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Optimization of Diclofenac Treatment in Synthetic Wastewater using Catalytic Ozonation with Calcium Peroxide as Catalyst

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ABSTRACT

This research studied the performance of ozonation process combined with calcium peroxide (CaO_2) as a catalyst for the removal of diclofenac (DCF) from synthetic wastewater. The experiments were conducted using venturi-type ozonation with an ozone production rate of 96.30 mg/h. Response surface methodology (RSM) with a Box-Behnken experimental design (BBD) was used to investigate the DCF removal efficiency by optimizing the catalytic ozonation process and analyzing the influence of key parameters: solution pH (5.0-9.0), initial DCF concentration (10-25 mg/L), CaO_2 dosage (1-3 g/L), and reaction time (30-90 min), on the DCF removal efficiencies. Analysis of variance (ANOVA) indicated that the experimental model derived from the RSM-BBD was best suited to a quadratic regression model, with a coefficient of determination (R^2) of 0.84. The model demonstrated that the optimal conditions for achieving the highest DCF removal efficiency of up to 100% were an initial DCF concentration of 10 mg/L, solution pH of 7, CaO_2 dosage of 2 g/L, and reaction time of 90 min. Using these conditions, the actual DCF removal efficiency from a confirmation test was 97.6%. The accuracy of the model was verified; the root mean square error (RMSE) was 5.90 and the mean absolute percentage error (MAPE) was 6.10%, indicating that the regression model could be used to predict the DCF removal efficiency under various conditions. The results showed that catalytic ozonation using CaO_2 as a catalyst could effectively remove DCF in synthetic wastewater.

1. INTRODUCTION

Diclofenac (DCF) is a non-steroidal anti-inflammatory drug of the phenylacetic acid class that is widely used in analgesics for humans, livestock, and domestic animals, for the treatment of muscle, joint, and bone pain from both rheumatic and non-rheumatic origins (Tra et al., 2023). The annual worldwide usage of DCF was approximately 940 t, as indicated by trend analysis from 2020 to 2027 based on pharmaceutical consumption (Alessandretti et al., 2021). Generally, DCF is continuously introduced into the environment in waste by pharmaceutical industries, hospitals, and household drainage, raising major environmental concerns. This emerging contaminant can readily enter wastewater and surface water through various routes, including excretion by humans and animals, as well as in discharges from industrial and municipal wastewater treatment facilities (Davies and Anderson, 1997; Sathishkumar et al., 2020; Thalla and Vannarath, 2020). DCF has been detected in the environment in both its original form and as metabolites at concentrations ranging from nanograms per liter (ng/L) to milligrams per liter (mg/L), with the actual value dependent on its source and the effectiveness of wastewater treatment methods (Lonappan et al., 2016). Although the contamination of DCF in water sources has been detected only at relatively low amounts (micro or nano levels), DCF is toxic to various aquatic organisms in the ecosystem, including green algae, microcrustaceans, and

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invertebrates (Zind et al., 2021). DCF was reported to induce lethal effects by causing damage to renal and gastrointestinal tissues in various vertebrates such as fish (Lonappan et al., 2016). In addition, DCF may present an adverse ecological risk to non-target organisms due to biomagnification within the food chain (Sathishkumar et al., 2020). Therefore, appropriate treatment of wastewater containing DCF is necessary prior to releasing it into natural water sources, to minimize its environmental impact.

Conventional wastewater treatment, such as activated sludge, cannot effectively remove DCF due to the complicated structure of DCF that resists biological degradation (Jabbari et al., 2020). An adsorption process can remove DCF in rapidly, however, it causes adsorbent disposal problems (Beltran et al., 2009). Nanofiltration (NF) and reverse osmosis (RO) are very effective at removing DCF and other pharmaceutically active compounds (PhAcs), however, retentate streams with high concentrations of pollutants must be removed before discharge into water sources (Maryam et al., 2020; Alonso et al., 2024). Chemical oxidation using potassium permanganate ($KMnO_4$) and chlorine (Cl_2) are effective in DCF treatment as they have strong oxidizing properties (Wang et al., 2023). However, they have a limitation on toxic residuals in the environment (Gomes et al., 2019; M'Arimi et al., 2020). Ozone oxidation is effective in the removal of DCF because ozone is a powerful oxidant with a high oxidation potential of 2.07 V (Alharbi et al., 2022). It reacts with the organic compounds either directly as molecular ozone or indirectly through the hydroxyl radical (OH·). Nevertheless, direct ozonation has a main drawback due to the selective nature of ozone, its limited mass transfer, and slow rate of reaction (Malik et al., 2020). Catalytic ozonation, an effective method of advanced oxidation processes (AOPs), is a promising technology for the treatment of recalcitrant contaminants present in wastewater (Bilińska et al., 2022). It generates reactive free radicals (primarily the hydroxyl radical) with a higher oxidation potential than that of ozone (E°=2.80 V). It is capable of oxidizing and completely mineralizing refractory organic compounds to CO_2 and H_2O with increasing rates of degradation, leading to reduction in the reaction time and operating cost (Rosales et al., 2019; Sun et al., 2019). Combining ozonation with a catalyst has been used to enhance the removal efficiencies of DCF and other PhAcs. Ozone combined with hydrogen peroxide (H_2O_2), known as peroxone, has been proved as an efficient method for the degradation of organic compounds, as the ozone is catalyzed to produce OH· (Chen and Wang, 2021). However, H_2O_2 is a strong oxidizer which enhances the combustion of other substances, causing restrictions in its use, storage, and transportation. To solve this limitation, calcium peroxide (CaO_2) has been introduced to use in combination with the ozonation process, because CaO_2 can release H_2O_2 and $Ca(OH)_2$ through a dissolution process (Lu et al., 2017; Xiang et al., 2021). The released H_2O_2 from CaO_2 can react with O_3 to generate OH· and accelerate the degradation of organic compounds (Nuar et al., 2023). Additionally, the released $Ca(OH)_2$ increases the alkalinity of the solution, which promotes O_3 to transform into more OH· (Wang et al., 2016; Javid et al., 2020). Therefore, ozonation using CaO_2 as a catalyst is considered to be a very practical technology for wastewater treatment, due to its high removal efficiency together with the advantages of easy handling, stability, safety, and reasonable cost (Xu et al., 2020). Other studies have revealed that CaO_2 could be effectively used as a catalyst in ozonation process to remove phenol, sulfamethoxazole, and oxytetracycline (Honarmandrad et al., 2021; Xiang et al., 2021). However, there is no published information regarding using CaO_2 as a catalyst in the ozonation process to degrade DCF.

