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Impact of Photolysis and TiO₂ on Pesticides Degradation in Wastewater

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Abstract: Pesticide residues are harmful to the environment and human and animal health even at low levels because of long-term bioaccumulation. In this study, photolysis was applied to treat three representative water samples: aqueous atrazine and dimethoate solutions as target pesticides, as well as wastewater and agriculture wastewater containing pesticide residue. It was performed using ultraviolet (UV) irradiation at two wavelengths (254 and 306 nm) with exposure times ranging from 2 to 12 h in the presence and absence of a photocatalyst to identify the optimal degradation conditions. Extraction and analyzation process were performed by the Quick Easy Cheap Effective Rugged Safe (QuEChERS) methods and gas chromatography–tandem mass spectrometry with triple quadrupole detector (GC–MSMS/TQD), respectively. Photodegradation increased with an increase in exposure time and the TiO₂ catalyst was beneficial for degradation. Both selected irradiation wavelengths were effective, although the wavelength of $\lambda = 306$ nm was the most efficient.

Keywords: photolysis; pesticides; degradation; wastewater; agriculture wastewater; TiO₂

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1. Introduction

Pesticides are used to improve crop plant quality and reduce losses because of insects. They are applied at various stages of cultivation and during post-harvest storage of various crops [1]. The wide-ranging use of pesticides has significant advantages in agriculture, but the inappropriate selection of pesticides, their over-use, and harvesting crops before washing off the residues can result in negative effects and undesirable pesticide levels in the produce that reaches consumers [2,3]. Exposure to pesticides can be direct, e.g., oral, inhalation, and dermal or indirect, e.g., through food, drinking water, residential, and occupational exposure. The consumption of pesticide-laden food crops is a major concern [4]. The persistent nature of pesticides can cause damage to the environment via transportation in water, soil, and air, leading to widespread environmental contamination [5–10].

Furthermore, the use of pesticides has been linked to human health risks, including acute effects such as nausea and headaches and chronic effects such as reproductive harm, endocrine system disruption, and cancer [11]. The potential damage of pesticides has been outlined in detail by Walker et al. [12].

Currently, many kinds of commodity pesticides are commercially available and are commonly used in agricultural practices. A commonly used pesticide worldwide is dimethoate (O, O-dimethyl-S-(N-methylcarbamoylmethyl) phosphorodithioate), an organophosphorus insecticide first registered in 1962 [13]. It can be applied to control

a wide range of insects including flies, aphids, mites, and plant hoppers [13] in crops including grains, vegetables, fruits, and ornamentals.

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is another commonly used chemical and a member of the s-triazine group of herbicides [14–16]. Serious negative effects and irritation to the eyes, nose, and throat can be caused by exposure to atrazine [17]. Atrazine had been found in rivers, high mountain lakes, ground water, drinking water supplies, rainwater, and even in fog [18].

Although several techniques have been reported to treat residual pesticides in the environment including electrochemical degradation [19,20] and membrane technology [21], photolysis and photocatalytic degradation of pesticides are widely used techniques to remove pesticides such as atrazine and dimethoate from the environment [22–28]. The photolysis process and photochemical approaches used to treat a wide range of pesticides were reviewed by Burrows et al. [29], Petala et al. [30], Pirsahab and Moradi [31] Kanan et al. [32] and Reddy and Kim [33]. Titanium dioxide (TiO_2) is the most suitable catalyst for industrial use, it has more photocatalytic efficacy and stronger stability with low cost [34]. Most importantly, it is safe for the environment and humans [35–37].

The importance of this work is in studying the photodegradation of very risky polluting chemicals such as pesticides in very needy sources of life, which is water, and to the best of knowledge, this is the first Saudi Arabian report of UV use in remediation of real samples of the pesticide atrazine and dimethoate-polluted water taken from the local environment, including treated wastewater and agriculture wastewater. It is strongly believed that the findings of this study will provide new data to environmental pollution and water remediation scientists, especially Saudi ones.

