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Comparison of direct UV photolysis and advanced oxidation technologies in the degradation efficiencies and kinetics of six typical organic pesticides

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ABSTRACT

Pesticide pollution has posed serious threats to human health and the ecological environment. This study comparatively investigated the degradation efficiencies and kinetics of six typical organic pesticides which were frequently detected in the nature water environment, namely cyromazine, dinotefuran, atrazine, chloridazon, diuron, and tebuconazole by ultraviolet (UV) based and ultrasound (US) based advanced oxidation processes, including UV/H_2O_2, UV/TiO_2, US, and US/TiO_2. Direct UV photolysis of the six pesticides was also examined for comparison. The results indicated that UV/H_2O_2 was substantially more efficient than the other technologies in the removal of the studied pesticides. All six pesticides could be removed 100% within 60 min at solution pH = 7 when the H_2O_2 dose was greater than 15 mg/L. The degradation rate of those pesticides by UV/H_2O_2 treatment was much higher than by the other methods. Direct UV photolysis worked well in the degradation of dinotefuran, followed by diuron. A 100% disappearance of dinotefuran and diuron could be achieved at 30 min and 90 min, respectively, independent of solution pH. However, the other four pesticides were found to be less susceptible to direct UV photolysis, particularly cyromazine, chloridazon, and tebuconazole. Although the UV/TiO_2 treatment also behaved well in the removal of dinotefuran and diuron, the decay of the two pesticides by this method was obviously slower than by the direct UV photolysis. UV/TiO_2 showed a similar ability to direct UV photolysis in the degradation of cyromazine, chloridazon, and tebuconazole. The performance of US treatment in the removal of the six pesticides was quite poor. An enhancement of the decay rate was observed when combined US and TiO_2, but the removal of the six pesticides by US/TiO_2 treatment was still less efficient.

Keywords: Degradation efficiency; Degradation kinetics; Direct UV photolysis; Organic pesticides; Ultrasound-based advanced oxidation processes; UV-based advanced oxidation processes

1. Introduction

To fulfill the increasing food demand arising from the growth of the global population, nowadays tons of pesticides are used yearly to protect crops from insects and pests and to enhance crops production in modern agriculture. However, only less than 3% of the pesticide applied to the crops reaches the target organisms, the rest either affects the

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no-target organisms or enters surface water and groundwater through runoff and infiltration processes [1]. The majority of the pesticides are persistent organic pollutants (POPs) and the residues persist in the ecosystem because of their elevated stability and some cases water solubility. Those pollutants characterized by high toxicity would cause potentially harmful effects on humans, and destroy the environment and biodiversity [2]. Even low levels of pesticides in drinking water may result in toxicity, with increased risk due to bioaccumulation and long-term chronic effect [3]. Examples of known chronic effects include cancers, birth defects, reproductive harm, neurological and developmental toxicity, immunotoxicity, and disruption of the endocrine system [4].

Due to the extensive application in agriculture, coupled with the low removal in the conventional drinking water and wastewater treatment processes, pesticides are becoming more and more ubiquitous in the environment. Pesticide pollution has been recognized as an important global issue [5]. Therefore, effective removal of pesticides from water would be of great significance for safe drinking water supply as well as the security of the environment.

In order to minimize the potential health risks of pesticides, various physical, chemical, and biological processes have been investigated to remove pesticides from water and wastewater, including membrane technologies [6], adsorption [7], chlorination [8], advanced oxidation processes (AOPs) [5], and biodegradation [9], etc. Among those methods, AOPs which are generally based on the in situ generations of highly reactive, unselective reactive oxygen species (ROS) such as $^{\bullet}OH$, a second strongest oxidant after fluorine, provides a viable and effective option for the removal of a wide range of organic compounds [10]. The most important advantage of those processes compared to conventional technologies is that AOPs are environmentally friendly as they do not transfer contaminants from one phase to another or produce massive amounts of sludge, and there is no generation of secondary waste [2,5]. The other advantages include the rapid reaction rate which means that less retention time and thus a smaller area would be required for processing the needed flow rate for the system [11].

Among the AOPs, the combination of ultraviolet (UV) irradiation with H_2O_2 or TiO_2 was usual option to remove pesticides from water and wastewater [12]. Recently, the use of ultrasound (US) in AOPs has received considerable attention due to the unique properties of US for generating $^{\bullet}OH$ and other oxygenated radicals, enhancing the rate of mass transfer and chemical reactions, and lowering the consumption of chemical reagents and generation of waste sludge [13]. US-based AOPs have been studied for the removal of various pollutants from wastewater such as aromatic compounds, chlorinated aliphatic compounds, pesticides, and pharmaceuticals and personal care products (PPCPs) [14].

The removal efficiencies of pesticides by different technologies would not be exactly the same. The choice of a suitable treatment method depends highly on the type of contaminants and the specific degradation methods, so the evaluation and optimal performance design of various technologies for the removal of targeted contaminants would be very beneficial. In this work, six typical organic pesticides belonging to five different commonly used classes, including triazines like atrazine and cyromazine, organochlorines such as chloridazon, triazoles, for example, tebuconazole, neonicotinoids like dinotefuran, and phenylureas like diuron, were chosen as the targeted pollutants. All of those selected pesticides had been characterized by their negative impact in environment given their toxicity, persistence, or potential of bioaccumulation [15–20]. Moreover, endocrine disrupting activity has been reported for atrazine, tebuconazole, and diuron [15–17]. This study aimed to investigate the suitability of UV-based and US-based AOPs for the degradation of the six typical organic pesticides from simulated water by comparatively evaluating their removal efficiencies and degradation kinetics in different processes. In a comparison, direct UV photolysis of the selected pesticides was also examined. Finally, a rapid and efficient method for removal of the six pesticides from aqueous solutions would be proposed. To the best of our knowledge, few direct comparisons of the removal of the selected pesticides by those treatment methods existed in the literature so far, and insufficient amounts of studies were found regarding the degradation of cyromazine, dinotefuran, and chloridazon by AOPs. Moreover, previous researches mainly focused on the degradation of the individual compounds, and few studies compared the removal efficiencies of those pesticides in mixtures where a competition effect would probably decrease the rate of degradation. The results of this work would provide the theoretical basis and technical support for the selection of removal technologies as well as the optimization of reaction conditions for the degradation of pesticides in aqueous solution.

2. Materials and methods

2.1. Materials

Tebuconazole (≥95%), diuron (≥98%), dinotefuran (≥97%), atrazine (≥97%), chloridazon (≥95%), cyromazine (≥95%), methanol (MeOH, HPLC grade), and acetonitrile (HPLC grade) which were used for the chromatographic analysis were purchased from J&K Scientific Ltd. (Darmstadt, Germany). NaH_2PO_4 (AR), Na_2HPO_4 (AR), HCl (38%, AR), and H_2SO_4 (98%, GR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). $Na_2S_2O_3$ (GR), NaOH (AR), and $Na_2B_4O_7$ (GR) were received from Tianjin Chemicals Reagent Ltd. (Tianjin, China). H_2O_2 (30%, w/w) and TiO_2 (P25, 80% anatase and 20% rutile) used in photo catalysis process were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and Evonik Degussa Co. (Dusseldorf, Germany), respectively. Ultrapure water (UPW, 18.2 MΩ·cm, TOC ≤ 1 μg/L) was produced by an Elga Purelab Ultra Analytic System (Bucks, UK). The basic information of the studied pesticides and their molecular structures are presented in Table S1.

2.2. Experimental procedure

2.2.1. Direct UV photolysis and UV-based AOPs

Direct UV photolysis and UV-based AOPs experiments were conducted in a photochemical reactor (V = 250 mL) schematically shown in Fig. S1. A 30 W low-pressure mercury UV (LPUV) lamp (monochromatic emission at 253.7 nm) was used as a light source. The average photon flux into the working solution was 1.18×10^{-7} Einstein/s determined by an iodide–iodate chemical actinometer [21]. Prior to the experiments, working solution containing the mixture of six pesticides with respectively initial concentration of 100 μg/L was first transformed into the photochemical reactor. In UV/H_2O_2 experiment, H_2O_2 solution was added into the working solution simultaneously with pesticides at 2~20 mg/L, similar to those used in the previous studies [22]. In UV/TiO_2 experiments, the working solution was prepared in the way as follows: pre-weighed Degussa P25 TiO_2 powder was added into UPW at 5~20 mg/L [22] first and mixed thoroughly by ultrasound for 30 min prior to the addition of pesticides. Then the suspension was transferred into photochemical reactor and the pesticides at fixed concentration were added. Immediately after that the working solution was allowed to react for 120 min under irradiation. During the experiments the reacting solution was stirred magnetically to maintain the solution homogeneous. A thermostatic water recirculation system was used to keep the solution temperature at 20°C ± 0.5°C during the irradiation treatment. To acquire stable output, the LPUV lamp was ignited for 30 min before the photooxidation experiments. During the reaction, sample aliquots were taken at defined time intervals and filtered using a 0.22 μm polyethersulfone ultrafiltration membrane for analysis. In UV/H_2O_2 experiments, excess $Na_2S_2O_3$ was added to the sample to quench any residual H_2O_2 immediately after sampling.

2.2.2. US-based AOPs

An open stainless steel ultrasonic bath (P = 600 W, f = 40 kHz) with a length, width, and height at 50, 30, and 20 cm was used as US reactor (Fig. S2). In US experiments, 250 mL working solution containing the mixture of six pesticides with the respectively initial concentration of 100 μg/L was transferred into the quartz break and placed in an open stainless steel ultrasonic bath (P = 600 W, f = 40 kHz) to react for 120 min in the dark. In US/TiO_2 experiments, the method of preparing working solution was similar with that of UV/TiO_2 experiments. Then the prepared working solutions were kept in the dark and allowed to react in the US bath for 120 min. The sampling method in US-based AOPs experiments followed similar procedures as UV-based experiments.

UPW was used to prepare all the working solutions in order to avoid the introductions of organic solvent which would scavenge the radicals produced in the AOPs and slow down the reaction rate. In all experiments, solution pH was buffered at 4.0, 7.0, and 10.0, respectively, using 2 mM phosphate and/or borate buffers, adjusted by small amounts of 1 M H_2SO_4 or 1 M NaOH. All experiments were conducted at least in triplicate and the average values of results were reported.

2.3. Analyses

The concentration of pesticides was detected using an ultra-performance liquid chromatography-electrospray ionization-triple quadrupole mass spectrometer (UPLC-ESI-MS/MS) (Waters Corporation, Milford, MA, USA) system equipped with an ACQUITYTM UPLC BEH C18 column (50 mm × 2.1 mm, 1.7 μm particle) (Waters Corporation, Milford, MA, USA). The detection was carried out using a TQD with ESI in positive multiple-reaction monitoring (MRM) mode. Masslynx 4.1 software (Waters Corporation, Milford, MA, USA) was used for data acquisition and processing. Parameters information of UPLC and MS for quantitative analysis of the six pesticides is presented in Text S1.

3. Results and discussion

3.1. Removal of six pesticides by direct UV photolysis

Photo-labile compounds could be directly degraded by UV irradiation as a consequence of light absorption [23]. The removal of the selected pesticides by direct UV photolysis was performed at solution pH of 4, 7, and 10, respectively. The results are presented in Fig. 1.

