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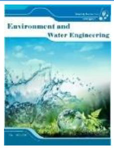

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Modeling optimal conditions for leachate chemical oxygen demand removal using the sononanocatalytic method

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ABSTRACT

The management, control, and treatment of industrial wastewater and municipal waste landfill leachate are crucial for environmental protection and the preservation of groundwater sources. The current research is an experimental study with an applied approach on a laboratory scale, which was conducted in a discontinuous system to remove leachate COD. To achieve this, the effects of four factors—pH, nanoparticle dose, contact time, and ultrasound wave intensity—were investigated at three levels in a Sononanocatalytic process using copper oxide nanoparticles to remove COD from leachate. Optimal conditions for COD removal and the analysis of variance (ANOVA) model were evaluated. The comparison between experimental and predicted COD removal efficiency indicated that the ANOVA model fit the data well. The optimal predicted values for pH, nanoparticle dose, contact time, and ultrasound intensity to achieve the highest COD removal efficiency were 6.39, 0.05 g, 60 min, and 84.89 kHz, respectively. Furthermore, the results showed that the response surface methodology is an efficient way to reduce the cost of tests, and examining the interactions between variables can lead to a better understanding of the effect of independent variables on the dependent variable.

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1. Introduction

Leachate from waste is recognized as one of the most polluted fluids on the earth and has long been considered one of the major challenges of landfill sites. Therefore, managing the control and treatment of leachate from municipal waste disposal sites is an environmental necessity and crucial for preserving groundwater resources. Therefore, the design and construction of appropriate leachate control and treatment systems, based on preliminary quantitative and qualitative studies, appear more necessary than ever. Thus, it is essential to evaluate methods that are economically less costly and, at the same time, free from the technical complexities of advanced leachate treatment systems (Kocakaplan et al., 2018).

Advanced oxidation processes are based on generating highly reactive species such as hydroxyl and superoxide radicals, which can rapidly oxidize a wide range of organic pollutants (Al-bsoul et al., 2020). The sonocatalytic process, like the photocatalytic process, is considered an advanced oxidation process. It operates based on the generation of hydroxyl and superoxide radicals, as well as the phenomenon of acoustic cavitation. These radicals are capable of oxidizing almost all organic compounds (Ran et al., 2022; Torkashvand et al., 2021). It is worth mentioning that the sonocatalytic process has been utilized for years as one of the environmental solutions in industrialized countries worldwide. Moreover, nanotechnology, by introducing an innovative approach to the sonocatalyst industry, promises a vast and promising future in this field.

The sonocatalytic process, either alone and directly or indirectly in combination with other methods such as ozone, ultraviolet radiation, and others, is highly effective in decomposing pollutants such as volatile organic compounds, chlorinated organic compounds, benzene derivatives, methyl tertiary-butyl ether, organic pesticides, and trihalomethanes. This approach yields better results compared to the separate application of each method (Al-bsoul et al., 2020). Research has also shown that nanometer-sized adsorbents have a significantly higher adsorption capacity for pollutant removal compared to their larger or bulk counterparts. Nanoparticles, due to their small size and unique molecular or atomic structure, exhibit distinctive mechanical, magnetic, optical, electronic, catalytic, and chemical properties. These properties have led to their increasing use in the treatment of environmental pollutants. The small size of nanoparticles facilitates effective and easy subsurface distribution, while their large surface area enhances their reactivity, enabling the rapid degradation of pollutants. The mechanism of pollutant removal by nanoparticles involves reducing pollutants to less hazardous products and subsequently adsorbing them onto their surfaces (Han et al., 2006).

Among metal oxides, the use of copper oxide nanoparticles has attracted significant attention from researchers since the 1990s. This is due to their large effective surface area, greater quantum size effects compared to bulk copper, low cost, ease of synthesis, and high efficiency as a catalyst (Han et al., 2006). Today, the use of advanced and precise statistical models to examine the relationships between variables and optimize various processes is increasingly expanding across different fields. One of the statistical models used in environmental health is the Response Surface Methodology (RSM). This technique is used to evaluate the effects of independent variables on the response variable. Additionally, based on this model, the optimal value for the response can be predicted. RSM is an optimization method that employs a set of statistical techniques to model the relationships between variables. It helps avoid costly and time-consuming experimental runs (Abdolalian et al., 2023). In this study, conducted to remove the chemical oxygen demand (COD) of landfill leachate through the sonocatalytic process using copper oxide nanoparticles, the experimental and predicted removal efficiency, the impact of key influencing variables such as acidity, nanoparticle dosage, contact time, and ultrasound intensity on removal efficiency, optimal removal conditions, ANOVA model analysis, and a comparison of removal efficiency using commercial and synthesized copper oxide nanoparticles under optimal conditions were examined.

