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Article

An Optimization Study of Advanced Fenton Oxidation Methods (UV/Fenton–MW/Fenton) for Treatment of Real Epoxy Paint Wastewater

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Abstract: The use of various advanced oxidation methods in the treatment of wastewater has become the subject of many studies published in recent years. In particular, it is exceedingly significant to compare these treatment methods for industrial wastewater to reduce environmental effects and optimize plant operations and economics. The present study is the first to deal with the treatability of real epoxy paint wastewater (EPW) using MW- and UV-assisted Fenton processes within an optimization framework. A three-factor, three-level Box–Behnken experimental design combined with response surface methodology (RSM) was conducted for maximizing the chemical oxygen demand (COD) and color removal efficiencies of ultraviolet (UV)/Fenton and microwave (MW)/Fenton processes in the treatment of the real epoxy paint wastewater (EPW, initial COD = 4600 ± 90 mg/L, initial color = 114 ± 4 Pt-Co), based on 15 different experimental runs. Three independent variables (reaction time ranging from 20 to 60 min (UV) and from 5 to 15 min (MW), power ranging from 20 to 40 W (UV) and from 300 to 600 W (MW), and H_2O_2/Fe^{2+} ratio ranging from 0.2 to 0.6 (for both UV and MW)) were consecutively coded as *A*, *B*, and *C* at three levels (−1, 0, and 1), and four second-order polynomial regression equations were then derived to estimate the responses (COD and color removals) of two distinct systems. The significance of the independent model components and their interrelations were appraised by means of a variance analysis with 99% confidence limits (α = 0.01). The standardized differences of the independent variables and the consistency between the actual and predicted values were also investigated by preparing normal probability residual plots and experiment-model plots for all processes. The optimal operating conditions were attained by solving the quadratic regression models and analyzing the surface and contour plots. UV/Fenton and MW/Fenton processes, which constitute combined Fenton processes, were performed using advanced oxidation methods, while Fenton processes were utilized as the standard method for wastewater treatment. When UV/Fenton and MW/Fenton processes were applied separately, the COD removal efficiencies were determined to be 96.4% and 95.3%, respectively. For the color parameter, the removal efficiencies after the application of both processes were found to exceed 97.5%. While these efficiencies were achieved in 1 h with a 38 W UV unit, they were achieved in 15 min with a MW power of 570 W. According to the RSM-based regression analysis results, the R^2 values for both processes were greater than 0.97 and *p* values were less than 0.003.

Keywords: epoxy paint wastewater; Fenton; microwave Fenton; ultraviolet Fenton; wastewater treatment

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1. Introduction

Paint consists of a blend of solvents, binders, additives/fillers, and suspended pigments in liquid form, serving as both a decorative coating and a protective material [1]. The "paint carrier" is defined as a mixture of solvent and binder, and the additives and pigment are diffused along this carrier. The compound's type and the ratios of the paint specify its characteristics. Paints are categorized as acrylic, alkyd or synthetic, cellulosic, epoxy, and polyurethane, depending on the type of resin content [2]. Epoxy resins are oligomers characterized by the presence of one or more epoxide groups in each molecule. They are synthesized through the reaction of phenols with epichlorohydrin in the presence of NaOH. The initial production of epoxy resins in the U.S. was carried out by Devoe & Raynolds Co., Inc. (NY, USA) [3]. Resins are preferred for their many advantageous properties, such as good mechanical and physical performance at high temperatures, low volatility while curing, high chemical and electrical resistance, excellent adhesion to various types of surfaces, and good adhesion to all substrates [3]. These exceptional characteristics are important reasons why epoxy resins are used as adhesives in concrete surface coatings; in the industry of paint surface coating; in dentistry, surgery, and prosthesis applications; in space fields and satellite applications; in electronic devices; in automobiles and plastics; as filling compounds in vessels; in decorative flooring; and in various aircraft production stages [1]. So far, few studies have been conducted on treating epoxy acrylate monomer industrial wastewater with high levels of organic compounds. As a result, efficient techniques should be created to produce wastewater effluent that is readily treated biologically in wastewater treatment plants or discharged into a body of water [4]. To achieve this, treatability experiments utilizing chemical and sophisticated oxidation techniques are required to treat epoxy paint wastewater properties [5].

The advancement of the paint industry aligns with progress in civil engineering and other interconnected industrial sectors. As a result, overall paint production has been increasing day by day; nevertheless, this increase also causes the high production of industrial wastewater. Hence, the paint industry is one of the industries which need to be evaluated in terms of their effects on the environment, particularly the aquatic ecosystem. Effluent generated by paint manufacturing facilities originates from packaging machines, floors, mixers, and the cleaning of reactors. Cleaning activities and products constitute 80% of the waste from the paint industry [6].

There is a challenge in the characterization of paint industry wastewater in terms of pollution parameters, such as physical, chemical, and biological parameters, due to the specific production type of each industrial unit [7]. Paint industry wastewater has a high pH level and is generally dark in color; it has low biodegradability and includes various heavy metals (e.g., Al, Cu, Cr, Zn and Pb) and a high amount of organic matter [8]. The discharge of toxic and colored wastewater not only causes visual pollution but also gives rise to deterioration in the water quality of receiving environments, inhibiting light transmission; this could be toxic for aquatic life and food chain organisms [8]. Accordingly, paint industry wastewater must be treated by a convenient method for both environmental health and economic reasons before being discharged into receiving waters. Various wastewater treatment methods, such as chemical treatment methods, methods using advanced oxidation processes (AOP), adsorption, and membrane processes, have been applied [8,9], and they have advantages and disadvantages [9]. For instance, adsorption studies were carried out with NiO and MgO silicate-based nanosorbents in the treatment of dye wastewater, and high removal efficiencies were achieved in synthetically prepared solutions [10]. There are also studies on pigment wastewater using membrane processes, and the removal of ionic type pollutants has also been examined [11]. Additionally, the removal of heavy metals and color from paint industry wastewater using polymers was also examined and high removal efficiencies were achieved [12]. Apart from dye wastewater, removal studies have been carried out with the photocatalytic degradation method on the treatment of tannery wastewater, and a 60% chemical demand oxygen (COD) removal could be achieved in this highly polluted wastewater [13]. Various auxiliary nanoparticles are also used in photodegradation. In a study using cadmium oxide (CdO) nanoparticles for this purpose, a dye removal efficiency of over 97% was achieved [14]. It has been noted that paint industry wastewater is toxic, but its components are stable. Due to these characteristics, advanced oxidation methods such as Fenton and Fenton-like (ultraviolet (UV)/Fenton, ozone/Fenton, microwave (MW)/Fenton, etc.) are efficient in the treatment of this type of wastewater [15,16].

