Synthesis and Environmental Application of BiOI/BiOCl Composites

Esraa N. Ismaeel* ***Hilal S. Wahab*****

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Abstract:

This work illustrates an enhanced visible light photocatalytic degradation of methyl orange dye (M.O.) by employing BiOI / BiOCl composites prepared under room temperature and without any organic precursors. Various experimental parameters have been studied, namely; composition of the composite, irradiation time and cell material. Composition D which implied 75% BiOI and 25% BiOCl has shown the highest bleaching of M.O. dye. This confirms the optimum photo-sensitization phenomenon for this composition in comparison to others. In the optimum photo-sensitized composite the electron of the conduction band reveals better reducing power and the hole of the valence band exhibits more oxidative power than those of pure BiOI electron and hole. Accordingly, under appropriate experimental conditions, methyl orange was significantly bleached using composite D.

Key words: Photocatalysis; Composites; Methyl Orange; Bismuthoxy halides

Introduction

Bismuth oxyhalides (BiOX (X = Cl, Br, I)) are another type of semiconductors that have been studied as potential candidates for photocatalytic applications in catalysis and pollution control[1] . The fabrication of semiconductor porous materials assembled from nanoscale building blocks has received intensive research interest due to its advantages of low cost, environmental friendly and mild synthesis conditions. The Semiconductor photocatalysis is driven by visible light which has become the world hot topic of intensive interest due to its potential applications in environmental purification and solar energy conversion by utilizing visible light in solar or indoor light source [2]. Furthermore, all the BiOX powders were more active than P25 (TiO_2) under UV–VIS light irradiation and C-doped TiO_2 under visible light illumination respectively. BiOI and BiOBr showed comparable photocatalytic activity in decomposing RhB (rhodamine B) under visible light. These products were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and infra-red spectroscopy (IR) [3]. In view of the fact that the unique properties of nanomaterials are structure dependent, scientists have paid much attention to the controllable and successful synthesis of BiOCl nanotubes, nanoplates , nanosheets and nano-flowers that are nanosized and of a particular morphology by means of hydrothermal and/or solvothermal treatment at 160–180 °C for 10–24 h [4]. Huizhong and his collaborators [5] have prepared a novel series of bismuth oxyhalide photocatalysts BiOX (X = Cl, Br, and I) by hydrolysis reaction. Their photocatalytic activities were evaluated by the photodecomposition of rhodamine B under visible light irradiation. They concluded that the main photocatalytic mechanism of BiOX is dye

*Department of Chemistry/ College of Sciences/ Al-Nahrain University

sensitization. Moreover, BiOCl can also degrade and even completely mineralize colorless isopropanol under visible light irradiation, indicating its high photocatalytic activity. For example, Zhang et al. [6] revealed that BiOCl exhibited better performance than TiO_2 (P25) at three-cycles on the photocatalytic degradation of methyl orange (MO) dye in 2006. At the same time, they discussed the electronic band structure of BiOCl using first-principles method based on density functional theory (DFT), and found that the open crystal structure and indirect optical transition of BiOCl played a crucial role in its excellent photocatalytic activity.

Nanobelts and nanotubes of bismuth oxyhalides have also been prepared via hydrothermal method, and the absorption patterns were found to be dependent on the synthetic conditions [7]. Here, we report the synthesis of BiOI / BiOCl composites from inorganic precursors (KI, KCl and Bismuthoxy nitrate) and its application in the bleaching of M.O.

Materials and Methods:

All chemicals used in this study were analytical grade and were used without further purification . Nanofiltered deionized water (NFDW) was used in all experiments.

1. Methyl orange (M.O.) $(CH_3)NC_6H_4$ N:N $C_6H_4SO_4Na$), BDH product.
2. $NH_3.H_2O$ (1M)./ $BiONO_3$ (5.74 g) 0.02 mol. (Purity = 79-82% and BDH product)

a) Preparation of chemical solutions

Model pollutant (Methyl orange)

0.05 grams of M.O. whose structure shown in Figure (1) was dissolved in sufficient volume of nanofiltered deionized water, diluted to the (1000ml) mark using (NFDW). 10ml of this stock solution were diluted into 100ml for spectroscopic measurements.

