Bismuth Oxide Carbonate Structures Synthesized by Microwave—Assisted Solvothermal Approach and Its Use as Catalyst for the Degradation of Azo Dye in a Solution

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Abstract
Because the textile industry wastewater is polluted with azo dyes, and in order to improve a process of wastewater remediation, the synthesized sample was evaluated in the photocatalysis of methylene blue and compared with commercial Bi₂O₃ and anatase TiO₂. Structures of bismuth oxide carbonate (Bi₂O₂CO₃) were successfully synthesized using a solution at 0.03 M concentration of sodium bismuthate as precursor and ethylene glycol as solvent by solvothermal microwave-assisted approach. The semiconductor catalyst samples were characterized by X-ray diffraction (XDR), scanning electron microscope (SEM) and Brunauer-Emmett-Teller analysis (BET). The application of the synthesized sample as catalyst, obtained a 68% of degradation. This result is better than the commercial Bi₂O₃ and close to the anatase TiO₂ degradation. This sample shows a variation in the formula (with the presence of carbonates) but also shows an acceptable degradation percentage according to TiO₂ results, making Bi₂O₂CO₃ a possible substitute of TiO₂.

Keywords
Carbonate Bismuth Oxide, Photocatalysis, Microwave-Solvothermal Synthesis, Methylene Blue, Degradation

1. Introduction
At the present time, the excess of residual liquids has become in a critical problem. There are a lot of pollutants in the water, among which are colorants and chemical substances. Industrial activities are significant contributors to the
wastewater pollution of all the water sources in the world, different industries, among which is textile as one of the largest generators of wastewater due to the dyeing and finishing process, where azo dyes are used [1]. There are a lot of attractive approaches that has been used as treatment for this wastewater. Heterogeneous photocatalysis is an advanced oxidation process widely used to the degradation of organic pollutants in water. It used semiconductors as catalyst for this process, normally. TiO$_2$ powder is employed for this purpose, however, different and economical materials as Bi$_2$O$_3$ have been studied to be used as substitute or complementary system [2].

On the other hand, the most used catalyst is titanium dioxide, TiO$_2$, which has proved that is highly efficient in degradation process of organic materials due to photocatalytic and photoconductor properties. This material has a band gap of 3.2 eV, which means that all UV radiation during a wavelength of 387 nm or less will have enough energy to turn on the catalyst [3]. It also has interesting properties such as transparency in visible light, refractive index, and low absorption coefficient [4]. Titanium dioxide has three different polymorphic structures: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Also, it is a semi-conductor, usually during its anatase and rutile phase [5].

There have been many researches to know bismuth oxide’s physicochemical properties. As a result, there is known that bismuth oxide has different structures which can be obtained with micro and nanometric structures. Besides this polymorphic characteristic, bismuth oxide is characterized for being a well ionic conductor because its band gap is between 2.7 - 2.8 eV and, it has a good photoconductivity [6].

Bismuth (III) oxide is one of the simplest oxides and it has the advantage of being economical and environmentally friendly. Nowadays, this oxide is used in different areas such as medicine and engineering, and also is used in cosmetics because of its low toxicity and, in the last few years, 43% of the bismuth production has been used as a replacement of lead [7].

According to several researches, this oxide has six polymorphic structures, yet, four of them are the most common: $\alpha$, $\beta$, $\gamma$, $\delta$, which two of them are stable; monocyclic phase $\alpha$ works at low temperatures and, cubic phase $\delta$ works at high temperatures, approximately at 1003.15 K; this phase is known because of its high ionic conductivity as oxide ions can move from side to side along bismuth arrangement. The other two intermediate meta-stables phases: tetragonal phase $\beta$ occurs at 923.15 K and, the $\gamma$ phase has a body centered cubic structure which is formed at 913.15 K [8].

In terms of this research, Mexico has maintained its second place in bismuth’s world production with a maximum quantity of 1000 ton in 2010 [9], so bismuth oxide can replace titanium dioxide as catalyst.