When utilized in combination, the interaction between O_3 and CaO_2 as a source of peroxide results in synergistic effects that influence removal efficiency. These effects vary depending on their interaction mechanisms; either O_3 acts as the activator for the peroxide, or the peroxide acts as the activator for O_3 (Chen et al., 2024). Furthermore, different control parameters, such as pH, CaO_2 dose, and reaction time, influence DCF removal efficiency. Currently, the optimization of these parameters is carried out on a trial-and-error basis. However, traditionally, this involves an experimental technique based on varying a single factor while fixing the remaining parameters at a certain set of conditions (Dwivedi and Sharma, 2015). Additionally, the single-dimensional factor of the experiment is not only time-consuming but also the attained optimum conditions are not accurate due to neglecting interactions between the operating variables (Ferreira et al., 2023). To solve this problem, response surface methodology (RSM) has been suggested to define the effects of individual parameters. RSM is a statistical and mathematical tools that has been proved valuable for the multifactor optimization of various processes (Dehghani et al.,

2016; Norabadi et al., 2020; Jafari et al., 2023). The Box-Behnken experimental design (BBD) is a widely exploited form of RSM, particularly tailored for 3 levels (-1, 0, and +1). BBD is more efficient than other factorial designs including the central composite design (CCD) and requires fewer experiments (Witek-Krowiak et al., 2014). More recently, RSM has been extensively used in the optimization of operating parameters in combined systems (Jasnia et al., 2020).

The novelty of the current research can be attributed to the use of calcium peroxide as a catalyst in the ozonation process for the degradation of DCF in wastewater, along with the statistical analysis using RSM with BBD to examine the effect of selected independent variables (initial DCF concentration, pH, CaO_2 dose, and reaction time) on the DCF removal efficiency. The mathematic model obtained from the study can be applied to determine the optimum conditions and to predict the performance of the catalytic ozonation process using CaO_2 as a catalyst in the removal of DCF. The expected results from this research should inform the use of CaO_2 combined with the ozonation process, with upscaling to treat wastewater contaminants such as DCF, other PhACs, and other emerging pollutants.

2. METHODOLOGY

2.1 Chemicals

Sodium thiosulfate ($Na_2S_2O_3$) and calcium sulfate ($CaSO_4$) were obtained from Ajax (Australia). Potassium hydroxide (KOH) and sodium hydroxide (NaOH) were purchased from KemAus (Australia). Hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), and ethanol (C_2H_6O) were obtained from Qrec (New Zealand). All chemicals used in this experiment were of analytical grade.

2.2 Preparation of CaO_2 catalyst

The CaO_2 catalyst was prepared from calcium sulfate ($CaSO_4$), according to Vijuksungsith et al. (2021). First, 40 g of $CaSO_4$ was dissolved in 400 mL of RO water; then, 160 mL of 1 M potassium hydroxide (KOH) and 208 mL of hydrogen peroxide (H_2O_2) were added to the solution. The mixture was stirred thoroughly for 2 h. After that, the solution was centrifuged at 5,000 rpm for 5 min and the CaO_2 obtained was washed twice using RO water and once again using ethanol. Next, the CaO_2 was dried at 90°C for 24 h before storing in a desiccator until use. The as-prepared CaO_2 was characterized using X-ray diffractometry (XRD) and Fourier-transform infrared spectroscopy (FTIR).

2.3 Preparation of synthetic wastewater

Different concentrations of DCF in the synthetic wastewater were investigated (10, 17.5, or 25 mg/L) to serve as a representative range of DCF contamination levels typically found in wastewater from the pharmaceutical industry. A stock solution of 25 mg/L DCF was prepared from an enteric-coated tablet containing 25 mg DCF. The tablet was ground into powder and dissolved in RO water. After that, the solution was adjusted to 1 L with RO water and then passed through GF/C filter paper to eliminate any residue. The stock solution was diluted to the desired concentrations (10 or 17.5 mg/L) and the DCF concentration was determined using a colorimetric method with a spectrophotometer at a wavelength of 275 nm (Mukkawi et al., 2021).