This study was performed to evaluate the presence of atrazine and dimethoate residues in local water sources in Riyadh city, the Kingdom of Saudi Arabia via extraction by the Quick Easy Cheap Effective Rugged Safe (QuEChERS) methods and analysis by gas chromatography/tandem mass spectrometry with triple quadrupole detector (GCMSMS/TQD). UV irradiation at various wavelengths and exposure times with and without catalyst was conducted to identify the optimal duration, wavelength for maximum degree of pesticide decomposition in the tested samples, and effect of catalyst addition on the photodegradation.

Chromatographic analysis was selected in this study because it is the only method which includes analyzing the pesticide residues and composition at the same time, ensuring no similarity or overlap with other compounds.

2. Materials and Methods

2.1. Sampling and Standards

Three water samples were used as targets in the study; deionized water from the Millipore deionized water system, Faculty of Food and Agriculture King Saud University. Also treated wastewater samples from the Almansuriyah treatment plant in Riyadh city in Saudi Arabia ($\text{pH} = 7.33$, $\text{EC} = 1.77 \mu\text{S}/\text{cm}$, $\text{TDS} = 1133 \text{ mg}/\text{L}$, turbidity = 1.89 NTU) where treatment process is performed by activated sludge method using tertiary treatment. Agriculture wastewater taken from the Alkharj agriculture region ($\text{pH} = 8.42$, $\text{EC} = 2.48 \mu\text{S}/\text{cm}$, $\text{TDS} = 1579 \text{ mg}/\text{L}$, turbidity = 3.24 NTU). The crops produced by the farms are date palm, grains and corn, some vegetables such as eggplant, pepper, zucchini and leafy crops such as mint, lettuce, parsley and watercress.

As for analytical parameters of gas chromatography, internal, calibration, and injection standards with declared 99.9% purities were purchased from AccuStandard, 153 Inc., New Haven, CT, USA, as individual or mixed standards at a concentration of $10 \mu\text{g}/\text{mL}$. All internal standards were ^{13}C 12-labelled, as the use of ^{13}C -labelled compound is preferable because quantification can be performed without clean-up (Maestroni et al., 2000; Maestroni 2002).

Methanol, dichloromethane, and acetonitrile obtained from Fisher Scientific (Fair Lawn, NJ, USA) were used as solvents for the extraction and analysis of the pesticides and were

of residue-analysis grade (99.9% purity). Quick Easy Cheap Effective Rugged Safe (QuEChERS) kits were purchased from Phenomenex, Madrid Avenue, Torrance, CA, USA. Titanium dioxide (TiO_2) as a photocatalyst was purchased from Sigma-Aldrich Chemie GmbH, Germany (molecular weight: 79.87, CAS Number: 13463-67-7, 718467nanopowder, 21 nm primary particle size (TEM), $\geq 99.5\%$ trace metals basis).

2.2. Remediation by Ultraviolet (UV) Photolysis

Photolysis of atrazine and dimethoate using UV irradiation at 254 and 306 nm for different durations was performed to investigate their effects on the pesticide photolysis process. Two devices of Boekel UV Crosslinker (BUV) model: 234100-2: 230 VAC, 175 W, 0.8 A, Boekel Scientific, 855 Pennsylvania Blvd. Feasterville, PA, USA. The first one was held with four 254 nm lamps and the second with four 306-nm lamps. The distance between lamps and water samples was 15 cm, and the UV irradiation intensity was $1071 \mu\text{Wcm}^{-2}$.

2.3. Sample Treatments

Natural water samples (10 mL) and those spiked with 2000 PPb of pesticides (2 ppm) were incubated for 12 h under UV light and aliquots (10 mL) were removed at intervals of 2 h to determine the remaining quantity of pesticides. The same procedure was applied after adding 0.001 g of TiO_2 as a photocatalyst to each 10 mL of water samples before UV remediation for 2 to 12 h.

