

RESEARCH ARTICLE

Photocatalytic Detoxification of NBB Dye Over Cerium Loaded Ag–ZnO Photocatalyst Under UV-A Light Irradiation

*B Subash¹, M Shanthi²

¹St. Joseph's College of Engineering, Department of Chemistry, Chennai 600119, Tamil Nadu, India.

²Photocatalysis laboratory, Department of Chemistry, Annamalai University, Annamalai Nagar, 608002, India.

Received- 17 August 2016, Revised- 19 November 2016, Accepted- 4 March 2017, Published- 25 March 2017

ABSTRACT

The Ce co-doped Ag-ZnO, expresses the photocatalyst Ce–Ag–ZnO, which was effectively produced by a simple solvothermal technique. In this catalytic process, several properties of the catalysts were taken into account to check that the catalyst gets characterized properly. These catalytic properties include X- ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM) images, Energy Dispersive Spectrum (EDS), Diffuse Reflectance Spectra (DRS), Photo-Luminescence spectra (PL), Cyclic Voltammetry (CV) and BET surface area measurements. In our research work, the process done in solvothermal method, which synthesized Ce co-doped Ag-ZnO, the so called photocatalyst Ce–Ag–ZnO, showed a positive effect. A part of our vision to find the photocatalytic activity of Ce-Ag-ZnO was carried out for the degradation process of Naphthol Blue Black (NBB) dye in aqueous solution as a medium under the irradiation of UV-A light. The ZnO which was present, absorbed in UV and visible region were shifted by the co-dopants. For the process of mineralization of NBB dye under UV-A light at pH value 9, the efficient one was proved to be Ce–Ag–ZnO when compared with Ag–ZnO, Ce–ZnO, commercial ZnO, prepared ZnO, TiO₂-P25 and TiO₂ (Merck). The impacts of operational parameters like, the amount of photocatalyst technically called as photocatalytic dosage, the concentration of the dye and initial pH value on photo mineralization of NBB dye were examined. The Chemical Oxygen Demand (COD) measurements also proved the mineralization process of Naphthol Blue Black (NBB) dye. Under UV-A light, the degradation of naphthol blue black dye is done by a degradation mechanism. The catalyst is finally proved to have the property of reusability.

Keywords: Ce doped Ag–ZnO, Photocatalysis, UV-A light, NBB dye, Reusability.

1. INTRODUCTION

Environmental issues have become a serious problem because of the pollutants from all over the world being accumulated in the living organisms thereby leading earth to a dangerous situation. There are different types of environmental pollutants like, adsorption, biodegradation, chlorination, combined coagulation and flocculation, electrochemical oxidation, ozonation, reverse osmosis and finally photocatalysis [1, 2]. For the treatment of dye wastes, the photocatalytic processes which involve ZnO semiconductor particles under the illuminations of UV light have been proved to be possibly valuable [3]. The

removal of toxic chemicals is offered by the semiconductor absorbents and photocatalyst, because of their extensive applications [4]. Even the organics can be totally oxidized into products that exhibit no toxicity and also water, CO₂, and some inorganic ions can also be subjected to oxidation by the Advanced Oxidation Processes (AOPs) [5]. Usually in organics, Advanced Oxidation Processes require active radicals like, [•]OH to attack and break C–C/C–H/C=O/C=N. Though it is viable to do the direct oxidation using UV (photolysis), high-power necessities and failure to treat refractory compounds make this direct oxidation a restricted one.

*Corresponding author. Tel.: +919976457199

Email address: chemsubash@gmail.com (B.Subash)

Double blind peer review under responsibility of DJ Publications

<https://dx.doi.org/10.18831/djchem.org/2017011004>

2455-5193 © 2017 DJ Publications by Dedicated Juncture Researcher's Association. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Heterogeneous photocatalytic oxidation process is a process in which semiconductor catalysts, like TiO₂, ZnO, SnO₂, CuO or CdS are added making it effective [6]. Just because of the high degradation tendency towards toxicity and recalcitrant chemical species conducted by comparatively simple and low-cost techniques, when compared to others, ZnO aided photocatalytic procedure occupies a noticeable place. Also there are other applications of this photocatalytic process which were recorded. As TiO₂, the typically used photocatalytic material, exhibits the band-gap energy as same as the band gap energy of ZnO, this theoretically proves that ZnO is proved to have the similar photocatalytic capability as TiO₂. In the early 1994, the synthesis of H₂O₂ on ZnO was detected [7]. All these information, have collectively proved the advantage of the low cost factor of ZnO when compared to TiO₂, suggesting that ZnO to be a favourable substitute to TiO₂ in photocatalysis [8]. Though all these issues favour ZnO, the application is limited because of the swift recombination of the photo-induced electrons and the holes get weak during photocatalytic process [9, 10]. To diminish this above mentioned restrictions, the photocatalytic activity of ZnO must be upgraded to be used in a large scale. For this, various methods have been established. The high capability of the hole-electron pair to combine again is a major problem, indicating that the photocatalyst is deactivated. Though oxygen, being a good hunter of electrons, many studies has proved that the incidence of transition metals like Pt, Ag and Fe only prompted the charge-transfer leading to the photochemical degradation process [11-14].

Instead of just using single element doping into semiconductor oxides, the change of using ZnO or TiO₂ by the process of co-doping was found to be an active method. This is due to the co-operative action of the co-doping which was able to increase the photocatalytic activity. Several studies were stated on co-doped materials like Cd and Al [15, 16], Zn and Al [17], N, S and C co-doped ZnO [18], Mn and Co [19], Ga/Al/Co co-doped ZnO [20], also co-doping technique uses the reactive donors (Ga, In, and Al [21-23]) to the acceptor (N or Li). Also, the double doping with the grouping of N and Li has been focused for further study [24]. And also

because of their 4f electron and multi-electron pattern, the features of polymorphism and good thermal stability were observed on rare earth oxides. Ce doping improved the photocatalytic activity of TiO₂ [25, 26]. For example, Lanthanide (Ln)-doped TiO₂ nanoparticles have been particularly preferred for their exclusive 4f electron pattern. Amongst others, due to the Ce³⁺/Ce⁴⁺ redox couple, Ce-doped TiO₂ nanoparticles have appealed attention, resulting from the move of cerium oxide between CeO₂ and Ce₂O₃ under oxidization and reduction situations [26-30]. The Ce-Ag-ZnO photocatalyst was subjected to photocatalytic activity using naphthol blue black dye under UV-A light irradiation and an outstanding photocatalytic activity was seen in the Ce co-doped Ag-ZnO photocatalyst substrates. The description about the creation of Ce doped Ag-ZnO and examination of its photocatalytic naphthol blue black dye action towards degradation, is nowhere found.

