatalytic degradation [6, 7]. Previous studies suggest that at an optimum pH, photocatalyst and dye concentration, the other operational parameters like oxidant concentration, salt concentration, dissolved oxygen and nitrogen also influence the photocatalytic degradation process. The study of the influence of metal ions like Fe^{3+} is important to study, as this are also present in the industrial effluents. It has been found that the addition of Fenton's reagent to the heterogeneous system has been proved as a promising technique to treat wastewater, thus its effect on the photocatalytic degradation of toluidine blue is also important to study. Literature supports that the presence of photocatalysts, with different shape size, morphology and chemical composition in the reaction mixture affect the degradation rate of the dyes differently [8,9].

This paper addresses the study of operational parameters like H_2O_2 and $K_2S_2O_8$ concentration $NaCl$ and Na_2CO_3 concentration, effect of $FeCl_3$ and Fenton's reagent, effect of purging N_2 and O_2, effect of other photocatalysts on the rate of photocatalytic degradation of toluidine blue utilizing nano BiOCl in solar light. For this study nano BiOCl has been prepared in laboratory and characterized through XRD and SEM techniques. To make the process environmentally momentous natural solar light has been used as radiation source for photocatalysis.

2. Materials and Methods

2.1. 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 used [10].

2.2. Measurement of Photocatalytic Activity

Dye 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 dye on the catalyst. For solar experiments, dye solution of 100 mL was taken in a double walled vessel with water circulation system, to this solution a known amount of catalyst was added and this complete setup was placed on a magnetic stirrer and illuminated in solar light of optimistic intensity, in clear weather. Water circulation system maintains the temperature and controls evaporation of reaction mixture. To measure the concentration changes due to dye degradation, the 3 ml aliquot was periodically withdrawn from the reaction mixture and centrifuged at 3500 rpm to remove BiOCl particles. The spectrophotometer 166 of Systronics was used for measuring absorbance at different time intervals. The light intensity was measured by a Lux meter (Lutron LX-101). The pH of the solution was constantly been monitored using a digital pH meter. pH was adjusted by the addition of either NaOH or H_2SO_4.

3.   Results and Discussions

3.1. Structural Studies

Fig. 1 shows the XRD pattern of as prepared nano BiOCl sample and it suggested that nano BiOCl was highly pure and well- crystallized. The average particle size of the sample has been calculated by applying Debye- scherrer formula[8], and it was found to be 45 nm [11, 12]**.** Fig. 2 shows the SEM image of the as-prepared nano BiOCl. It can be clearly seen that the overall morphology of BiOCl is composed of many plates with smooth surface.
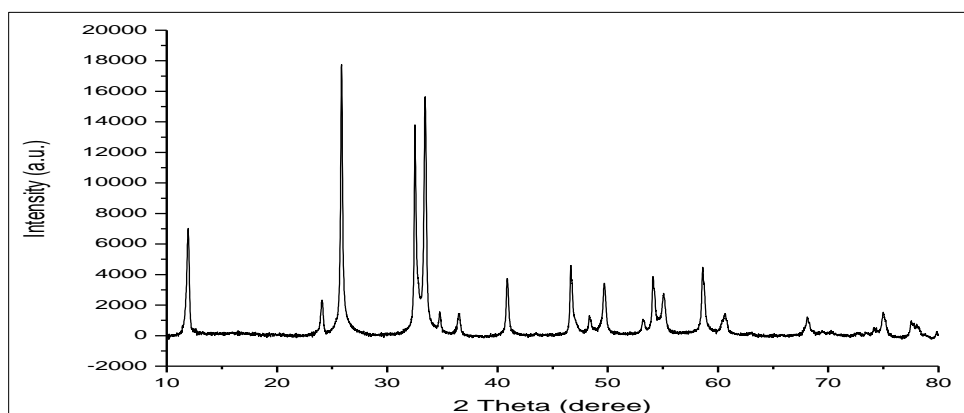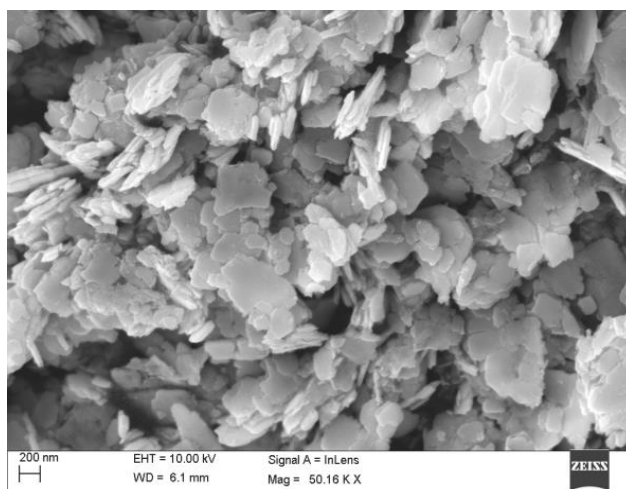