2.4. Samples Preparation and Extraction and Cleanup by Quick Easy Cheap Effective Rugged Safe (QuEChERS)

First, 10 mL of the water sample was transferred into a 50 mL centrifuge tube, and vortexed briefly. Then, 10 mL of acetonitrile was added to each sample. Samples were shaken (manually or mechanically) or vortexed for 5 min to extract pesticides. (In this study a Spex SamplePrep Geno/Grinder 2010 operated at 1500 rpm was used). After that, the contents of an ECQUEU750CT-MP (citrate salts) Mylar pouch were added to each centrifuge tube. Immediately samples were shaken for at least 2 min and centrifuge for 5 min at ≥ 3500 rcf. We transferred a 1 mL aliquot of supernatant to a 2 mL CUMPSC18CT (MgSO_4 , PSA, C18) dSPE tube. Samples were vortexed for 0.5–1 min. They were centrifuged for 2 min at high rcf (e.g., ≥ 5000). Purified supernatant was filtered through a $0.2 \mu\text{m}$ syringe filter directly into a GC sample vial. Finally, the samples were analyzed by GC-MS/MSTSQ 8000/SRM.

2.5. Analysis by Gas Chromatography–Tandem Mass Spectrometry with Triple Quadrupole Detector (GC–MSMS/TSQ) 8000/SRM

All measurements were carried out using the latest Thermo Scientific™ TSQ 8000™ triple quadrupole GC-MS/MS system equipped with the Thermo Scientific™ TRACE™ 1310 GC with SSL Instant Connect™ SSL module and Thermo Scientific™ TriPlus™ RSH auto sampler. Injection mode was spiltless, Splitless Time 1.0 min GC column TR™ 5 MS, $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, carrier gas He (99.999%, flow rate 1.2 mL/min, constant flow, temperature program 100°C , 1 min; $10^\circ\text{C}/\text{min}$ to 160°C , 4 min and $10^\circ\text{C}/\text{min}$ to 250°C , 2 min, transfer line temperature 280°C , total analysis time 22.4 min, TriPlus RSH Autosampler Injection volume 1 μL . Ionization mode EI, 70 eV, Ion source temperature 250°C , scan mode SRM using timed SRM SRM transition setup automatically built-up by AutoSRM software. Transition conditions are shown in (Table 1).

Table 1. Gas chromatography–tandem mass spectrometry with triple quadrupole detector (GC–MSMS/TSQ) 8000 SRM instrumental conditions.

GC Trace Ultra Conditions		TSQ Quantum MS/MS Conditions	
Column	TR-Pesticide 30 m × 0.25 mm × 0.25 µm	Operating mode	Selected Reaction Monitoring (SRM)
Injector	Splitless	Ionization mode	EI
Injected volume	1 µL	Electron energy	70 eV
Injector temperature	225 °C	Emission current	50 µA
Carrier gas	Helium, 1.2 mL/min	Q1/Q3 resolution	0.7 u (FWHM)
Oven program	80 °C hold 1 min 15 °C/min to 160 °C hold 1 min 2.2 °C/min to 230 °C hold 1 min 5 °C/min to 290 °C hold 5 min Run Time 57.15 min	Collision gas	Argon
Transfer line temperature	280 °C	Collision gas pressure	1 mTorr
		Polarity	Positive

2.6. QAQC Strategies and Method Performance

Quality control samples were prepared and analyzed in triplicate samples, blank and spiked, and certified reference material (CRM) was prepared for this purpose and processed with each batch (5–10 samples). QuEChERS and the GC–MSMS/TSQ 8000 method limit of detection (LOD) and limit of quantification (LOQ), repeatability, reproducibility, accuracy and precession also were determined for each compound of the pesticides (Table 2).

Table 2. Parameters of retention time (RT), limit of detection (LOD) and limit of quantification (LOQ), recovery % and GC–MS/TSQ target mass of SRM scanning mode.

Name	RT min	Mass	Product Mass	Collision Energy m/z	LOQ (ng/mL)	Lod (ng/mL)	r ²	Recovery %	SD
Dimethoate	21.37	176	124	9	3.55	1.23	0.8034	102.35	8.33
Atrazine	23.94	200	122	10	6.84	3.95	0.9643	108.07	6.52

3. Results and Discussion

Photoremediation of the pesticide residues for atrazine and dimethoate in different water media was studied: aqueous solutions (AS), wastewater (WW) and agriculture wastewater (Ag.W). The samples were irradiated at two different wavelengths ($\lambda = 254$ and 306 nm) in the presence and absence of a catalyst. The results are shown in Figures 1 and 2 and listed in Table 3.