2. EXPERIMENTAL

2.1. Materials

The commercial azo dye naphthol blue black dye synthesized from Aldrich was used and 99 percent of Oxalic acid dihydrates along with 99 percent of zinc nitrate hexahydrate were got from Himedia chemicals. The following chemicals were obtained from Himedia such as AgNO₃ and Ce(NH₄)₄(SO₄)₄.2H₂O were obtained from spectrochem ZnO, ozone and KBrO₃ whereas TiO₂ used as obtained was got from Merck. A sample of Degussa TiO₂-P25 was got from Evonik (Germany). This constitutes an 80:20 combination of anatase and rutile, possessing a particle size of 30nm and BET specific area of 50m²g⁻¹. K₂Cr₂O₇ (s.d.fine), Ag₂SO₄ (s.d.fine), HgSO₄, FeSO₄.7H₂O (Qualigens) and H₂O₂ (Rankem) were made use in the same form. For preparing experimental solution, water which was distilled twice was used. In prior to irradiation, the pH range of the solutions were adjusted with the help of H₂SO₄ or NaOH.

2.2. Analytical methods

X'Per PRO diffractometer prepared with a CuK α radiation with a wavelength value of 1.5406Å at 2.2kWMax was used to achieve powder X-ray diffraction patterns and their peak positions were matched with the standard files to find the crystalline phase and the

scanning electron microscope named, JEOL JSM-6701F cold Field Emission Scanning Electron Microscope (FE-SEM) examined the morphology of the catalyst. As a first step to organize FE-SEM measurements, the samples were placed on a gold platform located in the scanning electron microscope, for successive analysis of several magnifications. Shimadzu UV-2450 was found handy to record the diffuse reflectance spectra. The Perkin Elmer LS 55 fluorescence spectrometer, maintained at room temperature was used to record the Photoluminescence (PL) spectra. The carbon tetrachloride was used as a dispersion medium for the nanoparticles to be dispersed and after this, light with a wavelength of 300nm was used to excite these nanoparticles. CHI 60AC electrochemical analyzer was used as a process for the Cyclic Voltammetry (CV) calculations. Nitrogen adsorption maintained at 77K based on BET equation with micrometrics ASAP 2020 V3.00 H was used to find out the exact location of the samples. Hitachi-U-2001 spectrometer was used to perform the UV spectral calculations.

2.3. Irradiation experiments

A Heber Multilamp-photoreactor HML MP 88 was used for the degradation activity by using UV-A light at a range maintained at 365nm. In this model, an 8W medium pressure mercury vapour lamps were set in parallel which emits 365nm wavelengths. A reaction chamber with a specially designed reflector comprised of highly polished aluminum and cooling fan is constructed. A magnetic stirrer and 50mL capacity reaction glass tubes are also made available for this process. The coverage length of the light to be exposed is 330mm. Four parallel 8W medium pressure mercury lamps were used for the irradiation process. To totally mix the reaction solution, a pump is used in this process for the continuous aeration of the solution which has the catalyst and the dye.

To attain a maximum adsorption of naphthol blue black upon the semiconductor surface, a suitable amount of catalyst with 50mL of naphthol blue black at a range maintained at 2×10^{-4} M must be agitated for half an hour in a dark place before illumination. The solvent was found to be nonvolatile while illumination. By using the centrifugation process, at specific time gaps, 2mL to 3mL of the samples were taken and also the catalyst was taken aloof. The samples were then diluted appropriately and the naphthol

blue black concentration fluctuations were observed from the characteristic absorption. By the utility of UV-Visible spectrophotometer maintained at 320nm, the absorption in this range shows the aromatic portion of naphthol blue black and the reduction in the absorbance shows the dye's degradation.

3. RESULTS AND DISCUSSION

3.1. Characterization of catalyst

The process of preparing and characterizing the 3wt% Ce-Ag-ZnO and also its photocatalytic activity for the degradation of naphthol blue black dye with solar light were mentioned in [32, 33]. In the Ce-Ag-ZnO system, the occurrence of 1 new peak is achieved with 2θ value of 28.91 in correspondence with (111) plane of Ce^{4+} in CeO_2 (JCPDS 89-8436) on XRD analysis of Ce-Ag-ZnO. Figure 1 proves the settlement of Ce.

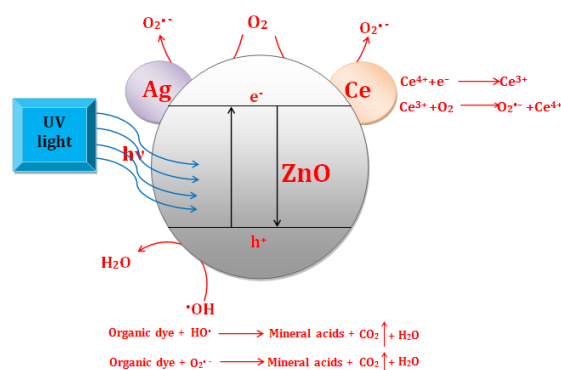


Figure 1. Mechanism of degradation of Naphthol Blue Black (NBB) by Ce-Ag-ZnO

Owing to very low concentration, 'Ag' was undetected by XRD [34]. At an increased focus of magnification, the hexagonal pattern of ZnO is obviously seen with the help of FE-SEM and HR-TEM images. 4nm to 100nm is observed to be the range of the size of Ce-Ag-ZnO particles and also the occurrence of Ce, Ag, Zn and O were exposed by the EDS spectrum. DRS spectra show that bare ZnO in the whole visible area has lower absorption when compared with Ce-Ag-ZnO. This has a chance to enhance the visible light activity of the photocatalyst. The value 3.15eV was observed to be the band gap of bare ZnO and the value 3.05 eV was observed to be the band gap of Ce-Ag-ZnO. The release of ZnO is not influenced with the stuffing of Ce and Ag with ZnO, the only thing that happens is the intensity of Photoluminescence discharge getting reduced

