

EFFECT OF TiO₂/UV-LED OPERATIONAL PARAMETERS ON THE
DEGRADATION OF PHARMACEUTICALS IN WATER

by

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Abstract

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The presence of pharmaceutical residues in water resources has alarmed water and health authorities. Among many treatment technologies for pharmaceuticals, ultraviolet (UV)-based oxidation has gained significant attention because it is capable of decomposing a variety of recalcitrant and toxic chemicals. As an alternative UV source to problematic conventional mercury lamps, light-emitting diode (LED) has shown many advantages for water treatment applications, so-called UV-LED. The overall goal of this study is to evaluate the high potential of the UV-LED technology to treat water contaminated with pharmaceuticals including sulfamethoxazole, ibuprofen, and triclosan. In particular, important operational parameters were investigated, including UV wavelength, irradiation intensity, reaction pH, and TiO₂ loading. The effect of the operational parameters on the decomposition of the pharmaceuticals was discussed, and optimized operation conditions were proposed. Photolytic decomposition of the pharmaceuticals was also compared with their photocatalytic decomposition. Photolytic decomposition of the pharmaceuticals was

solely determined by relation between their UV absorption characteristics and the UV emission spectra of LEDs. Both photolytic decomposition and photocatalytic decomposition were greatly affected by reaction pH. The presence of TiO_2 in cases that significant photolysis was present, rather inhibited the overall decomposition process. However, in all cases, photocatalysis showed better mineralization than photolysis.

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Chapter 1

Introduction

Pharmaceuticals and personal care products (PPCPs), including toothpaste, mouthwash, skin cream, hand-disinfecting soap, deodorant, and medicine, have become an integrated part of our daily life. Use of such products greatly contributes to contamination of our environment [1]. Some of PPCPs often found in drinking water sources are categorized into endocrine disrupting compounds [2]. Once released, the majority of PPCPs end up in sewage systems. However, large portion of PPCPs are not removed by conventional treatment processes because most of them are recalcitrant to chemical oxidation and toxic to microorganisms used for biological processes [3]. Due to the persistence and prevalence of PPCPs in the environment along with their toxicity, there have been significant research activities toward developing new treatment technologies to remove them [4].

Recently, various methods for water and air purification and soil remediation have been developed including chemical, electrochemical, and photochemical processes [5-6]. Among them, ultraviolet (UV)-based technologies have shown promising results [1-5]. Germicidal UV has been extensively used in disinfection process [3,7,8]. Chemical oxidation processes employing hydrogen peroxide and ozone combined with UV radiation are proposed to produce hydroxyl radicals which are strong oxidizing species enough to decompose many recalcitrant organic chemicals, so-called advanced oxidation technologies (AOTs) [9]. Photons from UV can provide energy to organic chemicals for direct photolytic decomposition (photolysis) while UV energy can also activate semiconducting photocatalysts such as titanium dioxide (TiO₂) to generate hydroxyl

radicals (photocatalysis) [10-11]. TiO₂ photocatalysis is known to be one of the most promising AOTs.

However, UV technologies have commonly used conventional mercury lamps, which have several important drawbacks such as long-term exposure instability, low photonic efficiency, and short lifetime [12-16]. In particular, mercury is specified as a hazardous air pollutant by US Environmental Protection Agency [12]. As an alternative UV source to problematic mercury lamps, light-emitting diode (LED) has been proposed for water treatment applications, so-called UV-LED [12-16]. UV-LED is characterized with optical stability, energy saving, long lifetime, and no mercury [12]. Recent studies have demonstrated successful decomposition of dyes, phenol, and natural organic matter by UV-LED [12-16].

Most of the studies emphasized introduction of LED as a new approach for UV-based water treatment. Meanwhile, less attention was given to evaluate the effect of various operational parameters of UV-LED technology. UV-LED exhibits higher photonic efficiency compared to mercury lamps, implying that even low intensity from UV-LED works for the photolytic and photocatalytic decomposition of organic chemicals [16-18]. The overall goal of this study is to evaluate the high potential of the UV-LED-based technology to treat water contaminated with PPCPs. Important operational parameters were investigated including wavelength and irradiation intensity of UV-LED. Photolytic decomposition of PPCPs was compared with their photocatalytic decomposition. The effects of reaction pH and TiO₂ loading under different wavelengths of UV-LED on the decomposition of PPCPs were also investigated to examine whether the use of UV-LED

varies the known performance of general UV-based technology employing mercury lamps. The effect of operational parameters on the decomposition of PPCPs was discussed, and optimized operation conditions were proposed. This research would help to fabricate and design UV-LED photoreactors and thus eventually to accelerate the application of the UV-LED technology for treatment of water contaminated with many recalcitrant organic chemicals.

Chapter 2

Materials and Methods

2.1. Chemicals

Among many PPCPs, sulfamethoxazole (SMX), ibuprofen (IBP), and triclosan (TCS) were chosen as target contaminants to decompose based on their prevalence, recalcitrance, and toxicity in the environment. SMX is an antibiotic commonly used for treatment of bronchitis and urinary tract infections [19]. Due to its antibacterial nature, SMX shows strong resistance to biological decomposition and thus is often found in wastewater treatment effluents [19]. IBP is one of the most widely used pain killers [20]. TCS commonly used as an antiseptic in various PPCPs is a precursor of more toxic dioxin [10]. They were purchased from Sigma-Aldrich, USA. For chromatographic analysis, acetonitrile and ortho-phosphoric acid were supplied from Sigma-Aldrich, USA. For pH adjustment, 0.01 N sodium hydroxide and hydrochloric acid (Sigma-Aldrich, USA) were used. High purity water made from a Milli Q-Water System (Millipore, USA) was utilized for the preparation of all solutions, suspensions, and chromatographic solutions. As a photocatalyst, P25 TiO₂ particles (Degussa, Germany) were used as received. P25 is nanocrystalline in a mixture of anatase and rutile (7:3) and characterized with surface area of around 50 m²/g and average primary particle size of 30 nm [15].

2.2 UV-LED photoreactor

UV lamps called UVCLEAN (TO39 UVLED) were equipped with multi-chip arrays of UV-LED with different wavelengths for UVA, UVB, and UVC. UV-LED was purchased

from International Light Technologies, USA for UVA, Crystal IS, USA for UVB, and Sensor Electronic Technology, USA for UVC. LED was packaged in a standardized transistor with an internal heat sink. The multi-chip array of UV-LED enabled to obtain higher UV intensity compared to conventional array configuration. Three LEDs were soldered to a circular-shaped programmable circuit board (Nex Logic, USA). An aluminum heat sink was used to dissipate heat from UV-LED. LED was powered by a constant-current power supply (KORAD KA3005D, USA). Standard distance between LED and reaction solution was 0.5 cm while the distance was varied up to 10 cm to change light intensity. The radiation intensity entering the reactor was measured as mW/cm^2 using a wide spectral range photodiode laser measurement sensor (PD-300RM-UV, Ophir Photonics, USA).

2.3. Batch experiment setup

A batch reactor was set up to carry out all the experiments. A 100 ml volume vessel was placed under UV-LED and was continuously mixed with a magnetic stirrer (note Fig. 2-1 for the configuration of the reactor setup). Each of the target PPCP was individually tested at concentration of 20 mg/L for SMX and IBP, while for TCS much reduced concentration at 10 mg/L was used due to its low solubility at around 11 mg/L. The different initial concentrations for the PPCPs would be justified by the fact that this study was not designed to directly compare the decomposition of the PPCPs but to study the effect of operational parameters on the decomposition of the PPCPs. In fact, higher concentrations are preferred for the accurate measurement of total organic carbon (TOC) later to determine total

mineralization efficiency of the system since a TOC analyzer is in general not sensitive enough to accurately measure low levels of TOC [3]. In addition, PPCPs in the environment are found at trace levels, e.g., several $\mu\text{g/L}$. However, in order to avoid analytical errors and observe obvious differences in reaction kinetics by the effect of operational parameters, much higher concentrations were used [3].

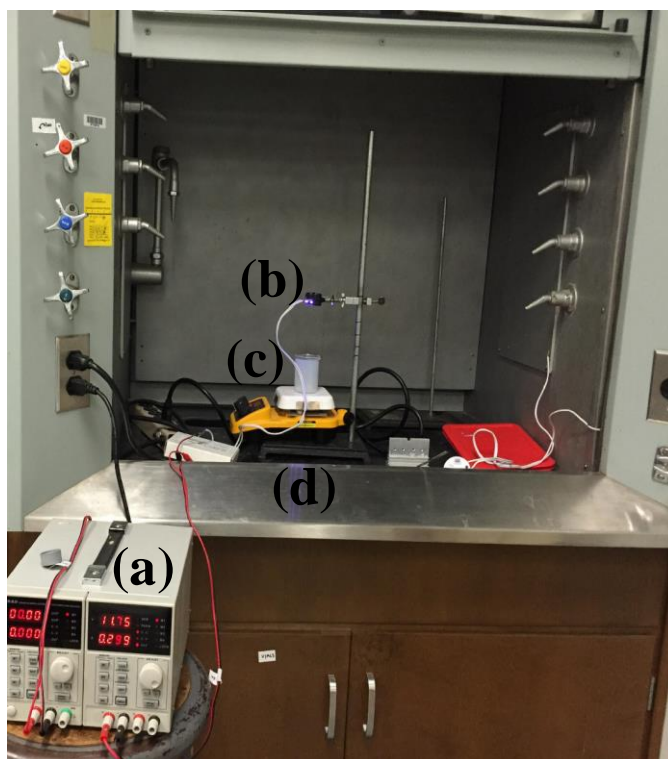


Figure 2-1. Configuration of reactor setup: (a) power supply and controller, (b) UV-LED lamps, (c) batch reactor with/without TiO_2 suspension, and (d) magnetic stirrer.

