JAEHR
Journal of Advances in Environmental Health Research
J Adv Environ Health Res, 2024; 12(4): 205-211. doi: 10.34172/jaehr.1365
http://jaehr.muk.ac.ir

Original Article

Enhancement of Photocatalytic Removal of 4-Chlorophenol from Aqueous Solutions by Manganese Oxide Doped ZnO Nanoparticles Using RSM

Shima Rezaei[1], Afshin Maleki[1], Reza Rezaee[1], Hajar Kashefi[2], Yahya Zandsalimi[1*]

[1]Environmental Health Research Center, Research Institute for Health Development, Kurdistan University of Medical Sciences, Sanandaj, Iran
[2]Vice Chancellor for Research and Technology, Kurdistan University of Medical Sciences, Sanandaj, Iran

Article history:
Received: December 9, 2023
Revised: February 3, 2024
Accepted: March 2, 2024
ePublished: November 12, 2024

***Corresponding author:**
Yahya Zandsalimi,
Email: yzandsalimi@gmail.com

Abstract
Background: Phenol and its derivatives as a toxic and dangerous substance produce by many industries. This pollutant must be removed from contaminated streams or fluids before discharging. The aim of this study was to enhancement of nano-photocatalytic removal of 4-chlorophenol (4-CP) from aqueous solutions applying manganese oxide doped ZnO nanoparticle (MnO_3-doped ZnO) catalyst via experimental designing of surface-response method.
Methods: In this study, MnO_3-doped ZnO NPs were fabricated using hydrothermal technique and ratio of Mn-doped ZnO NPs consisted of 0 (pure), 0.5, 1 and 1.5%. The characteristics of the synthesized NPs was studied by scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR), X-ray diffraction (XRD) and atomic force microscopy (AFM) analyses. For determined the doped ZnO quality, variables such as pH, initial 4-CP concentration, NPs dose and contact time were probed in 4-CP removal.
Results: Results demonstrate that the removal efficiency are significantly affected by the varied Mn-doped ZnO ratio. The ratio of 1% was optimal. The hexagonal shape of NPs confirmed by XRD and SEM analysis. The SEM indicated that no agglomeration of NPs observed. The sharp edges peaks in XRD indicate a proper crystallized ZnO NPs. Regression analysis showed a quadratic polynomial model was obtained for efficiency prediction. The data providing an acceptable model assumption for analyzing the variance. It was also realized that increasing the nanoparticles dose and the contact time led to reduce the removal rat.
Conclusion: Comparing the 4-CP removal efficiency of bare ZnO and Mn-doped ZnO showed that the Mn-doped ZnO have larger efficiency and improve up to 84%.
Keywords: 4-Chlorophenol, Zinc oxide, Photocatalyst, Doping, Surface-response

Please cite this article as follows: Rezaei S, Maleki A, Rezaee R, Kashefi H, Zandsalimi Y. Enhancement of photocatalytic removal of 4-chlorophenol from aqueous solutions by manganese oxide doped ZnO nanoparticles using RSM. J Adv Environ Health Res. 2024; 12(4):205-211. doi:10.34172/jaehr.1365

Introduction

Fast-growing of technology, human activities and the overuse of compound in medical terms has led introduction of frequently emerging organic compounds (EOCs) in water environment.[1] The EOCs includes amine, antibiotics, and phenols give rise to concern in environmental contaminants.[2,3] Among these pollutants, phenol derivatives (like chlorophenol) have been included in priority pollutant list regulated by the US-EPA's.[4] The primary nonpoint source of chlorophenol compounds were mainly by the chemical and petrochemical industry, and also, application of organochlorine pesticides and chlorination of phenol containing wastewater, burning of organic materials in the presence of chlorine.[5]

Among these organic pollutants, 4-chlorophenol (4-CP) which is used in the production of refrigerants, bactericides, herbicides, dyes, and pharmaceutical compounds, This recalcitrant compound is highly toxic with low biodegradability and very harmful for human health and ecosystem.[6] Long-term contacts with this substance can lead to headaches, fatigue, restlessness, affecting liver and kidneys, weakness of muscles, nausea, and finally coma and death.[5,6] Thus, effective removal of chlorophenols are important for the protection of the environment and human well-being. So, due to their high chemical stability and low biodegradability of CPs and the matters related with generation of toxic sludge, storage, handling and final disposal of sludge, conventional techniques cannot reached effective remove of organic contaminants.[7,8]

Using heterogeneous photocatalysis (HP) has grown due to its efficacy in removing EOCs. Among various semiconductors, ZnO is commonly used in HP due its high stability, a wide optical and magnetic characteristics, cost-effectiveness and also the large energy bandgap (60 meV) and strong exciton binding energy (3.37 eV). However, ZnO is effective only at the ultraviolet range of the electromagnetic spectrum. Various strategies such as doping have been applied to solve this matter. The doping process as an alternative for changing the chemical and photophysical properties of semiconductors is a common method used in HP applications. Manganese with unexpansive cost compared to other transitions elements employed to dope ZnO. The Zn^{2+}radius is higher than that of Mn^{2+}, Mn^{2+}can replace Zn^{2+}inside ZnO. So, making the doping process easier.[9-11]

The surface-response method is a set of mathematical and statistical techniques, which applied to develop, improve and optimize processes in which the desired surface affected by many variables, and the purpose is to optimize the response. The surface-response method is useful for evaluating several input variables that affects the efficiency scales or qualitative characteristics of the product or process. This method is also a useful tool in optimization studies.[12] The aim of this study was to enhancement the photocatalytic removal efficiency of 4-CP from aqueous environment using MnO/ZnO NPs and the process was optimized using the response surface methodology (RSM).