2.4 Experimental setup

Ozone was generated using a laboratory-scale ozone generator with a production rate of 96.30 mg/h. The ozonation experiment was carried out in batch mode using an acrylic rectangular reactor with dimensions of 12×12×15 cm. Synthetic wastewater containing DCF (1.5 L) was circulated using a pump through a venturi device where a vacuum was created. At this point, ozone gas was fed in and mixed with wastewater before the ozonated wastewater returned to the reactor, as shown in Figure 1. Unreacted ozone gas was trapped by the sodium thiosulfate ($Na_2S_2O_3$) solution contained in two gas absorption bottles in series. In the catalytic ozonation process, the as-prepared CaO_2 catalyst at a specified dosage was filled in the reactor. The catalyst was mixed simultaneously using turbulence from the circulation pump. Aliquot samples of 30 mL were collected at 30, 60, and 90 min. Sodium metabisulfite ($Na_2S_2O_5$) was used to quench any residual ozone in the sample. The samples were passed through 0.45-µm nylon filter to separate any CaO_2 residue prior to analysis. The DCF concentration was determined using a colorimetric method with a spectrophotometer at a wavelength of 275 nm (Mukkawi et al., 2021). All experiments were performed in triplicate. Data presented in figures and tables were averaged from three initial values. The percentage of DCF removal was calculated according to Equation 1.

$$\text{Removal (\%)} = \left(\frac{[DCF]_0 - [DCF]_t}{[DCF]_0}\right) \times 100 \quad (1)$$

Where; $[DCF]_0$ is the initial concentration of DCF and $[DCF]_t$ is the concentration of DCF at time t of the reaction.

2.5 Box-Behnken experimental design and statistical analysis

A Box-Behnken experimental design was used to evaluate the main effect on DCF removal from the operational factors, as well as to determine the operational factor values that achieved maximum DCF removal efficiency. The experimental design involved 4 factors, 3 levels, and 27 experiments. The factors considered as independent variables were initial DCF concentration (x_1), pH (x_2), CaO_2 dosage (x_3) and reaction time (x_4). The percentage DCF removal efficiency (y) was used as the response variable, as shown in Table 1.

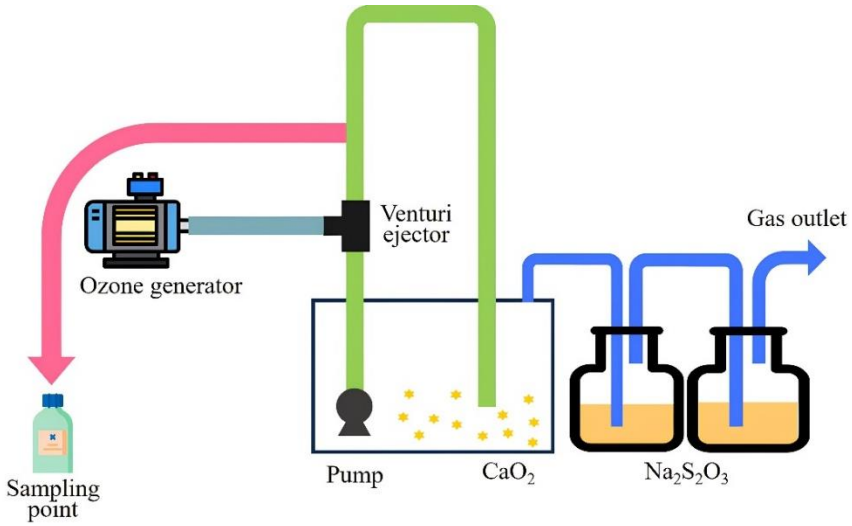

Figure 1. Catalytic ozonation system with venturi type

Table 1. Levels of each factor for Box-Behnken experimental design

Factor	Parameter	Code level		
		1-	0	1
x_1	Initial DCF concentration (mg/L)	10	17.5	25
x_2	pH	5	7	9
x_3	CaO_2 dosage (g/L)	1	2	3
x_4	Reaction time (min)	30	60	90

RSM was used to develop the optimization model and processes. RSM represents independent parameters quantitatively. The relationship between the independent and dependent variables can be illustrated using a quadratic model, as shown in Equation 2.

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_i x \sum_{<j=2}^{k} \beta_{ij} x_i x_j + e_i \quad (2)$$

Where; y is the dependent variable (response parameter); x_i and x_j are the independent variables; β_o is intercept; β_j is the linear coefficient; β_{jj} is the quadratic coefficient; β_{ij} is the interaction coefficient; k is the number of factors studied and optimized in the experiment; and e_i is the random error. The optimum conditions for DCF removal were analyzed based on RSM using different variable combinations, according to the BBD.

Statistical analysis was conducted using analysis of variance (ANOVA) at the 95% confidence level. The quality of fit of the polynomial model was expressed using the coefficient of determination (R^2), as shown in Equation 3. Model accuracy was analyzed using the root mean squared error (RMSE) and the mean absolute percentage error (MAPE), as shown in Equation 4 and Equation 5, respectively.

