

Article

UV and Zero-Valent Iron (ZVI) Activated Continuous Flow Persulfate Oxidation of Municipal Wastewater

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Abstract: Currently, sulfate-radical-based advanced oxidation processes are promising candidates to become viable post-treatment processes for wastewater purification. In this work, a continuous flow UV light/persulfate (PS)/zero-valent iron (ZVI) system has been applied for wastewater treatment for the first time. The influence of certain photo-Fenton-like process parameters, such as space time, PS concentration, and PS to ZVI molar ratio, on the removal of total organic carbon (TOC), was examined using the Box–Behnken design. First, synthetic municipal wastewater was used for the experiments, and the polynomial regression model was constructed utilizing the real data by using the response surface methodology (RSM). The adequacy of the RSM model was assessed by analysis of variance, which showed that the model was reliable and could be applied to improve the process parameters for TOC removal. Moreover, both synthetic and real municipal wastewater were spiked with carbamazepine (CBZ), which is commonly prescribed as an antiepileptic drug, to investigate its fate in the UV/PS/ZVI system. With a space time of 60 min, PS concentration of 60 mM, and PS to ZVI molar ratio of 15, it was possible to remove 71% of TOC and completely remove CBZ from the synthetic municipal wastewater, whereas a 60% TOC removal and complete removal of CBZ were achieved at a space time of 50 min, PS concentration of 50 mM, and PS/ZVI molar ratio of 15 for the real municipal wastewater. This difference in TOC removal could possibly be linked to the complex matrix of the real wastewater and the presence of radical scavenging agents.

Keywords: persulfate oxidation; municipal wastewater; carbamazepine; continuous flow photoreactor; zero-valent iron



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1. Introduction

Among different threats posing a variety of challenges to global water quality, municipal wastewater (MWW) discharges without complete treatment remain one of the most significant [1]. Although water-treatment plants relying on physical, biological, and chemical processes are embedded in the wastewater treatment system of developed countries, many developing countries still discharge MWW into natural ecosystems without any pre-treatment [2]. According to a United Nations World Water Report released in 2021, about 44% of MWW is not properly treated worldwide, i.e., treated effluents do not meet MWW discharge standards [3]. For example, in 2015, Kazakhstan had 87 registered MWW treatment facilities, with one-third of them found to be in unsatisfactory technical conditions [4]. Moreover, the villages and some small cities are not linked to the centralized municipal wastewater treatment plants (MWWTP). The example of the wastewater treatment plant situated in Aqtau city outskirts (Western Kazakhstan) is characteristic: the

construction has not been completed, and the domestic wastewater is being discharged into Koshkar Ata Lake [5]. Certain scientific works show that even in developed countries such as Germany, Italy, the USA, Sweden, the UK, and South Korea, the wastewater effluents contain trace organic contaminants such as diclofenac, ibuprofen, propranolol, bezafibrate, sulfamethoxazole, and carbamazepine (CBZ) with concentrations between the limit of quantification (LOQ) and $15 \mu\text{g L}^{-1}$ [6,7]. CBZ is a commonly prescribed antiepileptic drug, and its presence in wastewater, rivers, and groundwater has been extensively reported [8]. It is poorly removed using biological treatment systems. For example, Chtourou et al. reported about 36% removal of CBZ using a membrane bioreactor [9]. The poor efficiency of biological systems toward CBZ removal could be explained by its structure, which contains electron-withdrawing groups [10]. The potential release of emerging pollutants to the aquatic environment and the strengthening of wastewater disposal regulations stimulate the investigation of complementary wastewater treatment approaches such as advanced oxidation processes (AOPs) [11].

The hazardous components of MWW released to nature as a result of poor treatment include organic matter, phosphates, nitrates, and microorganisms [12,13]. Pharmaceuticals, not completely metabolized by humans and animals, also enter the environment as a part of organic matter. According to Wilkinson et al., the pharmacological fingerprint of almost half a billion inhabitants has been detected throughout 258 rivers in 104 nations across all continents [14]. Currently, they attract increasing attention due to the threat they represent to public health. Specifically, these compounds and the way they affect the organism is underresearched; therefore, the adverse consequences (carcinogenic, endocrine disrupting, mutagenic, etc.) are being prominently witnessed [15]. Furthermore, antibiotic resistance and the development of new types of hazardous microorganisms create a demand for advanced mineralization technologies [16,17], especially if wastewater is to be reused or reclaimed as a source of drinking water [18].

There are plenty of suggested modern approaches, and some of them are close to being applied in MWW plants [19,20]. However, the methods vary according to the type and strength of the MWW, and none of them guarantee 100% efficiency in real-life treatment [21]. Advanced oxidation processes (AOPs) have become a topic of leading interest nowadays due to the promising perspectives they demonstrate [22]. Processes with various combinations of oxidants, catalysts, and conditions are implemented to find the most appropriate method in terms of increased efficiency, low cost, and feasibility [23,24]. In wastewater treatment, photo-Fenton and photo-Fenton-like oxidation processes are increasingly investigated because of their high efficiency in eliminating target compounds in wastewater and leachate [25]. In a typical photo-Fenton process, an oxidant and an activator are used. Usually, peroxide and persulfate (PS) compounds are utilized as sources of oxidizing radicals [23,26].