For this research, a stable structure of bismuth oxide carbonate was used. It has parallel layers of bismuth atoms that are separated by layers of oxide ions. This allows the structure to have better superficial area. Also, due to low fusion point of bismuth, most of the methods that are used to synthesize different
structures do not apply to bismuth. Bismuth oxide carbonate was synthesized via solvothermal; however, to avoid long reaction periods, the experiment was microwave-assisted, which produces nanoparticles with low size dispersion, although it is hard to have control on morphology. This technique has been used during the last few years as an alternative method to synthesize materials at a nanometric scale because it is a fast and effective method that allows to get more quantity of product in a short period of time [10]. The synthesized material was tested as catalyst of heterogeneous photocatalysis in the reaction of degradation of methylene blue, as azo dye used in many textile industries.

2. Experimental Procedure

2.1. Preparation of the Bi$_2$O$_2$CO$_3$ Catalyst

BiNaO$_3$ (Sigma Aldrich) was dissolved in ethylene glycol (Reasol) to produce a 0.03M solution and maintained continuous stirring at 700 rpm for 15 min, then, the resulting solution was transferred into a digestion vessel (Parr mod. 4781). After that, the vessel was introduced into a microwave oven (Amana Commercial Mod. HDC12A2), the solution was irradiated at 1200 Watts for 10 seconds. Finally, the precipitates were centrifuged and washed several times using distilled water and isopropyl alcohol intercalary. The resulting precipitates were dried for 1 h in an oven (Neytech Qex mod. V1.2) at 100˚C for 1 hour.

2.2. Characterization Details

The surface morphology of the samples of commercial Bi$_2$O$_3$, Bi$_2$O$_2$CO$_3$ synthesized and commercial TiO$_2$ was characterized by scanning electron microscopy (SEM) in a JEOL microscope model JSM-7800F, with a resolution of 0.8 nm at 15 kV of acceleration in secondary electrons mode. A Rigaku diffractometer, model Miniflex 600 with X ray tube with Cu Ka (l = 1.54 Å) radiation and lineal focus was used for XRD, with 40 kV y 15 mA. Symmetric measurements from 3 to 70 degrees with step of 0.01 and a speed or 3 degrees/minute. Nitrogen adsorption and desorption isotherms were measured at 77 K using Quantachrome Autosorb 1. Prior to the measurements, the Bi$_2$O$_3$ 0.03 M and TiO$_2$ samples were outgassed at 100˚C for 25 h. and the commercial Bi$_2$O$_3$ sample was outgassed as the same temperature like the previous samples for 43 h. The specific surface area and the pore size distribution (average pore diameter and mean pore volume) were measured from the adsorption isotherm using the Brunauer-Emmett-Teller method and Barrett-Joyner-Halenda method, respectively.

2.3. Degradation of Methylene Blue

To verify the degradation of methylene blue (C$_{16}$H$_{18}$ClN$_3$S), it was prepared a 25-ppm solution (Sigma Aldrich). First a photolysis was made using 50 ml of the 25-ppm solution that was transferred to a quartz reactor. To make this experiment it was used a closed equipment that contained 8 UV lamps (50 W), and the solution was stirred at 600 rpm. During irradiation, 5 ml of the solution was re-
moved every 10 min for 2 h and went back inside the solution after being analyzed using a Perkin Elmer spectrophotometer 365 in a range of 400 - 700 nm to measure the absorbance of each sample. The commercial Bi₂O₃, synthesized Bi₂O₂CO₃ and TiO₂ catalyst were also studied under the same conditions.

3. Results and Discussion

3.1. DRX and SEM Analysis

The morphology of the samples was observed by SEM. Figure 1(a) shows the surface of the synthesized Bi₂O₃ sample composed by agglomerated foils of 5 µm maximum that might have very good results in photocatalytic activity because of the porosity found on the structure. These foils started to grow during the first 10 seconds of irradiation. The next two images are from the commercial Bi₂O₃ (Figure 1(b)) and TiO₂ (Figure 1(c)) respectively, these structures show difference between morphology and how it affects the degradation of methylene blue because the images show that TiO₂ particles are sphere shaped with an average diameter between 100 to 200 nm, while Bi₂O₃ shows compact agglomerate structures with a diameter of 10 µm.

