

## Sunlight Assisted Degradation of Methylene Blue as a Model Dye using Bismuth Oxychloride Nanoparticles: Ecofriendly and Industry Efficient Photocatalysis for Waste Chemical Treatment

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In this study, an efficient sunlight triggered dye degradation was demonstrated using methylene blue as a model dye and bismuth oxychloride nanoparticles were used as photocatalyst. Two different types of nanoparticles, nanoflower and nanodisk, were prepared to understand the effect of morphology on the photocatalysis. Both the particles were prepared following a straightforward and easy methodology from readily available chemicals. The particles were characterized using scanning electron microscope, Fourier transformed infrared spectroscopy, powder X-ray diffraction. UV-visible spectroscopy and colorimeter were used to evaluate the photocatalytic activity of the catalyst. Both the nanoparticles were able to degrade the dye completely within 3-4 h under visible light. The photocatalytic rate constant analysis demonstrates that out of two morphology, nanoflower is found to be more effective than nanodisk towards dye degradation. The sunlight was also used to understand whether the photocatalyst can degrade the dye or not in presence of sunlight only. Both nanoparticles were able to degrade the dye 100 % in presence of sunlight within maximum 4 h. The photocatalytic dye degradation in presence of sunlight was conducted in between 10 a.m. to 4 p.m. when the maximum amount of sunlight is available with high intensity and energy. The catalysts were 100 % active after the first cycle and upto four cycles the dye degradation efficiency remain around 60-80%. The study demonstrates that sunlight can degrade the dye in presence of these photocatalyst which clearly indicates its energy saving approach thus making it more economic and green methodology for the industries.

**Keywords:** Photocatalysis, Nanoflower, Nanodisk, Dye degradation, Bismuth, Sunlight.

### INTRODUCTION

For the last few decades, earth is suffering from many environmental problems like global warming, water pollution and water scarcity, waste disposal, land degradation and management, *etc.* [1]. Out of these problems, recently, waste management is one of the biggest challenges to the scientist worldwide because most of the industries produces and releases large amount of solid as well as liquid wastes every day [2]. According to the Press Information Bureau, India; almost 62 million tons of wastes is produced in India per year out of which almost 50 % is organic waste and most of it is exposed to the environment directly and proper disposal of this large amount of wastes is a real challenge to the industries [3,4]. Solid wastes are generally recycled in several steps or burned to produce energy through a process known as incineration [5]. When it comes to liquid waste, it is even more difficult to dispose or destroy them because

most of the time liquid wastes come with a mixture of several chemicals and majorly are soluble in water, which causes huge water pollution both in surface water and in ground water [6-8]. As the population increasing day by day, the demand for food, medicine, pesticide, fertilizers, clothes, paints, paper, dye, solvents and many more household materials are also increasing and so as the number of industries [9]. There are a number of industries *e.g.* pharmaceutical, dye, pesticides, paper, pulpwood, chemical industries, which produce lots of liquid wastes [10]. The proper disposal of these wastes is required for the reduction of many environmental problems like water and soil pollution, ground water contamination, landfill, *etc.* [11]. Industries release many toxic chemicals, which are highly dangerous to our health even if their concentration is very low (ppm or ppb level) in the environment [12]. So, destruction of these toxic chemicals is utmost important to reduce its bad effects on environment [13]. The conventional way to degrade these chemicals suffer

from many disadvantages like huge amount of energy requirement, inefficiency, *etc.* [14]. So, it is really important to develop an industry efficient and energy saving methodology to degrade these toxic chemicals. Out of several methods developed over the last few years for the degradation of toxic organic chemicals, photocatalytic degradation using nanoparticles due to its several advantages like energy saving, no pollution, more efficiency, remains one of the favorite techniques to the scientists [15].

Photocatalytic degradation is a technique which use ultra-violet or visible light as a source of energy to carry out the reactions and has been already applied in various field including the destruction or transformation of toxic chemicals to non-hazardous chemicals [16]. Several metal based nanomaterials are developed in the last few years *e.g.* copper, gold, silver, titanium dioxide, zinc oxide, bismuth oxide, *etc.* for the photocatalysis [17]. All these nanomaterials have one common property *i.e.* light absorption property which is the prime requirement for the photocatalytic activities of these materials which finally causes degradation of the organic pollutants [18]. Due to easy and free of cost availability of sunlight, environmental friendly nature, visible light triggered photocatalysis is always the ultimate choice of the scientist because it almost nullifies the energy cost which again benefits the industries and saves lots of money as well as indirectly save non-renewable energy resources like coal, petroleum, natural gas, *etc.* [19].

