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## Article

# Photocatalytic Degradation of 4-tert-butylphenol Using Solar Light Responsive $\text{Ag}_2\text{CO}_3$

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**Abstract:** In this work,  $\text{Ag}_2\text{CO}_3$  was prepared via a solution-based method and was further characterized by XRD, Raman spectroscopy, SEM/EDS analysis, and UV-VIS spectroscopy. SEM results revealed the formation of micro-sized particles with a rectangular shape. The photocatalytic activity of the catalyst was evaluated in the degradation of 4-tert-butylphenol (4-t-BP) under simulated solar light irradiation. The effects of 4-t-BP initial concentration (2.5–10 ppm), catalyst dosage (100–300 mg/L), different types of lamp sources, and water matrix were investigated. Complete 4-t-BP (5 ppm) degradation was achieved after 60 min by  $\text{Ag}_2\text{CO}_3$  (200 mg/L). The effect of anions such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  in the concentration range of 100–300 mg/L was also studied.  $\text{CO}_3^{2-}$  promoted the photocatalytic degradation process, while  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  exhibited an inhibition effect, which was marked with increasing  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  concentrations. The presence of  $\text{Cl}^-$  at the concentration of 100 mg/L increased 4-t-BP degradation, but higher concentrations inhibited the photocatalytic reaction. Cyclic experiments showed that the catalyst practically retained its catalytic activity toward 4-t-BP degradation after three successive experimental runs.

**Keywords:** 4-tert-butylphenol; degradation; heterogeneous photocatalysis; solar light



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## 1. Introduction

4-tert-butylphenol (4-t-BP) is an important organic chemical that is extensively used as an intermediate in the production of curing agents [1], phenolic, polycarbonate, and epoxy resins, etc., but is also an endocrine disrupting compound (EDC) [2]. Recently, 4-t-BP has been detected in water bodies from ng/L to  $\mu\text{g/L}$ , representing an environmental threat to aquatic life and human health [3–8]. Therefore, it is of great importance to seek an effective process to degrade 4-t-BP in water.

Several treatment technologies such as photochemical [9–11], physical [12], and biological [13] techniques have been investigated for the efficient elimination of 4-t-BP in contaminated water. Among these, advanced oxidation processes (AOPs) are considered promising to achieve a high degree of 4-t-BP degradation in an environmentally friendly manner [14,15]. Table 1 lists several works regarding AOPs previously used to degrade 4-t-BP. Particularly, heterogeneous photocatalysis, based on the activation of a solid semiconductor with solar light [16–18], has received increasing attention and is considered as an economically and environmentally viable method, since it applies an inexhaustible and sustainable energy source. The sunlight provides abundant irradiation energy; most of it is in the visible light range and only ~4% is ultraviolet light [19,20]. Thus, it is highly desirable to develop a solar-light responsive catalyst.

**Table 1.** Application of different AOPs for 4-t-BP degradation in recent years.

	Processes	Initial Pollutant Concentration (mg/L)	Catalyst Dosage (g/L)	Degradation Time (min)	Degradation Efficiency (%)	Reference
1	Visible light/Bi <sub>4</sub> O <sub>5</sub> I <sub>2</sub> nanoflakes	60	1	90	99.8	[11]
2	Visible light/Bi <sub>12</sub> O <sub>17</sub> Cl <sub>2</sub> /β-Bi <sub>2</sub> O <sub>3</sub> heterojunction (Bi:Cl ratio 1:8)	60	1	90	97	[21]
3	UV(254 nm)/Fe-TiO <sub>2</sub>	30	1	60	92	[22]
4	Solar light/Ti <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	5	0.2	150	89.8	[23]
5	UV (365 nm)/Cu-Mo-TiO <sub>2</sub>	15	0.1	60	100	[24]

To date, many new solar light active catalysts have emerged to degrade EDCs in water, such as metal and bimetal doped metal oxides [24], and binary and ternary composites [25–30]. Ag-based semiconductor materials like Ag<sub>2</sub>O [31,32], AgX (where X = Cl, Br, I) [33], etc. have spawned great interest in photocatalysis because of their non-toxicity [34] and useful photo-absorption ability, particularly in the visible light spectrum [35]. Among the Ag-based photocatalytic materials, Ag<sub>2</sub>CO<sub>3</sub> has a relatively narrow band gap of 2.3 eV [36], while the bottom of its conduction band (CB) consists of hybridized Ag s-Ag s states responsible for high dispersity, which in turn effectively hinders the recombination of electrons and holes [37]. Several researchers have previously reported the photocatalytic activity of Ag<sub>2</sub>CO<sub>3</sub> prepared via different methods. Dai et al. used highly visible-light responsive micro-sized Ag<sub>2</sub>CO<sub>3</sub> for the degradation of rhodamine B (RhB) [36]. Porous Ag<sub>2</sub>CO<sub>3</sub> nanorods prepared using a one-pot aqueous solution method were also applied for the degradation of RhB under visible light irradiation by Guo et al. [38]. In 2017, Lončarević et al. [39] and Zhou et al. [40] reported the photodegradation of methylene blue by means of Ag<sub>2</sub>CO<sub>3</sub> nano-rods and nanoparticles. Recently, Petala et al. found that Ag<sub>2</sub>CO<sub>3</sub> could completely degrade ethyl paraben with possible carcinogenic activity at the concentration of 0.5 mg/L after 120 min under solar light irradiation [37]. However, most of these studies focused on the degradation of organic dyes, while the photocatalytic activity of Ag<sub>2</sub>CO<sub>3</sub> toward the degradation of high estrogenic organic compounds is still under-researched. To the best of our knowledge, there is no study published on the photocatalytic degradation of 4-t-BP, which is a toxic and estrogenic compound, using Ag<sub>2</sub>CO<sub>3</sub>.

