

Comparison between bismuth oxy bromide and bismuth oxy bromide supported on strontium hydroxyapatite for Malachite green dye removal photocatalytic study.

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ABSTRACT

BiOBr and BiOBr/SrHA bismuth oxybromide and bismuth oxybromide supported on strontium hydroxyapatite can we get them both from simple hydrolysis method. BiOBr and BiOBr/SrHA were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), energy diffraction X-ray (EDX), Fourier transforms infrared spectroscopy (FTIR), and UV-visible (UV-vis) analysis. degradation of Malachite green in an aqueous solution was evaluated spectrophotometrically in the visible range from the area under the curve with peaks at 615 nm. BiOBr and BiOBr/SrHA showed the highest photocatalytic activity in degrading Malachite green and evolving O₂ for its proper valence band (VB), because of electron-hole pair separation through trapping electrons by oxygen vacancies. The kinetic constant of the degradation reaction can be calculated based on the pseudo-degradation mechanism of the first order, using UV, and 300 W Xe lamp were used as the light source. will use in this paper. There are some parameters different photocatalytic acceleration can be used, for example, the time of equilibrium, the initial concentration of the concerned dye, and the initial concentration of the photocatalysts.

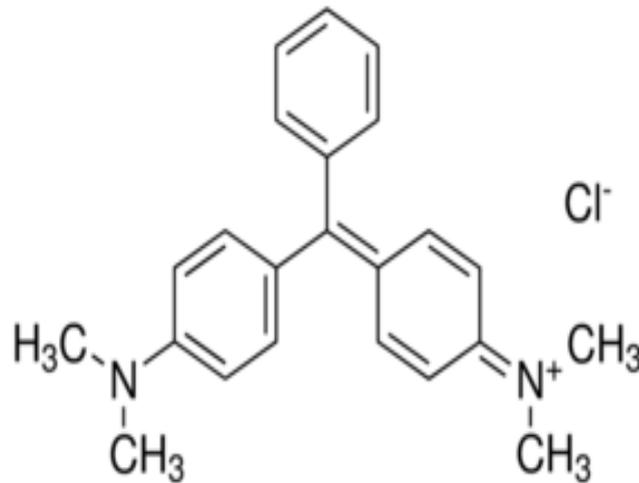
Keywords---- Adsorption , cationic dye , Photocatalytic, Kinetics , SEM , XRD

Introduction

Increase of Pollutants in the water Planet earth because wastewater, that produces from factories and Medical and industrial laboratories, all of that excess require for clean water sources. therapy these problems required fast and inexpensive solutions. Recently, modern technologies have appeared that work on treating sewage and removing pollutants from water, such as advanced oxidation processes (AOPs), which have contributed to solving many problems of pollution with dyes, for toxic organic removal are under continuous study[1-4]. Heterogeneous photocatalysis is kind of the most favorable and wonderful AOPs to control environmental pollution, due to its confirmed activity in the decay and

mineralization of an expanse of organic compounds. Heterogeneous photocatalysis is a process that Depends on utilizing light energy to stimulate a semiconductor at, rate of a chemical reaction without itself undergoing any permanent chemical change [5-6]. potential semiconductor compounds, titanium dioxide (TiO₂) P-25 is yet the most applied by industries today. It displays an interest in being inert, cheap, and stable. However, resultant of its bandgap of 3.2 eV this substance can only consume light energy in the UV region, which is ultimately around 5% of the solar spectrum. This may be TiO₂ considered unwanted for wastewater treatment Because the revitalization process needs high energy from natural sunlight [7-9]. newly, the photocatalytic properties of the bismuth oxyhalides family (BiOX, X = Cl, Br, I) have been scrupulous, performance favorable effects. between them, bismuth oxy bromide (BiOBr) has shown hopeful outcome hydrolysis, hydrothermal, solvothermal, microwave, microemulsion, and ion thermal all these methods of preparation of bismuth oxy bromide [10-11]. hydrolysis method, and physically and chemically describe in this study to produce bismuth oxy bromide. BiOBr has displayed major photocatalytic efficiency under sun radiation compared with the manufactory P25 [12]. Sr²⁺ element is very important in the human body its work decreases the activity of bone-resorbing osteoclasts and increases the activity of bone-forming osteoblasts [13-14]. there are more attempts were done by researchers replacing calcium (Ca²⁺) ion with strontium ion (Sr²⁺) to improve solubility and acid-reactive of hydroxyapatite. The presence of strontium element in hydroxyapatite in different proportions so that it does not affect the composition of the compound gives it some distinctive properties by increasing its solubility and vital activities if it is used inside the Vivo. and because the mismatch atomic radii occur a lattice expansion. we can get particles of hydroxyapatite (HA) by different processes and temperatures Some of them can be mentioned calcination method precipitation, wet mechanochemical process, calcination method [15]. Recently, great interest in the benefits of hydroxyapatite has been observed in modern chemistry due to the important biological activity in the human body [16]. The process of replacing strontium with calcium in proportion to the compound hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) is to obtain good solubility as well as to increase the acidity of apatite in this paper, we want to explain some differences between bismuth oxy bromide if it only and if it modified support on strontium bismuth oxy bromide to removal Malachite green dye [17]. Since Malachite green is a common pollutant in wastewater of biological labs, there is an increasing request for wastewater treatment contaminated by this compound. Due to the basic nature of Malachite green, it connects to proteins in acidic media. Malachite green is thought detrimental if it is swallowed, inhaled, or absorbed through the skin. newly, nanoparticles that were used to remove Malachite green by adsorption from aqueous solution by photodegradation depend on

using UV light, and 300 W Xe lamp [18]. In this study, we will discuss the process of removing Malachite green dye using BiOBr once and BiOBr/SrHA again and study which of the two compounds has the best effect on removing this dye. Scheme 1 shows the chemical structures of the studied Malachite green dye.