For photocatalytic experiments, standard loading of TiO_2 was at 0.75 g/L while the loading was also varied at 0.25 , 0.50 , 0.75 , and 1.0 g/L . In each time interval up to 3 hr, 1 ml of suspension was withdrawn and filtered with a $0.45 \mu\text{m}$ PTFE syringe (Sigma-Aldrich, USA). For those experiments, pH was not controlled. Later, initial pH was

adjusted without buffer at 3, 5, 7, 9, and 11 by adding sodium hydroxide and hydrochloric acid to examine the effect of reaction pH.

2.4. Analytical methods

UV absorption characteristics of SMX, IBP, and TCS were determined by using a UV-visible spectrophotometer (UV 2550, Shimadzu, Japan), which is helpful for interpreting their photolytic decomposition behavior under different UV wavelengths. High-performance liquid chromatography (HPLC, 1200 series, Agilent Technologies, USA) with a UV detector was used to quantify the PPCPs. Their concentrations were determined in a reversed-phase configuration with C18 column (Agilent Technologies, USA). A mixture of water and acetonitrile at 60:40 for SMX and 25:75 for TCS was used as a mobile phase [10]. For IBP, a mixture of 0.05 N phosphoric acid buffer and acetonitrile at 50:50 was utilized [20]. SMX, IBP and TCS were identified with a UV detector at 265 nm, 214 nm, and 280 nm, respectively. To determine total mineralization of the PPCPs along with their disappearance measured by HPLC, TOC was monitored by a TOC analyzer (TOC-VCSH/CSN, Shimadzu, Japan) at the end of each experiment.

Chapter 3

Results and Discussion

3.1. Effects of UV wavelength and intensity

LEDs for UVA, UVB, and UVC were found to emit different wavelengths at 378 ± 15 nm, 305 ± 15 nm, and 268 ± 15 nm, respectively (note Fig. 3-1 for UV emission spectra of the UV-LED lamps). The emission spectra well represented general UVA, UVB, and UVC wavelengths. Light intensity at various distances between UV-LED and reaction solution was measured and summarized in Table 3-1. Among them, LED for UV-A demonstrated highest and varied intensity at all distances while LED for UVB showed lowest intensity and meaningful intensity only at the closest distance of 0.5 cm. At the current advances in the LED technology, LEDs for UV-B and UV-C typically demonstrate low intensity [12]. There is no commercially available high intensity LED particularly for UVB. Meanwhile, an important factor for the degradation of PPCPs by photochemical reaction is their capacity to absorb photon energy from incident light. Figure 1 shows UV absorption spectra of the PPCPs in comparison to UV emission spectra of the UV-LEDs. SMX, IBP, and TCS were found to absorb mainly 265 nm, 214 nm, and 280 nm, respectively. For the experiments below, pH was not adjusted and no buffer was used. In all cases, initial pH at around 4-5 was slightly decreased.

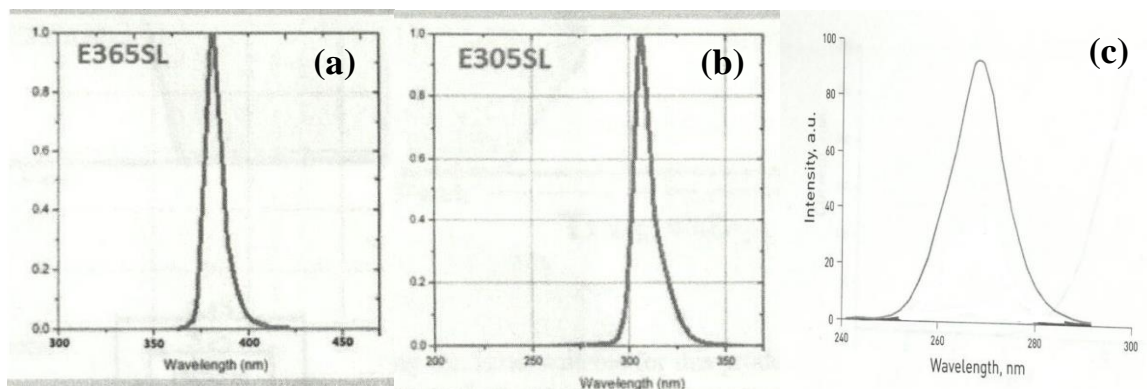


Figure 3-1. UV emission spectra of different UV LED lamps: (a) UVA, (b) UVB, and (c) UVC (source: Sensor Electronic Technology Inc., USA).

Distance (cm)	Intensity (mW/cm ²)		
	UVA	UVB	UVC
0.5*	8.6	0.1	0.5
2.5	3.6	0	0.2
5	1.2	0	0.1
10	0.4	0	0

Table 3-1. Light intensity of the different wavelength UV-LED lamps measured at various distances.

*This is standard condition for other tests on the effects of reaction pH and TiO₂ loading.

It should be noted that achieving the same light intensity for the three UV-LEDs at a given distance is technically almost impossible due to the characteristics of the LED lamps with different wavelengths.

3.1.1. SMX

Figures 3-2(a), 3-2(c), and 3-2(e) show the effect of UV radiation on the photolytic degradation of SMX. Solution pH decreased from 4.2 to 4.1 and from 4.7 to 3.8 during the photolytic and photocatalytic experiments, respectively. In case of UVA and UVB, no photolytic degradation of SMX was found because the wavelength of UVA at 378 nm and UVB at 305 nm is far from the absorption wavelength of SMX at 265 nm (note Fig. 3-3) [4,19]. In spite of significant increase in light intensity of UVA from 0.4 to 8.6 mW/cm², UVA was not absorbed by SMX at all. Only UVC showed significant photolysis of SMX. The peak wavelength emitted by UVC at 268 nm falls to the maximal absorption wavelength of SMX at 265 nm. When intensity of UVC increased, photolytic decomposition of SMX was enhanced significantly.

Figures 3-2(b), 3-2(d), and 3-2(f) show the effect of UV radiation on the photocatalytic degradation of SMX. The result on photocatalytic decomposition is interesting, in comparison to photolytic decomposition. Photocatalytic decomposition of SMX under UVA and UVC was significant. As intensity increased, faster decomposition of SMX was observed. UVB was not able to activate TiO₂ to decompose SMX most probably due to its low intensity used. At the same distance of 0.5 cm which gives highest intensity for each UV-LED (i.e., 8.6, 0.1, and 0.5 mW/cm²), around 80%, 7%, and 50% degradation was observed for UVA, UVB, and UVC, respectively. In comparison between UVA and UVC, adding TiO₂ accelerated SMX decomposition under UVA while it deteriorated SMX decomposition under UVC. Since SMX did not absorb UVA and thus did not show photolysis. UVA was absorbed only by TiO₂ to generate hydroxyl radicals for SMX

