



Diazinon and MCPA photo-reduction with sulfite excitation under UV irradiation and reducing agents' generation

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ABSTRACT

Diazinon (DIZ) and 4-Chloro-2-methylphenoxyacetic acid (MCPA) herbicide and widely used in agricultural lands. Present study investigates diazinon and 4-chloro-2-methylphenoxyacetic acid photo-reduction via UV/Sulfite (US) in as Advanced Reduction Processes (ARP). The ideal pH was Molar ratio of sulfite: DIZ or MCPA 1:1 and, 20 min reaction time, and pH 9, in which about 100 % reduction of DIZ and MCPA with a concentration of 10 mg L⁻¹ was achieved and the optimal conditions were considered. Kinetic investigation increasing DIZ and MCPA concentration from 5 to 20 mgL⁻¹, k_{obs} increase about from 0.151 to 0.234 for DIZ and from 0.231 to 0.589 min⁻¹. Also, reaction rate (r_{obs}) increases about from 0.755 to 4.68 for DIZ and from 1.155 to 11.78 mg L⁻¹.min. The amount of energy consumption in DIZ solution increased from 5 to 20, respectively, from 0.73 to 2.37, and in the reduction of MCPA from 0.47 to 1.49 kWh per cubic meter. According to experiments performed in 30 min with the US process, COD levels were reduced by about 46 % of both pollutants. It is important to note that the BOD/COD ratio rose from about 0.20 to 0.48 after 30 min. Since the index of biodegradability has grown high, it can be concluded that non-biodegradable COD (NBDCOD) convert to biodegradable COD (BDCOD) and toxicity is lower than of before of treatment. This study has been very suggesting that the UV/sulfite method produces effluent with a non-toxic and ecologically beneficial manner by biological treatment or discharge directly in environment.

1. Introduction

Diazinon (DIZ) and 4-Chloro-2-methylphenoxyacetic acid (MCPA) are herbicides and widely used in agricultural lands. Diazinon (DIZ) is a component of phosphorus toxins and an insecticide, and is widely used to kill flies and mites, especially Toulouse mites. This insecticide is also absorbed through the skin of the body, so contact with the skin should be avoided [1,2]. This insecticide can be used successfully to control pests that live inside plant tissues (minnows and stem eaters) by having the ability to penetrate the wax layers of plant tissues [3,4]. In recent years, DIZ is one of the most widely used organophosphate pesticides, which plays an important role in chemical pest control by controlling sucking pests in orchards and farms [5,6]. In our country, more than 3 million liters of DIZ are consumed annually. DIZ has a long-lasting effect due to its impact effect [7]. Also, diazinon and herbicide

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2-methyl-4-chlorophenoxyacetic acid pesticide are in the 2nd category of the World Health Organization (WHO) [8,9]. The Environmental Protection Agency (EPA) has determined the amount of DIZ in drinking water to be equal to $9 \times 10^{-6} \text{ mg L}^{-1}$ [10,11]. MCPA is a broad-leaved, used in agricultural products such as cotton, tobacco and sugarcane [12]. Also, EPA reports the maximum acceptable concentration in drinking water for MCPA toxin $0.1 \text{ } \mu\text{g L}^{-1}$. There are several methods for removal of organic and inorganic contaminants such as precipitation [13], electrochemical [14], hydrogels [15,16], adsorption [17,18], advanced oxidation processes [13, 19,20], advanced reduction processes [21–23], and Ozon/H₂O₂ [24,25] have been performed [26]. For persistent organic pollutants (POPs) removal and to enhance treatment, Advanced Oxidation and Reduction processes are effective methods [27,28]. In general, the kinetics of the oxidation and reduction reaction to ability of a process is determined by the removal of the target contamination [29]. Some anions can generate reducing species when excitation. Sulfite is a one of most applied anions to generate reducing species under UV irradiation [30,31]. Great UV absorption spectrum (ϵ) $220 \text{ M}^{-1} \text{ cm}^{-1}$ (and the $e_{\text{aq}}^{\bullet-}$ production per photon) 0.286 mol E^{-1} (of sulfite ions at 253.7 nm wavelength approved at many researches [21,30,31]). The benefits of using sulfite anion as a cutting-edge reduction technique include the production of reactive species, affordability, non-toxicity. Herein, the main purposes of this paper were to (1) investigate the elimination of contaminants by the UV/Sulfite system under UV irradiation; (2) Operational parameters effects; (3) examine the kinetic of contaminants oxidation and contaminants reduction; and (4) US-based MCPA and DIZ mineralization and biodegradability.