Malachite green

Scheme 1. Chemical structures of Malachite green dye.

2. EXPERIMENTAL

2.1 Preparation of photocatalysts

2.1.1 Preparation of photocatalysts BiOBr

In this work, BiOBr has been prepared using three different dissolvent syntheses were prepared by mixing ethanol and deionized water. These dissolvent syntheses include water: ethanol in ratios 30:70, 50:50,70:30 To prepare BiOBr, 100 ml of bismuth nitrate solution was prepared by dissolving 4.50gm of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in the first dissolvent i.e. water:ethanol:30:70 and 50 ml of KBr solution was synthesis by solving 1.19g of KBr in the first dissolvent. KBr solution was to insert to flow into the

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution in the conical flask at 2.5 ml/min with continuous stirring. 4 ml of 30% NH_3 solution was added to maintain the pH of the mixture as 2.5, and stirring was further continued for 6 h to ensure completion of the reaction, The resulting precipitates were collected by filtration on filter paper and washed several times with de-ionized water for the complete removal of undesired water-soluble products. The solid compound so obtained is subsequently dried at 75 C° for 8 h in an electric oven under normal atmospheric conditions. The above procedure was repeated to synthesize two other samples of BiOBr using solvent compositions: water: ethanol as 50:50, 70:30. The highest photodegradation rates of the Malachite green dye were observed for the sample synthesized with a solvent containing water to ethanol ratio as 50:50, in the particular series of BiOBr compounds.

2.1.2 Preparation HAP and Sr-HAP

HAP and Sr-HAP were prepared by the wet chemical precipitation path. To formation HAP, a 100-ml solution of 4g $(\text{NH}_4)_2\text{HPO}_4$ was added dropwise into 5.5g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution of 100 ml while constantly stirring the solution with a magnetic stirrer. pH was kept around 10 by adding the amount of NH_4OH . The prepared solution was kept at room temperature for 24 h. Sr-HAP was prepared by adding 4g $(\text{NH}_4)_2\text{HPO}_4$ solution dropwise into a solution comprised of 7g $\text{Ca}(\text{NO}_3)_2$ and 1.7g $\text{Sr}(\text{NO}_3)_2$ solutions, which is about 15 mol%. Can be represented with a chemical formula $\text{Ca}_{8.5}\text{Sr}_{1.5}(\text{PO}_4)_6(\text{OH})_2$.

2.1.3 Preparation of photocatalysts BiOBr/SrHA

BiOBr/SrHA was synthesis by a modification hydrolysis method using bismuth oxide, HBr, and SrHA as precursors [19]. In perfect preparation Bi_2O_3 (1.8g) was resolved in plus concentrated hydrobromic acid (10 mol/L, 10 mL) to get a transparent $\text{BiO}_3\text{-HBr}$ aqueous solution. To this solution, 1.3g of SrHA was inserted with continuous stirring. The acquired mixture was sonicated for 15 min. The pH of the solution was checked between 2 and 3 using ammonia. The specimen was heated at 90 C° for half an hour to get white precipitates. The sample was washed several times with water and ethanol and then dried at 85 C° for 6 h to obtain BiOBr/SrHA.

2-2. Photocatalytic degradation of dyes

Photocatalytic effectiveness test, the photocatalytic effectiveness of the BiOBr and BiOBr/SrHA photocatalyst was estimated by the degradation of Malachite green, under illumination. UV light and a 300 W Xe lamp were used as the light sources. The reaction specimens were synthesis by inserting 15 mg of BiOBr catalyst into 100 ml of Malachite green, solution (7.5 mg L^{-1}). Before illumination, The above procedure was repeated to BiOBr/SrHA. synthesize the suspension was ultrasonicated for 15 min and left in the dark for 30 min to insurance of the adsorption-desorption equilibrium. through irradiation, 10 mL of the samples were regularly taken from the reactor at different intervals. The photocatalysts powders and the Malachite green solution were separated by a centrifugal machine. Then, the Malachite green, dye concentration was analyzed through a (UV-vis Spectrophotometry PG Instruments Limited, model, T80 (EMC-LAB) and the area under the peaks at wavelength $\lambda = 615 \text{ nm}$ were noticed and concerning to the concentration of MG in the solution. The kinetic constant for the dye degradation reaction was calculated by supposing the pseudo-first-order mechanism for the degeneration reaction as per law $C = C_0 \exp(-kt)$, where C_0 and C are the concentrations of Malachite green, dye in the solution before irradiation and after irradiation respectively, for the time period “t” and “k” is the degeneration reaction rate constant.

