Environmental Research and Technology
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https://doi.org/10.35208/ert.872647

Research Article

Textile wastewater treatment by uv/fenton-like oxidation process using Fe-Cu doped pumice composite

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ARTICLE INFO

Article history
Received: 02 February 2021
Revised: 25 June 2021
Accepted: 05 July 2021

Key words:
Cu-Fe-pumice composite catalyst; SEM-EDX; UV/Fenton like process; textile wastewater

ABSTRACT

In this study, Fe-Cu-Pumice (Fe-Cu-P) composite was prepared to attempt it for UV/Fenton-like treatment of biologically treated textile wastewater by means of COD and color removal. SEM-EDX analysis showed that Fe-Cu-P composite contained Fe and Cu at 3.5% of each one. More than 95% color (RES-436, RES-525, RES-620) removal could be achieved using 3 g/L Fe-Cu-P in the Fenton-like process. The removal of COD and absorbances at Abs-254 nm and Abs-280 nm increased up to 5 g/L Fe-Cu-P concentration. In addition, the highest COD, Abs-254 nm and Abs-280 nm removal could be achieved at 250 mg/L H_2O_2 concentration pH 3. The removals of COD, Abs-254 nm and Abs-280 nm were obtained to be 63.7%, 66.3% and 72.9%, while the removals of RES-436, RES-525 and RES-620 were observed as 92.9%, 96.7% and 98.1%, respectively at optimum doses of catalyst (5 g/L Fe-Cu-P), oxidant (250 mg/L H_2O_2) and pH 3 after 3 h oxidation at room temperature.

Cite this article as: Çifçi Dİ, Meriç S. Textile wastewater treatment by uv/fenton-like oxidation process using Fe-Cu doped pumice composite. Environ Res Tec 2021;4(3):206–218.

INTRODUCTION

The textile industry, one of the largest industries worldwide, has the highest water consumption [1]. Since textile wastewater has high stability and low biodegradability, includes toxic dyes, treatment by conventional wastewater treatment processes is difficult [2, 3], thus advanced oxidation processes (AOPs) have gained importance. Among advanced oxidation processes, Fenton process is one of the most favoured one as it provides advantageous such as high efficiency, inexpensive, low reaction time, and easy application [4, 5]. On the other hand, Fenton oxidation has also some disadvantages such as excessive iron sludge. Thus, coating iron oxides on composites have been developed for AOPs applications [6, 7]. Studies have been carried out on dye or organic matter removal with Fenton-like and Photo Fenton-like oxidation processes by iron coated materials such as activated carbon, zeolite and clay and it was stated that these processes improved removal of dye or organic matter [4, 7, 8]. Dükkancı et al. (2010) reported a 100% removal of 100 mg/L Rhodamine 6G dye after 45 min of Fenton-like oxidation using a 1 g/L CuFeZSM-5 zeolite catalyst and 40 mmol H_2O_2 amounts at pH 3.4 [9]. The best Reactive black 5 (RB5) dye removal was obtained as 89.2% with 0.5 g/L catalyst of iron (III) oxide doped on rice husk ash and 4 mM H_2O_2 at pH 3 and 100 mg/L initial RB5 concentration

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by Fenton-like oxidation [10]. In addition, it was stated that the iron doped on materials such as zeolite and clay showed very good stability, and the iron concentration in treated wastewater was below 2 mg/L, which is the discharge standard in the EU directive [11, 12].

Having a high specific surface area and porous structure, pumice has been widely used for dye and metal adsorption [13]. Successful and remarkable results have been obtained in dye removal using the Fenton-like oxidation process with the synthesized magnetic iron coated pumice [14]. Furthermore, Fenton-like oxidation process proved the maximum COD, UV_{254}, UV_{436}, UV_{525} and UV_{620} removals to be 79.7%, 92.7%, 91.7%, 95.6% and 98.2% respectively using 7.5 g magnetite pumice composite catalyst at 500 mg/L H_2O_2, pH 3 during 120 min oxidation for a wastewater originated from a textile chemicals production industry [15].

However, the use of pumice bi-metal coated with Fe and Cu in the UV/Fenton-like oxidation process has not been studied so far that the aim of this study is to investigate the treatment of a biologically treated textile wastewater by Fenton-like oxidation process. For this purpose, the effect of Fe-Cu-P composite concentration, H_2O_2 concentration and pH on UV/Fenton like process performance was assessed in terms of COD, absorbances at 254 nm and 280 nm and color (RES-436, RES-525, RES-620) removal.

MATERIALS AND METHODS

Materials

The chemicals namely $CuSO_4.5H_2O$ (Cat No: 1.02790), hydrogen peroxide (H_2O_2 35% wt, Cat No: 1.08600), $FeCl_3.6H_2O$ (Cat No: 1.03943), NH_3 (25%, Cat No: 1.05422), $FeSO_4.7H_2O$ (Cat No: 1.03965), HCl (Cat No: 1.00314), HNO_3 (Cat No: 1.00456) and NaOH (Cat No: 1.06462) were purchased from Merck. All aqueous solutions were prepared using bidistilled water.

Treated Textile Wastewater

Biologically treated textile wastewater was collected from a dyeing and finishing textile industry located in Corlu, Tekirdag, Turkey. The sample kept at refrigerated (+4°C) without adding any conservative during analysis.

Synthesis of Fe-Cu-Pumice Composite (Fe-Cu-P)

Pumice was obtained from Nevşehir, Turkey. The particle size of pumice powder ranged from nano to micron (0–125 microns). $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ were first dissolved in 200 mL distilled water with the molar ratio of 2 between Fe^{3+} and Fe^{2+} in the solution according to literature [16, 17]. $CuSO_4.5H_2O$ was added into solution. Final Fe:Cu:Pumice ratio was adjusted to 5:5:100 as weight basis. An amount of 100 g pumice was added to this solution and the pH of the solution was adjusted to 9.5 by adding 6 N NaOH. The solution was ultrasonicated for 15 min and heated at 70°C for 1 hour. A 5 mL NH_3 solution was added into and stirred for 24 hours at room temperature. After 24 hours, composite was rinsed with distilled water for several times to remove dissolved ions from composite. Finally, the composite catalyst was dried at 105°C.

UV/Fenton-Like Oxidation Experiments

The UV/Fenton-like experiments were carried out in a UV Photoreactor equipped with ten UV-A light lamps (Philips, 8W, 350 nm wavelength). 3x2 lamps were positioned at left and right sides and 4 lamps were positioned on the top of the reactor. The lamps were switched off for 15 min as the dark adsorption process before starting the experiments. The experiments were carried out in 200 mL treated textile wastewater samples at a constant room temperature (25°C). pH was adjusted to the desired values by dosing 1 M NaOH and 1 M H_2SO_4. The effects of composite concentration, pH, H_2O_2 concentration on the process efficiency were studied ranging their values at the intervals of 1–5 g/L, 2–4 and 75–250 mg/L respectively.