2. Experimental

2.1. Reactor configuration

A pilot with quartz-coated UV lamp (power: 16 W, $\lambda = 254 \text{ nm}$) is placed in the center of the glass cylinder. The distance between the quartz surface and the glass cylinder was considered to be 1 cm. The reason for this short distance is the better effect of UV rays on sulfite and reducing species generation. Also, due to the production of heat, the reactor is cooled by circulating water around the glass cylinder to avoid the effect of excess heat on the reaction.

2.2. Analytical methods

MCPA concentration measured by high-performance liquid chromatograph A CECILCE-4100 with UV detector (CE-4900) and C18 column. Also, the mobile phase was distilled water with HPLC grade Contains 0.1 % acetic acid (50%) and acetonitrile (50%).

The following equation was used to calculate the MCPA photo-reduction efficiency [32]:

$$\text{Contaminants photo - removal} = \frac{C_0 - C_t}{C_0} \quad (1)$$

2.3. Kinetic model and energy consumption estimate

The Pseudo-first-order (PFO) model was used to explore the kinetic model of pollutant photo-reduction according to Equation (2)-3 [33].

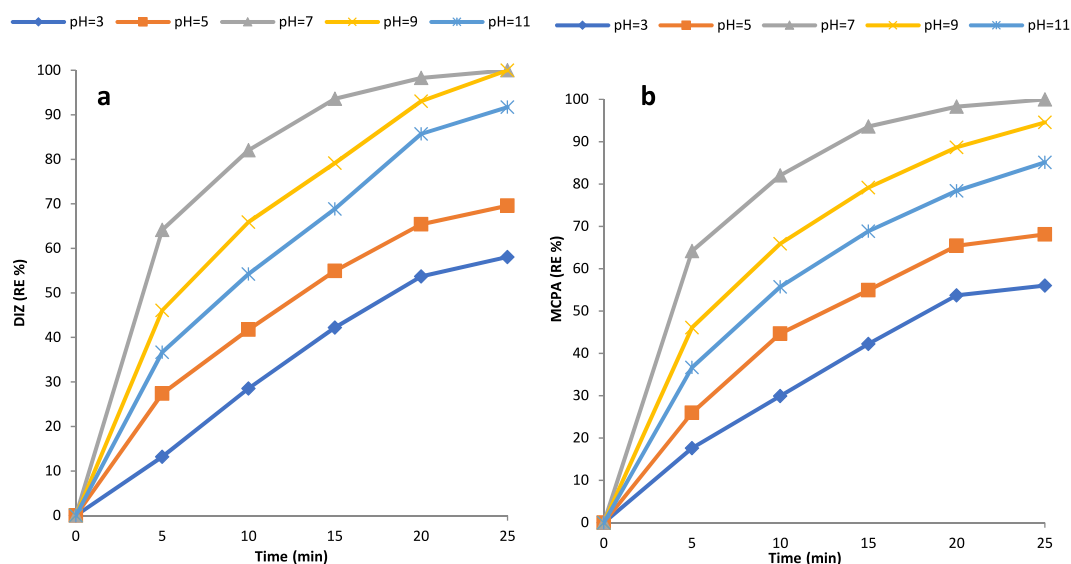


Fig. 1. Effect of pH on a) DIZ and b) MCPA reduction by UV/SO₃²⁻ (diazinon concentration = 10 mg l⁻¹).

$$\ln \frac{C_t}{C_0} = -K_{obs} t \quad (2)$$

$$r_{obs} = -k_{obs} C \quad (3)$$

The Electrical Energy per order (E_{EO}) parameter introduced by The International Union of Pure and Applied Chemistry (IUPAC) [27].