Regions under the absorption peak at 615 nm (in the visible area) was to the amount of MG present in the solution. We have registered the absorption spectrum of our specimens under two different exposure (UV and 300-W Xe lamp). Suppose “ C_0 ” is the initial concentration (before exposure) of MG dissolved in the solution, where $C = C_1, C_2, C_3, \dots$ etc. are the concentrations of MG remaining after 1, 2, and 3 hours of light exposure. The slope of the plot between $[(C/C_0)]$ vs. exposure time (min).

3. Results and discussion

Figure 1(a and b) shows the FT-IR spectra of BiOBr and BiOBr/SrHA, the range of $3417\text{--}3506 \text{ cm}^{-1}$ may refer to the stretching vibrations of --OH that existed in the adsorbed water molecule. As well the distinctive peaks at range $(1621\text{--}1647) \text{ cm}^{-1}$ are referring to the O-H bending vibrations. for pure BiOBr, 536.23 cm^{-1} corresponds to valence symmetrical A_{2u} -type vibrations of the Bi-O bond, a reference that the compounds of BiOBr are obtained. The broadband at 3417.84 cm^{-1} is refer to O–H vibration of H_2O absorbed in the specimen. 1403.52 cm^{-1} peak is refer to the carbon-related pollution and a small amount of $(\text{CO}_3)^{2-}$ caused by the CO_2 in an aqueous solution or air during the synthesis. 1631.84 cm^{-1} peak is refer to carbon-related pollution. The bands at 1023.42 cm^{-1} are a marker of asymmetric stretching. The two groups of bands in the low wavenumber ranging from 502.11 to

642.07 cm^{-1} (centered at 601.81 and 547.80 cm^{-1}) are attributed to the bending vibrations of O–P–O in $(\text{PO}_4)^{3-}$ groups. The phase structures of the as-synthesis BiOBr and BiOBr/SrHA specimens were examined by XRD. As displayed in [Figure 2](#), both BiOBr and BiOBr/SrHA specimens have highly strong and net diffraction peaks, which denote the perfect crystallinity of the patterns. All diffraction peaks can be guided to pure tetragonal BiOBr phase with network constants of standard JCPDS file (JCPDS# 9-432). As for BiOBr, the proportional diffraction intensities of peaks with (102) facets are clearly a lot stronger than those of others, which refer to a divergent development of the obtained BiOBr crystal over the (102) crystal face. anywise, it can be shown in BiOBr/SrHA XRD pattern that the peak of the (102) plane was clear repressed and the intensity of the (102) characteristic peak becomes thin than that of the (110) characteristic peak. In addition to the appearance of new peaks for a compound BiOBr/SrHA that was not present in a compound BiOBr, and this is an indication of the formation of a new compound that differs from the first compound.[20] describe the EDX pattern of BiOBr and BiOBr/SrHA. in [Figure 3](#) (a), and (b) respectively. The presence of elements O, P, Br, Sr, Ca, and Bi in BiOBr/SrHA and BiOBr. confirmed the formation of BiOBr/SrHA and BiOBr.

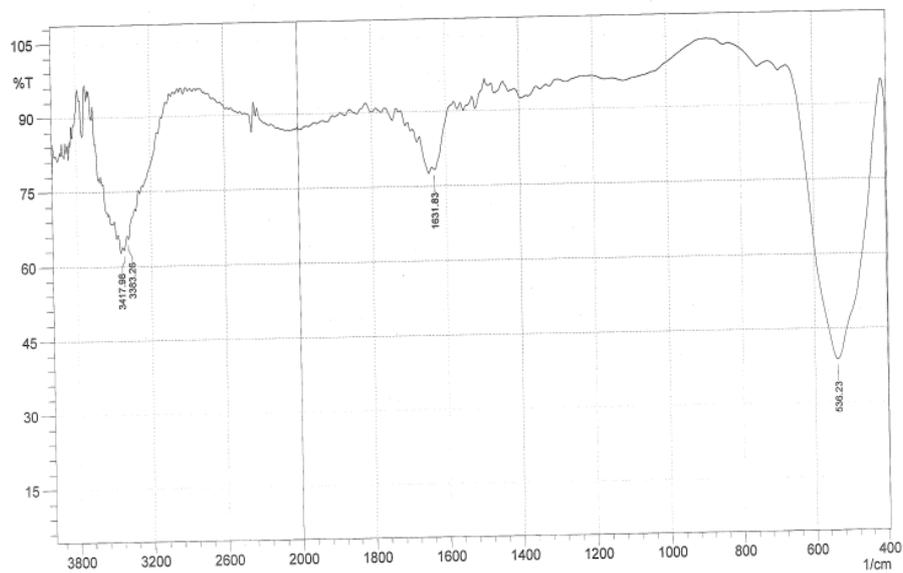
The BiOBr and BiOBr/SrHA photocatalysts [Figure 4](#) (a –b respectively). was sample BiOBr was and overlapped with each other to form 3D hierarchical flower-like structures. The morphology of BiOBr and BiOBr/SrHA respectively diagnosed by scanning electron microscopy (SEM) are fixed in SEM visual data of BiOBr shows a quite different morphology than for BiOBr/SrHA. notable, the surface structure of BiOBr/SrHA changes to marked rise with some holes that were not present and installed when modified with BiOBr, This explains the presence of a large surface area, which increased the adsorption process of the dyes. Malachite green, (MG), a widely used dye, was chosen as the test pollutant to evaluate the photocatalytic activity of synthesized BiOBr and BiOBr/SrHA. The same reaction conditions were also tested for comparison between, a blank control, a dark control, and a P₂₅. [Figure 5\(a\)](#) displays the photocatalytic action for Malachite green, degradation over BiOBr, BiOBr/SrHA, and the P₂₅, under 300W Xe lamp light irradiation. It can be a watch that the degradation of (MG), without photocatalysts under light irradiation is not observable, which reference that (MG), are stable under UV irradiation. moreover, the (MG), removal through BiOBr/SrHA, BiOBr, and the P₂₅ are about 91.5%, 69%, and 74% after 3 h of UV light irradiation. [Figure 5\(b\)](#) shows the photocatalytic activity of these photocatalysts under visible light irradiation ($\lambda > 420\text{ nm}$). It can be shown that, after 3 h of visible light irradiation, degrade (MG) dye, by P₂₅ can only about 25%, 79% for BiOBr, and 94% for BiOBr/SrHA. It is, therefore, obvious that BiOBr/SrHA, with almost all the (MG), dye complete degradation within 3 h irradiation, is yet the most effective photocatalysts of all

