Coprecipitation aided synthesis of bimetallic silver tungstate: a response surface simulation of sunlight-driven photocatalytic removal of 2,4-dichlorophenol

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Abstract
In the present study, the response surface methodology (RSM) model was used to investigate the photocatalytic performance of silver tungstate (Ag2WO4) in the removal of 2,4-dichlorophenol (2,4-DCP) under natural sunlight. The Ag2WO4 which has nanoflower-like structure was synthesized by a coprecipitation method. The synthesized photocatalyst was characterized for FESEM, TEM, EDX, XRD, FTIR, and UV–Vis spectroscopy. RSM was employed to scrutinize the suitable model to yield a profound pollutant removal rate. The four independent factors such as pollutant concentration, catalyst dosage, pH, and contact time are simulated using RSM. A total of 91% of 2,4-DCP degradation was achieved at a higher catalyst dosage and lower pollutant concentration with a contact duration of 8 h in an alkaline pH condition. The coefficient of regression (R2) and probability value (P) were 0.98 and 0.0472, respectively, which confirmed the ideality of RSM modeling. The study discusses on the possible photocatalytic degradation mechanisms of 2,4-DCP. The results showed a significant dependence of the photocatalytic removal of 2,4-DCP on the functional parameters.

Keywords Photodegradation · Nanocomposite · Phenolic pollutants · Silver tungstate · 2,4-dichlorophenol · RSM

Introduction
Water is a life-giving element for all humans and is widely regarded as the most valuable resource for human civilization (Zulfiqar et al. 2019). However, due to the rapid industrialization, population increase, and unsustainable use of natural resources, providing clean and safe water has become a significant challenge in many developing countries, resulting in the release of a massive amount of hazardous organic pollutants into water bodies (Nagaraju et al. 2020). Among them, chlorophenols are primarily employed in manufacturing pesticides, herbicides, preservatives, dyestuffs, and petrochemicals (Yashas et al. 2019; Guerrero-Araque et al. 2020), which are hazardous and likely to pollute the natural water systems. Out of various chlorophenols contaminants reported, 2,4-dichlorophenol (2,4-DCP) is a very stable compound resistant to conventional degradation when exposed to direct natural sunlight (Humaira et al. 2020). This pollutant is highly toxic to humans and aquatic organisms because it can be absorbed through the skin pores and induce a variety of ailments related to skin, kidney functioning, and melanoma (Hu et al. 2018). Due to its high toxicity, it deserves special attention and immediate response. Thus, it is appropriate to effectively remediate 2,4-DCP to maintain the aquatic system for human and animal health.

Over the last few decades, heterogeneous traditional water and wastewater treatment technologies have been replaced by photocatalytic degradation of organic contaminants, assuring high efficiency and no secondary pollutants (Rafiq and Majid 2020). Catalytic elimination of environmental pollutants driven by sunlight has gained considerable importance in recent years (Singh and Soni 2021). The evolution of sunlight-driven remediation...
technology will highlight specific features such as high activity, good recyclability, high stability, and efficient recovery of a photocatalyst (Huang et al. 2017). The photocatalytic function of semiconducting materials is due to the light-induced generation of charge carriers, such as electrons and holes, which can travel to the surface of the material, exhibit distinctive redox characteristics, and drive chemical transformations. However, such materials are frequently affected by a harmful electron–hole recombination process, which reduces the lifetime of charge carriers and limits their availability for photocatalysis. Charge recombination would seem to have a direct impact on the photocatalytic performance of semiconducting materials (Rafiq and Majid 2020). Hence, evaluation of different photocatalysts for pollutant degradation under sunlight is deemed essential to progress towards sustainability.

Furthermore, nanoscale photocatalysts have revolutionized water/wastewater treatment (Adelaye et al. 2016). In the recent years of decomposition of organic pollutants using visible light illumination by silver-based photocatalysts such as Ag₃PO₄, Ag₂WO₄, AgVO₃, Ag₂CO₃, AgX (X=Cl, Br, I), AgIO₃, Ag₃S, and Ag₂MoO₄ have recently received considerable attention (Senthil et al. 2020), due to its ease of reduction to metallic silver on its surface, silver tungstate (Ag₂WO₄) has received much interest, favoring the plasmon effect (Andrade Neto et al. 2020). To date, different synthesis methods have been reported in the literature to obtain Ag₂WO₄ metastable phases. In particular, Ag₂WO₄ was successfully prepared by a precipitation method using a surfactant-assisted route in the presence of polyvinylpyrrolidone (PVP) (Roca et al. 2017).

