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**HAL Id: hal-03098858**

<https://uca.hal.science/hal-03098858v1>

Submitted on 5 Jan 2021

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## Article

# Degradation of 2,4-Dichlorophenol by Ethylenediamine-*N,N'*-disuccinic Acid-Modified Photo-Fenton System: Effects of Chemical Compounds Present in Natural Waters

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**Abstract:** This paper describes a study of the treatment of 2,4-dichlorophenol (2,4-DCP) with an ethylenediamine-*N,N'*-disuccinic-acid (EDDS)-modified photo-Fenton system in ultrapure water and different natural waters. The results showed that the EDDS-modified photo-Fenton system is adequate for 2,4-DCP degradation. Compared with a medium containing a single organic pollutant, the removal of pollutants in a more complex medium consisting of two organic compounds is slower by around 25 to 50% as a function of the organic pollutant. Moreover, 2,4-DCP can be further effectively degraded in the presence of organic materials and various inorganic ions. However, the photodegradation of 2,4-DCP in different natural waters, including natural lake water, effluent from domestic sewage treatment plants, and secondary effluent from pulp and paper mill wastewaters, is inhibited. Chemical compounds present in natural waters have different influences on the degradation of 2,4-DCP by adopting the EDDS-modified photo-Fenton system. In any case, the results obtained in this work show that the EDDS-modified photo-Fenton system can effectively degrade pollutants in a natural water body, which makes it a promising technology for treating pollutants in natural water bodies.

**Keywords:** photo-Fenton; EDDS; 2,4-DCP; organic matter; inorganic ions; natural water bodies



**Citation:** Huang, W.; Huang, Y.; Wang, S.; Lin, H.; Mailhot, G. Degradation of 2,4-Dichlorophenol by Ethylenediamine-*N,N'*-disuccinic Acid-Modified Photo-Fenton System: Effects of Chemical Compounds Present in Natural Waters. *Processes* **2021**, *9*, 29. <https://dx.doi.org/10.3390/pr9010029>

Received: 24 November 2020

Accepted: 23 December 2020

Published: 25 December 2020

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## 1. Introduction

Advanced oxidation processes (AOPs) can effectively oxidize organic pollutants in water using active free radicals [1], which have been adopted to degrade pollutants from many types of wastewaters, such as tannery wastewaters and pharmaceutical wastewaters [2,3]. Fenton technology is one of the most simple and effective AOPs to degrade pollutants [4]. However, the Fenton reaction consumes a large number of chemical reagents and produces toxic by-products, resulting in secondary contamination [5]. In order to overcome the shortcomings of Fenton processes, different attempts have been carried out. First of all, irradiation has been introduced in the Fenton reaction, and the Fe(III)/H<sub>2</sub>O<sub>2</sub> mixture (Fenton-like reagent) can absorb photons of wavelengths up to 550 nm [6,7]. The efficiency of the photo-Fenton process has been proven by many previous studies, most of which were carried out at an acidic pH value [8–10]. Additionally, the introduction of chelating agents, especially organic carboxylic acid into the Fenton reaction, proved to be an effective method for broadening the applicable pH values. Several different organic carboxylic acids, such as citric acid, oxalic acid, NTA, and EDTA, were used to modify the Fenton process and proved to be efficient [11–14]. Ethylenediamine-*N,N'*-disuccinic-acid (EDDS), a biodegradable isomer of EDTA, was used as a chelating agent in homogeneous

and heterogeneous Fenton and photo-Fenton systems in our previous studies [15–18]. Therefore, the EDDS-modified photo-Fenton reaction is proven to be a promising approach to treat refractory pollutants.

However, most laboratory studies on pollutant removal using the EDDS-modified photo-Fenton system are currently conducted using deionized water, which is far from the complex chemical composition of natural water, in which the inorganic ions and dissolved organic compounds in water can significantly influence pollutant removal. In previous research, it was found that the water matrix could significantly influence the efficiency and mechanism of AOPs processes, especially the Fenton process. The presence of common inorganic ions had no substantial effect on herbicide removal when using the photo-Fenton system, but the  $H_2O_2$  (oxidant) consumption of this reaction was higher than that of the same reaction where inorganic ions were absent [19]. In the process of the photodegradation of 2,4-D by the photo-Fenton reaction, carbonate has little adverse effects, fluoride has a positive effect, and phosphate has an inhibitory effect [20]. The effect of typical inorganic water constituents (carbonates and chloride ions) and organic matter was also investigated and found to be different in the UVA-UVB activation of hydrogen peroxide and persulfate for advanced oxidation processes [21]. Therefore, it is necessary to study the influence of the natural water matrix on pollutant degradation efficiency in the EDDS-modified photo-Fenton system, including not only single inorganic ions or organic compounds but also natural water where various chemical compounds are present.

Chlorophenols (CPs) in wastewater represent a type of pollutant that greatly harms human health and the environment because they are toxic, teratogenic, and carcinogenic [22,23]. Nowadays, CPs are widespread in the environment, even in the most remote natural environments, as well as in aquatic and terrestrial food chains [24]. Among them, 2,4-DCP is present in most wastewaters generated by the textile and the pulp and papermaking industries and has attracted considerable attention because it is highly toxic and difficult to degrade. Furthermore, it is a kind of absorbable organic halide (AOX), which is the main pollution product in the pulping and papermaking industry [25]. It is poisonous, carcinogenic, and teratogenic. Direct discharge into water bodies can cause serious damage to the water environment. As a result, 2,4-DCP is usually degraded by AOPs and used as a target pollutant for developing new AOP methods.

In our previous study, we confirmed that the EDDS-modified photo-Fenton system can effectively degrade 2,4-DCP in deionized water in the laboratory. The effect of pH,  $H_2O_2$  concentration, and Fe(III)-EDDS dosage was investigated, and the optimal condition was determined [26]. On the other hand, it was found that 2,4-DCP could be effectively degraded in the EDDS-modified photo-Fenton system at pH 3–7. Furthermore,  $\bullet OH$  radicals were found to be the main active species of degradation. In this study, our purpose is to reveal the effect of chemical compounds (organic and inorganic compounds) on 2,4-DCP degradation using the EDDS-modified photo-Fenton system and the effect of the complex water matrix on the system. First, the effects of organic matter such as humic acids (HAs) (representing common organic matter in natural water) and 2,4,6-trichlorophenol (2,4,6-TCP) (representing the same kind of organic compounds always accompanying wastewater) on the degradation of 2,4-DCP are discussed. Second, the effects of inorganic ions on 2,4-DCP degradation are evaluated. Finally, three types of natural waters, including natural lake water (NLW), effluent from domestic sewage treatment plants (DSTP), and secondary effluent from pulp and paper mill wastewater (PPMW), are selected as the natural water matrix for 2,4-DCP degradation in the EDDS-modified photo-Fenton reaction. A metal halide lamp is used to mimic sunlight during these laboratory experiments. The expected selectivity of the EDDS-modified photo-Fenton reaction for 2,4-DCP in natural water is demonstrated by comparing the decrease in 2,4-DCP content in pure water with that in different natural waters. The results of these experiments on the efficiency of the EDDS-modified photo-Fenton system in removing pollutants from natural waters have important practical implications for advancing water treatment technologies.

