Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.792131

51 (2013) 6572–6579
October

Taylor & Francis
Taylor & Francis Group

Solar photocatalytic degradation of Naphthol Blue Black

B. Krishnakumar, M. Swaminathan*

Photocatalysis Laboratory, Department of Chemistry, Annamalai University, Annamalainagar, TamilNadu 608 002, India
Tel./Fax: +91 4144 220572; email: chemres50@gmail.com

Received 18 January 2012; Accepted 30 January 2013

ABSTRACT

The solar photocatalytic activity of AgBr–ZnO was investigated for the degradation of Naphthol Blue Black (NBB) in aqueous solution. Removal of azo dyes from wastewater is a challenging process, since these dyes are nonbiodegradable. Presence of a visible light absorbing component, AgBr, makes this catalyst solar active. AgBr–ZnO is found to be more efficient than commercial ZnO and prepared ZnO for solar degradation of NBB azo dye. The effects of operational parameters, such as the amount of photocatalyst, dye concentration, and initial pH on photo mineralization have been analyzed. The optimum pH and catalyst amount for the efficient removal of dye are found to be 11 and $3\,g\,L^{-1}$, respectively. Increase of initial dye concentration decreased the degradation rate. The mineralization of NBB has also been confirmed by chemical oxygen demand measurements. The higher photocatalytic activity of AgBr–ZnO towards NBB degradation in solar light is explained by a mechanism involving band energy levels of AgBr and ZnO. The catalyst was found to be reusable.

Keywords: AgBr loaded ZnO; Photocatalysis; Solar light; Naphthol Blue Black; Reusability

1. Introduction

Semiconductor oxides are acknowledged as the most important photocatalysts, since they have many advantages to other materials, such as stability, high activity, and low cost. The photocatalytic degradation of organic pollutants in water and air using TiO_2 and ZnO has been the focus of research due to their unique ability in the environmental detoxification [1–9]. ZnO, with a band gap = 3.2 eV, has become promising in the past few years because of its distinctive optoelectronic, photocatalytic, and photochemical properties [10,11]. In some cases, ZnO has revealed better photocatalytic activity than TiO_2 [12–17].

In photocatalysis, use of ultraviolet light for the treatment of huge quantity of industrial effluents is not feasible or economical. In the countries where ample amount of sunlight is available, photocatalysis involving sunlight will be a more economical and eco-friendly process. Therefore, there is a need of an effective photocatalyst which can degrade organic pollutants under sunlight or visible light irradiation. In order to enhance the solar activity of semiconductor oxides, many efforts have been taken to modify ZnO/TiO_2 by loading some metals/nonmetals/anions [18–24]. Recently, modification of the semiconductors with metal halides such as AgBr and AgCl has been found to enhance the visible light activity and certain other properties, such as stability and mesoporosity [25,26]. This makes semiconductor photocatalysis as an efficient chemical method of solar energy utilization. Azo dyes are the most important class of synthetic organic dyes used in the textile industry and so they

---

*Corresponding author.

are common industrial pollutants [27,28]. More than half of the global production of synthetic textile dyes are compounds having azo chromophore (–N=N–) in their molecular structures. During dyeing process 15% of the dye is lost and released in the effluent. These colored compounds in textile effluents should be removed before discharging into water bodies as they cause toxic effects on the ecosystem. Naphthol Blue Black (NBB) is one of the azo dye used widely in the dyeing industries. Earlier we reported the preparation and characterization of AgBr–ZnO and its catalytic activity in the dye degradation using UV light [29]. Characterization study revealed the higher visible light absorption of AgBr–ZnO than ZnO. Hence, present work focuses on solar photocatalytic activity of AgBr loaded ZnO for the degradation of NBB.

2. Experimental

2.1. Materials

The commercial azo dye NBB obtained from Aldrich was used as such. The chemical structure and absorption maxima are given in Fig. 1. Oxalic acid (99%) and zinc nitrate hexahydrate (99%) were obtained from Himedia chemicals. $AgNO_3$ and NaBr were obtained from sigma Aldrich. The double distilled water was used to prepare the experimental solutions. The pH of the solutions before irradiation was adjusted using H_2SO_4 or NaOH. $K_2Cr_2O_7$ (s.d.fine), Ag_2SO_4 (s.d.fine), ferroin indicator (s.d.fine), $HgSO_4$, and $FeSO_4{\cdot}7H_2O$ (Qualigens) were used as received. AgBr–ZnO was prepared by the coprecipitation of Zinc oxalate and AgBr, followed by calcination by a reported procedure [29].

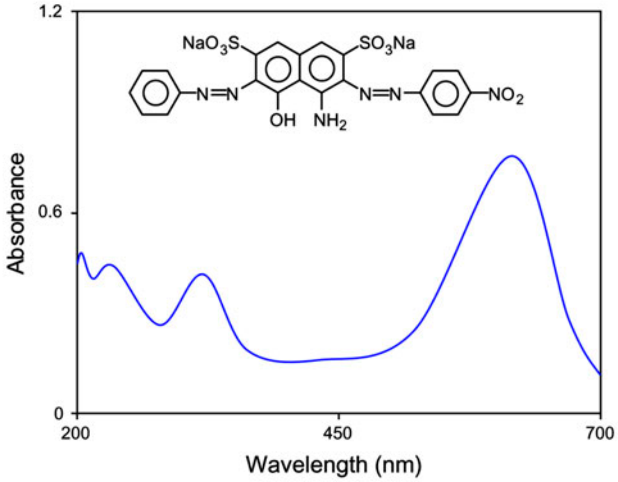


Fig. 1. The chemical structure and absorption maxima of NBB.