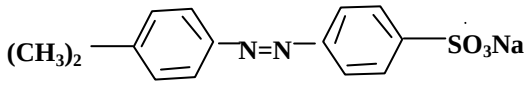


Fig. 1. Structure of Methyl –Orange (M.O.)

c) instrumentation

1. Shimadzu UV-VIS model (1650 PC) has been used throughout this work.
2. Hanna instruments pH meter model (pH 211).
3. Nanofiltered –deionization water supply unit model (Sm -11), waterpia.
4. Irradiation device (Image 1).

d) Absorbance measurement

The absorbance of dye solutions before and after bleaching were measured at different concentrations and time intervals, in the photon energy range of wavelength from 300-800 nm and with aid of quarts cell (10mm optical path length).

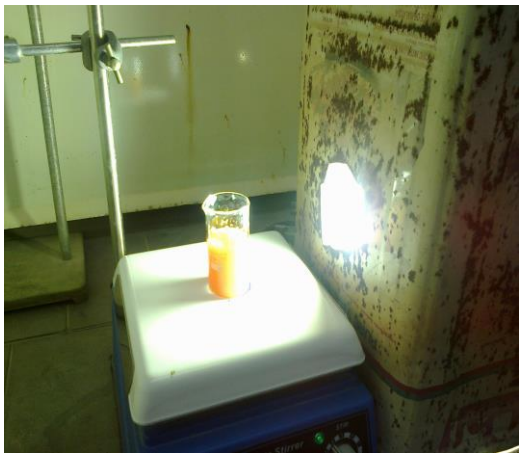
Figure (2) shows the visible absorption band of M.O. λ_{max} = 482 nm. The absorpitivity of the dye was calculated using Beer´s law as following

Abs = ϵ_{max} .b.c ; Average Absorbance value of several measurements = 0.661

ϵ_{max} = Molar Extinction Coefficient ; b = light path (1cm) ; c = concentration (1.5×10^{-5} mol/ L)

$\epsilon_{max} = 0.661/ (1cm\times1.5\times10^{-5} mol.\ L^{-1})$

$\epsilon_{max} = 0.44\times10^{5}$ $L.mol^{-1}cm^{-1}$ = 44000 $L.mol^{-1}cm^{-1}$



e)