the specimens. In the blank control and dark control test, the degeneration of (MG), dye is nearly shown under visible light irradiation, likewise to the visible light irradiation, which further refers that the effectiveness of adsorption is almost small.

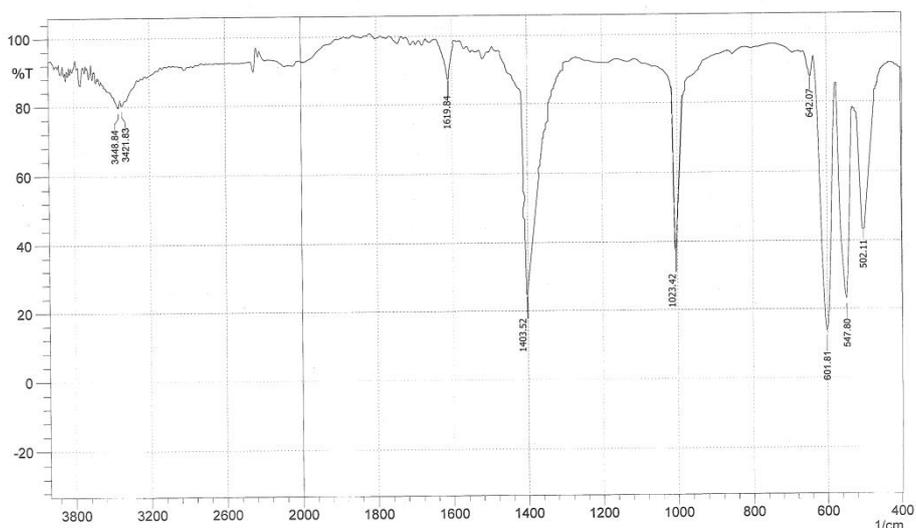
The lifetime of photocatalysts is significant for practical applications. that appreciate the photochemical stability of BiOBr/SrHA was recycled four times. The experimental conditions were $C_0 = 2 \times 10^{-5}$ mg/l, $V = 100$ ml, and BiOBr/SrHA = 0.2 mM. In addition, a 300W Xe lamp was used as the light source to provide visible-light irradiation. the photocatalytic fastness of the BiOBr/SrHA sample is promoted by repeating the decay processes four times under the same conditions, as shown in [Figure 6](#). After four recycles for the photo degeneration of MG, the photocatalyst was observed in the fourth cycle that its efficiency began to decrease. It references that the BiOBr/SrHA photocatalyst is constant during the photocatalytic oxidation of MG, which is particularly important for its application. To moreover realize the nature of the essential active species concerned in visible light degeneration of Malachite green, (MG), over BiOBr and BiOBr/SrHA, we executed the trapping experiments with the supplement of scavenger for the superoxide radical ($\cdot O^{-2}$) species, holes (h^+), and hydroxyl radicals ($\cdot OH$). [21] As shown in [Figure 7](#), with 0.3 mM of the superoxide radical ($\cdot O^{-2}$) scavenger Acrylamide (AC), the decay of (MG), was notably depressed, Also when 0.3 mM of Sodium oxalate ($Na_2C_2O_4$) as a hole scavenger inserts to the solution, the rate for the decay of (MG), notably decreased. In the meantime, with the insert of 0.3 mM isopropanol (IPA), as a scavenger for hydroxyl radicals ($\cdot OH$) species, was added, no apparent decrease in degradation rate was observed, reference the absence of hydroxyl radicals ($\cdot OH$) species. These results explain that holes (h^+) and the superoxide radical ($\cdot O^{-2}$) should be the essential active types for the decay of (MG), onto BiOBr/SrHA under visible light irradiation. [Figures 8 \(a\) and \(b\)](#) displayed the various time changes in the UV-vis irradiation of (MG), solutions through the photocatalytic degeneration over BiOBr and BiOBr/SrHA respectively. It is clear that (MG), could degenerate completely over BiOBr and BiOBr/SrHA photocatalysts under both UV light irradiation and visible light. The concentration of (MG) dye in each decay sample was determined by a spectrophotometer (UV-vis Spectrophotometry PG Instruments Limited, model, T80 (EMC-LAB) at $\lambda_{max} = 615$ nm. By this process conversion percent of (MG) can be obtained in various intervals. The decrease of absorption peaks of (MG) at $\lambda_{max} = 615$ nm in this figure indicates a rapid degradation of (MG). As displayed in [Figure 8 \(a,b\)](#), a blue shift of λ_{max} is frequently noticed through the oxidation of (MG), over BiOBr and BiOBr/SrHA. The shift is related to a stepwise also, it was found that the generation of N-de-methylated MG products during the attack of active oxygen types