The basic mechanism behind the visible light induced photocatalytic degradation of organic molecules is electron-hole pair generation within the nanoparticles [20]. As soon as the energy of the incident light crosses the band gap of nanoparticles, electrons are ejected and move to the conductance band keeping hole in the valance band, creating electron hole pair [21]. Now, because of the availability of huge surface area in the nanosized materials, electrons can easily move to the surface of the nanoparticles and performs various redox processes which is the basis for degradation or transformation of the chemicals. The easy availability of surface electrons in the nanoparticles result the creation of many reactive oxygen species (ROS) *e.g.* hydroxide radical, peroxide radical, ozone, *etc.* which destroy the chemicals through several intermediate chemical reactions [22].

Materials like BiOX (X = F, Cl, Br and I) oxyhalides have been considered because of its easy synthesis, tunable size, shape, morphology, less band gap which can work under visible radiations [23-27]. The BiOCl possess an outstanding photocatalytic performance for degradation of dyes under UV irradiation. Bismuth oxychloride possesses an open layered structure in which  $[\text{Bi}_2\text{O}_2]^{2+}$  layer is sandwiched by two  $[\text{Cl}_2]^{2-}$  layers in the crystal [28,29]. Because of its tunable nature, one can easily vary the morphology and band gap as per their requirement and it is possible to conduct photocatalysis under sunlight. Bismuth oxychloride was already reported to degrade many organic dyes and it exhibits an outstanding optical, electrical properties and non-toxicity [30,31]. The processes of removing effluents by heterogeneous photocatalysts under visible radiations are of low cost, clean and have biological photostability. The bulk BiOCl under visible light radiations does not degrade effluents, organic dyes effectively because of its large band gap. Recent studies revealed that nano-forms of

BiOCl like (fibre, flower, film, sheet and composite) is an effective photocatalyst to degrade organic-dyes under visible like radiations [32-34]. Although there are several reports, which shows the photocatalytic behaviour of BiOCl in presence of visible light but they lack two of the very important characteristics of visible light triggered photocatalysis *i.e.* the efficiency and effects of sunlight on photocatalytic activity.

The present work uses visible light as well as sunlight and have shown that nanoform of BiOCl (nanoflower and nanodisk) is able to degrade an important dye in presence of sunlight over a period of few hours. The efficiency of the system is also very high even after 3-4 catalytic cycles. Hereby, BiOCl is introduced with two morphology *e.g.* nanoflower and nanodisk, that have less band gap and these nanoforms degraded effectively effluents and organic dyes under visible light as well as in sunlight radiations. It has a band gap of around 3.34-3.46 eV, which is also close to the energy available with the sunlight thus it is quite possible that it can degrade the dyes in presence of sunlight [35-37].

## EXPERIMENTAL

Polyvinyl pyrrolidone (PVP), Bismuth nitrate pentahydrate, ferric chloride hexahydrate, bismuth trichloride, ammonia solution, methylene blue dye and ethanol were purchased from Loba Chemie Pvt. Ltd. Mumbai (India). The water involved in this work is double distilled water. Ethylene glycol was obtained from Qualigens Fine Chemicals, Mumbai (India).

X-Ray diffraction spectra were recorded over a range of 50 to 140° 2 $\theta$  on X ray diffractometer (X'Pert Pro), Netherlands which uses monochromatic CuK $\alpha$  radiation having a wavelength of 1.54 Å. The morphology was characterized by Field Emission Scanning electron microscope (FESEM) using a Merlin Compact, Germany. Fourier transform infrared (FT-IR) was recorded on an FT-IR spectrophotometer (FTIR-8400S) Shimadzu to examine the molecular structure. To measure photocatalytic activity of methylene blue solutions (UV-1800 Shimadzu) UV-Vis spectrophotometer was used.

### Preparation of photocatalyst

**Bismuth oxychloride nanodisk:** In a typical synthesis, 1.50 g of polyvinyl pyrrolidone was dissolved with 60 mL distilled water in a 100 mL beaker. Keep this solution under continuous slow stirring for 15 min. After the complete dissolution of polyvinyl pyrrolidone, 1.42 g of bismuth trichloride added into the above mixture. Ammonia solution was used to adjust the pH of the suspension to ~ 9 and keep the solution undisturbed for 20 min. Wet precipitates were collected and washed with ethanol and distilled water thrice, then products were collected and dried at 60-80 °C in an oven.

**Bismuth oxychloride nanoflower:** Bismuth nitrate pentahydrate (0.972 g) was added into 15 mL ethylene glycol in a 100 mL beaker. Keep this solution under vigorous stirring and sonication for 10 min. The mixture was dispersed to form a homogeneous solution. In another beaker, ferric chloride hexahydrate (0.541 g) was added into 15 mL distilled water under stirring for 5 min to form a homogeneous solution. Then, above two solutions were mixed and a white suspension was formed immediately. White suspension was filtered and washed

with distilled water and ethanol for several times to remove the residual ions. The final products were then collected and dried at 70 °C.