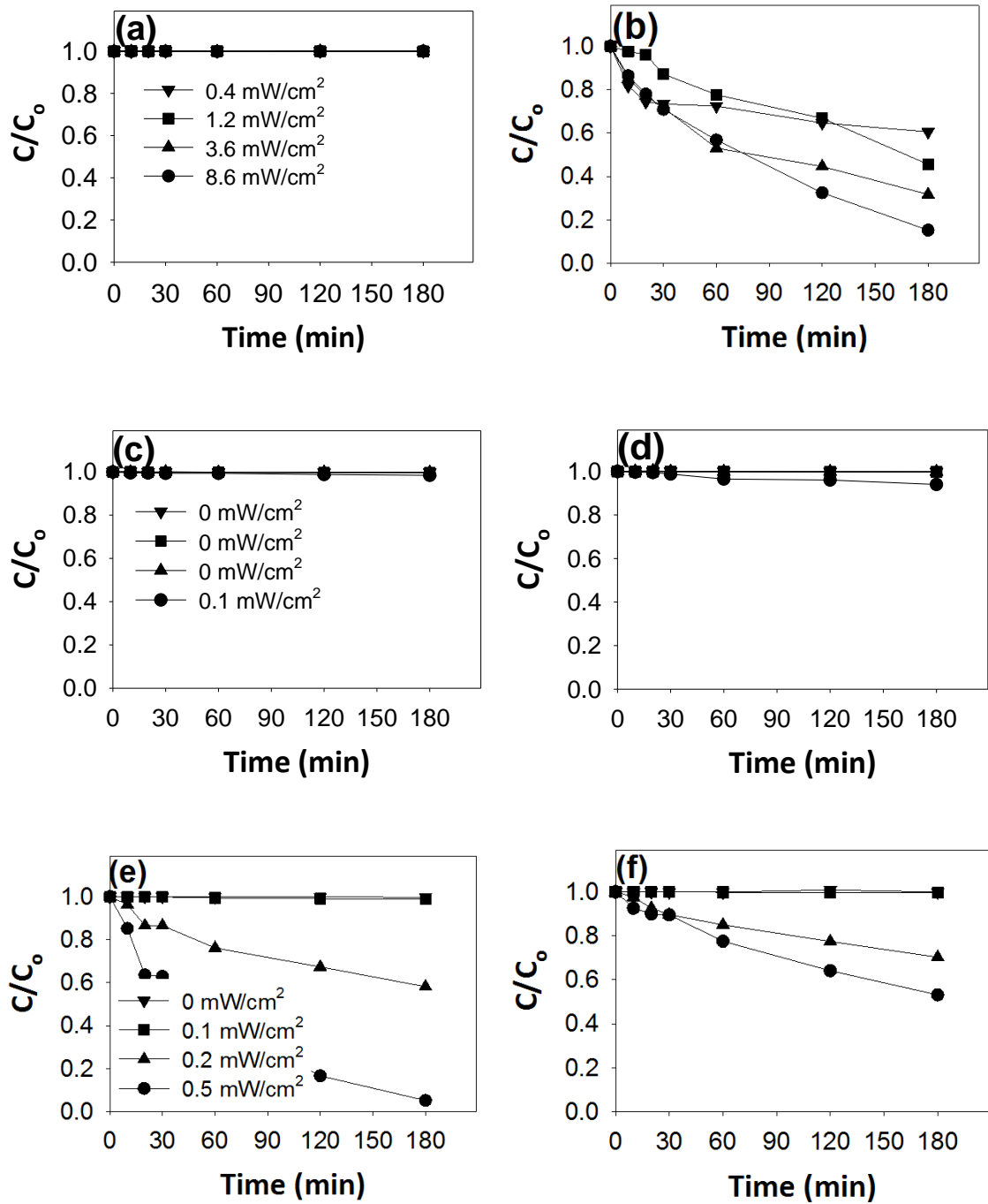


Figure 3-2. Effect of light intensity on the photolytic and TiO₂ photocatalytic decomposition of SMX ($C_0=20$ mg/L and TiO₂=0.75 g/L) under different UV wavelengths: (a) UVA, (b) UVA+TiO₂, (c) UVB, (d) UVB+TiO₂, (e) UVC, and (f) UVC+TiO₂.

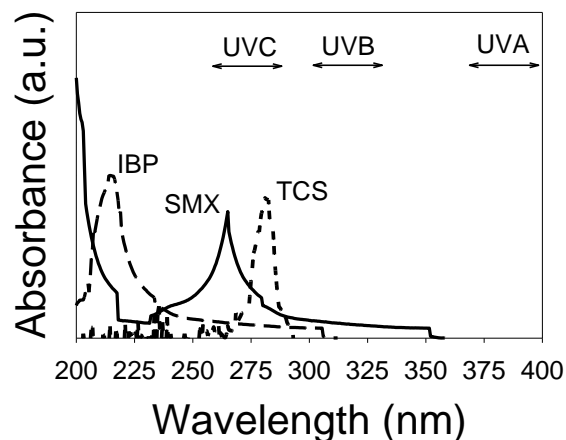


Figure 3-3. UV absorption spectra of SMX, IBP, and TCS in comparison to UV emission spectra of LEDs for UVA, UVB, and UVC.

decomposition. Meanwhile, SMX absorbed UVC well and showed significant photolysis. Once TiO_2 is added, there should be competition for UVC absorption between TiO_2 and SMX. Although photocatalytic decomposition of SMX is initiated, photolytic decomposition of SMX is significantly sacrificed due to the competition, resulting in decreased decomposition of SMX in the presence of TiO_2 [1,4,19]. In addition, scattered UV by TiO_2 particles might be less absorbed by SMX.

3.1.2. IBP

Figure 3-4 shows the effect of UV radiation on the photolytic and photocatalytic degradation of IBP. Solution pH decreased from 5.4 to 5.3 and from 5.1 to 4.4 during the photolytic

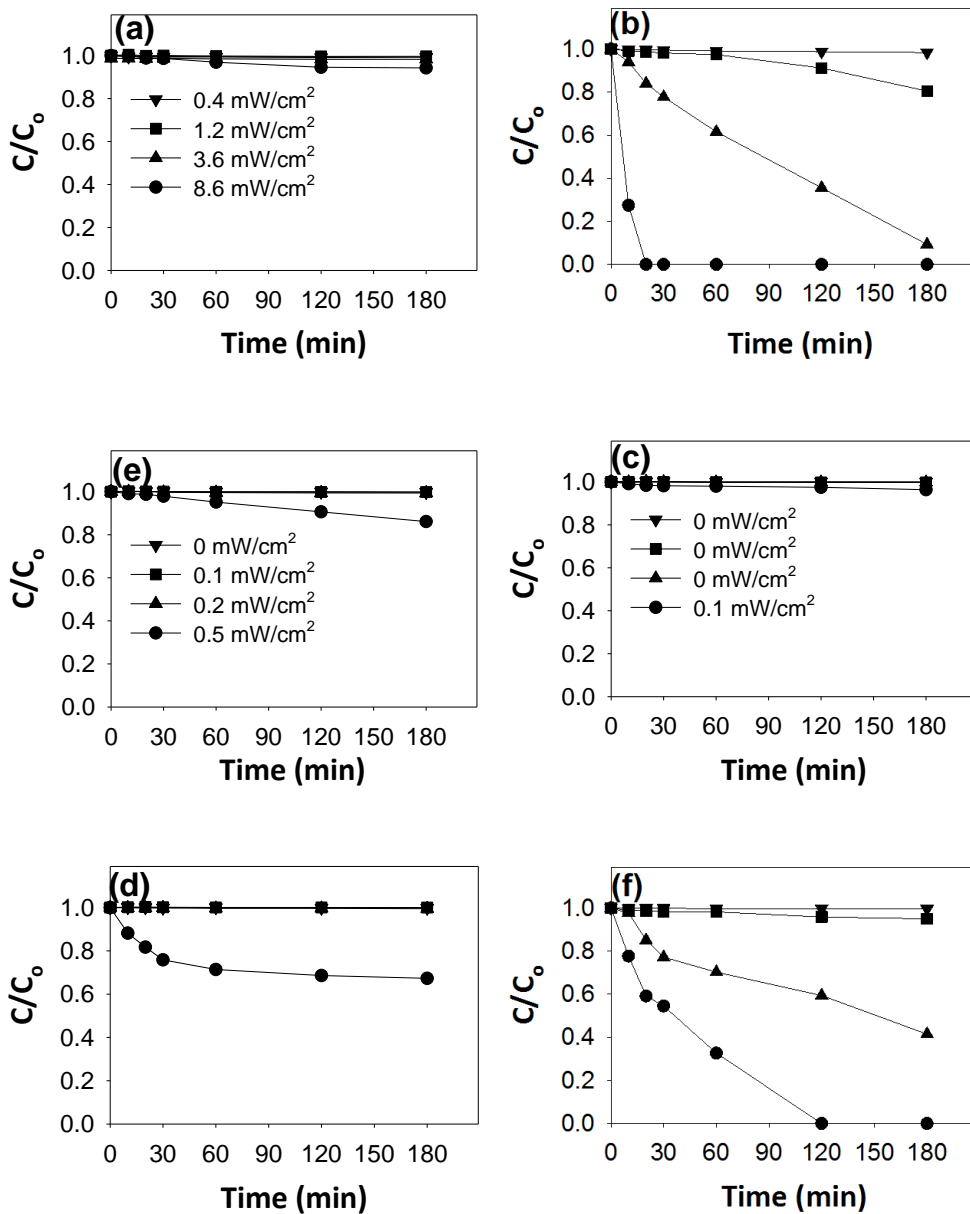


Figure 3-4. Effect of light intensity on the photolytic and TiO₂ photocatalytic decomposition of IBP ($C_0=20$ mg/L and TiO₂=0.75 g/L) under different UV wavelengths: (a) UVA, (b) UVA+TiO₂, (c) UVB, (d) UVB+TiO₂, (e) UVC, and (f) UVC+TiO₂.

and photocatalytic experiments, respectively. General observation for IBP is similar to SMX. In all cases of UVA, UVB, and UVC, no significant photolytic degradation of IBP was found since the wavelengths of UV-LEDs at 378, 305, and 268 nm, respectively are well above the absorption wavelength of IBP at 214 nm (note Fig. 3-3). In spite of significant increase in light intensity of UVA and UVC, no photon energy was absorbed by IBP for photolysis. Due to no significant photolysis of IBP, the presence of TiO₂ significantly improved decomposition of IBP [21-22]. Since IBP does not absorb UV, all photon energy can be used by TiO₂ to generate hydroxyl radicals for photocatalytic decomposition of IBP. In this case, the effect of light intensity on decomposition of IBP was apparent. Even in case of UVB, there was also noticeable photocatalytic decomposition of IBP, in comparison to negligible decomposition of SMX. This might suggest more vulnerability of IBP to hydroxyl radical attack than SMX [22].