As illustrated in Fig. 1, the photolysis efficiency of the six pesticides by LPUV irradiation followed the order below: dinotefuran > diuron > atrazine > cyromazine > tebuconazole > chloridazon. It was obviously seen that dinotefuran and diuron were easy to photolysis, and greater than 99% of the two pesticides could be removed after irradiation for 30 and 90 min, respectively, at all the examined solution pH. For atrazine, an elimination ratio of 71%, 68%, and 75% could be achieved at pH 4, 7, and 10, respectively, at the end of irradiation treatment. In comparison, cyromazine, tebuconazole, and chloridazon were more resistant to direct UV photolysis, only 37%~40% of cyromazine, 26%~40% of tebuconazole, and approximate 30% of chloridazon could be degraded after irradiation treatment for 120 min at the experimental solution pH.

Martins et al. [24] also reported a high-efficiency photolysis of diuron, an almost complete removal was observed after direct UV irradiation for 8 min. Similar results for diuron photodegradation were also described by Sanches et al. [12]. Different from the results observed in the present work, Prosen and Zupancic-Krajl [25] found that atrazine almost disappeared from the solution after 60 min of irradiation. Bianchi et al. [26] also observed an absolute degradation of atrazine within 100 min under photolysis at 254 nm. The distinction in the degradation efficiency might be ascribed to the different UV photon fluence, initial concentrations of atrazine, and the competition for photons between the six pesticides in mixtures. No obvious pH dependence was observed for the degradation of dinotefuran, diuron, chloridazon, and cyromazine by direct UV photolysis, but for atrazine, the highest removal efficiency was achieved at pH = 10, and the degradation degree of tebuconazole was larger at pH = 7.

The semi-log graph of the six pesticides concentration vs. irradiation time under the three solution pH conditions all presented straight lines (insets in Fig. 1), indicating that the degradation of six pesticides by direct UV photolysis followed pseudo-first-order reaction kinetic [27]. The reaction rate constants (k) at different solution pH were summarized in Table 1. As shown, dinotefuran presented the highest degradation rate (0.1016~0.1382 min^{-1}), followed by diuron (0.0481~0.0554 min^{-1}), atrazine (0.0093~0.0113 min^{-1}),

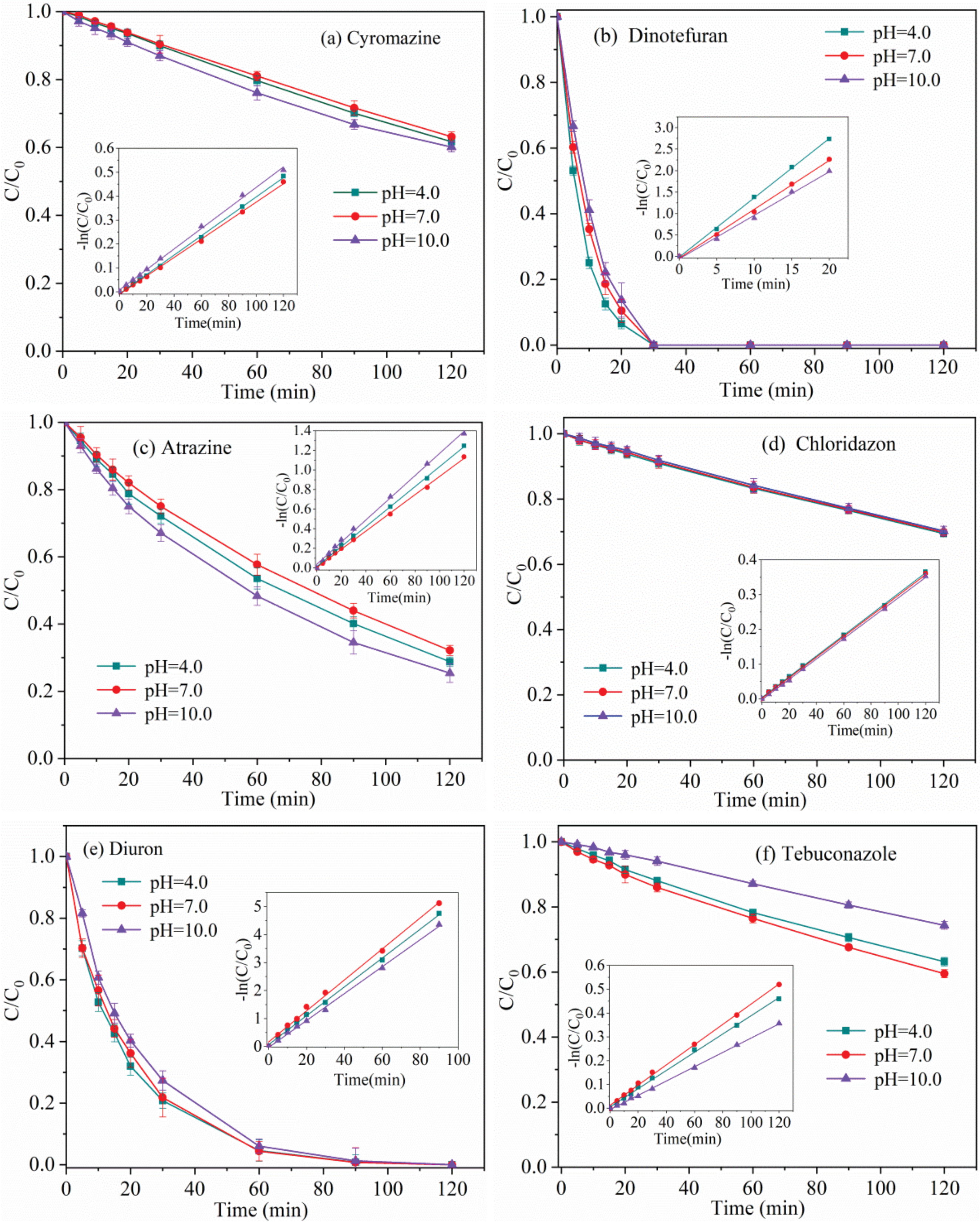

Fig. 1. The degradation of six pesticides at different solution pH by direct UV photolysis.

Table 1
Degradation rate constants k (min^{-1}) of the six pesticides by direct UV photolysis and various AOPs treatment

Pesticides	UV photolysis			UV/H_2O_2			UV/TiO_2			US			US/TiO_2		
	pH 4	pH 7	pH 10	pH 4	pH 7	pH 10	pH 4	pH 7	pH 10	pH 4	pH 7	pH 10	pH 4	pH 7	pH 10
Tebuconazole	0.0038	0.0043	0.0030	0.1702	0.1700	0.0251	0.0049	0.0060	0.0030	0.0007	0.0005	0.0006	0.0050	0.0035	0.0022
													0.0011	0.0013	0.0010
Diuron	0.0515	0.0554	0.0481	0.3207	0.3376	0.2610	0.0474	0.0375	0.0210	0.0012	0.0014	0.0015	0.0073	0.0053	0.0030
													0.0016	0.0014	0.0001
Dinotefuran	0.1382	0.1139	0.1016	0.1268	0.4818	0.1547	0.0270	0.0712	0.0373	0.0010	0.0014	0.0012	0.0073	0.0193	0.0117
													0.0013	0.0017	0.0016
Atrazine	0.0102	0.0093	0.0113	0.2601	0.1348	0.0394	0.0321	0.0115	0.0093	0.0006	0.0004	0.0005	0.0018	0.0075	0.0101
													0.0003	0.0011	0.0009
Chloridazon	0.0030	0.0030	0.0029	0.2610	0.3163	0.2333	0.0029	0.0065	0.0021	0.0009	0.0008	0.0011	0.0066	0.0259	0.0035
													0.0006	0.0022	0.0002
Cyromazine	0.0041	0.0039	0.0043	0.0342	0.0954	0.0117	0.0082	0.0052	0.0095	0.0014	0.0011	0.0016	0.0121	0.0098	0.0018
													0.0011	0.0012	0.0005

cyromazine (0.0039~0.0043 min^{-1}), and tebuconazole (0.0030~0.0043 min^{-1}). The photolysis rate of chloridazon was the slowest among the six pesticides, with a k value of about 0.0030 min^{-1} at all solution pH. The resulting values of k confirmed the trend noted above for the pesticide decay curves. Different molecular structures determined the difference of sensitivity to UV light, those pesticides which contain photosensitive groups in their molecular structures would exhibit faster degradation during UV hydrolysis. The k values reported in the present work were much lower than that observed in the literature. Benitez et al. [28] reported a rate constants of 51.1 × 10^3 min^{-1} for individual photo-oxidation of diuron. The slower degradation in the present study implied that there might be competition for incident photons between those pesticides in the mixture samples, which would retard the rate of degradation [24].

Direct UV photolysis was supposed to perform well in the degradation of photo-labile pesticides due to their potential to adsorb light. The degree of compounds degradation depended on two important parameters, namely molar adsorption coefficients (ε) and quantum yields (Φ) [29]. The ε of the selected pesticides at 254 nm was measured experimentally and the quantum yields were calculated according to the equation detailed in Text S2, the results are presented in Table 2.

No obvious dependency between ε and Φ of the six pesticides was observed, but the results of calculated Φ of the selected pesticides agreed well with the degradation trend and k observed above. Dinotefuran which degraded fastest possessed the highest Φ, followed by diuron, atrazine, and cyromazine. chloridazon and tebuconazole had comparable Φ. Although tebuconazole was measured to possess the highest ε which presented the highest probability to absorb UV light at 254 nm, the Φ was relatively small, indicating the low-utilization of photons. As a result, the decay of this pesticide by irradiation was relatively slow.

3.2. Removal of six pesticides by UV/H_2O_2 process

In general, H_2O_2 alone was not strong enough to oxidize most of the organic pesticides [24], this could be also confirmed by the results observed in the present work (Figs. S4 & S5 and Tables S3 & S4). The total removal efficiencies and rates of the six pesticides by H_2O_2 alone were all rather low. Thus the combination of H_2O_2 with other technologies like UV irradiation was essential. The removal of the six pesticides by UV/H_2O_2 treatment was examined at varying H_2O_2 concentration and solution pH. Fig. 2 presents the degradation efficiencies of the six pesticides at pH = 7 during H_2O_2 concentration of 2~20 mg/L.