Persulfate entered the field of AOPs relatively recently and attracted immediate interest due to its relative cost-effectiveness and high oxidation capacity [27]. Moreover, sulfate radicals possess greater oxidation potentials (2.5–3.1V) than hydroxyl radicals (2.8V) and are able to efficiently degrade organic contaminants in a pH range of 2–8 [28,29]. Unlike hydrogen peroxide, which is commonly used as a hydroxide radical source, persulfate is much safer and more convenient to utilize, store and transport [30]. Apart from oxidizing agents, the activating catalysts vary quite widely, too [23,29]. For example, photolysis [12], sonolysis [31], thermolysis [32], transition metals [33], carbon materials [34], and heterogeneous catalysts [35] may act as an activator. Some papers use activators in combination for synergetic effect [36,37]. Currently, heterogeneous catalysis using iron and iron minerals is considered to be highly effective [38]. In this study, persulfate was activated by zero-valent iron, which led to the production of sulfate radicals. Zero-valent iron has low toxicity, is chemically inert, exhibits biocompatibility with the environment, and is an excellent reducing agent [39,40]. The successful application of zero-valent iron-activated persulfate oxidation for the removal of organic pollutants has been previously reported [41,42].

The overwhelming majority of relevant studies include experiments with a single compound in ultrapure or distilled water [29]. The applicability of these methods remains questionable because the effect of the wastewater matrix on the reaction is paramount and unpredictable [11]. For example, mineral ions such as Cl^- , CO_3^{2-} , NO_3^- , and organic compounds may either promote or inhibit the action of the system during real-life application [43,44]. Therefore, to obtain a practical outcome, it is highly important to conduct comparative research between synthetic and real municipal wastewater. Moreover, most of the studies were performed using batch photochemical reactors [45]. However, the long-term performance and robustness of the process cannot be correctly assessed by batch systems [46]. In addition, batch photochemical reactors provide ideal conditions for the heterogenous process, but these conditions are far from real as they require additional steps increasing the cost of the process [47]. Therefore, the use of continuous flow systems is an essential step toward upscaling the process [48].

For the first time, a continuous flow photo-Fenton-like process was employed to remove organic contaminants from both synthetic and real municipal wastewater. The following factors' effects were investigated: space time, PS, and zero-valent iron (ZVI) concentrations. The municipal wastewater was also spiked with CBZ as a characteristic emerging pollutant. Moreover, Box–Behnken design, in combination with the response surface methodology, was used to design and optimize the experimental conditions in terms of TOC removal for the synthetic municipal wastewater. Finally, the findings of the study were used to treat real municipal wastewater. As far as the authors are aware, the continuous flow UV/PS/ZVI method has not yet been the subject of any published publication.

2. Results and Discussion

2.1. Characterization of Zero-Valent Iron

The characterization of ZVI included SEM and particle size analysis. The results are shown in Figure 1.

