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Insight into Nano Zero-Valent-Copper Process for Degradation Dye Wastewater – Optimization by Box-Behnken Design and Toxicity Evaluation

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ABSTRACT

This study focuses on utilization of a zero-valent metal (zero-valent iron, zero-valent aluminum, and nanoscale zero-valent copper) in conjunction with H_2O_2 conducted to treat real dye wastewater. Box-Behnken methodology was applied to describe effects of five independent factors involved in optimization of advanced oxidation system, which was type of zero-valent metals, dosage of zero-valent metals, pH, time and dosage of H_2O_2, for treating dye wastewater. Correlation coefficients for model, shown by the value R^2, were 0.9996 for removing color and 0.9708 for reducing COD. Mass of nZVC equaled 1.09 g/L, H_2O_2 equaled 5.39 mg/L were found to be the optimal reaction conditions when the pH was equal to 3.71. After 120 minutes of optimal settings, there was a reduction of 87.3% in COD and 98.72% in color of dye wastewater after heterogeneous treatments (nZVC/H_2O_2). The reusability of nZVC for degrading dye wastewater has been tested in four cycles and showed up to 70% COD removal. Ecotoxicological testing indicated that the raw textile effluent was extremely toxic to *Chlorella* sp. and *V. fischeri*. Even while wastewater after treatment collected definitely had a lower toxicity level with both *V. fischeri* and *Chlorella* sp. This research findings highlight the nZVC/H_2O_2 process as a feasible and effective method for real dye wastewater treatment and detoxification, positioning it as a valuable alternative oxidation process for treating organic contaminants.

Keywords: advanced oxidation process, Box-Behken design, dye wastewater, nano zero-valent copper.

INTRODUCTION

Since their potent reductive capacity, zero-valent metals (ZVMs) have been the subject of significant research and have found widespread application in the environmental remediation of a large variety of heavy metals and organic contaminants. ZVMs, for example, can remove aqueous pollutants such as arsenic, nitrate, phosphate, phenol, pesticides, inorganic anions, and chlorinated organic pollutants (Angai et al., 2022; Eljamal et al., 2020; Garg et al., 2022; Raman and Kanmani, 2016). This is achieved through a reduction reaction at the surface of the metal, where the pollutants are converted into less toxic or non-toxic forms. Using zero-valent metals has various benefits, including high removal efficiency, low cost, and the potential to be readily recovered and reused. Furthermore, zero-valent metals can be used in a variety of treatment setups, including batch and continuous flow systems, for a wide range of applications (Lee et al., 2010; Raman and Kanmani, 2016).

Nano-sized zero-valent copper (nZVC) was investigated because of its strong reactivity and vast surface area. nZVC refers to copper particles in the nanoscale range that have a zero oxidation state, which means they are completely reduced (no positive charge). These particles have unique physical and chemical characteristics, and their impacts have been discovered in possible applications, including environmental cleanup and wastewater treatment, particularly dye wastewater (Raut et al., 2016). The reduction of organic pollutants in water has utilized nano zero-valent copper (nZVC) as a catalyst (Ghorbanian et al., 2019; Liu et al., 2018; Zhou et al., 2016). Zhou et al. (2016) degraded benzoic acid in water using nZVC as a Fenton-like heterogeneous catalyst. All benzoic acid was destroyed in 25 minutes at 12 °C, pH 3, 1 mM/L of hydrogen peroxide, and 40 mg/L of nZVC. Shah et al. (2020) degraded Ciprofloxacin in water using nZVC as a Fenton-like heterogeneous catalyst. Their research revealed that 85% of antibiotics Ciprofloxacin was destroyed in 105 minutes at pH 8, 40 mg/L H_2O_2, and 0.5 g/L nZVC (Shah et al., 2020). As well as 2,4-dichlorophenol was degraded completely (> 98%) by nano zero-valent copper activated by persulfate with microwave irradiation for 90 min (Ghorbanian et al., 2019). Compared to other metal nanoparticles, nZVC provides benefits because they are affordable, widely available, and, compared to traditional adsorbents, give greater yields and faster reaction times under reasonable reaction conditions (Abdel-Aziz et al., 2021). According to Equation 1, the nZVC/H_2O_2 mechanism allows for gradually releasing Cu^+. Cu^+ then activates H_2O_2, increasing the generation of hydroxyl radicals, as seen in Equation 2. Thus, the fundamental advantage of the nZVC/H_2O_2 process is the use of nZVC rather than the usual copper salts commonly used in Fenton-like homogeneous procedures. Furthermore, Cu^{2+} can be transformed into Cu^+ on the surface of nZVC, according to Equation 3. (Shah et al., 2020). The RPB-nano-Cu^O/H_2O_2 method showed tremendous promise for efficient breakdown of Orange G in water with a 93% reduction of Orange G (Lin and Zhong, 2023). However, a limited study has been proposed in utilization of nZVC/H_2O_2 process and comparison with ZVA/H_2O_2 and ZVI/H_2O_2 treatment to the degradation of dye wastewater. Thus, this research applied nZVC/H_2O_2 process to remove dye wastewater