**Preparation of dye solution:** To prepare stock solution of M/1000 methylene blue, 0.0373 g of the dye is dissolved in 100 mL distilled water. Took a 1 mL of prepared M/1000 methylene blue stock solution in 100 mL conical flask to prepare 100 mL methylene blue solution of  $1 \times 10^{-5}$  M.

**Photodegradation using simulated sunlight:** Prepare methylene blue solution and then find out  $\lambda_{\max}$  of the solution by using colorimeter. Set observed  $\lambda_{\max}$  value on colorimeter then note down initial absorbance of prepared  $1 \times 10^{-5}$  M dye solution from colorimeter at zero time. Fixed the two rubber tubes, one tube in outlet and another one in inlet of the double walled beaker. Second side of rubber tube fix in tap and second side of rubber tube leave open in sink. Leave tap water on slowly for water circulation in outer wall of double walled beaker to maintain temperature. Place double walled beaker on magnetic stirrer. Pour 100 mL of prepared  $1 \times 10^{-5}$  M dye solution in double walled beaker. Then added 50 mg of BiOCl nanoflower/nanodisk in the methylene blue solution. Keep medium size Teflon coated magnet in the solution. Set halogen lamp 30 cm away from the double walled beaker. Switch on the magnetic stirrer in slow movement. After 15 min time interval, takeout about 4-5 mL of solution from beaker with pipette then pour in centrifuge tube and keep it inside the centrifuge machine and stir for 2 min till photocatalyst particles get settle down. Then takeout small amount of clean methylene blue solution from centrifuge tube carefully with the help of separate clean pipette then transfer solution to cuvette and note down absorbance on colorimeter at observed  $\lambda_{\max}$ . Repeat this process after every 15 min time interval and note down the reading till the absorbance of dye solution become 0.00.

**Photodegradation in presence of direct sunlight:** Prepare methylene blue solution and then find out  $\lambda_{\max}$  of the solution by using colorimeter. Set observed  $\lambda_{\max}$  value on colorimeter then noted the initial absorbance of prepared  $1 \times 10^{-5}$  M dye solution from colorimeter at zero time. Pour 100 mL of prepared  $1 \times 10^{-5}$  M dye solution in double walled beaker. Then added 50 mg of BiOCl nanoflower/nanodisk in methylene blue solution. Keep this solution in sunlight radiations and after 15 min time interval, small amount of methylene blue solution from beaker

carefully with the help of separate clean pipette was transferred to cuvette and noted the absorbance on colorimeter at observed  $\lambda_{\max}$ , repeat this process after every 15 min time interval and till the absorbance of dye solution become zero.

## RESULTS AND DISCUSSION

**SEM analysis:** The morphology of nanoparticles was characterized using field emission scanning electron microscope. Fig. 1 depicts both nanoflower and nanodisk morphology of the nanoparticles. Some larger nanoparticles were found because of some aggregation of the particles. The size of nanoflower particles were around 500-800 nm, whereas the size of nanodisk were around 100-150 nm.

**PXRD analysis:** Powder X-ray diffraction (PXRD) analysis was conducted to confirm the formation of BiOCl and to check the purity and crystal nature of the as-synthesized particles. Around 500 mg of dried powder samples were used to analyze the PXRD pattern. Fig. 2 shows the PXRD pattern of both nanoparticles. The major diffraction peak arises at  $2\theta$  values of 11.98°, 25.81°, 32.56°, 33.21°, 46.81° for nanoflower and at 11.88°, 25.92°, 32.56°, 33.53°, 46.59° for nanodisk. The  $2\theta$  values correspond to the 001°, 011°, 110°, 102° and 020° plane of the synthesized nanoparticles. All the peaks correspond to tetragonal structure of BiOCl nanoparticles which was indexed with JCPDS file number 06-0249. There were no other major peaks which clearly indicates the purity and single-phase structure of the synthesized particles.

**FT-IR analysis:** To understand the functional groups and chemical structure of the synthesized nanoparticles, Fourier transform infrared spectroscopy analysis was conducted for the both nanodisk and nanoflower. It is clear from Fig. 3 that both the particles show similar FT-IR spectrum because of the similarities in their chemical structure. The broad peak arises at 3350-3200  $\text{cm}^{-1}$  corresponds to the presence of surface -OH group in nanodisk and nanoflower, respectively. The most important feature of FTIR spectrum is the appearance of the peaks in fingerprint region. The peaks at 520 and 513  $\text{cm}^{-1}$  corresponds to the stretching vibration of Bi-O bond which is characteristic peak of bismuth oxide. The peak at 650 and 690  $\text{cm}^{-1}$  corresponds to the stretching vibration of O-Cl in solid state. Thus, all the peaks in FTIR spectrum also supports the formation of BiOCl nanoparticles.