As seen in Fig. 2, compared with H_2O_2 alone, there were significant enhancements in the degradation of all six pesticides when combined UV irradiation with H_2O_2. And the removal efficiency steadily increased with the incremental dose of H_2O_2. Specifically, at H_2O_2 dose of 2 mg/L, dinotefuran and diuron could be removed thoroughly within 30 min, while the 100% removal of chloridazon and atrazine needed about 120 min, tebuconazole and cyromazine failed to eliminate completely within the reaction time, especially for the latter which was proved to be the least susceptible to UV/H_2O_2 treatment. As H_2O_2 concentration

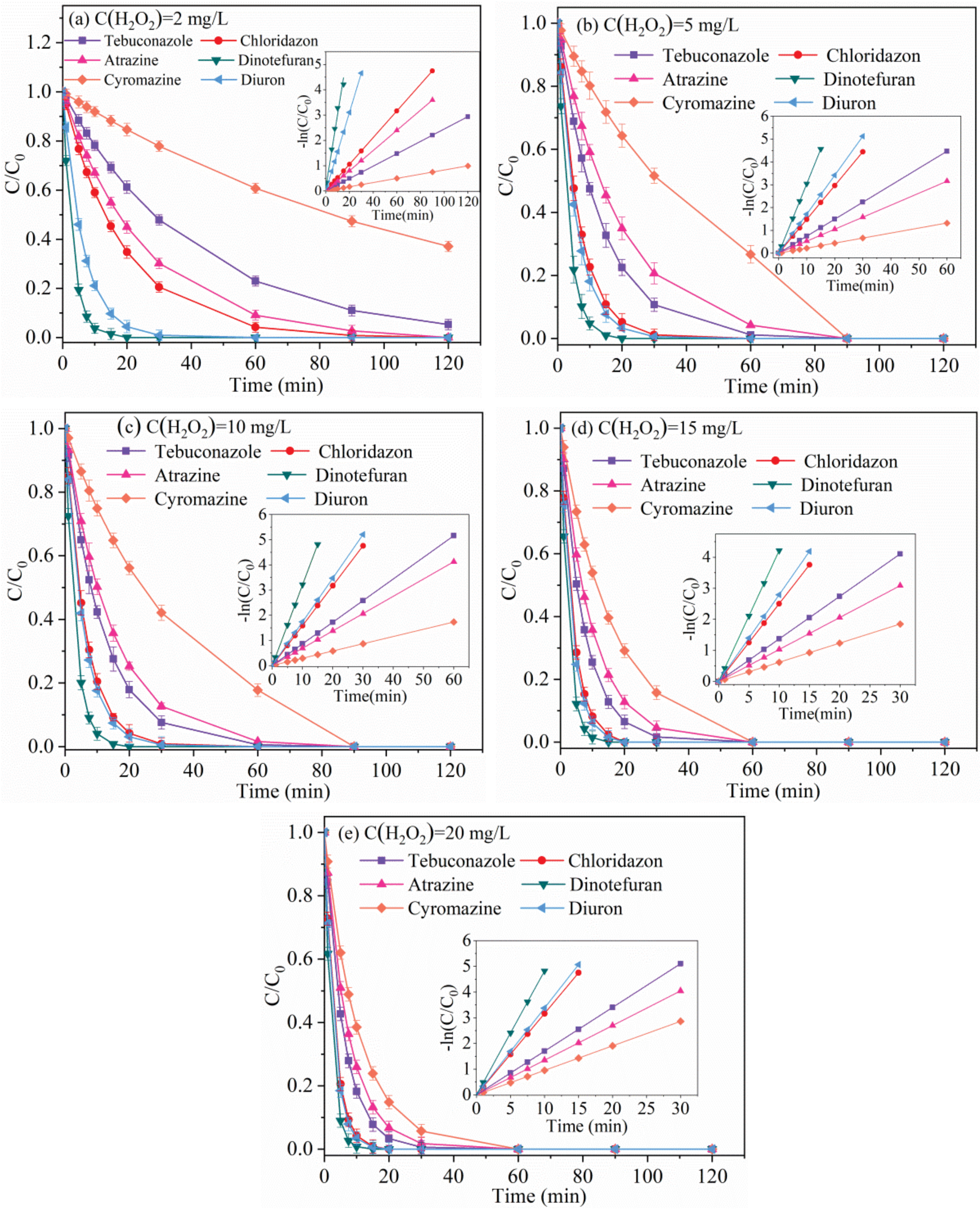

Fig. 2. The decay curves of six pesticides by UV/H_2O_2 treatment at different H_2O_2 dose.

increased to 5 and 10 mg/L, all the selected pesticides could be removed completely within 90 min. When H_2O_2 dose further increased to 15 mg/L, a faster elimination occurred, only 60 min was needed to remove the six pesticides. All the selected pesticides except for cyromazine could be removed completely within 30 min at H_2O_2 dose of 20 mg/L. Martins et al. [24] also reported that diuron could degrade rapidly by UV/H_2O_2 treatment and the diuron concentration was below the detection limit after reaction for 30 min.

The *k* values of the six pesticides by UV/H_2O_2 treatment at different H_2O_2 dose are listed in Table 3.

There was a noticeable increase in the degradation rate by UV/H_2O_2 treatment when compared with direct UV radiation. The removal rate of chloridazon, tebuconazole, and cyromazine by UV/H_2O_2 treatment at pH = 7 and H_2O_2 dose of 20 mg/L was approximately 105, 40, and 24 times faster than by direct UV photolysis at the same solution pH, indicated that the combination of UV irradiation and H_2O_2 was quite essential for the removal of those pesticides which were proved to be extremely resistant to direct UV photolysis. Chelme-Ayala et al. [30] also reported that UV/H_2O_2 process could enhance the oxidation rate of pesticides in comparison to direct UV photolysis. The degradation of pesticides in the UV/H_2O_2 system involved not only direct UV photolysis but also, more importantly, the reactions of $^{\bullet}OH$. It was known that H_2O_2 can be photolyzed by UV radiation at wavelengths ranging from 200 to 300 nm, yielding the hemolytic scission of the O–O bond of the H_2O_2 molecule and leading to the formation of $^{\bullet}OH$ which can contribute to the oxidation of pesticides [31]. The *k* of selected pesticides increased gradually as H_2O_2 dose increased from 2 to 20 mg/L. There was a low turnover of H_2O_2 and thus caused impairing generation of $^{\bullet}OH$ at low-dose H_2O_2 owing to the low ε of H_2O_2 at λ = 254 nm [10], thus a relatively high dose of H_2O_2 was necessary for an efficient oxidation of the selected pesticides. Although overdosed H_2O_2 would act as trap for radicals, thus compete with pollutants and result in lower degradation rates [10], no such phenomenon occurred in the examined H_2O_2 dose range in the present work. In consideration of the observed results, 20 mg/L was selected as the optimum H_2O_2 dosage.

The solution pH would also exert an effect on pesticides removal in UV/H_2O_2 process through affecting the production rate and oxidation power of free radicals [32,33]. Thus the influence of solution pH in the degradation of selected pesticides by UV/H_2O_2 process was examined at pH = 4, 7, and 10, respectively, the results are provided in Fig. 3.

The results suggested that solution pH almost did not affect the decay of chloridazon and diuron, but exerted moderate effect on dinotefuran removal, while the degradation of cyromazine, atrazine, and tebuconazole presented obviously pH-dependent. The most efficient removal was achieved at acidic conditions (pH = 4) for atrazine, neutral conditions (pH = 7) for cyromazine and dinotefuran, acidic and neutral conditions for tebuconazole. Alkaline condition (pH = 10) was the most unfavorable for the removal of those four pesticides. Those results might be explained as below: firstly, at acidic and neutral conditions, the –NH and –OH bonds existing in pesticide molecules would form hydrogen bonds with H_2O molecules, thus lower the bonds energy and make the reaction occur easier. Moreover, the OH group in pesticide molecules would be prone to bind with H^+ and leave as H_2O at acidic conditions. As a result, the degradation of those pesticides which have more –NH and –OH bonds in their molecules would occur easier in low solution pH and be more dependent on solution pH. Secondly, the decreased production and the attenuated oxidation power of $^{\bullet}OH$ at high solution pH would result in the reduced oxidation as well [32,33]. Hessler et al. [34] also observed that the degradation of atrazine slowed down at pH 11 compared with that at pH 3 and 7.

3.3. Removal of six pesticides by UV/TiO_2 process

Photocatalysis using TiO_2 which is chemically inert, easy to obtain and inexpensive shows high photo activity and

Table 3
The *k* (min^{-1}) of the six pesticides by UV/H_2O_2 treatment at different H_2O_2 dose

Pesticides	H_2O_2 dose (mg/L)				
	2	5	10	15	20
Tebuconazole	0.0249	0.0744	0.0859	0.1368	0.1700
Chloridazon	0.0527	0.1481	0.1586	0.2502	0.3163
Atrazine	0.0399	0.0525	0.0687	0.1028	0.1348
Dinotefuran	0.2900	0.3042	0.3208	0.4213	0.4818
Cyromazine	0.0083	0.0220	0.0288	0.0616	0.0954
Diuron	0.1552	0.1708	0.1735	0.2791	0.3376

Table 2
Molar absorption coefficients (ε) and quantum yields (Φ) of the six pesticides

Pesticides	pH 4		pH 7		pH 10	
	ε (M/cm)	Φ (mol/photon)	ε (M/cm)	Φ (mol/photon)	ε (M/cm)	Φ (mol/photon)
Tebuconazole	139.59	56.04	65.66	132.55	148.41	41.40
Diuron	84.57	1,247.50	45.68	2,482.06	73.09	1,348.17
Dinotefuran	62.14	4,555.96	20.27	11,503.95	49.49	4,202.36
Atrazine	81.61	255.94	50.94	373.07	72.02	321.59
Chloridazon	85.04	72.00	40.26	150.55	64.43	93.12
Cyromazine	58.55	141.66	38.79	203.23	56.50	155.49

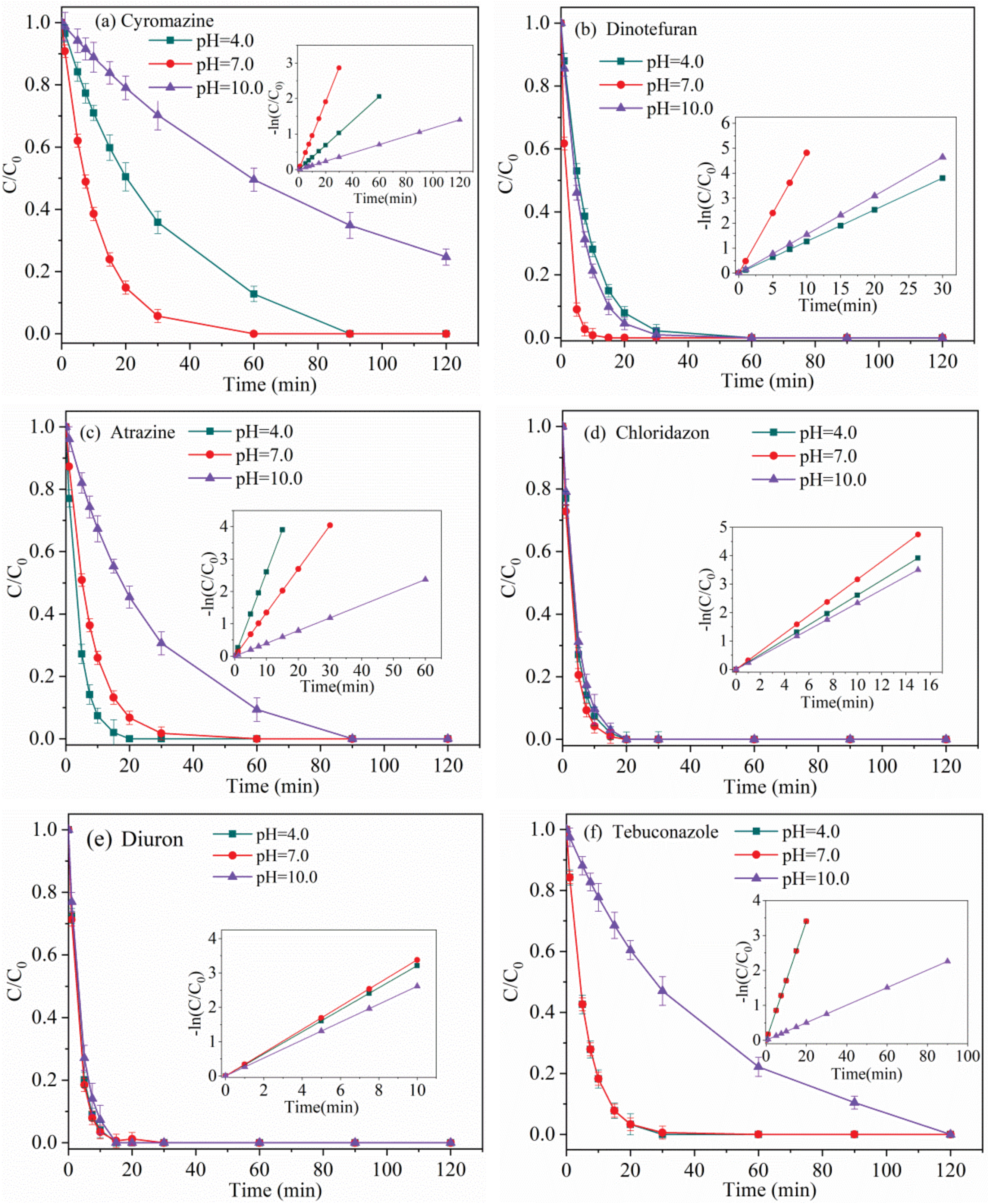

Fig. 3. The removal of six pesticides by UV/H_2O_2 process at different solution pH.