Image 1. UV-VIS illumination system using high pressure Hg lamp, 1000 watt

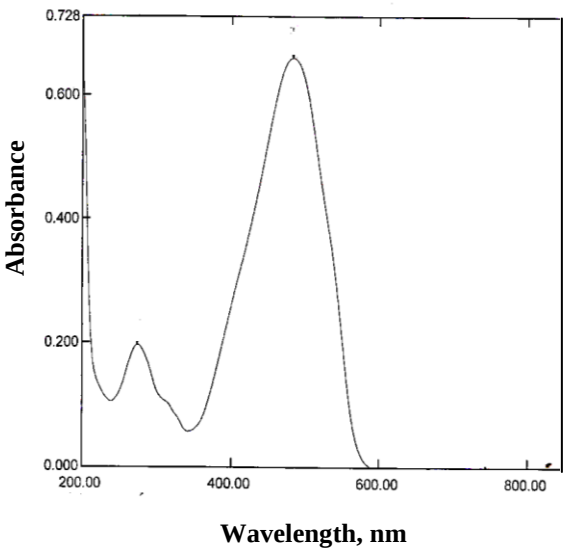


Fig. 2. UV-VIS Spectrum for Methyl Orange

procedure

BiOI/BiOCl composites were synthesized at room temperature (25^0C). In a typical synthesis, stoichiometric amounts of KCl and KI were dissolved in 150 ml of H_2O. 0.02 mol of $BiONO_3$ was added into the above solution slowly .The mixtures were adjusted to pH of 10 using 1M of $NH_3.H_2O$ solution and stirred vigorously for 12 h intermittently. After the stirring was complete, the resulting solid product was collected by filtration, washed several times with NF deionized water and then dried at 60^0 C to get the final sample. Depending on the molar ratio of KI to KCl (1:0, 0.25:0.75, 0.5:0.5, 0.75:0.25 and 0:1), different BiOI/BiOCl composites can be synthesized and labeled as BiOI (A), $BiOI_{0.25}Cl_{0.75}$ (B), $BiOI_{0.5}Cl_{0.5}$ (C), $BiOI_{0.75}Cl_{0.25}$ (D), and BiOCl (E), respectively. It was known that the hydrolysis of Bi $(NO_3)_3$ in water produced the $BiONO_3$ [4]. The formation of BiOI/BiOCl composites from the starting compounds following the Eqs. (1)-(4).

$$NH_3.H_2O \rightarrow NH_4^+ + OH^- \quad (1)$$

$$Bi(NO_3)_3 + H_2O \rightarrow BiONO_3 + 2H^+ + 2NO_3^- \quad (2)$$

$$H^+ + OH^- \rightarrow H_2O \quad (3)$$

$$BiONO_3 + xI^- + (1-x)Cl^- \rightarrow BiOI_XCl_{1-X} + NO_3^- \quad (4)$$

f) Irradiation Scheme

The following solid / liquid mixtures were irradiated for 2 and 7 minutes at a distance of 12 cm between the light source and sample:

M.O., M.O.+Composite A, M.O.+ Composite B, M.O.+Composite C, M.O.+Composite D and M.O.+ Composite E.

g) Incident light intensity measurement

The intensity of the incident light (I_0), was measured by the use of potassium ferrioxalate actinometer method as described in the literature [8]. The actinometer solution (6×10^{-3} mol/l) was prepared by dissolving (3gm.) of $K_3Fe(C_2O_4)_3.3H_2O$ in 800 ml of distilled water. A 100 ml of 1 N of H_2SO_4 solution was added and the whole solution was diluted to one liter with NF deionized water.

The intensity of incident light (I_0) was calculated according to the following method: Three milliliters of actinonmeter solution was irradiated in the irradiation cell for 3 minutes. After illumination, one ml of irradiated solution was transferred to 25 ml volumetric flask, 0.4 ml of hydroxyl ammonium chloride solution, 2 ml of 1, 10- phenanthroline solution and 0.5

ml of acetate buffer solution were added to the flask sequentially and then diluted to 25 ml with NFDW. A Blank solution was made by mixing one ml of unirradiated mixture solution with other components. The solution was left in dark for 30 minutes, afterwards, the optical density of ferrous-1,10-phenanthroline complex was measured at λ =510 nm. The intensity of incident light was then calculated using the following relationship:

$$\mathbf{I_o = \frac{A \times V_2 \times N_A}{{}_{\lambda}\Phi \times \epsilon_{max} \times V_1 \times t \times d}\ Photons.L^{-1}sec^{-1}} \quad || \quad \mathbf{I_o = \frac{A \times V_2}{{}_{\lambda}\Phi \times \epsilon_{max} \times V_1 \times t \times d}}$$

(mol)Ein /L.sec

Where:

I_o = Incident light intensity (Einstien L^{-1} sec^{-1})

A = Absorbance at (λ = 510 nm, Fe-phenanthroline complex)

V_2 = Final volume (25 ml)

${}_{\lambda}\Phi$ = Quantum efficiency = 1.21 [9]

ϵ_{max} = Molar extinction coefficient = 1.09455 × 10^4 $L.mol^{-1}.cm^{-1}$ (Fe-phenanthroline complex)

V_1 = Volume taken from irradiated solution (1 ml)

t = Irradiation time in second

N_A = Avogadro's number ($mole^{-1}$)

d = Light path of the cuvette (1 cm)

