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Comparative study of the degradation of carbamazepine in water by advanced oxidation processes

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Degradation of carbamazepine (CBZ) using ultraviolet (UV), UV/H₂O₂, Fenton, UV/Fenton and photocatalytic oxidation with TiO₂ (UV/TiO₂) was studied in deionized water. The five different oxidation processes were compared for the removal kinetics of CBZ. The results showed that all the processes followed pseudo-first-order kinetics. The direct photolysis (UV alone) was found to be less effective than UV/H₂O₂ oxidation for the degradation of CBZ. An approximate 20% increase in the CBZ removal efficiency occurred with the UV/Fenton reaction as compared with the Fenton oxidation. In the UV/TiO₂ system, the kinetics of CBZ degradation in the presence of different concentrations of TiO₂ followed the pseudo-first order degradation, which was consistent with the Langmuir–Hinshelwood (L–H) model. On a time basis, the degradation efficiencies of CBZ were in the following order: UV/Fenton (86.9% ± 1.7%) > UV/TiO₂ (70.4% ± 4.2%) > Fenton (67.8% ± 2.6%) > UV/H₂O₂ (40.65 ± 5.1%) > UV (12.2% ± 1.4%). However, the lowest cost was obtained with the Fenton process.

Keywords: carbamazepine; water; advanced oxidation processes; degradation; comparative assessment

1. Introduction

Pharmaceuticals, as emerging pollutants in aquatic environments, have received much attention recently [1–5]. A large variety of pharmaceuticals, including β -blockers, sympathomimetics, antiphlogistics, lipid regulators, antibiotics and so on, have been frequently detected in aquatic environments at concentration levels up to micrograms per litre in Europe, North America and South Asia [2,6,7]. A typical compound is carbamazepine (CBZ). Environmental pollution by CBZ is considered a pervasive problem because of its low biodegradability and inhibitory nature in wastewater [8]. A large volume of this kind of pharmaceutical is being used for treatment in humans (e.g. its annual usage ranks the second among all the anti-epileptic drugs used in China [9]). Carbamazepine is used for the treatment of seizure disorders, relief of neuralgia, and a wide variety of mental disorders. Approximately 72% of orally administered CBZ is absorbed, whereas 28% is unchanged and subsequently discharged through the faeces [10]. After it is absorbed, CBZ is heavily metabolized by the liver: only about 1% of the dosage leaves the body in an unaltered form. The CBZ metabolites undergo enterohepatic cycling and finally are excreted with urine. The elimination half-life time of CBZ is dose-dependent, but is usually in the range of 25–65 h post-administration [11]. Carbamazepine barely

attaches on to sludge. Its distribution coefficient between water and secondary sludge (K_d) is 1.2 L/kg, far from the value of 500 L/kg required for significant sorption on to sludge [12]. Therefore, the bulk of CBZ remains associated with the aqueous phase. Carbamazepine is highly persistent in the aquatic environment and has already been detected in municipal wastewater and surface water at concentrations ranging from 35 to 2440 ng/L. It has also been found in drinking water at a concentration of 30 ng/L [4,13,14]. Heberer [2] reported that the CBZ concentration was up to 1075 ng/L in the surface water in Berlin. In addition, CBZ has been detected in groundwater at concentrations up to 610 ng/L [1] and in sea water, although at a very low concentration (2 ng/L) [15].

Although the environmental risks of CBZ are largely unknown at the present, CBZ has been used as a model compound to evaluate the pharmaceutical removal efficiency in wastewater treatment plants [16]. The persistence of CBZ in the aquatic environment, with respect to abiotic transformation processes, as well as its toxicity and capability of accumulating in aquatic organisms (e.g. algae), has also been evaluated [17]. Oetken *et al.* [18] demonstrated that the antiepileptic CBZ had a significant and specific chronic effect against the oligochaete *Chironomus* at environmentally relevant concentrations. Carbamazepine