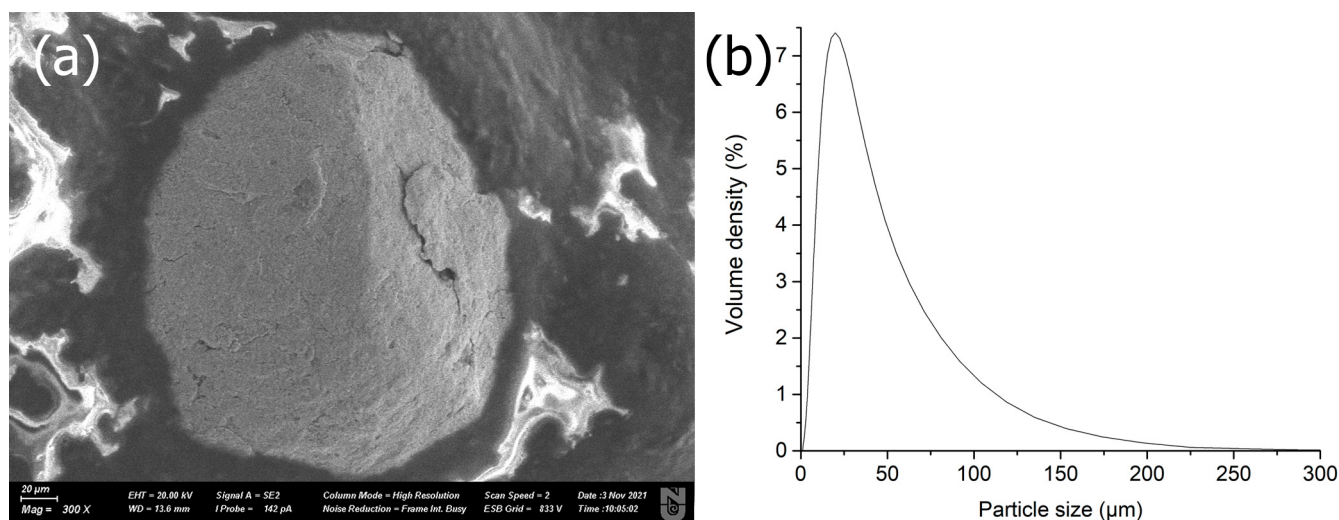


Figure 1. (a) SEM image and (b) particle size analysis of ZVI.

As can be seen from Figure 1, ZVI particles had a rounded shape, and their size ranged from 0.9 μm to 300 μm. The median particle size of ZVI particles was 20.2 μm. A total of 10% of ZVI particles had a size less than 6.87 μm, while 90% of ZVI particles were less than 60.2 μm. ZVI was estimated to have a specific surface area of 0.46 m² g^{−1} based on data from the Mastersizer 3000. The results are consistent with the existing literature, where the Brunauer–Emmett–Teller (BET) surface area is commonly reported. Kishimoto et al. used ZVI with a BET surface area of 0.21 m² g^{−1} and median diameter of 82 μm for removing

zinc ions [49], while Li et al. used ZVI with a BET surface area of $0.389 \text{ m}^2 \text{ g}^{-1}$ to activate persulfate for dye degradation [50].

2.2. Regression Model

With the use of the Box–Behnken design and response surface methodology (RSM) [51], 15 experimental runs using synthetic municipal wastewater were conducted. Experimental conditions, as well as predicted and achieved results, are presented in Table 1.

Table 1. Predicted and actual removal efficiencies for the continuous flow UV/PS/ZVI process.

Run	Independent Variables			Removal (Y, %)		
	A	B	C	Actual	Predicted	Actual
	Space Time, Min	PS, mM	PS/ZVI Molar Ratio	TOC	TOC	CBZ
1	20	20	10	23.42	24.12	86.97
2	60	40	5	33.60	36.19	97.18
3	40	20	15	21.83	23.71	95.56
4	40	20	5	36.31	34.3	100.00
5	40	60	15	41.79	43.8	99.71
6	60	20	10	31.79	31.22	98.10
7	20	40	15	26.54	23.95	99.61
8	60	60	10	46.55	45.85	99.39
9	40	60	5	42.59	40.71	99.56
10	20	40	5	49.91	51.22	99.50
11	60	40	15	57.27	55.96	96.78
12	40	40	10	31.10	31.48	97.60
13	20	60	10	35.40	35.98	96.23
14	40	40	10	30.63	31.48	98.79
15	40	40	10	32.70	31.48	99.43

It is clear in Table 1 that actual results and model-predicted values were close to each other. Subsequently, the actual results were used to derive a second-order polynomial equation, which predicted the response for each condition. The regression equation for TOC removal is shown in Equation (1). (coded):

$$\text{TOC removal (\%)} = 31.48 + 4.24A + 6.62B - 1.87C + 4.51A^2 - 1.69B^2 + 5.85C^2 + 0.695A \times B + 11.76A \times C + 3.42B \times C \quad (1)$$

where A, B, and C, represent space time (min), PS concentration (mM), PS/ZVI molar ratio, respectively.

In addition to TOC removal, Table 1 shows the degradation of CBZ, which was in the range of 86 and 100%. As high degradation of CBZ was observed for all runs, it was not feasible to construct a reliable model for CBZ degradation. Therefore, further analysis of the model and optimization of the experiments were conducted using TOC removal as the target response.

Figure 2 shows the plots for the normal probability versus residuals and the actual results versus predicted values obtained from the RSM regression equation.

Both the normal probability plot and the actual vs. expected data for TOC removal show a straight-line pattern. As further discussed in the next paragraph, this shows that the model followed the normal probability distribution and that there was a good agreement between the expected and actual outcomes.

