International Journal of Researches in Biosciences, Agriculture & Technology | January 2014 Issue-2, Volume-1 | ISSN No. (Online) 2347-517X

STUDY OF STRUCTURAL, PHOTOPHYSICAL AND PHOTOCATALYTIC PROPERTIES OF BiOCl

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Abstract

The BiOCl, a photocatalyst that could effectively utilize visible light, was prepared by hydrolysis method. The structural, photophysical and photocatalytic properties BiOCl have been investigated. Nile blue (NB) was selected as modal target to determine the photocatalytic activity of BiOCl. The photodegradation rate of this dye catalyzed by BiOCl under visible light irradiation. Complete removal of aqueous NB has been realized after visible light irradiation for 160 min with existing BiOCl as a catalyst. The reduction of the chemical oxygen demand (COD), and the evolution of CO_2 revealed complete mineralization of aqueous NB during the photocatalytic process by this photocatalyst.

Keywords: BiOCl; Nile blue; Visible light irradiation; photocatalysis; Mineralization

1. Introduction

During the past decades, besides the focused work on TiO_2 modifications, many efforts have been made to develop other novel efficient photocatalysts [1-3]. Several compounds have been prepared by different methods in order to develop new materials that can perform efficiently the redox reactions concerned in the photocatalysis process. In addition, these materials must be activated under visible light to have a sustainable process in photocatalytic reactions. However, most of these materials are titania-based oxides and their preparation is economically costly, time consuming and their activities are still low [4-7]. This situation made a big role of the development of new semiconductor materials that could be activated under both UV and visible light. Besides excellent performance in the oxidative cracking or

dehydrogenation reactions, layered bismuth oxyhalides have demonstrated outstanding photocatalytic activities and, more recently, attracting research interest in both the experimental and theoretical aspects [8-12]. Recently, bismuth oxyhalides (BiOX, X= Cl, Br, I) have been investigated because of their unique properties and potential applications. BiOX compounds crystallize in the tetragonal structure, a layer structure characterized by $[Bi_2O_2]$ slabs interleaved by $[Cl_2]$ [8,13]. They have been applied as catalysts which show high photocatalytic activity, because of the Bi^{3+} with s^2 configuration and the layer crystal [14]. The photocatalytic behaviour of BiOCl as a potential visible light photocatalyst was first studied by An et al [15]. This work revealed that BiOCl could perform as an excellent photocatalyst and solar-energy-conversion material. Photocatalytic activities for O_2 evolution/water splitting and the degradation of the RhB and isopropanol under visible-light irradiation were discussed in detail. Encouraged by this progress, we studied enhanced visible-light driven photocatalytic activity of the as-prepared BiOCl by performing the catalytic degradation of nile blue (NB) in aqueous solution. BiOCl can also degrade and even completely mineralize NB under visible light irradiation, indicating its high photocatalytic activity.

2. Experimental:

2.1 Synthesis of BiOCl

BiOCl powder was synthesized by a hydrolysis method. In this synthesis reagent Bi_2O_3 (AR, Aldrich) was dissolved in excessive concentrated hydrochloric acid (AR, Merck), to receive a transparent $BiCl_3$-HCl aqueous solution. When the pH value of the solution was adjusted between 2 to 3 with ammonia (AR, Shanghai), the yellowish color of Bi_2O_3 changed to white, suggests that the surface of Bi_2O_3 particle was converted to BiOCl. The obtained white precipitates were washed several times with distilled water, until no Cl^- was left in the solution as tested

by silver nitrate ($AgNO_3$) and then dried at 40° C in oven for 6 h before further characterization [13].

2.2 Photocatalytic degradation procedure:

The photocatalytic degradation of NB has been carried out in slurry type batch reactor having double walled pyrex vessel. The reaction temperature was kept at 25 °C by using a water circulation. For a typical photocatalytic experiment, 4 gm of the prepared BiOCl was added to 100mL of the nile blue (NB) aqueous solution. Suspension was kept in a dark for 15 min to establish adsorption-desorption equilibrium. The suspension containing NB and the photocatalyst was then irradiated under the visible light, and the photocatalytic reaction timing started. The irradiation was carried out by using 500 W halogen lamp (Philips, India) which emitted irradiation comparable to sunlight. The doubled wall pyrex vessel was placed on a magnetic stirrer. At specific time intervals, an aliquot (3 mL) of the mixture was withdrawn and centrifuged for 2 minutes at the rate of 3500 rpm to remove the BiOCl particles in order to access the extent of decolorization photometrically. The COD was determined by the potassium dichromate reflux method. [20, 21]. The efficiency of photocatalytic process was calculated as:

$$\%efficiency = \frac{C_0 - C}{C_0} \times 00 \qquad (1)$$

Where C_0 is the initial COD/ absorbance and C is the COD/absorbance at different time intervals of photocatalytic process.