Recently, Kokilavani and her team evaluated plasmonic CoS/Ag₂WO₄ (cobalt-sulfide coupled with silver tungstate) for photocatalytic degradation of toxic dye, Rhodamine B dye (Cen et al. 2021).

To complement the photocatalytic degradation, the present study employed response surface methodology (RSM). RSM is a powerful design tool for developing new processes, modifying the design, and optimizing their performances (Nagaraju et al. 2017; Rafaeely et al. 2021). By systematically adjusting all variables at the same time, it is the most reliable and empirical statistical technique for analyzing the influence of various process parameters on photocatalytic degradation (Zulfiqar et al. 2019). For instance, Malik and Sonawane employed RSM to simulate the sono-photocatalytic removal of Rhodamine B using bismuth-doped titanium dioxide, supported montmorillonite nanofluid (Malika and Sonawane 2021). Likewise, recently, Ataei and their team studied the photodegradation of antibiotics, where the process’s optimization and modeling were carried out using RSM (Ataei et al. 2021).

The present study focuses on the photodegradation of 2,4-DCP with Ag₂WO₄ prepared by soft-chemical technique and thoroughly characterized to uncover all the essential physico-chemical and photocatalytic properties. RSM was used for modeling and experimental validation for the removal of 2,4 DCP under natural sunlight with dependent parameters such as pH, contact time, pollutant concentration, and catalyst dosage. The study proposes the degradation mechanism and anticipates the potential application of the system for water/wastewater treatment.

**Materials and methods**

**Preparation of Ag₂WO₄**

Silver nitrate (AgNO₃), sodium tungstate (Na₂WO₄·2H₂O), polyvinylpyrrolidone (PVP·(C₆H₇NO)₉, M.W. 40,000), and ammonium hydroxide (NH₄OH·30%) were obtained from Sigma-Aldrich, India, and were used without any modifications. The deionized water was used as a solvent throughout the study. The synthetic route was in accordance with the earlier report by Neto and the team with slight modification (Andrade Neto et al. 2020). A 40 mL of 4 mM AgNO₃ was typically held under magnetic stirring until full solubilization was achieved.

The pH was then adjusted to 10.0 by adding ammonium hydroxide solution (I). Simultaneously, 40 mL of 2 mM Na₂WO₄·2H₂O was prepared and labeled as the solution (II). Subsequently, 0.3 g PVP was added to both (I) and (II), and the mixtures were stirred for another 30 min to achieve complete dissolution. Furthermore, solution (I) containing Ag⁺ ions was combined with solution (II) containing W⁶⁺ ions and agitated for 30 min at room temperature to form the final solution (III). The supernatant was then centrifuged, rinsed with deionized water and ethanol, and dried for 24 h at 60 °C.

The scheme of the synthesis is depicted in Fig. 1.

**Characterization of Ag₂WO₄**

The as-synthesized Ag₂WO₄ was subjected to various advanced characterizations to determine its physical, chemical, structural, and functional entities. Field emission scanning electron microscopy (FESEM, JSM-7100F, JEOL, Singapore) and transmission emission microscopy (TEM, Thermofisher, Talos F200 S) revealed the physical dimension of Ag₂WO₄. The elemental composition was analyzed with the FESEM machine. X-ray diffraction was used to examine the crystal structure of the photocatalyst (XRD, Microstar Proteum 8, Bruker). The functional properties of the catalyst were confirmed by Fourier transform infrared spectroscopy (FTIR, PerkinElmer RX-1) using potassium bromide. The band energy was determined using the Tauc plot and UV–Vis spectroscopy.
Photocatalytic study

The typical photocatalytic degradation experiments were run according to the design of the experiment using JMP Pro 15 software and RSM. Parameters (independent variables) like pH ranged from 5.0 to 10.0, contact time from 2 to 8 h, catalyst dosage of 10–100 mg, and pollutant concentration of 10–100 mg/L or ppm. The experimental studies were carried out under sunlight (average sunlight intensity = 15,285 Lumen/m²) as per the design. The concentration of 2,4-DCP was monitored using UV–Vis spectrophotometer (Agilent Cary 60 Spectrophotometer) where the maxima (λmax) was at 292 nm. The degradation percentage was calculated using Eq. (1) (Zabihi et al. 2015). The concentrations of 2,4-DCP at time 0 h and time t h of the photocatalytic run are C₀ and Cₜ, respectively.

\[ \% \text{Degradation} = \left( 1 - \frac{C_t}{C_0} \right) \times 100 \]  

(1)