Figure 1: XRD Pattern of Nano BiOCl

Figure 2: SEM Image of Nano BiOCl

3.2. Photocatalytic Studies

Effect of varying H_2O_2 Concentration
The presence of H_2O_2 in reaction mixture plays an important role in influencing rate of photocatalytic degradation. The decomposition of H_2O_2 generates extremely reactive hydroxyl radicals which enhances the rate of photocatalytic degradation. In this study, the H_2O_2

concentration was varied from 2.0×10^{-6} molL^{-1} to 16.0×10^{-6} mol L^{-1} with the increase in H_2O_2 concentration from 2.0×10^{-6} molL^{-1} to 6.0×10^{-6} mol L^{-1} the rate constant increased form 6.41×10^{-4} S^{-1} to 9.02×10^{-4} S^{-1} and was found maximum at 6.0×10^{-6} mol L^{-1} of 6.0×10^{-6} mol L^{-1}. An increase in H_2O_2 concentration to a certain level increases the rate constant while further increase in H_2O_2 concentration results into decrease in the decolorization rate of the toluidine blue dye. This may be accredited to the reason that he addition of H_2O_2 to a certain level increased the production of hydroxyl radicals, but the additional amount led to reduce the amounts of photoholes and hydroxyl radicals [13]. Fig 3 shows the effect of H_2O_2 on photocatalytic degradation of toluidine blue.
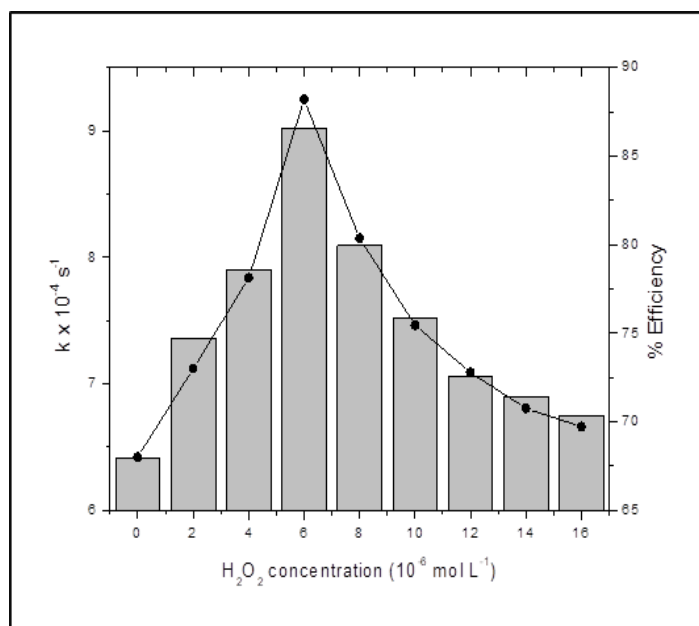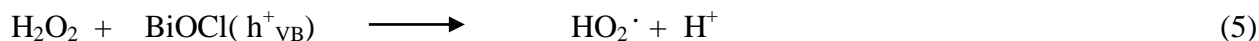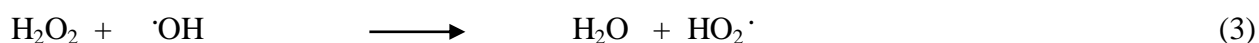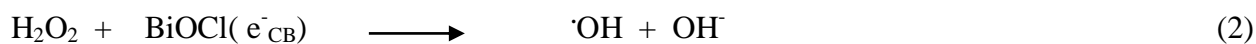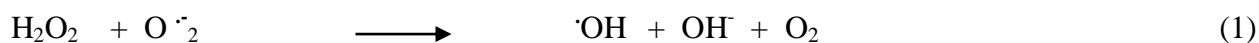

Figure 3: Effect of H_2O_2 Concentration on Photocatalytic Degradation of Toluidine Blue
Effect of H_2O_2: [TB] = 4×10^{-5} mol L^{-1}, pH = 11, BiOCl NPs = 30 mg/100 ml

$$H_2O_2 \ + \ O_2^{\cdot -} \longrightarrow \ ^{\cdot}OH \ + \ OH^- \ + \ O_2 \tag{1}$$

$$H_2O_2 \ + \ BiOCl(\,e^-_{CB}) \longrightarrow \ ^{\cdot}OH \ + \ OH^- \tag{2}$$

$$H_2O_2 \ + \ ^{\cdot}OH \longrightarrow \ H_2O \ + \ HO_2^{\cdot} \tag{3}$$

$$HO_2^{\cdot} \ + \ ^{\cdot}OH \longrightarrow \ H_2O \ + \ O_2 \tag{4}$$

$$H_2O_2 \ + \ BiOCl(\,h^+_{VB}) \longrightarrow \ HO_2^{\cdot} \ + \ H^+ \tag{5}$$