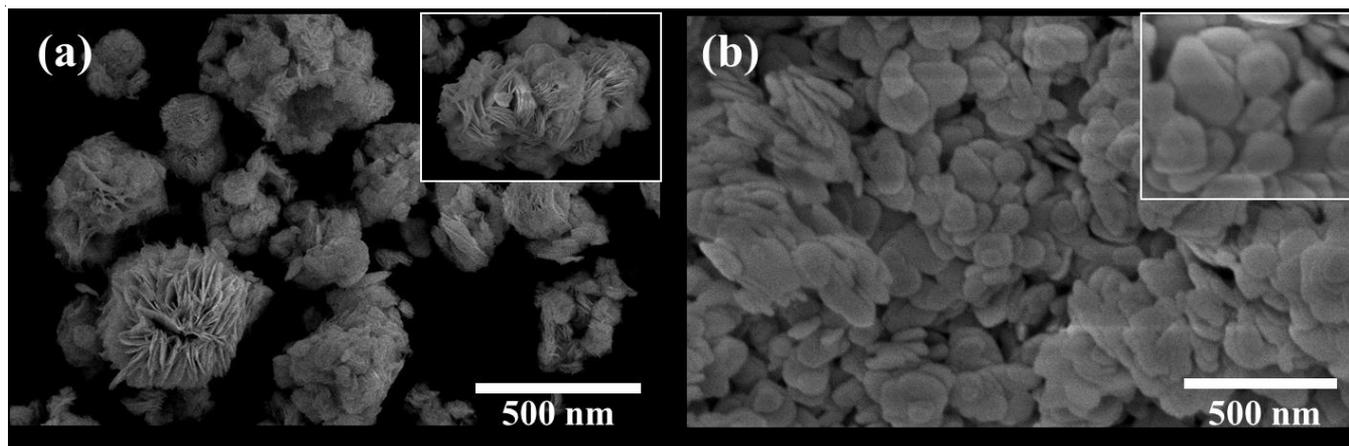


Fig. 1. SEM images of (a) nanoflower (b) nanodisk

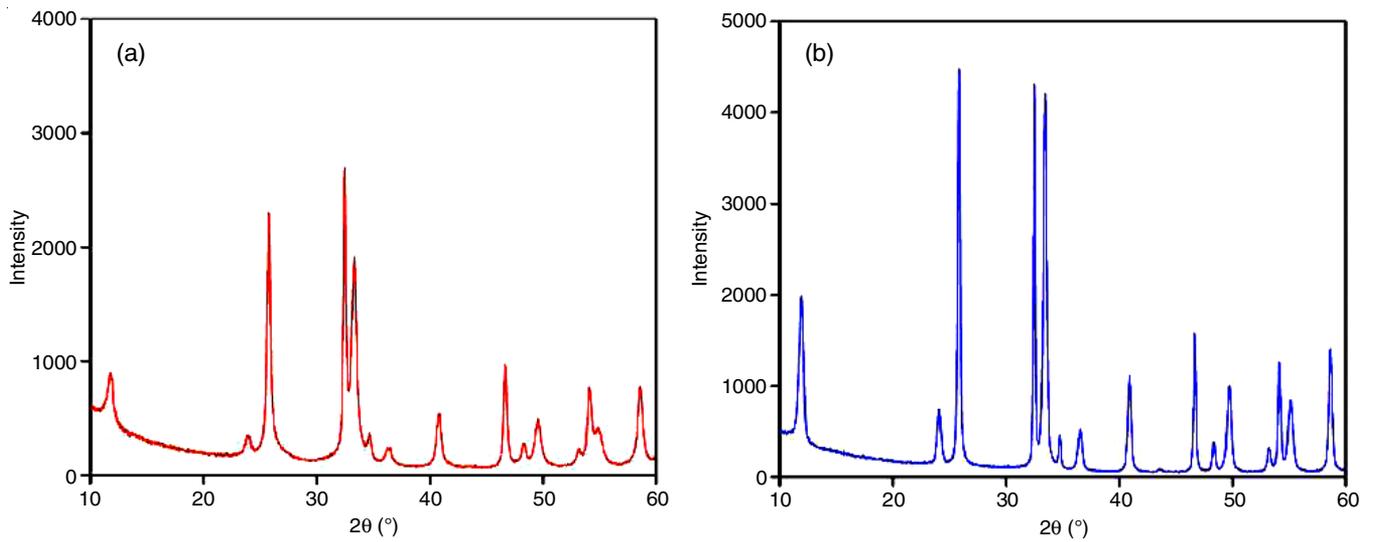


Fig. 2. PXRD pattern of (a) nanoflower (b) nanodisk

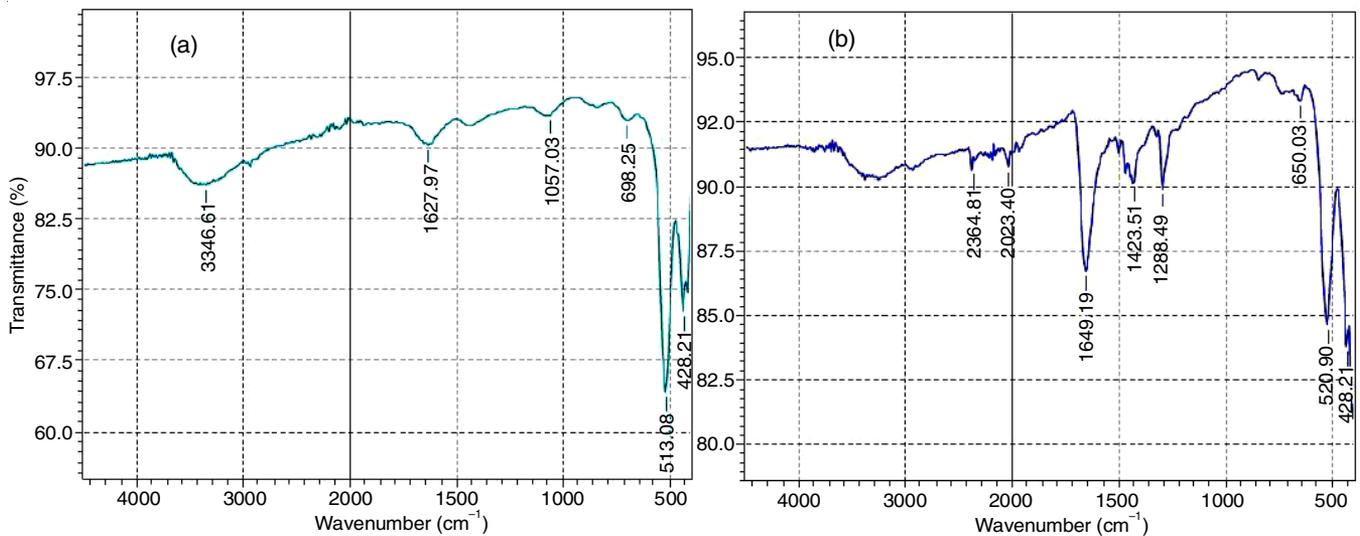


Fig. 3. FT-IR spectra of (a) nanodisk and (b) nanoflower

**UV-visible analysis:** To understand the absorption peaks and chemical structure of the synthesized nanoparticles, UV-Vis-spectroscopy analysis was conducted for the both nanodisk and nanoflower. Nanoflower and nanodisk size of BiOCl nano-

particles exhibit an absorption peak at 266 and 264 nm, respectively (Fig. 4).