Analysis

The wastewater samples were characterized for chemical oxygen demand (COD), total suspended and volatile solids (TSS and VSS), conductivity (WTW Cond 3210 Set 1 (2005), total khejdahl nitrogen (TKN) and ammonia-nitrogen (NH4-N), alkalinty, and pH (WTW pH 315i) parameters according to Standard Methods [18]. Absorbances at 254 nm and 280 nm and color (RES-436, RES-525, RES-620) were measured with a UV-Vis spectrophotometer (Shimadzu UV-2401) using 1 cm path length quartz cuvettes. Due to the aromatic nature of some organic compounds in wastewater, especially double bonds and aromaticity were characterized by Abs-254 nm and Abs-280 nm measurement, respectively [19].

Fe-Cu-Pumice composite was characterized by scanning electron microscope (SEM)-energy dispersive X-ray analyzer (EDX). FTIR analysis was performed using Bruker VERTEX 70 ATR in the range of 400–4000 cm^{-1}. The pH_{pzc} of the composite was determined according to the literature [20].

RESULTS AND DISCUSSION

SEM Analysis

SEM analysis and EDX profile of Fe-Cu-P composite are given in Figure 1. It is seen that Fe-Cu-P has irregular character. EDX spectrum of Fe-Cu-P composite showed that oxygen and silisium were the major elements. Fe-Cu-P mainly contains 50.9% O, 23.3% Si, 5.2% Al, 1.3% K, 12.5% Na, 0.22% Ca, 3.5% Fe and 3.5% Cu. It can be seen from Figure 1b that nano iron and copper particles were successfully doped on the surface of pumice as confirmed by EDX spectrum that Fe and Cu contents were at 3.5% in Fe-Cu-P

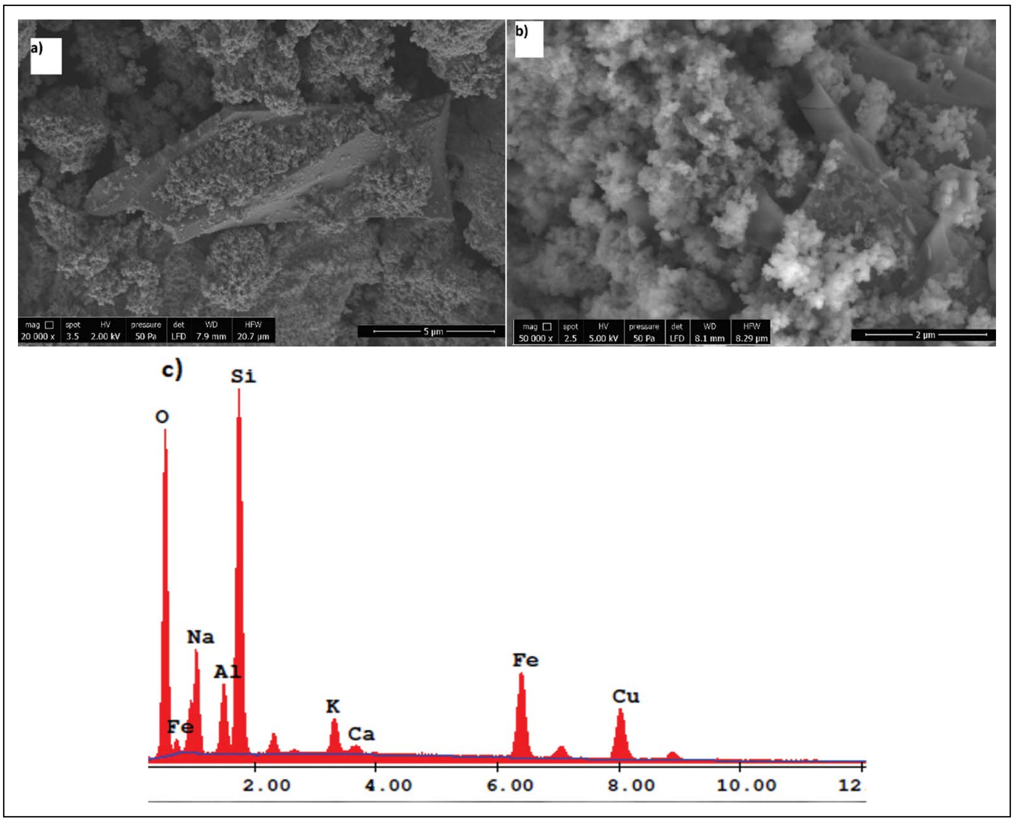

Figure 1. SEM images of Fe-Cu-P composite (a) 20000X (b)50000X (c)EDX analysis.

composite (Fig. 1c). The success of Fe and Cu coating on pumice in this study confirmed the study by Su [21] that coated zeolite with Fe and Mn metals for Fenton like oxidation of Reactive Brilliant blue dye.

FTIR analysis of Fe-Cu-P is given in Figure 2. At 995 cm^{-1} as the strongest peak is the Si-O-Si or Si-O-Al stretching vibration in pumice [22, 23]. The peak observed at 617 cm^{-1} is thought to be caused by Fe-O bond vibration [24, 25]. In addition, the peaks at 437 cm^{-1} and 617 cm^{-1} could also be due to Cu-O bonds [26, 27].

The pH_{pzc} is important to evaluate surface charge of the composite synthesized. If the solution pH is lower than pH_{pzc}, composite surface is positive and this provides a high adsorption capacity of anionic pollutants. On the contrary, if the pH of sample is above than the pH_{pzc}, surface of composite can be negative charged and this provides the increasing adsorption of cationic pollutants [20]. The value of pH_{pzc} was measured to be 5.87 and 10.09 of P and Fe-Cu-P composite, respectively. High value of pH_{pzc} of Fe-Cu-P composite gained affinity of a wide range anionic pollutions for adsorption.

Characterization of Biological Treated Textile Effluent

Characterization of the sample is given in Table 1. COD and color values need further removal according to Zero Discharge Hazardous Chemicals Limits [28].