## 2. Materials and Methods

### 2.1. Chemicals

EDDS (35% in water) was purchased from Shanghai Anpu Experimental Technology Co., Ltd. (Shanghai, China). 2,4-DCP and 2,4,6-TCP were purchased from Shanghai Macklin Biochemical (Shanghai, China). Ferric chloride hexahydrate, sodium chloride, sodium sulfate, sodium carbonate, sodium nitrate, sodium phosphate dodecahydrate, potassium chloride, magnesium chloride, calcium chloride, and H<sub>2</sub>O<sub>2</sub> (30% in water) were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. (Guangzhou, China). Humic acids (HAs) were purchased from Alfa (Shanghai, China). Methyl alcohol (HPLC grade) and acetonitrile (HPLC grade) were purchased from MERCK (Shanghai, China). The pH of the solutions was adjusted with sodium hydroxide (NaOH) and hydrochloric acid (HCl). The ferric carboxylic acid complex solution was prepared by mixing iron and EDDS aqueous solutions in a ratio of 1:1 (and left to stand for more than 1 h to ensure excellent chelation efficiency).

### 2.2. Analytical Procedures

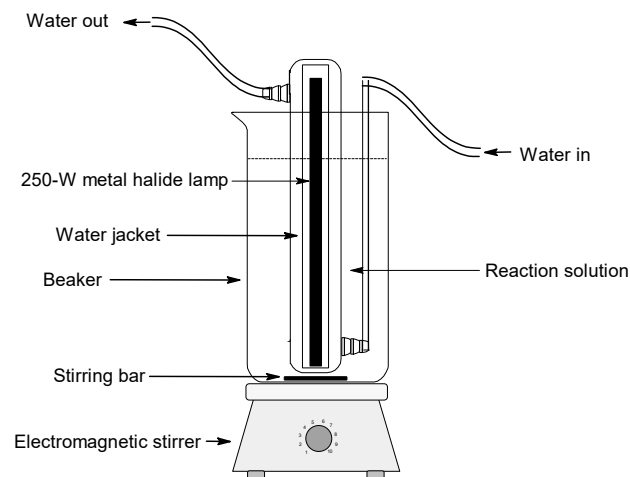
Total organic carbon (TOC) was measured using an Analytikjena TOC-VCSN analyzer (Jena, Germany). An ICS-5000 ion chromatography (IC) unit (Dionex Corporation, Sunnyvale, CA, USA) was used to monitor the release of chloride ions; this unit was equipped with a conductivity detector, an anion self-regenerating suppressor (ASRS<sup>TM</sup> 300 × 4 mm, Dionex Corporation, Sunnyvale, CA, USA), and the AutoSuppression<sup>TM</sup> Recycle Mode. Ultrapure water and 250 mM NaOH were supplied as the eluent to IC at a flow rate of 1 mL min<sup>-1</sup>. Degradation of 2,4-DCP, 2,4,6-TCP, and a mixture of 2,4-DCP and 2,4,6-TCP was determined using ultra-high-pressure liquid chromatography (Waters ACQUITY UPLC<sup>®</sup> H-Class, C-18 column, UV detector) (Waters, Milford, MA, USA). The UPLC operating conditions for the target compounds are listed in Table 1.

**Table 1.** UPLC methods for target compounds.

Compound	Mobile Phase	Flow Rate (mL min <sup>-1</sup> )	Column Temperature (°C)	Injection Volume (μL)	Detection Wavelength (nm)
2,4-DCP	Water/methanol (40:60. <i>v/v</i> )	0.35	35	5	280
2,4,6-TCP	Water/methanol (20:80. <i>v/v</i> )	0.35	35	5	210
Mixture of 2,4-DCP and 2,4,6-TCP	Water/methanol (20:80. <i>v/v</i> )	0.35	35	5	Dual channel: 210 and 280

### 2.3. Experimental System

All experiments were performed in a cylindrical Plexiglas container, which was covered with aluminum foil to protect against light and avoid side photochemical processes, placed on a homemade photoreactor (Figure 1). The photoreactor was designed with a cylindrical container, and the lamp with a glass-jacket was fixed through the central axes of the cell. For the experiment, the target pollutant solution and the Fe(III)-EDDS complex solution (0.1 mM) were added to a 1 L beaker. An adequate volume of the mixture was sampled and transferred into a 1 L volumetric flask, to which hydrogen peroxide solution (1.0 mM) was added. The 1 L flask containing the reaction solution was placed under agitation in a reactor equipped with a metal halide lamp (continuous spectrum of 290–800 nm), and samples were taken from the reactor at different time intervals. In order to simulate the natural pH, the initial pH value of all the single-effect experiments was set close to 7.0. Since the reaction may have continued after sampling, methanol was added to stop the reaction.



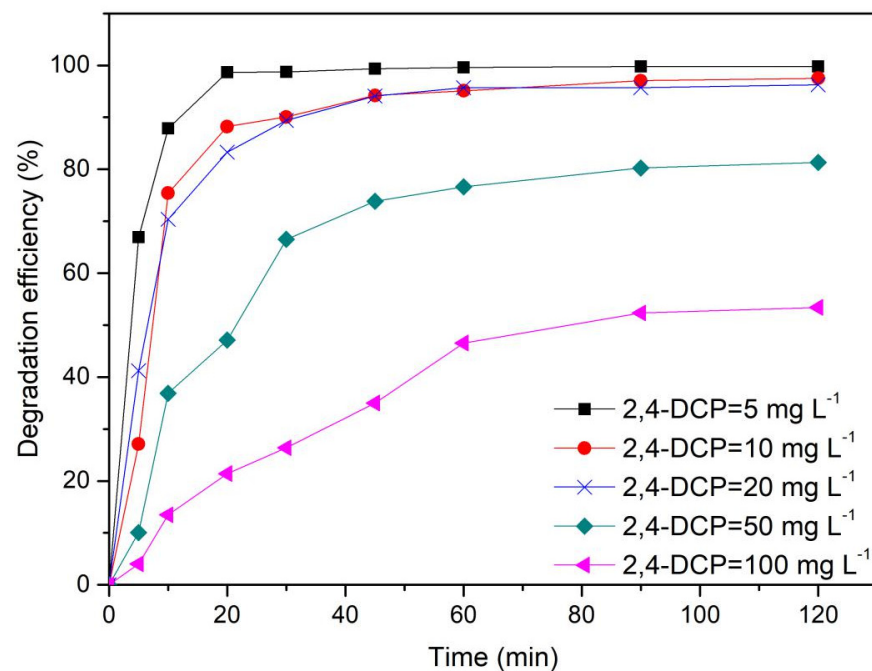
**Figure 1.** The scheme of the photoreactor used in this study.