Advanced oxidation methods have been used for many years and are especially preferred for pollutants that are difficult to remove [4,17]. The basic logic of this method is to remove especially organic pollutants in wastewater with its strong oxidant structure [18]. The most known of the processes is the Fenton process. The Fenton process consists of the reactions between hydrogen peroxide (H_2O_2) and homogeneous Fe^{2+}/Fe^{3+} catalysts [19]. Fenton reactions produce hydroxyl radicals, and these radicals are quite effective for the removal of stable paint wastewater components and toxins [20]. However, classical Fenton processes should be employed in a strong acid environment (pH < 3.0) to ensure the optimal removal of contaminants and to prevent the hydrolysis of Fe^{3+}. Furthermore, non-recyclable soluble Fe salts produce Fe_2O_3 sludge, which must be controlled before disposal [21].

There are many studies conducted with AOP, especially for the removal of synthetically prepared dye solutions. In these studies, up to a 100% herbicide removal rate and up to an 80% total organic carbon (TOC) removal rate were observed [22]. In a study conducted with a $LaCuO_3$ perovskite catalyst, a removal rate of 64.4% was achieved in a synthetically prepared Tartrazine solution under ultraviolet (UV) light irradiation [23]. Laterite soil was used as an iron source in the treatment of synthetic water containing 3-aminopyridine using the Fenton process, and it was observed that removal efficiencies ranged from 40% to 100%, depending on the iron dose added at the end of a 5 h period [24]. In a study using Fenton and Fenton-like wet oxidation processes, which are also used in the removal of organic radioactive waste, an organic matter removal rate of up to 99% was achieved [25].

Fenton reactions can be accelerated, and their efficiency can be increased by using different catalysts [26]. Ozone [27], ultrasound [28], and UV-assisted [29] studies have been carried out in this regard. In addition to these processes, microwave-assisted studies have been carried out in recent years [30]. The comparison of this process with other Fenton processes is limited [31]. It is considerably essential to optimize the operating conditions of Fenton and Fenton-like processes [27]. In this field, the response surface methodology (RSM) has been widely used in the literature [32]. It is noted that the Fenton process has a high organic matter removal potential. However, further increases in yield and reduction in treatment time may be possible. For this aim, adapting reaction accelerating factors, such as UV/MW, to the existing classical Fenton process can be beneficial in terms of efficiency increases. For example, in a Fenton- and photo-Fenton-based study conducted by Torrades and García-Montaño [33], a 5–15% increase was achieved in COD reduction from textile wastewater. Similarly, Carbajo et al. [34] reported a 10–20% difference between the classical Fenton process and the photo-Fenton process for TOC removal from landfill leachate wastewater effluent. In a study conducted by Yang et al. [35], it was observed that a 55% COD removal rate was achieved in 6 min with a power of 300 W using the MW/Fenton process for the treatment of highly concentrated pharmaceutical wastewater. Moreover, UV- and MW-supported Fenton studies showed remarkable results in terms of both acceleration and detoxification efficiency. The efficiency of Fenton, MW/Fenton, and UV/oxidant processes was reported in the treatment of a mixture of higher concentrations of azo dyes [36,37].

Although there are several studies in the literature on the classical Fenton process for the treatment of paint wastewater [38,39], there is no comparative study on the treatment of real paint wastewater with these extensively used methods. It should be noted that studies on MW-assisted Fenton processes are extremely limited in the literature. However, the present study, dealing with the treatment of real epoxy paint wastewater (EPW), consists of both the classical chemical treatment and Fenton processes. In addition to the classical Fenton processes, the current study is the first to include treatability studies using MW- and UV-assisted Fenton processes and compare these two processes within an optimization framework. Therefore, the primary aim of the present study is to determine and compare the performances of these two methods on the treatment of epoxy paint wastewater (EPW) and thus to pave the way for new developments by contributing to this field that seems untouched in the literature. Besides, the optimization of results has been carried out using a three-factor, three-level Box–Behnken experimental design combined with response surface methodology (RSM).

Based on the foregoing facts, the specific objectives of this study are as follows: (1) to characterize real EPW with low biodegradability for advanced Fenton oxidation studies; (2) to perform a series of treatability studies using UV- and MW-assisted Fenton processes as an advanced oxidation method and to compare their performance in the same wastewater; (3) to employ a three-factor, three-level Box–Behnken experimental design combined with RSM for maximizing the chemical oxygen demand (COD) and color removal efficiencies of UV/Fenton and MW/Fenton processes in the treatment of real EPW; (4) to create normal probability residual plots and experiment-model plots for the implemented processes using an optimization scheme; and (5) to demonstrate the treatability of a real and recalcitrant paint-based industrial effluent in a short time and with high efficiency through sophisticated oxidation processes.

2. Materials and Methods

2.1. Origin of Epoxy Paint Wastewater (EPW) and Characteristics

Industrial effluent was provided from a paint manufacturing facility within the Bursa Organized Industrial Zone (Bursa, Turkey). The effluent was stored at 4 °C until the analyses. Preceding each analysis, the EPW samples were acclimated to room temperature and subjected to a preliminary assessment of their components. The evaluation was carried out during the supernatant phase due to the extremely fast precipitation of the particulate matter content in the EPW. Due to the extremely rapid sedimentation of the particulate matter content in the EPW, the evaluation was performed during the supernatant phase.

The procedures described in the Standard Methods [40] were performed to determine the analytical parameters for the collected EPW samples. Assessed parameters were chemical demand oxygen (COD), color, pH, conductivity, and salinity. The COD was determined by using a thermoreactor (Hach Lange DRB 200, Hach Co., CO, USA) according to the Standard Method 5220 C (closed reflux titrimetric method). The color of EPW samples were measured by using a Hach Lange DR 5000, Hach Co., CO, USA spectrophotometer and determined spectrophotometrically as Pt–Co (platinum–cobalt) color unit according to the Standard Method 2120 C. The electrical conductivity (EC) was recorded by using a multimeter instrument (Hach Lange HQ 40D, Hach Co., CO, USA) based on the procedure described in the Standard Method 2510 B. Additionally, pH and salinity of EPW samples were measured using the multimeter device used for EC analysis. In this work, the analyses were performed at least three times to guarantee repeatability.

The characteristics of EPW used in the study are given in Table 1. According to the literature review, these parameters were selected as the most efficient ones [6,41]. Additionally, no evidence of iron was found in the wastewater. When the relevant literature was examined, it was seen that five different heavy metals were examined in wastewater containing five different paints, and the iron parameter was not examined in any of them [42]. For example, even if iron is present in the wastewater, it will be at the mg/L level, which may be negligible compared to the iron dose used in the advanced oxidation study.

Table 1. Properties of the raw wastewater generated from epoxy paint application (EPW) used in the study.

Parameters	COD	Color	pH	Conductivity	Salinity
Values/Units	4600 ± 90 mg/L	114 ± 4 Pt-Co	7.5 ± 0.5	1810 ± 60 µS/cm	1.11 ± 0.02%

2.2. Chemicals and Treatment Procedure

In the experimental studies, 1 N sodium hydroxide (NaOH, ≥99.0%) and 1 N sulfuric acid (H_2SO_4, ≥98.0%) were used for the adjustment of the pH values of the sample solution. Additionally, iron sulfate heptahydrate ($FeSO_4.7H_2O$, 99.5%) and hydrogen peroxide (H_2O_2, 30% (*w*/*v*)) were utilized for UV/Fenton and MW/Fenton processes, respectively. All chemicals utilized were procured from Merck Chemical Company (Darmstadt, Germany), were of analytical grade, and were used without any additional purification. Distilled water was employed in the formulation of the requisite solutions during the study.