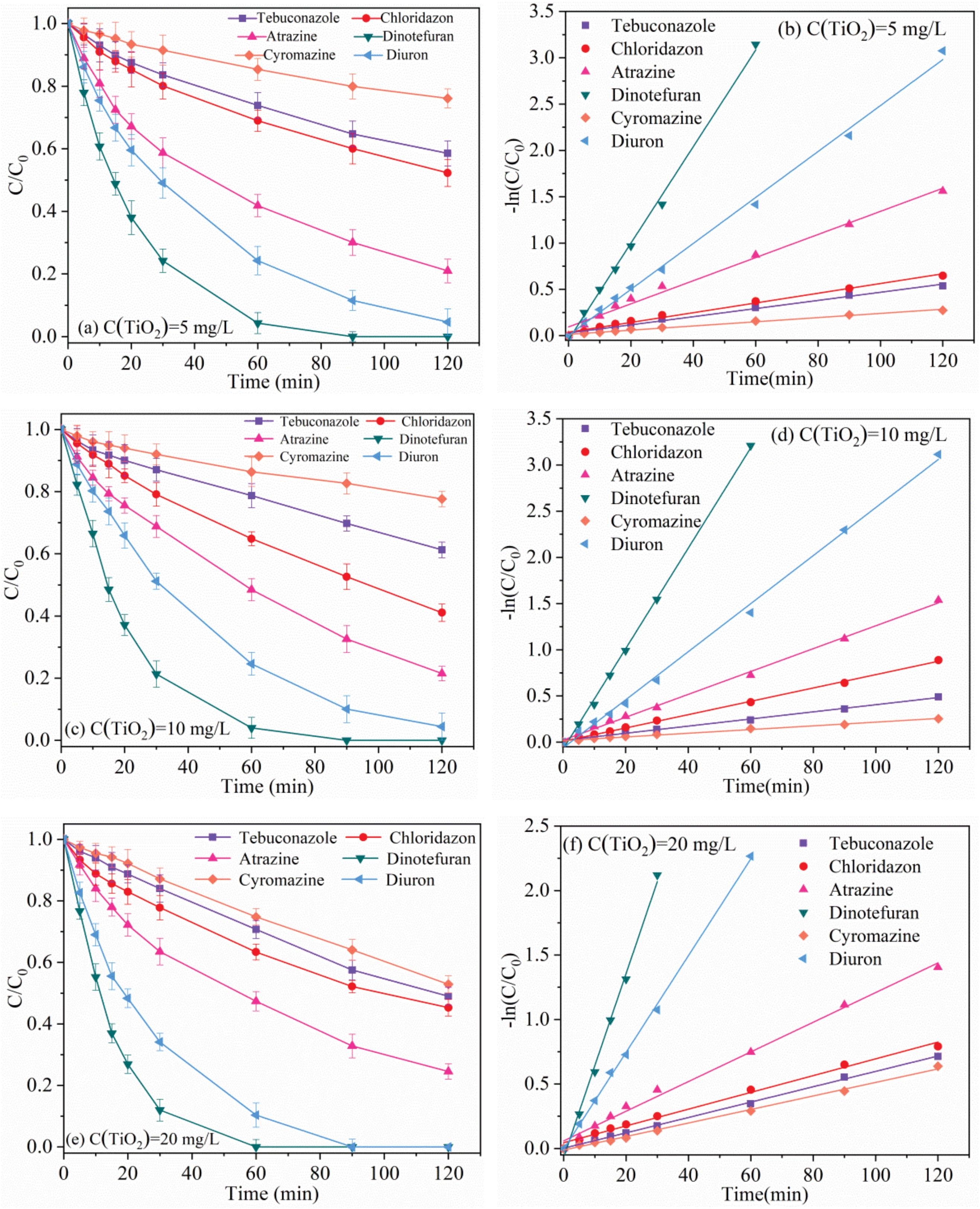

Fig. 4. The removal of six pesticides by UV/TiO$_2$ process at different TiO$_2$ loading: (a, c, e) were the decay curves of the six pesticides and (b, d, f) were the corresponding fitting results.

has been widely applied for the removal of various organic contaminants [31]. The degradation of the six pesticides by UV/TiO_2 treatment was examined by varying the dose of TiO_2 and solution pH, the effect of TiO_2 loading at pH = 7 is illustrated in Fig. 4.

As shown in Fig. 4, dinotefuran was the most vulnerable to UV/TiO_2 process, and exhibited the fastest degradation kinetics in spite of the TiO_2 dose, followed by diuron, atrazine, chloridazon, tebuconazole, and cyromazine. In the tested TiO_2 dose range, the degradation of the dinotefuran, diuron, tebuconazole, and cyromazine increased with the increase in TiO_2 dose. 100% degradation of dinotefuran could be achieved after reaction for 90 min at 5 mg/L TiO_2. The total disappearance of diuron occurred after 90 min at 20 mg/L TiO_2. However, the maximum removal of tebuconazole and cyromazine were only about 51% and 47%, respectively, at the end of the reaction and TiO_2 loading as high as 20 mg/L. The removal efficiency of chloridazon increased first from 48% to 59% with the improvement of TiO_2 dose from 5 to 10 mg/L, then slightly decreased to 55% as TiO_2 loading further increased to 20 mg/L. In comparison, the degradation of atrazine by UV/TiO_2 process was insensitive to TiO_2 dose, 75%~79% of atrazine could be removed after 120 min, longer reaction time would be needed to remove this pesticide completely. It was reported that almost complete atrazine degradation was achieved after reaction for 4 h in UV/TiO_2 process [33]. The degradation of diuron in UV/TiO_2 system was relatively slow compared with that reported in the literature. Malato et al. [35] observed that only 45 min was needed to attain a total disappearance of diuron by UV/TiO_2 treatment.

The k values of the selected pesticides removal by UV/TiO_2 process at different TiO_2 dose were summarized in Table 4.

The incremental number of catalyst particles would result in the increase of catalyst surface area, thus the growth in the number of absorbed photons and contaminating molecules, subsequently the creation of a higher number of active species, and ultimately the improvement of removal efficiency [36]. In consequence, the reaction rate constants k of the studied pesticides increased with TiO_2 loading increment except for atrazine (Table 4). A slight reduction in the degradation rate of atrazine was observed as TiO_2 dose increased. During the UV/TiO_2 treatment, contaminants could be removed by active species produced in UV/TiO_2 process or by direct UV photolysis, it could be speculated that direct photolysis played a key role in the removal of atrazine, when TiO_2 was added, the intensity of incident UV light was attenuated owing to the decreased light penetration and increased light scattering. And this influence would strengthen with the increase in TiO_2 dose. As a result, the degradation rate of atrazine decreased as TiO_2 loading increased.

Table 4
The k (min^{-1}) of the six pesticides by UV/TiO_2 treatment at different TiO_2 dose

Pesticides	TiO_2 dose (mg/L)		
	5	10	20
Tebuconazole	0.0039	0.0044	0.0060
Chloridazon	0.0053	0.0072	0.0065
Atrazine	0.0125	0.0124	0.0115
Dinotefuran	0.0521	0.0544	0.0712
Cyromazine	0.0023	0.0020	0.0052
Diuron	0.0248	0.0260	0.0375

In comparison, UV/TiO_2 was less efficient than UV/H_2O_2 process in the degradation of all six pesticides. At pH = 7, H_2O_2 and TiO_2 dose of 20 mg/L, the k values of chloridazon, tebuconazole, cyromazine, atrazine, diuron, and dinotefuran treated by UV/H_2O_2 were about 49, 28, 18, 12, 9, and 7 times higher than that by UV/TiO_2 process. And the k values of diuron and dinotefuran observed in UV/TiO_2 system was even lower than that in the direct UV photolysis system. This result agreed well with that reported in the literature. Kovacs et al. [37] observed a decrease of diuron degradation rate by UV/TiO_2 treatment compared with direct photolysis. The mechanism of heterogeneous photocatalysis involved in direct photolysis, •OH oxidation, and/or direct electron transfer between the photogenerated positive hole and absorbed organic substance, depending highly on the interaction between contaminant molecules and the TiO_2 surface [37]. Therefore the less efficient degradation of the six pesticides by UV/TiO_2 treatment could be explained as follows: (i) As noted above, the addition of TiO_2 would cause incident light obscured phenomenon and therefore reduce the degradation of those pesticides which were relatively susceptible to photolysis such as diuron and dinotefuran. (ii) The pK_a of the selected pesticides were all below pH 6, and the point of zero charge (PZC) of TiO_2 was reported to be around pH 6 [36], thus the six pesticides and the surface of TiO_2 were all negatively charged at pH = 7, consequently the adsorption of pesticides onto TiO_2 surface and the further oxidation of target contaminants would be hindered owing to the electrostatic repulsion between the negatively charged TiO_2 surface and pesticide species. (iii) The studied pH was close to PZC of TiO_2, thus the photocatalyst particles tended to agglomerate and form large clusters which would diminish the surface area of TiO_2 and the amount of active sites, consequently reducing the photodegradation rate [38]. (iv) There would be competition for the surface of TiO_2 between the studied pesticides. Furthermore, TiO_2 nanoparticles might also compete with pesticides for 254 nm photons, as a result, direct photolysis would be suppressed [39]. (v) The slower removal might be also related to the lower TiO_2 dose applied in the present study compared with that reported in the literature [37].

Solution pH which is correlated with the photocatalyst surface charge, the size of the aggregates formed by TiO_2 particles, the existing species of compounds, the formation and oxidation power of radicals and so on is an important parameter for the photocatalytic degradation of organic compounds [38]. The six pesticides removal under the influence of solution pH was examined at TiO_2 dose of 20 mg/L, the results are given in Fig. 5.