Figures 1 and 2a show the effect of exposure time of irradiation on the degradation of pesticides in aqueous solutions at two different wavelengths ($\lambda = 254$ and 306 nm) in the presence and absence of a catalyst. It is clear that the amounts of pesticides decreased with increased UV exposure time, indicating the degradation increases with increasing time, irrespective of the presence of the catalyst.

A similar trend is observed for the photoremediation of the pesticide residues in real water samples such as wastewater and agriculture wastewater (Figures 1 and 2b,c, respectively). To explain the obtained results, the mechanism of the process must be understood, and it can be described as follows:

For a non-catalytic process, the light energy from the radiation is absorbed by the pesticide molecules, which subsequently become activated and attain the excited state. These undergo homolysis, heterolysis, or photoionization, as illustrated in Figure 3a [38].

Figure 1. Concentration of pesticides (R = ppb) as a function of exposure time of irradiation for photolysis process of pesticides (non-catalytic process); (a) AS, (b) WW, and (c) Ag.W.

Figure 2. Concentration of pesticides (R(ppb)) as a function of exposure time of irradiation for photocatalysis process of pesticides (catalyst is TiO_2); (a) AS, (b) WW, and (c) Ag.W.

Table 3. Mean of concentration of pesticide residues degradation (R(ppb)) at two different wavelengths and irradiation time in the presence and absence of a catalyst ($\pm$ standard deviation (SD)). (spiked with 2000 PPb) and for catalytic process: 0.001 gm TiO_2 /10 mL.