For the UV/Fenton studies, the treatment process was carried out using a UVC multi lamp ultraviolet system (Eurotech Water Treatment Technol., Eurosan Water Treatment Syst. Indy Trade Joint Stock Co., Istanbul, Turkey) and a 304 stainless-steel UV reactor with a capacity of 500 mL. The pH was adjusted to 3.5 after adding the predetermined amounts of $FeSO_4.7H_2O$ (2.5 gr) and H_2O_2 (4 mL of 30%), and then the reaction was initiated by stirring the solution at 200 rpm for 2 min [43–45]. The sample was then placed in the UV reactor, and this reactor operated at certain power values (given in the next section) for a certain period of time. Following the completion of the reaction period, 450 mL of wastewater was decanted from the supernatant and transferred into a 500 mL beaker. Thereafter, the pH was increased to between 7.5 and 9.0, and the reacted solution was allowed to precipitate for 60 min. Since the pH was adjusted after adding Fe^{2+} and H_2O_2 to the sample, there was no significant pH change in the subsequent processes (during the reaction period). After the reaction period, the pH was immediately increased (e.g., >8.5), minimizing the effect of the possible presence of residual peroxide. After the precipitation process, the supernatant sample was collected for the subsequent color and COD analyses. It is noted that a small amount of peroxide may remain in the samples, and this may cause interference in the COD analysis. To prevent this formation, the remaining peroxide was first evaporated by keeping it at 50 °C for 30 min [41], then the residual peroxide concentration was measured using the permanganometric method before COD measurements [46]. No residual peroxide was found except for three samples with very low concentrations.

MW/Fenton experiments were conducted by using a 23-L microwave oven (MS23F300EEK, 800 W, Samsung, Istanbul, Turkey) similarly to the UV/Fenton studies and with the same H_2O_2/Fe^{2+} ratios as in the UV/Fenton process. However, in MW/Fenton studies, MW was used instead of UV as the Fenton catalyst. This also made it easier to compare the two processes. On the other hand, the experimental procedure (i.e., adding predetermined amounts of agents, pH adjustment during the reaction, pH increase after the reaction, preventing peroxide/radical from interfering with COD removal) was the same as the UV/Fenton process. It is noted that the initial concentrations of iron and hydrogen peroxide used in the experimental studies were selected according to a previous study [5]. A pictorial diagram is shown in Figure 1 for a visual understanding of the present investigation.

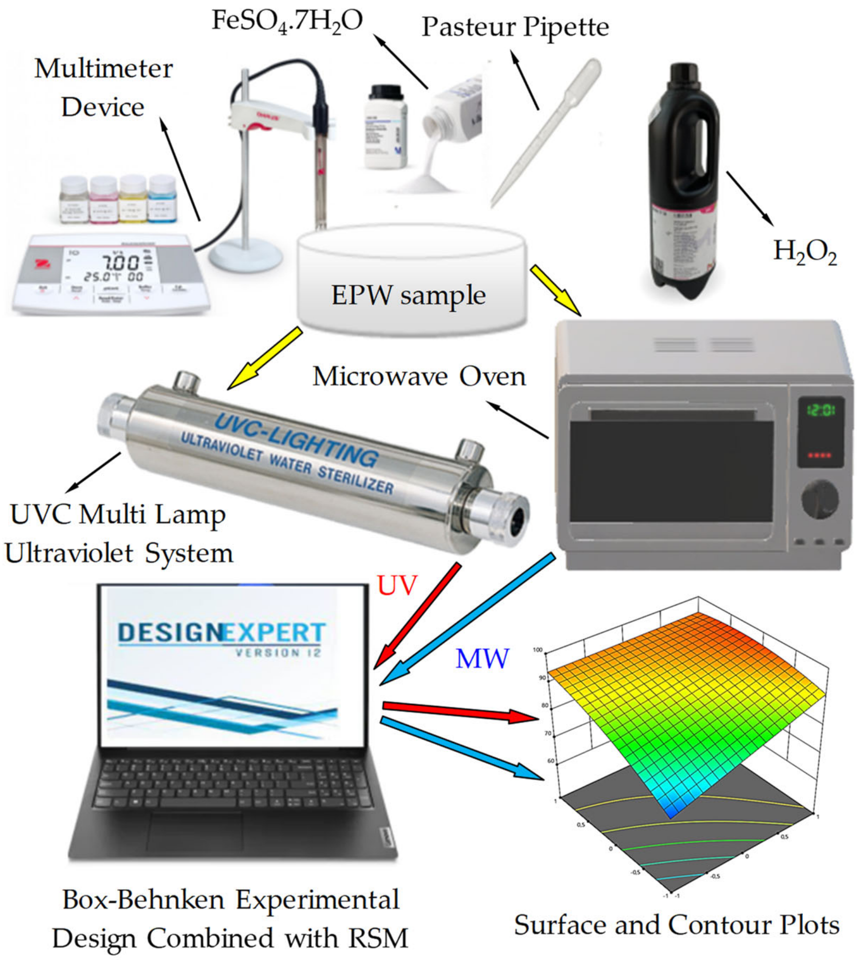

Figure 1. Pictorial diagram of the treatment process used for the advanced oxidation of EPW.

2.3. Box–Behnken Experimental Design

The operational conditions for all tests and the testing protocol designed using the Box–Behnken experimental design with three factors and three levels are presented in Tables 2 and 3, respectively. Since the operating parameters in Fenton and UV- and MW-assisted Fenton processes are very dependent on each other, the number of physical and chemical factors is kept low in the current experimental design. As a matter of fact, it is seen that three factors and three levels are used in the relevant literature [5,47–50]. One of the benefits of Box–Behnken designs is that they are all spherical and only need three levels of each factor running [51]. Table 3 shows that the proposed design contains only 15 experimental runs, compared to 27 experimental points in a 3^3 full factorial design. It is therefore important to note that by choosing the Box–Behnken experimental design over the full factorial design, several extra experiments have been avoided in this work. Moreover, a suitable equation derived in terms of coded factors can be used to estimate the response for the specified levels of each factor. High levels and low levels of the factors are coded as "+1" and "−1", respectively. The coded equation is a useful tool to identify the relative effect of factors by comparing factor coefficients.

In the present analysis, model variables and administered doses were selected in accordance with a previous work [5]. Additionally, Fenton stoichiometry [52] and synergistic effects [53] were also taken into account in this study. It is noted that although all processes have interrelated parameters, power and time are partially related in terms of the choice of certain independent variables. Notwithstanding the correlation between the $COD/H_2O_2/Fe^{2+}$ ratios, particularly in the Fenton process, the results in Table 3 demonstrate that the operating parameters chosen for this investigation were appropriate.

Table 2. Experimental range and levels of independent factors conducted for UV/Fenton and MW/Fenton processes.