In this study, aimed at removing the COD of landfill leachate through the sonocatalytic process using copper oxide nanoparticles, the experimental and predicted removal efficiencies were analyzed. The effects of key influencing variables, including pH, nanoparticle dosage, contact time, and ultrasound intensity, on removal efficiency were evaluated. Optimal removal conditions, ANOVA model analysis, and a comparison of removal efficiencies using commercial and synthesized copper oxide nanoparticles under optimal conditions were also investigated. A review of previous related studies indicates that the processes used in this research have not yet been applied to the leachate from the Zahedan landfill. Additionally, in this study, the advanced statistical method of RSM was utilized for experimental design, data collection, modeling the relationships between key factors, simultaneously considering their interactions, and achieving optimal conditions. The nanocatalyst used in the present study is copper oxide (CuO), which, according to the conducted reviews, has not been previously utilized or investigated for the leachate under study. It is worth mentioning that the results of this study will be valuable for identifying the role of pH, nanoadsorbents (catalysts), contact time, and ultrasound intensity in the sononanocatalytic process.

2. Materials and Methods

2.1 Materials

In this study, copper oxide nanoparticles from Sigma-Aldrich were used, with an effective surface area of 15–20 m²/g and an average size of less than 50 nm. The other materials used in this study were sourced from Merck, Germany. To ensure that the characteristics of the purchased commercial nanoparticles matched the specifications provided by the manufacturer, a sample of the commercial nanoparticles was sent to reputable laboratories for SEM, TEM, XRD, and XRF analyses prior to the start of the experiments. It is worth mentioning that for the synthesis of nanoparticles required in part of this study, copper oxide nanoparticles were prepared using the direct precipitation method in an aqueous solution (Zhou et al., 2006). Initially, to prepare a 0.1 M solution of ($Cu(NO_3)_2.3H_2O$), 2.416 g of that was dissolved in 100 ml of distilled water. Then, the pH of this solution was rapidly adjusted to 10 using a 1 M sodium carbonate solution, which was prepared by dissolving 10.56 g of sodium carbonate in 100 ml of distilled water, with continuous stirring. After allowing the solution to stand for 12 hours, the final product was collected through filtration using filter paper and was continuously washed with deionized water to effectively remove impurities. The separated precipitates on the filter papers were dried in an oven at 60 °C for 24 hrs. The precipitates were then transferred into a crucible and placed in a conventional furnace at 350 °C for 4 hrs. This process yielded the final product, which was prepared for laboratory analysis and subsequent work.

2.2 Experimental design

The present research is an experimental study with an applied approach conducted at the laboratory scale in a batch system. In this study, the advanced statistical method of RSM was employed for experiment design, data collection, modeling, analyzing the relationships between key factors, simultaneously considering their interactions, and achieving optimal conditions. The sample size, based on the specific objectives, was determined for landfill leachate using the RSM of the central composite design (CCD) type. The RSM identifies and predicts the optimal operational conditions within the range of the study's variables, including pH, copper oxide nanoparticle dosage, contact time, and ultrasound intensity. These conditions are presented as the best achievable process parameters. This program specifically searches for the optimal conditions for each variable and then optimizes the desired response based on the objective. The optimization process seeks a combination of variable levels that maximizes the removal of the target parameter during the desired process (Abdolalian et al., 2023; Hossini et al., 2014). Therefore, following this method and aiming to examine the effects of four factors at three different levels—pH (3, 7, and 11), copper oxide nanoparticle dosage (0.02, 0.035, and 0.05 g), reaction time (10, 35, and 60 minutes), and ultrasound intensity (35, 37, and 130 kHz)—in the sononano-catalytic process, a total of 93 experimental runs with three repetitions were required. This approach allowed for the analysis of interactions between these factors to achieve optimal COD removal conditions and develop the optimal regression model.