As presented in Fig. 5, the removal of all six pesticides was obviously influenced by solution pH. The highest removal was obtained in acidic conditions for atrazine and

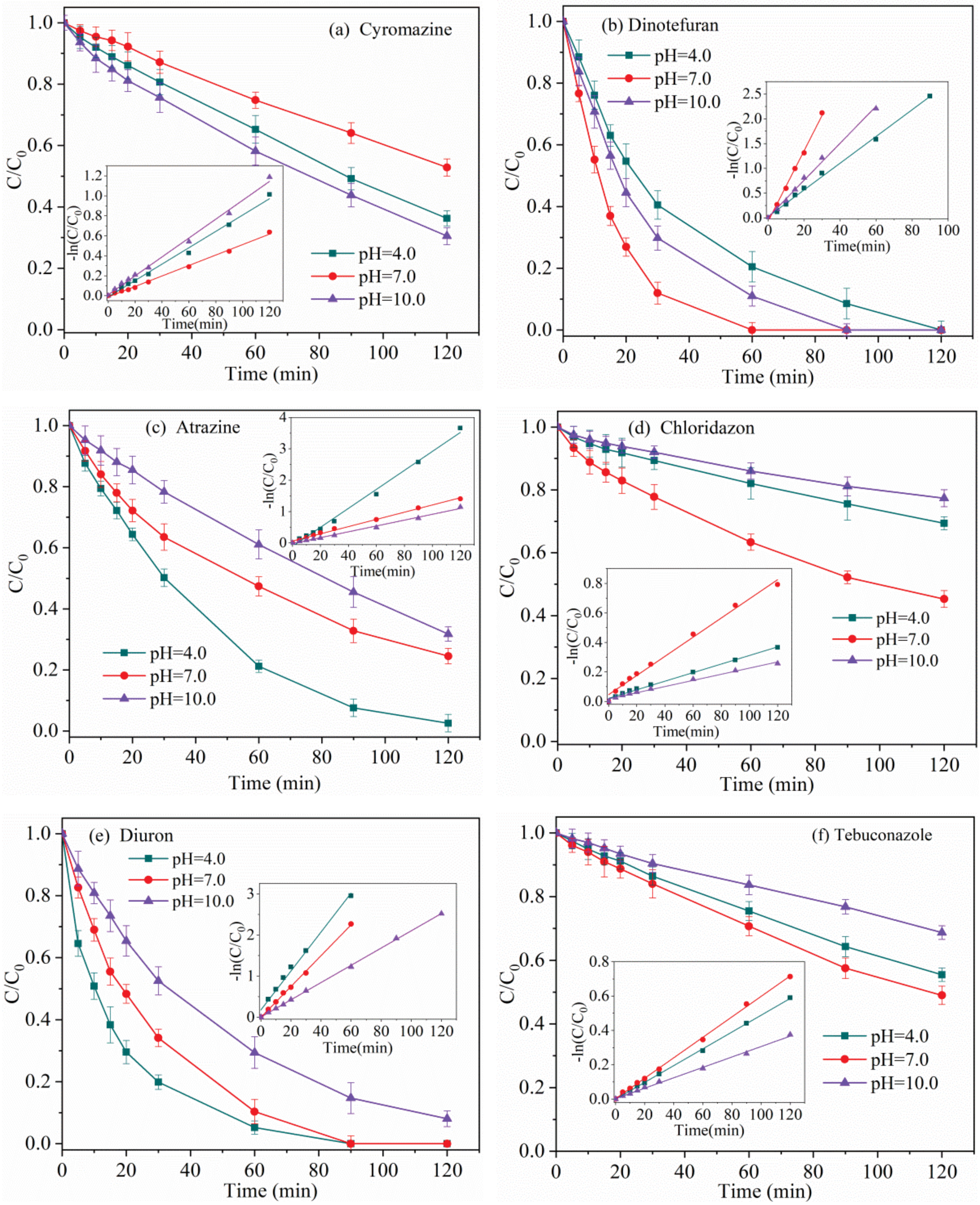

Fig. 5. The removal of six pesticides by UV/TiO$_2$ process at different solution pH.

diuron, neutral conditions for dinotefuran, chloridazon, and tebuconazole, and alkaline conditions for cyromazine. Similar results had been provided by our previous research that the fastest removal of atrazine by UV/TiO_2 treatment was observed in acidic conditions, a significant decrease of degradation occurred as solution pH increased from 4 to 10 [33]. Solution pH exerted a more significant influence in the removal of all six pesticides by UV/TiO_2 compared with UV/H_2O_2 process. This might be ascribed to the fact that the oxidation of target pesticides by heterogeneous UV/TiO_2 treatment involved initially the adsorption of those pollutants onto the surface of catalyst, and this process was highly depended on the characteristic of the adsorbent surface and the species of those pollutants, both the two factors were greatly influenced by solution pH.

3.4. Removal of six pesticides by US

Sonication of water by US (20~500 kHz) through cavitation involves the formation, growth and sudden collapse of micro-bubbles from acoustical wave-induced compression and rarefaction. These cavities implode violently after reaching a critical resonance size and generate transient high temperatures (>5,000 K), high pressures (>1,000 bar), and highly reactive radicals such as $^•OH$. Contaminants could be destructed in the bulk solution or at the interface between bubbles and the liquid phase by various radical reactions and thermal decomposition [10]. In recent years, US treatment has been applied to effectively degrade a wide variety of pollutants in wastewater [40]. The efficacy of US in the degradation of the selected pesticides was examined at different solution pH. The results are shown in Fig. 6.

According to the results, US irradiation was inefficient in the removal of the six pesticides, only 18%, 15%, 7%, 12%, 16%, and 8% of degradation efficiencies could be achieved for cyromazine, dinotefuran, atrazine, chloridazon, diuron, and tebuconazole, respectively, after reaction for 120 min under their optimal pH conditions. The degradation rate of the six pesticides was also extremely low (Table S5). Although US technology had been reported to demonstrate excellent performance in the degradation of organochlorine pesticides like dicofol, organophosphorus pesticides like azinphos-methyl and chlorpyrifos [40,41], it was not the case in the present work. Analogously, Bringas et al. [42] reported a 39% disappearance of diuron concentration by low-frequency US after irradiation time as long as 8 h. Papoutsakis et al. [43] found that only 20% of diuron could be removed even after 300 min by high-frequency US treatment alone.

The treatment efficiency of US was largely determined by the experimental conditions such as the frequency applied in the experiments, the working solution volume coupled with the concentration and nature of pollutants, and so on [31]. The inefficient degradation of the selected pesticides by US treatment in the present study was probably attributed to the factors below. Firstly, the sono-chemical destruction rate of contaminants was frequency-dependent. Ultrasonic frequency could influence the collapse period of cavitations, the collapse occurred more rapidly and consequently more radicals escaped from the cavitational bubble with the increase of frequency [44]. It was verified that the pesticide removal increased as the US frequency increased [40]. The frequency applied in the present study (40 kHz) was much lower than that in the literature (130 kHz, 1.7 MHz) [40,45,46]. Indeed, early research indicated that atrazine degradation proceeded only up to 20% after US irradiation for 6 h at 20 kHz [26]. US treatment of atrazine aqueous solutions at 20 kHz was much less efficient than at 500 kHz due to the lower production of H_2O_2 and $^•OH$ under cavitation. And low frequency US (i.e., at 20 kHz) could not be envisaged as a powerful degradation technique for atrazine in water [47]. Secondly, it was concluded that the degradation of pesticides decreased as the solution volume increased, and reacting solution volume (250 mL) used in the present study was several times greater than that applied in the literature (50 mL) [46]. Thirdly, the low initial concentrations of target contaminants would lead to the partial recombination of generated $^•OH$ to produce H_2O_2, thus reduced the amount of $^•OH$ and finally the efficiency of oxidation [48]. Finally, it was believed that contaminants in molecular species were easier to degrade by ultrasonic because that the protonated neutral states were prone to diffuse to gas–liquid interface and into cavitation bubbles to realize pyrolysis and oxidation by free radicals, while the deprotonated states, as ion form of contaminants, were harder to accumulate inside of cavitation bubbles or gas–liquid interface [49]. Thus the inefficient removal of the studied pesticides would also be partially ascribed to the fact that almost the six pesticides were all in their deprotonated species in the experimental pH.

The oxidation mechanism of targeted pollutants by US treatment depended largely on their characteristics, like solubility, hydrophilcity/hydrophobicity, volatility, and so on. The removal of atrazine was reported to be mainly radicals-involved oxidation, the pyrolysis in the vapor phase of cavitation bubbles was expected to be negligible because of the rather low volatility of atrazine in water [26]. As the $^•OH$ has a short lifetime, hydrophobic compounds like atrazine, diuron and tebuconazole were expected to be preferentially oxidized near the bubble/bulk interface due to their close proximity to the cavitation bubbles [43].

3.5. Removal of six pesticides by US/TiO_2 process

It was reported that catalytic processes involving TiO_2 assisted by US (US/TiO_2) was promising option for the destruction of resistant organic matter [13]. The removal of the six pesticides by US/TiO_2 treatment was examined at different TiO_2 loadings and solution pH = 7, the results are illustrated in Fig. 7.

Compared with US irradiation alone, a certain degree of enhancement in the degradation efficiency could be observed when treated by US/TiO_2 process. The removal of all six pesticides increased with TiO_2 loading except for tebuconazole, whose removal was almost TiO_2 load-independent. The maximum removal of the six pesticides was all achieved at TiO_2 dose of 20 mg/L, with a value of about 18% for tebuconazole, 22% for diuron, 52% for chloridazon, 23% for atrazine, 43% for dinotefuran, and 28% for cyromazine, respectively. The enhanced degradation of pesticides by US/TiO_2 could be attributed to the fact that the microbubbles tended to break up into