when associated with bare ZnO. This occurs as the suppression of the recombine process of electron-hole pairs by Ag and Ce. The occurrence of Ag⁰ and Ce⁴⁺ in the catalyst is exposed by XPS. Bare ZnO which ranges 11.5m²g⁻¹ is lower than that of BET surface area of Ce-Ag-ZnO which ranges 13.5m²g⁻¹. As the catalytic surface area is high, the photocatalytic action is also high.

3.2. Photocatalytic activities

The action of photodegradability process of naphthol blue black done with several photocatalysts under irradiation of UV light is expressed in figure 2. For this, various measurements must be maintained such as dye concentration=2×10⁻⁴molL⁻¹, catalyst suspended=3gL⁻¹, pH=9, I_{UV}=1.381×10⁻⁶einsteinL⁻¹s⁻¹, airflow rate=8.1mL s⁻¹.

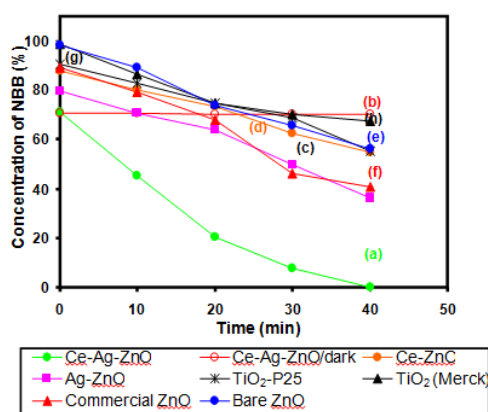


Figure 2. Photodegradability of NBB

The whole degradation process of the dye happens nearly at a period of 40 minutes with Ce-Ag-ZnO (expressed in curve a) under UV light. Due to the adsorption of the dye on the catalyst's surface, for the similar experiment done with Ce-Ag-ZnO without the incidence of UV light (curve b), a 29 percent fall in the concentration of the dye occurs. When the reaction took place in the incidence of UV light with no catalysts, minor degradation of about 0.2 percent occurred. With these interpretations, we can conclude that both catalyst and UV light are together needed for the best degradation of the dye. The achievements of various degradations of various photocatalysts happen only in the same conditions as expressed below. 63.9 degradation was achieved by the photocatalyst of

Ag-ZnO (curve c), 45.2 degradation was achieved by the photocatalyst of Ce-ZnO (curve d), 43.8 degradation was achieved by the photocatalyst of bare ZnO (curve e), 59.5 degradation was achieved by the photocatalyst of commercial ZnO (curve f), 44.8 degradation was achieved by the photocatalyst of TiO₂-P25 (curve g) and 32.0 degradation was achieved by the photocatalyst of TiO₂ (Merck) (curve h). This indicates that when compared to other degradation processes, the UV/Ce-Ag-ZnO process is more able.

The naphthol blue black dye that contains Ce-Ag-ZnO, which exhibits photocatalytic degradation, follows pseudo-first order kinetics. When the initial dye concentration is less the rate expression is expressed as,

$$\frac{d[c]}{dt} = k'[c] \quad (3.1)$$

Here, k' represents the pseudo-first order rate constant.

The equilibrium of adsorption and desorption is achieved in half an hour, as the dye is adsorbed onto the surface of the photocatalyst Ce-Ag-ZnO. The dye's equilibrium concentration is found out after adsorption. This equilibrium concentration is noted as the dye's initial concentration for analyzing kinetics. Integration of equation (3.1), with the limit C equals C₀ at t equaling 0 with C₀ acting as the equilibrium concentration of the solution in bulk, giving equation (3.2) expressed as follows,

$$\ln\left(\frac{C_0}{C}\right) = k't \quad (3.2)$$

Here, C₀ represents dye's equilibrium concentration and C represents the concentration at time t.

The naphthol blue black solution at different times of irradiation, which has the UV-vis spectra which ranges about 2×10⁻⁴M is given in figure 3. The following measurements are to be maintained as NBB=2×10⁻⁴M; pH=9; catalyst suspended=3gL⁻¹; I_{UV}=1.381×10⁻⁶einsteinL⁻¹s⁻¹. airflow rate= 8.1mL s⁻¹; (a) 0 min (b) 10 min (c) 20 min (d) 30 min and (e) 40 min. The UV-vis spectra, does not exhibit great change with the process of irradiation. While the degradation process happens, the intensity at 320 and the intensity at 615 decrease steadily. This clearly shows that no absorption is

done by the intermediates when the intensities of the wavelengths are at 320 and 615nm.

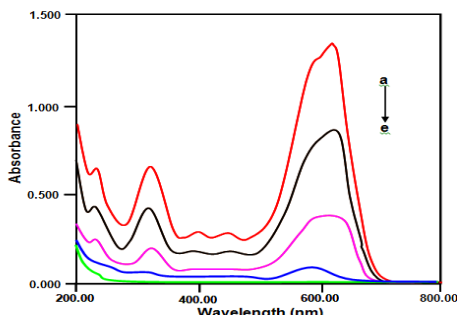


Figure 3. The changes in UV-vis spectra of NBB on irradiation with solar light in the presence of Ce-Ag-ZnO

3.3. Effects of photocatalytic parameters

3.3.1. Effect of solution pH

Depending upon the dye's adsorption on the catalyst's surface, the photodegradation process happens. The pH value maintained for the solution which is made used in this process appreciatively encourages dye's adsorption [35, 36]. This shows how pH acts as an important factor in the process of photodegradation. Figure 4 shows the pH's initial consequence on the degradation of naphthol blue black dye. The following measurements are to be maintained as, $[NBB]=2 \times 10^{-4} \text{ molL}^{-1}$, 3 wt% Ce-Ag-ZnO suspended = 3 gL^{-1} , airflow rate = 8.1 mL s^{-1} , $I_{UV}=1.381 \times 10^{-6} \text{ einsteinL}^{-1}\text{s}^{-1}$, irradiation time = 30 minutes.