Processes	Factors	Levels		
		−1	0	+1
UV/Fenton	Time (min) (*A*)	20	40	60
	UV (W) (*B*)	20	30	40
	H_2O_2/Fe^{2+} (*C*)	0.20	0.40	0.60
MW/Fenton	Time (min) (*A*)	5	10	15
	MW (W) × 10 (*B*)	30	45	60
	H_2O_2/Fe^{2+} (*C*)	0.20	0.40	0.60

Table 3. Design matrix based on the Box–Behnken approach with three factors and three levels.

Run	Levels			UV/Fenton COD Rem. (%)	UV/Fenton Color Rem. (%)	MW/Fenton COD Rem. (%)	MW/Fenton Color Rem. (%)
1	0	1	−1	74.5	95.1	71.6	91.6
2	−1	0	1	69.2	92.8	67.4	88.7
3	−1	0	−1	52.3	82.5	51.7	81.3
4	1	0	−1	57.1	85.6	56.1	84.4
5	0	0	0	61.7	91.9	61	89.2
6	1	−1	0	68.2	90.2	67.5	90.2
7	1	1	0	95.5	97.8	89.6	95.2
8	0	0	0	61.1	93.1	59.6	92.4
9	0	0	0	60.8	92.5	58.2	91.5
10	0	−1	1	63.4	94.4	61.4	93.4
11	−1	1	0	79.4	94.6	78.6	93.1
12	0	−1	−1	41.1	74.2	42.2	72.6
13	1	0	1	94.6	98.7	92.7	97.2
14	0	1	1	93.5	97.6	91.6	96.1
15	−1	−1	0	44.6	86.3	42.5	84.2

For two distinct processes (UV/Fenton and MW/Fenton), modeling and statistical analyses were carried out utilizing response surface methodology and regression analysis. Each process consisted of three replicates, and each replicate contained three parameters at varying levels. The optimization of each process was applied individually. In the last step, the comparison was performed on each optimization's regression coefficients. Statistical modeling, the generation of the results, and graphics were performed using Design Expert® software (Version 12.0.0, Stat-Ease Inc., Minneapolis, MN, USA). Response surface methodology (RSM) contains processes for optimizing factorial variable settings so that the response achieves the intended maximum, minimum, or target value. Within the implemented software, the optimization module looks for a set of factor levels that satisfy the criteria for each of the factors (e.g., reaction time, UV or MW power, H_2O_2/Fe^{2+} ratio) and responses (e.g., COD and color removal efficiencies) at the same time. A response needs to have a model fit through analysis or be provided through an equation-only simulation in order to be included in the optimization criterion [51]. Several procedures, including weighted linear functions (developed by Derringer and Suich), can be used to convert the response levels into desirability scores. Design Expert® aggregates individual desirabilities into a single value using Derringer and Suich's optimization technique, and then looks for the maximum overall desirability.

3. Results

3.1. Optimization of UV/Fenton Process

An optimization study was carried out in consideration of time (min), H_2O_2/Fe^{2+} ratio, and UV power (W) and an equation was obtained (Equation (1)). Accordingly, "*A*" represents time, "*B*" represents UV power, and "*C*" represents H_2O_2/Fe^{2+} ratio.

$$COD\ Removal\ Efficiency\ (\%) = 61.2 + 8.74 \times A + 15.7 \times B + 11.96 \times C + 5.45 \times A^2 + 5.28 \times B^2 + 1.65 \times C^2 - 1.88 \times A \times B + 5.15 \times A \times C - 0.825 \times B \times C \quad (1)$$

Regression coefficients and a variance analysis of each equation were also determined in in terms of ease of evaluation. When the results were analyzed on residual plots (normal probability plot), it was found that the data were normally distributed. The consistency of the experimental results with the model results for the COD parameter is shown in Figure 2. Moreover, the standardized differences and experiment-model plots for the color parameter are shown in Figure 3.

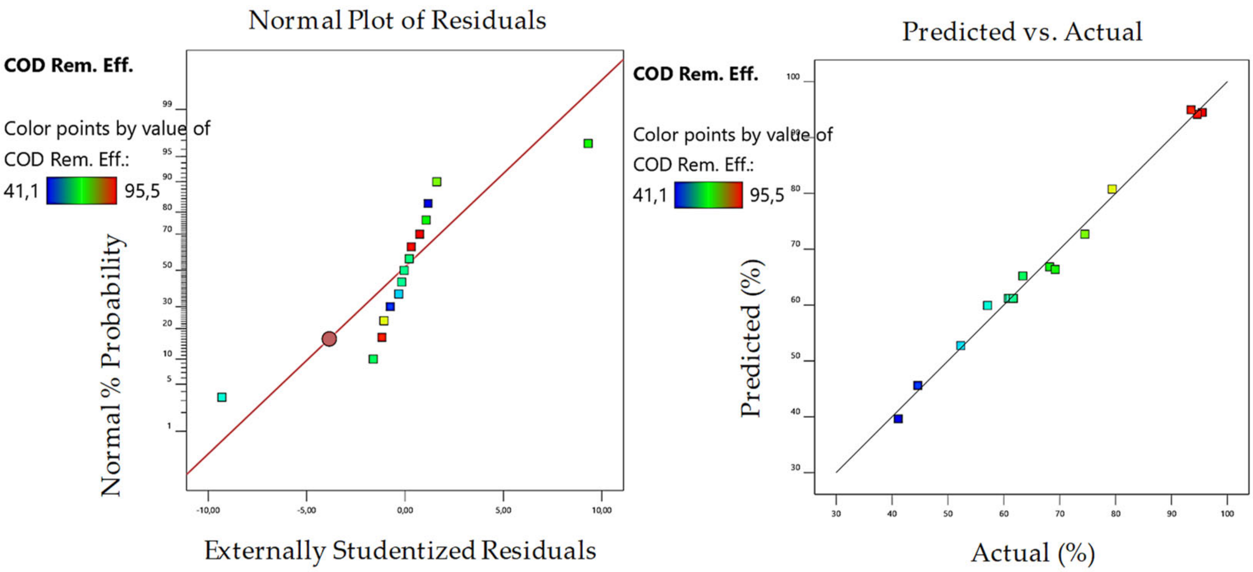

Figure 2. Normal probability residual plot and predicted vs. actual plot based on chemical oxygen demand (COD) removal efficiency values for the UV/Fenton process.