**Photophysical studies of methylene blue dye:** Methylene blue is a thiazine cationic dye. Its reduced form is colourless

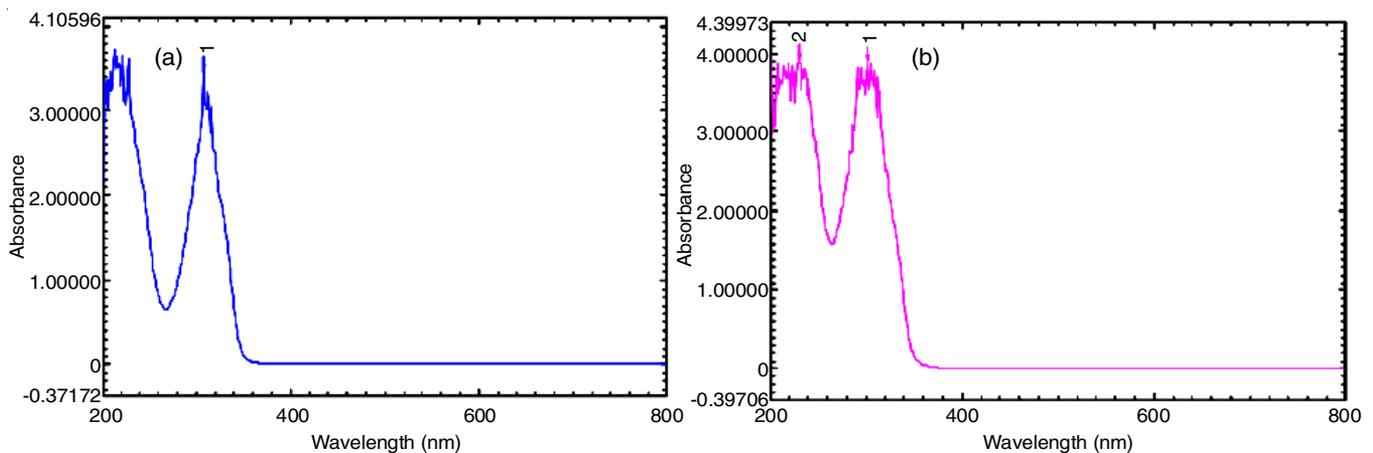


Fig. 4. UV-visible spectra of (a) nanoflower (b) nanodisk

and with oxidation, it changes to deep blue. Methylene blue is not sensitive towards pH change and stable under various solvent system (Fig. 5). So, this dye estimated to be degraded in air by photocatalytic reaction which uses either hydroxyl radicals or oxide ions produced on the surface of photocatalyst that helps in degradation of dye.