In this study, Ag<sub>2</sub>CO<sub>3</sub> microparticles were prepared and employed for 4-t-BP degradation under solar light irradiation. The crystal phase and morphology were investigated using X-ray diffraction analysis (XRD), Raman spectroscopy and Scanning electron microscopy (SEM). The influence of pollutant concentration, catalyst dosage, various light sources and the presence of anions (Cl<sup>−</sup>, HCO<sub>3</sub><sup>−</sup> and CO<sub>3</sub><sup>2−</sup>) was investigated. Radical trapping experiments were performed to study the mechanism of the photocatalytic degradation of 4-t-BP in Ag<sub>2</sub>CO<sub>3</sub>/solar light system.

## 2. Results and Discussion

### 2.1. Characterization

The phase purity and crystallographic structure of Ag<sub>2</sub>CO<sub>3</sub> was investigated through XRD analysis as displayed in Figure 1. The results reveal that Ag<sub>2</sub>CO<sub>3</sub> was in the monoclinic phase without impurities, corresponding to the JCPDS card No. 12-766 [37]. The characteristic diffraction peaks at 18.55°, 20.5°, 32.56°, 33.64°, 37.04°, 39.56°, 41.73°, and 44.32° were attributed to the (020), (110), (−101), (−130), (200), (031), (220), and (131) planes, which is in accordance with the standard XRD pattern of Ag<sub>2</sub>CO<sub>3</sub> [41,42]. Raman spectroscopy was applied in order to support the structural information obtained via XRD analysis. As shown in Figure 2, two peaks at around 701 cm<sup>−1</sup> and 1073 cm<sup>−1</sup> were observed, which corresponded to the characteristic Raman spectra of Ag<sub>2</sub>CO<sub>3</sub> [43,44].

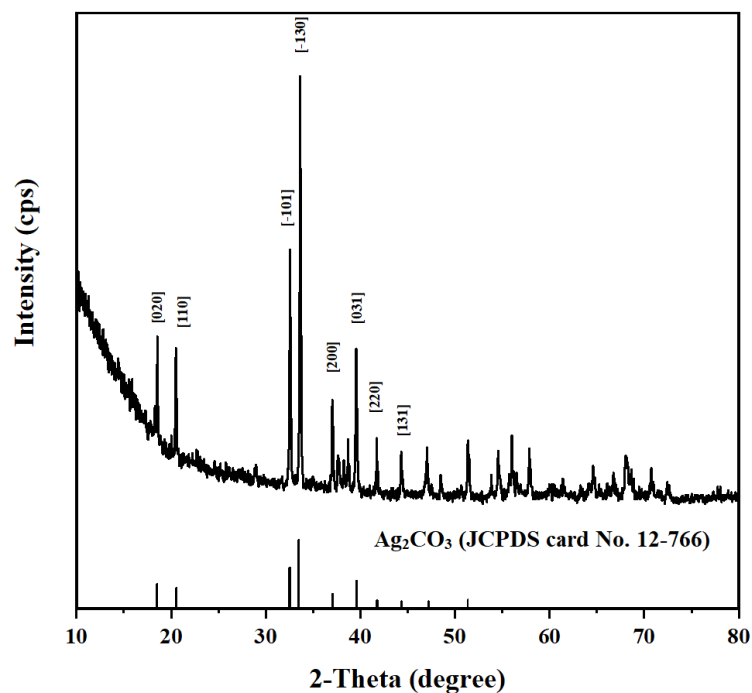


Figure 1. XRD pattern of  $\text{Ag}_2\text{CO}_3$ .

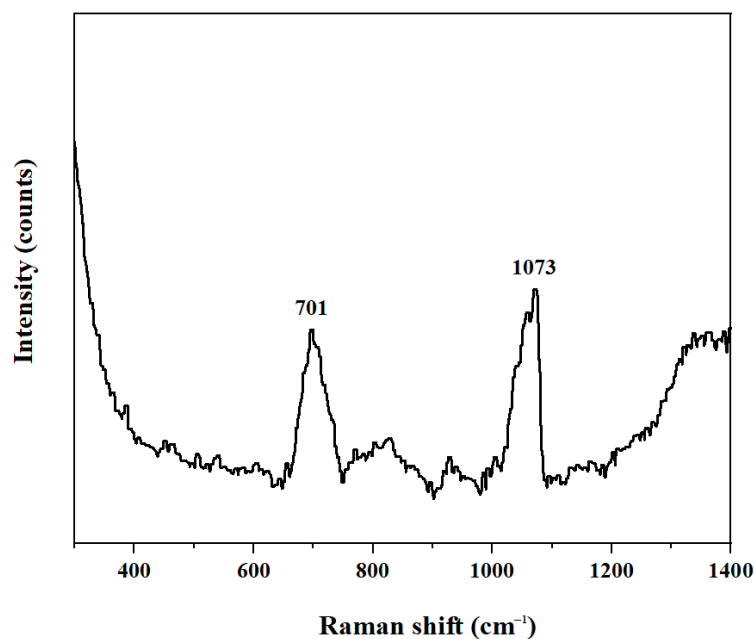
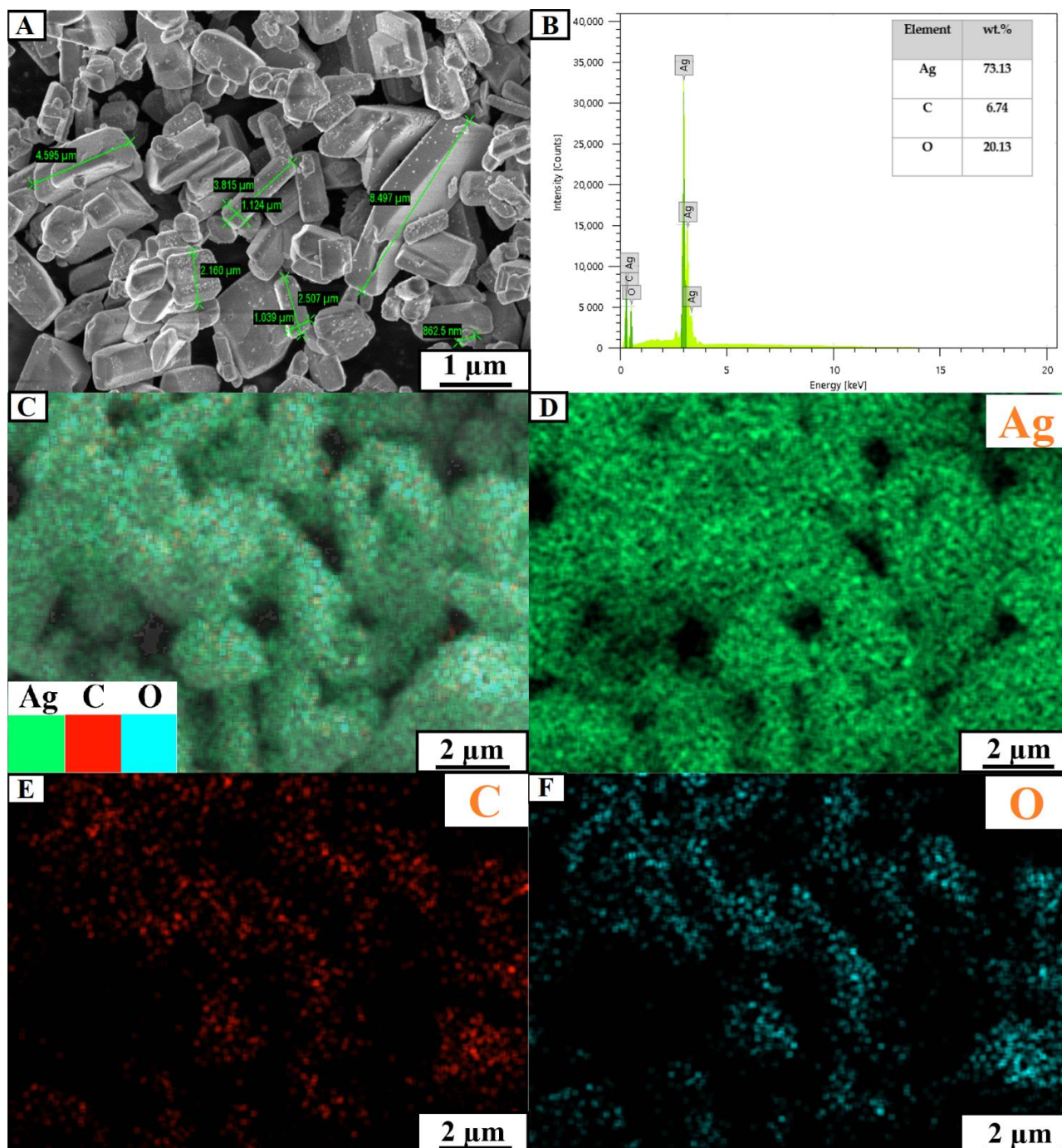