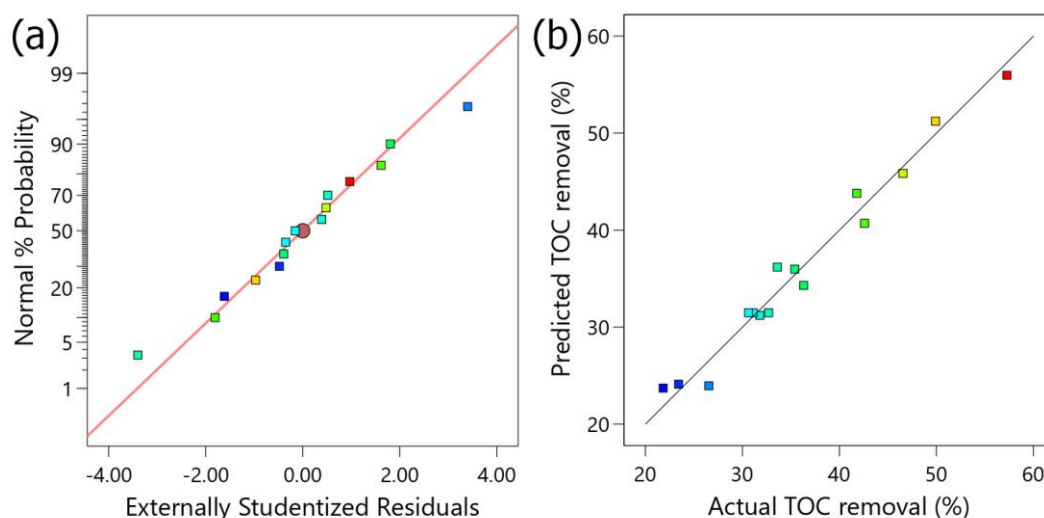


Figure 2. (a) Normal probability plot and (b) RSM predicted vs. actual values for TOC removal.

2.3. ANOVA

The effectiveness of the RSM model was evaluated using the analysis of variance (ANOVA). Regression coefficient (R^2), adjusted regression coefficient ($\text{Adj-}R^2$), predicted regression coefficient ($\text{Pred-}R^2$), coefficient of variance ($\text{CV}\%$), predicted residuals error sum of squares (PRESS), Fischer variation ratio (F-value), and probability values (p -value) were calculated as part of the analysis of variance (ANOVA). ANOVA is a crucial phase in the data analysis process because a poorly built model might produce false results [52]. The summary of ANOVA results for the TOC removal model is shown in Table 2.

Table 2. ANOVA results of the RSM model for the continuous flow UV/PS/ZVI treatment of synthetic wastewater.

Parameter	TOC Removal
Standard deviation	2.68
Mean	36.10
CV%	7.43
R^2	0.9737
$\text{Adj-}R^2$	0.9265
$\text{Pred-}R^2$	0.6035
Adequate precision	14.7219
PRESS	543.29
F-value	20.60
p -value	0.0019

The error between the fitted and actual data is indicated by the coefficient of variance ($\text{CV}\%$). The TOC values measured were well fitted by the model as the $\text{CV}\%$ was 7.43 since a $\text{CV}\%$ value less than 10 is acceptable [52]. The R^2 , $\text{adj-}R^2$, and $\text{pred-}R^2$ values of the RSM model for TOC removal were 0.9737, 0.9265, and 0.6035, respectively. R^2 and $\text{adj-}R^2$ showed adequate variation of the actual data, while the $\text{pred-}R^2$ represented the variation of the predicted data. Regression coefficients higher than 0.80 imply goodness of fit of the model [53]. F- and p -values were 20.60 and 0.0019, respectively. While a p -value less than 0.05 indicates the relevance of the model and model terms, the F-value shows the distribution of the actual values around the RSM model [12]. A, B, and AC, namely, space time, PS concentration, and the interaction between space time and PS/ZVI molar ratio, were the most significant parameters in the process as they had a p -value of less than 0.05. Moreover, the coefficients A^2 and C^2 , namely, space time to space time interaction and PS/ZVI molar ratio to PS/ZVI molar ratio interaction, had positive signs in the regression

equation, which suggests that the higher values of the space time and PS/ZVI molar ratio are, the more efficient the process is [54]. The adequate precision of the model was 14.7219. It describes the signal-to-noise ratio, and normally, its value should exceed four [53]. Finally, the difference between the actual and fitted data is described by PRESS. The lower the PRESS, the better the model is [52]. In this work, the PRESS value was reasonably low (543). For example, Davarnejad and Nasiri reported a PRESS value of 345 for a color removal model for slaughterhouse wastewater [52], while Biglarijoo et al. reported a PRESS value of 986 for the COD removal rate model from the landfill leachate [55]. Overall, all ANOVA parameters indicated that the model was significant and adequate and, therefore, the RSM model for TOC removal could be further used to navigate the Box–Behnken design within the selected ranges (space time: 20 to 60 min, PS concentration: 20 to 60 mM and PS/ZVI ratio: 5 to 15).

2.4. Three-Dimensional Plots for the RSM Model

Using the Design-Expert software, three-dimensional surface plots of the RSM model for TOC removal were obtained based on the earlier-presented polynomial function (Equation (1)). The surface plots are presented in Figure 3.