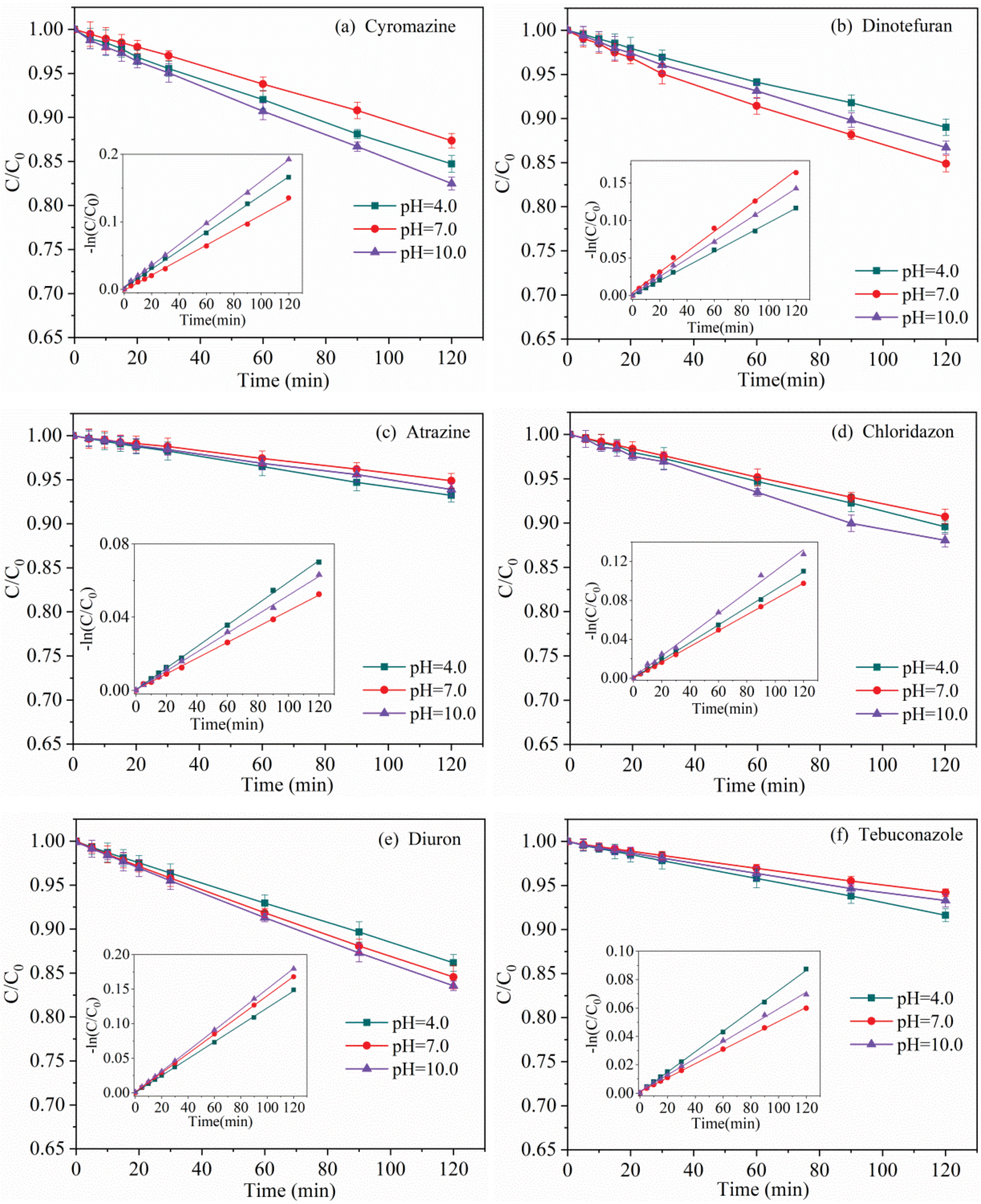

Fig. 6. The removal of six pesticides by ultrasound at different solution pH.

smaller ones in the presence of TiO_2 particles, consequently, the total number of regions of high temperature and pressure increased, which would result in the increase in the number of $^{\bullet}OH$ produced by the system and ultimately more efficient oxidation of the six pesticides [50]. Although the pesticide removal was enhanced compared to US treatment alone, the performance of US/TiO_2 in the degradation of the selected pesticides was still poor. The degradation rate constants of the six pesticides are shown in Table 5.

Table 5
The k (min^{-1}) of the six pesticides by US/TiO_2 treatment at different TiO_2 dose

TiO_2 dose (mg/L)	Pesticides					
	Tebuconazole	Chloridazon	Atrazine	Dinotefuran	Cyromazine	Diuron
5	0.0058	0.0100	0.0023	0.0171	0.0035	0.0015
	0.0007	0.0016	0.0010	0.0011	0.0009	0.0005
10	0.0027	0.0138	0.0067	0.0204	0.0031	0.0045
	0.0011	0.0025	0.0009	0.0017	0.0012	0.0011
20	0.0035	0.0259	0.0075	0.0193	0.0092	0.0053
	0.0013	0.0022	0.0011	0.0017	0.0014	0.0014

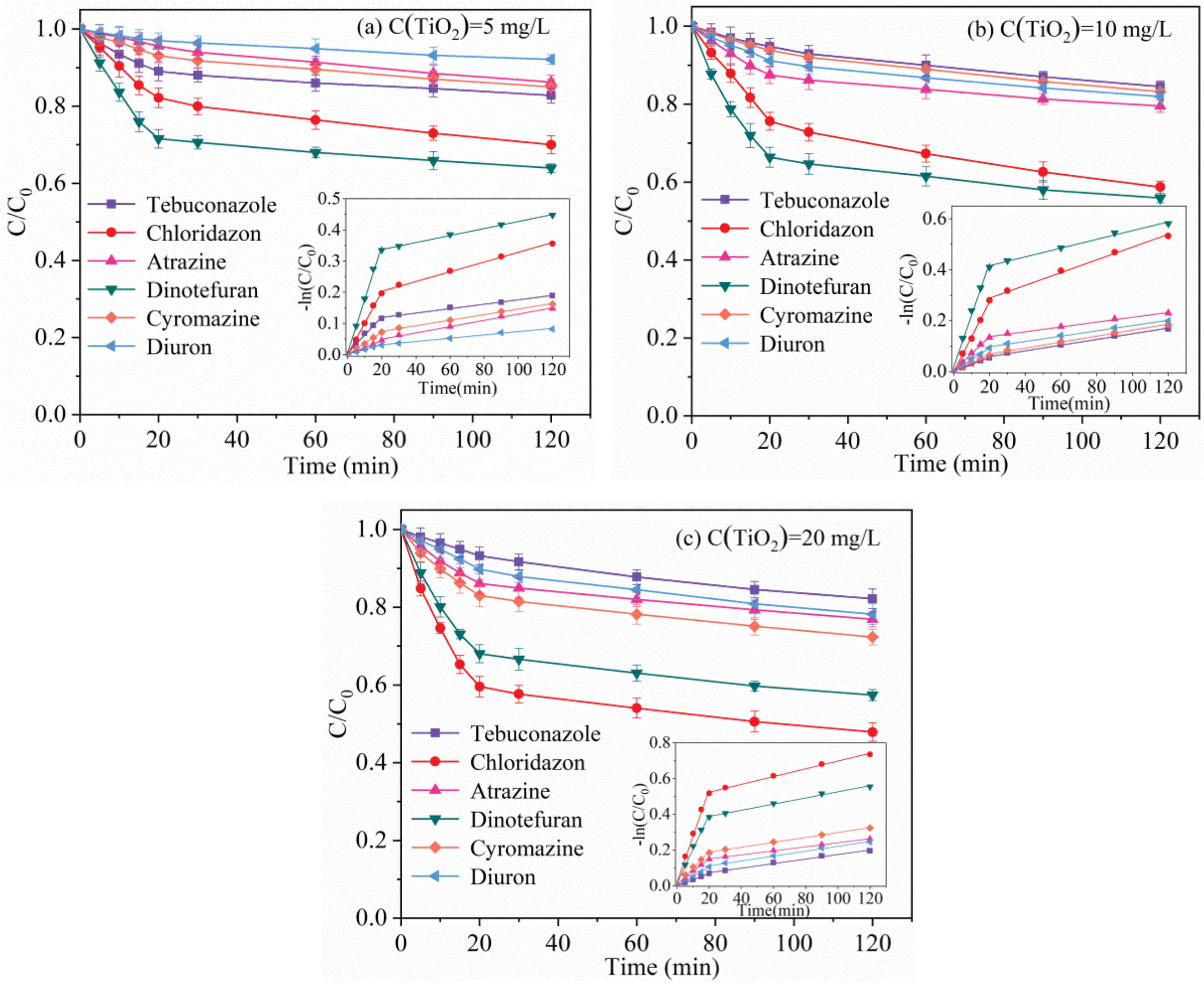

Fig. 7. The degradation of six pesticides by US/TiO_2 process as function of TiO_2 loadings.

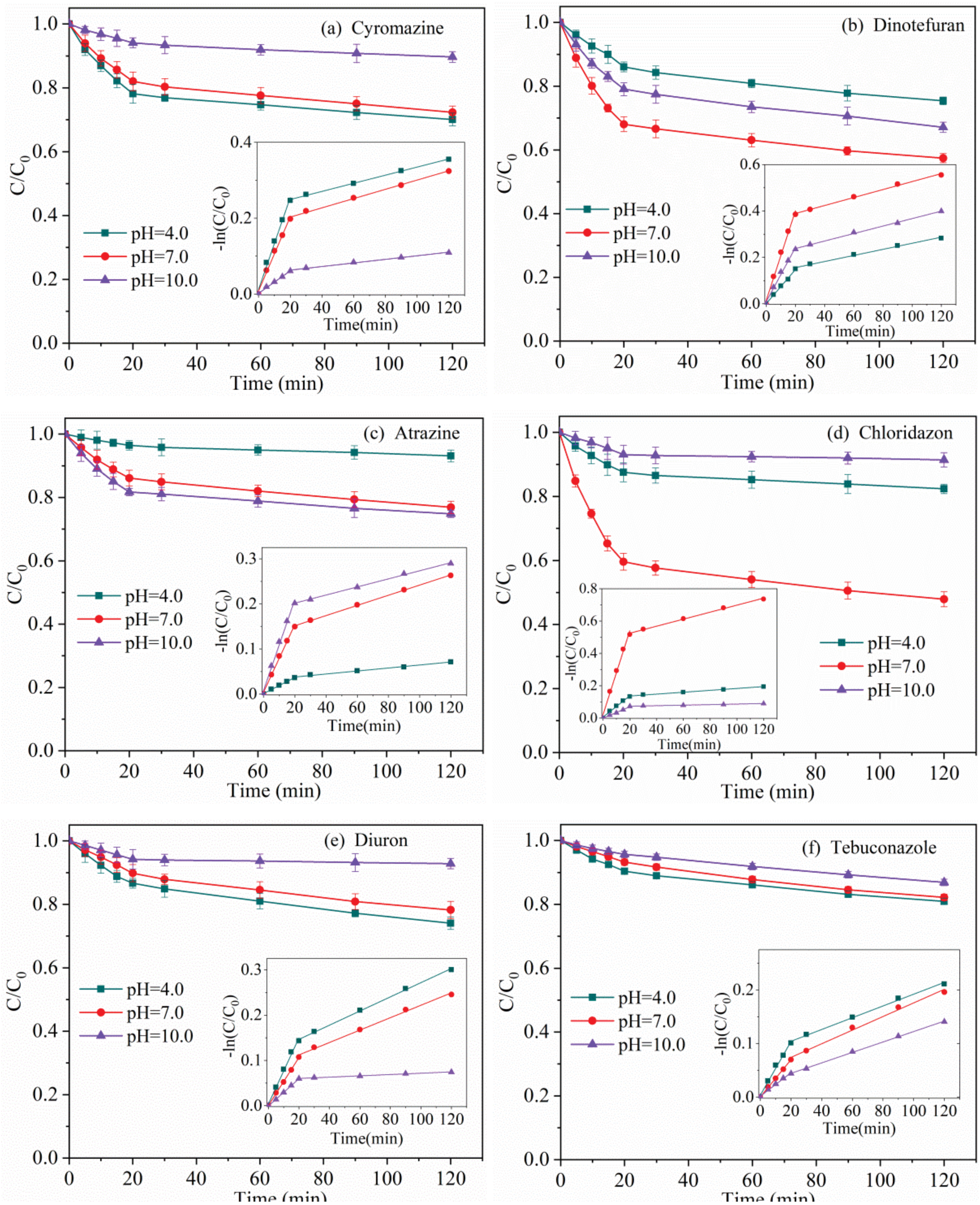

Fig. 8. The decay curves of six pesticides during US/TiO_2 process at different solution pH.

All the six pesticides initially experienced a rapid degradation phase (the first stage), then the degradation rate gradually reduced after an extended period (approximately 20 min) of irradiation (the second-stage). The retardation in the degradation rate was probably ascribed to the combination of the following factors: (i) the generation of intermediates in the solution competed for the oxidants with parent pesticides, which would retard the further degradation of those pesticides. In theory, such an effect would become more and more dominant as the intermediates accumulated to higher levels [51]; (ii) the low concentration of remaining degradable compounds would also lead to the low kinetic in the second-stage [24].