Figure 2. Raman spectrum of  $\text{Ag}_2\text{CO}_3$ .

In order to study the morphology of  $\text{Ag}_2\text{CO}_3$ , SEM analysis was conducted. The SEM image (Figure 3A) revealed that  $\text{Ag}_2\text{CO}_3$  particles are micro-sized with a smooth rectangular structure. The EDS spectrum of  $\text{Ag}_2\text{CO}_3$  (Figure 3B) showed that Ag, C, and O had an elemental distribution of 73.13 wt%, 6.74 wt%, and 20.13 wt%, respectively. At the same time, the elemental mapping showed a homogeneous distribution of Ag, C, and O elements (Figure 3C–F), confirming the purity of the  $\text{Ag}_2\text{CO}_3$  phase. These findings are in agreement with XRD and Raman measurements.



**Figure 3.** (A) SEM image, (B) EDS spectrum, and (C–F) Elemental mapping of  $\text{Ag}_2\text{CO}_3$ .

The optical absorption properties of  $\text{Ag}_2\text{CO}_3$  were examined using UV-VIS spectroscopy. Figure 4 shows that the catalyst had sufficient absorbance of light below 350 nm, and in the ranges of 350–450 nm and 450–800 nm, suggesting that  $\text{Ag}_2\text{CO}_3$  could be photocatalytically active under both UV and visible light as a result of the intrinsic absorption band of  $\text{Ag}_2\text{CO}_3$  [45]. The band gap estimated through Tauc plot of  $\text{Ag}_2\text{CO}_3$  was found to be 2.3 eV. These findings are in agreement with previous studies [46,47].

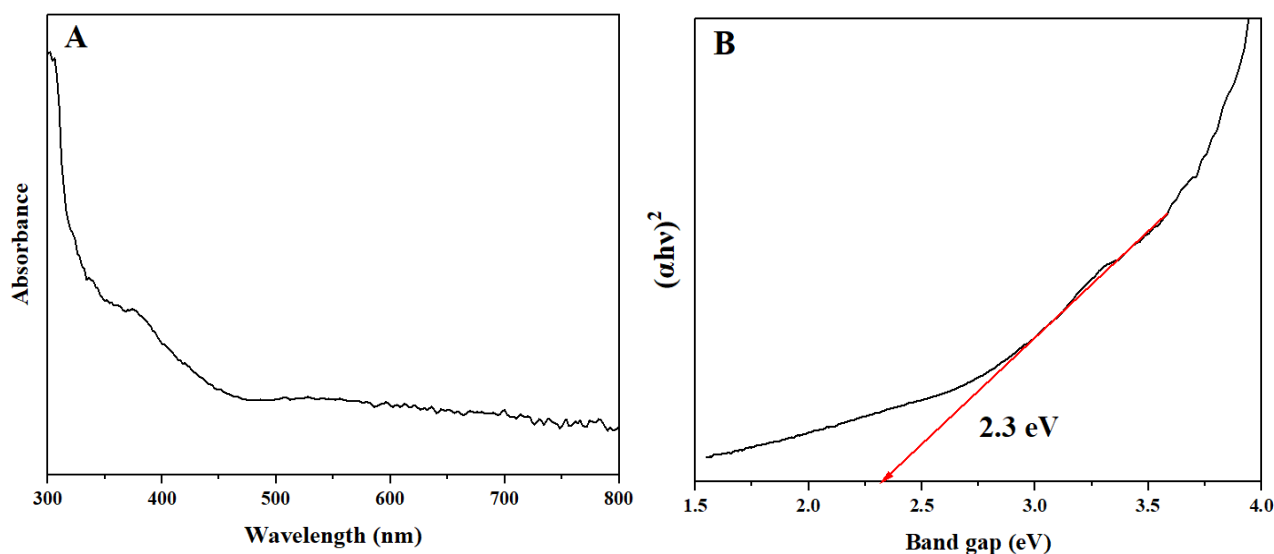


Figure 4. (A) UV-VIS spectra and (B) Tauc plot of  $\text{Ag}_2\text{CO}_3$ .