2.3 Research methodology

After procuring the required materials and equipment, all leachate samples were collected at specific times from the municipal landfill site in Zahedan, specifically from a reservoir located at the bottom of the waste pile. The samples were transported to the laboratory while maintaining a cold chain. After sampling and performing initial pretreatment, such as simple sedimentation and chemical coagulation using polyaluminum chloride, preliminary tests were conducted according to standard methods (Rice et al., 2012) to measure and record the initial COD levels in the leachate. The results were documented accordingly. Subsequently, each run, as determined by the randomized sequence provided in the RSM, was applied sequentially to the landfill leachate. At the end of each run, to evaluate performance and determine the removal efficiency in line with the study's objectives, the COD levels in the leachate were re-measured and recorded based on the standard method after removing the nanoparticles using a syringe filter (Rice et al., 2012). The overall removal efficiency of the target parameter in each run was calculated using Eq. 1:

$$R = (C_i - C_e)/C_i \times 100 \quad (1)$$

where, R = Removal efficiency (%), C_i and C_e are the initial and final concentration (mg/l), respectively.

2.4 Statistical analysis

To describe the data, considering the quantitative nature of the response variables, central tendency and dispersion indices such as mean and standard deviation were utilized. Additionally, analysis of variance (ANOVA) was conducted to identify significant effects, fit the model, estimate coefficients, calculate goodness-of-fit indices for the model, predict responses based on the fitted model, and compute residuals. It is worth mentioning that all data descriptions, analyses, and the plotting of three-dimensional and contour graphs were performed using Minitab software.

3. Results and Discussion

3.1 Initial characteristics of leachate

During each weekly sampling, the incoming leachate was analyzed for several key parameters, including biochemical oxygen demand (BOD), COD, total dissolved solids (TDS), total Kjeldahl nitrogen (TKN), and total phosphorus (TP). The results of the sample analysis and the permissible limits based on Iranian standards are presented in Table 1.

Table 1 Characteristics of the leachate sample

Parameters (mg/l)	Raw landfill leachate	After pretreatment by coagulation with PAC	After sonocatalysis process	Permissive levels (Ghasemi Masoumabad and Hajalifard, 2015)
BOD_5	1960	1120	168	30
COD	4083.5	2356.5	348.05	60
TDS	9960	5080	1016	-
TKN	107.52	84.56	16.912	2.5
TP	31.82556	18.5633	15.91278	6
BOD_5/COD	0.48	0.47	0.48	-

Table 2 Results of variance analysis of COD removal during sononanocatalytic process from waste leachate

Source	DF	Sum of squares	Mean Square	F-value	P-value (Prob>F)
Model	9	1143.76	127.085	391.25	<0.001
pH	1	224.55	224.550	691.30	<0.001
CuO	1	11.08	11.83	34.12	<0.001
Time	1	7.87	7.807	24.03	<0.001
US	1	73.76	73.758	227.07	<0.001
pH*pH	1	820.86	820.860	2527.12	<0.001
pH*time	1	0.80	0.786	2.45	0.121
pH*US	1	2.10	2.101	6.47	0.013
CuO*time	1	1.51	1.513	4.66	0.034
time*US	1	1.30	1.298	3.99	0.049
Residual Error	83	26.96	0.325		
Lack-of-Fit	15	7.44	0.496	1.73	0.066
Pure Error	68	19.52	0.287		
Total	92	1170.72			
R^2		97.70			
$R^2_{adjusted}$		97.45			

3.2 COD removal efficiency

Based on the recorded initial COD levels in the samples and the calculated remaining COD after the sononanocatalytic process, the removal efficiency for each experiment was determined. The highest removal efficiency (85.23%) was observed in the scenario where the ultrasound intensity was at its maximum level (130 kHz), while the other variables were at their midpoints (pH 7, nanoparticle dosage 0.035 g, and contact time 35 minutes). The comparison between the actual and predicted COD removal efficiencies in the sonocatalytic process using copper oxide nanoparticles indicates that the ANOVA model provided a good fit to the data. Using the statistical method of response surface methodology, the following analysis of variance (ANOVA) model, representing the relationship between the coded independent variables and the removal efficiency, was obtained as Eq. 2:

$$R = 83.96 - 2.03pH + 0.45\ CuO + 0.38\ time + 1.16\ US - 6.02\ pH^2 + 0.20\ pH\times US - 0.17\ CuO\times time - 0.16\ time\times US + \mathcal{E} \quad (2)$$

In this study, the high values of the coefficient of determination (R^2: 97.70) and the adjusted coefficient of determination ($R^2_{adjusted}$: 97.45) indicate that a very large proportion of the variations in the response variable is explained by the independent factors under consideration. Additionally, the non-significance of the lack-of-fit index (P = 0.06) confirms the good fit of the analysis of variance (ANOVA) model (Table 2).

The results of the analysis of variance (ANOVA) also indicate that the parameters of pH, copper oxide nanoparticle dosage, contact time, and ultrasound intensity have a significant impact on the COD removal process during the sonocatalytic process (pH>US>CuO>time). Therefore, the fitted model effectively describes the relationship between the independent variables and the dependent variable.