The cell was irradiated in the same position used for irradiated samples (Image 1).

$$\mathbf{I_0 = \frac{0.151 \times 25\ ml \times 6.02\ E\ 23\ photons.\ mol^{-1}}{1.21 \times 1.09455 \times 10^4\ L\ mol^{-1}.cm^{-1} \times 1ml \times 180\ sec \times 1cm}}$$

$$\mathbf{= 9.56 \times 10^{17}\ photons.L.sec.^{-1} = 1.59 \times 10^{-6}\ mol\ /L.sec. = 1.59 \times 10^{-6}\ Ein\ /L.sec}$$

Results and Discussion

1. Activity of BiOI / BiOCl composites

Photocatalytic activity of synthesized A, B, C, D and E composites have been studied through the bleaching (degradation) of M.O. solutions under irradiation conditions for two or seven minutes and twelve centimeters distance of the pyrex glass contained sample from the 1000 watt high pressure Hg lamp as illumination source. The pyrex glass reservoir absorbs usually the UV radiation of ≤ 390, i.e.; visible light is passed through glass wall. On the other hand , the medium and high pressure Hg lamp could also emit, other than UV radiation , visible radiation around the wavelengths of blue (440nm) to green (550nm) colores [10]. Several authors [2, 11-13] have reported the application of BiOX composites in the photodegradation of organic moieties. Cui et al. [11] have prepared BiOCl nanosheets in non–aqueous solvothermal medium. This nano structure composite has been characterised by x-ray diffraction (XRD) and scanning electron microscopy (SEM) and used successfuly for the degradation of organic dyes through hydroxyl radical generation. Whereas, Xiao et al.[12] have employed the BiOI/BiOCl miccrospheres for the decomposition of bisphenal–A molecule under visible

radiation. Moreover, other researchers [13] have adopted novel system composed of BiOCl / Bi_2O_3 as a notable photocatalyst in decomposition of 2-propanol using visible light illumination.

In the present study, a series of BiOI / BiOCl composite photocatalysts with different amounts of both bismuth oxy halides have been successfully synthesized under room temperature. These variable composition composites have been used for the photocatalytic bleaching of M.O. dye.

Figures 3 and 4 present the degradation of the dye using BiOI and BiOCl composites, respectively. The decomposition level (lower bands) is higher in the case of BiOI than BiOCl. This confirms the lower band gap energy of the former. This finding is in accordance with other published results in the literature [2, 12]. Furthermore, the stepwise decomposition at longer irradiation time (7 min.) in both Figures 3b and 4b are in a good agreement with the observation of Cui et al.[11] in the photodegradation of 7-hydroxycoumarine using BiOCl under UV-Visible light photons.

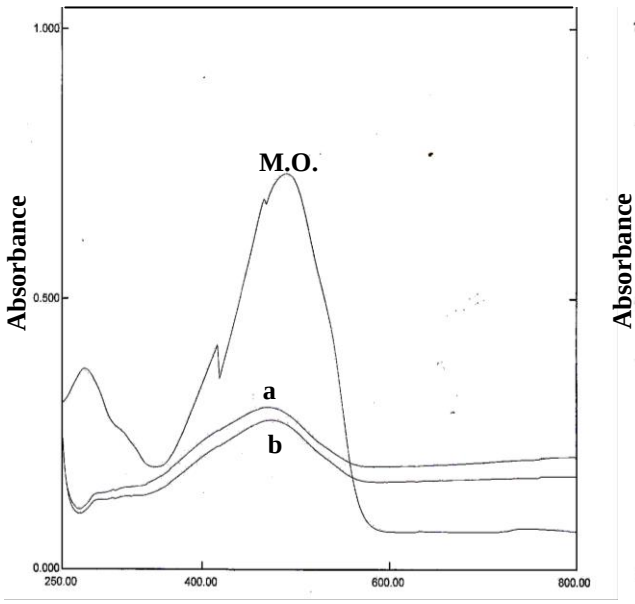


Fig. 3. Photodegradation of M.O. onto BiOI surface at a) Two and b) Seven minutes, of irradiation.