Materials and Methods

This research is a practical-experimental, which was conducted in experimental scale. Determination of 4-CP concentration was performed according to the standard method book (D 5530) by spectrophotometer tool (Spectrometer V/VIS, DR-5000, HACH) in 500 nm wavelength via colorimetric determination of amino antipyrine.[13] A 1000 mg/L stoke solution of 4-CP (Acros organics, 99%) was prepared in distilled water and used to prepare different concentrations of 4-CP. In order to adjust the pH, 1 N solution of HCl (37% purity, Catalog Number 100314, Merck) and NaOH (98-100% purity, Catalog Number 106482, Merck) were used. Equation 1 considered to calculate the 4-CP removal percentage[14]:

$$\%R = \frac{c_0 - c_t}{c_0} \times 100 \quad (1)$$

Where R% is removal percentage of 4-CP, C_0 = concentration of 4-CP at t = 0 (mg/L) and C_t = Concentration of 4-CP at the time of t (mg/L)

Characteristics of the Reactor and UV Radiation Source

As shown in Figure S1, in this probe, the experiments have been used in a discontinuous flow reactor with a volume of 500 mL of Plexiglas and 3 low-pressure lamp (6 w) with 20 cm length manufactured by Philips, Netherlands.

Synthesis Method of MnO_3-Doped ZnO

We utilized hydrothermal method for synthesis of both of the pure and doped ZnO NPs in various levels. The zinc oxide with catalog number 108849, 100% purity from Merck have been used. In this method, certain molar percentages (0, 0.5, 1 and 1.5%) of manganese oxide were added to the zinc oxide solution (2 N) in a Teflon liner. Then, 10 mL of sodium hydroxide (1 N) was added and also 0.5 mL of surfactant was added dropwise under gentle mixing. Then, the liner was placed in an oven for 12 hours at 120 °C. After that time, the liner contents were material was extracted and washed with distilled water several times at ambient temperature.[15] In the following, the undoped and doped ZnO with different Mn doping ratio used for the 4-CP photodegradation and removal efficiency investigated. So, the optimal doping ratio was determined

Materials Characterization

The dried product with optimized ratio MnO_3-doped ZnO was subjected to the characterization analysis including X-ray powder diffraction (Inel, EQUINOX 3000, France), scanning electron microscopy (SEM) (Tscan, MIRA3, Czech Republic), Fourier transform infrared spectra (FTIR) (Bruker-Tensor 27, Germany), atomic force microscopy (AFM) (Research Ara-Advance, Iran) in order to determine, the crystal structure, morphology, and surface chemistry, respectively.

Experimental Design

In this study, Central Composite Design (CCD)-RSM as one of the experimental design tools and the Design-Expert software version 7 were applied. The nanoparticle concentration, range of pH, initial 4-CP concentration and contact time were determined by the software, and the software determined the number of thirty thighs of the test. Surface-response method is a set of statistical and mathematical methods for modeling and analyzing in which the proposed response is a function of several variables. The purpose of this method is to optimize the response. Table 1 shows the experiments and their responses.

Results and Discussion

4-CP Photocatalytic removal efficiency under UV radiation by undoped ZnO and Mn-doped ZnO in different ratios shown in Figure 1. It was found that Mn-doped ZnO removed 4-CP much higher than undoped ZnO. Deposit a transition metal like manganese ions into the ZnO NPs cause modify magnetic, electrical and optical characteristic of material. Similar research has shown that the band gap for ZnO lattice after modification was smaller than the undoped ZnO.[16] The experiment demonstrated that the photodegradation efficiency of