## 2.2. Photocatalytic Activity of $\text{Ag}_2\text{CO}_3$

### 2.2.1. Effect of 4-t-BP Initial Concentration and Catalyst Dosage

4-t-BP was used as the target degradation compound to examine the solar photocatalytic activity of  $\text{Ag}_2\text{CO}_3$ . Figure 5A shows the effect of initial 4-t-BP concentration on 4-t-BP degradation. The degradation efficiency increased with the increase in pollutant initial concentration from 2.5 ppm to 5 ppm, while it was remarkably decreased after 60 min, with a further increase of pollutant initial concentration to 7.5 and 10 ppm. Such an observation implies a negative correlation between pollutant concentration and degradation efficiency, and can be associated with the fact that more molecules of 4-t-BP would compete to occupy limited reactive sites on the catalyst surface [48–50].

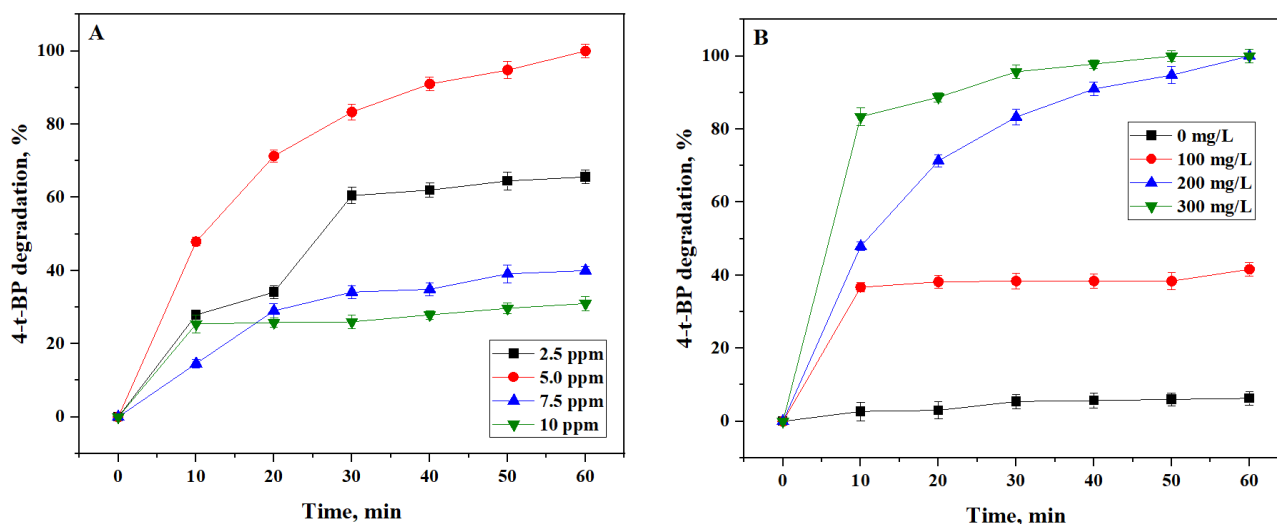


Figure 5. (A) Effect of initial 4-t-BP concentration (catalyst dosage = 200 mg/L) and (B) Effect of catalyst dosage ( $[4\text{-t-BP}]_0 = 5$  ppm) on the degradation of 4-t-BP under solar light.

To study the effect of  $\text{Ag}_2\text{CO}_3$  on the degradation of 4-t-BP, different  $\text{Ag}_2\text{CO}_3$  dosages (100, 200, and 300 mg/L) were used. As shown in Figure 5B, only 6.3% of 4-t-BP was degraded after 60 min in the absence of catalyst, indicating that 4-t-BP could not be effectively degraded by solar light only. As expected, 4-t-BP degradation was enhanced when the catalyst was added to the solution. The increase in catalyst dosage from 100 mg/L to 300 mg/L led to the increase of the final degradation efficiency from 41.6% to 100%. This

can be attributed to the existence of a higher amount of active sites, leading to significant increase in the 4-t-BP degradation [51–53]. On the other hand, the degradation performance of the catalyst was almost the same at the dosages of 200 mg/L and 300 mg/L after 60 min. This could be explained by the reduction of light penetration because of the agglomeration of catalyst microparticles [54,55]. Therefore, the dosage of 200 mg/L was used in the next experimental runs.

The results obtained in this work are compared to selected previous works on the use of Ag<sub>2</sub>CO<sub>3</sub>-based catalysts in the photodegradation of organic pollutants, in Table 2. Most of the recent studies focused on the preparation of composites, including ternary and quaternary, and their application under visible/solar light irradiation. Depending on the pollutant, its initial concentration, catalyst dosage, and light source, the degradation efficiency varies.

**Table 2.** The recent application of Ag<sub>2</sub>CO<sub>3</sub>-based catalysts for the degradation of organic compounds in water, under light irradiation.