3.1.3. TCS

Figure 3-5 shows the effect of UV radiation on the photolytic and photocatalytic degradation of TCS. Solution pH decreased from 5.7 to 5.6 and from 5.1 to 3.9 during the photolytic and photocatalytic experiments, respectively. In general, photolytic decomposition of TCS is similar to that of SMX while photocatalytic decomposition of TCS is similar to that of IBP. In cases of UVA and UVB, negligible photolytic degradation of TCS was found since the wavelength of UVA at 378 nm and UVB at 305 nm is far from the absorption wavelength of TCS at 280 nm (note Fig. 3-3). Only UVC showed significant photolysis of

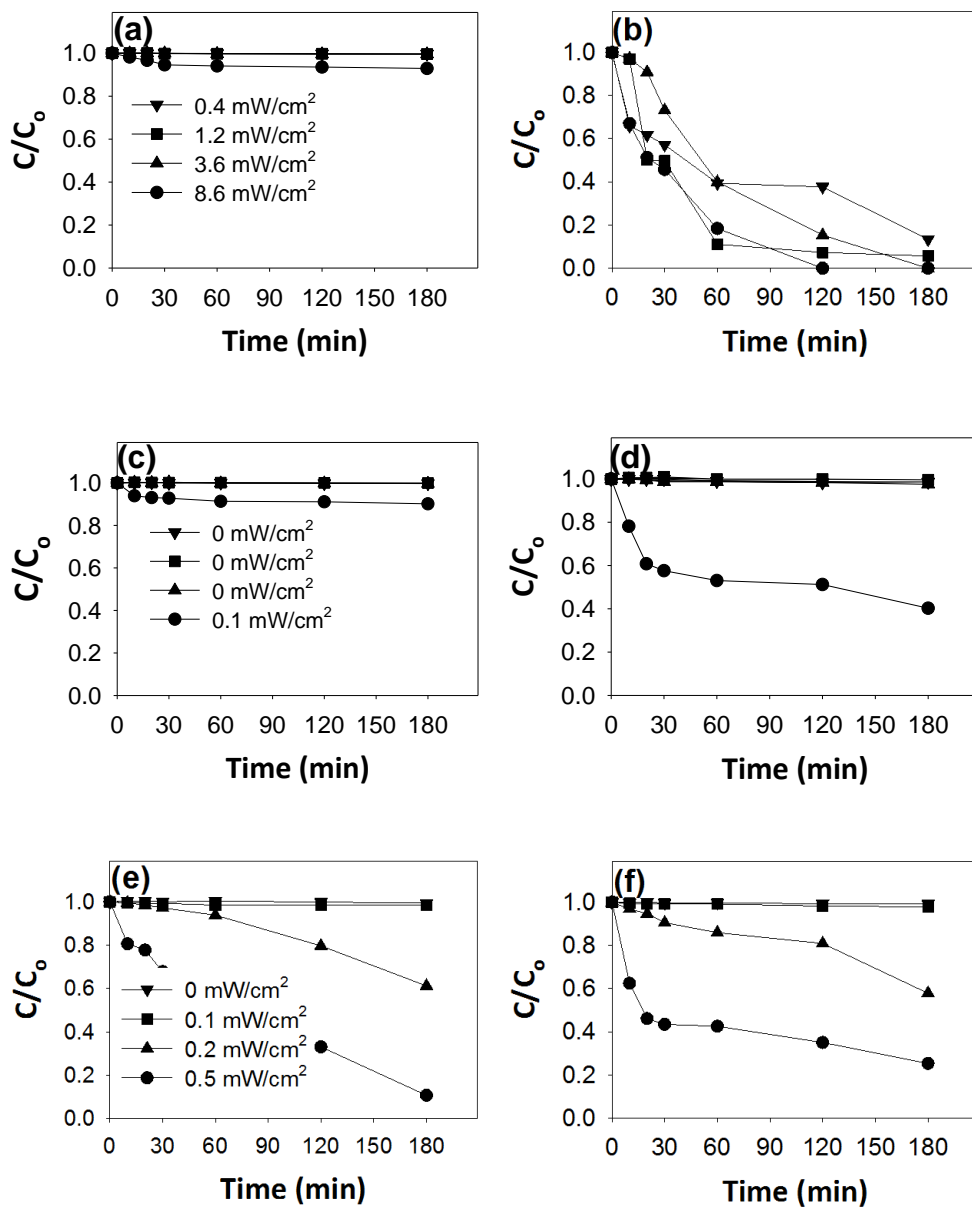


Figure 3-5. Effect of light intensity on the photolytic and TiO₂ photocatalytic decomposition of TCS (C₀=10 mg/L and TiO₂=0.75 g/L) under different UV wavelengths: (a) UVA, (b) UVA+TiO₂, (c) UVB, (d) UVB+TiO₂, (e) UVC, and (f) UVC+TiO₂. Note that lowered concentration of TCS at 10 mg/L was used due to its low solubility.

TCS since TCS with maximal absorption wavelength at 280 nm absorb UVC at 268 nm. Photocatalytic decomposition of TCS under UVA and UVC was significant. As intensity increased, faster decomposition of TCS was observed. Even in case of UVB, there was also noticeable photocatalytic decomposition of TCS, similar to IBP. In comparison between UVA and UVC, adding TiO₂ accelerated TCS decomposition under UVA while it deteriorated TCS decomposition under UVC, which is very similar to SMX and was explained with competition for UV absorption between TiO₂ and the PPCP.

3.1.4. Photolysis vs. photocatalysis

Photolytic decomposition of the PPCPs was solely determined by relation between their UV absorption characteristics and the UV emission spectra of the LED lamps. Shorter wavelength of UV-LED had high potential for photolytic decomposition. Increasing UV intensity to accelerate photolytic decomposition was meaningful only when the PPCP absorbed the UV wavelength. One should be careful about adding a photocatalyst TiO₂ for the purpose of increasing decomposition kinetics. There is competition for UV utilization between TiO₂ and PPCP. When no significant photolysis was observed, the presence of TiO₂ greatly helped to improve decomposition kinetics through hydroxyl radical generation [17]. On the other hand, when significant photolysis was observed, the presence of TiO₂ rather inhibited the overall decomposition process [1,4].

As discussed, testing the effect of the same intensity from UV-LEDs emitting different wavelengths is technically almost impossible (UV-LED technology has not been fully developed yet) [12]. Only comparison might be possible for UVA and UVC at

intensity of around 0.4-0.5 mW/cm². At the similar intensity, UVC with shorter wavelengths was much more effective for photolytic decomposition of all the PPCPs [22,23]. Results on photocatalytic decomposition were slightly different. UVC showed very similar (or slightly improved) performance to UVA for decomposition of SMX and TCS while UVC was superior to UVA for decomposition of IBP.

3.2. Effect of reaction pH

The effect of pH on the photolytic and photocatalytic decomposition of the PPCPs was investigated at 3, 5, 7, 9, and 11 under highest intensity of each UV-LED (i.e., at 0.5 cm distance). No buffer was used to remove any side effects of buffer species. Initial pHs at acidic and neutral conditions decreased slightly while those at basic conditions decreased significantly (e.g., initial pH at 11 changed to pH at around 7.0 after 3 hr reaction). Information on full scale decomposition kinetics of the PPCPs under different pHs is available in Figs. 3-6-3-8. Meanwhile, PPCP decomposition efficiency in each case for 1 hr is summarized in Figs. 3-9 and 3-10. Both photolytic and photocatalytic decomposition of the PPCPs was greatly affected by pH. In particular, photocatalytic decomposition is mediated by TiO₂ surface. The surface chemistry of TiO₂ used in this study (its point of zero charge is around 6.0) changes greatly over pH and thus the change influences adsorption and decomposition of the PPCPs [13]. Reaction pH may also affect the aggregation of TiO₂ particles and the ionic nature of the PPCPs.