Effect of Varying $K_2S_2O_8$ Concentration
The degradation rate of toluidine blue was found to be maximal at 6.0×10^{-1} mol L^{-1} of $K_2S_2O_8$ with rate constant 8.67×10^{-4} s^{-1}. The addition of persulphate led to form sulphate radical anion by trapping the photogenerated electrons. $S_2O_8^{2-}$ can generate sulphate radical anion (SO4$^{\cdot-}$) both thermally and photocatalytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes. The summarized results are presented in Fig. 4.
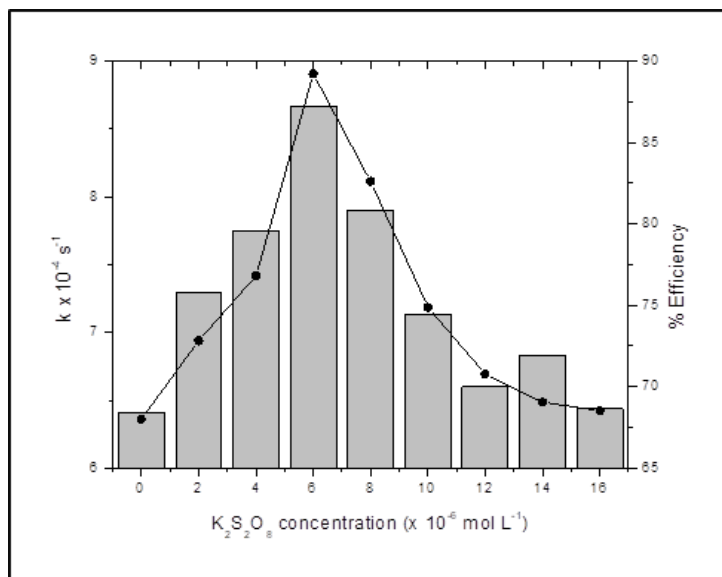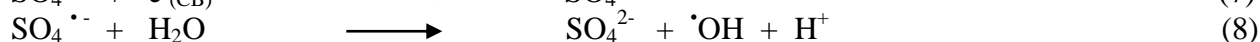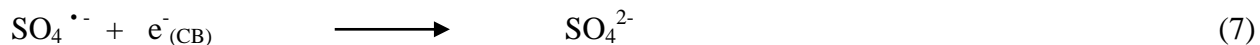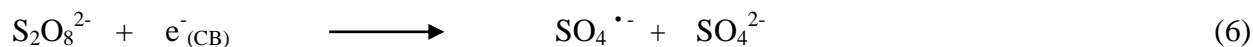
Figure 4: Effect of on $K_2S_2O_8$ Concentration
Effect of $K_2S_2O_8$: [TB] = 4×10^{-5} mol L^{-1}, pH = 11, BiOCl NPs = 30 mg/100 ml

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

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

$$SO_4^{\bullet-} + H_2O \longrightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \tag{8}$$

While, further increased concentration, resulted into a fall into rate, because after a certain optimum concentration, SO_4^{2-} produced may adsorbed on the photocatalyst surface and exert a competitive action for the oxidative species [14], which is explained in the equations below.