Table 1. Characterization of biological treated textile wastewater

Parameter		Unit	Biological treatment effluent
pH		-	7.74
Conductivity		Ms/cm	4.2
Alkalinity		mg $CaCO_3$/L	251±1.3
TSS		mg/L	115±7.1
TVSS		mg/L	80±5.7
COD		mg/L	246±4.5
TKN		mg/L	67±7.5
Ammonia Nitrogen		mgNH_4-N/L	37±3.4
Abs-254 nm		Abs	3.544
Abs-280 nm		Abs	2.848
	RES-436	Abs	0.66
Color	RES-525	Abs	0.852
	RES-620	Abs	0.468

Effect of Fe-Cu-P Concentration on UV/Fenton-Like Process Efficiency

The effect of Fe-Cu-P composite amount on the removal of Abs-254 nm and Abs-280 nm is given in Figure 3. As can be seen in Figures 3a and 3b, Abs-254 Abs-280 significantly decreased by increasing catalyst dose. Above 2 g/L catalyst dose, both Abs-254 and Abs-280 gradually decreased up to 1.5 oxidation time and after that time the absorbances started to decrease down during 3 h oxidation time. The highest Abs-254 (66.3%) and Abs-280 (68.6%) removal was ob-

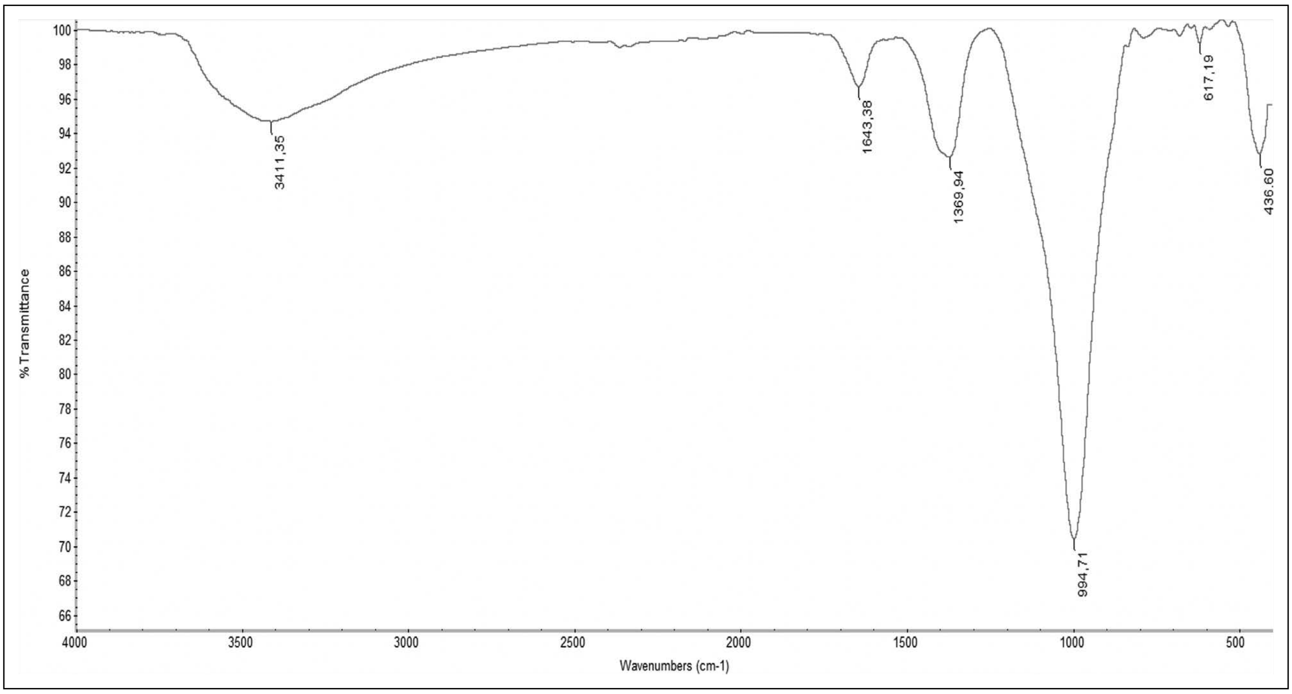

Figure 2. FTIR analysis of Fe-Cu-P composite.

tained with 5 g/L Fe-Cu-P composite dose at pH 3 and 250 mg/L H_2O_2. The effect of Fe-Cu-P amount on color removal (RES-436, RES-525 and RES-620) is given in Figure 4. The color (RES-436, 525 and 620) remained low in 1 g/L Fe-Cu P amount. RES-620 removal was seen to be similar in 2–5 g/L Fe-Cu-P amounts and over 98% removal was achieved. RES-525 and RES-620 removals were similar when Fe-Cu-P amounts of 4 and 5 g/L were used. After 3 hours of oxidation at 5 g/L Fe-Cu-P, the removal of RES-436, RES-525 and RES-620 were obtained as 95.6%, 98.7% and 98.9%, respectively.

The removal of COD using different Fe-Cu P amounts was given in Figure 5. While color removals were observed close at 2–5 g/L Fe-Cu P amounts, COD removal increased as the amount of Fe-Cu P increased in parallel with Abs-254 nm and Abs-280 nm removals. When increasing the amount of Fe-Cu-P composite from 4 to 5 g/L, the COD removal efficiency incremented from 53.7% to 63.7%, respectively. Not only organic matter removal but also aromatic structure degradation could be achieved in the treatment of textile wastewater by Fenton-like oxidation using Fe-Cu-P composite. Since the highest Abs-254 nm, Abs-280 nm and COD removal efficiencies were obtained at 5 g/L Fe-Cu-P, the optimum Fe-Cu-P amount was determined to be 5 g/L. Comparing with the previous literature, the removal of absorbance, color and COD was obtained lesser than the study that used 7.5 g of magnetite pumice composite as catalyst [15].

Effect of H_2O_2 Concentration on UV/Fenton-Like Process Efficiency

The changes of Abs-254 nm and Abs-280 nm removals depending on time and varying H_2O_2 concentration in the range of 75–250 mg/L, were given in Figure 6. While Abs-254 nm and Abs-280 nm removals were not observed below 150 mg/L H_2O_2 concentration, Abs-254 nm and Abs-280 nm removals improved from 19.2% to 66.3% and 36.0% to 72.9%, respectively when the H_2O_2 concentration was increased from 150 mg/L to 250 mg/L. At 250 mg/L H_2O_2 concentration, Abs-254 nm and Abs-280 nm removals continued for 2 hours, and no significant change in removals was observed after 2 hours of oxidation.

Similar removals of RES-436, RES-525 and RES620 were observed at all H_2O_2 concentrations. The RES-620 removal increased over 90% after 2 hours of oxidation, while RES-436 and RES-525 removals enhanced to above 90% after 2.5 hours (Fig. 7).