$$IUPAC E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log \frac{C_i}{C_f}} \quad (4)$$

Also, energy consumption can be evaluated with the E_{EO} kinetic method [28,34].

$$Kinetic E_{EOk} = \frac{P \times 38.4}{V \times K_{obs}} \quad (5)$$

3. Results and discussion

3.1. The effect of pH on DIZ and MCPA photo-reduction

The removal efficiency of DIZ and MCPA increased with rising pH, as shown in Fig. 1, and eventually reached to 100 % at pH 9. Also, by increasing the pH from 3 to 9 in 25 min, DIZ (Fig. 2a) removal efficiency rises from 68.55 to 100 % and the removal efficiency of MCPA (Fig. 2b) from 52 to 100 %; But when the pH goes from 9 to 11, the removal efficiency decreases slightly. At acidic pH, HSO_3^- is weaker species than e_{aq}^- and appear to be in charge of the effective decomposition of pollutants under acidic conditions. Nearly all sulfur species are present as SO_3^{2-} at higher pH, indicating that the reducing radicals e_{aq}^- and $\text{SO}_4^{\bullet-}$ are more common in alkaline environments. Therefore, at the pH of the neutral solution, all reducing species are present and improve further reduction of the substance [35].

In a study by Yu et al., In 2021 on the removal of Carbinamine using UV/Sulfite process, by raising the pH from 5.0 to 8.2 over the course of 40 min, a significant increase in reduction efficiency was discovered due to better e_{aq}^- formation. However, at the same time the reaction was stabilized by increasing the pH from 8.2 to 11 reduction efficiencies of about 99.7 %. They concluded that e_{aq}^- and $\text{SO}_3^{\bullet-}$ are mainly produced in this pH range and are responsible for the breakdown of carbamazepine [36].

3.2. Sulfite/pollutants molar ratio

In Fig. 2, the effect of different sulfite molar ratios on the removal efficiency of DIZ (Fig. 2a) and MCPA (Fig. 2b) using UV/ SO_3^- process, considering the concentration of 10 mg l⁻¹ diazinon, pH 9 was investigated and it was found that in a molar ratio of 1: 1 (Sulfite/pollutant) had the highest efficiency, about 100 % was obtained in 15 min. The results showed that the increase in efficiency is highly dependent on the ratio that is proportional to the bonds in the diazinon molecule and varies depending on the type of contaminant. In 2018, Yu et al. discovered that the constant rate of reduction of 2,4-dichlorophenol by the UV/Sulfite process