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{\sum_{i=1}^{n} (\bar{y} - y_i)^2} \quad (3)$$

$$RMSE = \sqrt{\sum_{i=1}^{n} \frac{(\hat{y}_i - y_i)^2}{n}} \quad (4)$$

$$MAPE = \frac{\sum_{i=1}^{n} \left| \frac{(\hat{y}_i - y_i)}{\hat{y}_i} \right|}{n} \times 100 \quad (5)$$

Where; $R^2$is the coefficient of determination; $\hat{y}_i$ is the actual value obtained from the experiment; $\bar{y}$ is the average value obtained from the experiment; y_i is the predicted value obtained from the model; and n is the number of experiments.

3. RESULTS AND DISCUSSION

3.1 Characterization of CaO_2

The CaO_2 was synthesized based on the chemical precipitation from mixing $CaSO_4$ and H_2O_2. The representative results of the XRD analysis of the CaO_2 are shown in Figure 2. The XRD spectra show the different diffraction peaks at 2θ values of 31.9°, 35.4°, 47.7°, 54.7°, and 55.2°. These dominant peaks aligned with the XRD patterns of CaO_2 nanoparticles reported by Madan et al. (2017) and Prameswari et al. (2023). However, the XRD spectra also showed diffraction peaks at 2θ values of 14.8°, 25.7°, and 29.7°, corresponding to $CaSO_4$ as reported by Moncea et al. (2016). The contamination by $CaSO_4$ was possibly caused by using excess $CaSO_4$ as the reactant or incomplete reaction of CaO_2 production or both, as shown in Equation 6.

$$CaSO_4 + H_2O_2 \rightarrow CaO_2\,(hydrate) + H_2SO_4 \quad (6)$$

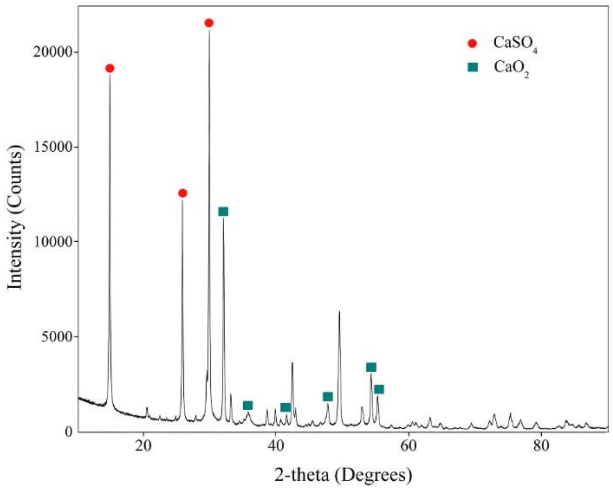

Figure 2. XRD pattern of as-prepared CaO_2 from $CaSO_4$

Figure 3 shows the FT-IR spectra in the wavenumber range 4,000-500 cm^{-1} to identify the functional groups present in the as-prepared CaO_2. According to the spectra, the peak at 599 cm^{-1} and the broad peak at 1,419 cm^{-1} were attributed to O-Ca-O stretching (Madan et al., 2017), whereas the peaks at 867 cm^{-1} corresponded to the O-O vibration of CaO_2 (Li et al., 2022; Dedecan et al., 2022). The FT-IR spectra also exhibited the presence of impurities from the unreacted $CaSO_4$ by the characteristic vibration bands of sulfate at the peaks of 659, 1,007, and 1,173 cm^{-1}. Furthermore, the peak at 1,621 cm^{-1} represented O-H stretching, related to the strongly held water molecules in the hydrated $CaSO_4$ (Melo et al., 2014). The peak at 3,612 cm^{-1} was attributed to O-H stretching vibrations, originating from moisture in the sample (Habte et al., 2019).

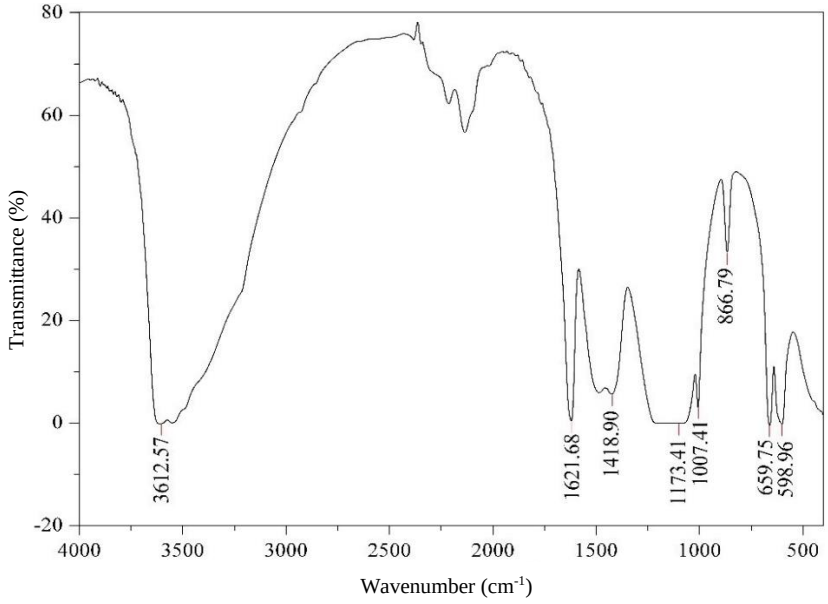

Figure 3. FT-IR spectra of CaO_2 synthesized from $CaSO_4$

3.2 Results from Box-Behnken experimental design and statistical analysis

The experiments involving the DCF removal based on catalytic ozonation using CaO_2 as a catalyst were conducted using a BBD, consisting of 27 experiment sets. The results of the DCF removal as the response variable affected by various factors are presented as a design matrix in Table 2. Statistical analysis revealed that the DCF removal percentage as response variable (y_1) was correlated with four design factors (x_1, x_2, x_3, x_4).