$$SO_4^{2-} + h^+ \longrightarrow SO_4^{\bullet-} \tag{9}$$

$$SO_4^{2-} + {}^{\bullet}OH \longrightarrow SO_4^{\bullet-} + OH^- \tag{10}$$
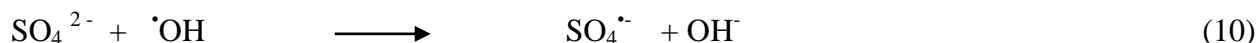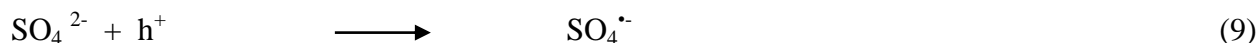
Effect of Varying Na$_2$CO$_3$ Concentration
Na$_2$CO$_3$ is mainly used to adjust the pH of dye bath and hence an important element of dyeing process. Since Na$_2$CO$_3$ is also present in textile effluents so it is important to study its effect on photocatalytic degradation of toluidine blue. The concentration of Na$_2$CO$_3$ was varied from from 2.0×10^{-5} mol L^{-1} to $12.0 \times 10^{-5.}$ mol L^{-1} in reaction mixture and with the increase in Na$_2$CO$_3$ concentration a gradual decrease in rate constant was found from 5.52×10^{-4} s^{-1} to 2.18×10^{-4} s^{-1}, which may be explained by the following equations [15] and results are presented in Fig. 5.
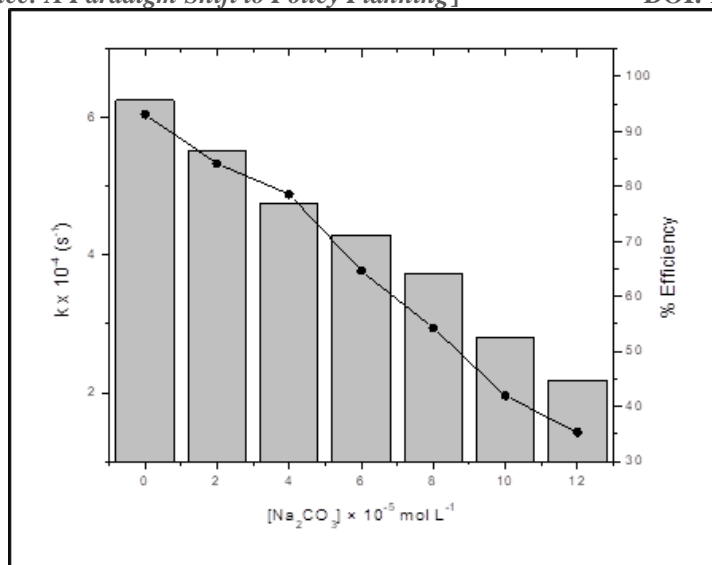
Figure 5: Effect of Na_2CO_3 Concentration
Effect of Na2CO3: [TB] = $4 \times 10\text{-}5$mol L-1, pH = 11, BiOCl NPs = 30 mg/100 ml

$$CO_3^{2-} + {}^{\bullet}OH \longrightarrow CO_3^{\bullet-} + OH^- \qquad (11)$$

$$HCO_3^- + {}^{\bullet}OH \longrightarrow H_2O + CO_3^{\bullet-} \qquad (12)$$
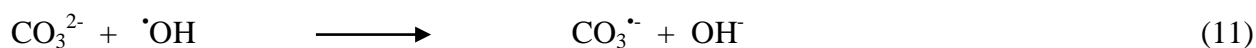
Effect of Varying NaCl Concentration
Sodium chloride is also a component of waste effluents from textile industries, so effect of NaCl is important to study for photocatalytic degradation of toluidine blue. The effect of interfering Cl^- ion for photocatalysis has been studied and it was found that rate constant was continuously decreased from $5.71 \times 10^{-4} S^{-1}$ to $1.99 \times 10^{-4} S^{-1}$ with increase in concentration of NaCl from 2.0×10^{-5} mol L^{-1} to $12.0 \times 10^{-5.}$ mol L^{-1}. The summarized results are shown in Fig. 6. This is because of hydroxyl radical scavenging properties of Cl^- ion, as presented in the equations below [15].
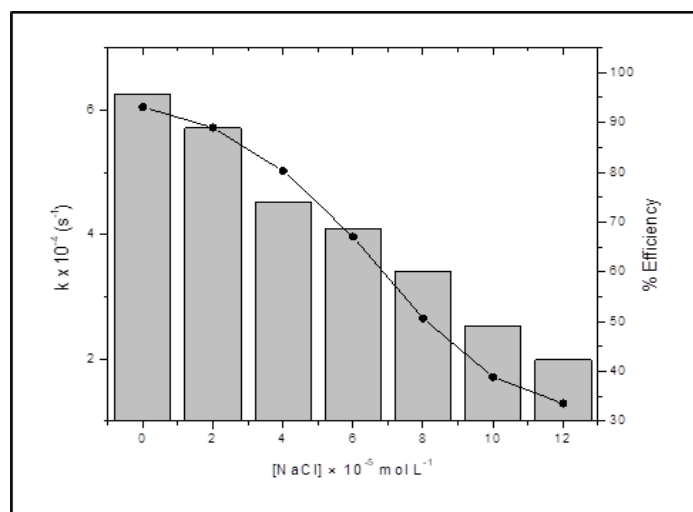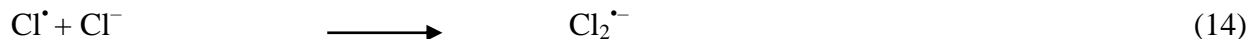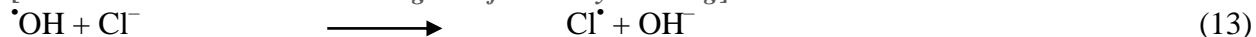