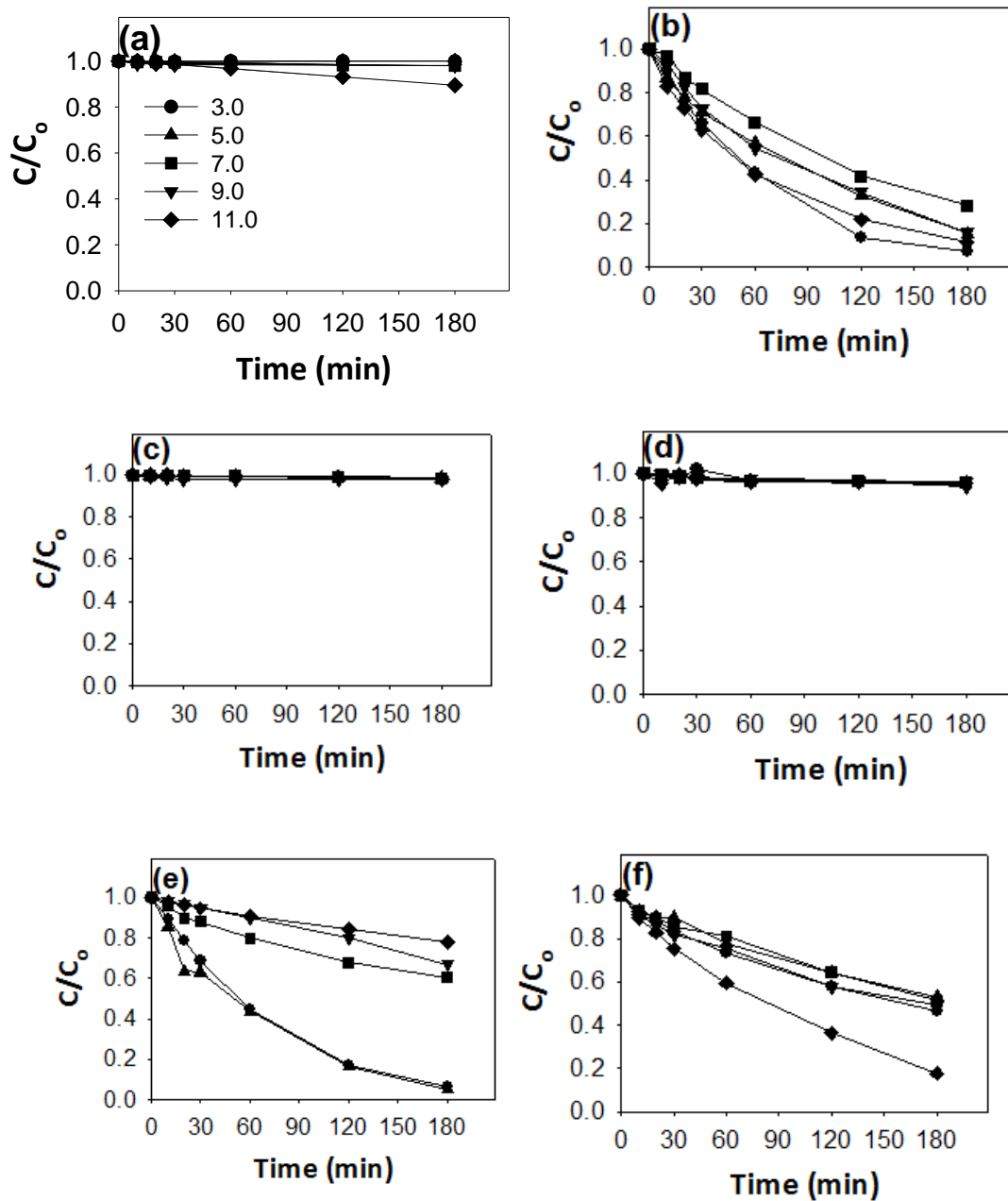


Figure 3-6. Effect of initial pH on the photolytic and TiO₂ photocatalytic decomposition of SMX ($C_0=20$ mg/L and TiO₂=0.75 g/L) under different UV wavelengths: (a) UVA, (b) UVA+TiO₂, (c) UVB, (d) UVB+TiO₂, (e) UVC, and (f) UVC+TiO₂.

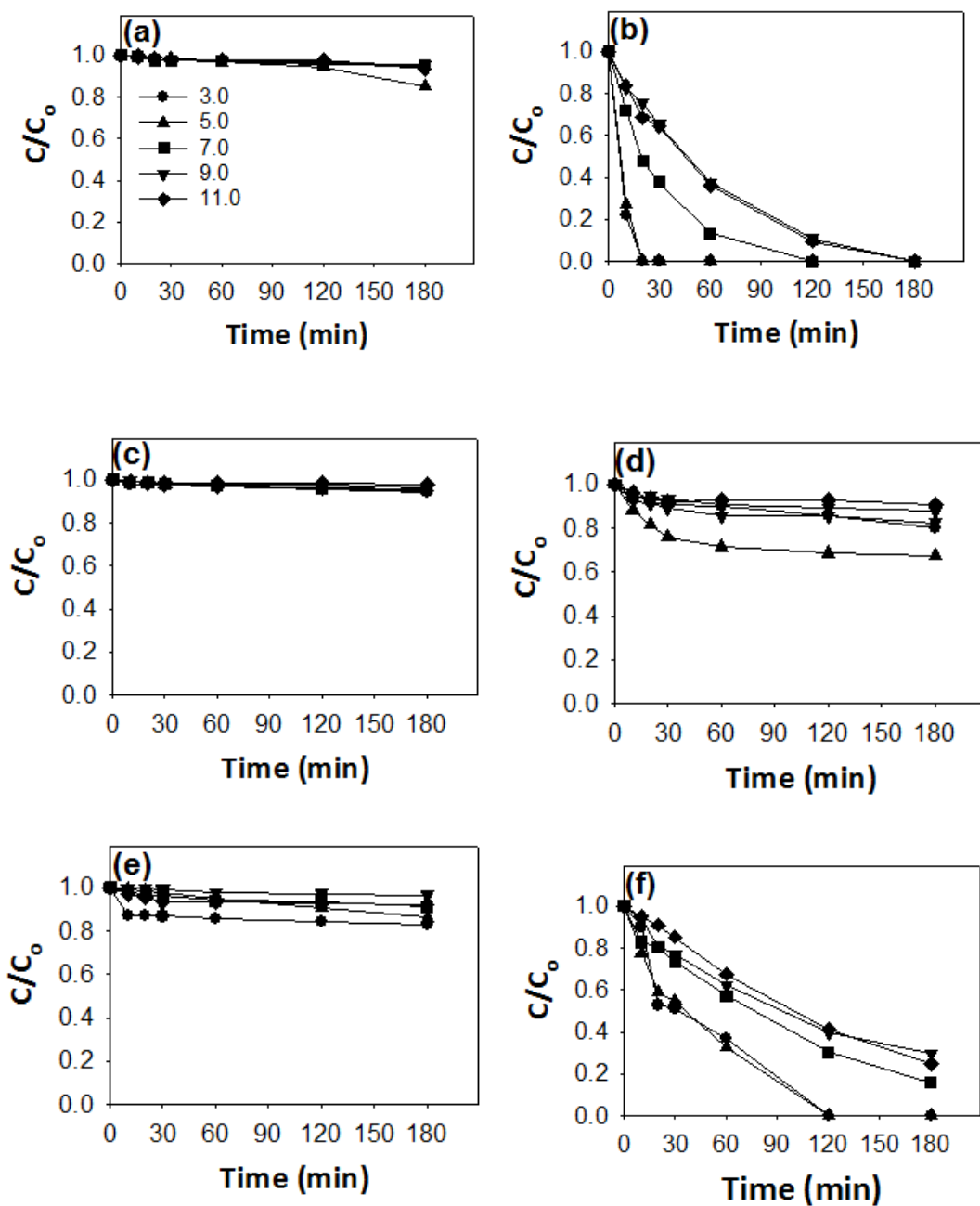


Figure 3-7. Effect of initial pH on the photolytic and TiO_2 photocatalytic decomposition of IBP ($C_0=20$ mg/L and $TiO_2=0.75$ g/L) under different UV wavelengths: (a) UVA, (b) UVA+ TiO_2 , (c) UVB, (d) UVB+ TiO_2 , (e) UVC, and (f) UVC+ TiO_2 .