### 3. Results

#### 3.1. Effects of Organic Matter

##### 3.1.1. Effect of Organic Compounds

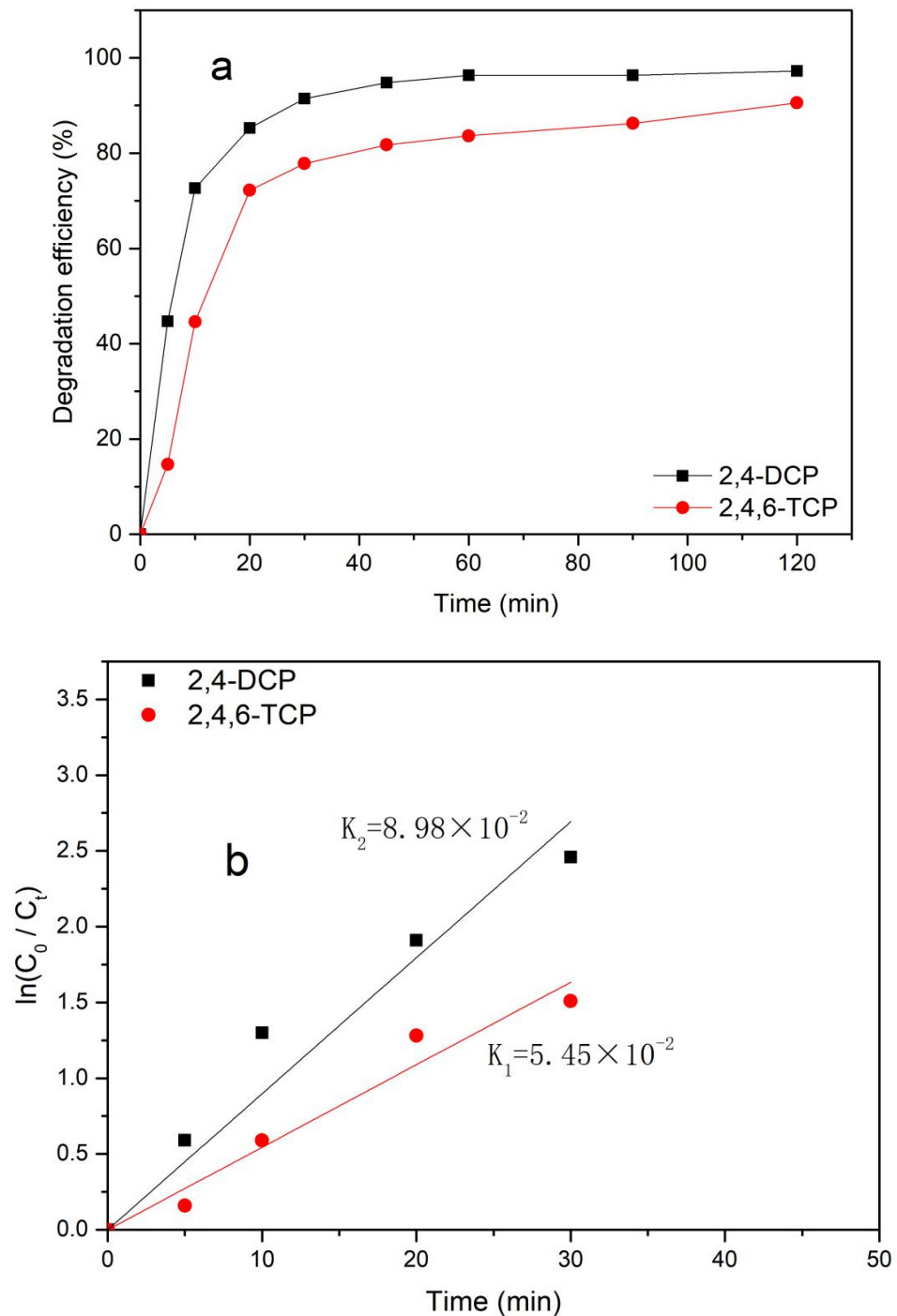
Changes in pollutant concentration could significantly influence the degradation efficiency in the photo-Fenton system. Therefore, the influence of different initial concentrations of 2,4-DCP on the photochemical experiment was studied while keeping the other reaction parameters unchanged. The pollutant was almost completely degraded at concentrations of 5 to 20 mg L<sup>-1</sup>. For 2,4-DCP concentrations equal to or exceeding 20 mg L<sup>-1</sup>, the degradation rate and efficiency decreased as the 2,4-DCP concentration increased (Figure 2). This phenomenon can be interpreted because the number of hydroxyl radicals did not increase proportionally as the pollutant concentration increased [27]. 2,4-DCP exhibited a significant degradation efficiency of around 53% even at the maximum pollutant concentration of 100 mg L<sup>-1</sup> considered in this study. The experimental results show that the EDDS-modified photo-Fenton process had an obvious degradation effect on 2,4-DCP, even at high initial concentrations.



**Figure 2.** 2,4-DCP degradation efficiency for different 2,4-DCP initial concentrations. [Fe(III)-EDDS] = 0.1 mM, [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM, and pH = 7.0 ± 0.1.

The toxicity of CPs can be ascribed to the number of Cl atoms on the benzene ring: the more Cl atoms in the chemical formula of CPs, the more toxic organic compounds there are [28]. Moreover, the quantity of Cl atoms on the benzene ring may affect the rate of degradation. Accordingly, we experimentally investigated the degradation of single 2,4,6-TCP and 2,4-DCP, as well as that of a mixture of these two pollutants.

In our photo-Fenton system and the single-substance experiments, the rate of 2,4-DCP pollutant removal was superior by around 65% to those of 2,4,6-TCP (Figure 3).



**Figure 3.** (a) EDDS-modified photo-Fenton degradation of 2,4-DCP and 2,4,6-TCP. (b) Variation of  $\ln C/C_0$  with time in 2,4-DCP and 2,4,6-TCP concentration using the EDDS-modified photo-Fenton system.  $[2,4\text{-DCP}] = [2,4,6\text{-TCP}] = 20 \text{ mg L}^{-1}$ ,  $[\text{Fe(III)-EDDS}] = 0.1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 1.0 \text{ mM}$ ,  $\text{pH} = 7.0 \pm 0.1$ .



This difference in 2,4-DCP and 2,4,6-TCP degradation rates could be attributed to the number of chlorine atoms on these CPs, possibly because the OH and Cl groups of 2,4-DCP are aligned along the ortho and para directions, and the  $\bullet\text{OH}$  radicals have the same preference for attack. By contrast, steric hindrance prevents the hydroxylation of 2,4,6-TCP [29]. It was reported that in the heterogeneous photo-Fenton system, the 4-CP removal rate was superior to that of 2,4,6-TCP, indicating that the quantity of Cl atoms significantly influenced the phenolic compounds' degradation rate [30]. However, our results showed the same effect but also that the EDDS-modified photo-Fenton process can be used to effectively treat 2,4-DCP and 2,4,6-TCP pollutants in deionized water.

Given that wastewaters contain multiple organic matters, we performed other experiments with a mixture of two soluble pollutant compounds (2,4-DCP and 2,4,6-TCP). The individual concentrations of 2,4-DCP and 2,4,6-TCP were set to  $10\text{ mg L}^{-1}$  (total pollutant concentration is  $20\text{ mg L}^{-1}$ ) while keeping the other experimental conditions unchanged from those employed in the single-substance experiments.

The removal rate of residual pollutants after 20 min of irradiation was considerably slower than that before 20 min of irradiation (Figures 3 and 4). This was primarily ascribed to the low concentration of residual pollutants (around 20% in the single-pollutant experiment and 40% in the mixture of the two pollutants of the initial concentration) after the first 20 min of reaction, resulting in a higher competition reaction of  $\bullet\text{OH}$  radicals with  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  able to scavenge  $\bullet\text{OH}$  radicals as well [31–33].