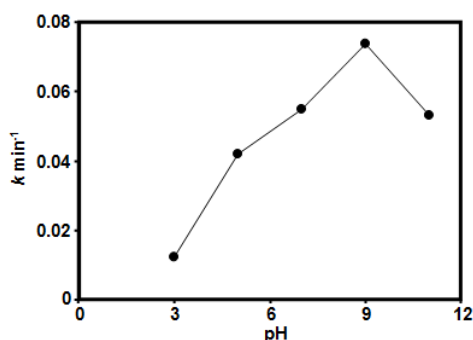


Figure 4. Effect of pH solution

For Ce-Ag-ZnO, the pseudo-first order rate constant at pH value 3 is 0.0123, at pH value 5 the pseudo-first order rate constant is 0.0418, at pH value 7 the pseudo-first order rate constant is 0.0548, at pH value 9 the pseudo-first order rate constant is 0.0738 and at pH value 11 the

pseudo-first order rate constant is 0.0531 with the unit min^{-1} . The elimination efficiency of naphthol blue black increases from the pH value 3 up to the pH value 9 and gradually decreases after that. For the best naphthol blue black dye's elimination on Ce-Ag-ZnO the optimum pH value 9 is suggested. At a range, when the pH possesses an acidic value, the effectiveness of elimination is less. This is because of the dissolution of ZnO, as the effectiveness of the photocatalytic process depends on dye's adsorption on the catalytic surface. At various pH ranges of values, the dye's adsorption is observed. The adsorption percentages after half an hour were observed to be 12.1, 21.5, 24.5, 29.0 and 23.2 at various pH values of 3, 5, 7, 9 and 11 respectively. This above mentioned adsorption equilibrium is attained only after half an hour. The effective degradation is found to be good at the pH value 9 since this is the range when the adsorption is more.

3.3.2. Effect of catalyst dosage

The consequence of the amount of catalyst on naphthol blue black dye's photodegradation under UV light was conducted by altering the amount of catalyst from 2 gL^{-1} to 6 gL^{-1} . These outcomes were expressed in figure 5. The following measurements are to be maintained as, $[NBB]=2 \times 10^{-4} \text{ molL}^{-1}$, 3wt% Ce-Ag-ZnO suspended = 3 gL^{-1} , pH=9, airflow rate = 8.1 mLs^{-1} , $I_{UV}=1.381 \times 10^{-6} \text{ einsteinL}^{-1}\text{s}^{-1}$, irradiation time = 30 minutes.

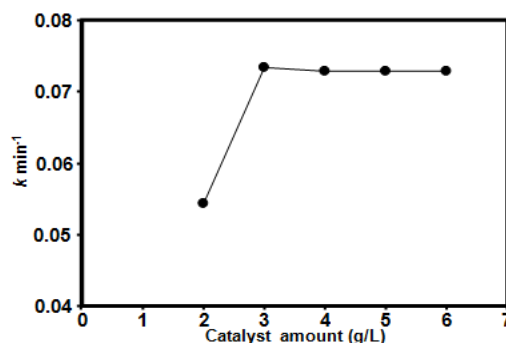


Figure 5. Effect of catalyst loading

This figure expresses that as the amount of catalyst, Ce-Ag-ZnO is maintained at 2 gL^{-1} , 3 gL^{-1} , 4 gL^{-1} , 5 gL^{-1} and 6 gL^{-1} the pseudo-first order rate constants are 0.0543 min^{-1} , 0.0734 min^{-1} , 0.0729 min^{-1} , 0.0728 min^{-1} and 0.0726 min^{-1} respectively. The activity of degradation increases as the amount of catalyst increases from 2 gL^{-1} to 3 gL^{-1} . After this the degradation

becomes constant. The best amount of catalyst to be used is observed to be at 3gL^{-1} . The improvement of the elimination rate is because of the below given factors.

- The increase in the dye's quantity adsorbed on the catalytic surface is influenced by the amount of the catalyst or catalytic dosage.
- Increase in the illumination area.

There is a chance of the catalytic light scattering effect to reduce NBB's effectiveness, when the dosage is high above the range 3gL^{-1} . This outcome has also found to be same when ZnO was subjected to the photodegradation process [36, 37].

3.3.3. Effect of initial dye concentration

The outcomes of several initial dye concentrations on the photocatalyst Ce-Ag-ZnO were examined for the process of degradation of Naphthol Blue Black (NBB) dye. All these outcomes revealed that as the dye's concentration increased, the rate concentration for the degradation decreased. For example, for degradation in half an hour, the rise in the concentration of the dye from $1 \times 10^{-4}\text{M}$ to $5 \times 10^{-4}\text{M}$ had declined the rate constant from 0.107min^{-1} to 0.0192min^{-1} which is expressed in figure 6.