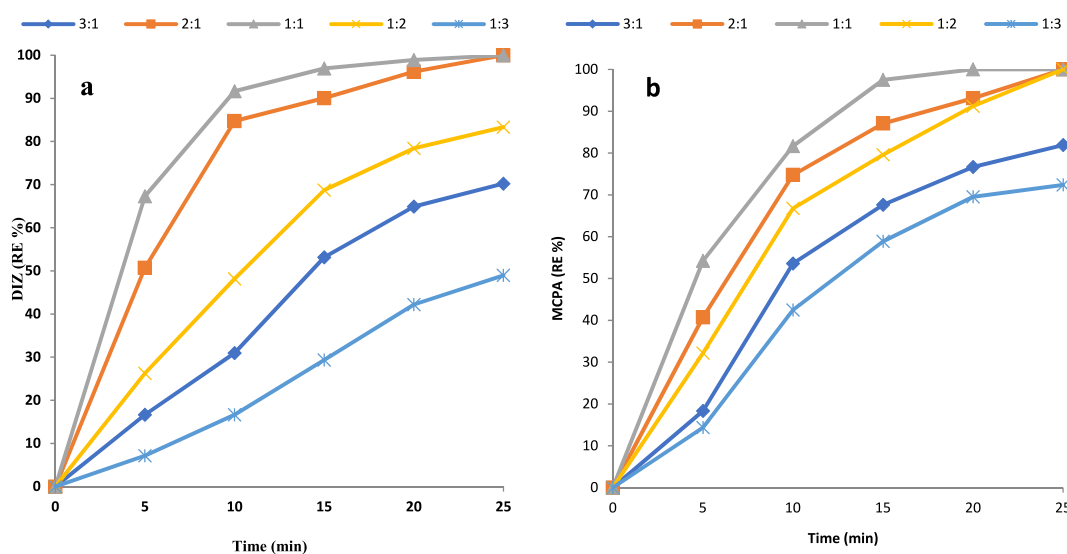


Fig. 2. Effect of a) Sulfite/DIZ and b) Sulfite/MCPA molar ratio on reduction by UV/ SO_3^- (diazinon concentration = 10 mg l⁻¹, pH 9 and temperature = 20 °C).

increased noticeably by raising the sulfite dose from 1 to 5 mm. While raising the initial sulfite concentration did not result in an increase in kobs they explained that higher removal efficiencies with a proportional increase in kobs resulted from the initial rise in the concentration of sulfite due to the greater uptake of UV light [37].

Xie et al., In 2016 showed that increasing the sulfite concentration increases the decomposition efficiency of 4-bromophenol in the UV/SO₃⁻ process. However, they stated that at aggregate concentrations of sulfite, the desired role fades, due to the absorption of light that could be used in direct photolysis [38]. Also, Yu et al. investigated the effect of different doses of sulfite on the breakdown of diclofenac molecules (initial concentration 0.3 mM) by irradiation of UV light to sulfide in the contaminant solution. They found that by increasing the sulfite dose from 0 to 8 mM, the reaction constant increased significantly. While with further increase of sulfite dose from 8 to 32 mM, the reaction constant decreased. The cause was attributed to reduced UV penetration and reduced quantum efficiency. This means that due to the reaction between the reacting species, the inhibition effect is created, the quantum efficiency is reduced and the efficiency is also reduced [37].

3.3. Investigation of the reaction mechanism of DIZ and MCPA degradation by UV/Sulfite process

The effects of reducing agents were examined by the addition of carbon tetrachloride reduction as species inhibitor DIZ and MCPA photo-degradation efficiency from 100 % to 40 % and 47 %, respectively, in optimal condition. In order to determine the potential impact of oxidizing species, *tert*-butyl alcohol (as oxidation species inhibitor), was also added to the reaction medium. As a result, the yield was oxidation by up to 4 %. This suggests that the mechanism of the reaction is photocatalytic reduction.

3.4. Kinetics and energy consumed

The pseudo-first order kinetic was used and the kinetic investigation and the results are given in Table 1. As can be seen, the reaction constant (k_{obs}) decreased with increasing concentration of DIZ and MCPA photo-reduction from 5 to 25 mg L⁻¹ concentration, observed rate constant (k_{obs}) increase about from 0.151 to 0.234 for DIZ and from 0.231 to 0.589 min⁻¹. Also, reaction rate (r_{obs}) increases about from 0.755 to 4.68 for DIZ and from 1.155 to 11.78 mg L⁻¹.min. The higher probability of collision of contaminant molecules with reducing species is what causes the constant increase and reaction rate [39]. Also, the amount of energy consumption in DIZ solution increased from 5 to 20, respectively, from 0.73 to 2.37, and in the reduction of MCPA from 0.47 to 1.49 kWh per cubic meter. Also, in IUPAC model it increases from 0.94 to 2.139 kWh.m⁻³ of treatment. Azarpira et al., in the diazinon photo-reduction by UV/Iodide method, concluded that in two conventional and baffled reactors, the pseudo-first-order reaction constant (k_{obs}) increased from 0.1 to 0.14 min⁻¹, and the reaction rate (r_{obs}) increased from 1.54 to 2.06 mg L⁻¹ min⁻¹ and also the E_{EO} changed from 8.61 to 5.37 kw h m⁻³ [4].