Aqueous Solution Samples, Non-Catalytic Process								
irradiation wavelength	Irradiation time	0 h	2 h	4 h	6 h	8 h	10 h	12 h
$\lambda = 254$ nm	Atrazine	2000 $\pm$ 0.0	2000 $\pm$ 0.0	1776 $\pm$ 15.13	1458.3 $\pm$ 7.51	1130.3 $\pm$ 2.08	905 $\pm$ 4	475.33 $\pm$ 4.04
	Dimethoate	2000 $\pm$ 0.0	1927.67 $\pm$ 6.51	1614.67 $\pm$ 8.14	1318.3 $\pm$ 6.51	1066.3 $\pm$ 5.51	817.67 $\pm$ 5.51	439.33 $\pm$ 9.61
$\lambda = 306$ nm	Atrazine	2000 $\pm$ 0.0	1971.3 $\pm$ 6.51	1666.67 $\pm$ 6.03	1402 $\pm$ 1	1042.67 $\pm$ 3.79	799 $\pm$ 5.29	413.3 $\pm$ 5.13
	Dimethoate	2000 $\pm$ 0.0	1913 $\pm$ 3.61	1583.67 $\pm$ 3.06	1252.3 $\pm$ 3.21	990.67 $\pm$ 1.53	708.3 $\pm$ 5.51	307.67 $\pm$ 5.69
Aqueous solution samples, catalytic process								
$\lambda = 254$ nm	Atrazine	2000 $\pm$ 0.0	1959.3 $\pm$ 3.79	1616.3 $\pm$ 4.73	1244.67 $\pm$ 4.51	994 $\pm$ 3.61	738.67 $\pm$ 2.52	ND
	Dimethoate	2000 $\pm$ 0.0	1843.3 $\pm$ 3.21	1410.3 $\pm$ 9.07	1111 $\pm$ 6.24	945.67 $\pm$ 5.03	527 $\pm$ 5.29	ND
$\lambda = 306$ nm	Atrazine	2000 $\pm$ 0.0	1895 $\pm$ 5.29	1408 $\pm$ 4.58	1112 $\pm$ 2	883.33 $\pm$ 3.21	584 $\pm$ 17.58	ND
	Dimethoate	2000 $\pm$ 0.0	1716.3 $\pm$ 11.02	1270.67 $\pm$ 7.02	1016.67 $\pm$ 5.03	805.67 $\pm$ 4.73	314.67 $\pm$ 6.66	ND
Wastewater samples, non-catalytic process								
$\lambda = 254$ nm	Atrazine	2144 $\pm$ 0.0	2037.3 $\pm$ 1.15	1726 $\pm$ 5	1432.3 $\pm$ 5.51	1150 $\pm$ 4.58	874 $\pm$ 4.58	391 $\pm$ 11.14
	Dimethoate	2041 $\pm$ 0.0	1911.67 $\pm$ 2.52	1559.67 $\pm$ 1.53	1150 $\pm$ 4.58	971 $\pm$ 8.89	749.33 $\pm$ 10.21	345.67 $\pm$ 4.04
$\lambda = 306$ nm	Atrazine	2144 $\pm$ 0.0	1972 $\pm$ 4.58	1633.3 $\pm$ 8.14	1371.67 $\pm$ 9.24	1007 $\pm$ 5.57	664 $\pm$ 4	353.67 $\pm$ 4.62
	Dimethoate	2041 $\pm$ 0.0	1183.67 $\pm$ 4.04	1408 $\pm$ 3.61	1042.67 $\pm$ 14.58	814.33 $\pm$ 2.89	454.33 $\pm$ 7.02	226.67 $\pm$ 6.51
Wastewater samples, catalytic process								
$\lambda = 254$ nm	Atrazine	2144 $\pm$ 0.0	1925 $\pm$ 7.21	1623.3 $\pm$ 4.04	1138.67 $\pm$ 6.81	924 $\pm$ 3.46	539 $\pm$ 7.21	ND
	Dimethoate	2041 $\pm$ 0.0	1811.3 $\pm$ 2.89	1406.67 $\pm$ 5.51	1015.67 $\pm$ 3.21	855 $\pm$ 3.46	324.33 $\pm$ 4.16	ND
$\lambda = 306$ nm	Atrazine	2144 $\pm$ 0.0	1936.3 $\pm$ 4.16	1336.3 $\pm$ 4.16	1064.67 $\pm$ 4.16	804.67 $\pm$ 2.52	459 $\pm$ 4.46	ND
	Dimethoate	2041 $\pm$ 0.0	1644 $\pm$ 3	1175.3 $\pm$ 3.21	892 $\pm$ 1.73	592.33 $\pm$ 6.11	266 $\pm$ 7	ND
Agriculture wastewater samples, non-catalytic process								
$\lambda = 254$ nm	Atrazine	2144 $\pm$ 0.0	2023.3 $\pm$ 2.31	1939.3 $\pm$ 4.16	1643.67 $\pm$ 2.52	1522.3 $\pm$ 5.51	1307 $\pm$ 5.29	779.3 $\pm$ 351.9
	Dimethoate	2184 $\pm$ 0.0	2006.3 $\pm$ 3.21	1853.3 $\pm$ 3.51	1613 $\pm$ 4.58	1416 $\pm$ 4.58	1126.3 $\pm$ 12.01	861.67 $\pm$ 6.51
$\lambda = 306$ nm	Atrazine	2144 $\pm$ 0.0	1993 $\pm$ 2.65	1883.3 $\pm$ 4.93	1587.3 $\pm$ 4.73	1403.3 $\pm$ 3.51	1144 $\pm$ 3	903 $\pm$ 2.65
	Dimethoate	2184 $\pm$ 0.0	1890.67 $\pm$ 7.09	1772 $\pm$ 2	1474 $\pm$ 4.58	1255.67 $\pm$ 2.08	989 $\pm$ 5.89	409 $\pm$ 3.61
Agriculture wastewater samples, catalytic process								
$\lambda = 254$ nm	Atrazine	2144 $\pm$ 0.0	1882 $\pm$ 5.20	1534 $\pm$ 3.61	1062.3 $\pm$ 8.08	884.3 $\pm$ 2.52	423 $\pm$ 4.58	39.33333
	Dimethoate	2184 $\pm$ 0.0	1778.3 $\pm$ 7.37	1108 $\pm$ 6.56	838.67 $\pm$ 6.51	555 $\pm$ 3.61	ND	ND
$\lambda = 306$ nm	Atrazine	2144 $\pm$ 0.0	1730.3 $\pm$ 3.06	1304.67 $\pm$ 3.51	988 $\pm$ 4.58	773 $\pm$ 3	339 $\pm$ 2	ND
	Dimethoate	2184 $\pm$ 0.0	1626.3 $\pm$ 4.51	985.3 $\pm$ 3.79	764.67 $\pm$ 2.31	416.33 $\pm$ 5.96	130.33 $\pm$ 8.33	ND