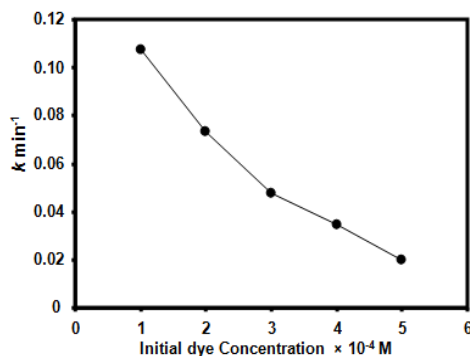


Figure 6. Effect of initial dye concentration

The following measurements are to be maintained as, $\text{pH}=9$, $3\text{wt}\%$ Ce-Ag-ZnO suspended= 3gL^{-1} , airflow rate= 8.1mLs^{-1} , $I_{UV} = 1.381 \times 10^{-6}\text{einsteinL}^{-1}\text{s}^{-1}$, irradiation time= 30 minutes. Because of the fall in the penetration of light by the molecules of the naphthol blue black dye, the efficiency also made a fall [37, 38].

3.3.4. Stability of the photocatalyst

If the reaction is either an organic transformation or the reaction is photodegradation, the reusable property of the photocatalyst is the main reason behind why the heterogeneous catalysts are used for reactions of any kind. Figure 7 shows the outcome of Ce-Ag-ZnO photocatalyst, when subjected to reusability for the (Naphthol Blue Black) NBB's degradation under UV light by 4 successive cycles. For this the following measurements must be maintained as, $\text{NBB}=2 \times 10^{-4}\text{molL}^{-1}$, $4\text{ wt}\%$ Ce-Ag-ZnO suspended= 3gL^{-1} , airflow rate= 8.1mL s^{-1} , $I_{UV}=1.381 \times 10^{-6}\text{einsteinL}^{-1}\text{s}^{-1}$, irradiation time= 40 minutes. At the 40^{th} minute, the complete process of degradation of the naphthol blue black dye happened in the first, second and the third runs while the fourth run gave a degradation value of just 96.0 percent. These outcomes clearly reveal that the catalyst prepared by us is stable as well as reusable.

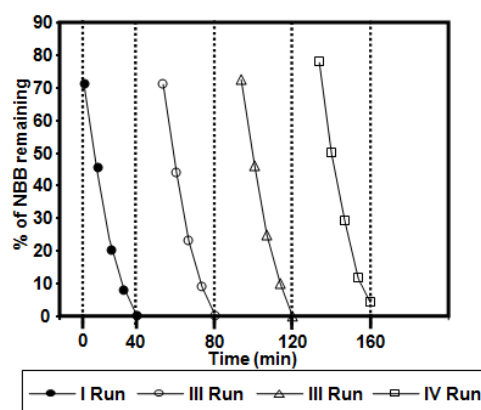


Figure 7. Catalyst reusability

3.3.5. COD analysis

Chemical Oxygen Demand (COD) values were used to prove the mineralization of (Naphthol Blue Black) NBB dye. Table 1 shows the percentage of reductions in the value of Chemical Oxygen Demand (COD). The percentage of Chemical Oxygen Demand (COD) reductions is expressed in table 1. The procedure is followed with a dye concentration of $2 \times 10^{-4}\text{mol/L}$, $3\text{ wt}\%$ Ce-Ag-ZnO suspended equals 3g/L , pH value equals 9 , airflow rate= 8.1mLs^{-1} , $I=1.381 \times 10^{-6}\text{einsteinL}^{-1}\text{s}^{-1}$. 94.9 percentage of COD value was attained after the photocatalyst Ce-Ag-ZnO, was subjected to 40 minutes of degradation. This reveals that the naphthol blue black dye is nearly mineralized.

Time in minutes	Percentage of COD reduction
10	12.8
20	30.6
30	64.2
40	94.9

3.3.6. Antiphotocorrosion property

The photocatalyst, Ce-Ag-ZnO was subjected under examination to test for its stableness by its property of antiphotocorrosion. The photocorrosion property of bare ZnO and Ce-Ag-ZnO was checked by us. After the process of photoreaction, the Zn^{2+} ionic concentration in the solution was observed by a spectrometer which performs the atomic absorption process to test how the ZnO is dissolved by the activity of photocorrosion. The outcomes offered in table 2 shows how bare ZnO is affected more with dissolution by the photocorrosion effect when compared to the photocatalyst Ce-Ag-ZnO. The following measurements are to be maintained as NBB= 2×10^{-4} M, catalyst suspended= 3 g L^{-1} , pH=7, airflow rate= 8.1 mL s^{-1} , irradiation time= 30 minutes. The photocatalyst Ce-Ag-ZnO is dissolved only 0.349 percent while the bare ZnO is dissolved only 2.49 percent. This dissolution is about 8.1 times the dissolution of CdS-Ag-ZnO. This shows that bare ZnO is less antiphotocorrosive when compared to the photocatalyst Ce-Ag-ZnO. This makes the photocatalyst to enjoy reusable and photostable property. Priorly, commercial ZnO was stated to be less antiphotocorrosive than the nanochain of ZnO [39].

3.3.7. Mechanism of degradation

Figure 7 mentioned above, reveals how the charges are separated and how the photocatalytic reaction happens mechanically for Ce-Ag-ZnO photocatalyst. A valence band electron proceeds to the conductance band leaving behind a hole in the valence band, when the irradiation process of UV irradiates the semiconductor. To minimize the photocatalytic action of semiconductors, these electron-holes are combined again. Nevertheless the incidence of 'Ag' and 'Ce' trap the electron from CB of ZnO at the same time, which prevents the electron-hole to recombine again. It is a well-

known fact that 'Ag' traps the electrons from CB of ZnO when UV is irradiated in the photocatalytic process for the purpose of photoreduction [32, 34 and 35]. When the property of dark adsorption is taken into account, the dark adsorption of Ce-ZnO and Ag-ZnO is lower than that of the dark adsorption process of Ce-Ag-ZnO. This activity improves the photocatalytic synergetic activity action between Ag and Ce in ZnO [40, 41]. It is clearly expressed that the photocatalytic activity of semiconductor is lower than that of the photocatalytic activity of Ce-Ag-ZnO photocatalyst.