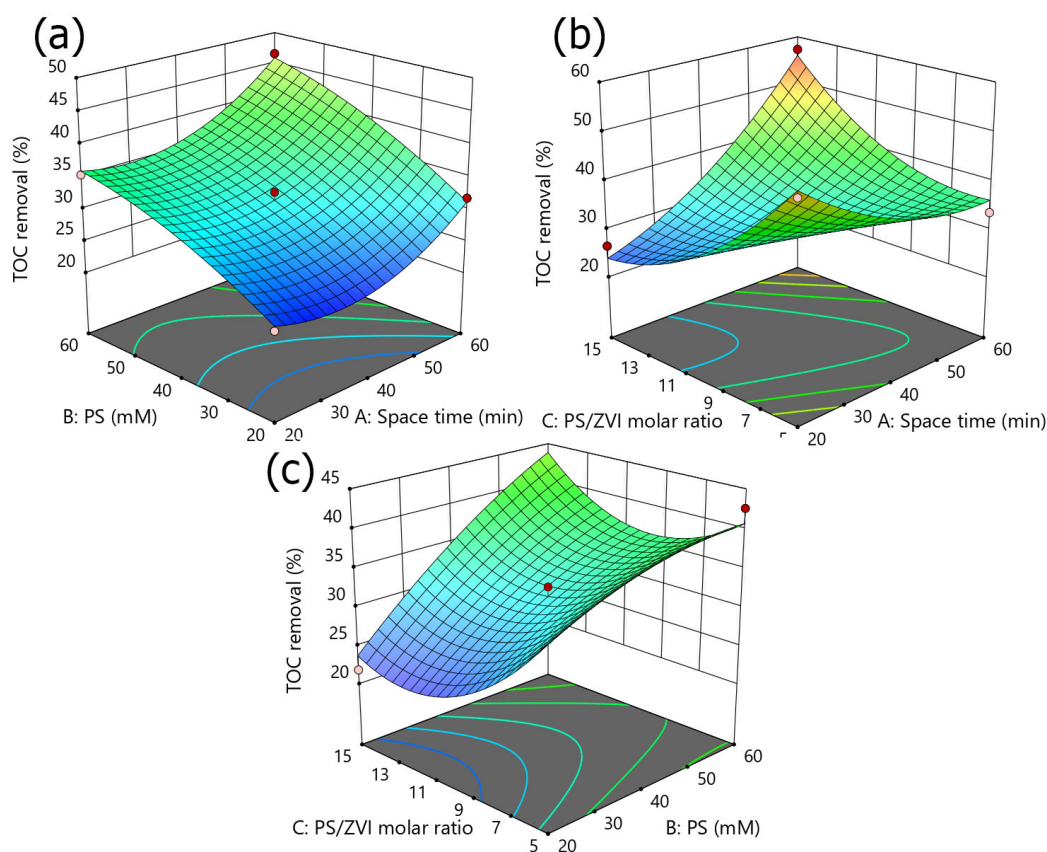


Figure 3. Three-dimensional plots of TOC removal in the continuous flow UV/PS/ZVI process as a function of: (a) space time (min) and PS (mM); (b) space time (min) and PS/ZVI molar ratio; and, (c) PS (mM) and PS/ZVI molar ratio.

Specifically, the interaction between variables and response was shown by 3D surface plots. These plots were made by keeping one variable at its center point while varying the other two within predetermined limits. It has been previously expressed in Equation (1) that PS concentration (B) has a directly proportional relationship with TOC removal. Moreover, the signs of the coefficients of the space time (A-A interaction) and PS/ZVI ratio (C-C interaction) were positive and significant, which also means that these factors

enhance the TOC removal. These suggestions were in line with the 3D surface plots discussed below.

It is obvious from the surface plot of Figure 3a that an increase in TOC removal was caused by both an increase in space time and in the concentration of PS. For example, TOC removal increased from 23.42% to 31.79% and from 35.4% to 46.55% with increasing space time at PS concentrations of 20 mM and 60 mM, respectively. The effect of space time was significant according to ANOVA results. Obviously, a higher space time enhances the generation of radical oxidative species and improves thus the TOC removal. Mergenbayeva and Pouloupoulos reported that increasing the space time from 10 min to 120 min under UV radiation caused the 4-tert-butylphenol degradation enhancement from 46% to 84% [56]. Both space time and residence time significantly impact the kinetics of the process [57]. For example, according to Petala et al., sulfamethoxazole was nearly entirely eliminated at the residence time of 22 min, while sulfamethoxazole removal dropped down to 40% at the residence time of 5.5 min [57]. Similarly, TOC removal increased from 23.42% to 35.4% and from 31.79% to 46.55%, with an increase in PS concentration at space time 20 min and 60 min, respectively.

Apparently, the increase in PS concentration leads to improved sulfate radical generation under UV light (Equation (2)) [11].



