Photocatalytic degradation of 2,4-dichlorophenoxyacetic acid from aqueous solutions by Ag₃PO₄/TiO₂ nanoparticles under visible light: kinetic and thermodynamic studies

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ABSTRACT

Between the countless chemical substances applied in agriculture, 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide is considered as a toxic and carcinogenic pollutant which is difficult to remove from water due to its biological and chemical stability and high solubility. The goal of this study was photocatalytic degradation of 2,4-D, using Ag₃PO₄/TiO₂ nanoparticles under visible light. The Ag₃PO₄/TiO₂ nanoparticles were characterized using XRD, FESEM and EDS analysis to investigate its crystal structure and elemental compounds. The effect of operating parameters such as pH, contact time, catalyst dose, and initial concentration of herbicide on the efficiency of the process was studied. Increasing the pH and initial concentration of herbicide led to the reduction of the efficiency of removing the herbicide, while increasing contact time and catalyst dose increased the efficiency. The best result (98.4% removal efficiency) was achieved at pH = 3, 1 g/L catalyst dose, 60 min contact time, and 10 mg/L initial concentration of 2,4-D. According to the results, 2,4-D removal efficiency with Ag₃PO₄/TiO₂ photocatalyst reached 96.1% from 98.4% after 5 cycles of reaction. The pseudo-first-order kinetics was the best fit for the 2,4-D degradation by Ag₃PO₄/TiO₂ with correlation coefficients (R² = 0.9945). The results demonstrated that the photocatalytic process using Ag₃PO₄/TiO₂ nanoparticles in the presence of visible light had a relatively good efficiency in removing 2,4-D. Moreover, Ag₃PO₄/TiO₂ can be used as a reusable photocatalyst for the degradation of such toxins from polluted water and wastewater.

Key words | 2,4-dichlorophenoxyacetic acid, Ag₃PO₄/TiO₂ nanoparticle, photocatalytic degradation, visible light

HIGHLIGHTS

● Photocatalytic degradation of 2,4-D by Ag₃PO₄/TiO₂ under visible light.
● Higher performance of Ag₃PO₄/TiO₂ compared with TiO₂.
● High stability of the Ag₃PO₄/TiO₂ photocatalyst after 5 cycles.
● Investigation of kinetics of 2,4-D degradation.
● Investigation of thermodynamics of 2,4-D degradation.

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INTRODUCTION

Water contamination has received much attention due to its harmful effects on human health and the whole ecology (de Souza et al. 2020). The growth of agricultural activities causes the wide use of many different types of herbicides by farmers, leading to the existence of their residues in water (Matias et al. 2019). More than 1,500 herbicide brand products comprise 2,4-dichlorophenoxyacetic acid (2,4-D) as the active ingredient (Li et al. 2020). 2,4-D is the most common systemic herbicide, which is applied to control broad-leaf weeds; it has also been used for many years because of its very low price and selectivity (Nunes et al. 2019). 2,4-D has a long half-life, which creates enough time for it to be transferred to surface and underground water and to create kidney and liver issues in animals and humans (Arroyave et al. 2018). Considering its high solubility and its link to many diseases including cancer and endocrine disorders, it is vital to remove the concentration of 2,4-D from water (Xu et al. 2020). The structure and properties of 2,4-D are shown in Figure 1 and Table 1.