Table 2. Zn^{2+} ionic concentration (ppm) in the solution mixture after photoreaction

No. of cyclic runs	Ce-Ag-ZnO at ppm	Bare ZnO at ppm
1 st run	1.76	2.1
2 nd run	2.39	16.2
3 rd run	3.86	31.4
4 th run	4.35	49.7
Average	3.09	24.9
Initial ZnO	1000.0	1000.0
Dissolution (%)	0.309	2.49

4. CONCLUSIONS

A simple technique called, solvothermal method was adopted for the efficient production of Ce-co-doped Ag-ZnO. When taking into account, the process of degradation of (Naphthol Blue Black) NBB, under the effects of UV-A light, Ag-ZnO, Ce-ZnO, bare and even commercial ZnO, TiO₂-P25 and TiO₂ (Merck), the process of degradation of naphthol blue black was outperformed by the photocatalyst Ce-Ag-ZnO. The optimal pH level of 9 g L^{-1} and the amount of catalyst should be maintained at a value of 3 g L^{-1} for effectively eliminating the dye. Chemical Oxygen Demand (COD) values were used to prove the mineralization of molecules of naphthol blue black. A process which performs the trap of Ag and Ce is performed to describe that the developed photocatalytic activity of the catalyst involves in electron trapping by Ag and Ce. Bare ZnO is found to be less antiphotocorrosive when

compared to the photocatalyst Ce-Ag-ZnO, making it possible for the cause of reusable and photostable properties.

ACKNOWLEDGEMENT

One of the authors (M. Shanthy) is highly thankful to UGC, New Delhi, India for financial support through research project F.No 41-288/2012 (SR). One of the authors B. Subash is thankful to UGC, New Delhi, India for BSR Fellowship.

REFERENCES

- [1] L.Hinda, P.Eric, H.Ammar, K.Mohamed, E.Elimame, G.Chantal and M.H.Jean, Photocatalytic Degradation of Various Types of Dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in Water by UV-Irradiated Titania, Applied Catalysis B: Environmental, Vol. 39, No. 1, 2002, pp. 75-90, [http://dx.doi.org/10.1016/S0926-3373\(02\)00078-4](http://dx.doi.org/10.1016/S0926-3373(02)00078-4).
- [2] I.K.Konstantinou and T.A.Albanis, TiO₂-Assisted Photocatalytic Degradation of Azo Dyes in Aqueous Solution: Kinetic and Mechanistic Investigations: A Review, Applied Catalysis B: Environmental, Vol. 49, No. 1, 2004, pp. 1-14, <http://dx.doi.org/10.1016/j.apcatb.2003.11.010>.
- [3] F.B.Bouaifel, B.Sieber, N.Bezzi, J.Benner, P.Roussel, L.Boussekey, S.Szuneritsa and R.Boukherroub, Synthesis and Photocatalytic Activity of Iodine-Doped ZnO Nanoflowers, Journal of Materials Chemistry, No. 21, 2011, pp. 10982-10989, <http://dx.doi.org/10.1039/C1JM11351H>.
- [4] C.Wu, L.Shen, Y.C.Zhang and Q.Huang, Synthesis of AgBr/ZnO Nanocomposite with Visible Light-Driven Photocatalytic Activity, Materials Letters, Vol. 66, No. 1, 2012, pp. 83-85, <http://dx.doi.org/10.1016/j.matlet.2011.08.030>.
- [5] S. Wang, A Comparative Study of Fenton and Fenton-like Reaction Kinetics in Decolourisation of Wastewater, Dyes and Pigments, Vol. 76, No. 3, 2008, pp. 714-720, <http://dx.doi.org/10.1016/j.dyepig.2007.01.012>.
- [6] H.Q.Sun, S.B.Wang, H.M.Ang, M.O.Tade and Q.Li, Halogen Element Modified Titanium Dioxide for Visible Light Photocatalysis, Chemical Engineering Journal, Vol. 162, No. 2, 2010, pp. 437-447, <http://dx.doi.org/10.1016/j.cej.2010.05.069>.
- [7] A.J.Hoffman, E.R.Carraway and M.R.Hoffmann, Photocatalytic Production of H₂O₂ and Organic Peroxides on Quantum-Sized Semiconductor Colloids, Environmental Science & Technology, Vol. 28, No. 5, 1994, pp. 776-785, <http://dx.doi.org/10.1021/es00054a006>.
- [8] P.M.Dasami, K.Parameswari, S.Chitra and K.Jayamoorthy, Experimental and Quantum Mechanical Studies on the Corrosion Inhibition of Mild Steel by Quinoline Schiff Bases, DJ Journal of Engineering Chemistry and Fuel, Vol. 1, No. 4, 2016, pp. 1-16, <http://dx.doi.org/10.18831/djchem.org/2016041001>.
- [9] A.V.Dijken, A.H.Janssen, M.H.P.Smitsmans, D.Vanmaekelbergh and A.Meijerink, Size-Selective Photoetching of Nanocrystalline Semiconductor Particles, Chemistry of Materials, Vol. 10, No. 11, 1998, pp. 3513-3522, <http://dx.doi.org/10.1021/cm980715p>.
- [10] H.Zeng, W.Cai, P.Liu, X.Xu, H.Zhou, C.Klingshirn and H.Kalt, ZnO-Based Hollow Nanoparticles by Selective Etching: Elimination and Reconstruction of Metal-Semiconductor Interface, Improvement of Blue Emission and Photocatalysis, ACS Nano, Vol. 2, No. 8, 2008, pp. 1661-1670, <http://dx.doi.org/10.1021/nn800353q>.
- [11] K.Hirano, H.Asayama, A.Hoshino and H.Wakatsuki, Metal Powder Addition Effect on the Photocatalytic Reactions and the Photo-Generated Electric Charge Collected at an Inert Electrode in Aqueous TiO₂ Suspensions, Journal of Photochemistry and Photobiology A:

- Chemistry, Vol. 110, No. 3, 1997, pp. 307-311,
[http://dx.doi.org/10.1016/S1010-6030\(97\)00201-3](http://dx.doi.org/10.1016/S1010-6030(97)00201-3).
- [12] A.Sclafani and J.M.Herrmann, Influence of Metallic Silver and of Platinum-Silver Bimetallic Deposits on the Photocatalytic Activity of Titania (Anatase and Rutile) in Organic and Aqueous Media, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 113, No. 2, 1998, pp. 181-188,
[http://dx.doi.org/10.1016/S1010-6030\(97\)00319-5](http://dx.doi.org/10.1016/S1010-6030(97)00319-5).
- [13] A.Blazkova, I.Csolleova and V.Brezova, Effect of Light Sources on the Phenol Degradation using Pt/TiO₂ Photocatalysts Immobilized on Glass Fibres, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 113, No. 3, 1998, pp. 251-256,
[http://dx.doi.org/10.1016/S1010-6030\(97\)00341-9](http://dx.doi.org/10.1016/S1010-6030(97)00341-9).
- [14] K.T.Ranjit and B.Viswanathan, Synthesis, Characterization and Photocatalytic Properties of Iron-Doped TiO₂ Catalysts, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 108, No. 1, 1997, pp. 79-84,
[http://dx.doi.org/10.1016/S1010-6030\(97\)00005-1](http://dx.doi.org/10.1016/S1010-6030(97)00005-1).
- [15] X.Wang, G.Li and Y.Wang, Synthesis and Characterization of Well-Aligned Cd-Al Codoped ZnO Nanorod Arrays, *Chemical Physics Letters*, Vol. 469, No. 4-6, 2009, pp. 308-312,
<http://dx.doi.org/10.1016/j.cplett.2009.01.006>.
- [16] M.Sharma and R.M.Mehra, Sol-Gel Derived Zinc Oxide Films Alloyed with Cobalt and Aluminium, *Thin Solid Films*, Vol. 518, No. 14, 2010, pp. 3725-3730,
<http://dx.doi.org/10.1016/j.tsf.2009.10.009>.
- [17] K.Dutta, S.Das and A.Pramanik, Concomitant Synthesis of Highly Crystalline Zn-Al Layered Double Hydroxide and ZnO: Phase Interconversion and Enhanced Photocatalytic Activity, *Journal of Colloid and Interface Science*, Vol. 366, No. 1, 2012, pp. 28-36,
<http://dx.doi.org/10.1016/j.jcis.2011.09.081>.
- [18] L.C.Chen, Y.J.Tu, Y.S.Wang, R.S.Kan and C.M.Huang, Characterization and Photoreactivity of N-, S-, and C-Doped ZnO under UV and Visible Light Illumination, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 199, No. 2-3, 2008, pp. 170-178,
<http://dx.doi.org/10.1016/j.jphotochem.2008.05.022>.
- [19] G.Li, D.Qu, W.Zhao and Y.Tong, Electrochemical Deposition of (Mn, Co)-Codoped ZnO Nanorod Arrays without any Template, *Electrochemistry Communications*, Vol. 9, No. 7, 2007, pp. 1661-1666,
<http://dx.doi.org/10.1016/j.elecom.2007.03.012>.
- [20] H.Serier, O.Toulemonde and D.Bernard, Dilute Magnetic Semiconductor Properties of Ga/Al/Co-Codoped ZnO Oxides, *Materials Research Bulletin*, Vol. 47, No. 3, 2012, pp. 755-762,
<http://dx.doi.org/10.1016/j.materresbul.1.2011.12.006>.
- [21] F.Zhu-Ge, Z.Z.Ye, L.P.Zhu, J.G.L, B.H.Zhao, J.Y.Huang, Z.H.Zhang, L.Wang and Z.G.Ji, Electrical and Optical Properties of Al-N Co-Doped p-type Zinc Oxide Films, *Journal of Crystal Growth*, Vol. 268, No. 1-2, 2004, pp. 163-168,
<http://dx.doi.org/10.1016/j.jcrysgro.2004.05.008>.
- [22] C.P.Liu and G.R. Jeng, Properties of Aluminum Doped Zinc Oxide Materials and Sputtering Thin Films, *Journal of Alloys and Compounds*, Vol. 468, No. 1-2, 2009, pp. 343-349,
<http://dx.doi.org/10.1016/j.jallcom.2008.01.053>.
- [23] T.Ratana, P.Amorpnitoksuk and S.Suwanboon, The Wide Band Gap of Highly Oriented Nanocrystalline Al Doped ZnO Thin Films from Sol-Gel Dip Coating, *Journal of Alloys and Compounds*, Vol. 470, No. 1-2, 2009, pp. 408-412,
<http://dx.doi.org/10.1016/j.jallcom.2008.02.081>.