In addition to sulfate radicals, the UV/PS system can generate hydroxyl and persulfate radicals by the following chemical equations [12,32]:

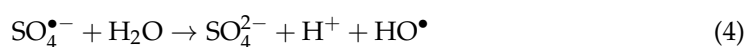
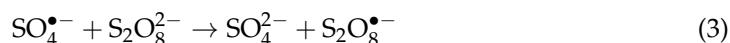
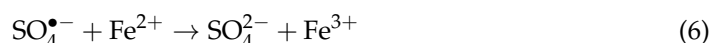


Figure 3b depicts the interaction between the space time and PS to ZVI molar ratio. It can be seen from the surface plot that the TOC removal decreased from 49.91% to 26.54% with an increase in PS/ZVI ratio at the space time of 20 min. In contrast, TOC removal was improved from 33.60% to 57.27% with an increase in the PS/ZVI ratio at the space time of 60 min. It is possible to explain this detrimental effect of the PS/ZVI molar ratio by the consumption of sulfate radicals through an excess of ferrous ions (Equation (6)) [58]:



In order to prevent this impact, it is crucial to choose the ideal molar ratio of Fe. ZVI is also capable of activating PS by reducing it into sulfate ions and radicals (Equation (7)) [38]. Produced ferrous iron is also capable of producing sulfate radicals (Equation (8)), while ferric iron can be reduced to ferrous iron under UV light (Equation (9)) [12,36]:

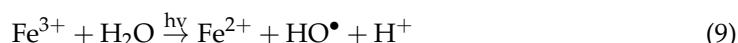
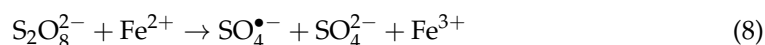
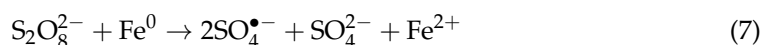


Figure 3c demonstrates the surface plot for PS concentration and PS/ZVI molar ratio. Overall, the increase in PS concentration improved TOC removal, whereas an increase in PS/ZVI molar ratio negatively affected TOC removal efficiency. Several studies have been performed using ZVI and UV light as persulfate-activating methods in a batch system. For instance, Samarghandi et al. applied the PS/nanoZVI (nZVI) process to degrade azo dye under UV and achieved 94% degradation of Acid Red 14 and TOC removal of 82% under these conditions: [Acid Red 14] = 100 mg L⁻¹, [PS] = 8 mM, [nZVI] = 0.05 g L⁻¹

and pH 3 [41]. In the absence of UV light, it was possible to achieve 63% degradation of Acid Red 14. Additionally, Samarghandi et al. reported that the process' removal efficiency was increased by increasing the amount of nZVI from 0.01 to 0.05 g L⁻¹, but a further increase in nZVI dosage higher than 0.05 g L⁻¹ resulted in the enhanced opacity of the solution, which limited the UV light's ability to penetrate it and decreased the removal efficiency [41]. Sharifi et al. also investigated UV/PS/ZVI process using a batch reactor and reported about almost complete degradation of p-chlorophenol after 45 min at the following conditions: [p-chlorophenol] = 0.44 mM, [PS] = 3 mM, [nZVI] = 1 mM and pH 3 [59]. The authors also reported that the increase in ZVI concentration was favorable for the efficient degradation of the target compound; however, an increase in pH led to the precipitation of ferric ions. In another study, para-chloronitrobenzene (p-CNB) was degraded in soil using the PS/ZVI process by Kang et al. [33]. The authors reported that the rate of p-CNB degradation significantly increased from 10.8 to 90.1% with increasing the ZVI concentration from 0.1 mmol g⁻¹ to 1.0 mmol g⁻¹, demonstrating the ZVI's persulfate activation ability [33].

2.5. Optimization of the Continuous Flow UV/PS/ZVI Process

The response surface methodology is an effective method for process parameter optimization. For photo-Fenton and photo-Fenton-like systems, it has previously been successfully used [12,53]. In this work, the optimization part was conducted by means of the Minitab software (v.19). The predicted optimal experimental conditions in terms of TOC removal are shown in Table 3.

Table 3. RSM optimal conditions and experimental verification for TOC removal.

Wastewater	Space Time, Min	PS, mM	PS/ZVI Molar Ratio	Removal, %			Error
				TOC	TOC	CBZ	
				Actual	Predicted	Actual	
Synthetic	60	60	15	71.14	65	100	6.14
Real	50	50	15	60.48	65	100	4.52

RSM predicted process parameters for TOC removal were as follows: space time of 60 min, PS concentration of 60 mM, and PS to ZVI molar ratio of 15. Under these process conditions, the model predicted 65% TOC removal for the synthetic municipal wastewater. In practice, a 71.14% removal of TOC was achieved. The treatment of actual municipal wastewater was then carried out using the RSM-derived parameters. The space time and PS concentration values for the optimum treatment of the synthetic municipal wastewater were recalculated by correlating them to the TOC of the actual municipal wastewater. The following conditions were obtained: space time of 60 min, PS concentration of 60 mM, and PS to ZVI molar ratio of 15. The PS to ZVI molar ratio remained unchanged as it depended on the PS concentration. At these conditions, 60.48% removal of TOC was observed, which was significantly lower than for the synthetic municipal wastewater. A possible explanation could be the greater concentration of the radical scavenging agents such as inorganic carbon in real municipal wastewater ([TIC] = 77.8 mgL⁻¹) in comparison with synthetic wastewater ([TIC] = 32.8 mgL⁻¹), which could inhibit the process efficiency [12]. In the case of carbamazepine, CBZ was completely removed in both synthetic and real wastewater under optimum experimental conditions.