	Catalyst	Pollutant	Light Source	Degradation Time (min)	Degradation Efficiency (%)	Reference
1	CaMg(CO <sub>3</sub> ) <sub>2</sub> @Ag <sub>2</sub> CO <sub>3</sub> /Ag <sub>2</sub> S/NCQD	phenol	Simulated solar	100	96.5	[56]
2	Ag <sub>2</sub> O/Ag <sub>2</sub> CO <sub>3</sub> /MWNTs	ciprofloxacin	visible light	60	76	[41]
3	In <sub>2</sub> O <sub>3</sub> /Ag <sub>2</sub> CO <sub>3</sub> S-scheme heterojunction	levofloxacin	visible light	90	86.1	[57]
4	Ag <sub>2</sub> CO <sub>3</sub> @Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> -NT	phenol	solar	240	96.2	[58]
5	g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> CO <sub>3</sub> /graphene oxide	tetracycline	visible	60	81.6	[59]
6	ZnO/Ag <sub>2</sub> CO <sub>3</sub> /Ag <sub>2</sub> O	ibuprofen	visible	480	99.3	[60]
7	Ag <sub>2</sub> CO <sub>3</sub> microparticles	4-tert-butylphenol	Simulated solar	60	100	this work

### 2.2.2. Effect of Lamp Type

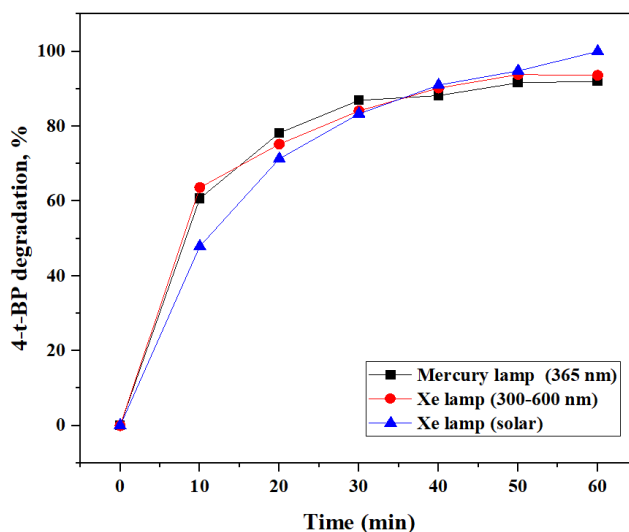
Photocatalytic degradation of 4-t-BP by Ag<sub>2</sub>CO<sub>3</sub> using a Mercury lamp (365 nm, 500 W) and a Xenon lamp (Xe, 300–600 nm, 500 W) was also conducted to compare results with the solar light simulating Xenon lamp (100 W). As displayed in Figure 6, after 10 min, the degradation efficiency of Ag<sub>2</sub>CO<sub>3</sub> using the Xe lamp (300–600 nm) was higher than for the solar light simulating lamp and Mercury lamp (365 nm), achieving 63.6% of 4-t-BP degradation. The application of the Xe lamp (300–600 nm) led to an almost similar degradation efficiency as that of the Mercury lamp (365 nm), though complete degradation of 4-t-BP was achieved only under the solar light simulating Xenon lamp (solar) after 60 min. Such behavior could be associated with the wide range of light absorption of Ag<sub>2</sub>CO<sub>3</sub>, showing concordance with the UV-VIS spectroscopy results of this study.

The energy cost of the photocatalytic process for the degradation of organic pollutants is one of the most important aspects influencing the implementation of these technologies at a larger scale. The energy consumption can be identified through the electrical energy per order (EE<sub>0</sub>), and calculated according to the Equation (1):

$$EE_0 = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_i}{C_f}\right)} \quad (1)$$

where P is the power of the lamp (W); t is the photocatalytic reaction time (min); V is the volume of the reactor (L); and C<sub>i</sub> and C<sub>f</sub> are the initial and final concentrations of 4-t-BP, respectively.

The calculated EE<sub>0</sub> value (Table 3) for the degradation of 4-t-BP, applying the Xe lamp (solar) is 0.98 kWh m<sup>-3</sup> order<sup>-1</sup>, which is significantly lower than the Hg lamp (365 nm) and Xe lamp (300–600 nm), for which values 8–9 times higher are estimated.



**Figure 6.** Effect of lamp types on the degradation of 4-t-BP. Experimental conditions:  $[4\text{-t-BP}]_0 = 5$  ppm, catalyst dosage = 200 mg/L.

**Table 3.**  $EE_O$  estimated for different type of lamps.

Light Source	$EE_O$ ( $\text{kW m}^{-3} \text{ order}^{-1}$ )
Hg lamp (365 nm)	9.12
Xe lamp (300–600 nm)	8.29
Xe lamp (solar light)	0.98

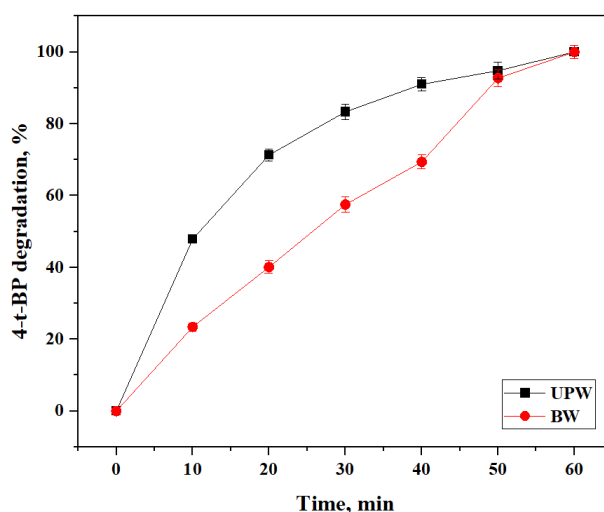
### 2.2.3. Effect of Water Matrix

Natural water matrices consist of a great number of organic and inorganic substances that can interfere with the target pollutant, either promoting or suppressing the efficiency of the process [61,62]. Bottled water is a typical representative of water matrices and therefore the photocatalytic efficiency of the  $\text{Ag}_2\text{CO}_3$ /solar system was also studied in commercially available bottled water (BW). The properties of BW are presented in Table 4. As can be seen from Figure 7, the degradation of 4-t-BP decreased during the first 40 min for BW, which could be attributed to the water matrix complexity [61]. Therefore, additional experiments were conducted to thoroughly investigate the hampering role of BW by adding anions like  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  in the range of of 100–300 mg/L.