Table 1. Test design with RSM

Std	Run	Block	Factor 1 A: pH	Factor 2 B: Nano Con. (g/L)	Factor 3 C: 4-CP Con. (mg/L)	Factor 4 D: Time (min)	Response1 4-CP Removal (%)
8	1	Block1	10	3	80	30	38.1
5	2	Block1	3	0.5	80	30	12.2
12	3	Block1	10	3	10	120	78.9
3	4	Block1	3	3	10	30	59.4
14	5	Block1	10	0.5	80	120	24.9
2	6	Block1	10	0.5	10	30	40.9
18	7	Block1	6.5	1.75	45	75	64.3
15	8	Block1	3	3	80	120	54.86
9	9	Block1	3	0.5	10	120	59.6
17	10	Block1	6.5	1.75	45	75	67.3
20	11	Block2	6.5	1.75	45	75	65.98
6	12	Block2	10	0.5	80	30	19.2
11	13	Block2	3	3	10	120	83.9
7	14	Block2	3	3	80	30	30.11
16	15	Block2	10	3	80	120	69.1
1	16	Block2	3	0.5	10	30	32.9
13	17	Block2	3	0.5	80	120	19.2
10	18	Block2	10	0.5	10	120	49.19
4	19	Block2	10	3	10	30	66.3
19	20	Block2	6.5	1.75	45	75	61.9
22	21	Block3	10	1.75	45	75	59.1
27	22	Block3	6.5	1.75	45	30	58.2
24	23	Block3	6.5	3	45	75	79.6
26	24	Block3	6.5	1.75	80	75	52.1
25	25	Block3	6.5	1.75	10	75	81
28	26	Block3	6.5	1.75	45	120	80.6
21	27	Block3	3	1.75	45	75	51.6
30	28	Block3	6.5	1.75	45	75	60.91
23	29	Block3	6.5	0.5	45	75	44.6
29	30	Block3	6.5	1.75	45	75	58.5

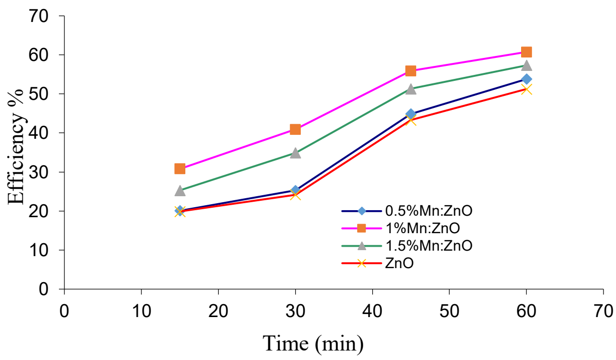

Figure 1. Photodegradation of 4CP Under UV Radiation in Different Ratio of Mn-Doped ZnO (4-CP concentration: 50 mg/L, NPs concentration: 1 g/L, pH: 6.5, Contact time: 60 min)

1%Mn-doped ZnO was significantly better than that of 0, 0.5 and 1.5 %. This is due to the particles size and particle agglomerate in 1% Mn-doped ZnO that is lowest rather than other percent and by rising in the weight ratio of manganese up to 1% Mn, the surface area of synthesized catalyst increases, but make smaller after that. Therefore, the surface area in 1% Mn-doped ZnO is highest. The results of the experiments are consistent with Abdollahi and colleagues' studies.[17]

Structure and Morphology of Nanoparticles

The SEM image of pure ZnO and 1% M MnO_3-doped ZnO with a magnification of 500 nm have been illustrated in Figure S2. The SEM image indicated that the MnO_3-doped ZnO NPs in this study has a hexagonal structure with a size smaller than 60 nm, which is suitable size in NPs range. In addition, the SEM image indicated that no agglomeration was observed for nanoparticles, and particles are completely separated and homogeneous distribution of particle size.

The X-ray diffraction (XRD) analysis of the synthesized pure ZnO and 1% MnO_3- doped ZnO are represent in Figure 2. The XRD spectrum provides information about phases and the structure of crystalline materials and indicate that the three major peaks in these spectra are (100), (002) and (101), are related to the crystalline structure of ZnO in the miller index. The XRD diagrams illustrate that the hydrothermal ZnO nanoparticles were effectively synthesized. The synthesis of stable hexagonal wurtzite polycrystalline nanostructures of ZnO was confirmed from XRD analysis indicating a good quality of ZnO formation, and also these findings have been proofed by SEM. The sharp edges peaks indicate a proper crystallized ZnO NPs. The maximum intensity of the spectra in the plan (101) appears at the angle of $2\theta = 36.045$.[18]

Figure S3 demonstrates the infrared spectroscopy of pure ZnO and 1% MnO_3-doped ZnO. Investigation of the FTIR spectra indicates that a strong bond is observed at 469 cm^{-1}, which is related to the Zn-O bond stretching frequency.[19] The bond in 1730 cm^{-1} is related to the starching bond of C=O in organic compounds. The starching vibrations for NH is located at 3448 cm^{-1} which is related to the NH bond in amine groups and was produced by addition of n-butyl amine surfactant. The band in 2930 cm^{-1} is related to H-C stretching bond to the organic material. In a study by Mote et al, which doped ZnO with chromium oxide, similar results were obtained. The band at 400-600 cm^{-1} is related to the Zn-O stretching bond and the band at 3600-3400 cm^{-1} indicated the presence of N-H bon.[20] Also, the effect of introducing manganese oxide on properties of the obtained manganese oxide doped ZnO nanoparticles was investigated by AFM (Figure 3).