Model suitability analysis was performed to explain the changes in the DCF removal efficiency resulting from the initial DCF concentration, solution pH, CaO_2 dosage, and reaction time. Table 3 presents the statistical analysis of the correlations among these parameters using four models. The coefficient of determination (R^2) is an important parameter for validating model adequacy and this value must be at least 0.80 for the model to be considered a good fit (Aguilar-Ascón et al., 2024). According to Table 3, the full quadratic model had a low standard error of 8.5866 with the highest R^2 and adjusted R^2 values of 84.00% and 65.34%, respectively, demonstrating a good fit to the data and that the quadratic regression model was the most suitable of the tested models to explain DCF removal efficiency.

Table 2. Experimental design matrix and DCF removal based on experimental data results compared to predicted values

Order	DCF concentration (mg/L)	pH	CaO_2 dosage (g/L)	Time (min)	DCF removal efficiency (%)		%Error
	x_1	x_2	x_3	x_4	Actual value	Predicted value	
1	10	5	2	60	96.45	93.96	2.65
2	10	7	1	60	88.00	87.45	0.63
3	10	7	2	30	69.51	66.80	4.06
4	10	7	2	90	95.07	100.00	7.53
5	10	7	3	60	96.00	94.45	1.64
6	10	9	2	60	100.00	98.81	1.21
7	17.5	5	1	60	80.80	76.44	5.70
8	17.5	5	2	30	54.63	57.29	4.66
9	17.5	5	2	90	87.49	85.43	2.40
10	17.5	5	3	60	81.28	78.58	3.44
11	17.5	7	1	30	39.39	46.28	14.90
12	17.5	7	1	90	76.21	77.50	1.66
13	17.5	7	2	60	83.48	83.81	0.39
14	17.5	7	2	60	81.96	83.81	2.21
15	17.5	7	2	60	86.25	83.81	2.91
16	17.5	7	3	30	51.03	57.11	10.65
17	17.5	7	3	90	77.26	77.76	0.64
18	17.5	9	1	60	77.89	70.50	10.48
19	17.5	9	2	30	52.76	56.97	7.40
20	17.5	9	2	90	81.21	80.69	0.64
21	17.5	9	3	60	85.20	79.45	7.24
22	25	5	2	60	80.37	89.08	9.78
23	25	7	1	60	72.93	76.64	4.85
24	25	7	2	30	82.47	64.61	27.63
25	25	7	2	90	87.84	80.47	9.16
26	25	7	3	60	78.01	80.73	3.37
27	25	9	2	60	69.27	79.17	12.50

Table 3. Statistical summary for models predicting DCF removal efficiency

Model	S	R^2 (%)	R^2 (adj) (%)
Linear	11.5778	46.67	36.98
Linear + square	7.7746	71.58	55.73
Linear + interaction	13.1001	50.35	19.32
Full quadratic	8.5866	84.00	65.34

Note: S=standard deviation, R^2=coefficient of determination and R^2(adj)=adjusted R^2

The model for predicting the DCF removal efficiency was obtained from statistical analysis using RSM. This quadratic regression model presented the relationship of DCF removal efficiency with the independent variables of pH, initial DCF concentration, CaO_2 dosage, and reaction time, as shown in Equation 7.

$$\text{DCF removal efficiency (\%)} = -41.1 - 2.23\ \text{DCF} + 6.8\ \text{pH} + 29.8\ CaO_2 + 2.815\ \text{Time} + 0.1335\ \text{DCF} \times \text{DCF} - 0.266\ \text{pH} \times \text{pH} - 6.50\ CaO_2 \times CaO_2 - 0.01405\ \text{Time} \times \text{Time} - 0.246\ \text{DCF} \times \text{pH} - 0.097\ \text{DCF} \times CaO_2 - 0.0224\ \text{DCF} \times \text{Time} + 0.85\ \text{pH} \times CaO_2 - 0.0184\ \text{pH} \times \text{Time} - 0.088\ CaO_2 \times \text{Time} \quad (7)$$

The results of the regression analysis are presented in Table 4, revealing that the initial DCF concentration (x_1) and reaction time (x_4) variables were significant based on the response variable (y) with a p-value of 0.006 (<0.05). These findings suggested that the changes in these parameters significantly affected the DCF removal efficiency at the 95% confidence level. The interactions between variables indicated that DCF^2 (x_1^2) and $Time^2$ (x_1^2) had significant effects on DCF removal efficiency at the 95% confidence level. All the 2-way interactions among the variables had p-values that were greater than the significance level (p>0.05), indicating that those interactions had no significant effects on DCF removal efficiency based on catalytic ozonation using CaO_2 as a catalyst. However, the lack of fit was not significant (p=0.052) in the model, indicating that the model could be used to predict the response of DCF removal efficiency.