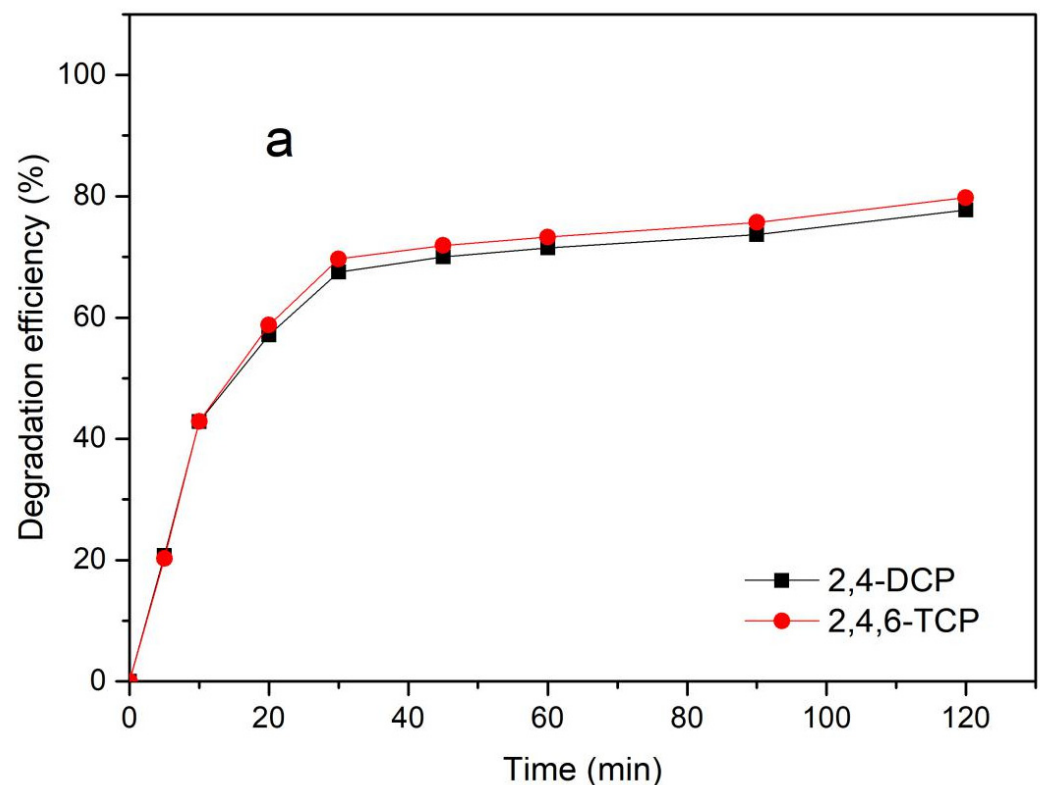
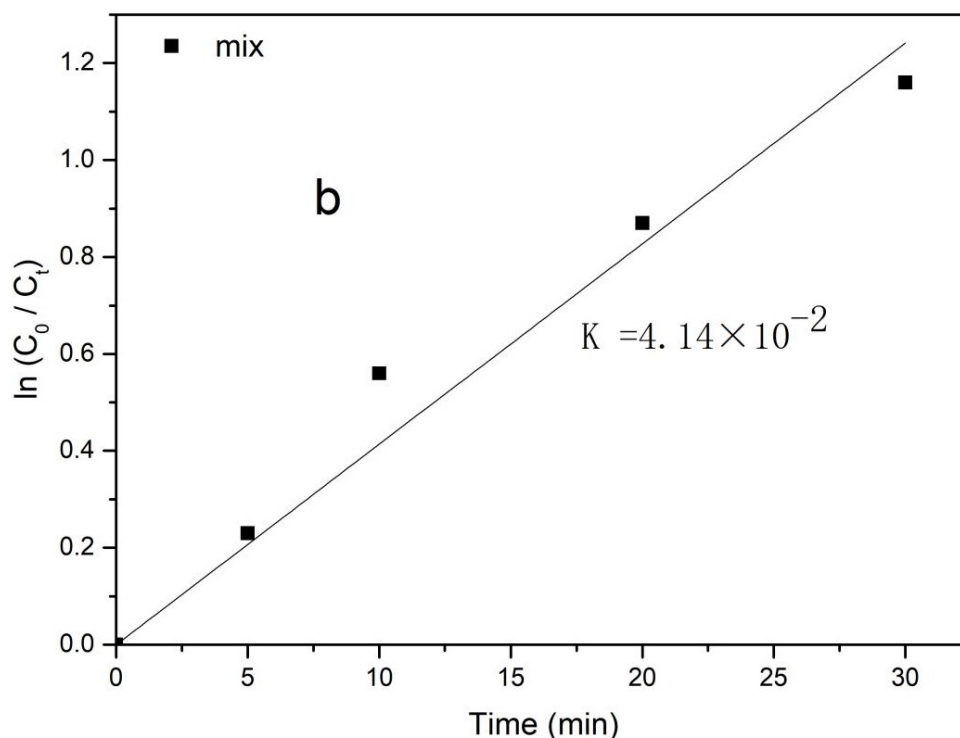


Figure 4. Cont.



**Figure 4.** EDDS-modified photo-Fenton degradation of a mixture of 2,4-DCP and 2,4,6-TCP in the two-pollutants experiment ((a) 2,4-DCP and 2,4,6-TCP degradation efficiency; (b) apparent rate constant of degradation of mixed pollutants). [2,4-DCP] = 10 mg L<sup>-1</sup>, [2,4,6-TCP] = 10 mg L<sup>-1</sup>, [Fe(III)-EDDS] = 0.1 mM, [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM, and pH = 7.0 ± 0.1.

In the two-pollutants experiment, approximately 80% of the two are degraded after 120 min. Compared with the single-pollutant experiment, the removal rate of the two pollutants was lower by around 54% for 2,4-DCP and 24% for 2,4,6-TCP. This result implies that the degradation of pollutants in complex media is slower. Therefore, our results demonstrate that the EDDS-modified photo-Fenton system is very effective for treating a single organic pollutant or a mixture of two organic pollutants.