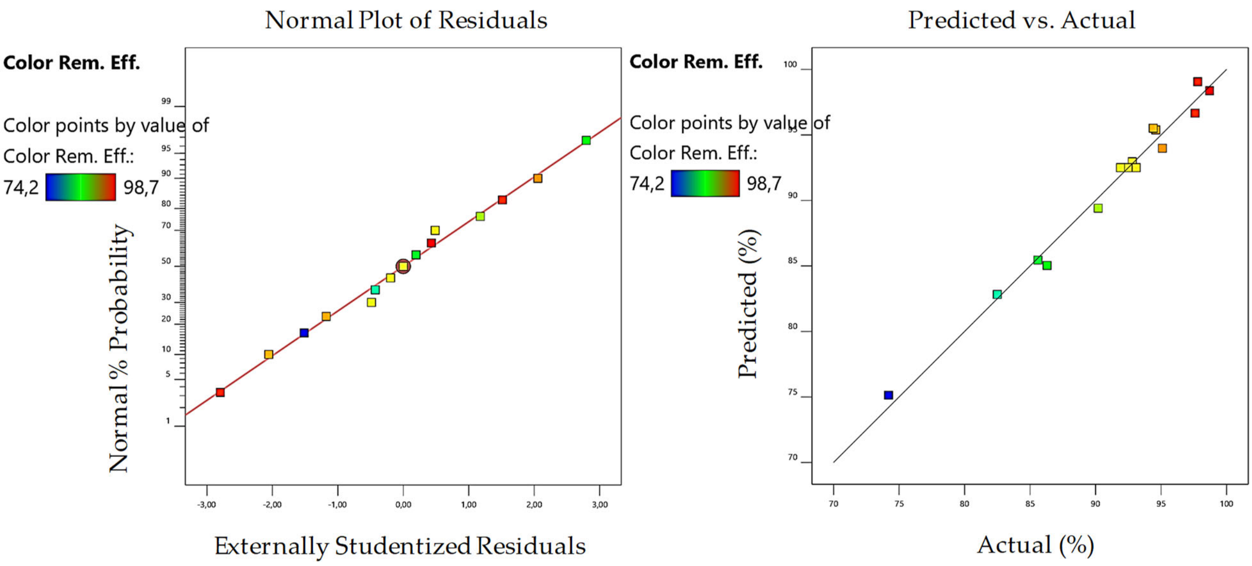

Figure 3. Normal probability residual plot and predicted vs. actual plot based on color removal efficiency values for the UV/Fenton process.

Equation (2) was obtained when the regression analysis and optimization study of the UV/Fenton process were performed for the color parameter.

$$\begin{aligned} &Color\ Removal\ Efficiency\ (\%) \\ &= 92.5 + 2.01 \times A + 5.0 \times B + 5.76 \times C - 0.35 \times A^2 + 0.075 \times B^2 - 2.25 \times C^2 \\ &- 0.175 \times A \times B + 0.7 \times A \times C - 4.43 \times B \times C \end{aligned} \quad (2)$$

These removal efficiencies are slightly higher compared to findings of other studies in the literature [6]. The reason for this situation is thought to be related to the structure of water. Since there are not enough studies with epoxy paint wastewater (EPW) in the literature, the findings are compared with the textile sector. The surface and contour graphs generated with the help of the equations (Equations (1) and (2)) obtained after the optimization of the UV/Fenton process are given in Figure 4.

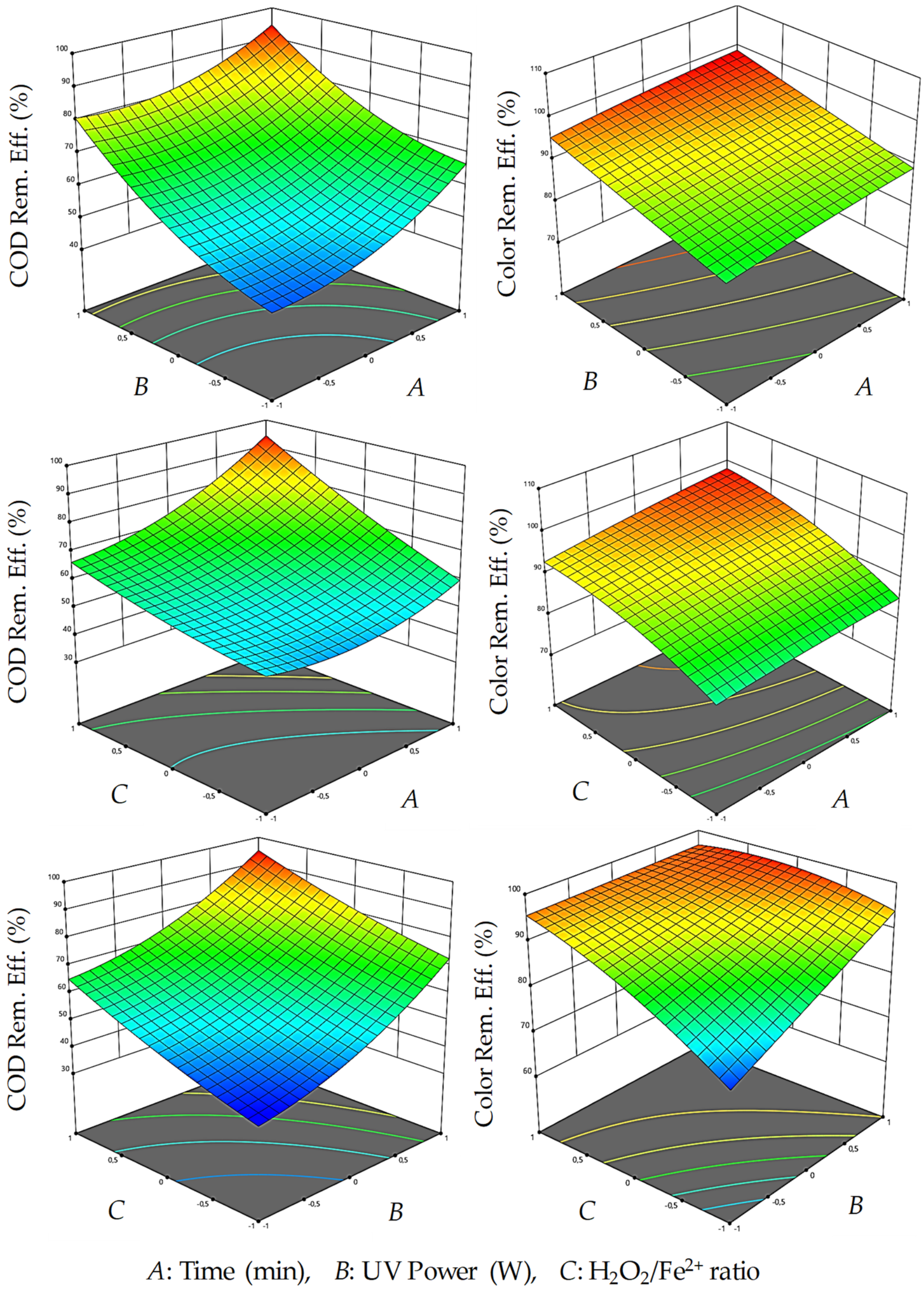

Figure 4. Surface and contour plots generated to illustrate the removal of pollutants, specifically addressing COD and color, through the UV/Fenton process.

Although the efficiency of COD removal has been found to be in the range of 45% and 95% (as depicted in Figure 4), as expected, it has been understood that the most important parameters were the applied UV power and H_2O_2/Fe^{2+} ratio. When the color removal efficiencies were examined, a removal rate between 75 and 95% was observed. This finding coincides with the data in other scientific reports [54,55].