Figure 6: Effect of NaCl Concentration
Effect of NaCl: [TB] = 4×10^{-5}mol L^{-1}, pH = 11, BiOCl NPs = 30 mg/100 ml

$$^{\bullet}OH + Cl^{-} \longrightarrow Cl^{\bullet} + OH^{-} \tag{13}$$

$$Cl^{\bullet} + Cl^{-} \longrightarrow Cl_2^{\bullet -} \tag{14}$$

Effect of FeCl₃

The previous studies suggested that Fe^{3+} ions facilitates the photocatalytic degradation of dyes, thus it is significant to study the effect of this ions. In this case, the $FeCl_3$ concentration has been varied from 2.0×10^{-5} mol L^{-1} to 12.0×10^{-5} mol L^{-1}, Fig. 7. The incorporation of $FeCl_3$ in the reaction mixture increased the rate constant from 7.36×10^{-4} s^{-1} to 8.78×10^{-4} s^{-1} upto the concentration 8.0×10^{-5} mol L^{-1}. The $Fe^{2+\bullet}OH$ species which is formed as a consequence of photoactivation of surface adsorbed complex ion ($Fe^{3+}OH^{-}$). The resulted species introduces electrons into the conduction band of nano BiOCl. The progression in rate is significant due to the reduced recombination because of rapid scavenging of conduction band electrons by molecular oxygen and formation of superoxide and hydroperoxide radicals [16]. In contrast, above optimal concentration, the rate constant decreased from 7.36×10^{-4} s^{-1} to 6.67×10^{-4} s^{-1} on the addition of FeCl3 from 10.0×10^{-5} mol L^{-1} to 12.0×10^{-5} mol L^{-1} due to the $Fe(OH)^{2+}$ ion which is expected to exist as the main monomeric iron (III)-hydroxy complex, which is also a major light absorbing species.
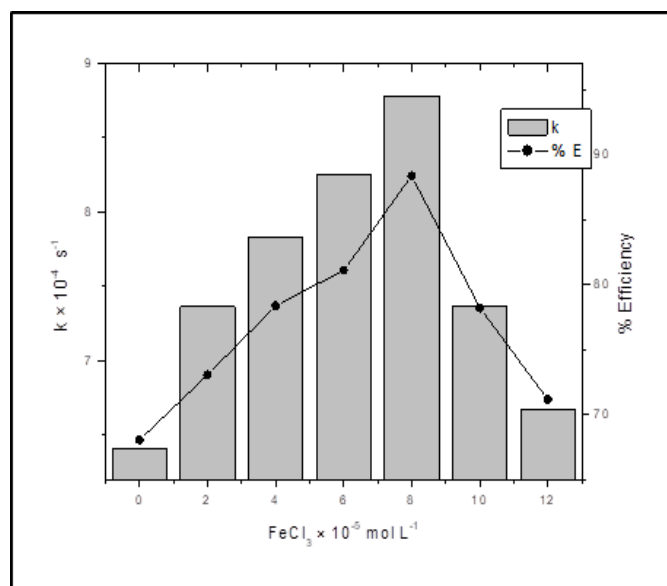

Figure 7: Effect of FeCl₃ Concentration
Effect of FeCl₃: [TB] = 4×10^{-5} mol L^{-1}, pH = 11, BiOCl NPs = 30 mg/100 ml

$$Fe^{3+} + e^{-}_{CB} \longrightarrow Fe^{2+} \tag{15}$$
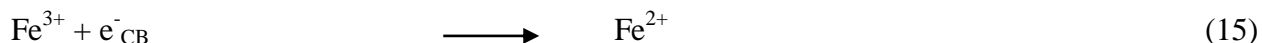
At the same time, there exist the following reactions:

$$Fe^{3+} + HO^{\bullet}_{2} + H^{+} \longrightarrow Fe^{2+} + H_2O_2 \tag{16}$$

$$Fe^{2+} + H_2O_2 + H^{+} \longrightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \tag{17}$$

The assistance of Fe^{3+} in toluidine blue degradation may be explained by the following reactions.

$$TB \ + \ h\nu_{solar} \longrightarrow \ _1TB^* \ or \ _3TB^* \tag{18}$$

$$_1TB^* \ or \ _3TB^* + BiOCl\,(\,Fe^{3+}OH^-\,) \longrightarrow \ BiOCl\,(\,Fe^{2+}OH^{\bullet}\,) + TB^{+\cdot} \tag{19}$$

$$BiOCl\,(\,Fe^{2+}OH^{\bullet}\,) + \ H_2O_2 \ \xrightarrow{\ h\nu\ } \ BiOCl(\,e^-_{CB}) \ + BiOCl\,(\,Fe^{3+}OH^-\,) \tag{20}$$