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often remains stable after conventional or even advanced biological wastewater treatment processes owing to its bio-refractory nature. It was constantly found at higher concentrations in treated sewage than in raw sewage [4]. Vieno *et al.* [4] qualitatively analysed CBZ-N-glucuronide in sewage samples by LC-MS/MS using three mass transitions for CBZ-N-glucuronide, and the result indicated that the increase in concentration was probably due to enzymatic cleavage of the glucuronic conjugate of carbamazepine and release of the parent compound in the treatment plant. In addition, it may be transformed to some mutagenic compounds during conventional oxidation processes [19]. In the classification scheme for pharmaceutical biodegradation, the removal status of CBZ was classified as 'no removal' [3]. If CBZ residues are not effectively removed from water by drinking-water treatment facilities, the CBZ is unintentionally consumed by humans. Therefore, it is pertinent to develop effective technologies to remove CBZ from water and wastewater [20].

Recently, advanced oxidation processes (AOPs) have been commonly applied to treat water and wastewater containing toxic and non-biodegradable pollutants [16,21,22]. Advanced oxidation processes use combinations of chemical oxidants, ultraviolet (UV) irradiation and homogeneous or heterogeneous catalysts to generate the hydroxyl radical ($\bullet\text{OH}$), an intermediate oxidant possessing a high oxidation potential ($E_0 = 2.8\text{ V}$), for the degradation of bio-refractory or hazardous organic compounds in wastewater. Organic pollutants are oxidized by free radicals and sometimes mineralized to water, carbon dioxide and mineral salts. A combined oxidation process usually has a higher reaction efficiency than an individual oxidation process because of the enhanced generation of $\bullet\text{OH}$. Taking the photo-assisted AOPs as an example (e.g. UV/ H_2O_2 , UV/ O_3 , UV/ $\text{H}_2\text{O}_2/\text{O}_3$, UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}[\text{Fe}^{3+}]$ and UV/ TiO_2), UV enhances the generation of $\bullet\text{OH}$, and H_2O_2 prevents the recombination of electrons and holes, thus leading to an effective degradation of many organic pollutants [23–26].

To the best of our knowledge, sufficient information on degradation of CBZ using AOPs is not available. In addition, a comparative study of different AOP technologies in a single manuscript is often missing. Therefore, the major objective of this study was to comparatively investigate the reaction kinetics and degradation efficiency for CBZ by UV irradiation, UV/ H_2O_2 , Fenton's reagent, UV/Fenton and UV/ TiO_2 to screen and select the most effective technology for the treatment of CBZ-containing wastewater. Cost evaluation was also performed for various AOP processes studied.

2. Materials and methods

2.1. Chemicals

Carbamazepine of high purity grade (99%) was purchased from Sigma (St Louis, MO, USA). Hydrogen peroxide

(30%, w/w) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were purchased from Shanghai Xingao Chemical Reagent Co., Ltd (Shanghai, China). Titanium dioxide (P25, particle size = 20–30 nm; Brunauer, Emmett, Teller (BET) surface area = 50–15 m^2/g , 70% anatase and 30% rutile) was purchased from Degussa (Essen, Germany). High-performance liquid chromatography (HPLC) grade acetonitrile was purchased from Tedia (Fairfield, OH, USA). Acetone was purchased from Shanghai Zhenxing NO.1 Chemical Plant (Shanghai, China). Ethyl acetate was purchased from the National Medical Group Chemical Reagent Co., Ltd (Beijing, China). Ultrapure water with a resistivity of 15–18 $\text{M}\Omega\text{-cm}$ was produced with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Hydrogen chloride and NaOH solutions were used to adjust the pH value of aqueous solutions.