2.2. Characteristics of AgBr–ZnO

Characterization of 44.4 wt.% AgBr–ZnO by Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy, diffuse reflectance spectra, photoluminescence spectra, cyclic voltammetry, and Brunauer Emmett and Teller (BET) surface area measurements and its photocatalytic activity for the degradation of Acid Black 1 (AB 1) by UV light were reported earlier [29]. XRD analysis of AgBr–ZnO reveals that there are five peaks with 2θ values of 31.06°, 44.44°, 55.14°, 64.58°, and 73.62° corresponding to AgBr. The band gap of bare ZnO and AgBr–ZnO are found to be 3.0 and 2.7 eV, respectively. XPS analysis reveals that Ag in the catalyst is present in the form of Ag^+. Crystalline size of AgBr–ZnO is found to be 51.3 nm which is larger than the size of prepared ZnO (30.1 nm). Morphology of AgBr–ZnO has been further analyzed by field emission scanning electron microscope (FE-SEM) and High-resolution transmission electron microscope (HR-TEM) images.

Fig. 2(a) and (b) shows FE-SEM images of AgBr–ZnO with 200 and 100 k magnifications. AgBr–ZnO exhibits a hexagonal structure at higher magnification of 200 k (Fig. 2(a)). AgBr is seen as small unshaped particles in both magnifications (Fig. 2(a) and (b)). HR-TEM images of AgBr–ZnO at different magnifications are shown in Fig. 3(a–c). ZnO particles are in the range from 20 to 100 nm. The hexagonal structure of ZnO present in AgBr–ZnO is also confirmed by HR-TEM images. It can be seen that AgBr nanoparticles (indicated by arrow marks in Fig. 3) are well dispersed on the surface of ZnO.

2.3. Irradiation procedure

All photocatalytic experiments were carried out under similar conditions on sunny days between 11 am and 2 pm. An open borosilicate glass tube of 50 mL capacity, 40 cm height and 12.6 mm diameter was used as the reaction vessel. Fifty milliliters of NBB (2×10^{-4} M) with the appropriate amount of catalyst was irradiated in the open air and continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. A time lag of 30 min was provided prior to illumination and the adsorption equilibrium was attained within 30 min. During the illumination time no volatility of the

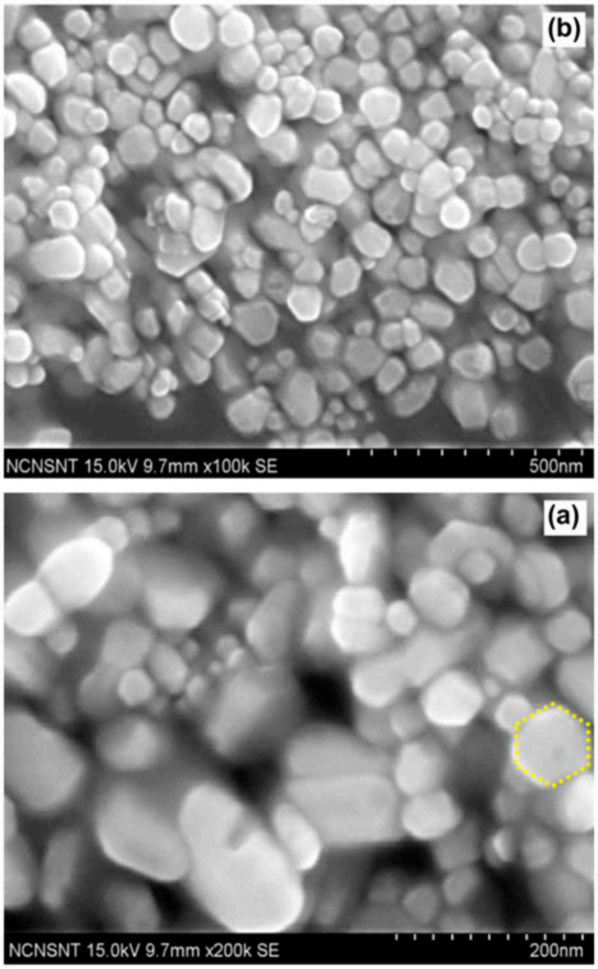


Fig. 2. FE-SEM images of (a) AgBr–ZnO (×200 k) and (b) AgBr–ZnO (×100 k).

solvent was observed. At specific time intervals, 2–3 mL of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the sample was suitably diluted and the concentration of dye was determined by measuring its absorbance at 306 nm, using a calibration graph. Each experiment was repeated thrice and the average value was taken as final concentration of the solution at time “*t*”. In the case of additives, the same procedure was followed. To find out the influence of additives on the degradation, experiments with the catalyst containing 0.1 M of anions/cations or 0.01 M oxidants were carried out.