In parallel with Abs-254 nm and Abs-280 nm removals, COD removal was also achieved above 150 mg/L H_2O_2 concentration (Fig. 8). Altogether, the removal of Abs-254 nm and Abs-280 nm were obtained as 66.3% and 72.9% respectively at 250 mg/L H_2O_2 which were lower than a previous study [15].

Effect of pH on Textile Wastewater Treatment Using UV/Fenton-Like Process Efficiency

The changes of Abs-254 nm and Abs-280 nm obtained with different pH values at 5 g/L Fe-Cu P amount and 250 mg/L H_2O_2 concentration are given in Figure 9. As seen in the figure, Abs-254 nm and Abs-280 nm removal was dropped at pH 2 and 4 values, and when the pH was increased from 2.5 to 3, Abs-254 nm removal enhanced from 57.7% to 66.3% and Abs-280 nm removal increased from 65.0% to 72.9%.

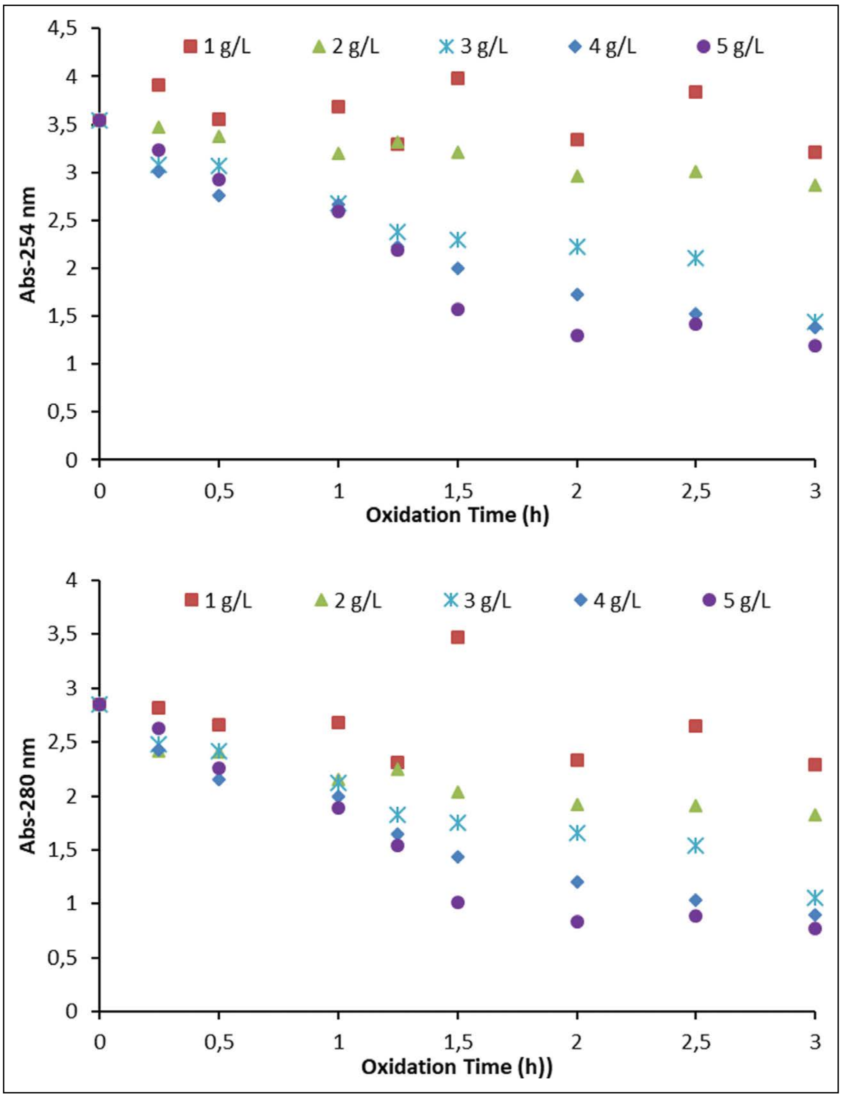

Figure 3. Effect of Fe-Cu-P catalyst amounts on the removals of Abs-254 nm and Abs-280 nm (pH: 3, H_2O_2 concentration: 250 mg/L)

Although the color removals (RES-436, RES-525 and RES-620) were similar in the pH range of 2–3, the removal of all colors at pH 4 values decreased (Fig. 10). RES-436, RES-525 and RES-620 removals were continued for 2 hours in the pH range of 2–3, and after 2 hours of oxidation, color removal as RES-436, RES-525 and RES-620 was observed over 90% between pH 2–3. RES-436, RES-525 and RES-620 removal were 92.9%, 96.7% and 98.1% at pH 3 after 3 hours oxidation. Both color and aromatic substance removals could not observed at pH 4. Although color removal observed at pH 2, aromaticity removal was low at Abs-280 nm and no removal was achieved at Abs-254 nm.

The COD removal at different pH values is given in Figure 11. Although the color removal as RES-436, RES-525 and RES-620 were similar in the pH range of 2–3, it was seen that the removal of COD, Abs-254 nm and Abs-280 nm gradually increased as pH increased from 2 to 3. The COD removal increased from 16.4% to 63.7%, when the pH was enhanced from 2 to 3 and 50.2% of COD could be achived at pH 2.5. In this study, optimum pH was obtained as 3 and this is generally the case in Fenton oxidation because H_2O_2 and HO. redox potentials decrease with increasing pH and H_2O_2 stability decreases at higher pH values [4]. In addition, iron hydro-complex which has the more photoactive properties become to dominate at near pH 3, as the pH increases less photo-active iron species begin to active and dominate [29, 30].