According to diffraction pattern, Figure 1(a) corresponds to a body centered tetragonal crystalline structure with unit cell parameters a = b = 3.865 and c = 13.675 and angles of α, β, γ de 90˚, this information matches accurately to the crystallographic PDF chart 41-1488, of the bismuth oxide carbonate (Bi₂O₂CO₃). Figure 1(b) shows the diffraction pattern of the alpha bismuth oxide (Bi₂O₃), where the corresponding PDF chart is 71-0465 and demonstrated the presence of a monoclinic system with space group P-21/c(14) and lattice parameters of a = 5.849, b = 8.164 and c = 7.510 and the angle β = 112.97. Finally, Figure 1(c) show the XRD of commercial TiO₂ anatase phase agree with the PDF chart 89-4921 where tetragonal system is reported with lattice parameters of a = b = 3.77 and c = 9.501, angles of 90˚ and space group I41/ad(141).

3.2. Nitrogen Adsorption - Desorption Measurements

The nitrogen adsorption-desorption isotherms of TiO₂ and Bi₂O₃ structures are shown in Figure 2. The TiO₂ and synthesized Bi₂O₃ are a type II isotherm curves. It is observed that the synthesized Bi₂O₃ adsorbed better the N₂ due to a bigger surface area and pore radius. The commercial Bi₂O₃ is a type III isotherm due to the small surface area and pore volume in comparison to the other isotherms.

The corresponding average pore diameter and total pore volume are calculated from the BJH pore size distribution curves and the values are given in Table 1, it is clear that the molecules synthesized of Bi₂O₂CO₃ exhibit a superior surface area and also a higher pore diameter and pore volume than TiO₂ particles. The commercial Bi₂O₃ surface area is 5.64 times smaller than the synthesized sample and it is because a precursor solution with low concentration was used for the synthesis and also the small period of time on the microwave affected positively the porosity of the structure. The specific surface area for the
Bi$_2$O$_2$CO$_3$, Bi$_2$O$_3$ and TiO$_2$ materials is also listed in Table 1.

### 3.3. Optical Properties

The band gap energy was measured using a Perkin Elmer spectrophotometer 365 with integration sphere at wavelength of 500 to 300 nm in Absorbance mode. The Kubelka-Munk method was used to determine the band gap energy. According to the Kubelka-Munk method the Equation (1) was be used:

Table 1. Surface area, total pore volume, and average pore diameter of commercial Bi$_2$O$_3$, anatase TiO$_2$ and synthesized Bi$_2$O$_2$CO$_3$.

| Sample           | Surface area (m$^2$/g) | Total pore volume (cm$^3$/g) | Average pore radius (Å) |
|------------------|------------------------|------------------------------|-------------------------|
| Bi$_2$O$_2$CO$_3$| 25.03                  | 0.1209                       | 90.37                   |
| Commercial Bi$_2$O$_3$ | 4.435                  | 0.006006                     | 21.04                   |
| Anatase TiO$_2$  | 9.819                  | 0.2302                       | 67.4                    |

Figure 1. XDR and SEM micrograph of (a) Synthesized Bi$_2$O$_2$CO$_3$, (b) commercial Bi$_2$O$_3$, (c) commercial TiO$_2$. 

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Figure 2. N$_2$ adsorption-desorption isotherms, (a) Bi$_2$O$_2$CO$_3$, (b) commercial Bi$_2$O$_3$, (c) commercial TiO$_2$, (d) isotherm comparison.

\[ (a\nu)^n = A(h\nu - E_g) \] (1)

where $a$, $\nu$, $A$, $E_g$ are the absorption coefficient, light frequency, a constant and the band gap energy, the $n$ is determined by the type of optical transition in the semiconductor (i.e. $n = 2$ for the direct transition and $n = 1/2$ for the indirect transition). Taking in consideration that the samples are an indirect semiconductor, the band gap energy is determined from a plot of $(a\nu)^{1/2}$ vs. Band gap energy, obtaining the results shown in Table 2.

As it can be observed, the value of Bi$_2$O$_2$CO$_3$ band gap is inside the range of the theoretical values which supports the theory that it is actual Bi$_2$O$_2$CO$_3$ and not another compound, and because of its higher value, it needs more energy than anatase, that is one of the reasons that degradation percentage is slower than anatase.