$$2Cu^0 + H_2O_2 + 2H^+ \rightarrow 2Cu^+ + 2H_2O \quad (1)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + HO^* \quad (2)$$

$$Cu^0 + Cu^{2+} \rightarrow 2Cu^+ \quad (3)$$

Employing an appropriate experimental design is tempting with so many potential factors at play. In order to draw inferences about variables and their connection which are the most meaningful response elements with the fewest feasible reactions, methods provide a systematic approach to working. The Box-Behnken designs (BBD), central composite design and three-level full-factorial designs are all examples of such experimental layouts (Tarkwa et al., 2019). BBD was used in various research to validate the degradation dye waster by advanced oxidation process (Dadban Shahamat et al., 2022; Jorge et al., 2023; Shakeel et al., 2014).

To discover the best advanced oxidation process for dye wastewater treatment, articles published use a statistical experiment design. Decomposition of azo dye wastewaters such as Orange G (Tarkwa et al., 2019), metyl Orange Azo dye (Adachi et al., 2022) has been researched. Likewise, nZVC have uncommonly been illustrated for the activation of H_2O_2 for degrading of real textile wastewater. Thus, this study's objective was to use BBD to determine the best conditions for degrading real dye wastewater by an advanced oxidation process activated by nZVC, ZVA, and ZVI. In addition, toxicity was assessed at different stages of the treatment process by *V. fischeri* and *Chlorella* sp. microalgae test. The reusability and mechanism of nZVC for treating dye wastewater were investigated.

MATERIAL AND METHODS

Sample of dye wastewater

Dye wastewater samples were collected for three months in winter of 2022 from sanitary sewers of Van Phuc Silk Village (Fig. 1.). Each month, 30 L of sampling dye wastewater was collected as well as held at 4 °C in pharmaceutical freezers (Panasonic, Japan) before being analyzed. Table 1 presents the properties of the dye wastewater.

Regents

Zero valent metals were included nano zero-valent copper (nZVC) (purity 99.99%, 25 nm particle size), zero-valent aluminum (ZVA) (purity 98%, 200 mesh), zero-valent iron (ZVI) (purity 98%, 200 mesh), was supplied from Merck (Germany). H_2SO_4, K_2CrO_7, Ag_2SO_4, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$; 1–10 phenanthroline were applied to analyze COD, also were purchased from Merck (Germany). Hydrogen peroxide (30%) was obtained for application in advanced oxidation process from Duc Giang Ltd. (Viet Nam). To adjust pH of dye wastewater, 0.1 M HCl or NaOH was added, to achieve the desired results. All solutions were produced daily with double-distilled water at room temperature (25 °C ± 1).

Analytical methods

The color of dye wastewater was measured by method 8025 in a spectrometer Hach Dr 3900, USA. pH levels of sollution were measured by a pH meter (Milwaukee MW102, Poland). And

Figure 1. Dye wastewater sample location

Table 1. Raw and treatment dye wastewater characteristics by nZVC/H_2O_2

No.	Parameter	Unit	Initial values	After treatment 120 min
1	Temperature	°C	40–45	25
2	pH		8.5	3.71
3	TSS	mg/L	1300	330
4	Color	Pt-Co	2600	853
5	BOD_5	mg/L	350	405
6	COD	mg/L	1500	190.5
7	TOC	mg/L	486	65.7
8	Total *Coliform*	MNP/100ml	25000	1200

COD was determined utilizing open reflux method SMEWW 5220B:2012 and a COD reactor (Hach, DRB 200, USA). Total organic carbon (TOC) values were measured with a torch TOC combustion analyzer (Tekmar, USA).

The color and COD reduction efficiency (H%) was calculated using (4) as follows:

$$H(\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (4)$$

where: C and C_0 are after and before concentration treatment of color (Pt.Co) and COD (mg/L) in textile wastewater, respectively.