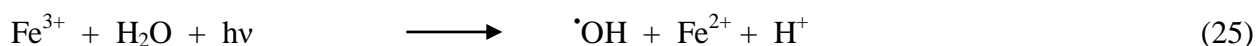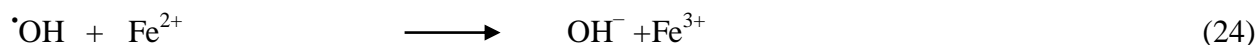$$BiOCl(\,e^-_{CB}) \ + \ O_2 \longrightarrow \ O_2^{\cdot -} \xrightarrow{\ H^+\ } \ HO^{\bullet} \tag{21}$$

$$TB \ / \ TB^{+\cdot} + OH^{\bullet} \ / \ O_2^{\cdot -} \ / \ HO^{\bullet}_2 \longrightarrow \ Degradation \ products \tag{22}$$
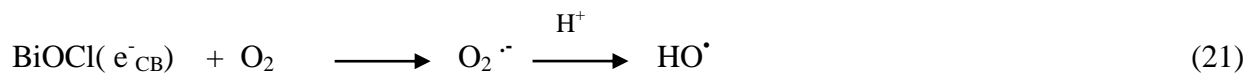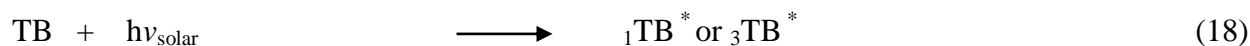
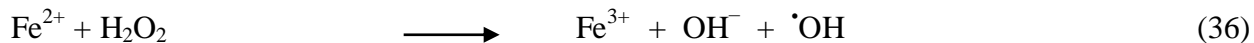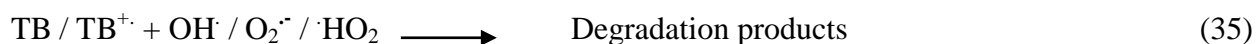**Effect of Fenton's Reagent (Fe^{3+}/H_2O_2)**
Treatment by Fenton's reagent is a cheaper and safe technique. It generates $^{\bullet}OH$ by reacting H_2O_2 and iron (II) salts. Fenton and photo- Fenton systems have demonstrated very good results even for complete mineralization of dyes [17]. In this work, the efficiency of fenton systems has been studied on decolorization of toluidine blue using nano BiOCl and solar light; the comparative results are achieved for the same reactions without nano BiOCl.
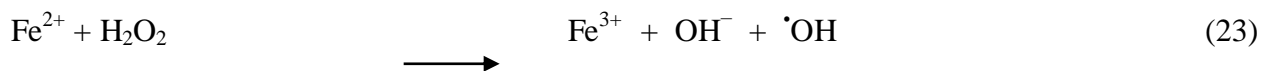
$$Fe^{2+} + H_2O_2 \longrightarrow \ Fe^{3+} \ + \ OH^- \ + \ ^{\bullet}OH \tag{23}$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+}:

$$^{\bullet}OH \ + \ Fe^{2+} \longrightarrow \ OH^- + Fe^{3+} \tag{24}$$

$$Fe^{3+} \ + \ H_2O \ + \ h\nu \longrightarrow \ ^{\bullet}OH \ + \ Fe^{2+} + \ H^+ \tag{25}$$

$$TB \ + \ h\nu_{Solar} \longrightarrow \ _1TB^* \ or \ _3TB^* \tag{26}$$

$$_1TB^* \ or \ TB^* + BiOCl(Fe^{3+}OH^-) \longrightarrow \ BiOCl\,(Fe^{2+}OH^-) + TB^{+\cdot} \tag{27}$$

$$BiOCl\,(\,Fe^{2+}OH^-\,) + \ H_2O_2 \longrightarrow \ BiOCl\,(\,Fe^{3+}OH^-\,) + OH^- + O \tag{28}$$

$$BiOCl\,(\,Fe^{3+}OH^-\,) \ + \ H_2O_2 \longrightarrow \ BiOCl\,(\,Fe^{2+}OH^-\,) \ + \ ^{\bullet}HO_2 + H^+ \tag{29}$$

$$BiOCl\,(\,Fe^{2+}OH^-\,) \longrightarrow \ BiOCl\,(Fe^{3+}OH^-) \ + \ BiOCl\,(\,e^-_{CB}) \tag{30}$$