It can be seen by AFM analysis that the morphology of MnO_3-doped ZnO was affected by increasing Mn^{2+} doping percentage. Figure 3 estimated rising in grain size

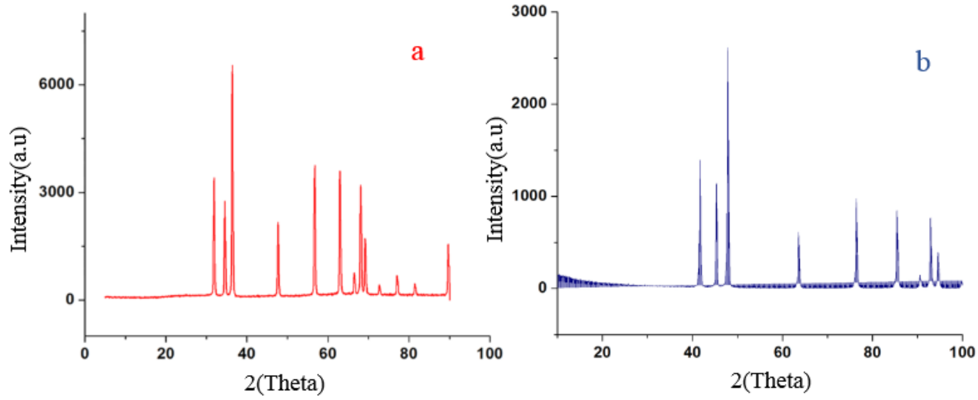

Figure 2. XRD Peak Pattern for (a) Undoped ZnO (b) MnO_3-Doped ZnO

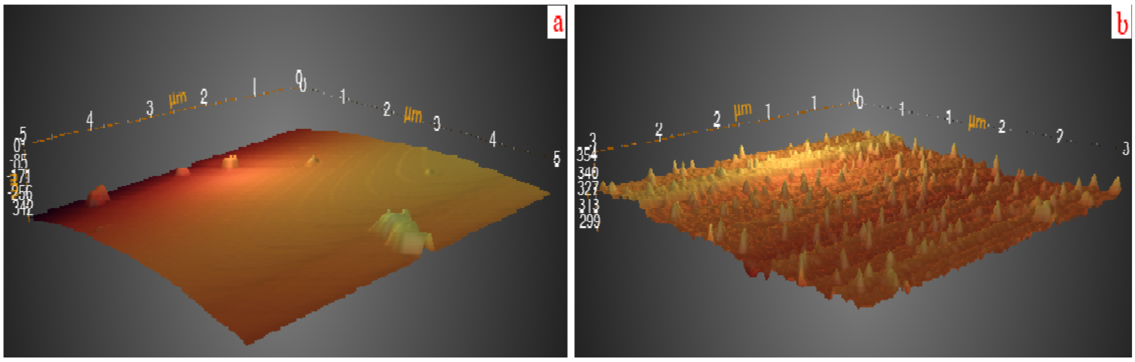

Figure 3. AFM image (a) undoped ZnO (b) MnO_3- doped ZnO

with enhanced surface roughness.[21]

Analysis of variance (ANOVA) was performed to assess the significant effects of independent variables on the response variable as the removal efficiency of 4-CP. Analysis of variance is the most widely used approach for predicting of statistical results.[22] Applying regression analysis, a quadratic (second-order) polynomial model was obtained for efficiency prediction.

In this study, to investigate the adequacy of the proposed model, various curves were used such as normal distribution and correlation curve, which were shown in Figure S4.

Regarding the results from variance analysis in Table 2, the proposed regression model for the removal efficiency of 4-CP is statistically significant at 95% confidence level. Also, for the proposed model was insignificant at 95% confidence level. The data providing an acceptable model assumption for analyzing the variance. This shows that the pattern for the response variable is acceptable and free of errors from incorrect data recording. In CCD-RSM model for 4-CP removal rat, it was found that *P* value < 0.0001, which shows the model parameters are considerable. It needs to be referred that *P* values > 0.1 indicate that the model is insignificant. In addition, *P* value < 0.05 demonstrates that the model is significant in the response, and the *P* value < 0.001 indicates that the model is highly significant in the response. In Figure S4 (A), the values from the internal residues indicate that the model is acceptable in satisfying the variance analysis assumptions. In Figure S4 (B), the proposed model was consistent with experimental data for the removal efficiency of 4-CP.

Table 2. The Results From ANOVA and Predictor Variables in CCD-RSM Model for Removal Rat of 4-CP

Source	Value F	*P* Value Prob > F	Sum of Squares	df
Model	33.71	<0.0001	10451.03	14
A: pH	6.51	0.0242	144.005	1
B: Nano Con.	178.31	<0.0001	3948.05	1
C: 4-CP Con.	146.12	<0.0001	3235.3	1
D: Time	74.18	<0.0001	1642.41	1
Residual	-	-	287.85	13
Lack of Fit	5.19	0.1010	272.12	10

The effect of independent factors on the photocatalytic removal efficiency of 4-CP are represented in Figure 4. The speed of chemical reactions directly correlated with the environment pH, and affects by the production of hydroxyl radicals.[23] In this study, pH was investigated at 3 levels of 3, 6.5 and 10. The results indicated that the acidic and alkaline pH ranges had less efficiency than the neutral pH and pH = 6.5 was the optimum value and led to better efficiency (Figure 4A). The reason can be interpreted to be that the level of H^+ions at high pH is high and the applied chlorophenol was existed as ion, so H^+ions compete with chlorophenol ions.[24] Also, in alkaline pH, OH^- ions compete with chlorophenol