In the analysis of experiments and the use of analysis of variance (ANOVA) models, it is assumed that the residuals have a normal distribution with a mean of zero and a constant variance (δ^2) and are independent of each other. Fig. 1 fully confirms the validity of these assumptions. Therefore, considering the above-mentioned figure that verifies the model's assumptions, as well as the values of R^2 and adjusted R^2, it can be concluded that the selected model is highly appropriate for describing and analyzing the data.

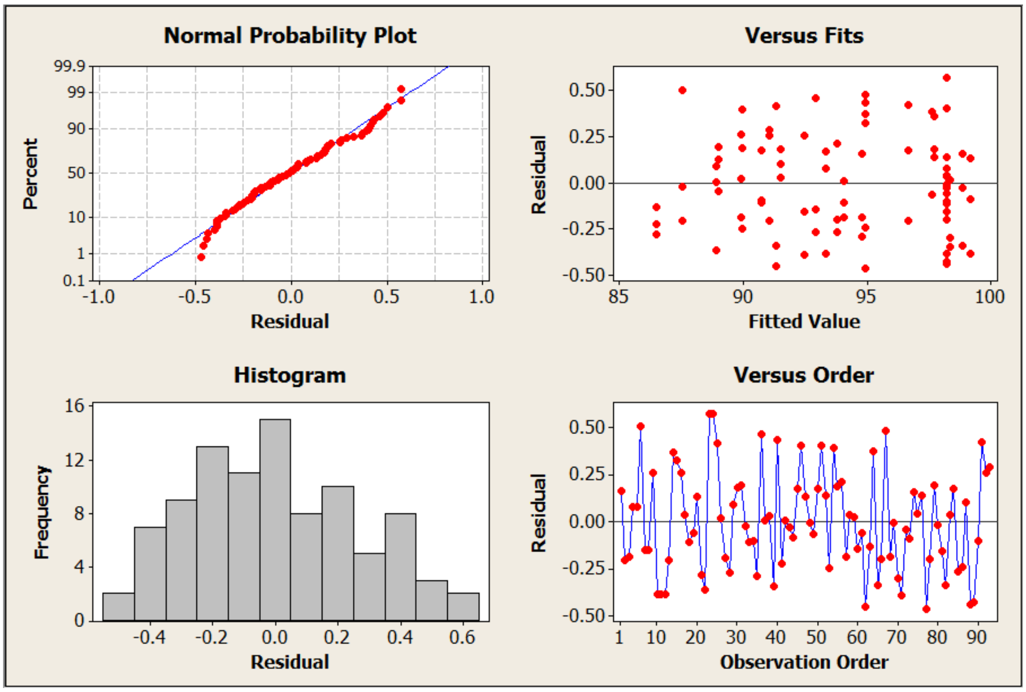

Fig. 1 Graphical review of the assumptions of the analysis of variance model in COD removal in the Sononanocatalytic process

3.3 Interaction effects of variables in COD removal efficiency

3.3.1 pH and US Intensity

As observed in Fig. 2(a), an increase in pH from 3 to 7 and an increase in US from 35 to 130 kHz result in improved COD removal efficiency. Specifically, at a pH of 7 and a US intensity of 130 kHz, COD removal efficiency exceeds 85%. However, as the pH increases from 7 to 11, a decline in removal efficiency is observed. At a pH of 11 and a US intensity of 35 kHz, the COD removal efficiency drops to less than 75%.

3.3.2 CuO dosage and contact time

In Fig. 2(b), with other variables held at their average levels, it is observed that increasing the nanoparticle dosage from 0.02 to 0.05 g/l and the contact time from 10 to 60 min leads to an improvement in COD removal efficiency. Specifically, more than 84.50% removal efficiency is achieved at a nanoparticle dosage of 0.05 g/l and a contact time of 60 min.

3.3.3 Contact time and US

In Fig. 2(c), it is observed that increasing the contact time from 10 to 60 min and the US intensity from 35 to 130 kHz leads to an improvement in COD removal efficiency. Specifically, more than 85% removal efficiency is achieved at a contact time of 60 min and a US intensity of 130 kHz.