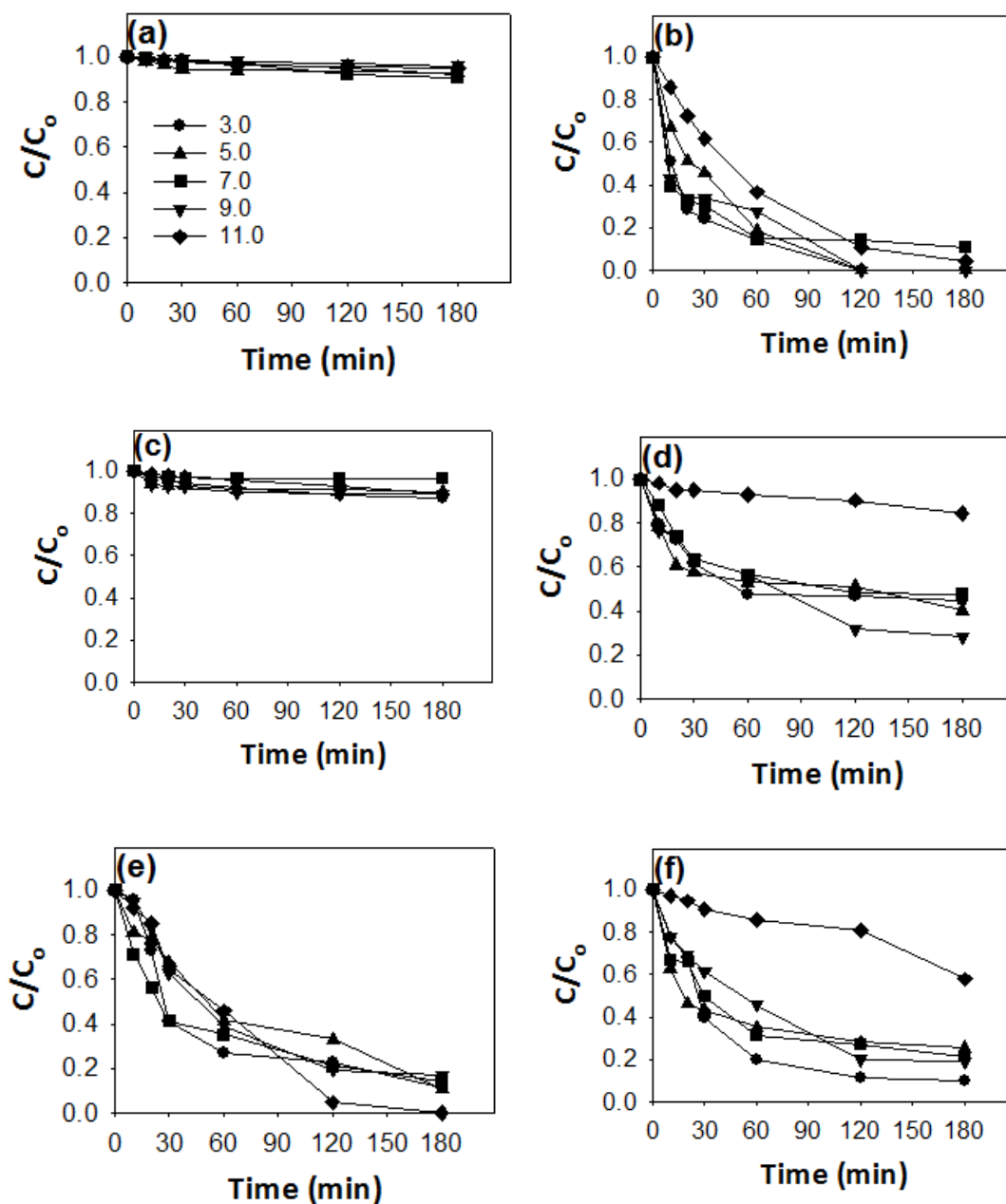


Figure 3-8. Effect of initial pH on the photolytic and TiO₂ photocatalytic decomposition of TCS ($C_0=10$ mg/L and TiO₂=0.75 g/L) under different UV wavelengths: (a) UVA, (b) UVA+TiO₂, (c) UVB, (d) UVB+TiO₂, (e) UVC, and (f) UVC+TiO₂.

3.2.1. SMX

Figure 3-9 shows photolytic decomposition of SMX under UVC at different pHs (there was negligible photolysis of SMX under UVA and UVB). Faster decomposition of SMX was observed under acidic condition (pH 5 followed by pH 3) under UVC. The significant dependency on pH under UVC was observed only for SMX. Figure 3-10 shows photocatalytic decomposition of SMX under UVA, UVB, and UVC at different pHs. Under UVB, there was no significant difference over pHs because the low intensity of the UV-LED caused negligible decomposition of SMX. Under UVA and UVC, SMX was decomposed faster at either acidic or basic condition. In particular, pH 11 resulted in the fastest decomposition of SMX under UVA and UVC. SMX has two pKa values at 1.7 and 5.6 [24]. At pH 1.7, SMX is mostly positively charged; at pH 5.6, its speciation is 50% neutral and 50% anion; and at pH 9.5 it is 100% negatively charged [24]. At acidic pHs, SMX is more or less neutral while TiO₂ becomes positively charged. Meanwhile, at neutral pHs, both TiO₂ and SMX are negatively charged, resulting in low interaction by repulsion force. However, the highest decomposition of SMX at pH 11 suggests that other mechanisms overcoming the repulsion were involved in the decomposition of SMX onto TiO₂. Many of organic chemicals including SMX under high pHs have been reported to undergo base-catalyzed hydrolysis reactions and thus their degradation can be significantly enhanced [4,19].

3.2.2. IBP

There was no photolysis of IBP under UVA and UVB, similar to SMX. Although photolytic decomposition of IBP even under UVC is very low, slightly faster photolytic

decomposition of IBP was observed under acidic condition. For photocatalytic decomposition of IBP, the result varied over UV wavelengths. Under UVB, IBP decomposition was enhanced at neutral pHs, i.e., 5 followed by 7 and 9 (but not significant). However, under UVA and UVC, IBP decomposition was much faster at acidic conditions, roughly 3<5<7<9<11. IBP has pKa of 4.9 above which ionic IBP is predominant species and below which IBP is found in the molecular form [25-26]. At low pHs, more IBP in the molecular form can be absorbed onto TiO₂ surface due to hydrophobic interaction.

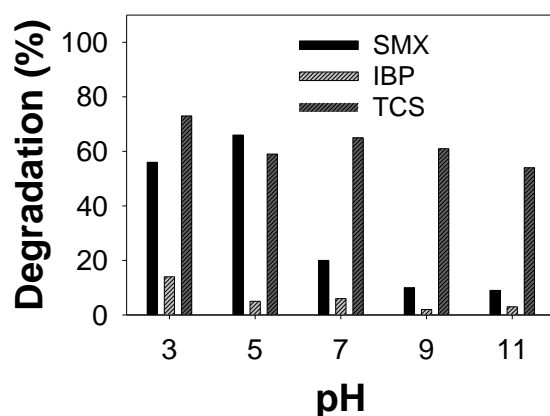


Figure 3-9. Effect of initial pH on the photolytic decomposition of pharmaceuticals for 1 hr (SMX=20 mg/L, IBP=20 mg/L, TCS=10 mg/L, and TiO₂=0.75 g/L) under UVC. Full scale kinetic results are shown in Figs. 3-6 – 3-8. Results on photolysis by UVA and UVB are not shown here since no degradation was observed under the condition.