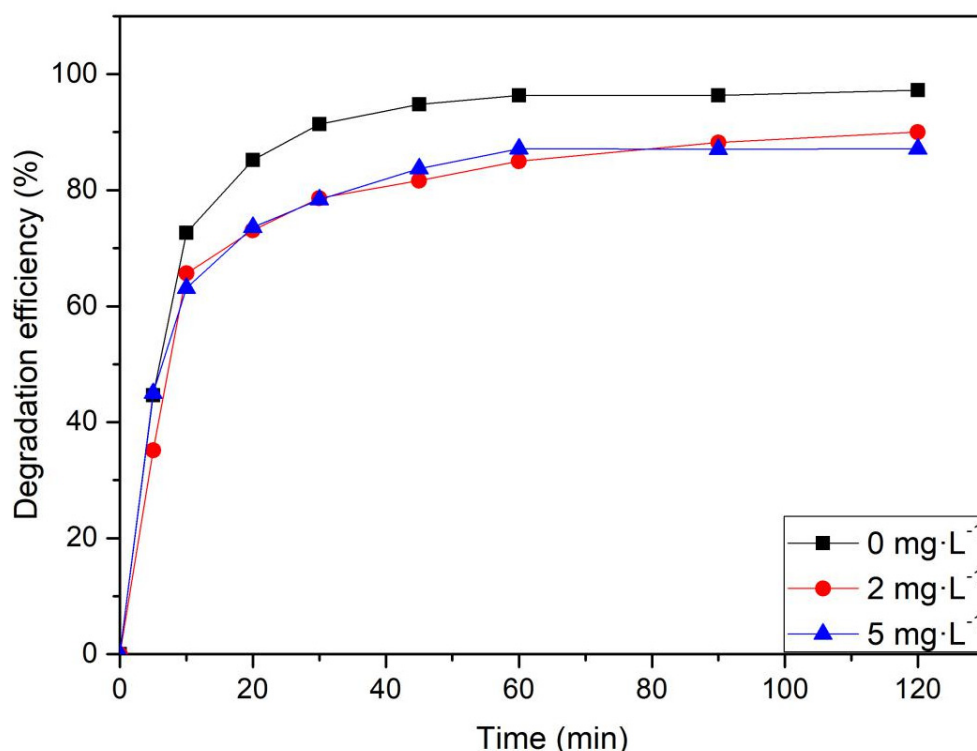
The apparent rate constant of degradation of mixed pollutants is lower than that of a single pollutant (Figures 3b and 4b), which indicates that 2,4-DCP degradation will be significantly affected in more complex natural media (a detailed analysis of 2,4-DCP degradation in complex natural media is provided in Section 3.3). Compared with a medium containing a single pollutant, a medium containing two organic pollutants will decrease the removal rate and weaken the removal effect. Nevertheless, in this experiment, the main goal (of pollutant removal) was achieved within a reasonable timespan.

### 3.1.2. Effect of Humic Acids (HAs)

HAs are ubiquitous in aquatic environments [34]. To a large extent, the degradation of organic pollutants is affected by their interaction with dissolved organic matter (DOM, such as HA) in aquatic environments [35]. When DOM absorbs ultraviolet or solar radiation, it forms reactive oxygen intermediates and can also have a shielding effect and inhibits the AOPs [36,37]. DOM can enhance or inhibit the photodegradation rate [38,39]. DOM in water, such as HA, can trap •OH radicals and also produce •OH radicals under irradiation [40]. HA is a potential electron donor and can reduce Fe<sup>3+</sup> in the system. For example, HA can significantly improve the degradation effect of pentachlorophenol by promoting the redox cycles of Fe(III) and Fe(II) in the photo-Fenton system [41,42]. Therefore, it is necessary to study the influence of HA on pollutant degradation in natural water. In our study, when HA was present in the solutions, the degradation rate of the EDDS-modified photo-Fenton system decreased marginally (around 10% less after 120 min of irradiation).



Moreover, when the HA concentration was increased from 2 to 5 mg L<sup>-1</sup>, the 2,4-DCP degradation rate was almost unchanged (Figure 5).



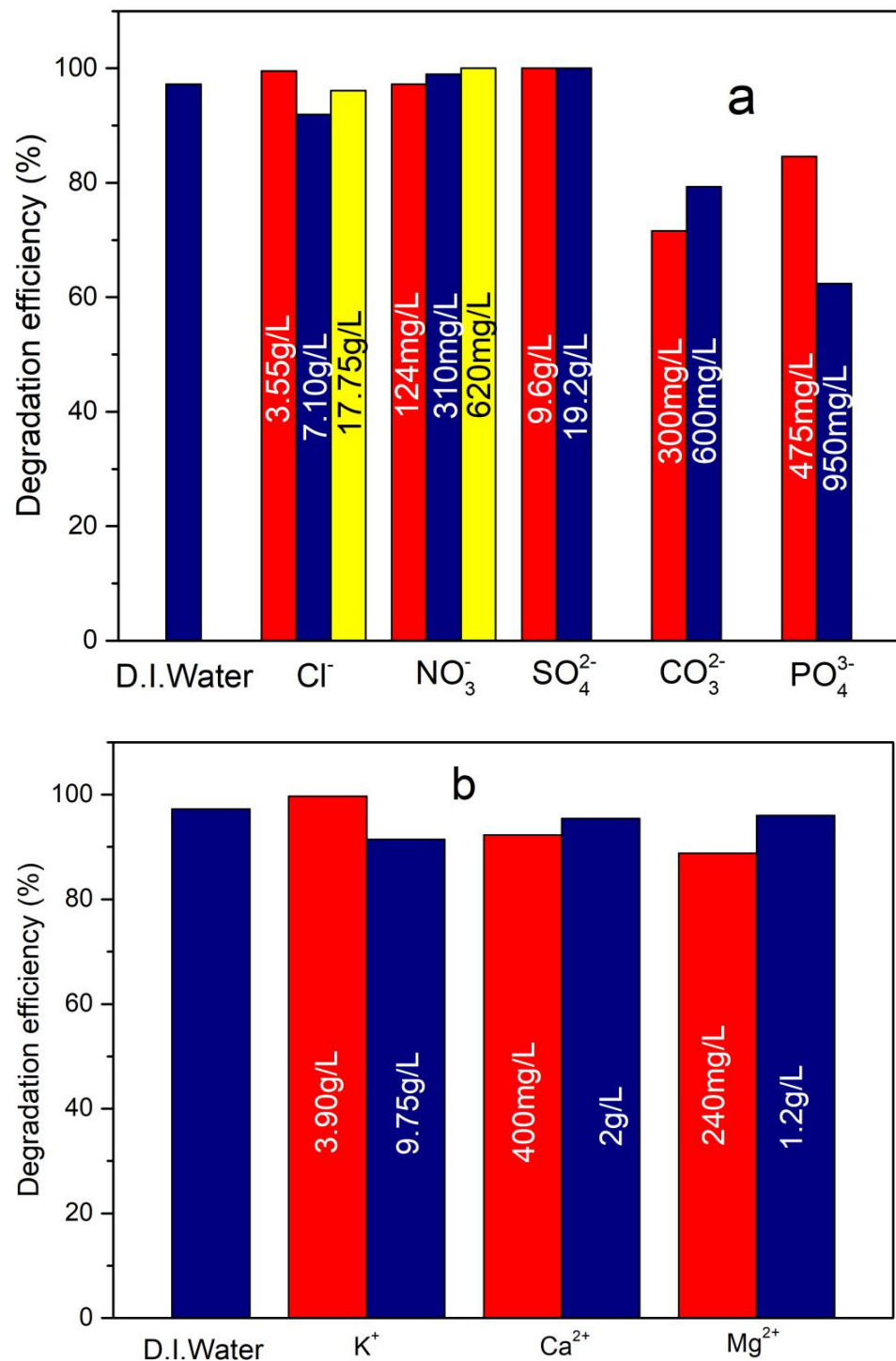
**Figure 5.** Effect of humic acid (HA) on 2,4-DCP degradation. [2,4-DCP] = 20 mg L<sup>-1</sup>, [Fe(III)-EDDS] = 0.1 mM, [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM, and pH = 7.0 ± 0.1.

The lower degradation rate could be ascribed to the fact that HA scavenged •OH radicals. Moreover, HA and the Fe(III)-EDDS complex compete for light absorption because HA is known to absorb sunlight, which reduces the photoredox process of the iron complex [35,43]. The photochemical properties of HA can be ascribed to complex phenomena and are influenced by multiple factors, including its origin and structural characteristics [35,44].