Experimental design for RSM

RSM compiled several statistical and mathematical methodologies that can be used to assess the relevance of various process factors. The reaction was analyzed using JMP Pro 15 software, and the predicted findings were calculated using the experimental design. Four variables with two central points and single replicates as the response were explored to determine the operating parameters for maximal deterioration of 2,4 DCP. Four independent parameters were taken into account: (i) pollutant concentration, (ii) catalyst dosage, (iii) contact time, and (iv) pH. The operational levels and ranges of independent variables investigated in this study are shown in Table 1. Table 2 shows the results of the seven experimental runs generated using the RSM method and custom design of JMP software. To investigate the impact of independent variables on the experimental investigation, the response percentage degradation of 2,4-DCP was calculated. To fit the experimental data, a model was developed that correlates the independent variables.

Results and discussion

Characterization of \( \text{Ag}_2\text{WO}_4 \)

Microscopic approach was used to analyze the morphology of as-synthesized \( \text{Ag}_2\text{WO}_4 \). Figure 2a and b shows the FESEM micrographs, captured at \( \times 2500 \) and \( \times 5000 \) magnifications, respectively. It is evident that \( \text{Ag}_2\text{WO}_4 \) has attained flower-like structures. Furthermore, TEM

| Table 1 Operating levels and independent variable ranges |
|---------------------------------------------------------|
| Level | Factors                   | Lower limit | Upper limit |
|-------|---------------------------|-------------|-------------|
| 1     | Pollutant concentration   | 10 ppm      | 100 ppm     |
| 2     | Catalyst dosage           | 10 ppm      | 100 ppm     |
| 3     | pH                        | 5           | 10          |
| 4     | Contact time              | 2 h         | 8 h         |

| Table 2 Experimental trials generated using custom design — RSM method |
|-----------------------------------------------------------------------|
| Pollutant concentration (ppm) | Catalyst dosage (mg) | pH | Contact time (h) |
|-------------------------------|-----------------------|----|-----------------|
| 100                           | 10                    | 5  | 8               |
| 10                            | 100                   | 5  | 2               |
| 55                            | 55                    | 7.5| 5               |
| 10                            | 10                    | 10 | 2               |
| 100                           | 100                   | 10 | 2               |
| 10                            | 100                   | 10 | 8               |
| 55                            | 55                    | 7.5| 5               |
was used to examine the detailed physical entity of Ag$_2$WO$_4$. The TEM micrographs of Ag$_2$WO$_4$ are shown in Fig. 2c and d confirming the flower-like structures.

EDX analysis was used to determine the material’s elemental composition. Figure 2e along with the inset table presents the percent weight of each element in the material. Notably, silver (Ag), oxygen (O), and tungsten (W) are showing respective peaks that correspond to their respective K shell, L shell, and K shell transitions, respectively. The sample comprises 45.6% Ag, 17.8% O, and 36.6% W, with atomic percentages of 64.1%, 24.4%, and 11.5%, respectively. The EDX results highlight the successful synthesis of Ag$_2$WO$_4$ with no additional trace elements. Table 3

The crystallographic data were collected using XRD, with the Cu K-radiation assisting the 2θ angular measurements between 10 and 80° at a scan rate of 2°/min. The XRD pattern for as-synthesized Ag2WO4 nano-flowers is shown in Fig. 3a. The intense peaks at 29.28°, 31.49°, 35.61°, 44.48°, and 53.03° were similar to those in JCPDS file number 861157 and earlier literature (Roca et al. 2017). The Ag2WO4 produced has high crystallinity, as evidenced by the narrow and sharp diffraction pattern.

Furthermore, Ag$_2$WO$_4$ was studied by FTIR, and the spectrum is shown in Fig. 3c. The broad peak at 3781.73 cm$^{-1}$ may be assigned to the stretching vibration of the O–H bond due to surface hydration. The peak at
1604.69 \text{ cm}^{-1} \text{ corresponds to } W–O–H \text{ bending. Two peaks at } 784.11 \text{ cm}^{-1} \text{ and } 1102.30 \text{ cm}^{-1} \text{ were due to the bridging stretching modes of } W–O \text{ and } W–O–W, \text{ respectively. An intense peak at } 471.08 \text{ cm}^{-1} \text{ was observed, which was ascribed to the characteristic asymmetric stretching vibration of } O–W–O \text{ bonds within the distorted } [W\text{O}_6] \text{ clusters. The peak at } 784.11 \text{ cm}^{-1} \text{ was attributed to the stretching modes of } W–O \text{ in } WO_6 \text{ octahedra (Nubla and Sandhyarani 2020; Elgorban et al. 2021).}