account for the notice absorption blueshift of the MG absorption through the MG photo degeneration over TiO₂. [22]

To find out why BiOBr and BiOBr/SrHA compounds give good results in photocatalytic under light irradiation, this has to do with photoelectrochemical properties where the process of electron transfer from the valence band to conduction band leaving behind a hole during irradiation process here, photocurrent will be generated and as it increases the strength of this current, this leads to the efficiency of the electron-hole separation process, and therefore the photocatalytic activity is high.[23]



(a)



(b)

Figure 1 FTIR patterns of BiOBr (a) and BiOBr/SrHA (b)

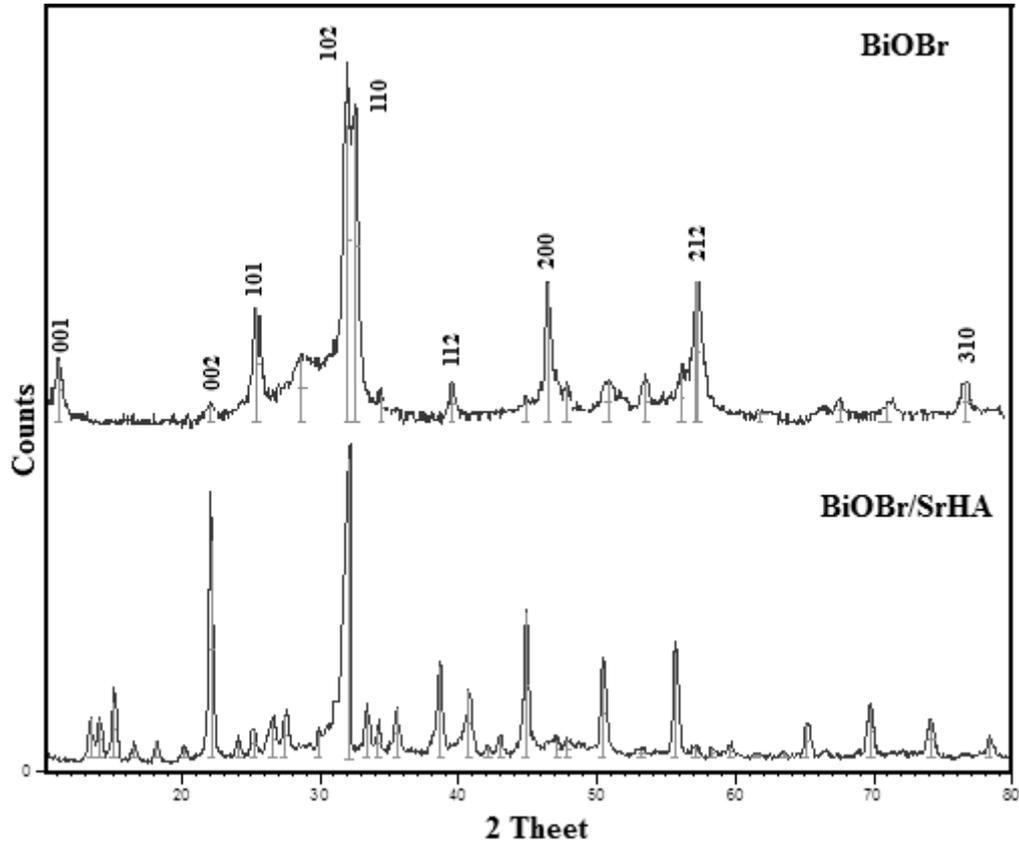


Figure 2 XRD patterns of BiOBr and BiOBr/SrHA

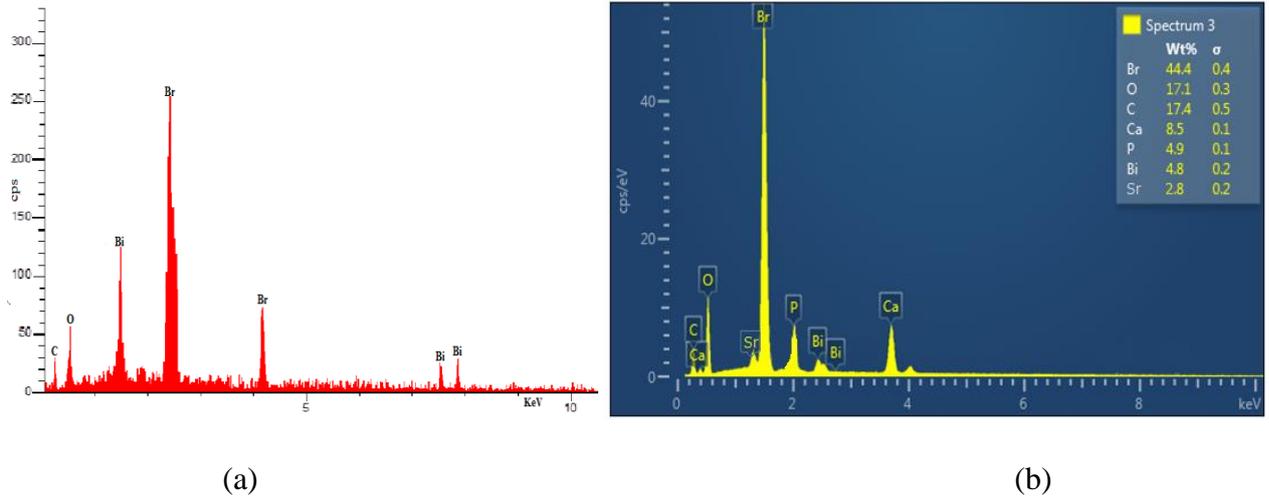


Figure 3 EDX patterns of BiOBr (a) and BiOBr/SrHA (b)

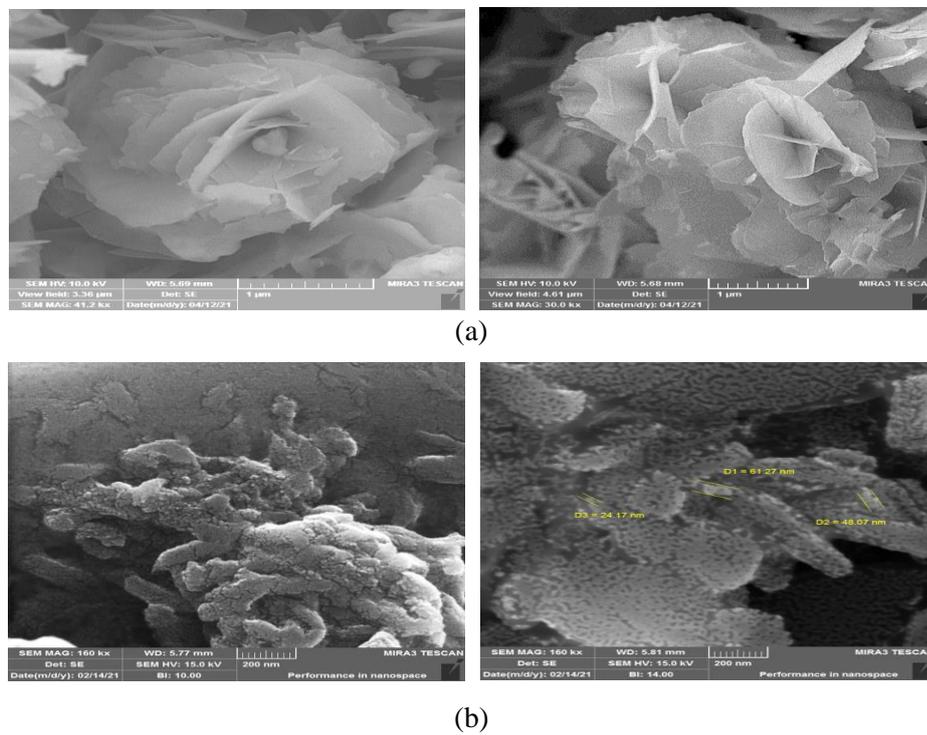


Figure 4 SEM of BiOBr (a) and BiOBr/SrHA (b)