### 3.2. Effects of Inorganic Ions

The results above indicate that the EDDS-modified photo-Fenton process is a promising and novel technology that can completely degrade 2,4-DCP. However, industrial wastewaters contain various inorganic ions. These inorganic anions and cations can play complex roles in the EDDS-modified photo-Fenton process.

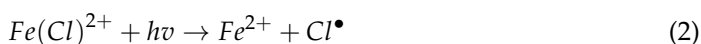
Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions could reduce the reaction efficiency by scavenging hydroxyl radicals and competing with the ligand for the complexation of iron ions [45]. The reaction of •OH radicals with SO<sub>4</sub><sup>2-</sup> ions occurs only at very high concentrations of SO<sub>4</sub><sup>2-</sup> ions [46]. Indeed, compared with the control experiment, the addition of SO<sub>4</sub><sup>2-</sup> (at concentrations of 100 to 200 mM) can marginally improve the 2,4-DCP photodegradation rate of the EDDS-modified photo-Fenton system (Figure 6a).



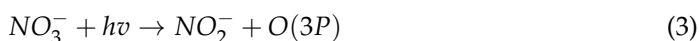
**Figure 6.** Effects of anions and cations on 2,4-DCP degradation. (a) Anions; (b) cations. [2,4-DCP] = 20 mg L<sup>-1</sup>, [Fe(III)-EDDS] = 0.1 mM, [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM, and pH = 7.0 ± 0.1.

From our results (Figure 6a), we show that the 2,4-DCP degradation efficiency decreased slightly at the chloride concentration up to 7.10 g/L, and the process continued to exhibit a significant degradation efficiency. The addition of chlorine ions to an aqueous solution of iron ions will result in the formation of the Fe(Cl)<sup>2+</sup> complex, which has a weaker (photo)reactivity than the Fe(III)-EDDS complex (R1) [47]. The effect of the concentration of chlorine ions is complicated in Fenton chemistry. When the Cl<sup>-</sup> concentration is equal to 17.75 g/L, the 2,4-DCP degradation efficiency is higher than when a 7.10 g/L Cl<sup>-</sup> concentration is added and lower than that in the deionized aqueous solution. This

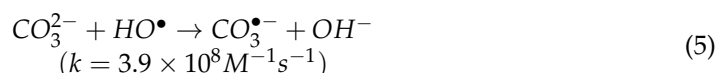
may be because of the increased concentration of chloride ions and the formation of  $\text{Cl}^\bullet$  radicals by the  $\text{Fe}(\text{Cl})^{2+}$  complex under irradiation (R2), which contribute toward 2,4-DCP degradation. The activity of  $\text{Cl}^\bullet$  radicals is weaker than that of  $\bullet\text{OH}$  radicals [48,49]. The inhibitory effect of chloride should also be attributed to the reactivity of  $\bullet\text{OH}$  radical with  $\text{Cl}^-$  leading to the formation of  $\text{Cl}^\bullet$  radical or  $\text{ClOH}^\bullet$  and after  $\text{Cl}^\bullet$  radical reacts with  $\text{Cl}^-$  to form the radical  $\text{Cl}_2^{\bullet-}$  [50,51]. These reactions are significant in the presence of  $\bullet\text{OH}$  radicals and  $\text{Cl}^-$ .



We found that  $\text{NO}_3^-$  ions had a small effect on the system. When the  $\text{NO}_3^-$  ion concentration was increased, the degradation rate slightly increased (Figure 6a).  $\text{NO}_3^-$  ions can produce other  $\bullet\text{OH}$  radicals (R3 and R4) under irradiation. However,  $\text{NO}_3^-$  ions have a strong ultraviolet (UV)-shielding effect, which is more significant than the formation of  $\bullet\text{OH}$  radicals through  $\text{NO}_3^-$  photolysis [52]. The fact that the presence of  $\text{NO}_3^-$  ions did not significantly influence the degradation of 2,4-DCP can possibly be ascribed to the interaction of all the above mentioned factors.



On the contrary, the degradation of 2,4-DCP was severely affected by the presence of carbonates (Figure 6a). When the carbonate concentration was 300 mg/L, the 2,4-DCP degradation efficiency decreased by approximately 25%. It has been reported that carbonates play an essential role in AOPs by acting as scavengers of hydroxyl radicals through the reaction R5, increasing oxidant consumption [53]. Papautsakis et al. [54] reported that carbonate can scavenge  $\bullet\text{OH}$  radicals and inhibit the degradation of imidacloprid in the Fe-EDDS photo-Fenton process. Moreover, carbonate has also been shown to have a destructive effect on the stability of soluble iron [53].



As the phosphate concentration increased, the 2,4-DCP degradation rate decreased, indicating that the  $\text{PO}_4^{3-}$  ion forms a complex with  $\text{Fe}^{3+}$  and reduces the efficiency of the EDDS-modified photo-Fenton system. It is reported in the literature that  $\text{Fe}^{3+}$  precipitation by  $\text{PO}_4^{3-}$  limited the Fenton and photo-Fenton reactions in aqueous solutions with high phosphate concentrations [55].

It is known that pH significantly influences the Fenton process. In the presence of carbonates and phosphates, the solution pH has a buffering capacity, owing to the hydrolysis of  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$  ions. Under this condition, the solution pH is neutral at the end of the experiment, while in deionized water, the corresponding solution pH is approximately 4.8. This may be also an important reason for the effect of carbonate and phosphate ions on the removal of pollutants.

When  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  ions were present in the solution, the degradation efficiency of the system decreased slightly (Figure 6b). Metal cations affect the degradation of the system by competing with Fe(III) ions for ligands. It has been shown that the higher the number of charges of metal ions, the greater their complexation ability [56]. The complexation ability of  $\text{Fe}^{3+}$  ions is the strongest, followed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, and  $\text{K}^+$  ions are the weakest. Therefore, even in the case of very high  $\text{K}^+$  concentration, the effect on the system is very small.

The above results made clear that the EDDS-modified photo-Fenton process can efficiently degrade organic pollutants in the presence of inorganic ions. Even at high concentrations of inorganic ions, the EDDS-modified photo-Fenton system exhibited significant degradation efficiency. Furthermore, inorganic ions affect degradation mainly by

competing with trivalent iron for ligands and scavenging hydroxyl radicals. Therefore, an investigation of 2,4-DCP degradation using the EDDS-modified photo-Fenton system in the presence of the main constituents of water will help to improve our understanding of their effects on pollutant degradation in real aquatic systems.