Table 4. Response surface model analysis of variance with variables

Source		SS	df	MS	F-value	p-value
Model		4,645.42	14	331.82	4.50	0.006
Linear		2,581.15	4	645.29	8.75	0.002
x_1	DCF	459.65	1	459.65	6.23	0.028
x_2	pH	17.63	1	17.63	0.24	0.634
x_3	CaO_2	93.94	1	93.94	1.27	0.281
x_4	Time	2,009.93	1	2009.93	27.26	0.000
Square		1,861.03	4	465.26	6.31	0.006
x_1^2	DCF×DCF	300.54	1	300.54	4.08	0.066
x_2^2	pH×pH	6.02	1	6.02	0.08	0.780
x_3^2	CaO_2×CaO_2	225.11	1	225.11	3.05	0.106
x_4^2	Time×Time	852.24	1	852.24	11.56	0.005
2-Way Interaction		203.24	6	33.87	0.46	0.825
x_1 x_2	DCF×pH	54.63	1	54.63	0.74	0.406
x_1 x_3	DCF×CaO_2	2.13	1	2.13	0.03	0.868
x_1 x_4	DCF×Time	101.94	1	101.94	1.38	0.262
x_2 x_3	pH×CaO_2	11.64	1	11.64	0.16	0.698
x_2 x_4	pH×Time	4.85	1	4.85	0.07	0.802
x_3 x_4	CaO_2×Time	28.05	1	28.05	0.38	0.549
Error		884.75	12	73.73		
Lack-of-fit		875.30	10	87.53	18.53	0.052
Pure error		9.45	2	4.72		

Note: SS=sum of squares, df=degree of freedom, MS=mean square error

3.3 Influence of parameters on DCF treatment by catalytic ozonation

DCF removal efficiency was optimized using RSM and a BBD, according to different variable factors. Contour plots were constructed to determine the optimum levels of the independent variables and the effects of individual factors were explained.

The regression analysis results indicated that initial DCF concentration and reaction time were significant parameters in the catalytic ozonation process. The effect of reaction time on DCF removal showed that as the reaction time increased, DCF removal efficiency increased. At 30 min, DCF removal efficiency was 69.51%, whereas DCF removal efficiency was 95.07% at 90 min. In the catalytic ozonation process, a long ozonation time was attributed to increased decomposition of the ozone and consequently the generation of the hydroxyl radical (OH·), which is a very powerful radical, that reacted with the DCF (Jabbari et al., 2020). The current findings were consistent with those of Norabadi et al. (2020) and Honarmandrad et al. (2021), which demonstrated that the removal percentage increased with longer reaction times. This observation could be attributed to the extended reaction time facilitating the generation of more hydroxyl radicals, thereby enhancing the degradation of pollutants. As shown in Figure 4, when the DCF concentration increased, the removal efficiency decreased. As a constant ozone concentration was applied to the system, when the DCF concentration increased, ozone and the hydroxyl radical had limited supply to oxidize DCF.

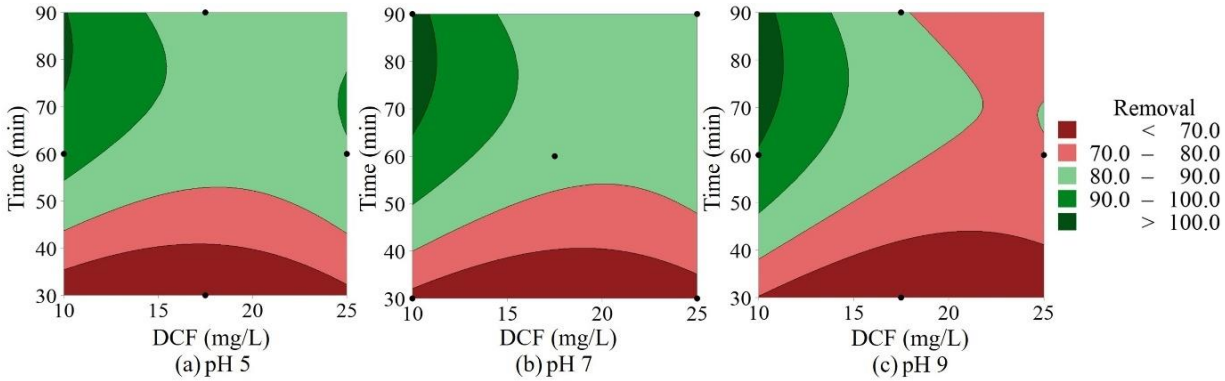

Figure 4. Contour plots of DCF removal efficiency as function of initial DCF concentration and reaction time at different pH levels (a) pH 5 (b) pH 7 and (c) pH 9

Figure 5 illustrates the RSM contour plots of DCF removal efficiency as a function of pH and reaction time at different initial DCF concentrations. It showed that the initial pH did not affect DCF removal efficiency during catalytic ozonation because the CaO_2 generated hydrogen peroxide (H_2O_2) and calcium hydroxide ($Ca(OH)_2$), leading to an increase in the pH, as shown in Equation 8. Under alkaline conditions, the ozone decomposed and produced hydroxyl radicals (OH·), a very powerful radical, as shown in Equations 9-11 (Castro et al., 2019; Wang and Chen, 2020).