Experiment design

Optimization of experimental conditions for treating color and COD in textile wastewater by advanced oxidation process activated by ZVA, ZVI and nZVC was totally conducted design of experiment by BBD with Design Expert ver. 11 software. To calculate the effect on experimental variables for the collar and COD degradation, five main factors were chosen: type of ZVMs (A), a mass of ZVMs (g/L) (B), pH (C), concentration of H_2O_2 (mg/L) (D), time of reaction (min) (E). The COD, color of dye wastewater removal was measured as the response, as described in Table 2.

To calculate the removal of COD and colour of dye wastewater, %COD and %color were suited by a second-order quadratic polynomial equation as followed:

$$Y = b_0 + \sum_{i=0}^{k} b_i X_i + + \sum_{i=0}^{k} b_{ii} X_i^2 + \sum_{i=0}^{k} \sum_{j=0}^{k} b_i b_j X_i X_j \quad (5)$$

where: Y is predicted response (COD and color reduction efficiency, %) employed as dependent value; X_i (A, B, C, D and E) are the independent variable factors, and b_0, b_i (i = 1, 2 and 3), b_{ii}, and b_{ij} (i = 1, 2 and 3; j = 1, 2 and 3) are model coefficients, respectively.

Ecotoxicity evaluation

Study the toxicity of raw influent and effluent dyeing wastewater from the 120-minute oxidation

Table 2. Code and levels of variables of DOE for advanced oxidation process activated by nZVC, ZVA and ZVI optimization

Factor	Variables	Units	Coded levels of variables		
			-1	0	1
Type of ZVMs	A		nZVC	ZVA	ZVI
Mass of ZVMs	B	g/L	0.5	1.25	2
pH	C		3	4	5
Concentration H_2O_2	D	mg/L	1	5,5	10
Time	E	min	60	90	120
%COD	Y_1	%			
%Color (TCU)	Y_2	%			

experiments with diluted ratio 1:1, 1:2 and 1:10 were examined by *V. fischeri* and *Chlorella* sp.

The toxicity of the photobacterium *V. fischeri* was measured follow (Khue et al., 2021) with a BioToxTM test kit (Aboatox Oy, Finland) based on the percent relative luminescence inhibition after an incubation period of 15 minutes in accordance with the ISO protocol. For assessing acute toxicity towards freshwater microalgae *Chlorella* sp., the Algaltoxkit FTM (MicroBioTests, Inc., Gent, Belgium) micro-biotests were employed. A concentrated microalgae *Chlorella* sp. cell suspension was introduced into each flask to achieve an initial cell concentration of 0.6×10^6 cells/mL. Flasks were stored at a temperature of 25 ± 1 °C with continuous illumination, and adjustments were made to light intensity according to *Chlorella* sp. requirements. Flasks were shaken twice daily for 3 days, and microalgae cell counts were performed using a counting chamber (Wälzlager, Germany). Percent relative growth inhibition rates were calculated after a 72-hour incubation period based on a toxicant-free control. The acute toxicity results were expressed as percent relative inhibition, and a positive control sample with potassium dichromate was included for each test.

RESULTS AND DISCUSSION

Response analysis and discussion via Box Behken design technique

COD in dye wastewater by advanced oxidation process mediated nZVC, ZVA and ZVI with H_2O_2

The efficiency of COD reduction was calculated using a variable design model illustrated in Table 3. By ANOVA test, many models (linear, two factorial, quadratic, and cubic) were explored for best fitting the data (Table 3). Based on the findings, a quadratic polynomial model is appropriate for describing COD elimination. This is an illustration of the model's Equation 6 in terms of coded factors:

$$\%COD = 78.36 - 2.30A + 0.4951B - 2.54C + 1.40D + 2.45E + 1.49AB + 0.2307AC + 1.17AD - 0.84AE + 2.56BC + 1.56BD + 0.1578BE - 2.10CD - 0.8245CE + 3.02DE + 0.3459A^2 - 1.2B^2 - 0.3349C^2 - 0.2150E^2 \quad (6)$$

The ANOVA analysis of the COD elimination model is illustrated in Table 3. F-value was 41.61, and the p-value was less than 0.05 (< 0.0001), indicating that model's fitness is statistically meaningful at 95%. In addition, the research obtains a good analysis coefficient (R2 = 0.9708) while examining null hypothesis to evaluate the effect of each model term (Nguyen et al., 2019). The five components of the created model were deemed significant. AC, AE, BE, CE, A^2, C^2, and E^2 were not important model variables in this model (Table 4).