2.3 Experimental technique

X-ray powder diffraction pattern of the prepared sample has been recorded on a Rigaku D/MAX B diffractometer equipped with Cu Kα (λ = 0.15418 nm) radiation under 40 kV and 1000 mA and scanning range 10-80°. The average crystallite size (D) of the particles was calculated according to the following Scherrer's equation [16]:

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos\theta} \qquad (2)$$

Where, D_{hkl} is the average crystallite size (nm), λ is the wavelength of Cu Kα radiation (λ = 0.154056 nm), β is the full-width at half maximum intensity (FWHM) of the peak obsereved at 2θ = 11.91 (converted to radian), θ is the Bragg's angle of diffraction, and k is constant usually applied as 0.9. Diffuse reflectance spectra (DRS) of the catalyst in wavelength range of 200-800 nm has been obtained by using UV-vis spectrophotometer (Perkin Elmer Lambda 950). Dye concentration in the aqueous solution was measured by Systronic Vis. Spectrophotometer (106).

3. Results and discussion:

3.1 Structural studies:

The XRD pattern of as-prepared BiOCl, shown in Figure 1. The intense and narrow diffraction peaks imply a well-crystallized BiOCl powder material. The XRD pattern shows that all the peaks are well indexed to the tetragonal phase according to the PDF # 850861 data files. The crystal lattice parameters of BiOCl were calculated to be a = b = 0.38953 Å, c = 0.73734 Å, which were consistent with the literature [13]. The strong and sharp diffraction peaks confirmed the highly crystalline nature of BiOCl. The average crystallite size calculated by using the Scherrer formula is 39.6 nm.

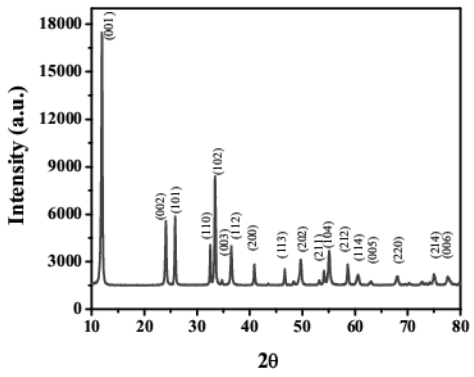

Figure 1. XRD pattern of BiOCl particles

3.2. Optical properties

The optical properties of the BiOCl sample were measured using UV–vis spectroscopy. The UV–vis spectra of as prepared BiOCl is shown in Figure 2. The result revealed that the sample exhibit significant increase in the photoabsorption at wavelength ≥ 400 nm. The band gap energy for BiOCl can be estimated from a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) (inset of Fig. 2). The intercept of the tangent to the plot can give a good approximation of the band gap energy for BiOCl. The band gap energy estimated from the intercept of the tangent to the plot is 3.2 eV, this observation was also made by Wang et al and Zhang et al [17,18]. Usually, the photoabsorption of the photocatalyst depends on the mobility ability of electron-hole pairs, which determines the probability of electrons and holes to reach reaction sites of the photocatalyst surface **[8].**

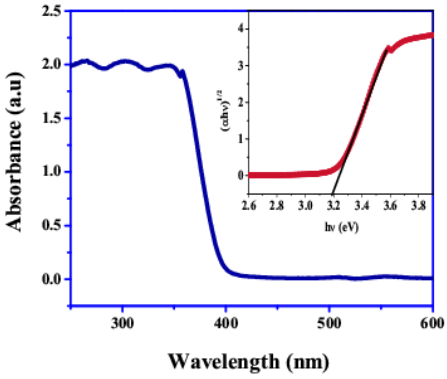

Figure 2: (a) UV-Vis absorption spectra for BiOCl particles
(b) Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for BiOCl.

3.3 Photocatalytic properties:

Figure 3 shows the photodegradation efficiency of NB mediated by the BiOCl photocatalysts. The experimental results showed that the degradation of NB solution was extremely low under visible light irradiation in the absence of catalyst and the BiOCl suspension was unable to initiate the dye degradation in dark. Both visible light and

BiOCl semiconductor particles were indispensable for the degradation of NB aqueous solution. By comparing the processes with blank tests, it was revealed that in the degradation of NB the photocatalytic process was the predominant process though photosensitization might also contribute some.