2.4. Solar light intensity measurements

Solar light intensity was measured using LT Lutron LX-10/A digital Lux meter for every 30 min and the average light intensity over the duration of each experiment was calculated. The solar intensity (1,250 × 100 ± 100 Lux) was nearly constant during the experiments.

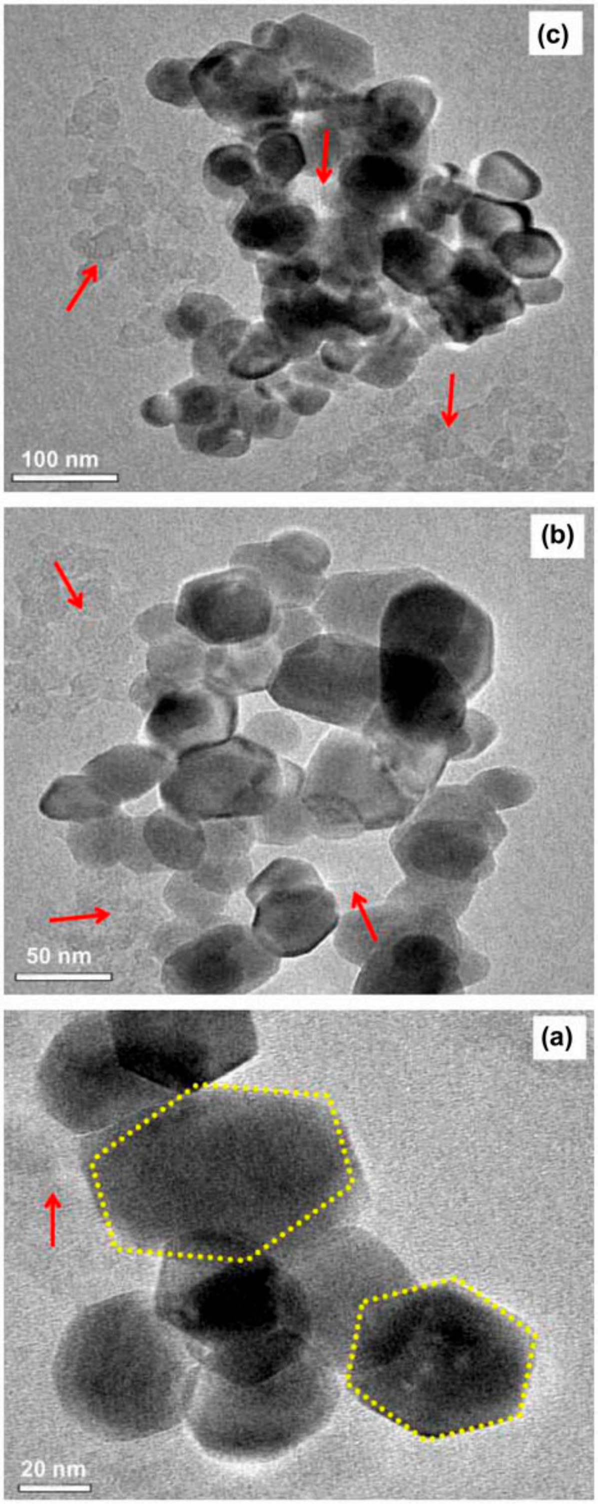


Fig. 3. HR-TEM images of AgBr–ZnOAgBr–ZnO; (a) 20 nm (b) 50 nm and (c) 100 nm (→ AgBr).

2.5. Analytical methods

UV absorbance measurements for the determination of dye concentration were done with Hitachi-U-2001 spectrometer. FE-SEM images were obtained using a JEOLJSM-6701F FE-SEM. HR-TEM images were taken using a JEOL JEML-3010 with the working voltage of 300 keV. chemical oxygen demand (COD) measurements were done according to standard methods [15].

3. Results and discussion

3.1. Photodegradability of NBB

The photocatalytic activities of the AgBr–ZnO catalysts with 25.7, 34.1, 40.9, 44.4, and 50.9 wt.% of AgBr loading were evaluated by the degradation of NBB under solar light. Catalyst loaded with 44.4 wt.% of AgBr shows a highest percentage of degradation for NBB (Table 1). Further increase of AgBr content decreased the percentage of degradation. Hence, 44.4 wt.% of AgBr is found to be the optimum concentration of AgBr in ZnO.

Experiments with 44.4 wt.% AgBr–ZnO, bare ZnO, and commercial ZnO for NBB degradations were carried out. Fig. 4 shows the percentage of NBB remaining during degradation process with different catalysts. It has been observed that almost complete degradation of the pollutants takes place at the time of 90 min with AgBr–ZnO under solar light. This was contrasted with 6% decrease in dye concentration that occurs for the same experiment performed with AgBr–ZnO in the absence of solar light and this may be due to the adsorption of the dye on the surface of the catalyst. Negligible degradation (0.2%) was observed, when the reaction was allowed to occur in the presence of solar light without any catalyst. These observations reveal that solar light and photocatalyst are needed for effective destruction of NBB. When the photocatalyst bare ZnO and commercial ZnO were used under same conditions only 51.8 and 84.8% degradations occurred, respectively. This shows that solar/AgBr–ZnO process is more efficient in NBB degradation than solar/bare (prepared) ZnO and solar/Commercial ZnO processes. Since, the degradation was effective with AgBr–ZnO, the influence of operational parameters had been carried out to find out the optimum conditions.