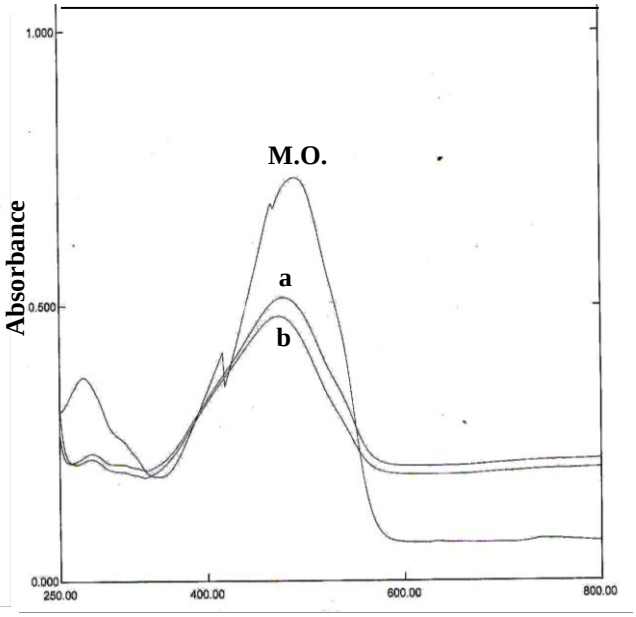


Fig. 4. Photodegradation of M.O. onto BiOCl Surface at a) Two and b) Seven minutes of irradiation

Figures 5-7 for various BiOI / BiOCl composition composites exhibit clearly the influence of synergestic phenonemenon on the decomposition of the dye, particulary for the couple of $BiOI_{0.75}/BiOCl_{0.25}$ (composite D) composition. This is attributed to the sensitization process which lead to up lifted conduction band (CB) edge (more photo reducible electron) and down lowered valance band (VB) edge (more powerful oxidative holes) as shown in scheme 1. Tables 1 and 2 present clearly the photodegradation of M.O. at different illumination time intervals (2 and 7 minutes) for the synthesized composites. For composite D (Figure 7), one can foresee that these are no real absorption band (NAB), which consequently a significant percent of decomposition is attained.

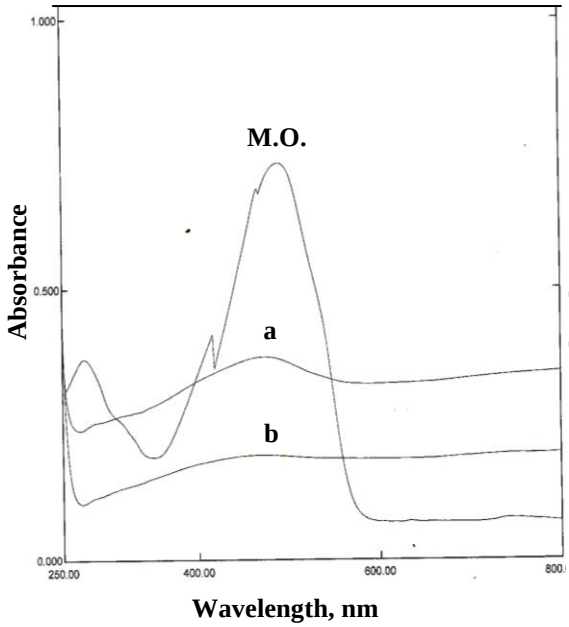


Fig. 5. Photodegradation of MO onto composite B after a)Two and b) Seven minutes of irradiation