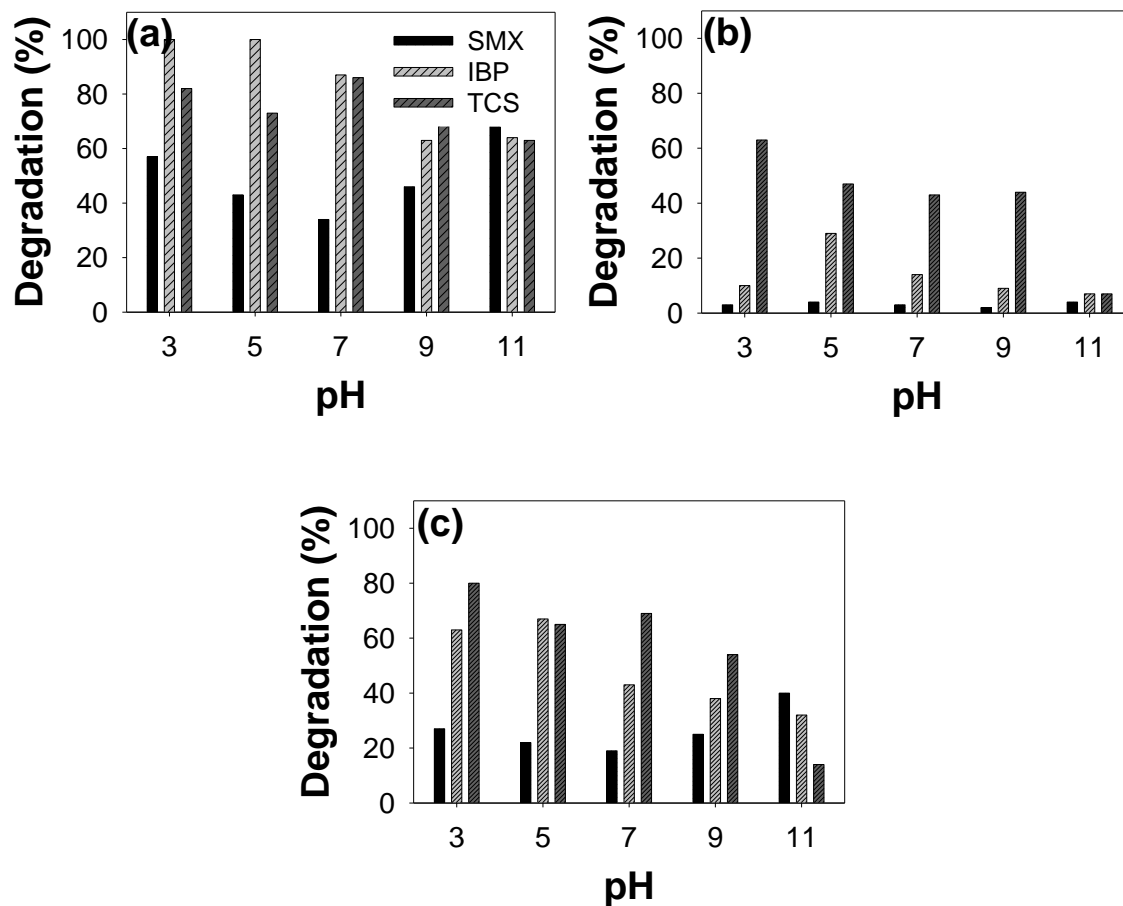


Figure 3-10. Effect of initial pH on the TiO_2 photocatalytic decomposition of pharmaceuticals for 1 hr (SMX=20 mg/L, IBP=20 mg/L, TCS=10 mg/L, and TiO_2 =0.75 g/L) under different UV wavelengths: (a) UVA, (b) UVB, and (c) UVC. Full scale kinetic results are shown in Figs. 3-6 – 3-8.

3.2.3. TCS

Photolytic decomposition of TCS is significant only under UVC but pH effect was marginal, showing fastest decomposition at pH 3. For photocatalytic decomposition, acidic pHs generally showed better decomposition of TCS under all UV wavelengths. Only under

UVA, TCS decomposition at 7 was slightly better than that at pH 3. TCS has pKa of around 8.0 [27]. At basic pHs, TCS is deprotonated. Increase in pH results in loss of positive charges and thus buildup of negative charges [28]. Both TiO₂ and TCS are negatively charged, causing strong repulsion force.

3.2.4. TOC removal

Mineralization capability of a treatment system might be more important and relevant than its decomposition capability toward target chemicals [19]. Table 3-2 summarizes TOC removal of various systems treating the PPCPs for 3 hr under different solution pHs and UV wavelengths. Under certain conditions, significant mineralization of the PPCPs was achieved. Mineralization of the PPCPs was slightly retarded, following their disappearance, as expected [1,10,22]. Observed trends in the mineralization capability of each system in combination of target PPCP, UV wavelength, and pH are well aligned with those found in its decomposition capability. Previously, photocatalytic decomposition with respect to disappearance of the PPCPs was less effective than photolytic decomposition in some cases where photolysis was significant. However, with respect to mineralization, photocatalysis showed better mineralization than photolysis in almost all cases. PPCPs are decomposed by hydroxyl radicals in photocatalysis via various oxidation mechanisms and oxidized PPCPs might be more vulnerable to further mineralization than reaction intermediates formed in photolysis mainly via bond breakage [4,19,28].

Wavelength	pH	Photolysis			Photocatalysis		
		SMX	IBP	TCS	SMX	IBP	TCS
UVA	3	9	9	15	72	61	43
	5	6	9	0	71	59	40
	7	5	10	0	51	62	24
	9	7	6	7	28	1	12
	11	10	7	1	55	20	10
UVB	3	7	3	16	9	27	18
	5	8	1	18	10	27	18
	7	7	2	10	3	17	10
	9	6	3	6	1	20	6
	11	10	7	0	0	17	3
UVC	3	17	13	20	47	43	48
	5	13	16	18	24	43	48
	7	6	18	0	26	29	42
	9	5	10	12	31	32	40
	11	13	10	4	52	1	17

Table 3-2. TOC removal for 3 hr at various pH conditions under different UV wavelengths

3.3. Effect of TiO₂ loading

The effect of TiO₂ loading on the photocatalytic decomposition of the PPCPs under different UV wavelengths was investigated at 0.25, 0.50, 0.75, and 1.0 g/L. In general, photocatalytic activity can be enhanced by increasing catalyst loading [19].

TiO ₂ (g/L)	UVA			UVB			UVC		
	SMX	IBP	TCS	SMX	IBP	TCS	SMX	IBP	TCS
0.0	6	9	0	7	1	18	13	4	20
0.25	11	1	18	8	24	20	16	32	29
0.50	32	47	32	10	25	23	22	35	26
0.75	71	59	40	10	27	18	24	43	48
1	70	57	44	13	35	18	12	43	51

Table 3-3. TOC removal for 3 hr at various catalyst loadings under different UV wavelengths

However, due to many other factors such as UV penetration and scattering through reaction solution containing TiO₂ suspension, an optimum TiO₂ loading might exist. Figure 3-11 and Table 3 summarize degradation of PPCPs, with respect to disappearance and mineralization, respectively, while full scale decomposition kinetic data is available in Figs. 3-12 – 3-14. Under UVA, adding TiO₂ affected the PPCP decomposition positively but the effect of TiO₂ loading in the range of 0.25-1.0 g/L was marginal. Although it is hard to determine an optimum TiO₂ loading under UVB due to the overall low reactivity, 0.75 g/L showed best decomposition of the PPCPs. Under UVC, SMX was decomposed faster in the absence of TiO₂ while IBP was decomposed faster in the presence of TiO₂ at around 0.75 g/L. Decomposition of TCS was not affected by TiO₂. In most cases, an optimum catalyst loading was found to be around 0.75 g/L. These observations were also supported by results on TOC removal. As observed in the effect of pH, photocatalysis showed better mineralization than photolysis in all cases.

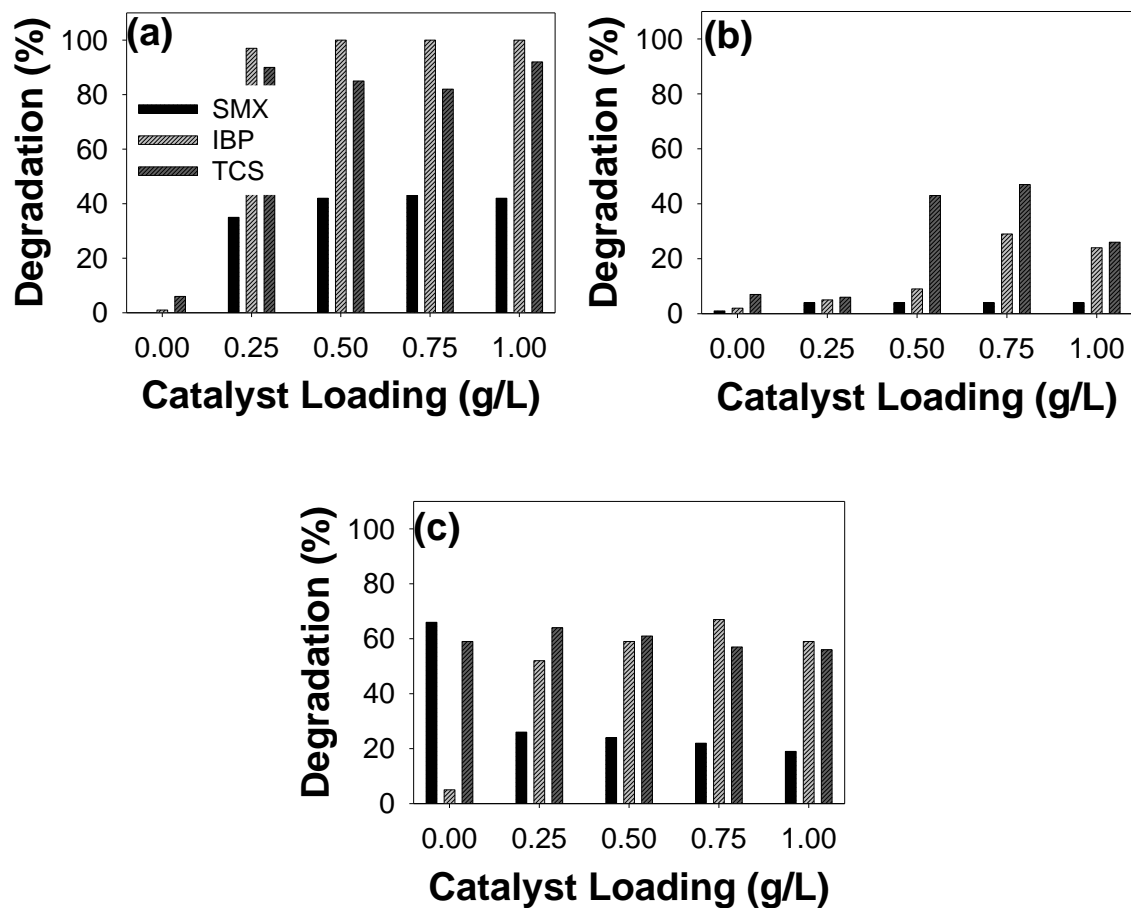


Figure 3-11. Effect of catalyst loading on the TiO₂ photocatalytic decomposition of pharmaceuticals for 1 hr (SMX=20 mg/L, IBP=20 mg/L, and TCS=10 mg/L) under different UV wavelengths: (a) UVA, (b) UVB, and (c) UVC.