Table 1
Effect of different wt.% AgBr on ZnO for the degradation of NBB under solar light

Wt.% of AgBr	% of degradation
25.7	38.1
34.1	43.5
40.9	47.3
44.4	50.8
50.9	42.1

Notes: [NBB] = 2×10^{-4} M, catalyst suspended = 2 g L^{-1}, pH = 11, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min.

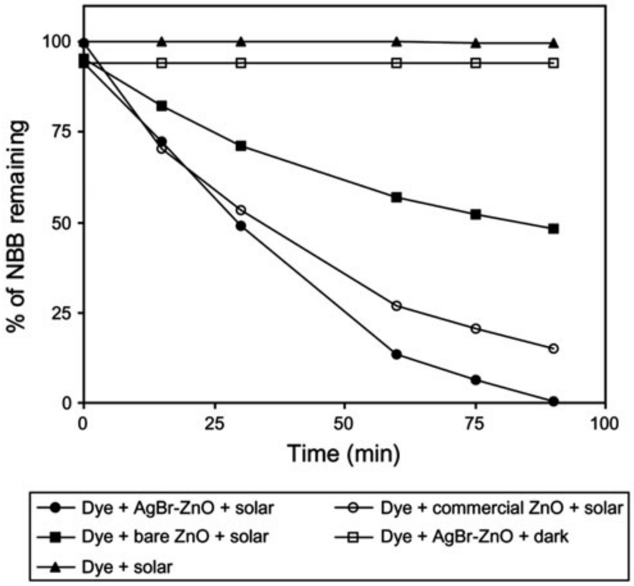


Fig. 4. Photodegradability of NBB: [NBB] = 2×10^{-4} M, pH = 11, catalyst suspended = 2 g L^{-1}, airflow rate = 8.1 mL s^{-1}.

The photocatalytic degradation of NBB dye with AgBr–ZnO obeys pseudo-first-order kinetics. At low initial dye concentration the rate expression is given by

$$d[C]/dt = k'[C] \quad (1)$$

where k' is the pseudo-first-order rate constant. The dye is adsorbed onto the AgBr–ZnO surface and the adsorption/desorption equilibrium is reached in 30 min. After adsorption, the equilibrium concentration of the dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integration of Eq. (1) (with the limit of $C = C_0$ at $t = 0$ with C_0 being the equilibrium concentration of the bulk solution) gives Eq. (2),

$$\ln(C_0/C) = k't \quad (2)$$

where C_0 is the equilibrium concentration of dye and C is the concentration at time t. Rate constant "k" was determined from the plot of ln (C_0/C) vs t.

3.2. Effect of operational parameters

3.2.1. Effect of solution pH

The effect of pH on the photodegradation of NBB was studied in the pH range 3–12 for AgBr–ZnO and bare ZnO (Fig. 5). It is observed that the raise in pH from 3 increases the degradation rate constant of NBB

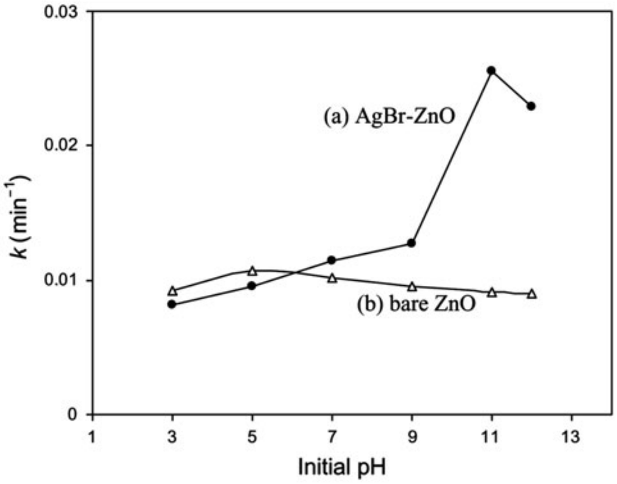


Fig. 5. Effect of solution pH: [NBB] = 2×10^{-4} M, catalyst suspended = 2 g L^{-1}, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min.

up to 11 and then decreases. The optimum pH for efficient NBB removal on AgBr–ZnO is 11 which is less than the optimum pH 12, observed with UV-A light ($I_{UV} = 1.381 \times 10^{-6}$ einstein $L^{-1} s^{-1}$) [29]. ZnO can react with acids to produce the corresponding salt at low acidic pH values. At high pH value AgBr–ZnO surface is negatively charged by means of adsorbed OH^- ions. The presence of large quantities of OH^- ions on the particle surface as well as in the reaction medium favors the formation of $^{\cdot}OH$. As seen in Fig. 5 the degradation rate constant increases, slightly from pH 3 to 5 and then decreases. The optimum pH for bare ZnO is 5. Degradation efficiency with bare ZnO is less than AgBr–ZnO in neutral to alkaline pH range (pH 7–12). This shows that AgBr–ZnO is more efficient than bare ZnO in the neutral and alkaline pH.