2.2. Sample preparation

The stock solution of CBZ was prepared by dissolving 84.6 μmol of CBZ in 2 L of deionized water. After the stock solution was magnetically stirred for several hours and filtered through 0.2 μm cellulose nitrate filters (Millipore, Bedford, MA, USA) to remove residual solids, it was stored in an amber vial at -20°C . The stock solution was renewed monthly. All the working solutions of CBZ were prepared freshly by diluting the stock solution that had been brought back to room temperature ($\sim 24^\circ\text{C}$) with deionized water. Prior to each experiment, the working solution was sparged with a gentle stream of humidified air for 15 min, to make it reach a similar concentrations of dissolved oxygen and bicarbonate. The working solution was then buffered with phosphate salts (K_2HPO_4 and KH_2PO_4) to adjust its pH to 7.0.

A ferrous sulphate solution (2 mM) was prepared in 0.01 M HCl, which was replaced weekly with a fresh solution to prevent the formation of $\text{Fe}(\text{OH})_2 \cdot \text{H}_2\text{O}_2$. The working solutions used in the experiments were prepared by appropriate dilutions of the stock solution.

2.3. The photoreactor with a UV irradiation system

A custom-made photoreactor was used to conduct all the experiments (Figure 1). It is made of glass and is covered with an aluminium sheet to prevent loss of UV light. The photoreactor is cylindrical with a UV lamp (a 30 W medium-pressure mercury lamp) situated in the centre of a quartz tube. The reaction space, between the quartz tube and the reactor shell, allows for an effective reaction solution of 2.75 L. The solution can be sampled via a sampling port at various time intervals and mixed by means of a closed external circulating loop with a peristaltic pump (Bt100-2J, Baoding Longer Precision Pump Co., Ltd, Baoding, China). A magnetic stirrer (RH basic 2, IKA® Werke GmbH & Co. KG, Staufen, Germany) is located at the base of the reactor for agitation. Both mixing modes ensure the

Figure 1. Schematic diagram of the UV irradiation system.

solution can remain homogeneous throughout the reaction. In addition, the photoreactor is provided with inlet valves for feeding reactants and measuring temperature. A cooling water jacket was used to maintain the reaction solution at room temperature ($\sim 25^\circ\text{C}$).

2.4. Experimental design

Degradation of CBZ by five AOPs was investigated in the reactor (Figure 1) under the conditions shown in Table 1. For each test, the reaction vessel was filled with 2.75 L of solution and exposed to UV light (except for Fenton tests, Table 1) with the circulating pump being connected and the magnetic stirrer being switched on. For each test condition, triplicates were conducted; the averages of the results of

these triplicates are reported in this study. For each AOP, details of the methods and test conditions are described as follows.

2.4.1. UV and UV/ H_2O_2 processes

Irradiation experiments with UV were carried out in the photoreactor with CBZ concentrations of 4.2, 12.7, 29.6 and 42.3 μM . The UV dose was 172 mJ/cm^2 . The UV/ H_2O_2 experiments were carried out with a CBZ concentration of 4.2 μM and H_2O_2 concentration of 5 and 10 mM.

2.4.2. UV/ TiO_2 process

Photocatalytic (UV/ TiO_2) degradation experiments were conducted under UV irradiation in combination with TiO_2 . Titanium dioxide was added into Milli-Q water and sonicated for at least 30 min prior to the experiment. Before irradiation, the CBZ solution and TiO_2 suspension were mixed together to make the final concentration of CBZ = 4.2 μM , TiO_2 = 0.5, 100, 1.5 and 2.0 g/L and the solution pH = 6.5. After irradiation, the samples were followed by centrifugation and filtered through 0.45 μm membrane filters (Millipore) for analysis of the CBZ.

2.4.3. Fenton and UV/Fenton processes

Fenton and UV/Fenton oxidation experiments were carried out in the photoreactor at an initial pH of 3.5, a CBZ concentration of 4.2 μM and three different Fenton solutions (i.e. hydrogen peroxide at a fixed initial concentration of 5 mM and ferrous ions at varied initial concentrations of 0.5, 1.0 and 2.0 mM) with or without UV irradiation. These concentrations were chosen to allow measurable degradation of CBZ over a reaction period of 7 min, in accordance with the UV irradiation time. The experiments were conducted

Table 1. Rate constants of degradation of CBZ in five advanced oxidation processes.