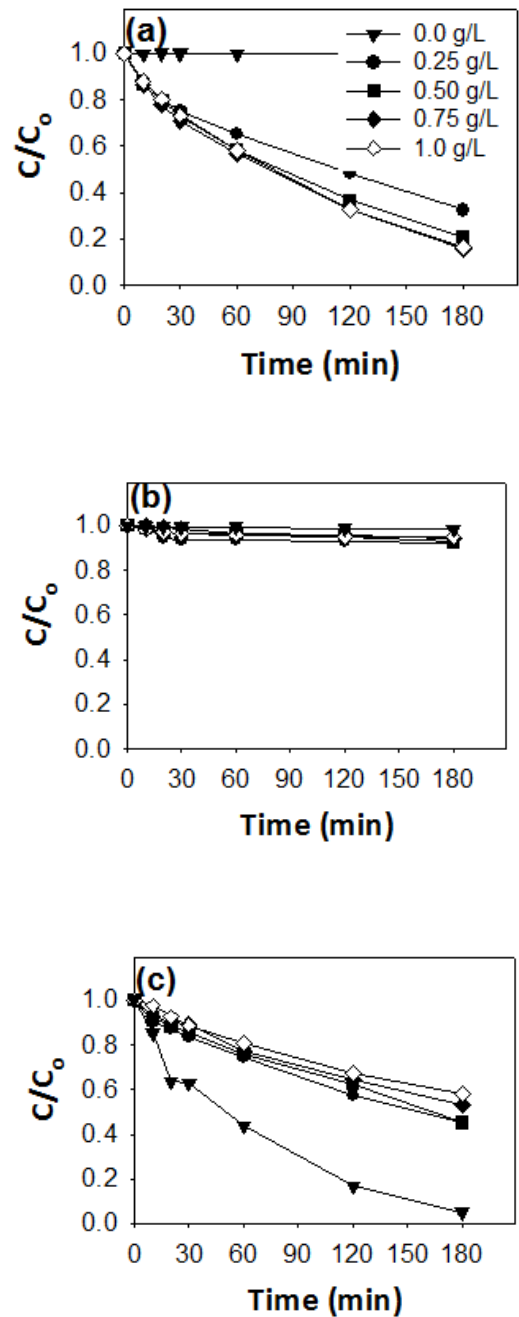


Figure 3-12. Effect of catalyst loading on the TiO_2 photocatalytic decomposition of SMX ($C_0=20$ mg/L) under different UV wavelengths: (a) UVA, (b) UVB, and (c) UVC.

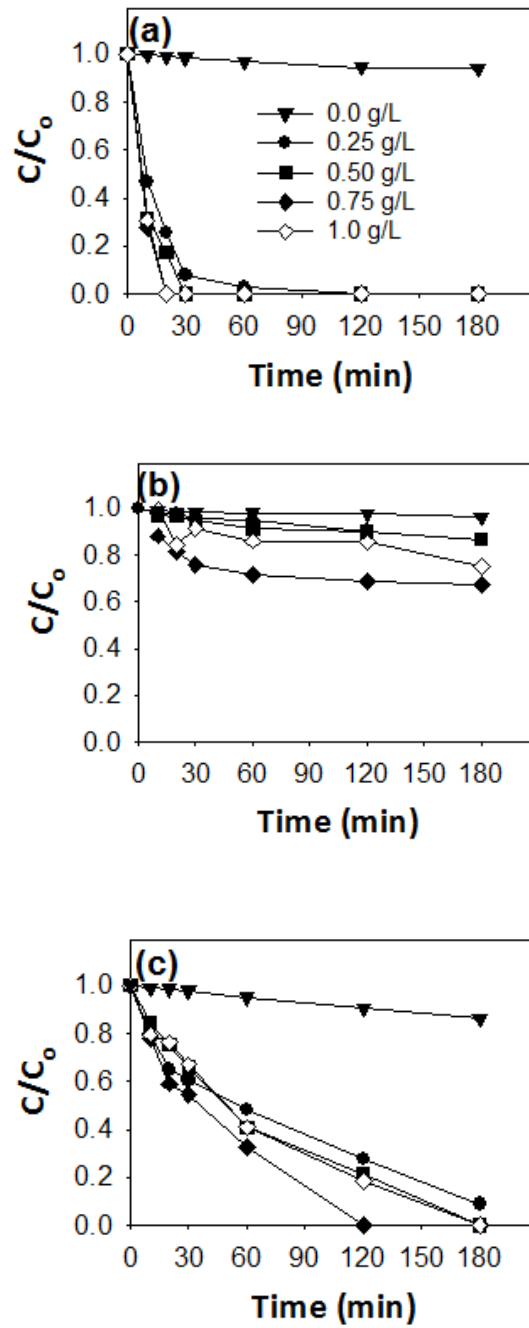


Figure 3-13. Effect of catalyst loading on the TiO_2 photocatalytic decomposition of IBP ($C_0=20$ mg/L) under different UV wavelengths: (a) UVA, (b) UVB, and (c) UVC.

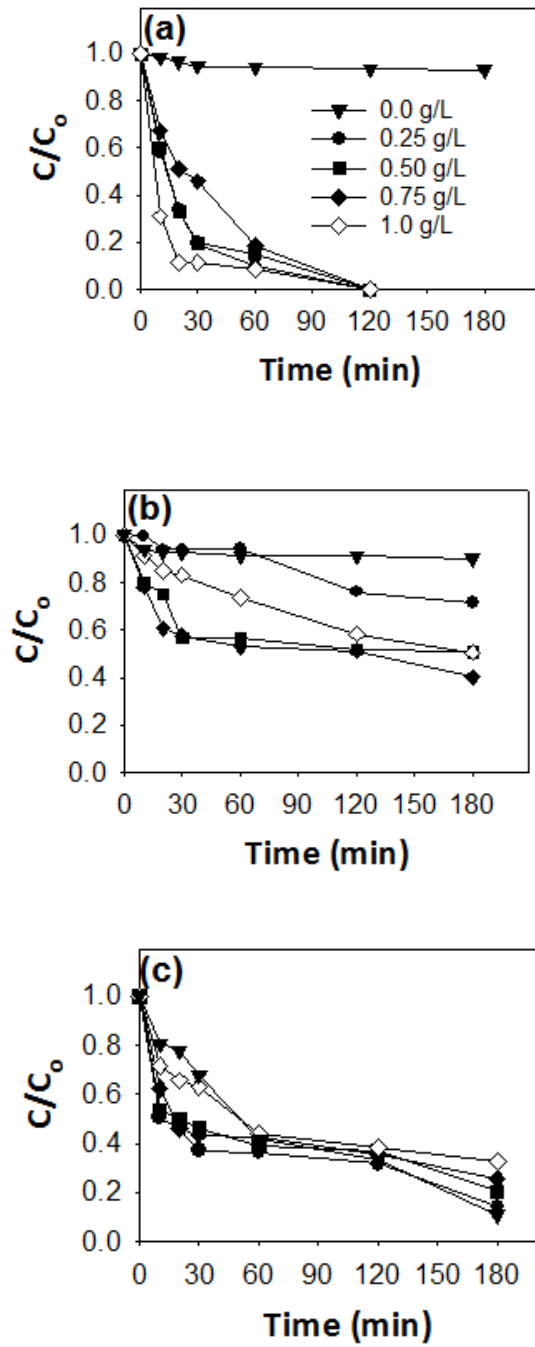


Figure 3-14. Effect of catalyst loading on the TiO_2 photocatalytic decomposition of TCS ($C_0=10$ mg/L) under different UV wavelengths: (a) UVA, (b) UVB, and (c) UVC.

Chapter 4

Conclusion

This study investigated the performance of UV LED for photolytic and photocatalytic decomposition under different operating parameters such as pH, light intensity, and catalyst loading. UV LED which possesses several economic and environmental advantages over conventional UV lamps. They have a very low light intensity compared to low-pressure lamps which is an important parameter that could control the size of reactors. Significant photolysis degradation occurs only under UVC, while UVB and UVA do not produce any satisfactory result. The photocatalytic degradation was significantly observed under UVA wavelength because of its high intensity and longer wavelengths than the target pollutants. The pH experiments revealed that degradation is favored in order of acidic>neutral>alkaline due to positive nature of TiO₂ at acidic pH. More detailed studies on the decomposition of the chemicals at more environmentally relevant concentrations (µg/L), simultaneous and competitive decomposition of the chemicals in a mixture, elucidation of reaction pathways and mechanisms such as identification of reaction intermediates. Development of high-intensity UV-LED lamps, reactor vessels made of materials that would capture maximum light for degradation and seize of the catalyst particles present in aqueous suspension would help in utilizing photo-oxidation to pilot scale to full-scale levels.

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