3.2. Optimization of MW/Fenton Process

At this point in the research, operational parameters similar to those used for the UV/Fenton processes were selected to make the comparison more accurate, as shown in Table 1. An optimization study was performed with MW power, H_2O_2/Fe^{2+} ratio, and time as operating conditions [7]. The regression equation obtained as a result of the optimization of the MW/Fenton process is given in Equation (3). In this equation, *A*, *B*, and *C* represent the time (min), MW power (W), and H_2O_2/Fe^{2+}, respectively.

$$COD\ Removal\ Efficiency\ (\%) = 59.60 + 8.21 \times A + 14.72 \times B + 11.44 \times C - 3.50 \times A \times B + 5.22 \times A \times C + 0.2 \times B \times C + 5.11 \times A^2 + 4.84 \times B^2 + 2.26 \times C^2 \quad (3)$$

Upon analyzing the residual plots, specifically the normal probability plot, it was determined that the data exhibited a normal distribution. The consistency of the experimental results with the model results for the COD parameter is also shown in Figure 5.

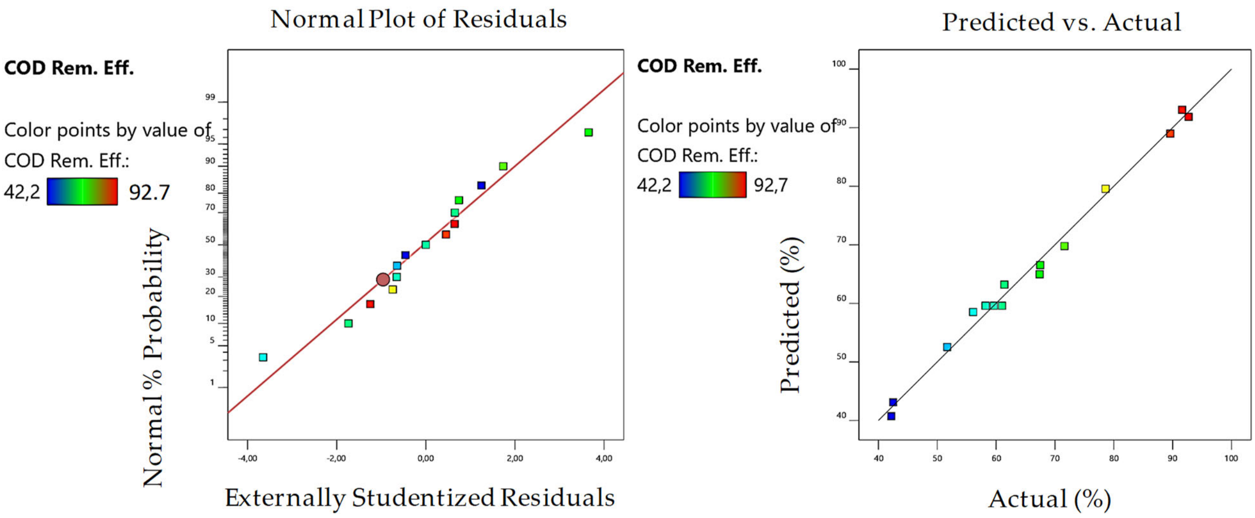

Figure 5. Normal probability residual plot and predicted vs. actual plot based on chemical oxygen demand (COD) removal efficiency values for the MV/Fenton process.

Equation (4) was attained when the regression analysis and optimization study of the MW/Fenton process were performed for the color parameter.

$$Color\ Removal\ Efficiency\ (\%) = 91.03 + 2.46 \times A + 4.45 \times B + 5.69 \times C - 0.9750 \times A \times B + 1.35 \times A \times C - 4.08 \times B \times C - 0.4417 \times A^2 + 0.0833 \times B^2 - 2.69 \times C^2 \quad (4)$$

The residual plots and predicted vs. actual plots obtained for the color parameter are shown in Figure 6, showing that the model results are representative of the experimental results.

Surface and contour plots of the MV/Fenton process created using Equations (3) and (4) are illustrated in Figure 7.

Although the efficiency ranged between 40% and 95% (as shown in Figure 7), it has been observed that the most effective parameters for the MW/Fenton process were the power and H_2O_2/Fe^{2+} ratio, as expected. These results are consistent with the literature data [8].

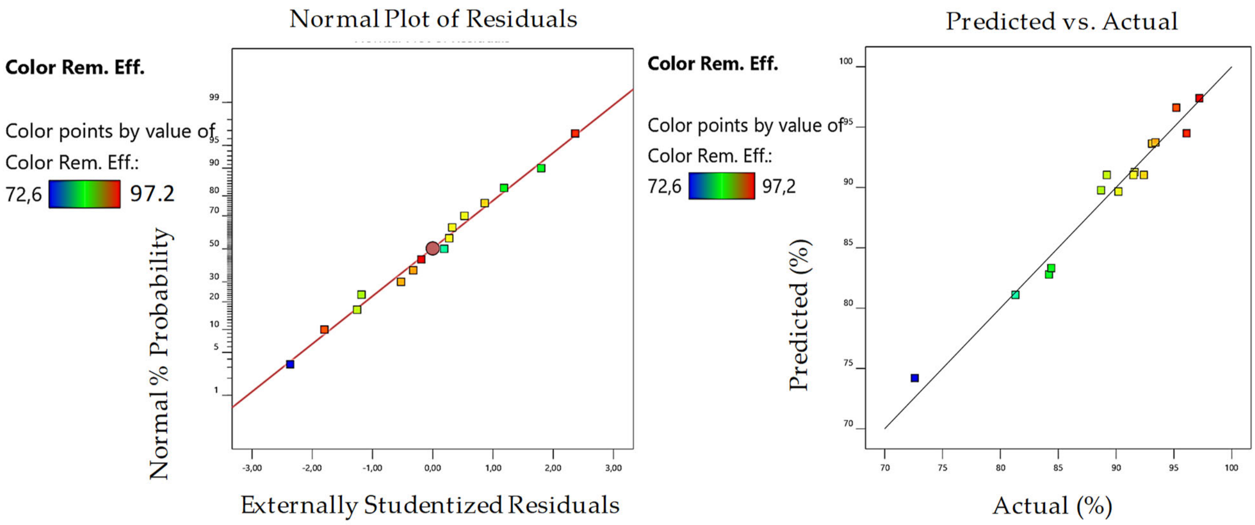

Figure 6. Normal probability residual plot and predicted vs. actual plot based on color removal efficiency values for the MV/Fenton process.

The derived models underwent a thorough evaluation, involving the scrutiny of the regression coefficients and variance analysis [56]. The corresponding regression values and optimal operating conditions for each study are detailed in Table 4.

Table 4. A comparison of optimized processes in relation to efficiency and statistical measures.