### Photocatalytic activity

**Photocatalytic evaluation using visible light lamp:** The photocatalytic activity of BiOCl nanoparticles was assessed by measuring the degradation of methylene blue dye under visible light radiations. The concentration of methylene blue dye was analyzed by Colorimeter (Labtronics-LT12). A 500 W Halogen Luminaire lamp (Crompton) was used as the light source. The distance between the surface of solute and light source was about 15 cm during stirring the solution. In 100 mL dye solution, 50 mg sample of photocatalyst was added and the solution was stirred till absorbance is zero. The temperature of double walled beaker containing dye solution was maintained by continuous circulating water. At given irradiation time intervals (after 15 min), about 2 mL of solution was taken out for the analysis of remaining dye concentration. The gradual decrease of absorption value indicates the depletion of dye concentration in the solution, which clearly suggests that dye degradation occurred in presence of the catalyst.

**Nanoflower versus nanodisk:** In order to investigate the photocatalytic activities of the photocatalysts, methylene blue

is adopted as the target pollutant. The photocatalysts are firstly stirred in the degradation system under visible light radiations. Under visible light radiations, photocatalytic degradation of methylene blue are performed with variation in concentrations with irradiation time over different photocatalysts (Fig. 6).

The rate constant for nanoflower is  $0.94 \text{ s}^{-1}$  and for nanodisk is  $0.52 \text{ s}^{-1}$ . This analysis revealed that rate constant for nanoflower is almost two times higher than nanodisk. In the presence of visible light as well as in sunlight radiations, an electron-hole pairs are generated on the surface of BiOCl nanoparticles. The oxygen vacancies reduced the band gap between the conduction and valence band that enhance the harvesting of low energy photons in the visible range, which facilitates the generation of photogenerated carries. In addition, due to the band alignment, the as-generated electrons could be injected to the conduction band of BiOCl. The positively charged holes remained in valence band could directly function as oxide species and hydroxyl radicals for dye degradation. In addition, compared with pure BiOCl, nanoparticles of BiOCl could also improve the adsorption capability on methylene blue molecules, which finally results in the improved photocatalytic degradation efficiency of the BiOCl nanoparticles. The result demonstrates that nanoflower is more efficient than nanodisk for degradation of methylene blue dye.

**Comparative study of nanoflower in dark, visible and sunlight radiations:** It is observed that nanoflower in visible radiations is more efficient with high rate constant and takes

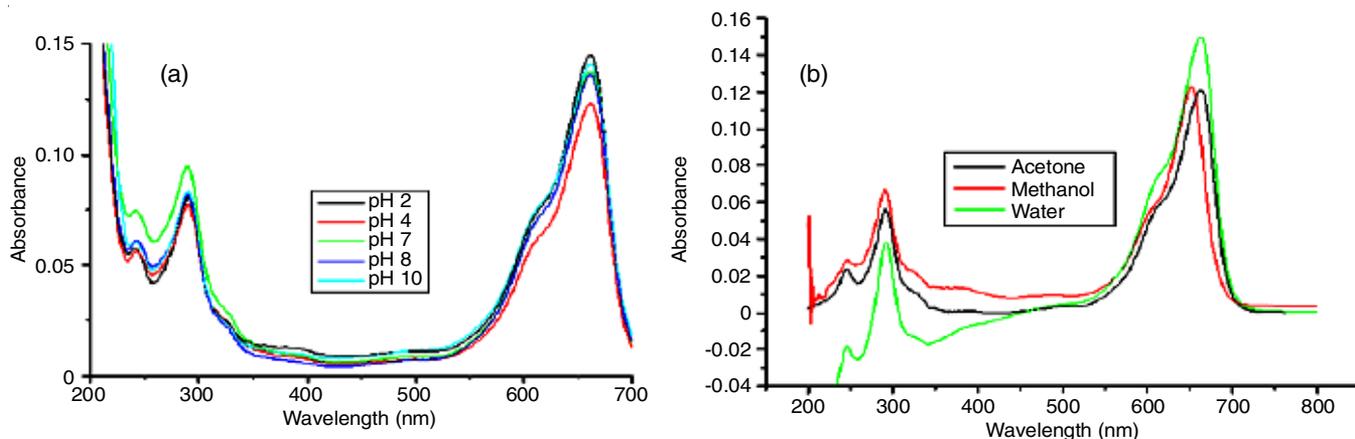


Fig. 5. Absorption spectra of methylene blue (a) at different pH (b) in different solvent system