Process	CBZ (μM)	Oxidant/Catalyst	$k_1 \times 10^{-4}$ (s^{-1})	$t_{1/2}$ (min)	R^2
UV	4.2	MP lamp	1.35 ± 0.03	84.9	0.998
	12.7		1.08 ± 0.02	106.2	0.998
	29.6		0.703 ± 0.03	159.3	0.9029
	42.3		0.352 ± 0.06	325.4	0.9846
UV/ H_2O_2	4.2	5 mM H_2O_2	5.66 ± 0.01	21.9	0.993
		10 mM H_2O_2	6.42 ± 0.03	17.6	0.9975
UV/ TiO_2	4.2	0.5 g/L TiO_2	9.99 ± 0.02	10.8	0.9507
		1.0 g/L TiO_2	18.1 ± 0.02	6.63	0.9981
		1.5 g/L TiO_2	29.7 ± 0.09	4.5	0.9982
		2.0 g/L TiO_2	21.6 ± 0.03	5.2	0.9917
Fenton	4.2	0.5 mM Fe^{2+}	16 ± 0.06	7.2	0.9929
		1.0 mM Fe^{2+}	20.9 ± 0.08	5.4	0.9878
		2.0 mM Fe^{2+}	23.4 ± 0.07	4.8	0.974
UV/Fenton	4.2	0.5 mM Fe^{2+}	26.3 ± 0.09	4.8	0.9663
		1.0 mM Fe^{2+}	33.8 ± 0.02	3.4	0.9682
		2.0 mM Fe^{2+}	41.5 ± 0.05	2.7	0.9535

with room lights on and under the UV irradiation condition for the Fenton and UV/Fenton reactions, respectively.

2.5. Analytical methods

Carbamazepine concentration was determined by HPLC (Agilent 1200, Agilent Technologies Co. Ltd, Palo Alto, CA, USA) equipped with a diode array detector. The HPLC system consisted of a binary pump, a vacuum degasser and an auto sampler. The UV detection wavelength was 210 nm. A Shimadzu C₁₈ reversed-phase column (250 mm × 4.6 mm i.d., particle size 5 μm) was used for separation with its temperature controlled at 30 °C, and the separation of CBZ was accomplished using a mobile phase consisting of a mixture of acetonitrile and water (31:69, v/v) at a constant flow rate of 1 mL/min. The injection volume was 20 μL for each analysis.

3. Results and discussion

3.1. Pre-experiment: thermodegradation and adsorption

Thermodegradation of CBZ was performed before the photodegradation experiments to evaluate the possible degradation due to temperature. One litre of CBZ solution with 5 mg/L initial concentration was placed in the stirred tank and heated at 20, 40, 60 and 80 °C. Once the set temperature was reached, an aliquot was taken for HPLC analysis. Concentration profiles in all cases were always constant and close to the initial concentration. No thermodegradation decrease was observed for CBZ tested in the 20–80 °C range.

On the other hand, to evaluate the decrease in the pollutant due to adsorption on the catalyst, different compositions of CBZ and TiO₂ solution were prepared in 20 mL hermetic closed flasks, which were submerged in a thermostatic bath at constant temperature (25 °C). The equilibrium concentration of each adsorbed CBZ was determined after measuring the supernatant concentration after 24 h darkness. A very low percentage of CBZ adsorption (2.75%) was obtained. Therefore, from a practical point of view, the adsorption stage between CBZ and the TiO₂ catalyst does not represent a significant reduction in the concentration of the substrate during the main photocatalytic process.

3.2. CBZ degradation with UV and UV/H₂O₂ processes

Different initial CBZ concentrations were studied in UV irradiation. The results (Figure 2) showed that the initial CBZ concentration had a significant effect on the CBZ degradation rate. The degradation rate was higher for lower initial concentrations of CBZ than for higher initial concentrations. At the initial concentration of 4.2 μM, nearly 34% of CBZ was degraded in 50 min whereas, at 42.3 μM initial concentration, the degradation percentage was only 13%. Several studies confirmed that the initial

Figure 2. Degradation of CBZ at different initial concentrations in deionized water by UV.