The UV–Vis spectra revealed the light scattering capability, which was used to determine the bandgap of as-prepared semiconductor material (Makula et al. 2018). The UV–Vis spectra were obtained in the range of 280–800 nm as shown in Fig. 2c. The optical bandgap (E_g) was found to be 2.8 eV, which could be compared to previous studies (Shi et al. 2016; Andrade Neto et al. 2020). Equation (2) was used to compute E_g, where \( \alpha \) is the absorption coefficient, \( h \) is the Planck constant, \( \nu \) is the frequency, and \( h\nu \) is the incident photon energy.

\[
(ah\nu)^2 = A(h\nu - E_g)
\]

Response surface modeling for 2,4-DCP degradation

RSM analysis was conducted to optimize degradation at each design level using four different variables and seven different tests. Over the course of each experiment, the chlorophenol residual concentration was calculated at regular intervals, and the chlorophenol degradation percentages are represented in Fig. 4a. The response factor was 2,4-DCP degradation (percent), and the calculated data over multiple variable-level sequences were statistically behaved to create the model. The connection between predicted and actual data, as shown in Fig. 4b, is used to determine if the model is significant or insignificant for phenol removal. The anticipated \( R^2 \) for chlorophenol degradation is 0.98. The model’s relevance is also checked in terms of \( F \)-value, \( P \)-value, and sufficient precision. The root mean square error is 6.7951, and the probability value is 0.0472.

The total sum of squares is the sum of the squared differences between the response values and the sample mean. It refers to the entire spectrum of possible responses (3773.0824). The erroneous sum of squares is the sum of squared differences between the fitted and actual values. It illustrates the variability that the model is unable to account for (92.3462). The model sum of squares is the difference between the total sum of squares and the error sum of squares, and it represents the variability explained by the model. In this case, the model’s explained variability is 3773.0824, which is much higher than the 92.3462 that remains unexplained. The sum of squares divided by the relevant degree of freedom yields the mean square.

The \( F \) ratio is a statistical test that compares the error mean squares of the model with the error mean squares of the model. The \( F \)-test has a \( p \)-value of probability > F. The \( p \)-value is used to determine the statistical significance of a finding under a null hypothesis. The \( p \)-value indicates the possibility of getting an \( F \) ratio as high as that observed. In other words, a low \( p \)-value suggests that if the null hypothesis was true, such an extreme observed outcome would be exceedingly implausible. The probability > F is less than 0.0001, indicating that the model has at least one significant effect.

The graphs of studentized residuals vs. run number and anticipated degradation, respectively, are shown in Fig. 5a and b. The residuals vs. run graph was quite helpful. Lurking variables that may have influenced the response during

![Fig. 3](image-url)
experimental work were used to examine the acceptability of a constant variance plot of residuals vs. predicted values. As seen in Fig. 5b, they do not develop any evident pattern containing an abnormal structure. In addition, the expression of equal scatters down the x-axis demonstrates the sufficiency of the proposed model.

Effects of independent operating parameters on pollutant removal

To visualize the influence of the independent operating factors on 2,4-DCP degradation, three-dimensional (3D) response surfaces and contour plots were developed. Overall, the effective degradation of 2,4-DCP was observed with the higher dosage of photocatalyst, lesser pollutant concentration in alkaline medium and the study carried out for a longer duration. In addition, 85% removal was observed with lesser contact time in acidic pH with a higher dosage of catalyst. On the other hand, the minimal removal efficiency was noted with the increased pollutant and photocatalyst dosage in the alkaline pH for lesser contact time. Figure 6, 7, and 8 represent the 3D responses in the form of contour plots. Figure 6a is the 2,4-DCP removal as a function of catalyst dose and the pollutant concentration. It is seen that 91% degradation was achieved when the photocatalyst concentration was higher and the initial pollutant concentration was lesser.
At a higher dosage of photocatalyst and pollutant concentration, the degradation efficiency of 2,4-DCP was lesser. Figure 6b shows the influence of pH and pollutant concentration on the photodegradation of 2,4-DCP. It is well established that pH between 5–8.5 and lower pollutant concentrations (10–45 ppm), there would be maximum mineralization of 2,4-DCP (> 80%). Conversely, in an alkaline medium with a higher contaminant load, the degradation rate decreases obviously.