**Table 4.** The properties of bottled water.

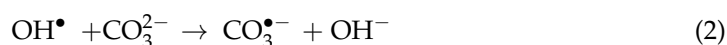
Properties	Value
Conductivity	158.8 $\mu\text{S}/\text{cm}$
pH	7.2
Total organic carbon (TOC)	1.02 mg/L
Total inorganic carbon	16.72 mg/L
$\text{Na}^+$	1–15 mg/L
$\text{K}^+$	0–5 mg/L
$\text{Ca}^{2+}$	10–45 mg/L
$\text{Mg}^{2+}$	5–25 mg/L
$\text{HCO}_3^-$	50–200 mg/L
$\text{Cl}^-$	3–35 mg/L
$\text{SO}_4^{2-}$	1–30 mg/L



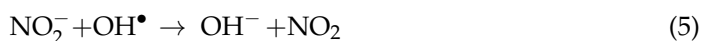
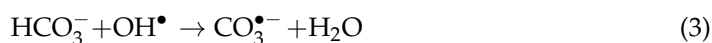


**Figure 7.** Effect of the type of water on the degradation of 4-t-BP under solar light. Experimental conditions:  $[4\text{-t-BP}]_0 = 5$  ppm, catalyst dosage = 200 mg/L.

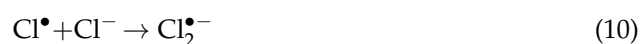
As shown in Figure 8A, the presence of  $\text{CO}_3^{2-}$  enhanced the 4-t-BP degradation. Increasing the concentration of  $\text{CO}_3^{2-}$  from 100 mg/L to 300 mg/L led to the improvement of catalyst performance. Such behavior could be attributed to the generation of more active species ( $\text{CO}_3^{\bullet-}$ ) in the reaction system (Equation (2)). Although  $\text{CO}_3^{\bullet-}$  has a lower redox potential than that of  $\text{OH}^{\bullet}$ , it exhibits higher selectivity and longer survival time in solution, resulting in fast 4-t-BP photocatalytic degradation in the reaction system [63,64].



As for  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  (Figure 8B,C), the significant inhibition effect on the performance of  $\text{Ag}_2\text{CO}_3$  stems from the formation of less reactive radicals [65,66] (Equation (3)) and the consumption of photons,  $\text{OH}^{\bullet}$  and  $\text{h}^+$  by  $\text{NO}_3^-$  [67] (Equations (4)–(6)). The most pronounced inhibition effect of  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  was observed with an increase of  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  concentrations to 300 mg/L. The degradation efficiency of 4-t-BP decreased to 55.1% and 50.6% in the presence of  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ , respectively.

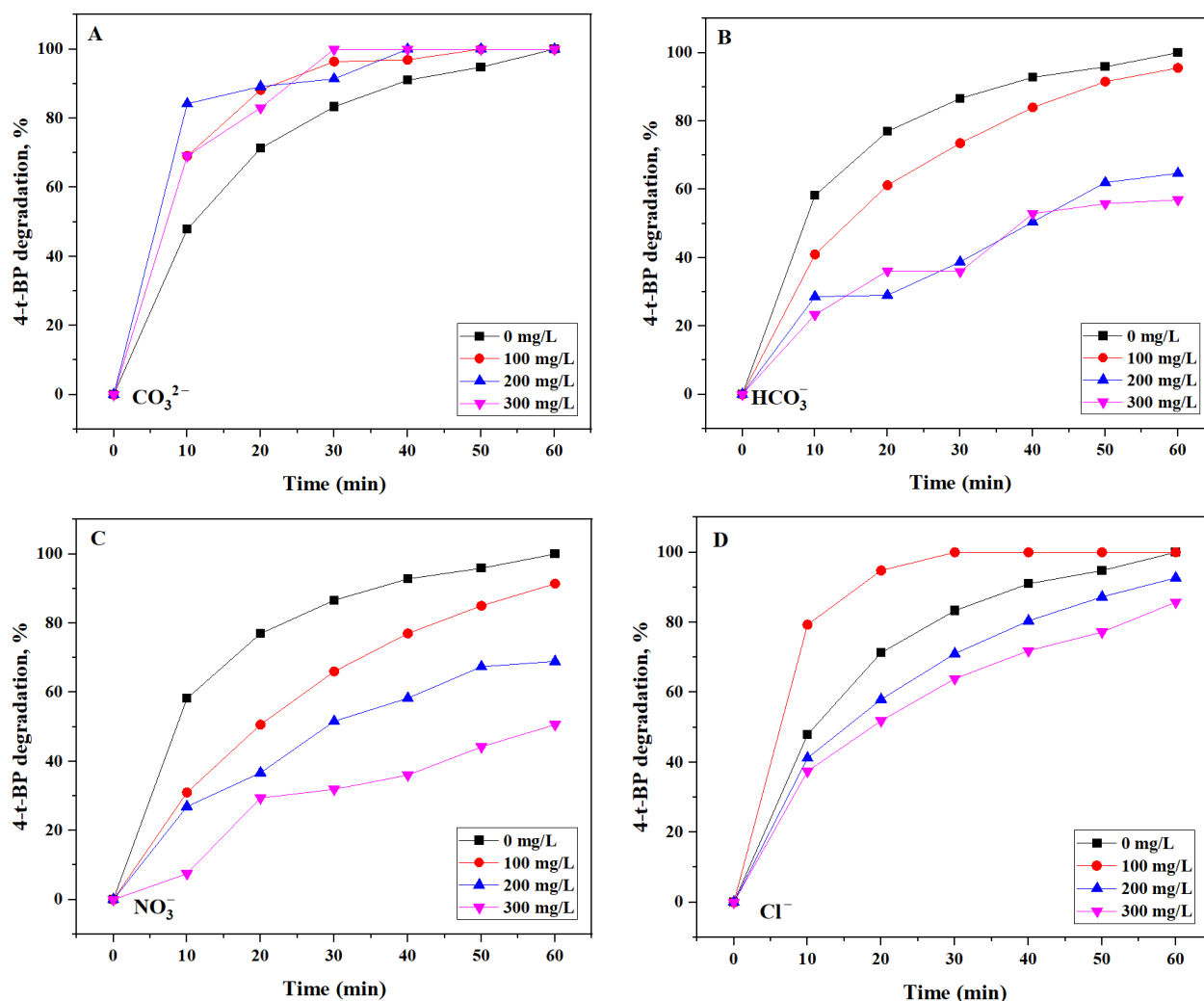


The addition of 100 mg/L of  $\text{Cl}^-$  had a positive effect on the degradation process ascribed to the selectivity of chloride radicals [68], while a further increase in  $\text{Cl}^-$  concentration inhibited the photocatalytic degradation of 4-t-BP (Figure 8D). This can be associated with the generation of less oxidative species via the following reactions [69,70] (Equations (7)–(14)):