3.2.2. Effect of catalyst loading

Experiments were carried out to find out the optimum catalyst loading for efficient degradation by varying the amount of AgBr–ZnO from 1 to 5 g L^{-1} (Fig. 6). NBB degradation increases with the increase in catalyst amount from 1 to 3 g L^{-1}. Further increase of catalyst amount decreased the rate constant of degradation. The increase in dye degradation rate up to 3 g L^{-1} is due to the increase in the amount of catalyst which increases the number of dye molecules adsorbed, whereas the decrease in the degradation efficiency of NBB above 3 g L^{-1} may be due to the light reflectance by catalyst particles. It is found that the optimum catalyst loaded for solar process (3 g L^{-1}) is less, as compared to the degradation using UV-A light (4 g L^{-1}) [29].

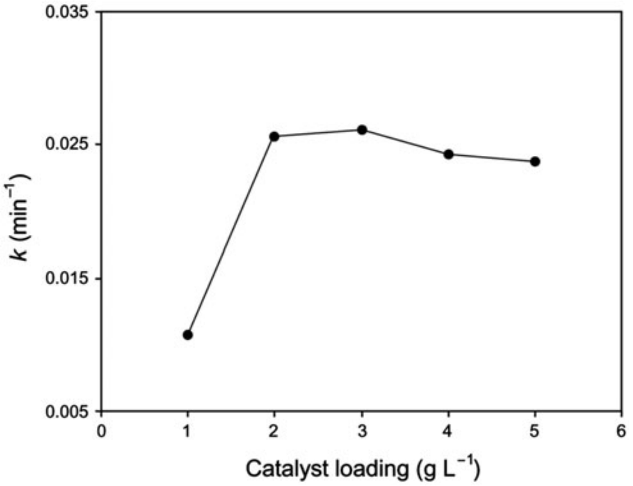


Fig. 6. Effect of catalyst loading: [NBB] = 2×10^{-4} M, catalyst = 44.4 wt.% AgBr–ZnO, pH = 11, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min.

3.2.3. Effect of initial dye concentration

The effect of various initial dye concentrations on the degradation of NBB on AgBr–ZnO surface has been investigated (Fig. 7). Increase of dye concentration from 1 to 5×10^{-4} M decreased the rate constant from 0.0301 to 0.0064 min^{-1} for degradation in 30 min. The rate of degradation relates to the $^{\cdot}OH$ radical formation on the catalyst surface and probability of $^{\cdot}OH$ radical reacting with dye molecule. For all the initial dye concentrations, the catalyst amount and light

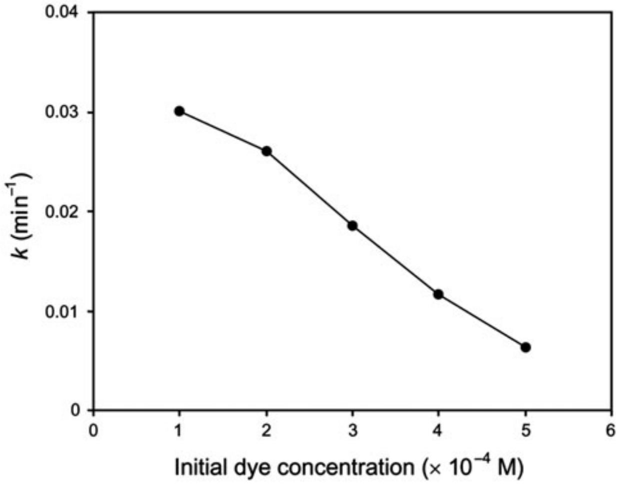


Fig. 7. Effect of initial dye concentration: pH = 11, 44.4 wt.% AgBr–ZnO suspended = 3 g L^{-1}, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min.

Table 2
Effect of oxidants on photodegradation of NBB with AgBr–ZnO by solar light

Oxidants	% of degradation
AgBr–ZnO	53.7
AgBr–ZnO + oxone	55.9
AgBr–ZnO + KIO_4	5.0
AgBr–ZnO + H_2O_2	48.0

Notes: [NBB] = 2×10^{-4} M, 44.4 wt.% of AgBr–ZnO suspended = 3 g L^{-1}, pH = 11, oxidants = 0.01 M, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min.

intensity are same. Since, the generation of hydroxyl radical remains constant, the probability of dye molecule to react with hydroxyl radical decreased. At high initial dye concentrations, the path length of photon entering into the solution also decreases [23,29].

3.2.4. Effect of additives

The effect of oxidants such as $H_3K_5O_{18}S_4$ (oxone), KIO_4, and H_2O_2 in addition to molecular oxygen on the degradation kinetics of the NBB was investigated at pH 11 under solar light. It was found that the addition of these oxidants except oxone, decreases the photodegradation of NBB (Table 2). The high degree of degradation in this process with oxone is due to the formation of highly reactive radical intermediates by oxone (Eqs. (3) and (4)).

$$HSO_5^- \xrightarrow{hv} SO_4^{\cdot -} + {}^{\cdot}OH \tag{3}$$

$$SO_4^{\cdot -} + H_2O \rightarrow {}^{\cdot}OH + SO_4^{2-} + H^- \tag{4}$$

ZnO on irradiation with aqueous dye solution produces hydrogen peroxide. Hence, by the addition of H_2O_2, optimum concentration of H_2O_2 is exceeded. This is the reason for the inhibition of photodegradation by the addition of H_2O_2. The decrease in the mineralization efficiency of dye with KIO_4 is mainly due to its hydroxyl radical scavenging effect [30].