The response simulated for the variation in pH and contact time is shown in Fig. 7a. Uniquely, the percentage degradation of 2,4-DCP reaches above 85% at two distinct operating conditions. Firstly, at a pH of 8.5–10.0 and a longer contact time of 7–8 h, the degradation observed attains around 85%. Secondly, the degradation reaches 80–85% at lower pH (5–6) for shorter contact time, as well as a neutral pH (7.5) for average run time. Hence, there exists a positive effect of pH on both pollutant concentration and contact time. Figure 7b illustrates the 3D response as the function of contact time and catalyst dosage. The simulated response unveils that the maximum degradation of the target is with the higher catalyst load and extended reaction time (Nourieh et al. 2020).

Figure 8a notifies on the variation of 2,4-DCP removal as a function of pollutant concentration and contact time. It is straightforward that, for a broad range of pollutant concentrations (10–65 ppm) and contact duration of 4–8 h, approximately 80% or higher rate of degradation would be accomplished. Hence, the present system driven by Ag2WO4 stands potential under sunlight to treat 2,4-DCP. Finally, Fig. 8b represents the probable degradation with the influence of catalyst dosage and pH of...
the reaction solution. The degradation percentage would reach above 80% at moderate pH of 5–6 for higher catalyst loading (60–100 mg).

**Photocatalytic mechanism**

The 2,4-DCP undergoes systematic breakdown under the action of sunlight and the Ag$_2$WO$_4$ catalyst. The typical photoactivation of the catalyst takes place upon absorbing suitable photons (energy $> E_g$ of Ag$_2$WO$_4$, 2.8 eV). The redox reactions at the conduction and valence bands of Ag$_2$WO$_4$ generate reactive oxidants that act on the 2,4-DCP to disintegrate the molecule and finally form simple organic compounds like water and carbon dioxide (Ali et al. 2020). The specific chemical reactions are represented in Eqs. 3–6. Figure 9 shows the schematic of photodegradation of 2,4-DCP using Ag$_2$WO$_4$.

$$\text{Ag}_2\text{WO}_4 + h\nu \rightarrow \text{Ag}_2\text{WO}_4 + h^+ + e^-$$  \hspace{1cm} (3)

$$h^+ + \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H}^+$$  \hspace{1cm} (4)

$$e^- + \text{O}_2 \rightarrow \text{O}_2^- \rightarrow \text{OH}^-$$  \hspace{1cm} (5)

$$e^- + h^+ \text{or} O_2^- + 2,4-\text{DCP} \rightarrow \text{Intermediate compounds} + \text{CO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (6)

Furthermore, the possible degradation pathway includes the dehalogenation and ring fragmentation, forming a few intermediates and finally resulting in chloride ions, water, and carbon dioxide (Ai et al. 2019). Specifically, the 2,4-DCP adsorbed on the surface of Ag$_2$WO$_4$ firstly undergoes dechlorination to form ortho- and para-chlorophenols, and phenol. Subsequently, these
are reduced to para-benzoquinone, which in turn decomposes into benign intermediates and ions (Rakibuddin and Ananthakrishnan 2016).

**Conclusions**

In summary, the present work showcases photocatalytic treatment of a toxic, yet recurrently occurring chlorophenol, 2,4-DCP in water and wastewater. The optimization of the whole process was done through RSM, a reliable statistical tool. Specifically, a promising Ag$_2$WO$_4$ photocatalyst was synthesized easily by coprecipitation method and analyzed to confirm its intrinsic properties which favored the photocatalytic action. There existed a reliable and convincible correlation between the experimental and predicted efficiencies with $R^2$ of 0.98 and probability index of 0.0472. Furthermore, the 3D responses generated based on response modeling revealed the significant influence of pH, contact

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**Fig. 8** Response surface and contour plots showing the effects of the independent variables on the 2,4 DCP photodegradation, a effects of contact time and pollutant concentration on 2,4 DCP removal, and b effects of pH and catalyst dosage on 2,4 DCP removal

**Fig. 9** Schematic of photocatalytic removal of 2,4-DCP using Ag$_2$WO$_4$ under the sunlight irradiation
time, catalyst dose, and initial concentration of 2,4-DCP on the percentage removal. Finally, a plausible photocatalytic mechanism was proposed. Hence, the model presented is foreseeable to be applied in real-time water and wastewater treatment.

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Author contribution RR executed the experiment and analyzed the obtained results. BMG and SHKD assisted in the interpretations of the results. NP hypothesized and supervised the study.

Data Availability All data generated or analyzed during this study are included in this article (and its supplementary information files).

Declaration Ethics approval Not applicable. Consent to participate Not applicable. Consent for publication Not applicable. Competing interests The authors declare no competing interests.

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