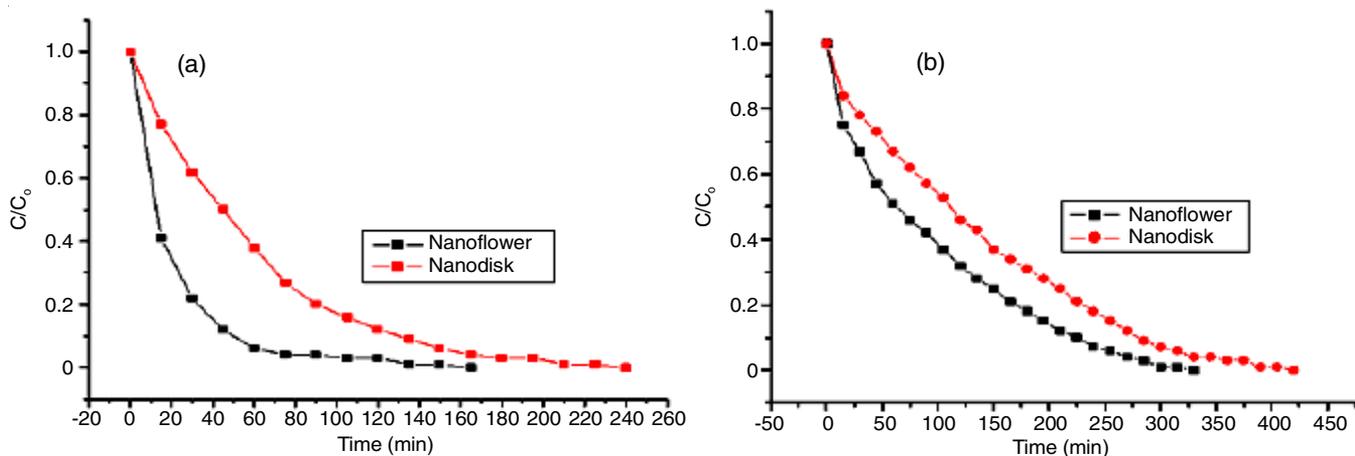


Fig. 6. Absorption value of methylene blue in presence of nanoflower and nanodisk (a) in visible light radiation (b) in sunlight radiations

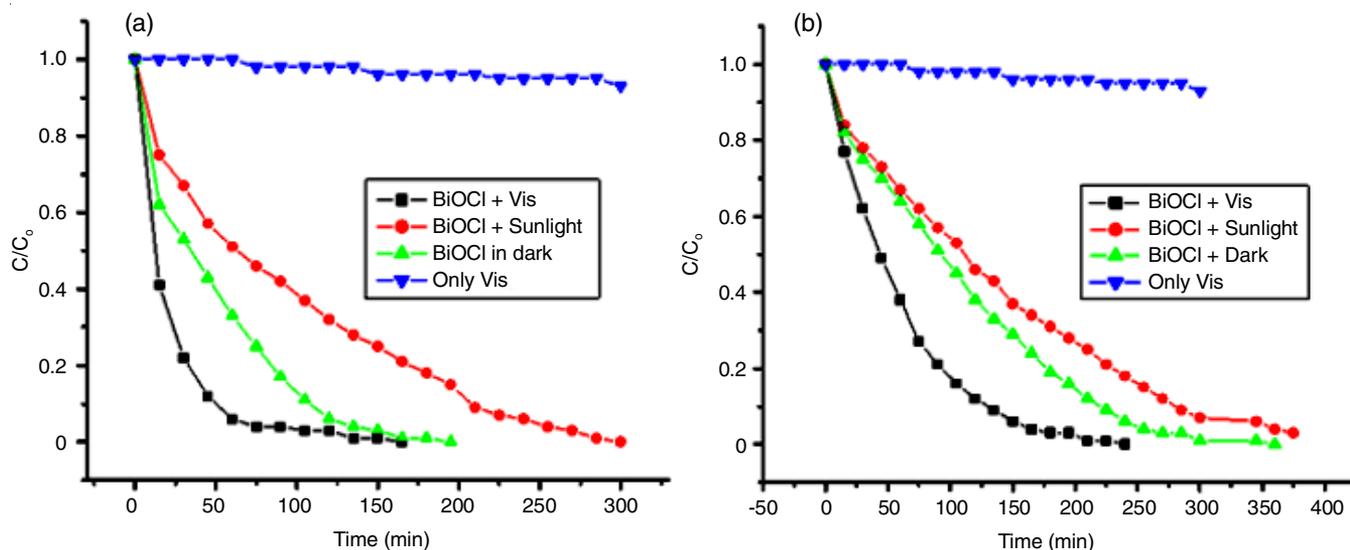


Fig. 7. Comparative study of methylene blue degradation by photocatalyst (a) nanoflower (b) nanodisk in visible, sunlight radiations and in dark

less time (approx. 170 min) for degradation of dye than in sunlight and dark (Fig. 7). In dark and sunlight radiations, dye takes more time to degrade and had less rate constant value than in visible light radiations.