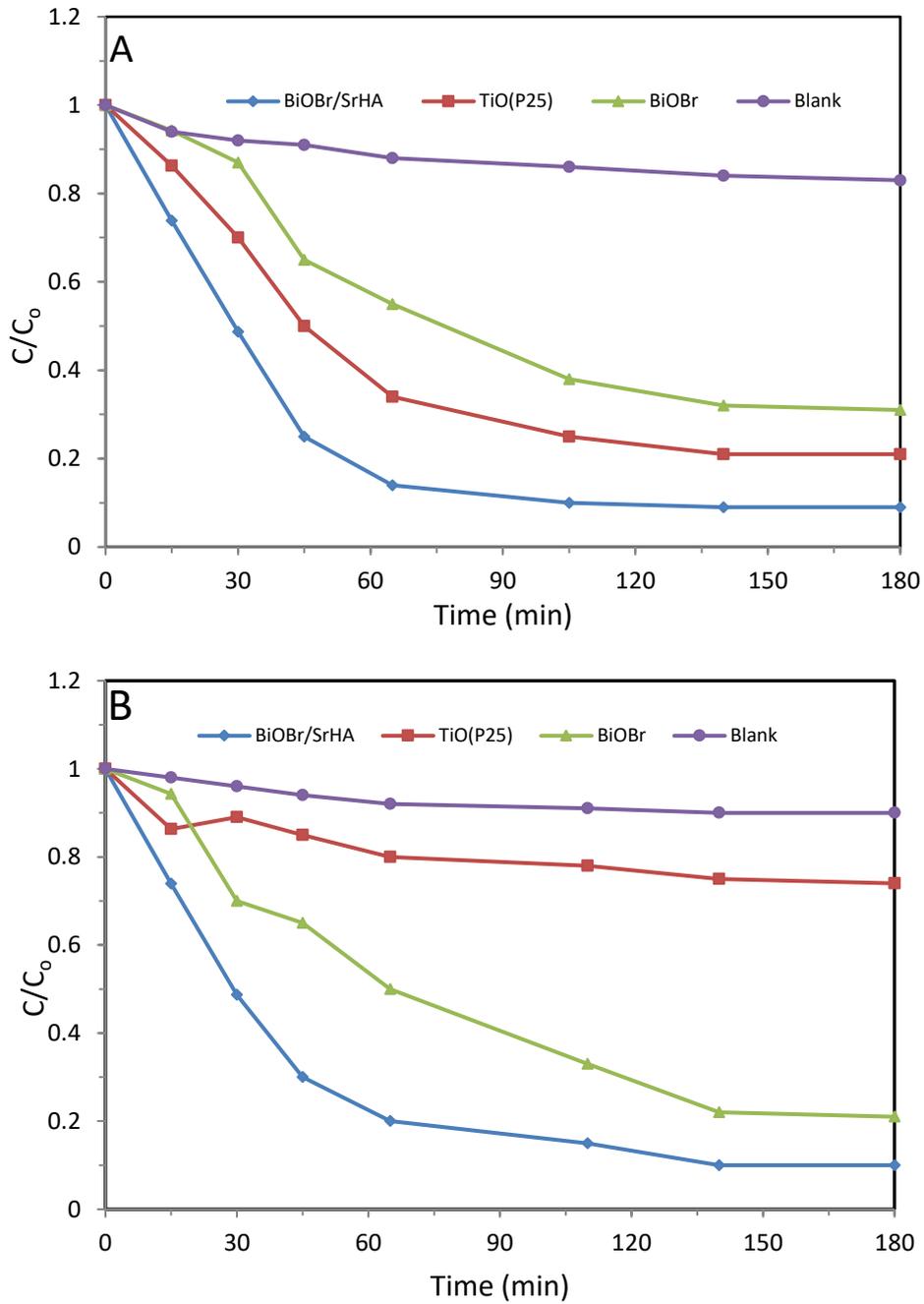


Figure 5 .Time profile of Malachite green (MG), dye degradation by BiOBr and BiOBr/SrHA under (A) UV irradiation, (B) vis-light irradiation

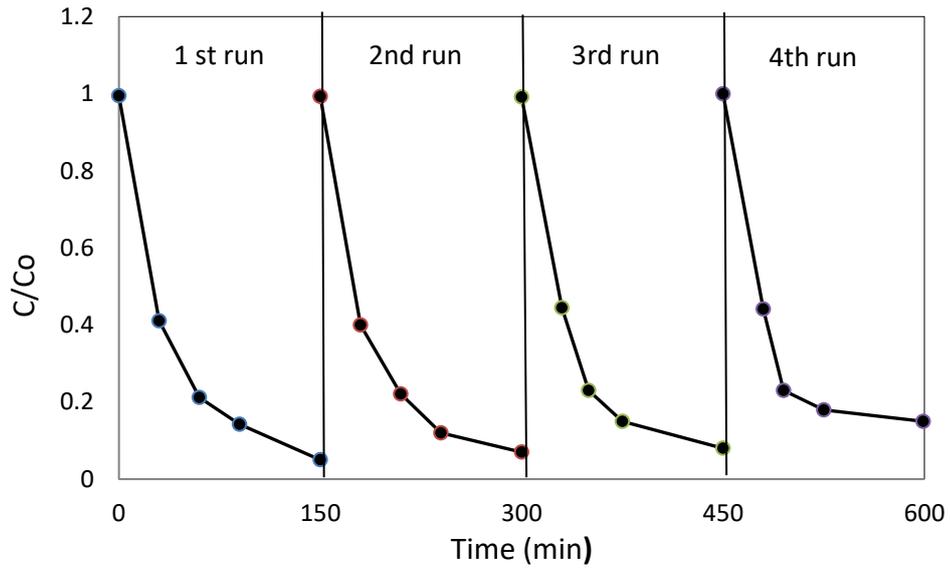


Figure 6. Recycle experiments degradation of MG under visible light irradiation over the BiOBr/SrHA.