$$BiOCl\,(\,e^-_{CB}) \ + \ O_2 \longrightarrow \ O^{\cdot -}_2 \xrightarrow{\ H^+\ } HO_2 \tag{31}$$

$$H_2O_2 \ + \ O^{\cdot -}_2 \longrightarrow \ ^{\bullet}OH \ + \ OH^- \ + \ O_2 \tag{32}$$

$$H_2O_2 \ + \ BiOCl(\,e^-_{CB}) \longrightarrow \ ^{\bullet}OH \ + \ OH^- \tag{33}$$

$$\cdot OH \ + \ H_2O_2 \longrightarrow H_2O \ + \ \cdot HO_2 \tag{34}$$

$$TB \ / \ TB^{+\cdot} + OH^{\cdot} \ / \ O_2^{\cdot -} \ / \ \cdot HO_2 \longrightarrow \text{Degradation products} \tag{35}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} \ + \ OH^- \ + \ \cdot OH \tag{36}$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+}:

$$\cdot OH \ + \ Fe^{2+} \longrightarrow OH^- + Fe^{3+} \tag{37}$$

$$Fe^{3+} \ + \ H_2O \ + \ h\nu \longrightarrow \cdot OH \ + \ Fe^{2+} + \ H^+ \tag{38}$$
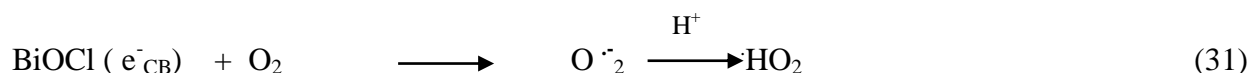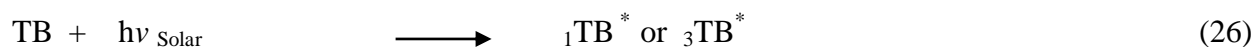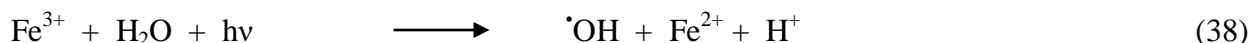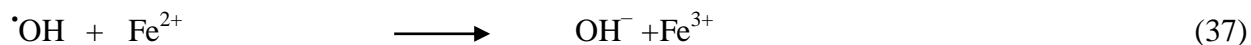
The results are specified in Fig. 8. For Fe^{3+}/ H_2O_2 system with nano BiOCl in solar light, the degradation rate constant has a value 7.4×10^{-4} s^{-1} on addition of Fe^{3+}: H_2O_2 in molar ratio 1:2, on increasing molar ratios between 1:2 and 5:6, the maximum decolorization of toluidine blue was attained at 3:4 with the degradation rate constant 9.17×10^{-4} s^{-1} which again began to decline by increasing molar ratios further upto 5:6, where the rate constant was 7.83×10^{-4} s^{-1}. In a system Fe^{3+}/ H_2O_2 and solar light, without BiOCl, the rate of toluidine blue decolorization was found to increase gradually from 3.14×10^{-4} s^{-1} to 4.95×10^{-4} s^{-1} with an increase in molar ratio of Fe^{3+}/ H_2O_2 from 1:2 to 5:6.
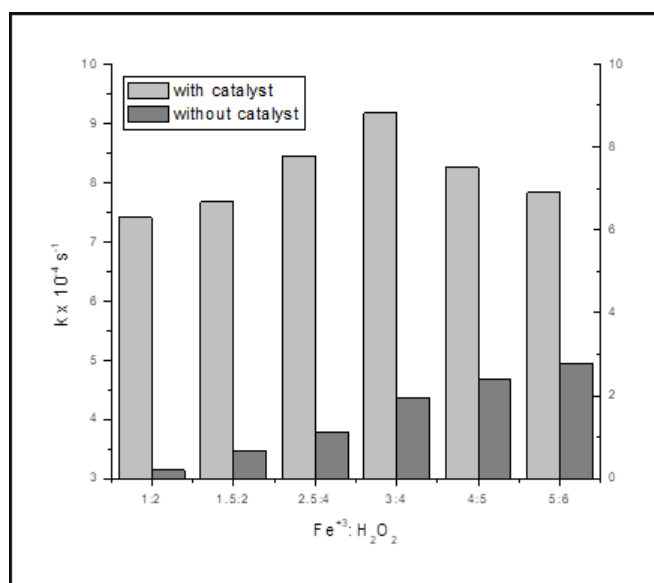

Figure 8: Effect of Fenton's Reagent

Effect of Fenton's Reagent: $[TB] = 4 \times 10^{-5} mol \ L^{-1}$, pH = 11, BiOCl NPs = 30 mg/100 ml

Effect of N_2 and O_2 Purging

In the presence of N_2, the degradation rate severely retarded by blocking the initial step of photocatalysis, where the photogenerated e^- and h^+ starts the photocatalytic degrareaction. As the reactions of conduction Band (CB) electrons were obstructed by N_2 purging, the valence Band (VB) holes were involved in the recombination process which finally reduced the photocatalysis.