CBZ concentration has a remarkable effect on the photolytic degradation percentage of the parent compound; the higher the initial concentration, the lower the degradation percentage [19]. A reason could be the complete absorption of the incident photon flux by the higher initial pharmaceutical concentrations over a shorter path length [27]. So the absorbed photon flux of the lower and higher initial pharmaceutical concentrations was probably not proportional to the initial concentration of the pharmaceuticals.

In the UV irradiation experiments, the concentration of CBZ decreased nearly exponentially during irradiation (Figure 2). The data were fitted by a pseudo-first-order kinetic law described in Equation (1), where c_0 and c_t are the CBZ concentration at time 0 and t respectively, k is the degradation rate constant (1/min) and t is the irradiation time (min).

$$-\frac{dc}{dt} = kc \text{ or } c_t = c_0 e^{-kt} \quad (1)$$

For the calculation of the degradation rate constant, k , of the photodegradation (Table 1), only the concentration values with $c_t/c_0 \geq 0.5$ were used, because the degradation products influenced the rate at higher losses by scavenging reactive intermediates and by competitive spectral absorption. Doll and Frimmel [27] reported a kinetic constant for solar UV degradation of CBZ of 1×10^{-5} 1/s, which is lower than the rate constants (0.3×10^{-4} to 1.35×10^{-4} 1/s) obtained in this study.

Addition of H₂O₂ to the aqueous solution resulted in faster degradation of CBZ (Figure 3), compared with its direct photolysis (H₂O₂ = 0). The UV radiation causes the photolysis of H₂O₂ into hydroxyl radicals as a result of the primary photolytic process. The degradation mechanism of CBZ in the presence of H₂O₂ is oxidation by the very strongly oxidizing hydroxyl radicals ($E_0 = 2.8$ V). The quantum yield for generating hydroxyl radicals using the UV/H₂O₂ process is 1.0 [28]. Hence the rapid degradation of the CBZ occurs in the presence of H₂O₂. Only a minor

Figure 3. Degradation of CBZ in deionized water by UV/H₂O₂ ($c_0 = 1$ mg CBZ/L = 4.2 μ M).

increase in the degradation rate was observed between 5 and 10 mM H₂O₂. This may be attributed to autodecomposition of H₂O₂ to oxygen and water, and the recombination of $\bullet$ OH radicals. Moreover, higher concentrations of hydrogen peroxide act as a free-radical scavenger itself, thereby decreasing the concentration of hydroxyl radicals and reducing compound elimination efficiency [29], as shown in Equation (2).

Rate constants in the UV/H₂O₂ process varied from 5.66×10^{-4} to 6.42×10^{-4} 1/s at different H₂O₂ concentrations (Table 1). The constants calculated here for CBZ are far lower than that (0.02 1/s) reported in the literature [30].

It was found that CBZ ($\text{p}K_a = 13.9$) degradation by UV and UV/H₂O₂ process was not affected by varying the pH of the solution in the range of 2.0–8.0 (data not shown). At these pH values (below $\text{p}K_a$), there is no change in the ionic charge of the organic molecule and therefore the pH of the

solution did not alter the structure or subsequent degradation of CBZ.

3.3. CBZ degradation with Fenton and UV/Fenton processes

The pH has a significant role in determining the efficiency of Fenton and UV/Fenton oxidation. The maximum degradation carried out by H₂O₂/Fe²⁺ or UV/H₂O₂/Fe²⁺ is expected at a pH between 2 and 4. At pH < 2.5, (FeOH)²⁺ is formed, which reacts more slowly with H₂O₂ and therefore reduces the degradation efficiency. At pH > 4, degradation rates decrease owing to the formation of Fe(II) complexes and precipitation of ferric oxyhydroxides [31], thereby lowering the ferrous iron's ability to catalyse H₂O₂. Furthermore, the oxidation potential of hydroxyl radicals is known to decrease with an increase in pH [32].