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \quad (8)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (9)$$

$$H_2O_2 + e^- \rightarrow OH\cdot + OH^- \quad (10)$$

$$O_3 + OH^- \rightarrow 2OH\cdot + O_2{}^-\cdot \quad (11)$$

Figure 6(a-c) show the RSM contour plots for DCF removal efficiency as a function of CaO_2 dosage and reaction time at different pH levels. They show that the CaO_2 dosage affected DCF removal efficiency; specifically, as the CaO_2 dosage increased, the removal efficiency increased. This could be explained by during the ozonation process, the CaO_2 produced H_2O_2 and $Ca(OH)_2$ through dissolution. The released H_2O_2 from the CaO_2 reacted with O_3 to generate OH· and accelerated the degradation of the DCF, as mentioned earlier (Xu et al., 2020; Xiang et al., 2021).

3.4 Optimization of DCF treatment based on catalytic ozonation and confirmation test

The regression model obtained from the RSM with BBD provided predicted data from different experimental conditions. The predicted values were calculated using the regression quadratic model with

training and test datasets, and then compared with the experimental data, as listed in Table 2. Figure 7 shows both the experimental and predicted values from the regression model. The observed and predicted values were close to linearity, with RMSE and MAPE values of 5.90 and 6.10%, respectively, suggesting that the regression model could accurately predict DCF removal efficiency.

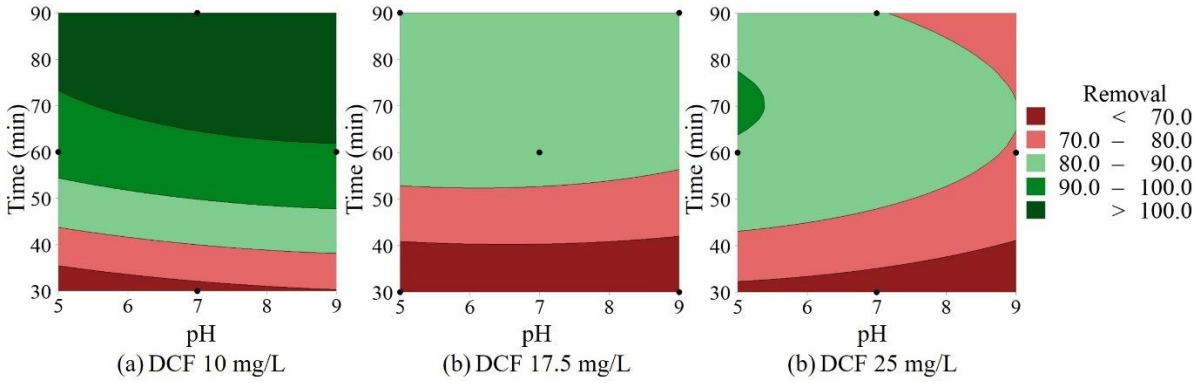

Figure 5. Contour plots of DCF removal efficiency as function of pH and reaction time at different initial DCF concentrations (a) 10 mg/L (b) 17.5 mg/L and (c) 25 mg/L

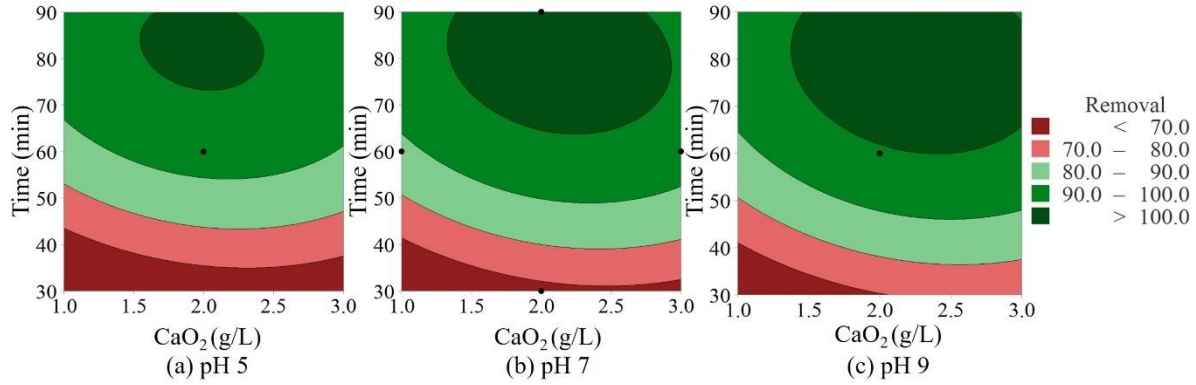

Figure 6. Contour plots of DCF removal efficiency as function of CaO_2 dosage and reaction time at different pH levels (a) pH 5 (b) pH 7 and (c) pH 9