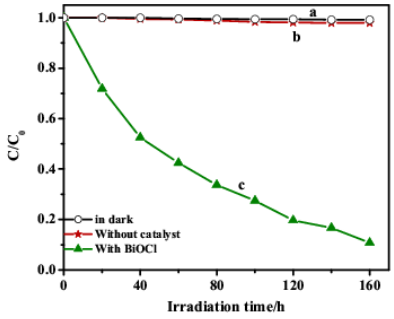

Figure 3: The photodegradation of NB (a) in dark (b) without catalyst (d) with BiOCl. Experimental conditions: [NB] = 50 mgL^{-1}, [BiOCl] = 4 gmL^{-1}, initial pH 6.1

We investigated the pH dependent photocatalytic activity of BiOCl, as shown in Figure 4. A variation in pH from 2.53 to 10.27 greatly influences the photodegradation of NB in aqueous BiOCl suspension. The photodegradation efficiency increases with the decreasing of pH value. Since NB dye is cationic it is obvious that their adsorption on the photocatalyst surface is not possible in acidic medium due to repulsive forces between BiOCl surface and dye. But, it is possible to formation of hydroxyl radicals which react with dye molecules in acidic medium. Therefore degradation efficiency of dye was observed in acidic solution. The prevailing pH of the solutions affects the mode and extent of adsorption of NB on the BiOCl surface and thus, indirectly, photodegradation rate of NB. The decrease in degradation at higher pH value such as 8.65 and 10.27 may be because BiOCl particle surfaces should mainly neutral. This probably causes agglomerization of BiOCl catalyst.

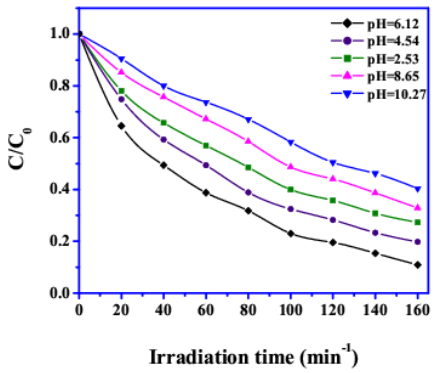

Figure 4: Dependence of photocatalytic properties over BiOCl on pH

To have a further insight, whether NB is mineralized or not, the COD (chemical oxygen demand) observation has been carried out during the photodegradation of NB and results are shown in Figure 5(a). It was observed that the COD exhibited a substantial decrease with irradiation time. For instance, after a period of 2 h, the COD was reduced to about 60% of its initial value while at the end of the experiment (6h) more than 98% of the COD has been removed (Figure 5(a)). Consequently, the complete mineralization of NB was achieved after 6 h of visible light irradiation in the presence of BiOCl. The COD analysis also showed dye sensitizations of catalyst. As shown in Figure 5(a), the COD removal of NB has been nearly maintained unchanged when NB was almost decolorized after 4 h, which indicated that the dye sensitization involving an interaction between BiOCl and NB [17].

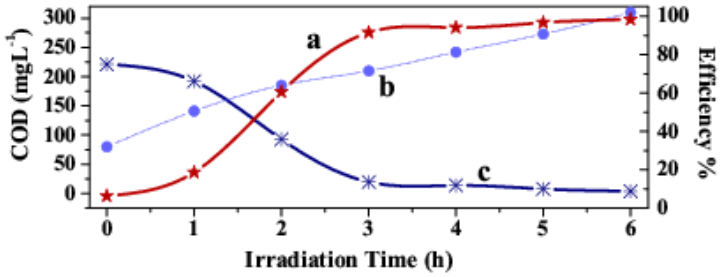

Figure 5: (a) COD removal of the solution, (b) efficiency % and Formation of CO_2 during the photodegradation of NB (50 mgL^{-1}) in BiOCl aqueous dispersions (4 mgL^{-1}) under visible irradiation, pH = 6.1

4. Conclusion:

In conclusion, the BiOCl as photocatalyst with layered structure has been synthesized by a hydrolysis route. The mineralization of aqueous NB led to the formation of end products such as carbon dioxide and remarkable decrease of COD during the reaction was observed which suggests that BiOCl/ visible light system might be regarded as an effective way for treating of textile industry wastewater.

Acknowledgement

Authors acknowledge support and laboratory facilities provided by department of Chemistry, Madhav Science College, Ujjain, India. Also the authors would like to thank the UGC-DAE CSR, Indore for their help in XRD and UV-Vis measurements.

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