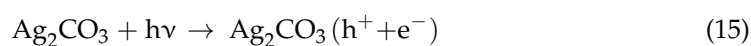


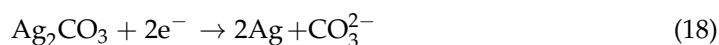
To investigate the photocatalytic mechanism of  $\text{Ag}_2\text{CO}_3$ , radical quenching experiments were performed using several scavengers, namely KI, IPA, and p-BQ to identify the major active species ( $\text{h}^+$ ,  $\text{OH}^\bullet$ , and  $\text{O}_2^{\bullet-}$ ) responsible for the degradation of 4-t-BP. The degradation efficiency was enhanced in all three cases (Figure 9), suggesting that the presence of KI, IPA, and p-BQ was beneficial for the  $\text{Ag}_2\text{CO}_3$ /solar light system in terms of 4-t-BP degradation. The introduction of KI into the reaction contributed to the production of more  $\text{OH}^\bullet$  radicals through the scavenging of photo-generated  $\text{h}^+$  [63,71], while the addition of IPA decreased the recombination of electron-holes [72], hence increasing the photocatalytic activity.



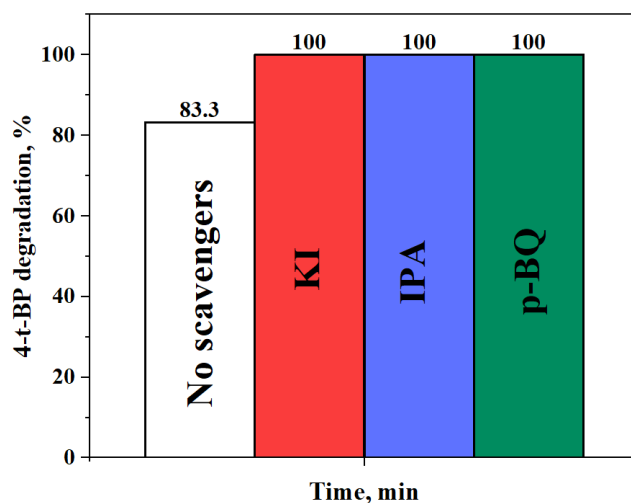
**Figure 8.** The effect of (A)  $\text{CO}_3^{2-}$ , (B)  $\text{HCO}_3^-$ , (C)  $\text{NO}_3^-$ , and (D)  $\text{Cl}^-$  on the degradation of 4-t-BP. Experimental conditions:  $[\text{4-t-BP}]_0 = 5 \text{ ppm}$ , catalyst dosage = 200 mg/L.

As previously reported [36], the visible light irradiation of  $\text{Ag}_2\text{CO}_3$  catalyst results in the formation of electrons/holes in  $\text{Ag}_2\text{CO}_3$  (Equation (15)), resulting in electron transfer. Positive holes react with water generating  $\text{OH}^\bullet$  (Equation (16)), while electrons may induce both oxidation (Equation (17)) and reduction reactions (Equation (18)) leading to the formation of  $\text{H}_2\text{O}_2$  and  $\text{CO}_3^{\bullet-}$  radicals.





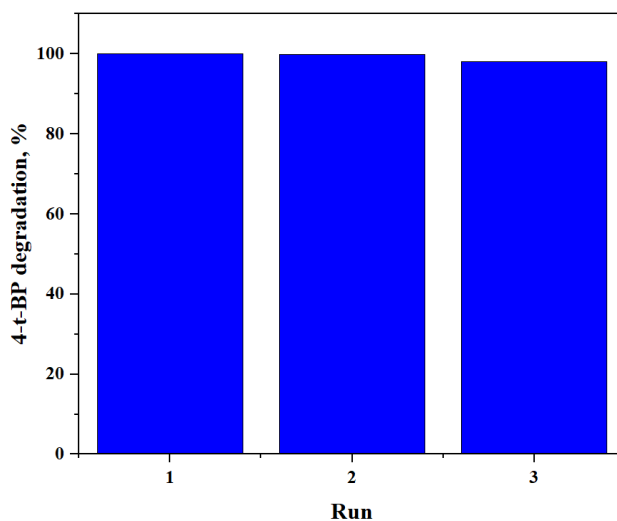
It has also been reported that in some cases, radical scavenging tests had no remarkable impact on the degradation of persistent organic pollutant, suggesting the presence of surface-bound reactive species and electron transfer in the reaction solution between the oxidant and the molecule of the target organic compound [63]. In such cases,  $\text{H}_2\text{O}_2$  formed under the absorption of visible light by  $\text{Ag}_2\text{CO}_3$  (Equation (17)) can serve as an oxidant in the degradation process, while the generated  $\text{CO}_3^{2-}$  radical (Equation (18)) promotes the degradation of 4-t-BP, as discussed earlier.



**Figure 9.** Effect of KI, IPA, and p-BQ on the degradation of 4-t-BP. Experimental conditions:  $[\text{4-t-BP}]_0 = 5$  ppm, catalyst dosage = 200 mg/L.

#### 2.2.4. Reusability and Stability of $\text{Ag}_2\text{CO}_3$

Cyclic experiments were carried out to investigate the stability and reusability of the  $\text{Ag}_2\text{CO}_3$  catalyst. Figure 10 illustrates the performance of the  $\text{Ag}_2\text{CO}_3$  catalyst for three successive experiments. After each run, the catalyst was filtered, washed with UPW for several times, and dried. It is obvious that the loss in catalytic activity of  $\text{Ag}_2\text{CO}_3$  was insignificant, thus indicating the good stability of the catalyst.