Kinetic Evaluation of UV/Fenton-Like Process

The first order kinetic values obtained in this study are given in Table 2. The k_1 values for Abs-254 nm and Abs-280 nm were calculated with the data obtained in the first 2 hours as there was no significant change in Abs-254 nm

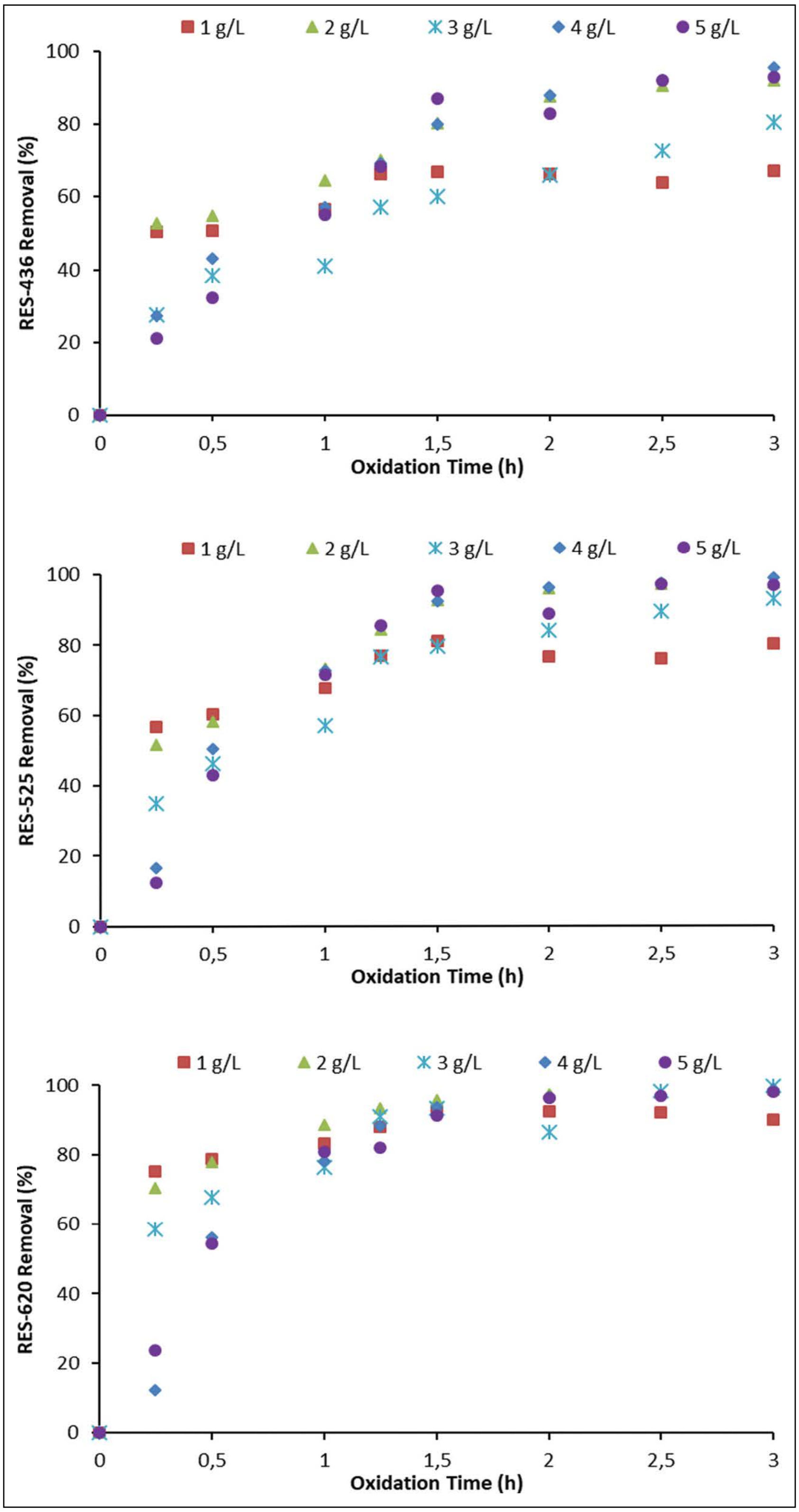

Figure 4. Effect of Fe-Cu-P amounts on color (RES-436, RES-525 and RES-620) removal (pH: 3, H_2O_2 concentration: 250 mg/L)

and Abs-280 nm in the 2–3 hours interval. With the same reason k_1 was calculated from the data obtained within the first 1.5 hours as the removal of RES-436, RES-525 and RES-620 occurred within the first 1.5 hours [14, 29]. Above a 90% removal of RES-436, RES-525 and RES-620 could be achieved at 5 g/L Fe-Cu-P composite concen-

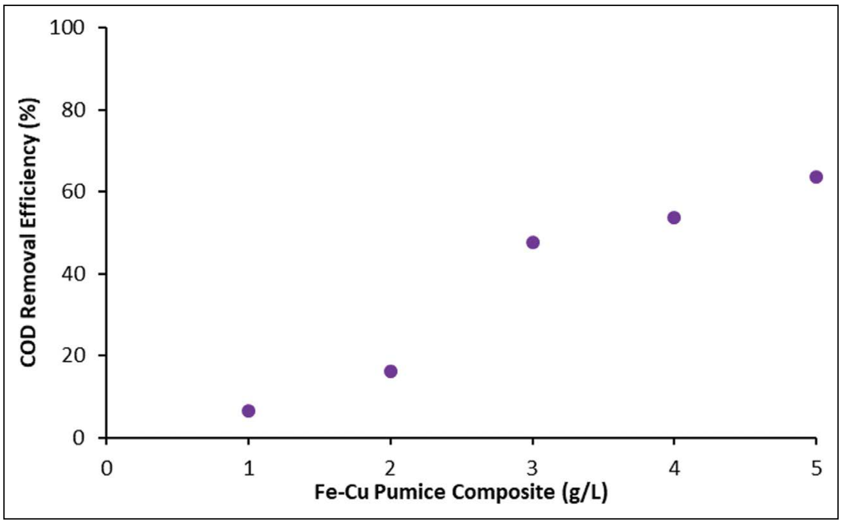

Figure 5. COD removal at varying amount of Fe-Cu-P composite (pH: 3, H_2O_2 concentration: 250 mg/L, oxidation time: 3h)