3.5. The impact of anion in real sample on DIZ and MCPA photo-reduction

Effect of interfering anions presence in neutral water were investigated and shown in Table 2. After 20 min, all concentrations of DIZ and MCPA from various water matrixes were reduced to less than 10 mg L⁻¹, demonstrating the US process has a high potential for use in real-world applications for the removal of both. The results show that the removal of DIZ (10 mg L⁻¹) in the presence of anions in the process showed an adverse effect on the performance of the reduction process, so that the reduction percentage of DIZ from 100 % (solution made with distilled water) to 64 % in the presence of nitrate anion decreased. Also, the reduction of MCPA in the presence of nitrate anion was reduced from 100 % to 73 %, respectively. While sulfate, chloride and phosphate slightly (less than 10 %) reduced the decomposition process efficiency. In 2019, Yu et al. studied the effect of nitrite and nitrate anions on UV/Sulfite process performance in diclofenac reduction. They reported that nitrate and nitrite had a significant inhibitory effect on hydrated electrons (e_{aq}^-) and in alkaline conditions (pH = 9.2) in the presence of nitrate the DCF reduction rate decreased from 0.2091 to 0.0125 min⁻¹ and the DCF reduction by NO₃⁻ Demonstrated the inhibitory effect of nitrate, proving the major role of e_{aq}^- in this process [40]. Possible reactions between anions and e_{aq}^- are as follows [13,32]:



Table 1

The PFO kinetics and electrical energy used in in different initial DIZ and MCPA concentration.

	Concentration (mg L ⁻¹)	R ²	K_{obs} (min ⁻¹)	r_{obs} (mg/L.min)	E_{EO} (kwh/ /m3)
DIZ	5	0.9687	0.151	0.755	0.73
DIZ	10	0.9712	0.1718	1.718	1.61
DIZ	20	0.9837	0.234	4.68	2.37
MCPA	5	0.9921	0.231	1.155	0.47
MCPA	10	0.9678	0.487	4.87	1.05
MCPA	20	0.9755	0.589	11.78	1.49

Table 2
Chemical parameters of real sample before and after the photo-reduction.

Parameters	Row water	UV/SO ₃
pH (unit)	8.87	7.64
DIZ and MCPA (mg L ⁻¹)	10	0.1
HCO ₃ ⁻ (mg L ⁻¹)	117.46	91.24
CO ₃ ²⁻ (mg L ⁻¹)	47.02	46.12
NO ₂ ⁻ (mg L ⁻¹)	17.27	2.14
Cl ⁻ (mg L ⁻¹)	75.27	73.64
SO ₄ ²⁻ (mg L ⁻¹)	49.91	78.68
HPO ₄ ²⁻ (mg L ⁻¹)	9.68	7.31



3.6. US-based MCPA and DIZ mineralization and biodegradability

Water, carbon dioxide and salt are very stable mineral compounds that are created in the mineralization of organic compounds to reduce pollution. Mineralization of MCPA and DIZ at 20 mg L⁻¹ MCPA and DIZ is investigated under optimal conditions. To determine the degree of biodegradability and mineralization, chemical oxygen demand (COD) and total organic carbon (TOC) indices and their ratios (BOD/COD) were monitored in the UV/Sulfite process effluent. According to the data from Fig. 3 for MCPA reduction by UV/Sulfite process the BOD/COD ratio started at about 0.19 and after 30 min the photo reaction time reached 0.48. During this time, COD decreased about 42 % but biochemical oxygen demand (BOD) increase from 16.72 to 24.4 mg L⁻¹, indicating the breakdown of MCPA molecules to linear biodegradable mediators [41]. Also, Fig. 4 shows that for DIZ reduction by UV/Sulfite process the BOD/COD ratio started at about 0.19 and after 30 min the photo reaction time reached 0.48. During this time, COD decreased from 96.72 to 63.84 and (about 34 %) but BOD increase from 21.41 to 23.81 mg L⁻¹. From this data it can be concluded that from these data, it can be concluded that the non-biodegradable COD (NBDCOD) convert to biodegradable COD (BDCOD) and some of these materials have also been mineralized.