**Figure 10.** Cyclic experiments of  $\text{Ag}_2\text{CO}_3$  toward the degradation of 4-t-BP. Experimental conditions:  $[\text{4-t-BP}]_0 = 5$  ppm, catalyst dosage = 200 mg/L.

### 3. Materials and Methods

#### 3.1. Materials

Silver nitrate ( $\text{AgNO}_3$ , 99.0%), 4-tert-butylphenol ( $\text{HO-C}_6\text{H}_4\text{-C(CH}_3)_3$ , 99.0%), sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99.5%), sodium bicarbonate ( $\text{NaHCO}_3$ , 99.7%), sodium nitrate ( $\text{NaNO}_3$ , 99.0%), sodium chloride ( $\text{NaCl}$ , 99.8%), methanol ( $\text{CH}_3\text{OH}$ , 99.9%) were obtained from Sigma-Aldrich (Saint Louis, MO, USA), while potassium iodide ( $\text{KI}$ , 99.0%), isopropanol ( $\text{C}_3\text{H}_8\text{O}$ , 99.5%) p-benzoquinone ( $\text{C}_6\text{H}_4\text{O}_2$ , 98.0%) were obtained from Merck KGaA (Darmstadt, Germany) and used without further purification. UPW (18.25  $\text{M}\Omega\cdot\text{cm}$ ) was applied for preparing required solutions.

#### 3.2. Preparation of $\text{Ag}_2\text{CO}_3$

A simple solution-based method was used to synthesize  $\text{Ag}_2\text{CO}_3$  [73]. Under continuous stirring, two solutions were prepared: (1) 0.5 g of  $\text{NaHCO}_3$  was mixed in 60 mL of UPW and (2) 2.04 g of  $\text{AgNO}_3$  was mixed in 60 mL UPW. Then, the obtained  $\text{AgNO}_3$  mixture was added dropwise to  $\text{NaHCO}_3$  mixture and kept under a stirring condition for 240 min at room temperature. Finally, the formed precipitate was collected by centrifugation, washed with UPW, and dried at 60 °C for 12 h.

#### 3.3. Characterization of the Prepared Catalyst

The XRD pattern of prepared  $\text{Ag}_2\text{CO}_3$  was recorded on the Rigaku Smartlab system (Rigaku, Tokyo, Japan) in a  $2\theta$  range of 10–80°, while the Raman spectra was obtained using Raman spectrometer (Horiba, LabRam HR evolution, Kyoto, Japan). SEM imaging and EDS elemental mapping of  $\text{Ag}_2\text{CO}_3$  analysis was performed using a SEM/EDS (Crossbeam 540, Carl Zeiss, Oberkochen, Germany) instrument. UV-VIS spectroscopy was used to investigate the optical properties of the catalyst by Thermo Scientific Genesys 150 UV-Visible spectrophotometer (Thermo Fisher Scientific Inc., Waltham, MA, USA).

#### 3.4. Photocatalytic Degradation of 4-t-BP

Photocatalytic experiments were conducted in a 50 mL batch reactor under continuous stirring. A solar simulator (100 W Xe lamp, AM1.5G filter, LCS-100, Newport) was used as an irradiation source. The initial concentration of 4-t-BP ranged from 2.5–10 ppm (mg/L), while the catalyst dosage amounted in the range of 0–300 mg/L. A 30-min magnetic stirring was applied before the start of irradiation to allow for adsorption-desorption equilibrium. Samples were periodically withdrawn from the reactor, filtered by means of 0.22  $\mu\text{m}$  Millipore filters, and sent for high-performance liquid chromatography (HPLC, Agilent 1290 Infinity II, Santa Clara, CA, USA) analysis. A mixture of  $\text{CH}_3\text{OH}$  and UPW (50%:50% by volume) was used as a mobile phase.

The following equation was used to estimate the 4-t-BP degradation:

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100\%$$

where  $C_t$  is the concentration of 4-t-BP after regular intervals of time (t), and  $C_0$  is the initial concentration of 4-t-BP.

For comparison, the 4-t-BP solution in the presence of  $\text{Ag}_2\text{CO}_3$  was also exposed using a Mercury lamp (365 nm, 500 W) and a Xenon lamp (300–600 nm, 500 W) source under the same conditions using photocatalytic reactors (Lanphan industry, Zhengzhou City, Henan Province, China).

The active species in the  $\text{Ag}_2\text{CO}_3$ /solar light system were investigated with the addition of potassium iodide (KI), isopropanol (IPA), and p-benzoquinone (p-BQ) into the reaction system to identify holes ( $\text{h}^+$ ), hydroxyl radicals ( $\text{OH}^\bullet$ ), and superoxide radicals ( $\text{O}_2^{\bullet-}$ ), respectively. Prior to irradiation, 1 mL of each scavenger solution, with a concentration of 2 mmol/L was added to the mixture of 4-t-BP solution and  $\text{Ag}_2\text{CO}_3$ .

#### 4. Conclusions

$\text{Ag}_2\text{CO}_3$  was synthesized by a simple solution-based method and was applied toward 4-t-BP degradation under simulated solar light irradiation. The crystal structure, purity, morphology, and optical properties of the catalyst were studied using XRD, Raman Spectroscopy, SEM, and UV-VIS spectroscopy. The effect of different factors, including the initial concentration of 4-t-BP, catalyst dosage, types of light source, and water matrix on 4-t-BP degradation were further investigated. Complete degradation of 4-t-BP (5 ppm) was achieved within 60 min using 200 mg/L of  $\text{Ag}_2\text{CO}_3$ . The presence of  $\text{CO}_3^{2-}$  had only a positive effect on the performance of  $\text{Ag}_2\text{CO}_3$ /solar light system and enhanced 4-t-BP degradation. Low amounts of  $\text{Cl}^-$  (100 mg/L) in the reaction system enhanced 4-t-BP degradation; however, a further increase of  $\text{Cl}^-$  concentration to 300 mg/L inhibited the degradation process. Through three successive experimental runs, the catalyst exhibited excellent stability and reusability properties.

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