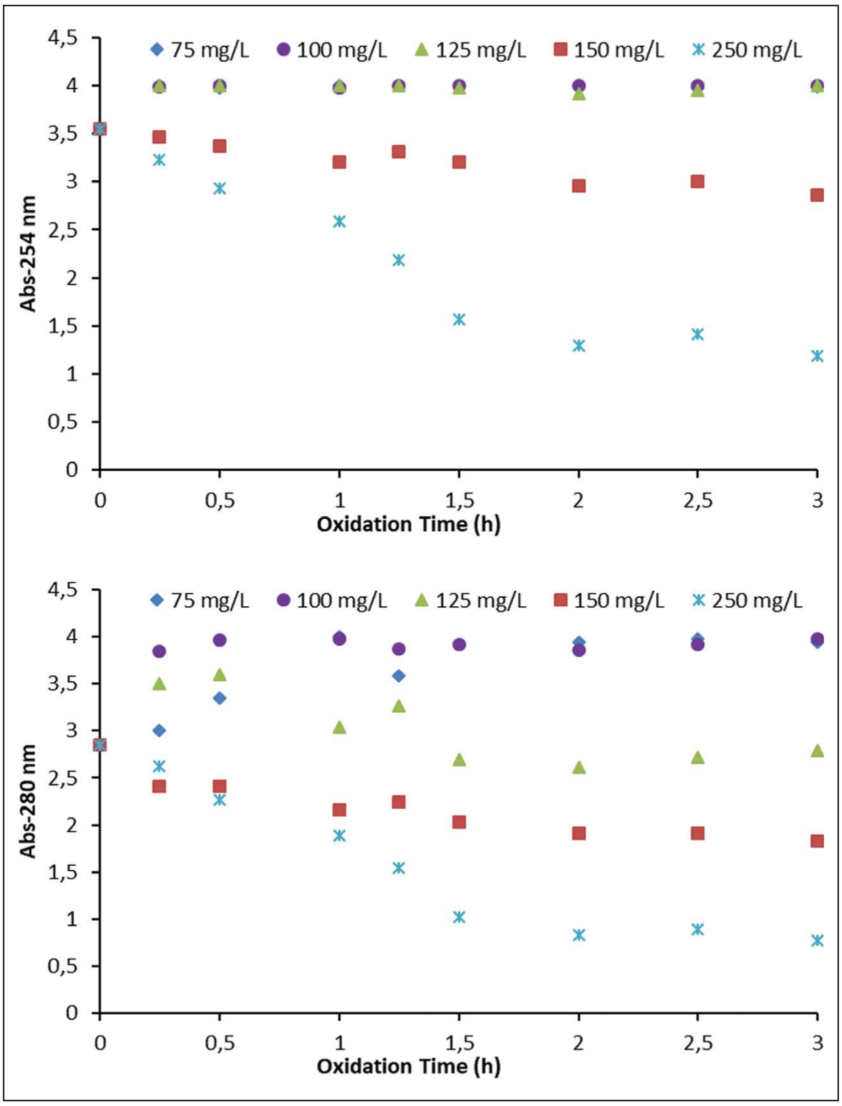

Figure 6. Effect of H_2O_2 concentration on absorbance removal (Abs-254 nm and Abs-280 nm) (pH: 3, Fe-Cu-P concentration: 5 g/L)

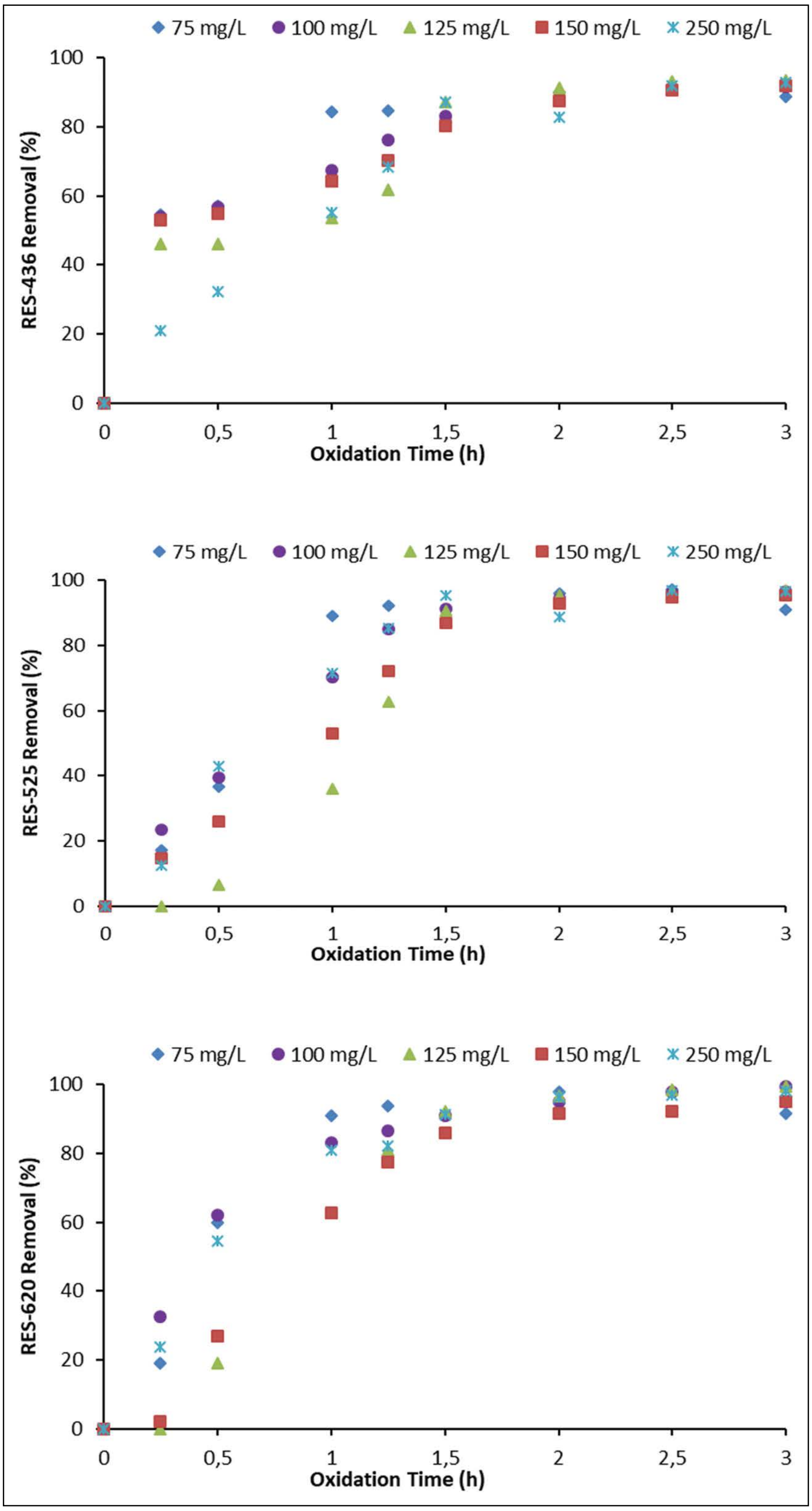

Figure 7. Effect of H_2O_2 concentration on color (RES-436, RES-525 and RES-620) removal (pH: 3, Fe-Cu-P concentration: 5 g/L)

tration, 250 mg/L H_2O_2 concentration and pH 3 after 1.5 hours degradation. Mahamallik and Pal found over a 92% of decolorization when textile wastewater was oxidized with photo Fenton process using 10 g/L Co-SMA (Co(II) adsorbed surfactant-modified alumina) catalyst, 37.9 mM H_2O_2 after 1 hour of oxidation [31].