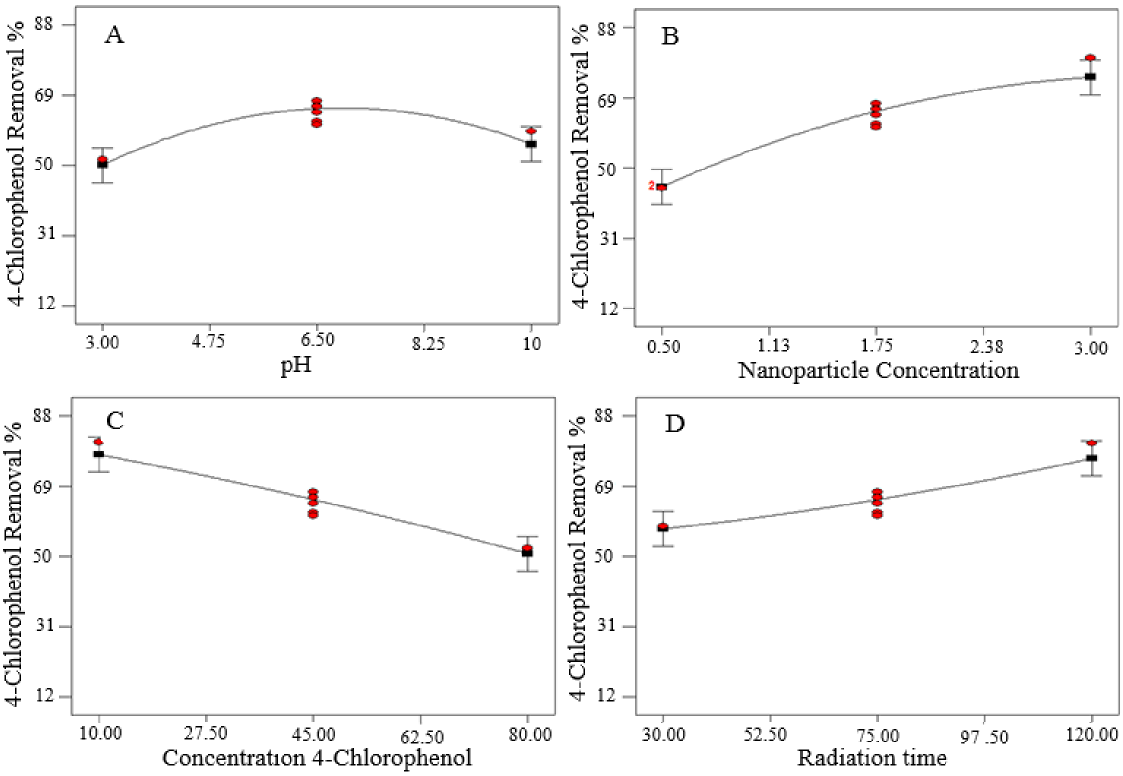

Figure 4. 4-CP Photocatalytic Removal Experiments on Pure and Doped ZnO; Effect of (A) pH, (B) NPs Dose, (C) 4-CP Concentration, and (D) Radiation Time on the % Removal of 4-CP

molecules, and ultimately the removal efficiency led to be decreased.[25] Lathasree et al investigated the effect of pH on photocatalytic degradation of phenol, o-chlorophenol and p-chlorophenol using the ZnO/UV process, and the decomposition level of phenol in mild acidic and neutral conditions was shown to be desirable.[26]

Determination of the dose of NPs is one of the most important problems due to economic considerations. The concentration of NPs was investigated in doses of 0.5, 1.75 and 3 g/L. The results indicated that increasing the catalyst concentration led to increase the removal efficiency. In the expression of the effect of MnO_3-doped ZnO loading, on the photocatalytic degradation of 4-CP (Figure 4B), it can be mentioned that increasing the catalyst concentration, led to increase the number of absorbed photons, which led to raise the number of activated sites available at the photocatalyst surface from which, the number of adsorbed 4-CP molecules was increased. The effect of initial concentration of 4-CP was investigated at the levels of 10, 45 and 80 mg/L, and the results indicated that the increasing the initial concentration of the pollutant cause to reduce the photocatalytic removal efficiency (Figure 4C). The photocatalytic process by NPs in the presence of UV light is justified by producing active hydroxyl radicals and decomposition of 4-CP. By keeping constant the UV irradiation and increasing the concentration of 4-CP molecules in a determined volume, the number of active hydroxyl radicals produced by adding the oxidizable organic compound per unit volume of solution remains constant, and on the other hand by increasing 4-CP concentration, the free sites available to the catalyst can be reduced by oxidizing the pollutant molecules.[25,27] In their study which was performed on photocatalytic removal of day, it was concluded that dye elimination depends on the produced level of $OH^{\cdot}$ and increasing the initial concentration of dye, causes the pollutant molecule to absorb the irradiated UV photons and prevent it from reaching to the catalyst, resulting in lesser production of active hydroxyl radicals.[28] The contact time was also being checked at 30, 75 and 120 minutes, the result showed that the removal efficiency increased by increasing the contact time (Figure 4D). The reason is probably due to increase the time and producing the enough reactive hydroxyl radicals to make reaction, and also active hydroxyl radicals have enough time to react to and attack to the 4-CP molecules.[14]

Figure 5 indicated the overlapping between the independent variables on the photocatalytic removal efficiency of 4-CP indicated, and determine which variables have had a greater impact on elimination process.