Color in dye wastewater by advanced oxidation process by mediated nZVC, ZVA and ZVI

A BBD was utilized to evaluate the impact of various parameters on the removal of color from dye effluent. Table 3 displays the percentages of color in dye wastewater reduction using a design matrix with various parameters. Given F-value (2947.92), p-value (< 0.0001), and a substantial analysis coefficient (R2 = 0.9999), a quadratic polynomial model provides the best match for color removal. The model's signal-to-noise rate of created model (10.41) (> 4) demonstrated enough accuracy, indicating that the model for color removal is accurate (Khue et al., 2021). Similarly, the model fits the data at the 95% significance level. Table 5 demonstrates the ANOVA analysis for this model. Equation 7 reflects the model Equation for color reduction is dependent on coded parameters:

Table 3. Design of five-level experiments applying BBD, COD and color reduction responses to treat dye wastewater by advanced oxidation process mediated nZVC, ZVA and ZVI with H_2O_2

No.	Factor A type of ZVMs	Factor B dosage of ZVMs (g/L)	Factor C pH	Factor D concentration H_2O_2 (g/L)	Factor E time (min)	% COD reduction (%)	% Color reduction (%)
1	ZVI	1.25	4	1	90	16.29	69.25
2	ZVI	1.25	4	5.5	120	67.12	78.32
3	ZVA	1.25	4	5.5	90	24.18	78.42
4	ZVA	1.25	4	10	120	79.43	79.26
5	nZVC	1.25	4	5.5	60	3.459	77.68
6	nZVC	1.25	4	1	90	14.87	75.15
7	ZVA	1.25	4	5.5	90	24.18	78.42
8	ZVA	1.25	3	5.5	60	39.12	76.63
9	ZVI	1.25	4	5.5	60	21.25	74.13
10	ZVI	1.25	5	5.5	90	42.78	74.4
11	ZVA	1.25	4	5.5	90	24.18	78.17
12	ZVA	1.25	4	5.5	90	24.18	79.09
13	nZVC	1.25	4	5.5	120	70.96	85.23
14	ZVA	1.25	4	1	120	58.75	70.19
15	ZVA	1.25	4	1	60	12.98	71
16	ZVA	2	3	5.5	90	37.43	78.9
17	ZVA	0.5	4	5.5	60	16.98	74.92
18	nZVC	0.5	4	5.5	90	43.78	81.5
19	nZVC	1.25	5	5.5	90	52.63	77.97
20	ZVA	1.25	5	5.5	120	98.32	76.28
21	ZVI	1.25	3	5.5	90	52.90	78.56
22	ZVA	2	4	10	90	32.62	74.75
23	nZVC	1.25	3	5.5	90	29.09	83.05
24	ZVA	1.25	3	1	90	36.16	71.05
25	ZVA	2	4	1	90	33.96	69.41
26	ZVI	1.25	4	10	90	31.62	74
27	ZVA	1.25	4	5.5	90	24.18	78
28	ZVA	0.5	4	1	90	17.43	71.26
29	ZVA	0.5	4	10	90	38.32	70.36
30	ZVA	1.25	5	5.5	60	34.37	73.64
31	ZVA	1.25	5	1	90	42.87	70.53
32	nZVC	2	4	5.5	90	10.30	77.45
33	nZVC	1.25	4	10	90	19.09	75.23
34	ZVI	0.5	4	5.5	90	12.98	72.91
35	ZVA	2	4	5.5	60	27.96	75.83
36	ZVA	0.5	5	5.5	90	38.72	70.02
37	ZVA	1.25	5	10	90	52.65	69.91
38	ZVA	1.25	4	5.5	90	24.18	78.06
39	ZVA	2	4	5.5	120	79.08	80.38
40	ZVA	2	5	5.5	90	76.92	77.68
41	ZVI	2	4	5.5	90	56.17	74.81
42	ZVA	1.25	4	10	60	11.84	68
43	ZVA	0.5	3	5.5	90	64.79	81.47
44	ZVA	1.25	3	10	90	45.94	78.81
45	ZVA	1.25	3	5.5	120	87.23	82.57
46	ZVA	0.5	4	5.5	120	79.22	78.84

Table 4. ANOVA test of a quadratic polynomial model for COD degradation of dye wastewater