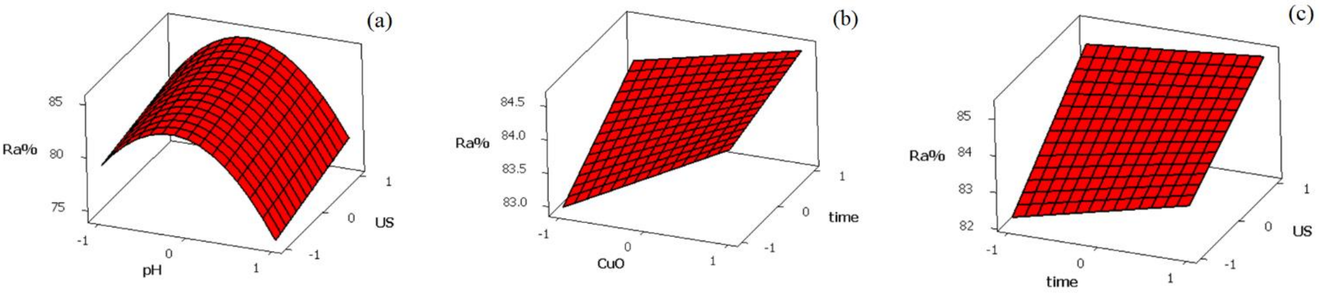

Fig. 2 The 3D surface plots of the interaction effects of: a) pH and US intensity, b) CuO nanoparticle dose and contact time, and c) US intensity and CuO nanoparticle dose and contact time on COD removal efficiency

3.4 Optimization of COD removal process and validation

As illustrated in Fig. 3, the predicted optimal values of the variables for achieving the highest COD removal efficiency are as follows: pH = 6.39; nanoparticle dosage = 0.05 g; contact time = 60 min; and US intensity = 84.89 kHz.

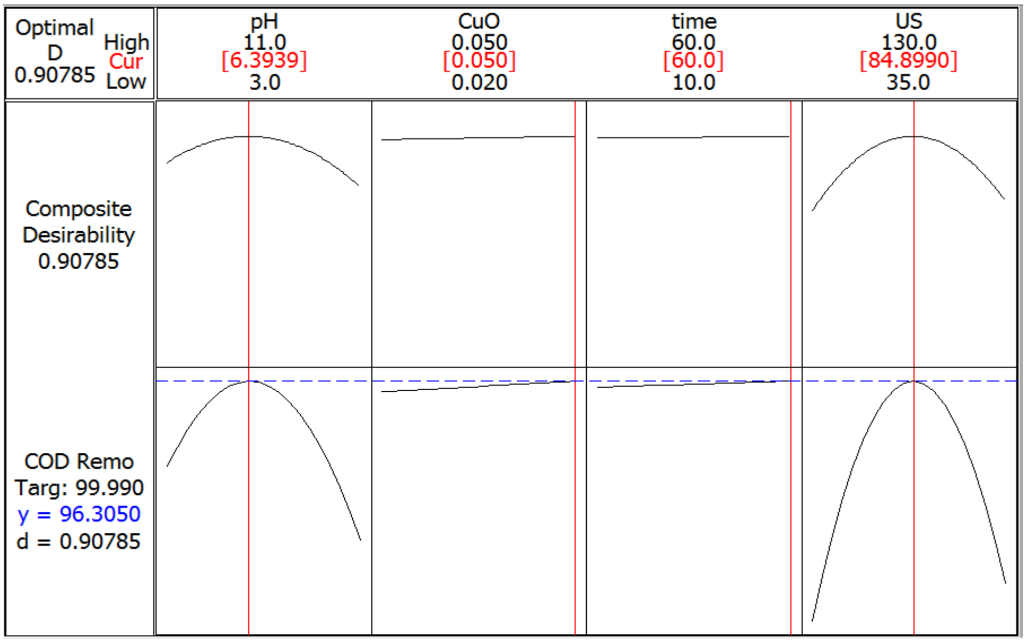

Fig. 3 Optimum conditions designed by RSM to remove COD from waste leachate during sononanocatalytic process

To validate the optimization results, the optimal conditions were tested three times. The experimental mean values reported were consistent with the predicted values from the ANOVA model, confirming the accuracy of the optimization process (Table 3).

Table 3 Optimum values of variables and predicted value, and average experimental efficiency of COD removal

Parameters	Optimum value	COD degradation rate (%)	
		Predictive	Experimental
pH	6.39	96.30	94.93
CuO	0.05 g/l		
Time	60 min		
US	84.89 kHz		

Furthermore, after conducting three experiments, it was determined that the average removal efficiency of all target parameters under optimal conditions during the sononanocatalytic process was higher when using commercial nanoparticles (94.93%) compared to synthetic nanoparticles (90.40%). The comparison between the actual and predicted COD removal efficiency in the sononanocatalytic process using copper oxide nanoparticles indicates that the ANOVA model provided an excellent fit to the experimental data. Moreover, in this study, the high values of the R^2 and $R^2_{adjusted}$ indicate that a significant proportion of the response variable's variability is explained by the independent variables.