- [24] T.T.Zhao, T.Yang, B.Yao, C.X.Cong, Y.R.Sui, G.Z.Xing, Y.Sun, S.C.Su, H.Zhu and D.Z.Shen, Growth Ambient Dependent Electrical Properties of Lithium and Nitrogen Dual-Doped ZnO Films Prepared by Radio-Frequency Magnetron Sputtering, *Thin Solid Films*, Vol. 518, No. 12, 2010, pp. 3289–3292, <http://dx.doi.org/10.1016/j.tsf.2009.09.008>.
- [25] M.Palacio, P.I.Villabrille, G.P.Romanelli, P.G.Vazquez and C.V.Caceres, Ecofriendly Liquid Phase Oxidation with Hydrogen Peroxide of 2,6-Dimethylphenol to 2,6-Dimethyl-1,4-Benzoquinone Catalyzed by TiO₂-CeO₂ Mixed Xerogels, *Applied Catalysis A: General* Vol. 359, No. 1–2, 2009, pp. 62–68, <http://dx.doi.org/10.1016/j.apcata.2009.02.032>.
- [26] Y.Xie and C.Yuan, Visible-Light Responsive Cerium Ion Modified Titania Sol and Nanocrystallites for X-3B Dye Photodegradation, *Applied Catalysis B: Environmental*, Vol. 46, No. 2, 2003, pp. 251–259, [http://dx.doi.org/10.1016/S0926-3373\(03\)00211-X](http://dx.doi.org/10.1016/S0926-3373(03)00211-X).
- [27] F.B.Li, X.Z.Li, M.F.Hou, K.W.Cheah and W.C.H.Choy, Enhanced Photocatalytic Activity of Ce³⁺-TiO₂ for 2-Mercaptobenzothiazole Degradation in Aqueous Suspension for Odour Control, *Applied Catalysis A: General*, Vol. 285, No. 1–2, 2005, pp. 181–189, <http://dx.doi.org/10.1016/j.apcata.2005.02.025>.
- [28] N.Sasirekha, S.John, S.Basha and K.Shanthi, Photocatalytic Performance of Ru Doped Anatase Mounted on Silica for Reduction of Carbon Dioxide, *Applied Catalysis B: Environmental* Vol. 62, No. 1–2, 2006, pp. 169–180, <http://dx.doi.org/10.1016/j.apcatb.2005.07.009>.
- [29] K.Nagaveni, M.S.Hegde and G.Madras, Structure and Photocatalytic Activity of Ti_{1-x}M_xO_{2+δ} (M = W, V, Ce, Zr, Fe, and Cu) Synthesized by Solution Combustion Method, *The Journal of Physical Chemistry B*, Vol. 108, No. 52, 2004, pp. 20204–20212.
- [30] W.K.Jo, J.T.Kim and J.Hazard, Application of Visible-Light Photocatalysis with Nitrogen-Doped or Unmodified Titanium Dioxide for Control of Indoor-Level Volatile Organic Compounds, Vol. 164, No. 1, 2009, pp. 360–366, <http://dx.doi.org/10.1016/j.jhazmat.2008.08.033>.
- [31] B.Krishnakumar and M.Swaminathan, Influence of Operational Parameters on Photocatalytic Degradation of a Genotoxic Azo Dye Acid Violet 7 in Aqueous ZnO Suspensions, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol. 81, No. 1, 2011, pp. 739–744, <http://dx.doi.org/10.1016/j.saa.2011.07.019>.
- [32] Andrea Sandra Christine D’Cruz and K.R.Sankaran, Optical and Self-Assembly studies of some New Perylene Tetracarboxylic Diimides, *DJ Journal of Engineering Chemistry and Fuel*, Vol. 1, No. 4, 2016, pp. 23–42, <http://dx.doi.org/10.18831/djchem.org/2016041003>
- [33] B.Subash, B.Krishnakumar, M.Swaminathan and M.Shanthi, Synthesis and Characterization of Cerium–Silver Co-Doped Zinc Oxide as a Novel Sunlight-Driven Photocatalyst for Effective Degradation of Reactive Red 120 dye, *Materials Science in Semiconductor Processing*, Vol. 16, No. 4, 2013, pp. 1070–1078, <http://dx.doi.org/10.1016/j.mssp.2013.04.001>.
- [34] B.Subash, B.Krishnakumar, M.Swaminathan and M. Shanthi, Highly Efficient, Solar Active, and Reusable Photocatalyst: Zr-Loaded Ag–ZnO for Reactive Red 120 Dye Degradation with Synergistic Effect and Dye-Sensitized Mechanism, *Langmuir*, Vol. 29, No. 3, 2013, pp. 939–949, <http://dx.doi.org/10.1021/la303842c>.

- [35] B.Subash, B.Krishnakumar, M.Swaminathan and M.Shanthi, ZnS–Ag–ZnO as an Excellent UV-Light-Active Photocatalyst for the Degradation of AV 7, AB 1, RR 120, and RY 84 Dyes: Synthesis, Characterization, and Catalytic Applications, *Industrial & Engineering Chemistry Research*, Vol. 53, No. 33, 2014, pp. 12953–12963, <http://dx.doi.org/10.1021/ie5018145>.
- [36] B.Subash, B.Krishnakumar, M.Swaminathan and M.Shanthi, Enhanced Photocatalytic Performance of WO₃ Loaded Ag–ZnO for Acid Black 1 Degradation by UV-A Light, *Journal of Molecular Catalysis A: Chemical*, Vol. 366, 2013, pp. 54–63, <http://dx.doi.org/10.1016/j.molcata.2012.09.008>.
- [37] B.Subash, B.Krishnakumar, M.Swaminathan and M. Shanthi, β-Ag₂S–ZnO as a Novel Sunshine Photocatalyst for the Effective Degradation of RR 120 dye, *Powder Technology*, Vol. 241, 2013, pp. 49–59, <http://dx.doi.org/10.1016/j.powtec.2013.03.002>.
- [38] B.Krishnakumar, K.Selvam, R.Velmurugan and M.Swaminathan, Influence of Operational Parameters on Photodegradation of Acid Black 1 with ZnO, *Desalination and Water Treatment*, Vol. 24, No. 1-3, 2012, pp. 132-139, <http://dx.doi.org/10.5004/dwt.2010.1466>.
- [39] R.Velmurugan, K.Selvam, B.Krishnakumar and M.Swaminathan, An Efficient Reusable and Antiphotocorrosive Nano ZnO for the Mineralization of Reactive Orange 4 under UV-A Light, *Separation and Purification Technology*, Vol. 80, No. 1, 2011, pp. 119–124, <http://dx.doi.org/10.1016/j.seppur.2011.04.018>.
- [40] A.Mills and M.McGrady, A Study of New Photocatalyst Indicator Inks, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 193, No. 2–3, 2008, pp. 228–236, <http://dx.doi.org/10.1016/j.jphotochem.2007.06.029>.
- [41] G.M.Mura, M.L.Ganadu, P.Lombardi, G.Lubinu, M.Branca and V.Maida, A Preliminary Comparison between Hydrogenase and Oxygen as Electron Acceptors in Irradiated Aqueous Dispersion of Titanium Dioxide, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 148, No. 1–3, 2002, pp. 199–204, [http://dx.doi.org/10.1016/S1010-6030\(02\)00043-6](http://dx.doi.org/10.1016/S1010-6030(02)00043-6).