In Figure S5, the optimum condition in photocatalytic removal of 4-CP *according* to the CCD-RSM model is illustrated as operating parameters and its removal percentage has been shown. The optimum conditions obtained as follow: pH = 7.66, concentration of NPs = 2.18 g/L, concentration of contaminant = 14.07 mg/L, and contact time = 91.23 min. In this condition, the optimum removal efficiency of 4-CP is 83.18%.

Conclusion

We synthesize bare ZnO and Mn-doped ZnO (0.5, 1

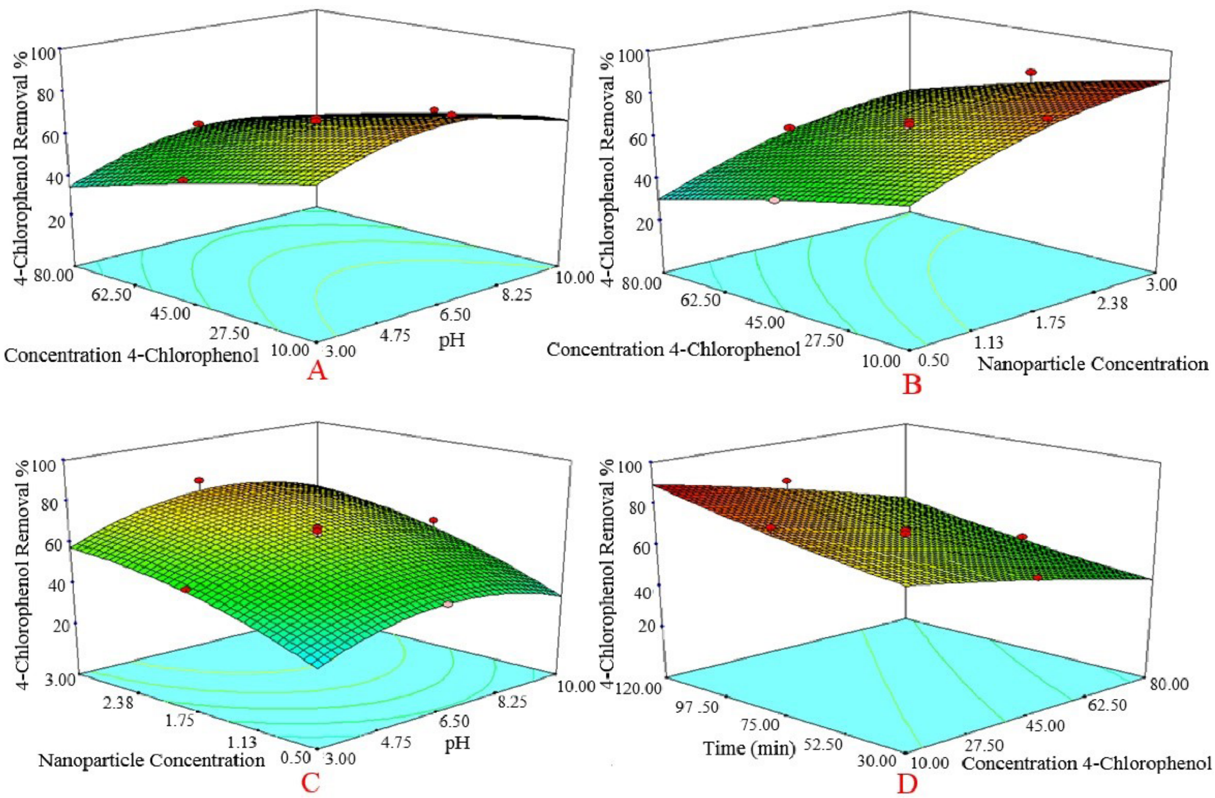

Figure 5. Overlap Diagram of the Independent Variable Effects on 4-CP Removal Efficiency.

and 1.5 % wt.). Characterization techniques verified the Mn doping process. The findings revealed that Mn-doped ZnO have higher removal efficiency. XRD patterns indicated a reduction in the crystalline size after the doping process. AFM confirmed the surface roughness and surface morphology of the thin films and strongly agreed with SEM results. Modification of the ZnO morphology provides an excellent opportunity to improve the performance of 4-CP removal be obtained by the low-cost, easy, and high yield for photocatalytic process. Also, the experiment values obtained for the 4-CP removal were found to agree satisfactorily with the CCD-RSM model values ($P < 0.0001$).

Acknowledgements

This research was funded by the Student Research Committee with registration number of 366/95. We also thanked the health faculty of Medical University of Kurdistan for providing the necessary facilities.