Table 3
Effect of transition metal ions on photodegradation of NBB with AgBr–ZnO by solar light

Cations	% of degradation
AgBr–ZnO	53.7
Fe^{2+}	45.5
Cu^{2+}	14.6
Mn^{2+}	23.9
Mg^{2+}	63.7

Notes: [NBB] = 2×10^{-4} M, 44.4 wt.% of AgBr–ZnO suspended = 3 g L^{-1}, pH = 11, cations = 0.1 M, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min.

Table 4
Effect of anions on photodegradation of NBB with AgBr–ZnO by solar light

Anions	% of degradation
AgBr–ZnO	53.7
$NaHCO_3$	33.0
Na_2CO_3	28.2
NaCl	74.0
Na_2SO_4	69.7

Notes: [NBB] = 2×10^{-4} M, 44.4 wt.% of AgBr–ZnO suspended = 3 g L^{-1}, pH = 11, anions = 0.1 M, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min.

Table 3 shows the effect of addition of metal ions like Fe^{2+}, Cu^{2+}, Mn^{2+}, and Mg^{2+} (0.1 M) as sulfates at pH 11. Except Mg^{2+} all the metal ions decrease the rate of degradation. Addition of metal ions generally decreases the efficiency of the catalyst due to blocking of active sites of catalyst by adsorption. In case of Mg^{2+}, interaction of dye with Mg^{2+} may decrease the adsorption.

Table 4 shows the effect of addition of inorganic anions like bicarbonate, carbonate, chloride, and sulfate of sodium salts at pH 11. The degradation efficiency of solar/AgBr–ZnO was significantly decreased in the presence of HCO_3^- and CO_3^{2-} whereas addition of Cl^- and SO_4^{2-} enhanced the degradation rate. Addition of

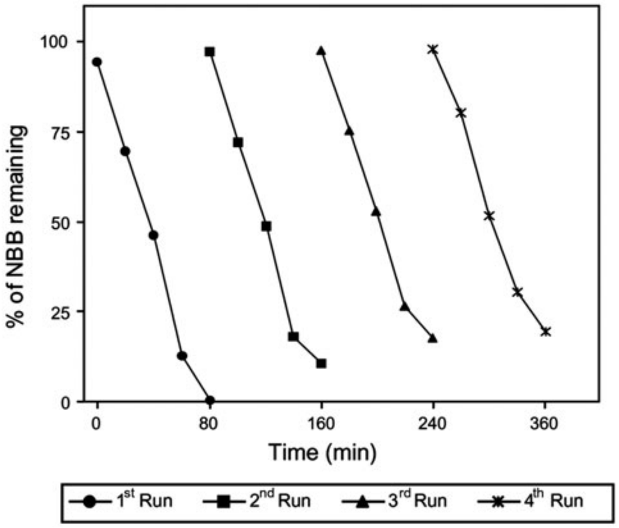
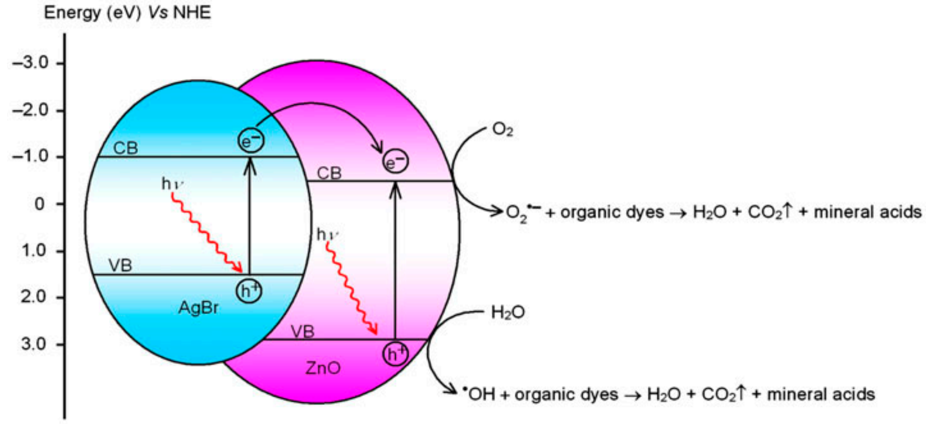


Fig. 8. Catalyst reusability: [NBB] = 2×10^{-4} M, pH = 11, 44.4 wt.% AgBr–ZnO suspended = 3 g L^{-1}, airflow rate = 8.1 mL s^{-1}.



Scheme 1. Proposed degradation pathway of NBB with AgBr–ZnO.

inorganic anions generally decreases the efficiency of TiO_2 and ZnO due to hydroxyl radical scavenging property. But in case of AgBr–ZnO, Cl^-, and SO_4^{2-}, ions may interact with the AgBr in the catalyst. Due to the mixed interactions of these anions with the catalyst, the trend observed is different. The decrease in the degradation efficiency with HCO_3^- and CO_3^{2-} is due to their hydroxyl radical scavenging property.