The continuous flow UV/PS/ZVI process has not been previously studied; there is scarce information in the literature regarding the application of persulfate oxidation in a continuous-flow mode in general. According to a study by Fan et al., continuous flow persulfate oxidation was utilized to successfully degrade Orange G in an aqueous solution, where biochar made from sludge and linked with manganese oxide was used to activate persulfate [60]. The authors reported that the increase in PS concentration from 1 to 5 mM promoted the dye degradation; however, a further increase did not lead to

significant change as excessive PS saturated the activation sites. Moreover, similarly to our work, the decrease in the flow rate from 1.2 mL min^{-1} to 0.4 mL min^{-1} improved the dye degradation from 10% to 60% [60]. On the contrary, Ishak et al. used the lab-scale continuous flow UV/PS system for the landfill leachate treatment and found no significant difference in COD removal between the flow rates of 50 mL min^{-1} and 100 mL min^{-1} [48]. The authors reported that about 70% removal of COD was achieved at the flow rate of 50 mL min^{-1} , PS of 12 mM, pH of 6, and reaction time of 10 h. In another study, utilizing persulfate oxidation in a continuous flow 3D electrode dynamic reactor, Yu and Pei treated landfill leachate [61]. They reported that the flow rate decrease from 1.5 L h^{-1} to 0.75 L h^{-1} improved ibuprofen degradation from 51% to 86 %; however, a further flow rate decrease down to 0.375 L h^{-1} and 0.1875 L h^{-1} resulted in 87.5% and 88% degradation of ibuprofen, respectively. Overall, they were able to remove 60% of the TOC at a flow rate of 0.75 L h^{-1} and a current density of 16 mA cm^{-2} [61].

3. Materials and Methods

3.1. Chemicals

Potassium persulfate ($\geq 99\%$), peptone, glucose monohydrate, ammonium chloride ($\geq 99\%$), anhydrous potassium monohydrogen phosphate ($\geq 98\%$), disodium hydrogenphosphate dehydrate ($\geq 98\%$), sodium hydrogen carbonate ($\geq 98\%$), sodium chloride ($\geq 99\%$), iron (III) chloride hexahydrate ($\geq 99\%$) were purchased from Fisher-Chemical. Lab lemco powder (TN 12.4, aminonitrogen 2.5, chloride 1.1) was obtained from Oxoid. Carbamazepine (analytical standard, $\geq 99.0\%$) and zero-valent iron (powder, $\geq 99\%$) were supplied by Sigma-Aldrich (St. Louis, MO, USA).

3.2. Wastewater Characteristics

The synthetic municipal wastewater composition was adapted from the ISO11733 Standard [62]. Table 4 provides information about its content.

Table 4. Synthetic wastewater composition adapted from ISO11733 Standard.

Content	Concentration, mg/L
Peptone	192
Lab lemco powder	138
Glucose monohydrate	19
Ammonium chloride (NH_4Cl)	23
Anhydrous potassium monohydrogen phosphate (K_2HPO_4)	16
Disodium hydrogenphosphate dihydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$)	32
Sodium hydrogen carbonate (NaHCO_3)	294
Sodium chloride (NaCl)	60
Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)	4
Carbamazepine	2

The real municipal wastewater was collected from the “Astana su arnasy” wastewater treatment plant after mechanical screening stage (Astana, Kazakhstan, $51^\circ 08' 35.9'' \text{ N}$ $71^\circ 20' 10.9'' \text{ E}$) in November, 2021. Table 5 lists the key analytical parameters for both synthetic and real municipal wastewater, including total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC), and pH.

Table 5. Characteristics of municipal and synthetic wastewater samples.

Type of Wastewater	TC, mg/L	TOC, mg/L	TIC, mg/L	pH
Synthetic	209.2 ± 3.3	176.3 ± 2.9	32.8 ± 1.2	7.65 ± 0.1
Real	223.6 ± 0.2	145.8 ± 0.2	77.8 ± 0.2	7.51 ± 0.1

3.3. Experimental Procedure

The sketch of the photochemical apparatus is shown in Figure 4. Photochemical experiments took place in a continuous-flow photoreactor. A detailed description of the photoreactor has been given in the previous work [56]. The photoreactor consisted of a 300 mL vessel and a UV lamp ($\lambda = 254$ nm, 10 W). The mixture consisting of wastewater, PS, and ZVI was mechanically stirred in a 300 mL glass cylinder. The space time of 20, 40, and 60 min corresponded to the flow rate of 15 mL min^{-1} , 7.5 mL min^{-1} , and 5 mL min^{-1} , respectively. The duration of each experiment depended on the order of the experiment in statistical design shown in Table 1. Standard deviation at central point was 1.09. pH was measured for both initial and final samples.