Authors' Contribution

Conceptualization: Shima Rezaei, Afshin Maleki, Reza Rezaee, Hajar Kashefi, Yahya Zandsalimi.
Data curation: Hajar Kashefi, Yahya Zandsalimi.
Formal analysis: Afshin Maleki, Yahya Zandsalimi.
Funding acquisition: Shima Rezaei, Afshin Maleki.
Investigation: Reza Rezaee, Hajar Kashefi, Yahya Zandsalimi.
Methodology: Reza Rezaee, Hajar Kashefi, Yahya Zandsalimi.
Project administration: Afshin Maleki, Yahya Zandsalimi.
Resources: Reza Rezaee, Yahya Zandsalimi.
Software: Afshin Maleki, Yahya Zandsalimi.
Supervision: Shima Rezaei, Afshin Maleki.
Validation: Shima Rezaei, Afshin Maleki.
Visualization: Reza Rezaee, Yahya Zandsalimi.
Writing–original draft: Reza Rezaee, Yahya Zandsalimi.
Writing–review & editing: Shima Rezaei, Afshin Maleki.

Competing Interests

The authors declare that there is no conflict of interest concerning the publication of the study.

Ethical Approval

This study was approved by the Ethics Committee of the Kurdistan University of Medical Sciences (Ethical code: IR.MUK.REC.1395/366). The authors certify that this study has not been published separately elsewhere, nor will it be in the future.

Funding

This work was financially supported by the Student Research Committee of Kurdistan University of Medical Sciences (1395/ 366).

Supplementary Files

Supplementary file 1 contains Figure S1-S5.

References

1. Saravanakumar K, Yun K, Maheskumar V, Yea Y, Jagan G, Park CM. Construction of novel In2S3/Ti3C2 MXene quantum dots/SmFeO3 Z-scheme heterojunctions for efficient photocatalytic removal of sulfamethoxazole and 4-chlorophenol: degradation pathways and mechanism insights. Chem Eng J. 2023;451(Pt 1):138933. doi: 10.1016/j.cej.2022.138933.
2. Mukhopadhyay A, Duttagupta S, Mukherjee A. Emerging organic contaminants in global community drinking water sources and supply: a review of occurrence, processes and remediation. J Environ Chem Eng. 2022;10(3):107560. doi: 10.1016/j.jece.2022.107560.
3. Wang G, Bi W, Zhang Q, Dong X, Zhang X. Hydrothermal carbonation carbon-based photocatalysis under visible light: modification for enhanced removal of organic pollutant and novel insight into the photocatalytic mechanism.