3.3. Catalyst stability

Degradation was carried out with the used catalyst for four cycles. Fig. 8 shows the percentage of dye remaining at each cycle. Although the degradation efficiency of AgBr–ZnO is slightly decreased after each cycle, the catalyst exhibited 80.5% activity after three successive cycles under the solar irradiation. These results indicated that AgBr–ZnO catalyst remained effective and reusable under solar light.

3.4. COD analysis

To confirm the mineralization of NBB, the degradation was also analyzed by COD values. The COD value of 1,344 ppm for 2×10^{-4} M dye concentration decreased to 89.6 ppm (93.3% dye degradation) after 1 h of irradiation with AgBr–ZnO. Mineralization of dye was also revealed by the formation of CO_2 during degradation. CO_2 evolution was tested by the precipitation of $CaCO_3$ when the evolved gas was passed into lime water.

3.5. Mechanism of the degradation

Band energy levels for AgBr and ZnO with respect to NHE are shown in Scheme 1. Since, there was no leaching of AgBr from the catalyst and the catalyst was found to be more solar light active as compared to bare ZnO and commercial ZnO; a mechanism based on the band energy levels of AgBr and ZnO is proposed for the degradation of dye. Electrons generated by solar light are transferred from CB of AgBr to CB of ZnO. This electron transfer process is faster than electron-hole recombination in AgBr. The electrons in CB of ZnO produce $O^{2\cdot-}$ which degrades the dyes. The holes in the AgBr and the holes produced in ZnO by photoexcitation react with H_2O and ^-OH to produce $^\cdot OH$ radicals for the degradation of the dye. A similar mechanism has also been reported earlier for AgBr–TiO_2 [31].

4. Conclusions

AgBr–ZnO is found to be more efficient than commercial and bare ZnO for degradation of NBB azo dye under solar light. The optimum pH and catalyst amount for the efficient removal of dye are found to be 11 and $3\,g\,L^{-1}$, respectively. Increase of initial dye concentration decreased the degradation rate. Except oxone, other oxidants decrease the degradation of NBB. Except Mg^{2+}, all metal ions Fe^{2+}, Cu^{2+}, and Mn^{2+} inhibit the degradation efficiency of AgBr–ZnO. The catalyst was found to be reusable. Reusability of the solar active catalyst makes this process more economical and eco-friendly. COD measurements confirm 93.3% mineralization of NBB molecule. The higher photocatalytic activity of AgBr–ZnO towards NBB degradation in solar light is explained by a mechanism involving band energy levels of AgBr and ZnO. Since, less amount of catalyst is required for solar process ($3\,g\,L^{-1}$) as compared to UV process ($4\,g\,L^{-1}$); this catalyst will be much useful for solar treatment of dye wastewater.

Acknowledgments

The authors thank the Ministry of Environment and Forests (MOEF), New Delhi, India for the financial support through research grant No. 315-F-36, F. No. 19/9/2007-RE. One of the authors B. Krishnakumar is thankful to CSIR, New Delhi, India for the award of Senior Research Fellowship.

References

[1] B. Swarnalatha, Y. Anjaneyulu, Studies on the heterogeneous photocatalytic oxidation of 2,6-dinitrophenol in aqueous TiO_2 suspension, J. Mol. Catal. A: Chem. 223 (2004) 161–165.

[2] A. Akyol, M. Bayramoglu, Photocatalytic degradation of Remazol Red F3B using ZnO catalyst, J. Hazard. Mater. 124 (2005) 241–246.

[3] M.J. Height, S.E. Pratsinis, O. Mekasuwandumrong, P. Praserthdam, Ag-ZnO catalysts for UV-photodegradation of methylene blue, Appl. Catal., B 63 (2006) 305–312.

[4] C.C. Chen, Degradation pathways of ethyl violet by photocatalytic reaction with ZnO Dispersions, J. Mol. Catal. A: Chem. 264 (2007) 82–92.

[5] M.N. Esfahania, A. Khakifirooz, N. Tavakoli, M.H. Soleimanic, Preparation, characterization and photocatalytic activity of a novel nanostructure ZnO composite film derived sol-gel process using organic binder materials, Desalin. Water Treat. 21 (2010) 202–209.

[6] P. Bansal, N. Bhullar, D. Sud, Studies on photodegradation of malachite green using TiO_2/ZnO photocatalyst, Desalin. Water Treat. 12 (2009) 108–113.

[7] N. Sobana, M. Swaminathan, The effect of operational parameters on the photocatalytic degradation of Acid Red 18 by ZnO, Sep. Purif. Technol. 56 (2007) 101–107.

[8] M. Muruganandham, N. Sobana, M. Swaminathan, Solar assisted photocatalytic and photochemical degradation of Reactive Black 5, J. Hazard. Mater. 137 (2006) 1371–1376.

[9] B.H. Hameed, U.G. Akpan, K.P. Wee, Photocatalytic degradation of Acid Red 1 dye using ZnO catalyst in the presence and absence of silver, Desalin. Water Treat. 27 (2011) 204–209.