Source	Sum of squares	df	Mean square	F-value	p-value	Comment
Model	751.48	20	37.57	41.61	< 0.0001	significant
A-type of ZVMs	85.00	1	85.00	94.12	< 0.0001	
B-ZVMs	3.92	1	3.92	4.34	0.0476	
C-pH	103.00	1	103.00	114.05	< 0.0001	
D-H_2O_2	31.58	1	31.58	34.96	< 0.0001	
E-time	96.30	1	96.30	106.63	< 0.0001	
AB	8.85	1	8.85	9.80	0.0044	
AC	0.2129	1	0.2129	0.2357	0.6315	
AD	5.46	1	5.46	6.05	0.0212	
AE	2.82	1	2.82	3.13	0.0893	
BC	26.13	1	26.13	28.93	< 0.0001	
BD	9.72	1	9.72	10.77	0.0030	
BE	0.0996	1	0.0996	0.1103	0.7426	
CD	17.56	1	17.56	19.45	0.0002	
CE	2.72	1	2.72	3.01	0.0950	
DE	36.40	1	36.40	40.30	< 0.0001	
A^2	1.04	1	1.04	1.16	0.2926	
B^2	13.62	1	13.62	15.08	0.0007	
C^2	0.9790	1	0.9790	1.08	0.3077	
D^2	274.73	1	274.73	304.21	< 0.0001	
E^2	0.4034	1	0.4034	0.4467	0.5100	
Residual	22.58	25	0.9031			
Lack of fit	121.78	20	1.09	6.87	0.209	not significant
Pure error	0.7930	5	0.1586			
Total	774.06	45				
R2	0.9708					

$$\%TCU = 607.8126 + 18.11618A - 100.55873B - 212.76312C + 0.520819D - 3.3352E + 25.55403AB - 8.41667AC + 0.617407AD + 0.180333AE + 21.85222BC - 1.64617BD + 0.123481BE - 1.33195\ 10^{-15}CD + 0.131988CE + 0.040395\ DE - 1.82544A^2 + 14.73403B^2 + 22.06013C^2 - 0.092071D^2 + 0.020452E^2 \quad (7)$$

In this model, A, B, C, D, E, AB, AC, AD, AE, BC, BD, BE, CE, DE, A^2, B^2, C^2, D^2, E^2 are significant model terms.

Optimization of advanced oxidation process activated by nZVC, ZVA and ZVI with H_2O_2 for dye wastewater degradation

The primary objective of optimization is to determine the ideal values of the variables for COD and color reduction in dye wastewater treatment by using experimental inputs. A maximum target value with the lowest concentration of ZVMs and H_2O_2 was chosen as the desired response goal, which was determined by the kind of ZVMs, the dosage of ZVMs and H_2O_2, pH, and operating duration. At a pH of 3.71, the best conditions of the experimental variables were determined to be current nZVC, mass of nZVC equal to 1.09 g/L, and H_2O_2 equal to 5.39 mg/L. The actual experimental results measured for COD treatment were 62.9% and for color removal were 76.3%.

Effect of parameters in treating dye wastewater by nZVC/H_2O_2 process

Given that pH directly impacts both the rate at which nZVC corrodes. It should come as no surprise that the pH level is a crucial metric. In addition, pH is another factor that regulates the formation of free radicals during advanced oxidation process. Hoa et al. (2020) were studied to treat of Ciprofloxacin efficiently at pH 4 utilizing persulfate oxidation mediated by ZVC (Hoa et al., 2020). Generation of HO^* improved in acidic

Table 5. ANOVA examination of a quadratic polynomial model for color degradation of dye wastewater

Source	Sum of squares	df	Mean square	F-value	p-value	Comment
Model	24553.18	20	1227.66	2947.92	< 0.0001	significant
A-Type of ZVMs	202.53	1	202.53	486.31	< 0.0001	
B-ZVMs	111.38	1	111.38	267.46	< 0.0001	
C-pH	135.69	1	135.69	325.82	< 0.0001	
D-H_2O_2	382.04	1	382.04	917.37	< 0.0001	
E-Time	12777.68	1	12777.68	30682.40	< 0.0001	
AB	1469.27	1	1469.27	3528.08	< 0.0001	
AC	283.36	1	283.36	680.42	< 0.0001	
AD	30.88	1	30.88	74.14	< 0.0001	
AE	117.07	1	117.07	281.12	< 0.0001	
BC	1074.42	1	1074.42	2579.95	< 0.0001	
BD	123.47	1	123.47	296.48	< 0.0001	
BE	30.88	1	30.88	74.14	< 0.0001	
CD	0.0000	1	0.0000	0.0000	1.0000	
CE	62.71	1	62.71	150.59	< 0.0001	
DE	118.96	1	118.96	285.64	< 0.0001	
A^2	29.08	1	29.08	69.83	< 0.0001	
B^2	599.47	1	599.47	1439.48	< 0.0001	
C^2	4247.12	1	4247.12	10198.40	< 0.0001	
D^2	30.34	1	30.34	72.85	< 0.0001	
E^2	2956.98	1	2956.98	7100.45	< 0.0001	
Residual	10.41	25	0.4164			
Lack of fit	10.41	20	0.5206			not significant
Pure error	0.0000	5	0.0000			
Total	24563.59	45				
R2	0.9996					

conditions, strengthening the removal of organic pollutants in dye wastewater. Consequently, as pH decreases, both nZVC corrosion and HO* production increase (Sun et al., 2019). In Figure 2,