Fig. 4.49 shows the effect of N_2 purging on phoocatalytic degradation of toluidine blue [18]. The presence of oxygen in reaction mixture plays a major role. By accepting the electron, oxygen molecule prevents electron-hole recombination. To determine the effect of dissolved oxygen on photocatalytic degradation of dye, the reaction mixture was purged with O_2 [19]. The results presented in Fig. 9 shows that the photodegradation rate was rigorously increased by purging O_2 in reaction mixture. The rate constant was increased from 6.25×10^{-4} s^{-1} to 6.41×10^{-4} s^{-1}.
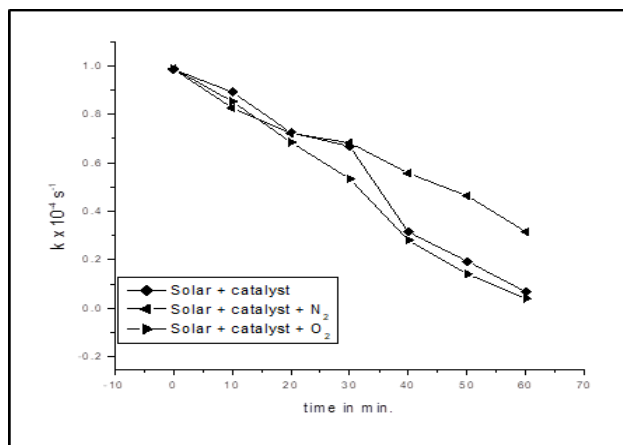

Figure 9: Decolorization of TB in Different Photocatalytic Systems
[TB] = 4×10^{-5} mol L^{-1}, pH = 11, BiOCl NPs = 30 mg/100 ml

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. Generally, semiconductors having large band gaps are good photocatalysts. It has already been reported that semiconductors such as ZnO, and BiOCl have band gaps larger than 3 eV show strong photocatalytic activity. The degradation rate constant for flower-like BiOCl, nano plate-like BiOCl, nano ZnO, Bulk BiOCl and bulk ZnO was found to be 7.06×10^{-4} s^{-1}, 6.25×10^{-4} s^{-1}, 6.02×10^{-4} s^{-1}, 5.75×10^{-4} s^{-1}, 5.36×10^{-4} s^{-1} respectively [20]. The graphical results have been presented in Fig 10.
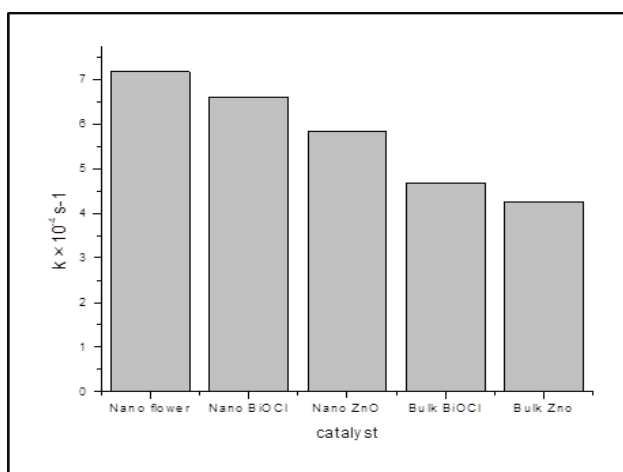

Figure 10: Effect of Other Catalysts
Effect of Other Catalysts: [TB] = 4×10^{-5} mol L^{-1}, pH = 11

4. Conclusions

The results suggested that toluidine blue dye can be efficiently degraded by as-prepared nano BiOCl in the presence of solar light, and operational parameters like oxidant's concentration, salt concentration, N_2, O_2 purging and other photocatalysts greatly alters the rate of potocatalytic degradation. The optimum oxidants concentration was found as 6.0×10^{-6} mol L^{-1} for both H_2O_2 and $K_2S_2O_8$. With increase in NaCl and Na_2CO_3 concentration rate of photocatalytic degradation was decreased for both. Dissolved O_2 increased the rate constant while dissolved N_2 decreased the rate constant. Different photocatalysts showed variable rate constants for same reaction conditions of toluidine blue degradation, the maximum photocatalytic degradation was obtained for flower like nano BiOCl.

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