Additionally, the non-significant values of the lack-of-fit index further confirm the excellent fit of the ANOVA models. The results of the ANOVA analysis indicate that the parameters pH, copper oxide nanoparticle dosage, and ultrasound intensity have a significant impact on the COD removal process during the sononanocatalytic procedure. Therefore, the fitted model effectively describes the relationship between the independent variables and the dependent variable. Considering the graphical evaluation of the assumptions of the analysis of variance model in the removal of COD parameter during the sononanocatalytic process, as well as the confirmation of the model assumptions and the values of the R^2 and $R^2_{adjusted}$ presented in the analysis of variance table, it can be concluded that the selected model is entirely appropriate for describing and analyzing the data.

To evaluate the reusability of the synthesized nanocomposite, adsorption and desorption processes were carried out over 10 cycles. The results showed that the performance of the COF@MOF nanocomposite remained stable with negligible change across the 10 adsorption-desorption cycles. According to desorption results, the adsorbent showed a 33% reduction in CO_2 adsorption efficiency (from 100 to 9 ppm) and an 18% decrease in CH_4 adsorption efficiency (from 2500 to 2186 ppm) after 10 cycles, indicating the efficiency of the hybrid adsorbent.

3.5 Effect of pH values on removal efficiency

The pH value of the solution is one of the most critical and influential parameters in chemical reactions, affecting the structure of the pollutant under investigation, the surface properties of the nanoparticles, and the pathway and kinetics of the reactant materials (Ayare et al., 2019). On the other hand, in heterogeneous catalytic systems, pH can influence the surface properties of metal oxides produced by hydroxyl groups in the presence of water. Moreover, under natural conditions, the effective surface charge of various types of catalysts can be either positive or negative, depending on their surface characteristics, particularly the surface functional groups and the components of the catalyst. As the pH increases, the dominant surface charge of the catalyst becomes negative, while a decrease in pH results in a positive dominant surface charge on the catalyst. This phenomenon is crucial in studying sonocatalytic mechanisms. At high pH values, surface functional groups become deprotonated, while at low pH values, these surface functional groups become protonated (Jiang et al., 2002). The deprotonation and protonation of surface functional groups enable the catalyst to act as a Lewis acid and base, which is one of the most significant phenomena influencing the performance of copper oxide nanoparticles as a catalyst. An increase in the solution's pH enhances the rate of heterogeneous sonocatalytic reactions. These reactions lead to the formation of highly reactive hydroxyl radicals and other radicals such as OH, HO_2, and HO_3. Consequently, this can result in an increased degradation of pollutants (Jiang et al., 2002). In examining the interaction effects of variables on the removal of the COD parameter from landfill leachate during the sononanocatalytic process, the interaction between pH and ultrasonic wave intensity was found to be significant. Specifically, a simultaneous increase in pH from 3 to 7 and ultrasonic frequency (US) from 35 to 130 kHz resulted in an increase in COD removal efficiency. The highest COD removal efficiency was observed at a pH of 7 and a US of 130 kHz. However, as the pH increased from 7 to 11, the removal efficiency decreased, with the lowest COD removal efficiency observed at a pH of 11 and a US of 35 kHz. Overall, the results indicate that the pH variable plays a critical role in the removal of the target pollutant from landfill leachate during the sononanocatalytic process. As the pH increases up to a neutral level, the removal efficiency of all pollutants improves. However, with further alkalinity, the removal efficiency decreases, and the highest removal efficiency of the target pollutant occurs at a neutral pH. This phenomenon may be attributed to the substantial formation of reactive radicals such as hydroxyl, OH, HO_2, and HO_3 at a pH of 7. From acidic to neutral pH, the production of hydroxyl radicals gradually increases during catalytic processes. At lower pH levels, the positive surface charge of the catalyst limits the availability of hydroxyl groups needed for the formation of hydroxyl radicals. In contrast, at higher pH levels, a significant amount of hydroxyl ions is generated to react with holes and form hydroxyl radicals. However, as the pH exceeds 7, the removal efficiency decreases because, under these conditions, hydroxyl ions intensely compete with organic molecules for adsorption on the surface of the nanocatalyst. This competition reduces the efficiency of pollutant removal from the solution (Chen et al., 2010). It is also worth noting that among the four main variables influencing the sononanocatalytic process, pH has the most significant impact on pollutant removal, as reported in the analysis of variance model. This is clearly evident from the analysis of the coefficients. In a study conducted by a group of researchers on the removal of humic acid in the presence of chromium via photocatalytic degradation using titanium dioxide nanoparticles, the efficiency increased as the pH rose from 4 to 7 but decreased when the pH was further increased from 7 to 11 (Yang et al., 2006). In another study on the photocatalytic removal of aniline using magnesium oxide nanoparticles, it was observed that the removal efficiency increased with a rise in pH up to neutral levels but decreased with further alkalinity. In this study, the optimal pH for the photocatalytic removal of aniline was reported to be 7 (Bazrafshan et al., 2016). The results of studies indicate that the decrease in efficiency in alkaline environments is because high pH levels provide favorable conditions for the formation of carbonate ions, which are effective scavengers of OH^- ions and can reduce the decomposition rate (Fang et al., 2011). Studies have also shown that the addition of nanoparticles gradually makes the solution alkaline. When the pH is adjusted to alkaline conditions, the environment can become excessively alkaline. Under such conditions, nanoparticles react with water molecules and decompose. As a result, at very high (alkaline) pH levels, the nanoparticles lose their functionality, leading to a reduction in pollutant removal efficiency (Sasaki et al., 2011). Moreover, an excessive increase in pH leads to the elevated formation of HO_2^- ions and the consumption of OH radicals by carbonate and bicarbonate ions (Bobu et al., 2008).