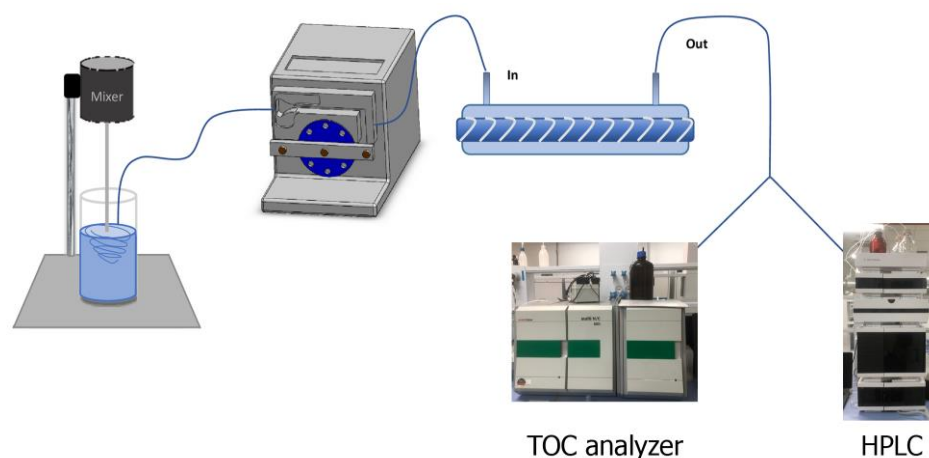


Figure 4. Experimental setup for CFPR.

3.4. Analytical Procedure

All samples were filtered using $0.2 \mu\text{m}$ glass fiber filters before analysis. Measurements of TC, TIC, and TOC were made using the Analytik Jena AG Multi N/C 2100S (Germany); the details of the measurement are given in previous work [11]. Five easy FE20 pH meter (Mettler Toledo, Greifensee, Switzerland) was used for pH measurements. Using an Agilent 1290 Infinity high-performance liquid chromatography (HPLC) system with an Agilent ZORBAX SB-C8 column (100×2.1 mm, particle size $1.8 \mu\text{m}$), carbamazepine (CBZ) was determined. Acetonitrile and water (in a ratio of 40:60) made up the mobile phase, and the flow rate was 0.35 mL min^{-1} . CBZ was monitored at 225 nm using 1290 Infinity Variable Wavelength Detector. Using scanning electron microscopy (SEM-EDS, Crossbeam 540, Zeiss, Germany) and a particle size analyzer (Mastersizer 3000, Malvern, United Kingdom), the specific surface area and particle size distribution of zero-valent iron were studied.

3.5. Statistical Design and Analysis

The experimental design was created using the statistical tool Design-Expert (v.13). Space time (min), PS concentration (mM), and PS/ZVI molar ratio were the three different corresponding variables in the design, which had three levels (-1 , 0 , and $+1$). (Table 6). Process optimization was carried out with the help of Minitab software (version 19).

Table 6. Independent variables and their levels in continuous flow UV/PS/ZVI process.

Symbol	Factor	Levels of Variables		
		-1	0	$+1$
A	Space time (min)	20	40	60
B	PS concentration (mM)	20	40	60
C	PS/ZVI molar ratio	5	10	15

There were 15 experiments used in the Box–Behnken design. Maximizing the TOC removal in both synthetic and real municipal wastewater was achieved by means of the response surface methodology (RSM).

4. Conclusions

In the present work, the continuous flow UV/PS/ZVI process was used to treat municipal wastewater spiked with carbamazepine. Synthetic municipal wastewater was first prepared and used for experiments. Box–Behnken design and response surface methodology were applied in combination to build the experimental design and optimize the process in terms of TOC removal. The RSM model was successfully applied since it effectively matched the experimental results, according to the analysis of variance. In the case of synthetic municipal wastewater, 71% of TOC and 100% of CBZ were removed at the space time of 60 min, PS concentration of 60 mM, and PS to ZVI molar ratio of 15. The RSM-derived optimum conditions were recalculated considering the TOC of the real wastewater, and 60% of TOC and 100% of CBZ were removed at the space time of 50 min, PS concentration of 50 mM, and PS/ZVI molar ratio of 15. This difference in TOC removal could be explained by the complex matrix of the real wastewater and the possible presence of radical scavenging agents. Overall, the response surface methodology proved to be an effective tool in wastewater treatment, which is of paramount importance as moving from synthetic to real wastewater is a highly challenging task.

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