In this study, Fenton and UV/Fenton reactions were carried out at pH 3.5, an initial H₂O₂ concentration of 5 mM, and ferrous ion initial concentrations of 0.5, 1.0 and 2.0 mM, respectively. Degradation of CBZ by Fenton and UV/Fenton oxidation also exhibited pseudo-first-order kinetics (Figure 4 and Table 1). In the Fenton process, ferrous ions are used as a catalyst for hydrogen peroxide reduction and, at acidic pH, for production of hydroxyl radicals, according to Equation (3):

An approximate 20% increase in the CBZ removal efficiency occurred with the UV/Fenton reaction as compared with the Fenton oxidation after 7 min reaction, at all three initial ferrous ions concentrations (Figure 4). By applying UV light to the Fenton process (UV/Fenton), additional hydroxyl radicals are generated and ferric ions are reduced to ferrous as follows:

Figure 4. Degradation of CBZ in deionized water by (a) Fenton and (b) UV/Fenton processes ($c_0 = 1$ mg CBZ/L = 4.2 μ M).

Recycling of Fe^{2+} (Equation (5)) also leads to further generation of $\bullet\text{OH}$ according to Equation (3). An increase in the gross hydroxyl radical concentration results in acceleration of the degradation of CBZ using the UV/Fenton reaction as compared with the Fenton reaction. To our knowledge, no data have yet been published for CBZ degradation by UV/Fenton and Fenton processes.

The degradation rate (Table 1) and removal efficiency (Figure 4) for CBZ by both Fenton and UV/Fenton reactions were improved with an increase in the Fe^{2+} concentration from 0.5 to 1 mM. For example, the removal of CBZ by UV/Fenton reaction increased from 63% at a molar ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:10$ to 78% at a molar ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:5$ over 7 min reaction time. Only a minor increase in the degradation rate was observed between 1 and 2 mM Fe^{2+} . This is due to the fact that, at an Fe(II) concentration higher than the optimum, the initial formation rate of hydroxyl radicals, originating mainly from the decomposition of H_2O_2 , was so high that much of the hydroxyl radicals were consumed by the side reactions before they could be utilized effectively for oxidizing CBZ. Moreover, it resulted in a brown turbidity that hindered the absorption of the UV light required for photolysis [33,34]. Therefore, overdosing with Fe^{2+} impedes the CBZ degradation efficiency.

The above results indicated that the Fenton and UV/Fenton processes were promising choices for CBZ degradation. However, the use of ferrous or ferric salts in Fenton oxidation usually suffers from two major drawbacks: (a) the narrow pH range of operation to avoid the formation and subsequent precipitation of iron oxyhydroxides, and (b) the need to recover dissolved ions from the treated solution, thus requiring an additional treatment stage. To overcome these drawbacks, the immobilization of Fenton catalyst on a heterogeneous matrix would enable its use under non-controlled pH conditions as well as its easy recovery from the treated effluent, which is perhaps a future research direction [35].

3.4. CBZ degradation with UV/ TiO_2

Oxidation of organic compounds by means of TiO_2 was achieved by hydroxyl radical generation through the e^-/h^+ pair generated when the semiconductor TiO_2 is exposed to UV radiation. Specifically, the valence band hole (h_{vb}^+) may react with surface-bound H_2O or OH^- to produce the hydroxyl radical, and the conduction-band electron (e_{cb}^-) is picked up by oxygen to generate superoxide radical anion (O^{2-}), as indicated in the following equations [36].