3.6 Effect of nanoparticle dosage on removal efficiency

One of the most important parameters influencing the efficiency and optimal performance of hybrid processes, adsorption processes, and catalytic oxidation is the dosage of the nanoparticle or adsorbent used in the process. As observed in the results of the analysis of variance and graphical representation of the variables' effects on the removal efficiency of the target parameter from landfill leachate, the interaction between the dosage of copper oxide nanoparticles and contact time was significant for all parameters. Specifically, simultaneous increases in the nanoparticle dosage from 0.02 to 0.05 g/L and the contact time from 10 to 60 minutes resulted in improved removal efficiency. The results of this study indicate that an increase in the dosage of copper oxide nanoparticles leads to an improvement in removal efficiency. Studies have shown that increasing the presence of copper oxide nanoparticles in sonocatalytic processes generates additional nuclei, which subsequently increases the number of bubbles and radicals. Additionally, the cavitation threshold may decrease due to the vapor and gases present in the pores of the nanoparticles. In other words, nanoparticles provide additional surfaces for cavitation (Haddadi et al., 2007; Mason et al., 2002). Another reason for the increased pollutant removal efficiency with higher nanoparticle dosages is the extension of the induction phase, which strongly depends on the intensity and dosage of nanoparticles. The improved removal efficiency with higher nanoparticle dosages is likely due to the presence of more active sites on the catalyst surface, the increased likelihood of interactions between the pollutant and copper oxide nanoparticles, and the greater effect of ultrasonic wave frequencies at higher dosages (Liao et al., 2003). Studies have shown that removal efficiency is significantly influenced by the number of active sites and adsorption by the catalyst. Increasing the nanoparticle dosage up to an optimal level improves removal efficiency. However, experimental findings suggest that exceeding this optimal dosage no longer enhances removal efficiency and may even result in decreased performance (Dianati et al., 2014). This behavior of the catalyst can be explained by the fact that, with an increase in catalyst dosage, the catalyst itself acts as a scavenger, inhibiting the production of hydroxyl radicals and even consuming the generated hydroxyl radicals. In other words, as the catalyst dosage increases, the catalyst functions as an adsorbent, leading to enhanced physical adsorption of pollutants on its surface (Molinari et al., 2006). The results of studies conducted by some researchers showed that increasing the dosage of nanoparticles can enhance the efficiency of nitrate removal (Dianati et al., 2014). Another study demonstrated that increasing the concentration of nanoparticles leads to improved removal efficiency of the antibiotic metronidazole (Fang et al., 2011). In a study on the removal of azo dyes from industrial wastewater using MgO nanoparticles, it was found that increasing the nanoparticle dosage enhances the removal efficiency (Moussavi et al., 2009).