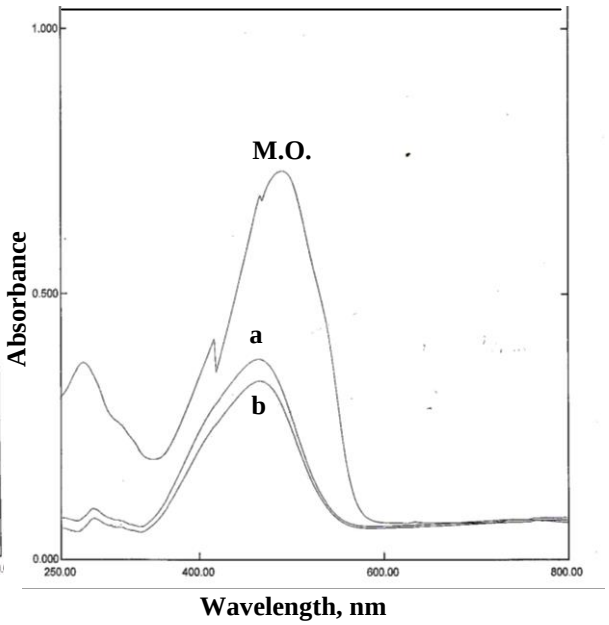


Fig. 6. Photodegradation of MO onto composite C after a) Two and b) Seven minutes of irradiation

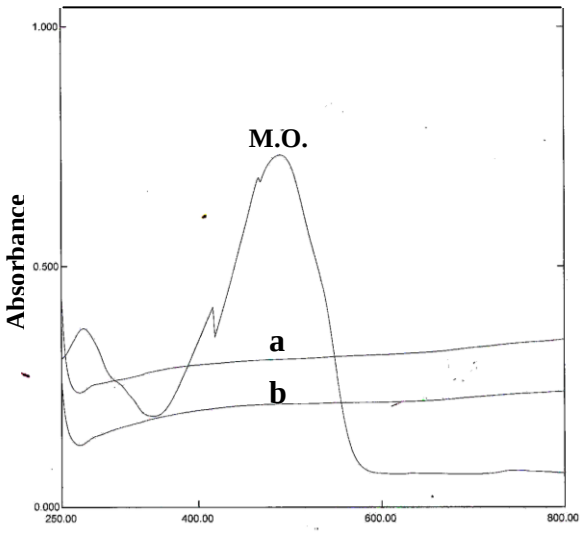
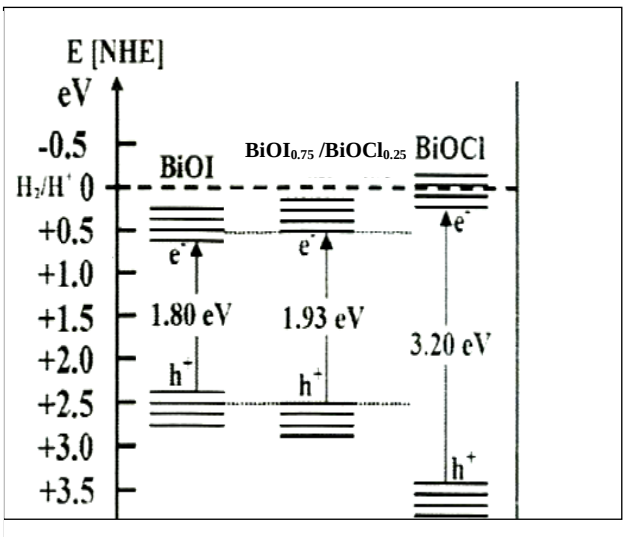


Fig. 7. Photodegradation of M.O. onto composite D surface at a) Two and b) Seven minutes of irradiation.