3.4. Kinetics of Degradation of Methylene Blue

The degradation of methylene blue is until the final stage of the process shown in Figure 3, give as result the formation of CO$_2$ and water, removing the dye in the original solution. In this work, we follow the reaction only with the dye concentration respect the time.
Figure 3. Degradation process of the methylene blue [16].
Table 2. Band gap data obtained from the Kubelka-Munk method and the theoretical ones.

| Band gap   | Bi$_2$O$_2$CO$_3$ | Commercial Bi$_2$O$_3$ | Anatase TiO$_2$ |
|------------|-------------------|------------------------|-----------------|
| Measured   | 3.35 eV           | 2.6 eV                 | 3.0 eV          |
| Theoretical| 2.25 - 3.55 eV    | 2.7 - 2.9 eV           | 2.86 - 3.34 eV  |

The experimental section of the application was carried out following the next procedure: first a calibration curve was obtained, in order to know the concentration of dye in the solution, a photolysis to know the degradation caused by the lamps and finally, the three catalysts were proved at the same conditions.

The calibration curve of methylene blue was obtained to calculate the concentration of the solutions in relation to time. It is clearly observed that the adjusted R-squared value is equal to 0.99756, with an adjusted equation $y = 0.1103x - 0.01103$. This data allows to obtain the concentration of each sample of methylene blue solutions that were taken during the degradation experiments.

To obtain the data for Table 3 some equations were used. Langmuir-Hinshelwood was employed to obtain the first approximation, considering a first order kinetics, as is used in organic dyes in low concentrations. The different concentrations of each solution were calculated using the adjusted equation of the calibration curve (Equation (2)).

$$C_{MB} = \frac{Abs + 0.1148}{0.1148}$$

(2)

The equation above needs the Absorbance in different time ($Abs$), and the result is the concentration of methylene blue in the solution ($C_{MB}$). Then, the percentage of methylene blue in solution was calculated in order to obtain the degradation efficiency, the Equation (3) was used

$$\%C_{MB} = \frac{MBs \times 100}{Co}$$

(3)

$Co$ is the initial concentration of each experiment and finally, the degradation efficiency of each catalyst was calculated by the Equation (4):

$$\%D_{MB} = 100 - \%MB_s$$

(4)

where $D_{MB}$ is the degradation efficiency of catalysts and MBs is the percentage of methylene blue in solution. The table below shows the degraded methylene blue percentage in relation to time.

**Figure 4** shows the comparison of the different experiments to show the degradation percentage of the methylene blue along the 120 min. TiO$_2$ degrades 85.64% of the solution while Bi$_2$O$_2$CO$_3$ shows a degradation percentage of 68.25, showing that the morphology affects positively on the photocatalytic activity.

Morphology plays an important role in photocatalytic activity because commercial Bi$_2$O$_3$ is formed by agglomerated compacted structure that reduces its surface area. A serial of factors influence the photocatalytic reaction with Bi$_2$O$_3$, among which are: due to its hybridisation (Bi 6s and O 2p orbital), it is a strong oxidizer and can successfully degrade organic compounds and favors the mobility of photoholes in the valence band [17].
Table 3. Degraded methylene blue percentage.

| Time (min) | Photolysis | Bi$_2$O$_2$CO$_3$ | Commercial Bi$_2$O$_3$ | Anatase TiO$_2$ |
|-----------|------------|-------------------|------------------------|---------------|
| 0         | 0          | 0                 | 0                      | 0             |
| 10        | 10.4679    | 60.2842           | 29.5348                | 14.3705       |
| 20        | 10.7898    | 62.8541           | 30.0239                | 26.1621       |
| 30        | 10.8316    | 63.2387           | 30.1803                | 35.4951       |
| 40        | 10.8339    | 64.4867           | 31.4892                | 41.4745       |
| 50        | 10.8674    | 65.2364           | 36.2470                | 47.9653       |
| 60        | 11.0419    | 65.2746           | 38.0888                | 55.4298       |
| 70        | 11.1100    | 65.7818           | 38.9539                | 63.9367       |
| 80        | 11.3709    | 66.6508           | 40.2249                | 71.1749       |
| 90        | 11.5032    | 67.7182           | 40.2810                | 77.5477       |
| 100       | 11.6802    | 67.9340           | 41.4341                | 80.2620       |
| 110       | 20.2549    | 68.1760           | 42.9989                | 82.5338       |
| 120       | 24.7961    | 68.2573           | 50.3846                | 85.6415       |