Processes/Parameters	UV/Fenton COD		UV/Fenton Color		MW/Fenton COD		MW/Fenton Color	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real
R^2	0.9918		0.9841		0.9917		0.9697	
p Value	0.0001		0.0006		0.0001		0.0028	
Time (min) (*A*)	1	60	1	60	1	15	1	15
UV (W) (*B*)	0.9	38	0.9	38	-	-	-	-
MW (W) (*B*)	-	-	-	-	0.8	570	0.8	570
H_2O_2/Fe^{2+} (*C*)	0.4	0.48	0.4	0.48	0.8	0.56	0.8	0.56
Model Predictions	97.35		98.44		99.89		97.2	
Experimental Results	96.41		97.89		95.25		97.5	

Upon reviewing Table 4, it becomes evident that the regression coefficients for all four models are notably high. Additionally, the results were found to be statistically significant at a very high level ($p < 0.01$). When these results are evaluated, it could be stated that processes are slightly more successful in terms of chemical material utilization, but both UV and MW processes, which are advanced models, have been found to give consistent outcomes regarding both efficiency and the model compatibility. This state supports the findings of previous studies [57]. Particularly, in classical Fenton studies applied in the same water, a COD removal efficiency of 88.6% could be reached in 1 h [5]. In other wastewater treatments, the duration is around 1–2 h [58]. In these processes, both higher removal efficiencies (>95% for COD) were achieved at the end of 15 min, especially with the MW/Fenton process.

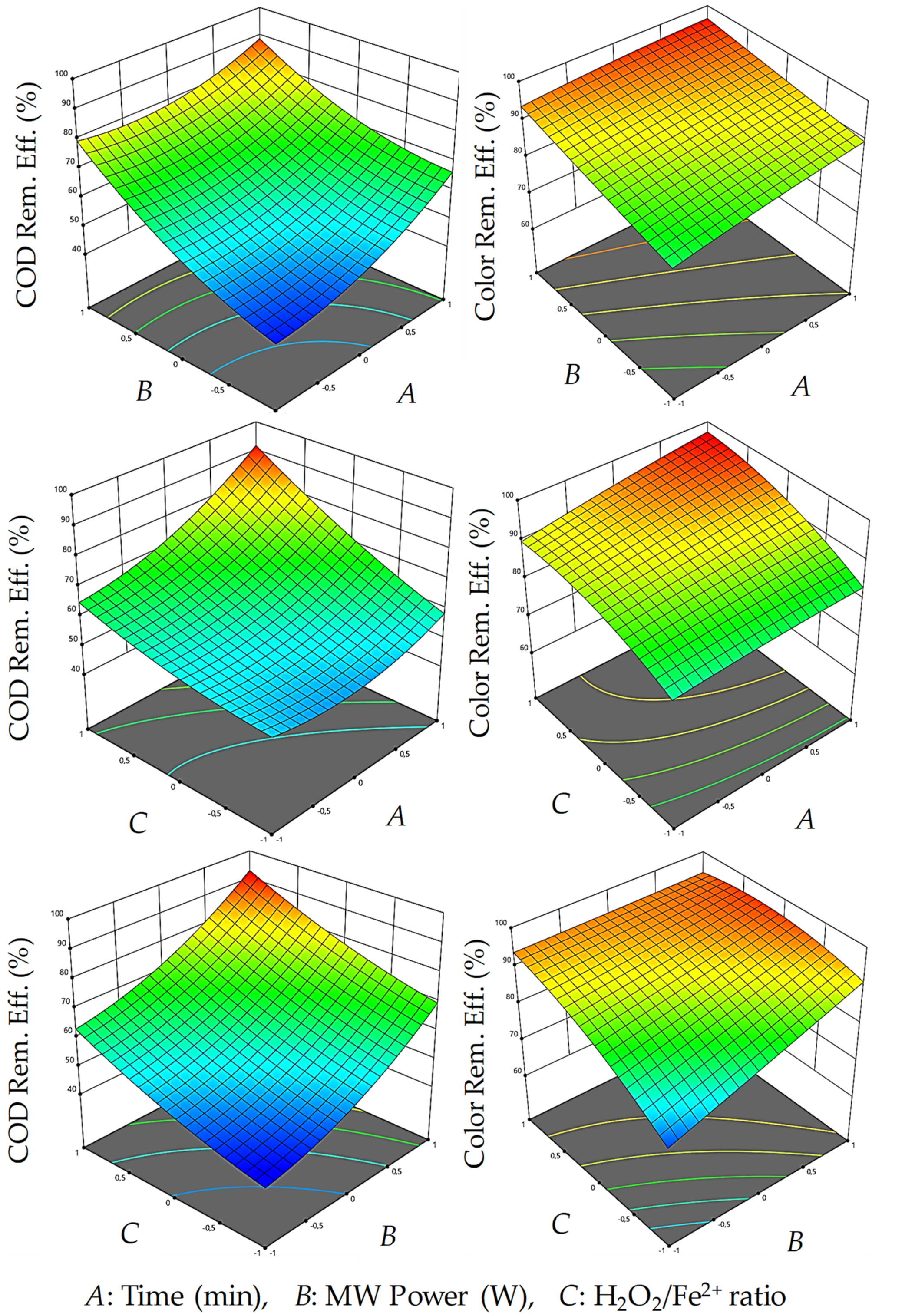

Figure 7. Surface and contour plots generated to illustrate the removal of pollutants, specifically addressing COD and color, through the MW/Fenton process.

4. Discussion

The difficulties of the model building process include basic stages such as defining the problem, collecting sufficient data, creating a mathematical model, and developing a solution suitable for the model. Defining the current problem can be expressed as the most important and most difficult stage of the model creation process. During the problem definition phase, critical research is carried out such as clearly determining the purpose of the model (e.g., maximization and minimization), defining the factors affecting the purpose (what the decision maker can and cannot control), and determining the constraints. In the data collection phase, data are collected under certain standards experimentally (through observation), from the relevant literature, field conditions, expert opinions, or using computer technology (automatically). While creating the numerical model for the purpose of measuring the performance of the system, the types of decision variables, their activity levels (operating limits), parameters (i.e., constants used in the objective function and constraints), and the objective function, depending on the decision variables, must be expressed mathematically accurately. It should be noted that modeling the system and finding a solution to the developed mathematical model are different concepts. In the solution phase, the most appropriate approach, such as simulation techniques, mathematical analysis techniques (such as regression analysis), optimization techniques, and heuristic or meta-heuristic techniques, should be investigated in detail. In addition, the success/performance of the model should be tested with a sufficient number of suitable statistical performance indicators. In other words, modeling studies should be handled in an integrated manner with statistical science. Moreover, the number of variables in the model should not be so insufficient that the model does not represent the real situation or so excessive that it makes the model too complex for practical applications. For this purpose, unnecessary or low-contributing variables should be eliminated with appropriate techniques. For the applicability of the model, it is also very important to verify it with real data. As a result, even a well-established forecasting model will have a certain approximation error. The tolerance for this error must be determined accurately by the researcher/data analyst according to the characteristics of the actual process being modeled.

When the relevant literature data are examined, it is seen that epoxy paint wastewater studies are limited [5]. In addition, although there are studies with classical chemical processes, there are almost no studies with different catalyzed Fenton reactions. In the present study, MW- and UV-catalyzed Fenton studies were conducted, extending the previous classical chemical methods and Fenton processes, and it has been observed that the long time (1–2 h) [59–61], which is one of the most important disadvantages of the Fenton process, can be reduced to 15 min. This is on average a quarter of the time of conventional Fenton studies [46]. In addition, the amount of sludge was also observed to be less compared to traditional Fenton studies. Based on all these issues, it was concluded that the MW/Fenton process gave better results than the UV/Fenton process, and the UV/Fenton process gave better results than the classical Fenton process. Furthermore, within the scope of this study, it was observed that the duration of the Fenton process could be shortened, and the efficiency could be increased with different catalysts (e.g., MW, UV). This will serve as a guide for future studies.