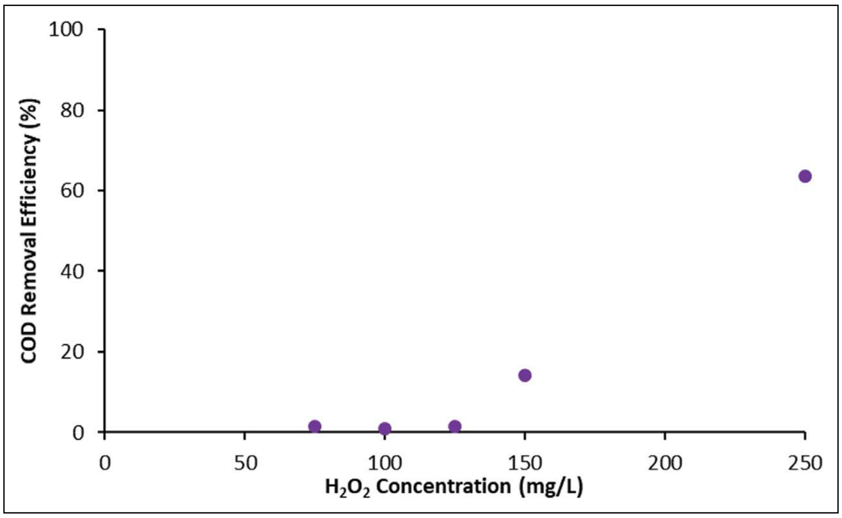

Figure 8. COD removal at different H_2O_2 concentration (pH: 3, Fe-Cu-P concentration: 5 g/L, oxidation time: 3h)

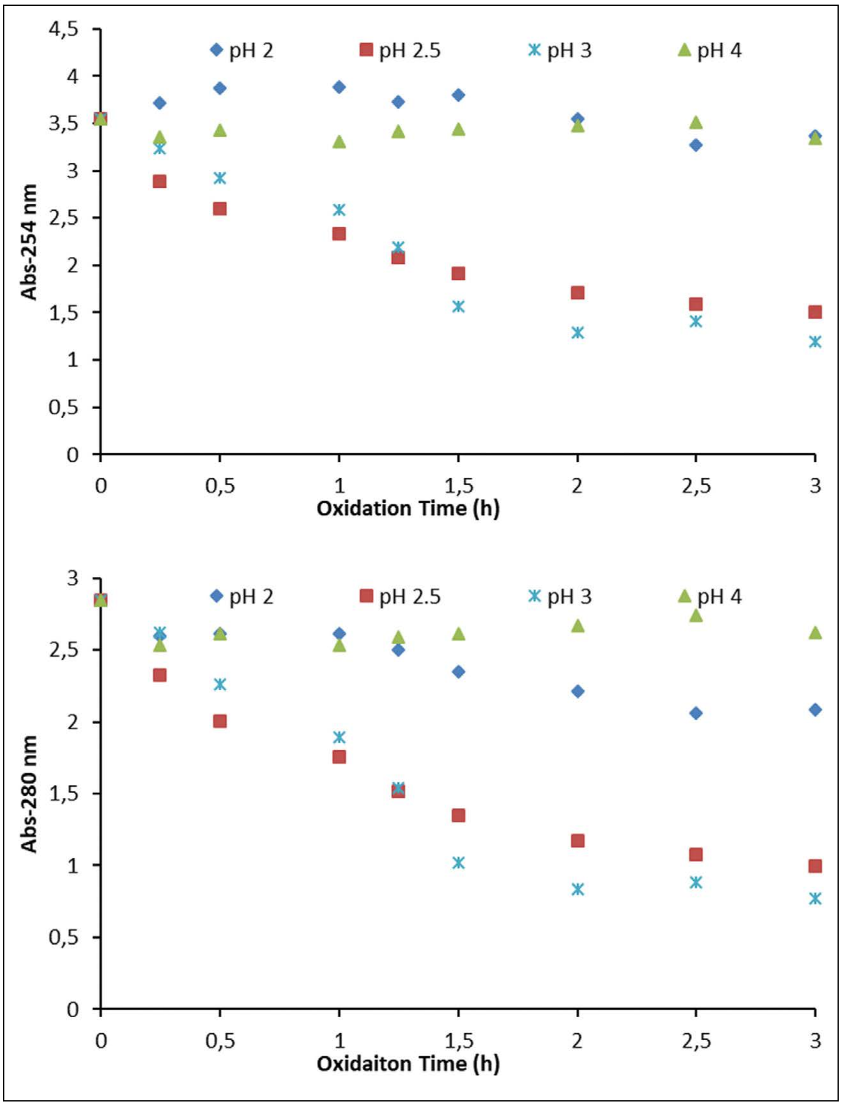

Figure 9. Effect of pH on the removals of Abs-254 nm and Abs-280 nm (Fe-Cu-P concentration: 5 g/L, H_2O_2 concentration: 250 mg/L)