### 3.3. Effect of Natural Water Bodies

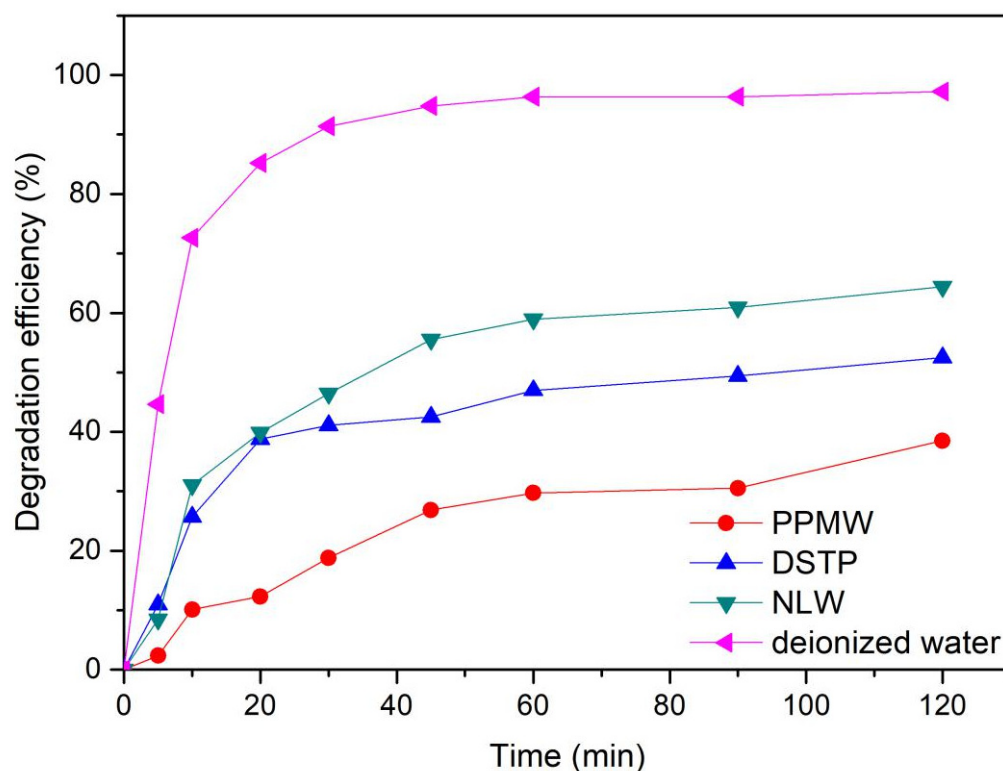
TOC and ionic chromatography analyses of the three natural water bodies show significantly different matrix contents. In terms of ions, the amounts of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  detected in the DSTP, PPMW, and NLW water samples varied significantly.  $\text{NO}_3^-$  was not detected in NLW (Table 2). The chromaticity of the three water bodies varied considerably, which is of great importance for the photo-Fenton system. In conclusion, the chemical compositions of the three water samples differed considerably, and the influences of ion concentration and chromaticity were non-negligible.

**Table 2.** Physicochemical parameters and chemical compositions of natural water bodies.

Water Bodies	Color	pH	TOC ( $\text{mg L}^{-1}$ )	TC ( $\text{mg L}^{-1}$ )	IC ( $\text{mg L}^{-1}$ )	Anion	Concentration ( $\text{mg L}^{-1}$ )
PPMW	Dark yellow	7.84	49.8	88.0	38.2	$\text{Cl}^-$	188.1
						$\text{SO}_4^{2-}$	67.7
						$\text{NO}_3^-$	20.1
DSTP	Light yellow	7.05	6.6	17.0	10.4	$\text{Cl}^-$	37.2
						$\text{SO}_4^{2-}$	21.9
						$\text{NO}_3^-$	16.4
NLW	Yellow	8.47	6.4	9.4	3.0	$\text{Cl}^-$	7.6
						$\text{SO}_4^{2-}$	21.8
						$\text{NO}_3^-$	Not detected

Pollutant degradation in natural water is a more complex process than degradation in the presence of single inorganic ions and organic matter. The EDDS-modified photo-Fenton system was used to evaluate the photocatalytic removal of 2,4-DCP dissolved in natural waters, including NLW, DSTP, and PPMW. The 2,4-DCP degradation rate in deionized water was considerably faster than that in natural waters. The degradation efficiencies after 120 min of irradiation were 52.5%, 64.4%, and 38.5% in DSTP, NLW, and PPMW, respectively (Figure 7) and around 100% in deionized water after 60 min of irradiation.

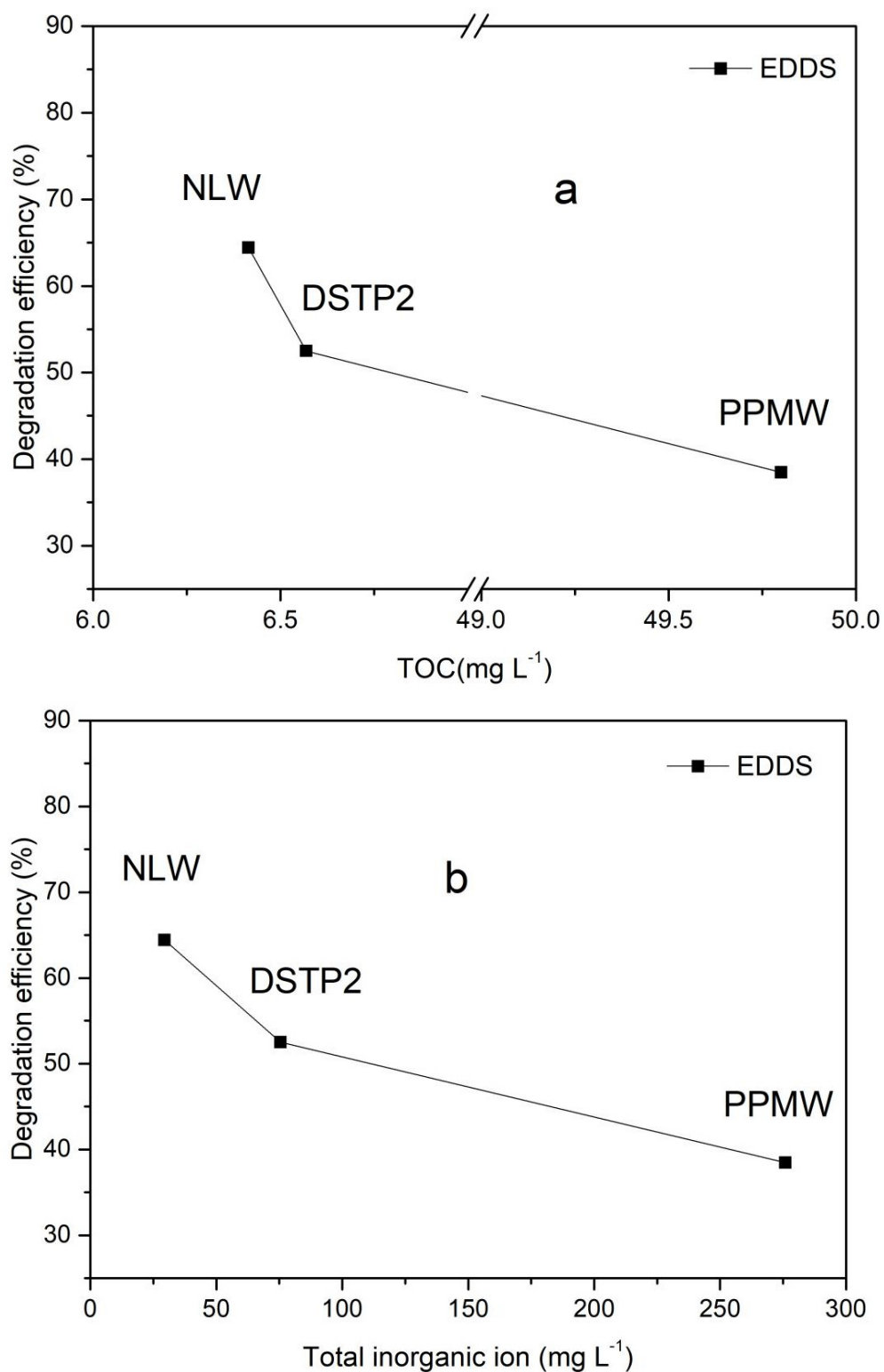
The lower 2,4-DCP degradation rate in NLW, DSTP, or PPMW than that in deionized water could be ascribed to the presence of inorganic ions and dissolved organic compounds. As given in Table 2, we determined some of the chemical constituents. The concentrations of chloride, sulfate, and nitrate ions in the studied natural waters were different. Among the three aforementioned water systems, 2,4-DCP degradation was most severely inhibited in PPMW, which may be ascribed to the relatively higher concentrations of inorganic ions in this compartment than those in the other two other water systems. Secondly, PPMW is dark yellow in color, which means it can cause a screen effect and thus decrease the Fe(III)-EDDS photoredox process. Thirdly, the presence of higher TC concentration can affect the degradation efficiency of 2,4-DCP. A more comprehensive understanding of the influence of TOC and total inorganic ion concentration in water on pollutant removal is therefore needed.