Scheme 1. Band gap structures and photo-sensitization phenomenon

Table 1. Photodegradation of 10 ppm M.O. at illumination time of two minutes onto synthesized composites synthesized composites

Code	Composite	Abs.	Remained Abs.	%deg.	Remained conc.,ppm
A	BiOI	0.73	0.3	57	4.5
B	A25-E75	0.73	0.35	54	4.7
C	A50-E50	0.73	0.37	49	5
D	A75-E25	0.74	0.3 *NAB	60 (100)	4.5 (NIL)
E	BiOCl	0.74	0.51	31	6.5

*** NAB stands for no absorption band**

Table 2. Photodegradation of 10 ppm M.O. at illumination time of seven minutes onto synthesized composites synthesized composites

Code	Composite	Abs.	Remained Abs.	%deg.	Remained conc.,ppm
A	BiOI	0.73	0.27	61	4
B	A25-E75	0.73	0.25	64	3.2
C	A50-E50	0.73	0.33	55	4.6
D	A75-E25	0.74	0.2 *NAB	73 (100)	2.5 (NIL)
E	BiOCl	0.74	0.49	34	6.8

*** NAB stands for no absorption band**

2. Influence of Irradiation Cell

Since glass material absorbs UV light at ≤390 nm, the only light which is involved in photo decomposition is visible light (Figure 8). While, when quartz cell is used for irradiation, UV and Visible radiations take part in illumination process. Accordingly, higher decomposition percents are a achieved (Figure 9).

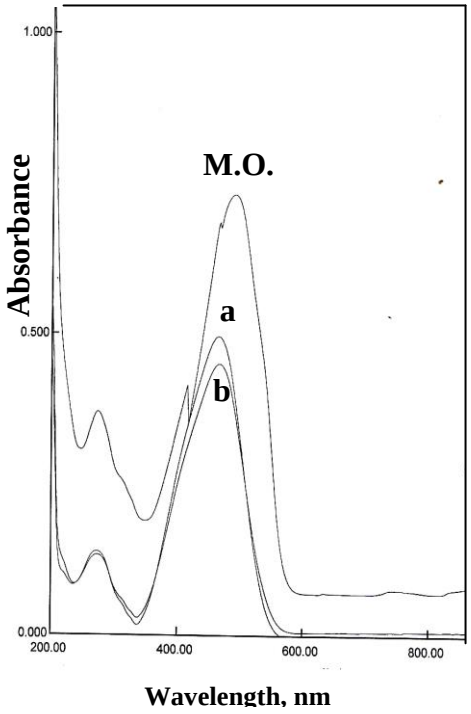


Fig. 8. Effect of irradiation on photodegradation of M.O. in a pyrex glass container at a) Two and b) Seven minutes of irradiation

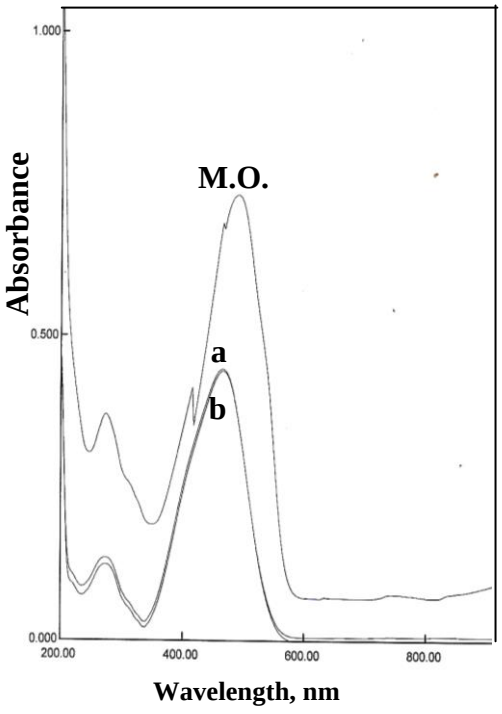


Fig. 9. Effect of irradiation on photodegradation of M.O. in a quartz container at a) Two and b) Seven minutes of irradiation

Conclusions

1- Bismuth oxy halide composites are efficient photocatalysts for degradation of M.O. dye.

2- Sensitization plays significant role is the photocatalytic process.

3- Synergistic effect could be observed in the present study.