3.7 Effect of contact time on removal efficiency

Reaction time is one of the most critical variables influencing the design and performance of any chemical process, including oxidation processes. In fact, reaction time refers to the duration required to achieve the desired treatment objectives (Bazrafshan et al., 2013a; Bazrafshan et al., 2013b). As observed in the results of the analysis of variance and the graphical representation of the variables' effects on the removal efficiency of the target parameter from landfill leachate, the interaction of contact time with the dosage of copper oxide nanoparticles and the intensity of ultrasonic waves was significant. Specifically, simultaneous increases in contact time from 10 to 60 minutes, nanoparticle dosage from 0.02 to 0.05 g/L, and ultrasonic wave intensity from 35 to 130 kHz resulted in enhanced removal efficiency. Overall, the results indicate that increasing the contact time enhances the removal efficiency of the target pollutant. Studies have also shown that increasing the contact time enhances the pollutant removal efficiency. This is attributed to the prolonged excitation of nanoparticles over time, which subsequently increases the production of OH radicals and positive holes, leading to an expanded adsorption surface area and improved removal efficiency (Parastar et al., 2012). In a study conducted by Kakavandi et al., (2014) titled Evaluation of the Efficiency of Magnetic Powdered Activated Carbon Modified with Iron Oxide Nanoparticles for Amoxicillin Removal from Aqueous Environments, the optimal removal efficiency of amoxicillin was achieved at a contact time of 90 minutes (Kakavandi et al., 2014). Some researchers, in the photocatalytic degradation of ciprofloxacin using NaCl/TiO_2, reported the highest antibiotic removal efficiency under irradiation at 60 minutes (Liu et al., 2014).

3.8 Effect of US wave intensity on removal efficiency

The frequency of sound waves is a crucial parameter influencing the size, number, and collapse of bubbles, the production of hydroxyl radicals, and ultimately the overall performance of the sonocatalytic process (Joshi et al., 2019). As observed in the results of the analysis of variance and the graphical representation of the variables' effects on the removal efficiency of the target parameter from landfill leachate, the interaction of ultrasonic wave intensity with pH and contact time was significant. Specifically, simultaneous increases in ultrasonic wave intensity from 35 to 130 and pH from 3 to 7, as well as increases in ultrasonic wave intensity from 35 to 130 kHz and contact time from 10 to 60 min, resulted in enhanced removal efficiency. Overall, the results indicate that increasing the frequency of ultrasonic waves enhances the removal efficiency of all target pollutants. This is due to the increased excitation of nanoparticles, the greater number of positive holes generated, and consequently, the higher production of hydroxyl radicals, leading to improved removal efficiency (Khataee et al., 2015).

3.9 Removal efficiency under optimal conditions

The results indicate that the removal efficiency of the target parameter under optimal conditions is higher when using commercial nanoparticles. The specific surface area of nanoparticles is an influential parameter affecting the physical and chemical properties of the nanoparticle. Commercial copper nanoparticles have a larger specific surface area (15–20 m^2/g) compared with synthetic nanoparticles (10–15 m^2/g). A larger specific surface area provides more active sites for reactions, which is why commercial copper nanoparticles exhibit a higher reaction rate with pollutants (Joo et al., 2006).

4. Conclusion

The findings of this study are as follows:

1. The quadratic model is suitable for pollutant removal using the integrated process, and the response surface design enables the

evaluation of numerous variables with the minimum number of experiments.

2. There was a good correlation between the values predicted by the model and the results obtained from the experiments.

3. The response surface methodology proved to be an efficient approach in reducing costs and experiments. Additionally, analyzing the interaction effects of variables aids in better understanding the influence of independent variables on the dependent variable.

4. In general, the reduction of chemical oxygen demand (COD) in leachate using the sononanocatalytic method with copper oxide nanoparticles is highly feasible. Employing this model can achieve high efficiency at a low cost.

The variations in the characteristics of the incoming leachate and parameters such as TDS, TSS, organic matter, and colors, which can act as confounding factors influencing the model and its P-Value, are uncontrollable in this study. Considering the use of a batch system in this study, it is suggested that a continuous system be investigated as well. Additionally, it is recommended to explore the combined application of copper oxide nanoparticles with other nanoparticles for the removal of COD from leachate.

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Statements and Declarations

Data availability

The data from this study will be made available upon request.

Conflicts of interest

The author of this paper declared no conflict of interest regarding the authorship or publication of this paper.

Author contribution

I. Homayoonnezhad: Study Design, Conducting Experiments, Data Acquisition, Data Analysis and Interpretation, Drafting the initial manuscript. P. Amirian: Conducting Experiments, Plotting Graphs, Literature Review, Drafting Discussion and Conclusion Sections.

AI Use Disclosure

During the preparation of this manuscript, the authors used ChatGPT for language translation. All content has been carefully reviewed and revised by the authors, who take full responsibility for the final version of the manuscript.

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