Since in this study, a maximum of 40 W was used in the UV/Fenton process and a minimum of 300 W was used in the MW/Fenton process (Table 2), it can be seen that the optimized times (Table 4) are reasonable for existing processes. When the relevant literature is examined, it is seen that the reaction can be completed in 10–15 min in the MW-assisted Fenton process, which means that the removal efficiency obtained during this timeframe is sufficient for the treatment of EPW. The main purpose of the UV/Fenton study is to make the relatively long-term classical Fenton studies shorter and more efficient [62]. It is clear from the current results that this goal was achieved by the advanced oxidation process applied for treatment of EPW (Table 4). MW/Fenton investigations, on the other hand, have been commonly employed in the literature for shorter time periods because of the solution loss over a longer duration [35].

Considering the Fenton stoichiometry, it seems that 2.125 units of H_2O_2 and 3.5 units of Fe^{2+} are required for 1 unit of COD removal, but in the literature, attempts have been made to obtain high removal efficiencies by using lower H_2O_2/Fe^{2+} ratios [52]. Regarding the effect of this ratio on the current process, it was seen that when the H_2O_2/Fe^{2+} ratio increased under equivalent operating conditions (Run 4 and Run 13), the COD removal, which was 57.1% in the UV/Fenton study, increased to 94%. In the MW/Fenton study under equivalent operating conditions, it was observed that while COD removal was 56.1%, the removal efficiency reached up to 92.7% when the H_2O_2/Fe^{2+} ratio increased.

In a study comparing classical Fenton processes, UV-assisted H_2O_2 processes, and UV/Fenton processes, removal efficiencies of 40%, 50%, and 60% were achieved, respectively, at the end of a 1 h period [62]. In a different advanced oxidation study, while the antibiotic removal efficiency obtained by the conventional Fenton process was only around 70% at the end of a 3 h period, it was observed that this removal efficiency reached up to 90% with the UV-assisted process under the same operating conditions [63]. Additionally, in another study where the microwave-assisted Fenton process was applied, a removal efficiency of around 60% was achieved after 6 min [35].

It is noted that there is a dearth of comparative studies on the application of MW- and UV-assisted Fenton processes to the treatment of actual epoxy paint wastewater, despite the fact that numerous studies have been conducted on the traditional Fenton method for paint wastewater treatment. Since epoxy paint was used instead of normal paint in the current study, it may not be appropriate to make a direct comparison for data obtained from studies involving textile dyes or residential paints. Nonetheless, Table 5 presents the performance comparison of research primarily focused on exterior paints for residential buildings.

Table 5. A comparison of some different methodologies applied in paint wastewater treatment with respect to COD removal.

Wastewater	Treatment Method	COD Removal Efficiency	Reference
Paint wastewater	Biological (Aerobic)	43%	[64]
Epoxy paint wastewater	Chemical Coagulation	44%	[5]
Epoxy paint wastewater	Electrocoagulation	48%	[5]
Water-based paint wastewater	Adsorption	62%	[65]
Water-based paint wastewater	Electrooxidation	68%	[6]
Water-based paint wastewater	Fenton	80%	[38]
Water-based paint wastewater	UV/Fenton	81%	[66]
Epoxy paint wastewater	UV/Fenton MW/Fenton	96.4% 95.3%	This study

Furthermore, when looking at sector-based studies, it can be said that the BOD/COD ratio (i.e., biodegradability index) of the epoxy paint wastewater is around 0.2–0.3. Therefore, it would be much more logical and appropriate to treat such recalcitrant wastewater with chemical or even advanced oxidation processes rather than biological treatments. For example, the biodegradability of this type of wastewater can be increased using effective oxidation techniques such as the Fenton process. Thus, long-chain non-biodegradable compounds can be converted into smaller-chain biodegradable compounds after the oxidation process [67].

In recent years, the use of environmentally friendly approaches in the treatment sector has become increasingly important. A study comparing electrocoagulation, Fenton, and membrane distillation procedures to treat paint industry effluent found that the Fenton process is more sustainable and environmentally benign than the other methods [68]. Since the end products in advanced oxidation processes are carbon dioxide and water, there is no need to examine the toxicity resulting from the post-treatment process [69]. The residual peroxide that may remain in the effluent prevents the possible toxicity [70]. It is also known that the current method increases the level of biodegradability [67]. Finally, since very high removal efficiencies can be achieved with the AOP-based methods, pollutant concentrations in the purified water are almost non-existent. This shows that the advanced oxidation technique is a method that benefits ecology.

5. Conclusions

In this study, the feasibility of treating real epoxy paint wastewater was investigated using two distinct processes. In addition to testing different applications, modeling studies were carried out employing the methodology of response surface analysis and the evaluation of these modeling results were also conducted. As a general evaluation, it was observed that Fenton processes have consistent findings concerning both effectiveness and the model data compared to advanced oxidation processes. Using only Fenton process (i.e., UV and MW power not applied), the efficiency remained at 68%, and therefore, we aimed to increase the removal efficiency by using different processes. To facilitate a straightforward comparison, pH, added Fe, and current values were maintained at consistent levels. Although this rate could reach 96% experimentally using advanced oxidation processes, up to a 98% removal rate could be achieved according to the model results. While a 68% COD removal rate was obtained at the end of 60 min with classical Fenton processes for COD removal in this study, a 96.4% COD removal rate was achieved after UV catalysis was applied in the same amount of time. A color removal rate of 97.9% is also achieved under similar operating conditions. In the MW-catalyzed studies, similar efficiencies (95.3% and 97% for COD and color, respectively) could be achieved in a quarter of the time (15 min). The regression values and optimal operating conditions revealed that R^2 values > 0.984 and p values < 0.028 were found in all models. This proved that the implemented RSM-based strategy worked consistently and appropriately.

Given the paucity of previous research on the treatment of real EPW, the current study has made a significant contribution to filling the literature gap in this field. Faster and more efficient models of the traditional Fenton process have been studied in the treatment of real EPW. In this respect, the current study is the first research on this subject, as there is no comparative study of UV/Fenton and MW/Fenton processes for the treatment of real EPW. Therefore, the significance of the current work is demonstrated by the lack of prior research comparing these two distinct processes in the same wastewater. In this study, which is unique in this respect, both comparison and optimization studies of UV/Fenton and MW/Fenton studies were carried out and very high regression coefficients were achieved. As a result, a COD removal rate of over 95% and a color removal efficiency of over 97% in a period of 15 min are very important in the treatment of a recalcitrant wastewater such as real EPW. Consequently, this study revealed that real epoxy paint effluent, which has not been extensively researched previously and which has a low biodegradability, could be significantly treated using sophisticated oxidation techniques such as UV- and MW-assisted Fenton processes.

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