Figure 4. Degradation curves of methylene blue.
According to Levenspiel, the equation used to get the parameters come from the reaction rate equation in terms of the concentration of the reactant

\[-r_d = -\frac{dC_A}{dt} = kC_A^n\]  

(5)

where \(n\) means the order of the reaction, \(k\) is the rate constant and the \(C_A\) is the concentration of the reactant, which in this case is methylene blue.

It is well known that the concentration of the reactants in time \(t\) can be explained by the Equation (6)

\[C_A = C_{A0} (1 - X_A)\]  

(6)

\(C_{A0}\) is the initial concentration of the catalyst and \(X_A\) is the degree of conversion of the reactant. Then, the substitution of Equation (6) in Equation (5) is next

\[-r_d = C_{A0} \frac{dX_A}{dt} = k \left( C_{A0} (1 - X_A) \right)^n\]  

(7)

Knowing the time of the experiment, the change of concentration in time \(t\) due to absorbance measurement and the initial concentration of each experiment, the equation to know the rate constant is shown below as Equation (8).

\[k = \frac{1}{t} \int_0^t \frac{dX_A}{C_{A0} (1 - X_A)^{n-1}}\]  

(8)

Table 4 shows the results of the calculus made to get the approximately kinetic constant of each catalyst and to understand their behavior during the photocatalysis. Even that they are first order kinetics, the speed constant of Bi$_2$O$_2$CO$_3$ shows a bigger constant than TiO$_2$ Anatase because during the first 20 minutes of UV radiation, Bi$_2$O$_2$CO$_3$ degrades better than TiO$_2$. The same behavior is shown with Commercial Bi$_2$O$_3$. For the experiment anatase TiO$_2$ was used because its properties are well known, the superficial area has a value of 10 - 17 m$^2$/g [18] [19]. TiO$_2$ Anatase band gap experimental value is 3.0 eV which shows that needs more energy to get excited and to degrade in a higher way.

**Table 4.** Kinetic parameters of the catalysts used.

|                  | Photolysis | Bi$_2$O$_2$CO$_3$ | Commercial Bi$_2$O$_3$ | Anatase TiO$_2$ |
|------------------|------------|-------------------|------------------------|-----------------|
| \(k\) (rate constant) [min$^{-1}$] | 0.0031 min$^{-1}$ | 0.01310 min$^{-1}$ | 0.0105 min$^{-1}$ | 0.02606 min$^{-1}$ |
| Kinetic model    | \(r_{MB} = -0.0031 C_{MB}\) | \(r_{MB} = -0.0131 C_{MB}\) | \(r_{MB} = -0.0105 C_{MB}\) | \(r_{MB} = -0.02606 C_{MB}\) |

**4. Conclusions**

Anatase TiO$_2$ clearly has the highest degradation percentage of all samples. However, the Bi$_2$O$_3$ structure that was synthesized by solvothermal method using microwave irradiation shows a variation in the formula indicating traces of CO$_3$ but also shows an acceptable degradation percentage according to TiO$_2$ results, making Bi$_2$O$_2$CO$_3$ a possible substitution of TiO$_2$. It needs to be mentioned
that BET area shows that Bi₂O₂CO₃ is clearly superior than Anatase TiO₂ including pore radius. This will indicate in the future that with the proper conditions, it can degrade better than TiO₂. Also, the morphology highly affects degradation process: if the structure possesses high porosity, it will have a high degradation percentage. In terms of band gap, the experimental value of Bi₂O₂CO₃ is inside of theoretical values, but the amount of energy needed in the degradation experiment is higher than anatase; that is one of the principal reasons why anatase has a higher degradation percentage, however, Bi₂O₂CO₃ presents acceptable results, especially in the first minutes of reaction. It is important to consider that Mexico has the second place in bismuth oxide production worldwide, and this allows to reduce costs and to get the catalyst inside the country. Waste-water problem could be decreased considerably using a system like the presented in this research.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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