J Hazard Mater. 2022;426:127821. doi: 10.1016/j.jhazmat.2021.127821.
4. Li Z, Mao Y, Liu Z, Song Z, Qu S, Wang Z, et al. Efficient adsorption and removal mechanism of 2,4-dichlorophenol by MoS2@C6H12O6 floral activated carbon with intercalated structure. Mater Sci Eng B Solid State Mater Adv Technol. 2024;299:116807. doi: 10.1016/j.mseb.2023.116807.
5. Harini G, Subhiksha V, Okla MK, Abdel-maksoud MA, Al-ghamdi AA, Alatar AA, et al. Construction of sandwich like RGO/BiVO4/ZSM-5 hybrid heterostructure for the enhanced photocatalytic removal of p-chlorophenol. Surf Interfaces. 2024;44:103774. doi: 10.1016/j.surfin.2023.103774.
6. Barrera A, Hernández-Amezcua J, López-Álvarez MA, Carbajal-Arízaga GG, Casillas JE, Velásquez-Ordoñez C, et al. Promotion effect of Ga3+in ZnAlGa-x mixed oxides obtained from their layered double hydroxides on the enhancement in the transient photocurrent response, the inhibition in the recombination rate of photogenerated (e−, h+) charges and the photocatalytic activity in the photodegradation of 4-chlorophenol. J Photochem Photobiol A Chem. 2024;449:115403. doi: 10.1016/j.jphotochem.2023.115403.
7. Yadav S, Kumar S, Haritash AK. A comprehensive review of chlorophenols: fate, toxicology and its treatment. J Environ Manage. 2023;342:118254. doi: 10.1016/j.jenvman.2023.118254.
8. Bayramoglu G, Gursel I, Tunali Y, Arica MY. Biosorption of phenol and 2-chlorophenol by *Funalia trogii* pellets. Bioresour Technol. 2009;100(10):2685-91. doi: 10.1016/j.biortech.2008.12.042.
9. Rakshitha R, Chethan R, Pallavi N. Photocatalytic removal of emerging contaminants from water using metal oxide-based nanoparticles. Curr Nanosci. 2024;20(3):339-55. doi: 10.2174/1573413719666230331111906.
10. Vallejo W, Cantillo A, Díaz-Uribe C. Improvement of the photocatalytic activity of ZnO thin films doped with manganese. Heliyon. 2023;9(10):e20809. doi: 10.1016/j.heliyon.2023.e20809.
11. Sharma A, Kumar P. Review on structural, magnetic, optical properties of manganese doped zinc oxide nanoparticles. Mater Today Proc. 2023. doi: 10.1016/j.matpr.2023.01.248.
12. Bezerra MA, Santelli RE, Oliveira EP, Villar LS, Escaleira LA. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta. 2008;76(5):965-77. doi: 10.1016/j.talanta.2008.05.019.
13. Gouvea MEV, Boldrin FH, da Silva BH, Paiva LK, de Moraes NP, Gonçalves de Aguiar L, et al. Fluidized bed reactor for 4-chlorophenol photodegradation via solar and visible radiation using ZnO/g-C3N4/carbon xerogel as a photocatalyst. Chem Phys Impact. 2024;8:100428. doi: 10.1016/j.chphi.2023.100428.
14. Reda SM, Khairy M, Mousa MA. Photocatalytic activity of nitrogen and copper doped TiO2 nanoparticles prepared by microwave-assisted sol-gel process. Arab J Chem. 2020;13(1):86-95. doi: 10.1016/j.arabjc.2017.02.002.
15. Shahmoradi B, Soga K, Ananda S, Somashekar R, Byrappa K. Modification of neodymium-doped ZnO hybrid nanoparticles under mild hydrothermal conditions. Nanoscale. 2010;2(7):1160-4. doi: 10.1039/c0nr00069h.
16. Nkamuo CJ, Okoli NL, Nzekwe FN, Egwunyenga NJ. Tuning the properties of manganese-doped zinc oxide nanostructured thin films deposited by SILAR approach. Chem Inorg Mater. 2024;2:100038. doi: 10.1016/j.cinorg.2024.100038.
17. Abdollahi Y, Abdullah AH, Zainal Z, Yusof NA. Synthesis and characterization of manganese doped ZnO nanoparticles. Int J Basic Appl Sci. 2011;11(4):44-50.
18. Jahan Tamanna N, Sahadat Hossain M, Mohammed Bahadur N, Ahmed S. Green synthesis of Ag2O & facile synthesis of ZnO and characterization using FTIR, bandgap energy & XRD (Scherrer equation, Williamson-Hall, size-train plot, Monshi- Scherrer model). Results Chem. 2024;7:101313. doi: 10.1016/j.rechem.2024.101313.
19. Umashankar R, Harshitha Devi S, Gurushantha K, Manjunatha SO, Al-Dossari M, Shobha G, et al. Improved photocatalytic, antimicrobial and photoelectrochemical properties of nanocrystalline Cu2+-doped ZnO nanoparticles. Ceram Int. 2023;49(13):22449-59. doi: 10.1016/j.ceramint.2023.04.077.
20. Sachin, Singh N, Shah K, Pramanik BK. Synthesis and application of manganese-doped zinc oxide as a potential adsorbent for removal of Congo red dye from wastewater. Environ Res. 2023;233:116484. doi: 10.1016/j.envres.2023.116484.
21. Safdar H, Aydın R, Şahin B. Syntheses, structural evolution, electrical and optoelectronic characterization of ZnO/CuO composite films doped with transition metal Mn2+ions. Ceram Int. 2022;48(18):26678-88. doi: 10.1016/j.ceramint.2022.05.362.
22. Behnajady MA, Modirshahla N, Hamzavi R. Kinetic study on photocatalytic degradation of CI Acid Yellow 23 by ZnO photocatalyst. J Hazard Mater. 2006;133(1-3):226-32. doi: 10.1016/j.jhazmat.2005.10.022.
23. Gholizadeh A, Kermani M, Gholami M, FarzadkiaM M. Comparative investigation of 2-chlorophenol and 4-chrorophenol removal using granulated activated carbon and rice husk ash. Tolooebehdasht. 2013;11(3):66-78. [Persian].
24. Uddin MT, Islam MS, Abedin MZ. Adsorption of phenol from aqueous solution by water hyacinth ash. ARPN J Eng Appl Sci. 2007;2(2):11-7.
25. Akhtar S, Khan AA, Husain Q. Potential of immobilized bitter gourd (*Momordica charantia*) peroxidases in the decolorization and removal of textile dyes from polluted wastewater and dyeing effluent. Chemosphere. 2005;60(3):291-301. doi: 10.1016/j.chemosphere.2004.12.017.
26. Lathasree S, Rao AN, SivaSankar B, Sadasivam V, Rengaraj K. Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions. J Mol Catal A Chem. 2004;223(1):101-5. doi: 10.1016/j.molcata.2003.08.032.
27. Tehrani-Bagha AR, Gharagozlou M, Emami F. Decolorization of CI Reactive Red 120 in the presence of hydrogen peroxide and magnetic nanoparticles of cobalt-iron oxide as a catalyst. J Color Sci Technol. 2012;6(1):77-86. [Persian].
28. Fouad SM, El-Shazly YM, Alyoubi MA, Nosier SA, Abdel-Aziz MH. Enhanced photocatalytic degradation of cationic dyes using slurry of anatase titania in a falling film reactor. Case Stud Chem Environ Eng. 2023;8:100518. doi: 10.1016/j.cscee.2023.100518.