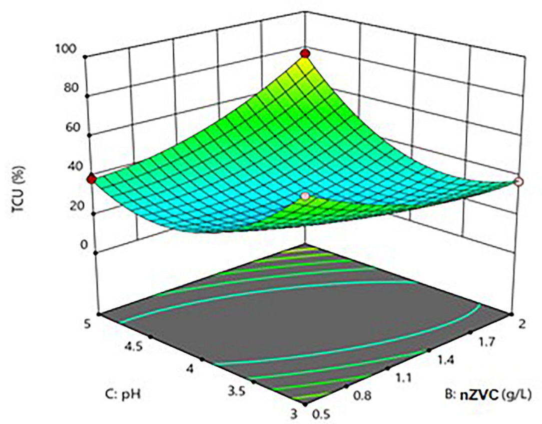

Figure 2. Three-dimensional response surface graphs depicting the interaction of pH and nZVC mass in relation to color (TCU) removal

contour lines and response surface plots are depicted to show the correlation between pH and the mass of nZVC. The study found that hydrogen peroxide alone, as an oxidant, had an insignificant impact on removing color and COD (%TCU = 38.4% and %COD = 25.3%). This suggests that the direct interaction between hydrogen peroxide and RB4 molecules was not significant. The highest removal of COD and color (measured in TCU) occurred at a pH of 3.71. The findings indicate that an increase in H_2O_2 concentration has an impact on both TCU and COD reduction. At an H_2O_2 dosage of 5.39 mg/L, the maximum COD removal was 62.89%, and the maximum TCU removal was 76.3% (Figure 3).

Mechanism of nZVC/H_2O_2 process for treating dye wastewater

In the same way that zero-valent iron corrodes via three distinct mechanisms (Hoa et

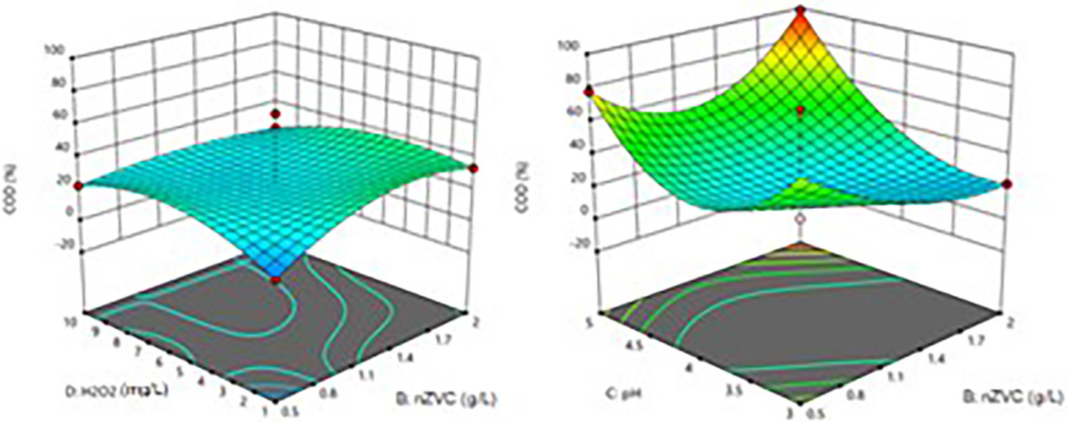

Figure 3. Three-dimensional response surface graphs depicting the relationship between H_2O_2 and mass of nZVC (left); pH and mass nZVC (right) of COD removal

al., 2020), nZVC corrosion can release Cu^+ via three specific mechanisms:

1. Cu^+ release through an indirect pathway via deoxygenated water (9),
2. Instantaneous release of Cu^+ via H_2O_2 (10), and
3. Indirect discharge of Cu+ via O_2 (8) (Zhou et al., 2016).

$$Cu^o + ½ H_2O_2 \rightarrow Cu^+ + OH^- \quad (9)$$

$$Cu^o + ¼ O_2 + ½ H_2O \rightarrow Cu^+ + OH \quad (10)$$

Inside the presence of a catalyst, hydrogen peroxide (H_2O_2) breaks down into the hydroxyl radical (HO^*), as indicated in reactions (1)–(3). Because of its high oxidation potential, the hydroxyl radical reacts extremely quickly with organic pollutants (Shah et al., 2020). Due to the high reactivity of HO^* had a quick interaction with the pollutants it was targeting, which caused the contaminants in dye wastewater to degrade.