Khan et al. observed that atrazine could be degraded by direct photolysis at 254 nm by absorbing the photons from UV light and transforming into the excited state, which subsequently decomposes [22]. The mechanism for the direct photolysis of atrazine involves photoinduced solvolysis via the heterolytic cleavage of the C–Cl bond [39,40].

In a photocatalytic process, a semiconductor catalyst is photoexcited by absorbing electromagnetic UV radiation. Upon light absorption, the electrons in the valence band are excited to the conduction band, leaving a positive hole in the valence band [33]. The empty hole in the valence band and the electron in the conduction band can induce reduction or oxidation of the pesticide adsorbate [41], as illustrated in Figure 3b [31].

Thus, the increase in the photodegradation of pesticides with increasing the contact time could be attributed to the higher opportunities of electron transforming into the excited state, and in the case of the catalytic process, leads to generation of more free radicals which are powerful for degradation.

Previous studies reported the importance of the contact time as an effective factor in the photodegradation process. A previous study showed a result in agreement with our results, demonstrating that this phenomenon occurs because of more process of oxidation, and the chance of atrazine photodegradation is higher with increasing exposure time to radiation [42]. The study pointed to the importance of determination of the required time to reach to equilibrium stage wherein the reaction rate reached a plateau at this stage [42].

Figure 3. Scheme of photoremediation process; (a) direct photolysis process (the scheme is quoted from [27]) and (b) photocatalysis process (the scheme is quoted from [31]).

Furthermore, it is observed that the addition of a catalyst enhances the photoremediation over the irradiation time. After 12 h of irradiation, Pesticides were not detected at either tested wavelengths, but only atrazine was detected at 254 nm. These results agree with the findings reported in the literature. The potential of common pollutants like dimethoate, chlorpyrifos, and malathion in the complete mineralization by photodegradation was investigated by direct and indirect sunlight exposure [23], and it was found that the degradation efficiencies of the various methods of photolysis follow the order, benzophenone sensitized > β -carotene sensitized > direct exposure. Evgenidou et al. observed that the degradation of dimethoate occurred at a very low rate in the absence of the catalyst, while it was positively influenced by the presence of semiconducting oxides (TiO_2 and ZnO) as catalysts [43]. It was reported in another study [24] that the efficiency of atrazine degradation by a combination of UV and chlorine was better than that by UV or chlorine alone. Pesticides such as atrazine, thiobencarb, dimethoate, lindane, dipterex, malathion, and bentazone were photodegraded effectively in the presence TiO_2 ceramics as catalysts [44]. Atrazine also underwent an effective photocatalytic degradation via microwave-assisted photocatalysis in the presence of nanocatalyst of titania-coated multiwall carbon nanotube [45].

The role is played by the photocatalyst is to facilitate degradation, as suggested by Yola et al. [46]. According to them, the separation of electrons (e^-) and holes (h^+) is enhanced by the catalyst molecules (TiO_2), which help in producing $\bullet O_2^-$ and $\bullet OH$ radicals. The

•OH radical attacks the pesticides, causing their degradation in a stepwise manner that ends up in the generation of small molecules such as Cl^- , NO_3^- , CO_2 , and H_2O [45].