**Figure 7.** Degradation of 2,4-DCP in natural water bodies.  $[2,4\text{-DCP}] = 20 \text{ mg L}^{-1}$ ,  $[\text{Fe(III)-EDDS}] = 0.1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 1.0 \text{ mM}$ , and  $\text{pH} = 7.0 \pm 0.1$ .

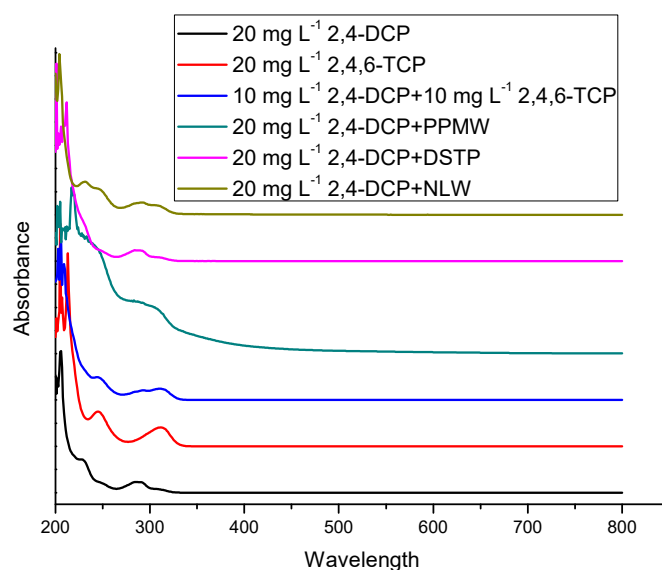
The TOC concentration of NLW, DSTP, and PPMW increased successively, contrary to the decreased 2,4-DCP degradation efficiencies (Figure 8a). The high concentration of TOC in the natural water body was in competition with the target pollutant for the reactivity of  $\bullet\text{OH}$  radicals, which is an essential reason for the resulting low degradation efficiency. Moreover, compared with that in deionized water, the decreased 2,4-DCP photodegradation efficiency in natural water may be ascribed to the optical filter effect of organic matter in natural water. Indeed, organic matter can be one of the critical absorbers of sunlight in aquatic environments [35]. We speculate that TOC concentration is not the only factor affecting 2,4-DCP degradation in the studied water bodies. The effect of total inorganic ion concentration in water on 2,4-DCP removal was explored. Overall, the 2,4-DCP degradation efficiency decreased as the total inorganic ion concentration increased (Figure 8b). The same effect was observed in the study by Sakkas et al. [25]. As the salinity of water increased, chlorothalonil combined with DOM through hydrophobic interaction or weak van der Waals forces, thus affecting the photodegradation of the pollutants. Obviously, the factors affecting the 2,4-DCP removal in natural water included inorganic ion concentration, TOC concentration, and chromaticity.

The UV–visible absorption spectrum of different water matrices containing 2,4-DCP is shown in Figure 9, and it was noted that most change in UV–visible absorption occurred in the UV zone (lower than 290 nm), which was out of the wavelength range of the lamp used in this study. As a result, it was preliminarily indicated that the influence had nothing to do with UV–visible absorption.



**Figure 8.** Effects of (a) TOC and (b) total inorganic ion concentration on 2,4-DCP degradation efficiency in different water bodies. [2,4-DCP] = 20 mg L<sup>-1</sup>, [Fe(III)-EDDS] = 0.1 mM, [H<sub>2</sub>O<sub>2</sub>] = 1.0 mM, and pH = 7.0 ± 0.1.





**Figure 9.** UV-visible absorption spectrum of different water bodies.

The degradation of 2,4-DCP was affected differently by different natural water compositions. However, the more the water is loaded with organic/inorganic compounds, the more significant the inhibition of 2,4-DCP degradation. Regardless, the EDDS-modified photo-Fenton system still removed more than 50% of 2,4-DCP in NLW and DSTP and more than 30% in PPMW. This finding indicates that the EDDS-modified photo-Fenton process can be used to effectively treat pollutants in natural waters and potentially simulate solar photocatalytic water treatment. Thus, 2,4-DCP degradation in natural water bodies justifies a more in-depth study to understand and evaluate the parameters that are essential for the efficiency of the process.

#### 4. Conclusions

The results indicate that the EDDS-modified photo-Fenton system is suitable for 2,4-DCP removal. It is a promising route for treating 2,4-DCP by simulating natural sunlight, which is a low-cost alternative light source and significantly reduces the process cost. The system could effectively degrade single 2,4-DCP and 2,4,6-TCP pollutants and the mixture of 2,4-DCP and 2,4,6-TCP. Furthermore, it could effectively degrade pollutants in the presence of common inorganic ions. The effect of anions on 2,4-DCP degradation was found to be stronger than that of cations. Finally, the degradations of 2,4-DCP in different water bodies, including NLW, DSTP, and PPMW, were remarkably different. The 2,4-DCP degradation rate in PPMW was severely inhibited, which may be related to the high absorption of light, high TOC concentration, and high inorganic ion content in this water compartment. The use of several different natural waters to treat 2,4-DCP with the EDDS-modified photo-Fenton process shows the efficiency of this process for industrial applications. Nevertheless, the application will be particularly more efficient when this process is used in a ternary treatment when the water is not too loaded.

**Author Contributions:** Conceptualization, W.H. and G.M.; methodology, W.H. and Y.H.; software, Y.H.; validation, W.H. and S.W.; formal analysis, W.H. and G.M.; investigation, W.H. and Y.H.; resources, G.M.; data curation, G.M.; writing—original draft preparation, W.H.; writing—review and editing, G.M.; visualization, H.L.; supervision, G.M.; project administration, W.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Acknowledgments:** This work was partially supported by the National Natural Science Foundation of China (No. 21367003), Guangxi Science and Technology Research Program (No. AA17202032) and Open Fond of Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control (KF201724).

**Conflicts of Interest:** The authors declare no conflict of interest.

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