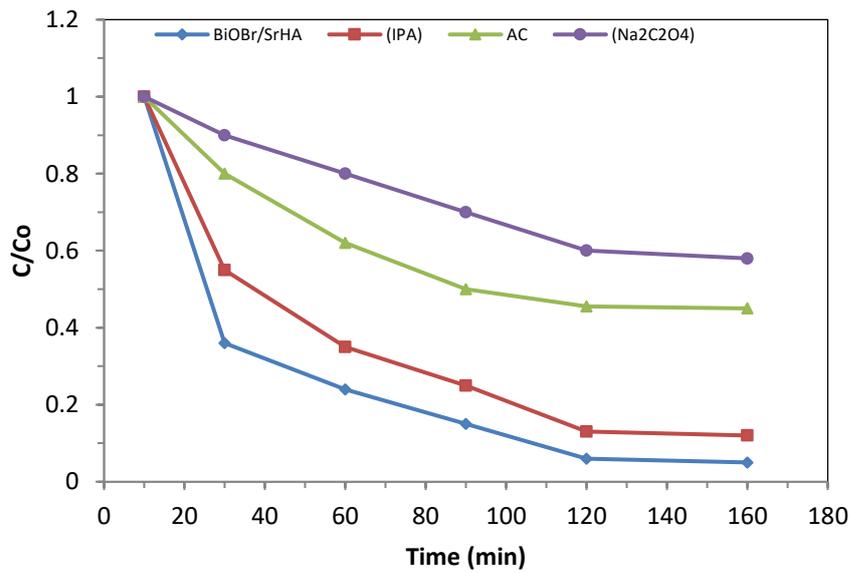


Figure 7. Trapping test of active species through the photocatalytic decay of MG reaction by BiOBr/SrHA

a

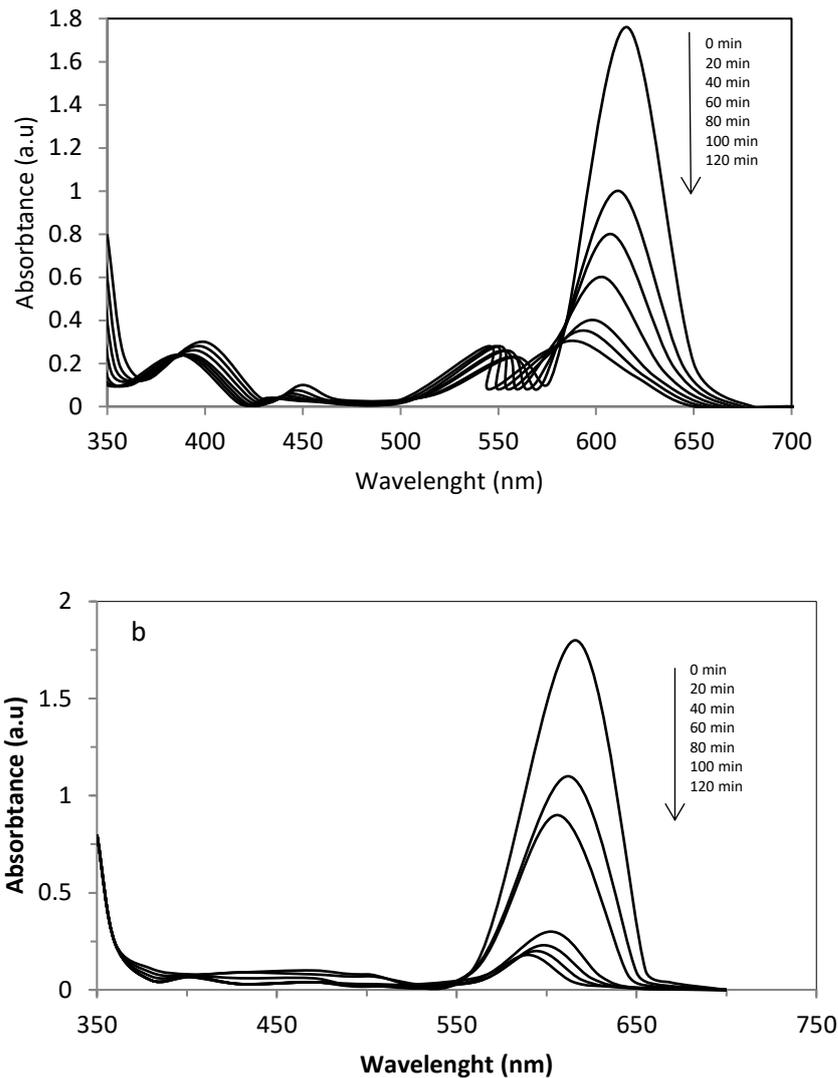


Figure 8. Photocatalytic degradation of MG: (a) UV-vis spectrum of MG over BiOBr/SrHA under vis-light irradiation. and (b) UV-vis spectrum of MG over BiOBr under vis-light irradiation.

4. Conclusions

The results obtained from preparing BiOBr and BiOBr/SrHA compounds confirmed that these two compounds can give excellent results in removing MG dye from its aqueous solutions compared to TiO₂ P₂₅ compound. especially when stimulated under visible light, although TiO₂ P₂₅ compound has a 3.2 bandgap that enables it to function properly. However, the photocatalytic activity of the BiOBr and BiOBr/SrHA models may be related to the effective electron-hole pair separation at the photocatalyst mediator under visible light. in addition to These results reference that the suggested process was a

fast, facile, cheap, and green path to synthesize BiOBr and BiOBr/SrHA photocatalysts, and can become its industrial application and commercial production.

5. REFERENCES

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