The effect of the wavelength of irradiation (254 and 306 nm) on the degradation of pesticides in the different water media is presented in Figure 4 and Table 3. Although both of them were effective, it was observed that the photoremediation at $\lambda = 306$ nm was better than that at $\lambda = 254$ nm, in the presence and absence of a catalyst, in agreement with previous studies [47]. This indicates that the increase in wavelength increases the photodegradation because of the destructive effect of UV radiation on molecular bonds, and the enhancement of the electron transmission between the valence and conduction bands, which makes the degradation process easier and faster.

Figure 4. Concentration of pesticides (R = ppb) as a function exposure time of irradiation at both wavelengths of ultraviolet (UV) for the photo-remediation process, with and without catalyst, of pesticides; (a) AS, (b) WW, and (c) Ag.W.

In addition, the results reveal that the tendency of degradation in dimethoate upon irradiation is greater than that in atrazine in both the presence and absence of the photocatalyst. This can be an attribute of the pesticide structure. The difference in the structure of the two pesticides is distinct: atrazine is an aromatic compound, while dimethoate is an aliphatic compound (Figure 5), which can be degraded more easily than the aromatic ring.

Figure 5. Structures of pesticides; (a) dimethoate and (b) atrazine.

Furthermore, and although the effect of dissolved constituents in water samples on photodegradation of pesticides in the water samples was out of the scope of our study, it is worth indicating the role which is played by this kind of matter. In general, UV radiation has a destructive effect on molecular bonds. Therefore, it is expected that the organic matter in water samples can be affected the radiation by absorbing the UV light to be excited and entering in series of reactions [48–51]. Despite the fact that this matter might be good for our experiment because most of pesticide residues is adsorbed or absorbed in the organic part in the targeted wastewater samples, an inhibitory effect of them on the photodegradation process is also possible [52,53]. A study reported that the dissolved organic matter in the excitation state act as a photosensitizer, enhancing phototransformation of pesticides in addition; it may act as an antioxidant decreasing phototransformation rates through various mechanisms [52]. Inhibition mechanisms by natural organic matter were also reported in another study [53].

The differences in the response of the different water media towards photodegradation could be explained by this factor although it needs to be confirmed by further experiments (Figure 6). However, previous published works highlighted the effect of different organic species on the photodegradation process of pesticides in some aquatic systems and discussed this factor in detail [48,54]. In a recently published review [55], challenges in a photocatalytic process of natural water were compiled by analyzing the cyanotoxins' remediation, and the critical influence of natural organic matter was discussed.

Figure 6. Cont.

Figure 6. Comparison of photodegradation, with and without catalyst, of pesticides in different water media: concentration of pesticides (R(ppb)) as a function exposure time of irradiation at both wavelengths of UV; (a) Dimethoate (noncatalytic process), (b) Dimethoate (Catalytic process), and (c) Atrazin (noncatalytic process). (d) Atrazin (Catalytic process)

4. Conclusions

In this study, the photodegradation of atrazine and dimethoate in aqueous solutions and in real water samples such as wastewater and agricultural wastewater collected from Riyadh, Saudi Arabia, was investigated. UV irradiation at $\lambda = 254$ and 306 nm was used to induce the photodegradation in the presence and absence of TiO_2 as a photocatalyst. The study of effect of time and selected wavelength on the photodegradation was the aim of this work. The samples were extracted by the QuEChERS method and analyzed using

gas chromatography–mass spectrometry. The findings show that photoremediation was successfully achieved; the conclusions are the photodegradation increased with the increase of process time under the selected wavelengths of irradiation, particularly at $\lambda = 306$ nm. The catalyzed process with TiO_2 was more efficient than the uncatalyzed process, although the applied conditions of photodegradation were effective for both the selected pesticides; dimethoate was more easily degradable than atrazine. The photodegradation process conditions are applicable for pesticides residues in real environments. The effect of the structure of the pesticides on the photodegradation process needs to be confirmed by further studies in future. Studying other factors such as the effect of the dissolved constituents in water on the photodegradation process and the effect of other catalysts with evaluating their recyclability is recommended.

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