4. Conclusions

Advanced treatment processes based on nanoparticles have problems such as high energy consumption, their distribution in the reaction environment and the release of these nanomaterials into the environment. To overcome these problems in this study, the reduction of two contaminants viz MCPA and DIZ under UV irradiation and Sulfite excitation in charger-transfer-to-solvent (CTTS) states of anions in polar solvents to produce reducing species was investigated. Over time, the reduction rate increases and in a short time 100 % of these organic matters are degraded organic matter from the reaction medium. The reduction of these pollutants also produces a large number of organic radicals, which leads to the production of various oxidizing and reducing species. Therefore, the

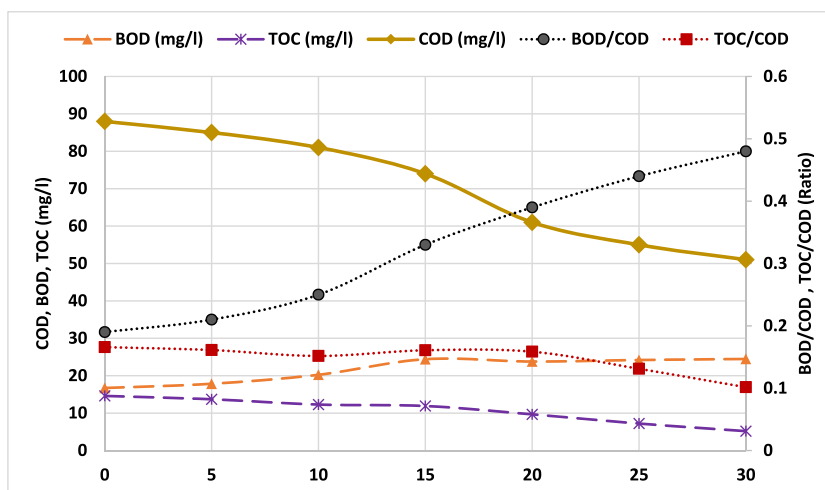


Fig. 3. COD, BOD, TOC (mg L⁻¹) and BOD/COD, TOC/COD (ratio) change in 30 min reaction time for MCPA reduction.

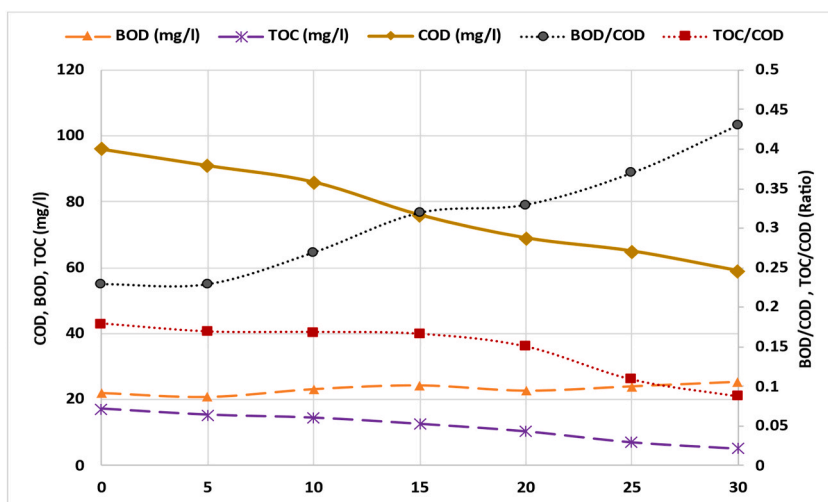


Fig. 4. COD, BOD, TOC (mg L^{-1}) and BOD/COD, TOC/COD (ratio) change in 30 min reaction time for DIZ reduction.

molar ratio is an important issue in this type of process. since the index of biodegradability has grown high, it can be concluded that non-biodegradable COD (NBDCOD) convert to biodegradable COD (BDCOD) and toxicity is lower than of before of treatment. Although this method is very efficient, increasing COD removal requires more time and energy. Considering that the ratio of BOD to COD is suitable, it is suggested to use the biological treatment after this process.

Author contribution statement

- 1 - Conceived and designed the experiments.
- 2 - Performed the experiments.
- 3 - Analyzed and interpreted the data.
- 4 - Contributed reagents, materials, analysis tools or data.
- 5 - Wrote the paper.

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Data availability statement

All data generated or analyzed during this study are included in this article.

Additional information

No additional information is available for this paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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