References:

1. Paolaa A., Lopez E., Marci G. and Palmisanoa G.L. 2012 "A survey of photocatalytic materials for

environmental remediation" J.Hazard. Mater. 211-212: 3-29.
2. Dong F., Suna Y., Fu M., Wu Z. and Lee S.C. 2012 "Room temperature synthesis and highly enhanced visible light photocatalytic activity of porous BiOI/BiOCl composites nanoplates microflowers" J. Hazard. Mater. 219-220 : 26-34.
3. Zhoua S. X., Ke Y., Li J. and Lu S. 2003 "The first mesostructured bismuth oxychloride synthesized under hydrothermal condition" Mater.lett. 57 : 2053-2055.
4. Chen L. , Yin S. F., .Huang R, Zhou Y., Luo S. L. and Au C. T. 2012 "Facile synthesis of BiOCl nano-flowers of narrow band gap and their visible-light-induced photocatalytic property "Catal.Comm. 23: 54-57.
5. Huizhong A. N., Yi D. U., Tianmin W., Cong W., Weichang H. and Junying Z. 2008 "Photocatalytic properties of BiOX (X = Cl, Br, and I)" Rare Metals. 27: 243-250**.**
6. Zhang K. L., Liu C.M., Huang F.Q., Zheng C. and Wang W. D. 2006 "Study of the electronic structure and photocatalytic activity of the BiOCL photocatalyst" Appl catal. B.Enviromental 68: 125-129.
7. Huang W. L. and Zhu Q. 2009 "Structural and electronic properties of BiOX (X = F, Cl, Br, I) considering Bi 5f states" Comp. Mater. Sci. 46: 1076-1084.
8. Attwan S. M. 2012 "Spectroscopic and photochemical study of riboflavin", M.Sc. Thesis, Al–Nahrain University, College of Sciences, Department of Chemistry.
9. Hatchard C. G. and Parker C. A. 1956 "A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer" Proc. R. Soc. Lond. A 235: 518-536.
10. Sansonetti C. J., Salit M.L. and Reader J. 1997 "Wavelengths of spectral lines in mercury pencil lamps" Applied Optics 35: 74-77.
11. Cui Z., Mi L. and Zeng D. 2013 " Oriented attachment growth of BiOCl nanosheets with exposed {110} facets and photocatalytic activity of the hierarchical nanostructures "J. All. Compound 549: 70-76.
12. Xiao X., Hao R., Liang M., Zuo X., Nan J., Li L. and Zhang W. 2012 " One-pot solvothermal synthesis of three-dimensional (3D) BiOI/BiOCl composites with enhanced visible-light photocatalytic activities for the degradation of bisphenol-A" J. Hazard. Mater. 233-234: 122-130.
13. Chai S.Y, Kim Y.J. and Jung M.H., Chakraborty A.K. Jung D., Lee W.I. 2009 "Heterojunctioned BiOCL/Bi2O3,a new visible light photocatalyst" J. Catal. 262: 144-149.

الاستخدام البيئي لمركبات BiOI/BiOCl المحضرة مختبريا

اسراء نهاد اسماعيل ***هلال شهاب وهاب****

*جامعة النهرين – كلية العلوم - قسم الكيمياء

الخلاصة:

يبين البحث التفكك المتحفز للملوث العضوي (المثيل البرتقالي) بأستخدام مخاليط هالوجينات اكاسيد البزموث في الظروف المختبرية وبأعتماد الضوء المرئي. تم دراسة عوامل تجريبية مختلفة مثل محتوى المخلوط وفترة التشعيع وطبيعة الخلية.توصل البحث الى ان المخلوط المتكون من 75% من اليوديد اوكسيد البزموث و 25% كلوريد اوكسيد البزموث اظهرنتائج جيدة في قصر او تفكيك المثيل البرتقالي ، وتوافقت هذه الاستنتاجات مع النتائج المنشورة في الادبيات ، وتطرق البحث كذلك الى مسألة الاختلاف في طاقة الفجوة بأختلاف مكونات المخاليط.