[10] C.C. Chen, C.S. Lu, Mechanistic studies of the photocatalytic degradation of methyl green: An investigation of products of the decomposition processes, Environ. Sci. Technol. 41 (2007) 4389–4396.

[11] T.J. Kuo, C.N. Lin, C.L. Kuo, M.H. Hung, Growth of ultralong ZnO nanowires on silicon substrates by vapor transport and their use as recyclable photocatalysts, Chem. Mater. 19 (2007) 5143–5147.

[12] F.D. Mai, C.S. Lu, C.W. Wu, C.H. Huang, J.Y. Chen, C.C. Chen, Mechanisms of photocatalytic degradation of Victoria Blue R using nano-TiO_2, Sep. Purif. Technol. 62 (2008) 423–436.

[13] B. Krishnakumar, K. Selvam, R. Velmurugan, M. Swaminathan, Influence of operational parameters on photodegradation of Acid Black 1 with ZnO, Desalin. Water Treat. 24 (2010) 132–139.

[14] B. Krishnakumar, M. Swaminathan, Solar photocatalytic degradation of Acid Black 1 with ZnO, Indian J. Chem., Sect A 49 (2010) 1035–1040.

[15] B. Krishnakumar, M. Swaminathan, Influence of operational parameters on photocatalytic degradation of a genotoxic azo dye Acid Violet 7 in aqueous ZnO suspensions, Spectrochim. Acta, Part A 81 (2011) 739–744.

[16] A. Akyol, H.C. Yatmaz, M. Bayramoglu, Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions, Appl. Catal., B 54 (2004) 19–24.

[17] St. Christoskova, M. Stoyanova, Degradation of phenolic waste waters over Ni-Oxide, Water Res 35 (2001) 2073–2077.

[18] M. Pelaez, P. Falaras, V. Likodimos, A.G. Kontos, A.A. de la Cruz, K. O'shea, D.D. Dionysiou, Synthesis, structural characterization and evaluation of sol–gel-based NF-TiO2 films with visible light-photoactivation for the removal of microcystin-LR, Appl. Catal., B 99 (2010) 378–387.

[19] S. Suwanboon, P. Amornpitoksuk, A. Sukolrat, Dependence of optical properties on doping metal, crystallite size and defect concentration of M-doped ZnO nanopowders (M = Al, Mg, Ti), Ceram. Int. 37 (2011) 1359–1365.

[20] K.C. Barick, S. Singh, M. Aslam, D. Bahadur, Porosity and photocatalytic studies of transition metal doped ZnO nanoclusters, Microporous Mesoporous Mater. 134 (2010) 195–202.

[21] S. Chusaksri, J. Lomda, T. Saleepochn, P. Sutthivaiyakit, Photocatalytic degradation of 3,4-dichlorophenylurea in aqueous gold nanoparticles-modified titanium dioxide suspension under simulated solar light, J. Hazard. Mater. 190 (2011) 930–937.

[22] M. Xing, J. Zhang, F. Chen, New approaches to prepare nitrogen-doped TiO_2 photocatalysts and study on their photocatalytic activities in visible light, Appl. Catal., B 89 (2009) 563–569.

[23] B. Krishnakumar, K. Selvam, M. Swaminathan, Product selectivity in semiconductor mediated dehydrazonation of benzophenone hydrazone, Synth. Commun. 41 (2011) 1929–1937.

[24] C. Han, M. Pelaez, V. Likodimos, A.G. Kontos, P. Falaras, K. O'Shea., D.D. Dionysiou, Innovative visible light-activated sulfur doped TiO_2 films for water treatment, Appl. Catal. B: Environ 107 (2011) 77–87.

[25] G. Li, K.H. Wong, X. Zhang, C. Hu, J.C. Yu, R.C.Y. Chan, P. K. Wong, Degradation of Acid Orange 7 using magnetic AgBr under visible light: The role of oxidizing species, Chemosphere 76 (2009) 1185–1191.

[26] P. Huo, Y. Yan, S. Li, H. Li, W. Huang, Floating photocatalysts of fly-ash cenospheres supported AgCl/TiO_2 films with enhanced Rhodamine B photodecomposition activity, Desalination 256 (2010) 196–200.

[27] V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, Adsorption of basic dyes on granular acivated carbon and natural zeolite, Water Res. 35 (2001) 3357–3366.

[28] W.S. Kuo, P.H. Ho, Solar photocatalytic decolorization of methylene blue in water, Chemosphere 45 (2001) 77–83.

[29] B. Krishnakumar, B. Subash, M. Swaminathan, AgBr–ZnO: An efficient nano-photocatalyst for the mineralization of Acid Black 1 with UV light, Sep. Purif. Technol. 85 (2012) 35–44.

[30] B. Gozmen, M. Turabik, A. Hesenov, Photocatalytic degradation of Basic Red 46 and Basic Yellow 28 in single and binary mixture by UV/TiO_2/periodate System, J. Hazard. Mater. 164 (2009) 1487–1495.

[31] M.A. Asia, C. He, M. Su, D. Xia, L. Lin, H. Deng, Y. Xiong, R. Qiu, X.Z. Li, Photocatalytic reduction of CO_2 to hydrocarbons using AgBr/TiO_2 nanocomposites under visible light, Catal. Today 175 (2011) 256–263.