Mineralization degree

Besides the decomposition of organic pollutants, an adequate quantity of mineralization has to be performed on contaminants for them to transform them into water, carbon dioxide, and other mineral ions. This approach is regarded as a viable option to the treatment of wastewater contaminated with organic contaminants (Jaafarzadeh et al., 2018; Khue et al., 2021). TOC degradation was illustrated to show the mineralization extent of dye wastewater by $nZVC/H_2O_2$ systems, and the results are shown in Figure 4. It has been proven that an efficient level of mineralization could be achieved using the $nZVC/H_2O_2$. As can be seen, roughly 86.7% of dye-waster was mineralized by the

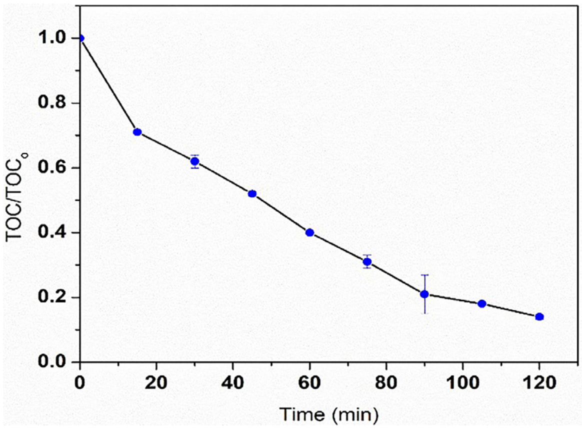

Figure 4. Mineralization of dye wastewater applying $nZVC/H_2O_2$. Condition of experiments: pH = 3.71, nZVC = 1.09 g/L, and $[H_2O_2]$ = 5.39 mg/L

$nZVC/H_2O_2$ system within 120 min reaction time. In contrast to other research on treating real dye wastewater by advanced oxidation processes such as $ZVI/PMS/H_2O_2$ or photo – fenton like support from carbon nanotube, this $nZVC/H_2O_2$ process offers enhanced treatment efficacy (Ghanbari et al., 2014) (García et al., 2017). It has been reported that hydroxyl radical is exceedingly effective in mineralizing organic pollutants (Xu et al., 2016).

Toxicity assessment

Previous research has shown that releasing untreated textile wastewater into water bodies has significant negative impacts on the environment and poses a danger to various life forms. Unlike previous findings, Raptis et al. (2014) also found that the growth of *V. fischeri* and reproduction of *Chlorella* sp. were negatively correlated with COD and BOD concentrations, respectively, in dye wastewater influent (Raptis et al., 2014). Textile wastewater influent with initial COD from 545 to 860 mg/L exhibited elevated levels of toxicity (EC50 for *V. fischeri* were 4.9–211.2) (Liang et al., 2018). Therefore, it is necessary to evaluate the toxicity of treated dyeing wastewater to apply the nZVC/H_2O_2 process on an industrial scale.

Wastewater from dyeing textiles with an initial COD concentration of 1200 mg/l treated under optimal conditions, the treated water was diluted at ratios of 1/1, 1/2, and 1/10, with pH adjusted to 7.8–8.5, suitable for *Chlorella* sp. The survey results after 48 hours revealed a correlation between the mortality rate of *sp.* at 48 h and the diluted treated water samples. The control sample showed 10.42% mortality of *Chlorella* sp. after 48 h. In contrast, the mortality rates in the treated textile wastewater at dilution ratios of 1/1, 1/2, 1/10, and control samples were significantly higher at 69.4%, 56.2%, and 27.4%, respectively. The mortality rate *of Chlorella* sp. could be attributed to toxins, particularly Cu^{2+} ions, in the wastewater.

The *V. fischeri* bioassay is by far simpler and less time-consuming than most other toxicity test procedures. The photobacteria can be stored for several months and used promptly on demand (Arslan-Alaton et al. 2014). Figure 5 displays relative inhibition rates obtained by dye wastewater after treatment by nZVC/H_2O_2 during 120 min in the *V. fischeri* growth medium. From Figure 2 it is evident that its inhibitory effect declined rapidly from 46.2% in the original sample down to 30.2% of dilution ratio 1:2.