The effect of different concentrations of TiO_2 on CBZ degradation is shown in Figure 5. It was found that UV

Figure 5. Effect of TiO_2 concentrations on the degradation of CBZ by UV/ TiO_2 ($c_0 = 1 \text{ mg CBZ/L} = 4.2 \mu\text{M}$).

irradiation in the absence of TiO_2 catalyst (direct photolysis) showed extremely low CBZ removal (about 10%). Likewise, using TiO_2 (1.5 g/L) alone without UV resulted in no obvious decrease in CBZ. In the UV/ TiO_2 process, when the TiO_2 concentration increased from 0.5 to 1.5 g/L, the CBZ degradation rate increased with an increase in the catalyst dose (Figure 5 and Table 1). Therefore, TiO_2 is capable of promoting the interaction between hydroxyl radicals and CBZ. A further increase in the TiO_2 concentration led to a decrease in the degradation efficiency (Figure 5 and Table 1). Similar observations have been reported in other heterogeneous photocatalytic systems where the efficiency of photodegradation was not always proportional to the catalyst load. An optimal point exists where catalyst loaded showed a maximum degradation rate. Many studies have demonstrated that the rate of photodegradation for organic pollutants was strongly affected by the number of active sites and the photo-absorption ability of the catalyst used [37]. An adequate dosage of the catalyst increases the generation rate of electron/hole pairs and thus the formation of $\bullet\text{OH}$ for enhancing photodegradation. However, an excess dosage of the catalyst will cause light scattering that precludes the UV light permeation in the reactor system and hence reduces the photodegradation rate [38]. The TiO_2 concentration of 1.5 g/L was found to be the optimum value to achieve a maximum degradation of CBZ (Figure 5). Above this value, scattering phenomena can appear, and active sites on the surface of TiO_2 do not bring more e^-/h^+ , and therefore the degradation rate does not increase any more [39].

The photocatalytic degradation of CBZ increased as the initial concentration of CBZ decreased (Figure 6). Possible explanations for this phenomenon are the wavelength used and the composition or incomplete dispersion of TiO_2 . Another possible explanation for this behaviour was that the CBZ molecules at high concentrations exceeded the capacity of the sorbent (TiO_2), which influenced the

Figure 6. The photocatalytic degradation of CBZ at different initial concentrations (pH = 7.0, TiO₂ = 1.5 g/L).

degradation rate. The photocatalytic degradation of CBZ by means of illuminated TiO₂ can be formally described by the Langmuir–Hinshelwood (L–H) kinetics model. For high concentrations of organic contaminants, where saturation coverage of the TiO₂ surface was achieved, the L–H kinetics simplified to a zero-order-rate equation. For lower concentrations of organic contaminants, the L–H equation simplified to a pseudo-first-order kinetic law (Equation (1)) [40].

The two extreme cases are shown in Figure 6 for CBZ at two different initial concentrations (4.2 and 42.3 μM) as a function of the irradiation time. At high initial concentration, the pollutant decay was according to zero-order kinetics whereas the degradation kinetics at low concentrations could be interpreted as an example of first-order kinetics.

By further investigations, the kinetics of CBZ degradation in the presence of different concentrations of TiO₂ (0.5, 1.5 and 2.0 g/L) was found to follow the first-order degradation, which was consistent with the L–H model resulting from the low coverage of the sorbent (TiO₂) in the experiment with a low CBZ initial concentration (4.2 μM) (Figure 5). The photocatalytic degradation rate constants, k , (Table 1) were calculated by taking only the concentration values of $c_t/c_0 \geq 0.5$, to avoid the competition between the daughter compounds and CBZ [21]. As shown in Table 1, the effect of the TiO₂ concentration on k was significant, confirming the positive influence of the increased number of TiO₂ active sites on the process kinetics. The high photoreactivity of P25 is explained by its slow electron/hole recombination rate, because the rutile/anatase combination promotes charge pair separation and inhibits recombination [33]. The rate constant of 1.8×10^{-3} 1/s (Table 1) was determined at 1 g/L TiO₂, which is lower than that (11×10^{-3} 1/s) reported by Doll and Frimmel [41] using a 1000 W Xe short-arc lamp under identical conditions. This is mainly due to the different UV lamps with different UV doses used in our study and Doll and Frimmel's study.