**Comparative study of nanodisk in dark, visible and sunlight radiations:** Similarly, when we compared nanodisk in visible, sunlight and in dark. It was observed that nanodisk in visible radiations is more efficient with high rate constant and take less time (approx. 250 min) for degradation of dye than in sunlight and dark. In sunlight radiations and dark, dye takes more time to degrade and had less rate constant value than in visible light radiations.

**Variation of dye concentration under visible light radiations:** After the comparative study of nanoflower and nanodisk in visible, sunlight radiations and in dark, dye concentration was varied to observe the effect of dye on the efficiency of the photocatalyst by keeping the photocatalyst concentration constant. Fig. 8 shows that upto  $1 \times 10^{-2}$  M dye concentration, photocatalyst works efficiently and had high rate constant value. As the concentration increases, the rate constant decreases since the dye molecules to photocatalyst ratio decreases.

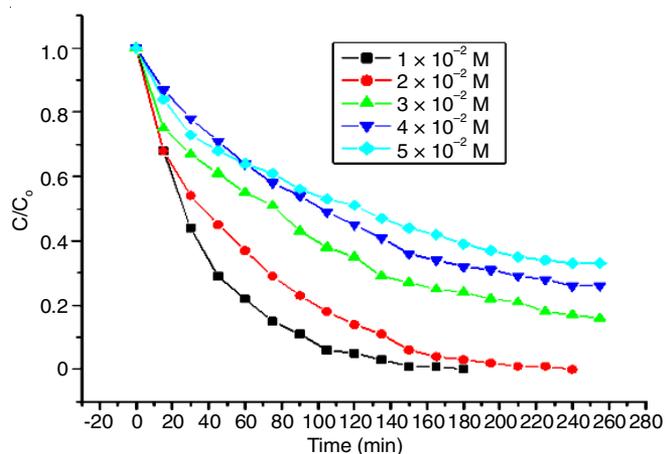


Fig. 8. Variation of dye concentration with nanoflower in visible light radiations

**Variation of photocatalyst (nanoflower) concentration under visible light radiations:** After observing that nanoflower is more efficient than nanodisk for degradation of dye and upto  $1 \times 10^{-2}$  M dye concentration, nanoflower is working very efficiently with high rate constant value. Fig. 9 shows that as soon as the amount of photocatalyst increases the rate constant increases because the dye molecules to photocatalyst ratio increases which further helps to degrade dye molecules much faster.

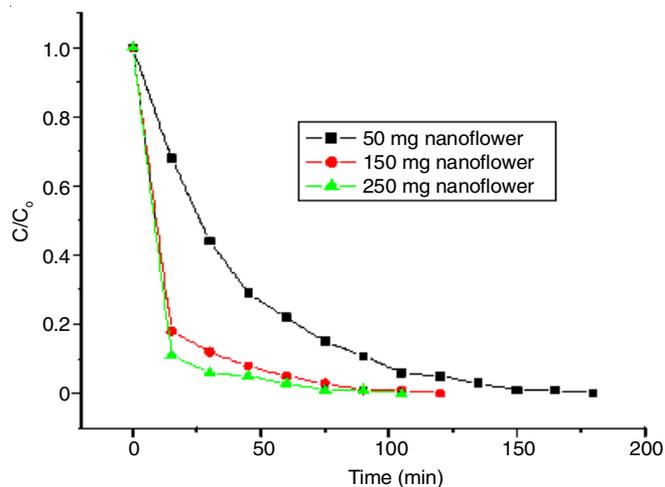


Fig. 9. Variation of photocatalyst (nanoflower) concentration under visible light radiations

## Conclusion

In this study, we have successfully synthesized BiOCl nanoflower and nanodisk following a straightforward method. Both the nanoparticles were able to degrade methylene blue dye completely within 3-4 h under visible light. However, out of two morphology, nanoflower is found to be more effective than nanodisk towards dye degradation. Dye degradation efficiency of nanoflower is higher than nanodisk and bulk BiOCl. Both the nanoparticles were able to degrade dye 100 % in presence

of sunlight within maximum 4 h of time. The catalysts were active after the first cycle and upto three cycles, the dye degradation efficiency remains around 60 %. The band gap structure of BiOCl nanoparticles was also the critical factor for the excellent photocatalytic activities under visible light irradiation. This study demonstrates that sunlight can degrade the dye in presence of these photocatalysts which minimize its energy cost and hope that it will help the future development of the application of nanoparticles in liquid wastes management.

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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