The degradation of the six pesticides by US/TiO_2 process under the influence of solution pH is shown in Fig. 8.

As shown in Fig. 8, the degradation of all the selected pesticides was pH-dependent, the impact of pH followed the order below: chloridazon > cyromazine ≈ atrazine ≈ dinotefuran ≈ diuron > tebuconazole. The maximum degradation ratio of chloridazon was obtained at the neutral conditions with a value of 52% after reaction for 120 min, while the removal efficiencies were only 18% and 9% in acidic and alkaline conditions, respectively. The highest removal was observed in acidic conditions for cyromazine (30%), diuron (26%), and tebuconazole (19%), at the neutral conditions for dinotefuran (43%), at the alkaline conditions for atrazine (25%). All the selected pesticides failed to disappear completely within the reaction time, further indicating the poor performance of US/TiO_2 process in the degradation of the six pesticides.

4. Comparison of various oxidation methods and conclusions

The comparison in the degradation rate constants k of the six organic pesticides by direct UV photolysis and various AOPs is shown in Table 1. In summary, the six pesticides all exhibited the fastest decay rates when treated by UV/H_2O_2 process compared with the other methods. The degradations of dinotefuran and diuron by direct UV photolysis were faster than by UV/TiO_2, but the other four pesticides presented similar removal kinetics in the two process. The decay of the six pesticides by US/TiO_2 treatment was generally slower than that by UV-based AOPs and direct UV photolysis. The degradations of those pesticides by US were slowest. In conclusion, UV/H_2O_2 would be an effective method for the removal of the six pesticides among the five processes.

For UV/H_2O_2 treatment, a noticeable enhancement of the degradation rate was observed as H_2O_2 dose increased. All the selected pesticides could be removed completely within 60 min when H_2O_2 dose was greater than 15 mg/L at pH = 7. Dinotefuran was the most susceptible to UV/H_2O_2 process, followed by diuron, chloridazon, tebuconazole, atrazine, and cyromazine. Solution pH influenced the removal of cyromazine, atrazine, tebuconazole, and dinotefuran by UV/H_2O_2 to different extent, but the degradation of chloridazon and diuron were almost pH-independent.

Direct UV photolysis performed well in the degradation of dinotefuran, a 100% disappearance of this pesticide occurred within 30 min, followed by diuron and atrazine. But cyromazine, tebuconazole, and chloridazon were found to relatively resistant to this process, less than 40% of the three pesticides were removed after irradiation for 120 min. When treated by UV/TiO_2 process, dinotefuran, diuron, and atrazine could be totally removed after reaction for 60, 90, and about 120 min under their optimum conditions, respectively, while the other three pesticides failed to decay thoroughly (around 51%~70%) within the reaction time. US treatment behaved poorly in the removal of the six pesticides, only less than 20% degradation of those pesticides was observed. US/TiO_2 process could enhance pesticides removal to some extent, but the removal efficiencies of the six pesticides were still relatively low (19%~52%), probably mainly owing to the low irradiation frequency and the large volume of reacting solution adopted in the present work.

Appendix A. Supplementary information

Supplementary texts, figures and tables are shown in supplementary information.

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Supporting information

S1. Parameters information of UPLC and MS for quantitative analysis of the six pesticides

The flow rate of the mobile phase, which was composed of MeOH (A) and UPW (B), was 0.2 mL/min. The separation started with 10% A for 0.50 min, then increased to 70% at 9.00 min, and further increased to 100% at 11.00 min and maintained for 0.50 min. Finally it was reduced back to 10% at 13.00 min and maintained 3 min for equilibrium before the next injection. The column temperature and sample room temperature were maintained at 35°C and 25°C, respectively. The full loop injection volume of the autosampler was 10 µL. After each injection, the sample injection needles were flushed automatically to avoid the disturbance between the injections.

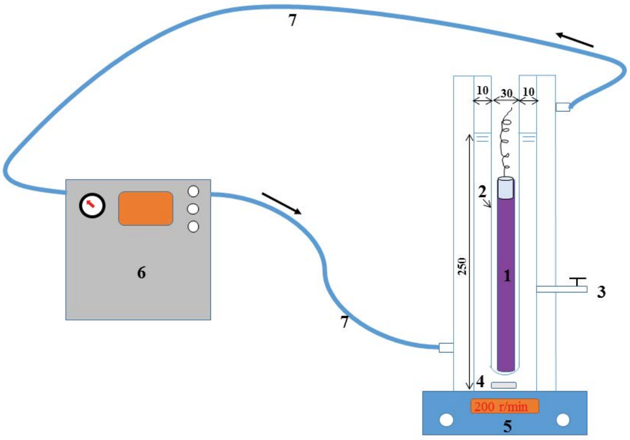


Fig. S1. Schematic diagram of photochemical reactor: (1) low-pressure mercury UV lamp; (2) quartz glass well; (3) sampling point; (4) magnetic stirrer; (5) magnetic stirrer apparatus; (6) thermostatic water recirculation system; (7) silicone tube. All dimensions are in millimeter (mm).

Detection was carried out using a TQD three quadrupole mass spectrometer with electrospray ionization (ESI) in positive multiple-reaction monitoring (MRM) mode (Waters Corporation, Milford, MA, USA). The desolvation temperature was set at 350°C and the source temperature at 110°C. The capillary voltage and cone voltage were set at 2.5 kV and 20 V, respectively. The desolvation gas and cone gas

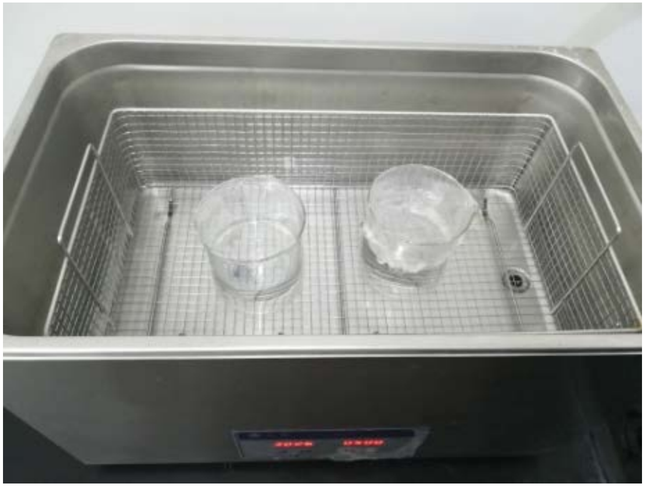


Fig. S2. Photograph of the ultrasound reactor used for the degradation of pesticides.

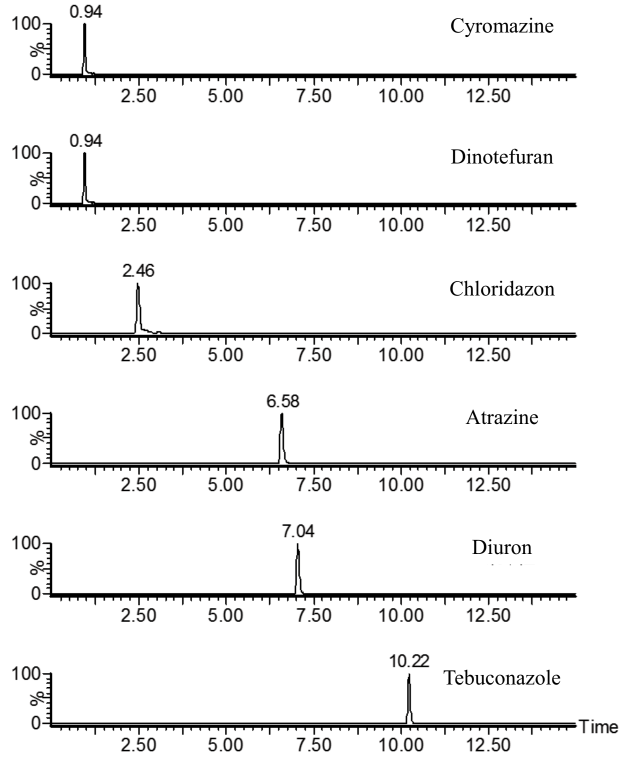


Fig. S3. UPLC-MS/MS chromatograms of extracted quantitative identification ions of the six pesticides in MRM mode obtained with mixed standard solution at 10 µg/L for the individual analytes.

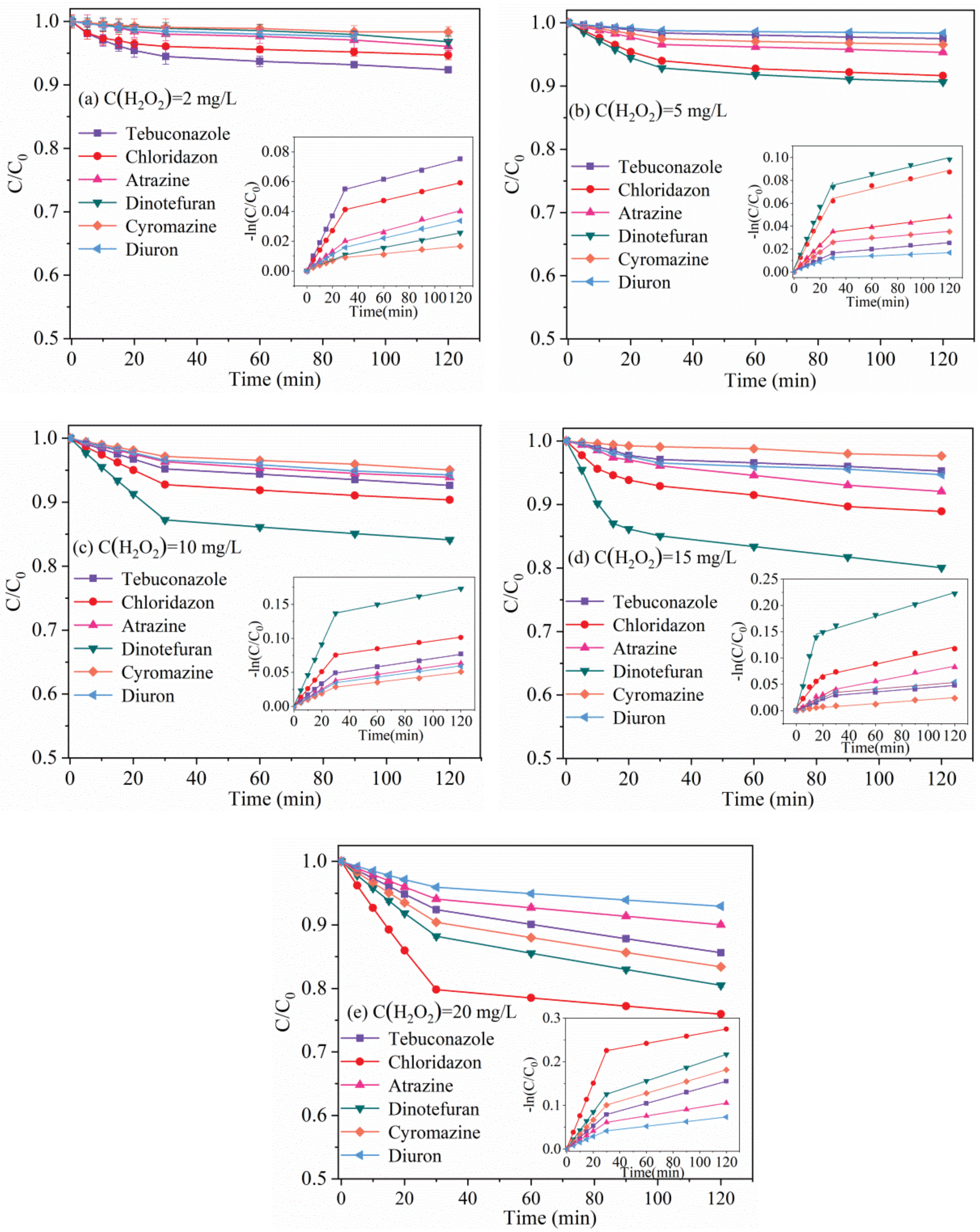


Fig. S4. Effect of H_2O_2 concentration on the removal of pesticides by H_2O_2 oxidation.