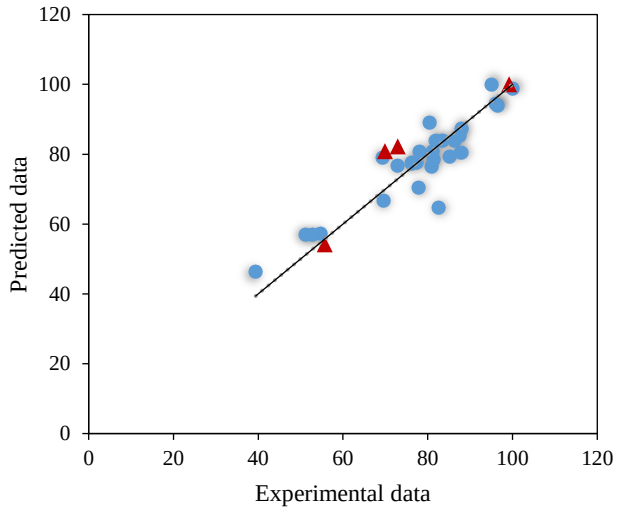

Figure 7. Comparison of predicted and experimental data for DCF removal efficiency (blue dots: training dataset, red triangles: test dataset)

According to Table 2, the DCF removal efficiency of the predicted values was up to 100% for the optimal conditions (initial DCF concentration 10 mg/L, solution pH 7, CaO_2 dosage 2 g/L, and reaction time 90 min). The confirmation test was performed with those optimum factors to validate the predicted optimal conditions. A new experiment was carried out and 97.6% DCF removal efficiency was achieved, as shown in Figure 8. Compared to the experimental data, the RMSE and MAPE values were 4.02 and 6.47%, respectively. These results showed that the regression model obtained from RSM could be effectively used to predict the optimal conditions for DCF treatment based on ozonation catalyzed with CaO_2. Furthermore, the DCF removal efficiency based on catalytic ozonation was compared with that by ozonation alone for the same conditions, which showed that the DCF

removal efficiency based on catalytic ozonation was higher than from using ozonation alone (48.1%), proving that CaO_2 could be effectively used as a catalyst in catalytic ozonation for treatment of DCF contamination in wastewater.

While catalytic ozonation presents an attractive technology for removing emerging contaminants, several studies have indicated that other constituents in wastewater, such as total dissolved solids, total organic carbon, nitrite, and alkalinity, may impair its performance (Kolosov and Yargeau, 2019; Merkus et al., 2023). Additionally, the degradation by-products generated during this process could be more toxic and hazardous than the parent compounds (Malik et al., 2020). Therefore, it is recommended to undertake further investigations into the combined effects of these constituents, the toxicity of by-products, and the cost-effective aspect to ensure the development of more sustainable wastewater treatment solutions.

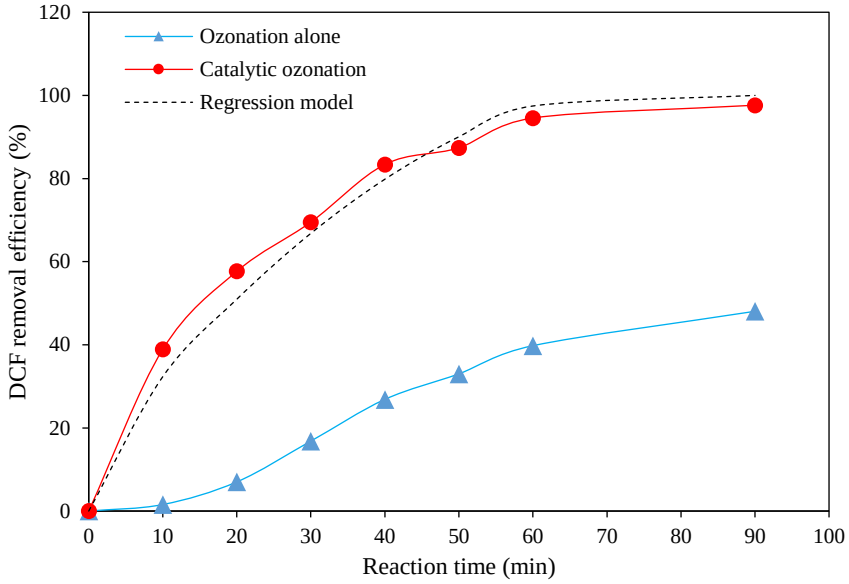

Figure 8. Removal of DCF in synthetic wastewater based on catalytic ozonation using CaO_2 as catalyst (initial DCF concentration 10 mg/L, pH 7, and CaO_2 dosage 2 g/L)

4. CONCLUSION

Catalytic ozonation using CaO_2 as a catalyst was successfully applied to remove DCF in synthetic wastewater. The as-prepared CaO_2 was characterized using XRD and FT-IR to confirm the existence of CaO_2. The results from the RSM with BBD showed that the quadratic regression model was suitable to describe the influence of the studied variables on the DCF removal efficiencies with an R^2 value of 84.00%. According to regression analysis, the initial DCF concentration and reaction time were the key parameters in the catalytic ozonation process. The predicted data obtained from the model were verified with the experimental data, producing RMSE value of 5.90 and a MAPE of 6.10%, indicating that the regression model could be used to optimize and predict DCF removal efficiency. Using the optimal conditions (initial DCF concentration 10 mg/L, solution pH 7, CaO_2 dosage 2 g/L, and reaction time 90 min), the DCF removal efficiency obtained from the experiment was 97.6%, whereas that from the regression model was up to 100%, which was higher than that obtained from ozonation alone (48%). The results from the current research proved that CaO_2 could be effectively used as a catalyst for catalytic ozonation treatment of DCF contamination in wastewater.

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