Table 2. Degradation of CBZ by UV, UV/H₂O₂, Fenton, UV/Fenton and UV/TiO₂ processes.

Process ^a	Degradation (%)
UV	14.2 ± 1.4
UV/H ₂ O ₂	40.6 ± 5.1
Fenton	67.8 ± 2.6
UV/Fenton	86.9 ± 1.7
UV/TiO ₂	70.4 ± 4.2

^aCBZ = 4.2 μM; H₂O₂ = 5 mM; Fe²⁺ = 2 mM; TiO₂ = 1.5 g/L. Reaction time in Fenton systems = 7 min. Irradiation time = 7 min.

3.5. Comparison of CBZ degradation by various processes

The same operating parameters (temperature, volume, reaction time, etc.) were applied in the UV, UV/H₂O₂, Fenton, UV/Fenton and UV/TiO₂ processes in order to compare their efficiency for the degradation of CBZ. On a time basis, the CBZ degradation efficiencies are in the following order, UV/Fenton > UV/TiO₂ > Fenton > UV/H₂O₂ > UV (Table 2), with the UV/Fenton process being the most effective for partial mineralization or complete mineralization of CBZ. The differences in degradation efficiencies are mainly due to the difference in production of hydroxyl radicals during the process. In the UV/Fenton process, the hydroxyl radicals were produced by various sources, as it had a combined effect. An approximate 20% increase in the CBZ removal efficiency occurred with the UV/Fenton reaction as compared with the Fenton oxidation. Iron-catalysed decomposition of H₂O₂ was more significant than UV-catalysed H₂O₂ decomposition. Hence, the Fenton process was more efficient than the UV/H₂O₂ process. The efficiency of the UV/TiO₂ process was comparable to the Fenton process. Also, the degradation rate with the UV/Fenton process was higher than the other three processes, as evidenced by the kinetic constant values (Table 1).

3.6. Cost estimation

Cost evaluation is one of the important aspects in wastewater treatment. The overall costs are represented by the sum of the capital costs, the operating costs and maintenance costs. For a full-scale system these costs strongly depend on the nature and the concentrations of the pollutants, the flow rate of the effluent and the configuration of the reactor [42]. The costs of reagents and electricity are shown in Table 3. An estimation of the operating costs was made (Table 4) for the processes given in Table 2. Among all the treatment processes studied, the operating costs of photocatalysis and UV were considerably more expensive than the others. However, it should be pointed out that costs can decrease considerably for photocatalytic treatments when solar light is used [34].

Table 3. Cost of reagents used in the studied processes [43,44].

Reagent	Basis	Cost (US\$)
H ₂ O ₂	kg	0.93
FeSO ₄ · H ₂ O	kg	13.5
TiO ₂	kg	0.86
Electricity	kWh	0.0948

Table 4. Operating costs of the different treatment processes.

Process	Treatment cost (US\$/kg)
UV	210.4
UV/H ₂ O ₂	42.6
Fenton	5.4
UV/Fenton	26.7
UV/TiO ₂	70.2

4. Conclusions

A study was carried out to compare different AOPs for the removal of CBZ in water. From the results obtained in the present work, it can be concluded that UV/Fenton, UV/TiO₂, UV/H₂O₂ and Fenton processes are effective for CBZ degradation in aqueous solutions under certain simple operational conditions and within a short time. The degradation of CBZ was more efficient by the Fenton process than by the UV/H₂O₂ process, and the mineralization efficiency was also improved; the efficiency of the UV/TiO₂ process is between that of the UV/Fenton and Fenton processes; and the UV/Fenton process was the most effective for partial mineralization or complete mineralization of CBZ. Therefore, the degradation rate and the lower costs obtained with UV/Fenton make it the most appealing choice for CBZ degradation. The results of this study are useful for selection, design and evaluation of an AOP process for the abatement of CBZ in water.

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