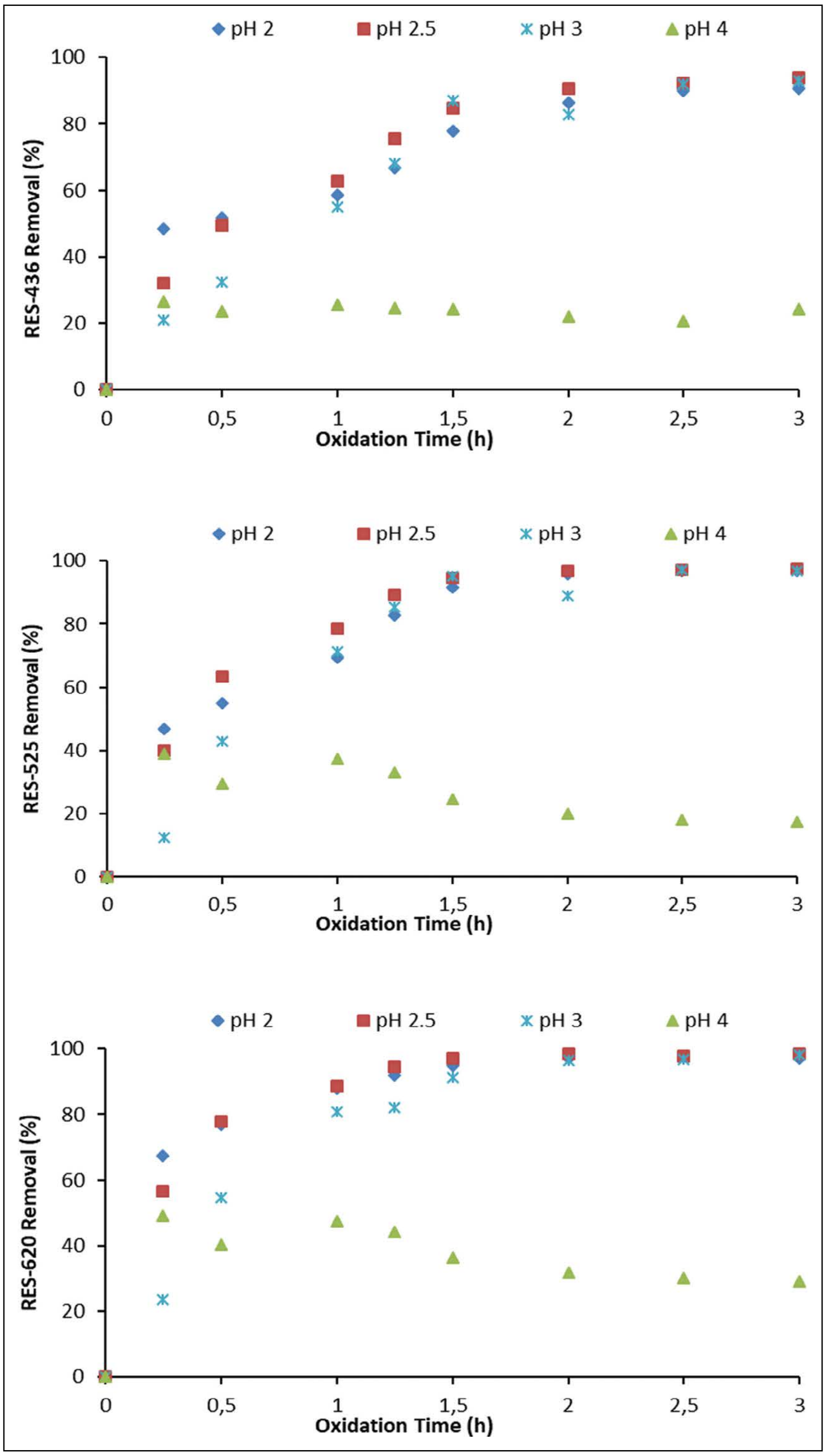

Figure 10. Effect of pH on (a) RES-436, (b) RES-525 and (c) RES-620 removals (Fe-Cu P concentration: 5 g/L, H_2O_2 concentration: 250 mg/L)

Assessment of Treatment with UV/Fenton-Like Process
Standardized industrial wastewater discharge limits by the Zero Discharge of Hazardous Chemicals Program (ZDHC) are given in Table 3. The COD concentration of treated textile wastewater decreased from 246 mg/L to 78 mg/L with UV/Fenton-like proses using Fe-Cu-P composite catalyst in this study. According to ZDHC limits, this textile wastewater is in the progressive part as seen in Table 3 [28]. In addition, RES-436, RES-525 and RES-620 values of the treated textile wastewater with UV/Fenton-like were obtained as

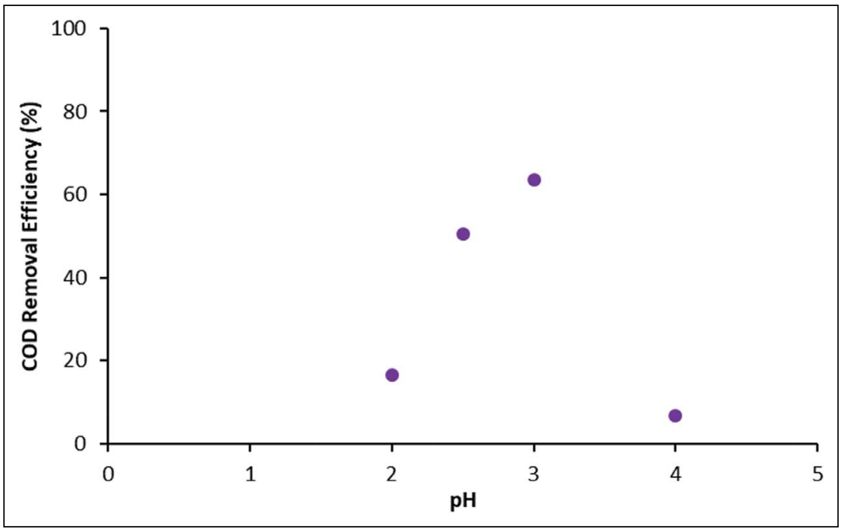

Figure 11. COD removal at different pH values (Fe-Cu-P concentration: 5 g/L, H_2O_2 concentration: 250 mg/L, oxidation time: 3h)

Table 2. Kinetic parameters of UV/Fenton-like proses

Parameter	k_1	R^2
Abs-254 nm	0.3246	0.9731
Abs-280 nm	0.3735	0.9762
RES $_{436}$ (m^{-1})	0.5704	0.9852
RES $_{525}$ (m^{-1})	0.6738	0.9798
RES $_{620}$ (m^{-1})	0.6895	0.8886

Table 3. Characterization of UV/Fenton-like treated wastewater and ZDHC limits

Parameter	Biological treated wastewater	Fenton treated wastewater	ZDHC limits [14]		
			Foundational	Progressive	Aspirational
COD (mg/L)	246	78	150	80	40
RES $_{436}$ (m^{-1})	66.0	4.7	7	5	2
RES $_{525}$ (m^{-1})	85.2	2.8	5	3	1
RES $_{620}$ (m^{-1})	46.8	0.9	3	2	1

4.7 m^{-1}, 2.8 m^{-1} and 0.9 m^{-1}, respectively, and these values also comply with the discharge limits in the progressive class [28]. As a result, treated textile wastewater complies with the ZDHC progressive discharge limits, however it needs additional treatment for compliance with the aspirational class [28].

CONCLUSIONS

In this study, the treatment of biologically treated textile wastewater with the prepared Fe-Cu pumice composite (containing 3.5% Fe and 3.5% Cu) by UV/Fenton-like oxidation was investigated. A high color removal (RES-436, RES-525 and RES-620) was achieved at 3–5 g/L Fe-Cu-P concentration, 125–250 mg/L H_2O_2 concentration and pH 2–3 range. However, the conditions that can provide the highest COD, Abs-254 nm and Abs-280 nm removals were obtained at 5 g/L Fe-Cu-P and 250 mg/L H_2O_2 concentrations and at pH 3. As a result of the study, it has been observed that UV/Fenton-like oxidation process using the Fe-Cu-P is a very suitable process in terms of obtaining color and organic matter removal of biologically treated textile wastewater before discharging to the receiving environment.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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