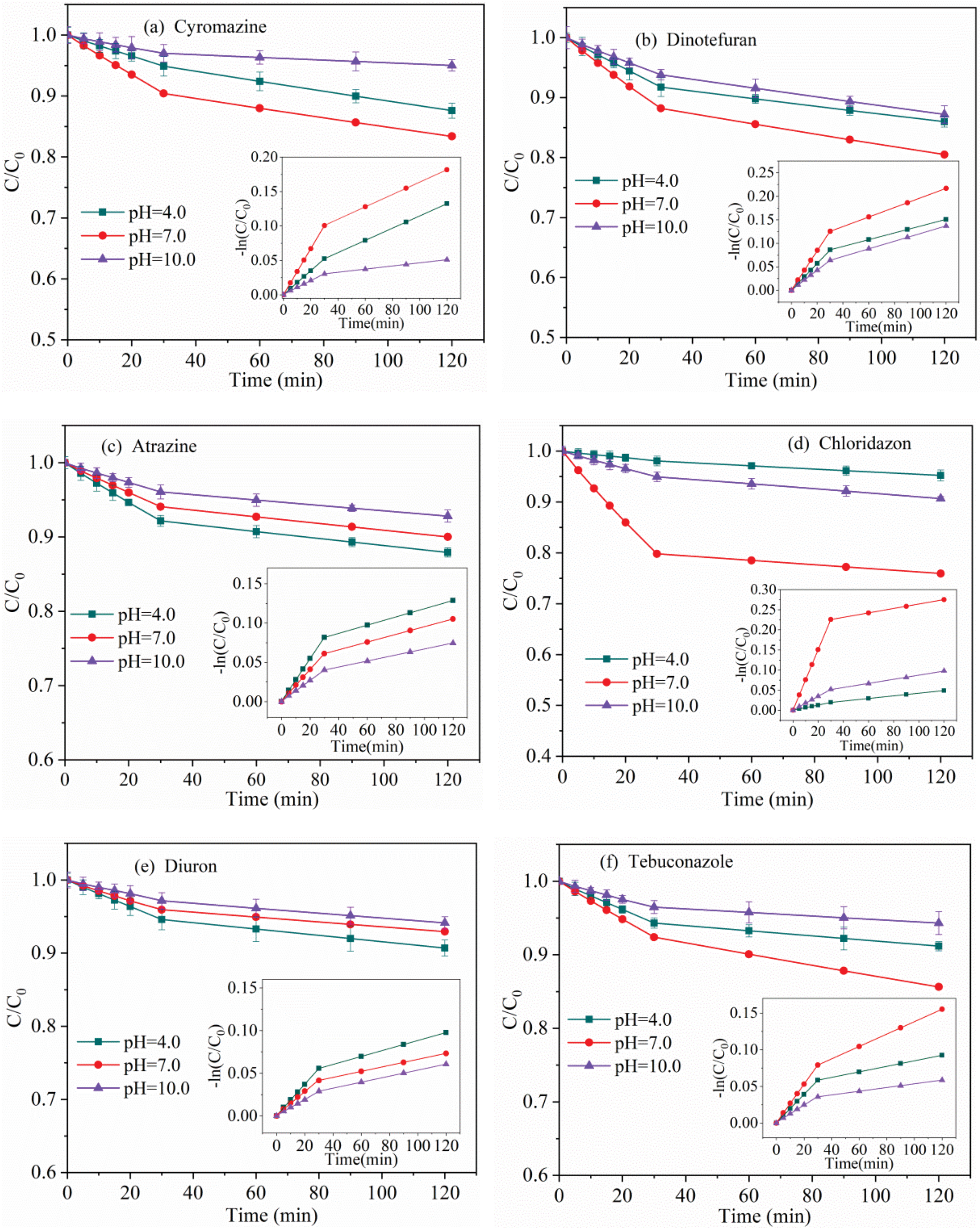
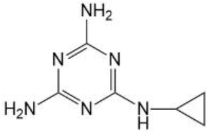
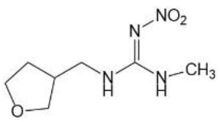
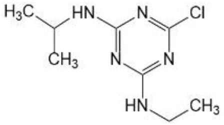
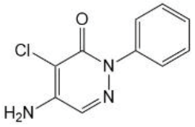
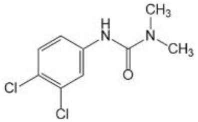
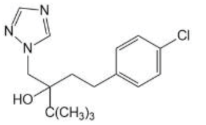


Fig. S5. Effect of solution pH on the removal of pesticides by H_2O_2 oxidation.

Table S1
Basic information of the six pesticides

Pesticides	Molecular formula	MW[a] (g/mol)	pK$_a$	Water solubility (mg/L at 20°C)	logK_{ow}[b]	Classification	CAS number	Molecular structure
Cyromazine	$C_6H_{10}N_6$	166.2	5.22	11,000	–0.2	Triazines	66215-27-8	
Dinotefuran	$C_7H_{14}N_4O_3$	202.2	3.24	54,300	–	Neonicotinoids	165252-70-0	
Atrazine	$C_8H_{14}ClN_5$	215.7	1.7	30	2.2–2.8	Triazines	1912-24-9	
Chloridazon	$C_{10}H_8ClN_3O$	221.0	3.38	340	0.8	Organochlorines	1698-60-8	
Diuron	$C_9H_{10}C_{12}N_2O$	233.1	–1~–2	42	–	Phenylureas	330-54-1	
Tebuconazole	$C_{16}H_{22}ClN_3O$	307.8	5.0	36	3.7	Triazoles	107534-96-3	

[a]MW: Molecular weight;
[b]logK_{ow}: Octanol/water partition coefficient;
–: No exact data.

Table S2
Retention time, transition ions, collision energy for the six pesticides

Analyst	Retention time (min)	Precursor ion (m/z)	Product ion (m/z)			
			Quantitative ion (m/z)	Collision energy (eV)	Qualitative ion (m/z)	Collision energy (eV)
Cyromazine	0.93	167.06	84.99	17	125.06	16
Dinotefuran	0.94	203.07	129.06	10	113.06	8
Chloridazon	2.47	222.03	104.05	22	92.05	26
Atrazine	6.58	215.96	173.92	16	95.78	18
Diuron	7.05	231.01	185.98	20	150.13	23
Tebuconazole	10.24	308.03	70.02	20	125.03	34

Table S3
The *k* (min^{-1}) of the six pesticides by H_2O_2 treatment at different H_2O_2 dose

Pesticides	H_2O_2 dose (mg/L)				
	2	5	10	15	20
Tebuconazole	0.00056	0.00103	0.00163	0.00103	0.00263
	0.00010	0.00082	0.00031	0.00021	0.00085
Chloridazon	0.00209	0.00159	0.00250	0.00319	0.00751
	0.00027	0.00050	0.00029	0.00054	0.00055
Atrazine	0.00115	0.00099	0.00124	0.00138	0.00202
	0.00014	0.00015	0.00029	0.00048	0.00049
Dinotefuran	0.00251	0.00170	0.00454	0.00949	0.00418
	0.00027	0.00052	0.00040	0.00075	0.00102
Cyromazine	0.00084	0.00061	0.00095	0.00019	0.00334
	0.00010	0.00012	0.00024		0.00090
Diuron	0.00047	0.00052	0.00115	0.00121	0.00138
	0.00040	0.00013	0.00027	0.00021	0.00035

Table S4
The *k* (min^{-1}) of the six pesticides by H_2O_2 treatment at different solution pH

Pesticides	4	7	10
Tebuconazole	0.00194	0.00263	0.00119
	0.00038	0.00085	0.00025
Chloridazon	0.00064	0.00751	0.00172
	0.00033	0.00055	0.00051
Atrazine	0.00271	0.00202	0.00133
	0.00052	0.00049	0.00031
Dinotefuran	0.00286	0.00418	0.00212
	0.00072	0.00102	0.00081
Cyromazine	0.00174	0.00334	0.00101
	0.00089	0.00090	0.00023
Diuron	0.00184	0.00138	0.00095
	0.00047	0.00035	0.00035

were nitrogen (99.999%) with flow rates of 500 and 30 L/h, respectively. The collision gas was argon (99.999%) with a flow rate of 0.12 mL/min. Masslynx 4.1 software (Waters Corporation, Milford, MA, USA) was used for data acquisition and processing.

The six pesticides were fragmented using collision induced dissociation (CID) with settings shown in Table S2. Each of those analytes was quantified by MRM using the protonated molecular ion as its precursor. The most abundant MRM transition was used for quantitation with a second

Table S5
The k (min^{-1}) of the six pesticides by US treatment

Solution pH	Pesticides					
	Tebuconazole	Chloridazon	Atrazine	Dinotefuran	Cyromazine	Diuron
4	0.0007	0.0009	0.0006	0.0010	0.0014	0.0012
7	0.0005	0.0008	0.0004	0.0014	0.0011	0.0014
10	0.0006	0.0011	0.0005	0.0012	0.0016	0.0015

transition used for confirmation. The extracted ion chromatograms (EICs) of the quantitative ion of the six analytes in MRM mode are shown in Fig. S3.

S2. Calculation method of quantum yields

The quantum yields (Φ (mol/photon)) of the selected pesticides degradation by direct UV photolysis was calculated according to the following equation [S1]:

$$\Phi = \frac{10 \cdot U_\lambda \cdot k_{\text{obs}}}{\varepsilon \cdot \ln(10)} \tag{S1}$$

where Φ (mol/photon) is the quantum yields, k_{obs} (min^{-1}) is the pseudo-first-order rate constant, U_λ (J/Einstein) is the energy of 1 molar photo quantum at wavelength λ, and the value of U_λ at 254 nm was equal to 471,528 J/Einstein (Bolton and Stefan [S1]), ε (M/cm) was the molar adsorption coefficients at wavelength λ and could be determined by Berr–Lambert's law as expressed in Eq. (S2).

$$\varepsilon = \frac{A}{l \cdot c} \tag{S2}$$

where A is the absorbance of the solution, l (cm) is the length of the cuvette and is equal to 1 cm in the present study, c (mol/L) is the molar concentration of pesticides.

Reference

[S1] J.R. Bolton, M.I. Stefan, Fundamental photochemical approach to the concepts of fluence (UV dose) and electrical energy efficiency in photochemical degradation reactions, Res. Chem. Interm., 28 (2002) 857–870.