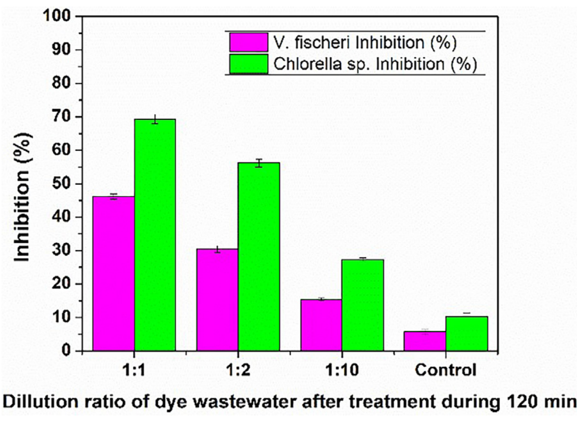

Figure 5. Toxicity reduction of dye wastewater by nZVC/H_2O_2 after 120 min

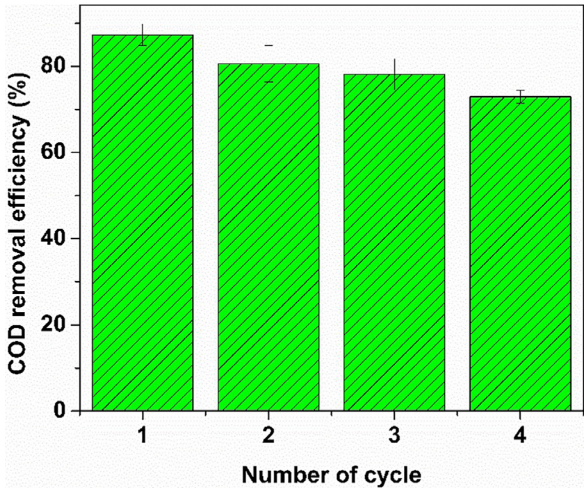

Figure 6. Reusability of nZVC after four cycles of experiment by nZVC/H_2O_2. Condition of experiments: pH = 3.71, nZVC = 1.09 g/L, and $[H_2O_2]$ = 5.39 mg/L

Inhibition rates decreased to 15.5% of dilution ratio 1:10. Percent inhibition rates of control sample were at around 10.4%. A rapid decrease in *V. fischeri* toxicity in dye wastewater has already been reported.

The difference in toxicity levels between these two methods may be attributed to the creation of distinct compounds during treatment. With aromatic compounds and simple organic acids forming at different stages, it appears that *Chlorella* sp. displays resistance to Cu^{2+}, while *V. fischeri* exhibits resilience to organic acids. As similar outcomes are seen with the UV/oxidant process, toxicity assessment in such systems could be conducted using either of these methods (Thakur and Chauhan, 2018).

Reusability of nZVC

Reusability is a critical factor for any catalyst to be suitable for large-scale applications. To evaluate, the nZVC was subjected to four cycles of reuse. After dye wastewater was completely treated, nZVC was easily separated through centrifugation, followed by washing with 99% ethanol as an organic pollutant in nZVC surface removal. Afterward, it was dried in an air oven at 60 °C for 3 hours before the next treatment cycle (Abdelfatah et al., 2021). Remarkably, even after four nZVC cycles, efficiency of COD degradation by nZVC/H_2O_2 system is almost 70% (Fig. 6). It is true that nZVC is an eco-friendly, cost-effective, and sustainable natural catalyst.

CONCLUSIONS

Compared with ZVA, ZVI, nZVC activates H_2O_2 based to treat textile wastewater efficiently. Box-Behken design was an acceptable strategy that was used to optimize the operational state of advanced oxidation process mediated ZVMs with H_2O_2 for a decrease in COD and color of dye wastewater. At a pH of 3.71, the best reaction conditions were determined to be a mass of nZVC equal to 1.09 g/L and a concentration of H_2O_2 equal to 5.39 mg/L. Chemical oxygen consumption was reduced by 62.9% and dye wastewater color by 76.3% following heterogeneous treatments (nZVC/H_2O_2) after 120 minutes under optimum conditions. Dye wastewater has been shown to benefit greatly from the combined efforts of nano-zero-valent copper and H_2O_2 process. However, treating dye wastewater on an industrial scale by nZVC/H_2O_2 is carefully calculated due to high costs, difficulties in maintaining an acidic environment, and the recovery of nanomaterials after the reaction.

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