Until now, various techniques have been used to remove 2,4-D from aqueous solutions such as adsorption (Trivedi et al. 2019), biological degradation (Quan et al. 2015), electrochemical (Fontmorin et al. 2012), irradiation, Fenton (Chen et al. 2015), ozonation (Piera et al. 2000), chemical oxidation (Kwan et al. 2007), photocatalytic degradation (Baloochi et al. 2018), and many others (Youssef et al. 2017). Photolysis has attracted many considerations in the removal of 2,4-D in recent years (Bian et al. 2015). The use of photocatalyst in
degradation is considered a green, clean, and environmental-friendly technology (Lü et al. 2018; Wang et al. 2019). During photocatalytic oxidation processes, pollutants are degraded completely and electron-hole pairs created and hydroxyl radicals (OH) released as a result of radiation in the presence of the photocatalyst (Giovannetti et al. 2015). Semiconductor metal oxides are often used for photocatalytic processes. Nanoparticles such as TiO₂, SnO₂, WO₃, CeO₂, Bi₂O₃, ZnO, Ag-based photocatalyst (Suganya Josephi & Arumugam 2018) and also Nb₂O₅ (Niobium-based metal oxides) (Batista et al. 2017; Dos Santos et al. 2019) are investigated for their photocatalytic activities under irradiation of UV and visible light.

Titanium dioxide (TiO₂) is known as a superb choice for photocatalytic degradation. This is because TiO₂ is a low cost, non-toxic, stable, and highly efficient semiconductor (Olama et al. 2018; Heydari et al. 2019; Rahmat et al. 2020). In addition, TiO₂ has a relatively large band gap (about 3.2 eV) that requires ultraviolet (UV) light (about 4% of the solar spectrum) for activation, limiting its application in the visible light region (Cui et al. 2012). Recent studies have focused on the modified photocatalysts that can be activated in the presence of visible light, which contains the larger portion (46%) of the solar light (De la Cruz et al. 2015). Ag₃PO₄ has been reported to be successfully utilized under visible light for water treatment and organic contaminant photodegradation (Huang et al. 2013; Bian et al. 2020). Photocatalytic degradation is one of the most advanced oxidation processes, causing the degradation of pollutants by producing hydroxyl free radicals. This process begins with exposing a heterogeneous photocatalyst to the photons of a light source. With light radiation, electrons in the valence layer are transferred to the conduction layer, and electron holes are created; these holes react with the water molecules on the surface and produce hydroxyl radicals that can oxidize the contaminant. Finally, the organic compounds will be degraded into minerals according to the following equations (Dos Santos et al. 2019).

\[
\text{photocatalyst} + hν \rightarrow e^- + h^+ \quad (1)
\]
\[
h^+ + H_2O \rightarrow H^+ + OH \quad (2)
\]
\[
e^- + O_2 \rightarrow [O_2]^- \quad (3)
\]
\[
e^- + H_2O_2 \rightarrow OH + OH^- \quad (4)
\]
\[
[O_2]^- + H_2O_2 \rightarrow OH + OH^- + O_2 \quad (5)
\]
\[
H_2O_2 + hν \rightarrow 2OH \quad (6)
\]

In this study, the photocatalytic activity of Ag₃PO₄/TiO₂ for degradation of 2,4-D under visible light was evaluated. The effects of the practical parameters, including pH, initial 2,4-D concentration, time, catalyst dosage, temperature, and water matrices, on the degradation of 2,4-D were further investigated. Therefore, the stability and reusability of the photocatalyst were also checked.

**EXPERIMENTAL**

**Materials**

2,4-dichlorophenoxyacetic acid (C₈H₆Cl₂O₃)(98%) and silver nitrate (AgNO₃, CAS number 7761-88-8) were purchased from Merck company (Germany). P25 titania (TiO₂, CAS number 13463-67-7) was purchased from Degussa (Germany), and the Na₃PO₄ used for catalyst synthesis was purchased from Sigma-Aldrich.

**Synthesis of Ag₃PO₄/TiO₂ photocatalyst**

Synthesis of silver phosphate deposited onto Degussa titania (P25) was carried out using the *in situ* precipitation method reported by Yao et al. (2012). 1.6 g of titania (P25 with 80% anatase and a surface area of 50 m² g⁻¹) was dispersed in 50 ml of distilled water and sonicated for 5 min. After sonication, 3.05 g of AgNO₃ was added to the titania dispersed water and the resulting solution was magnetically stirred for 10 min at 200 rpm. Sodium phosphate was previously dispersed in 50 mL distilled water and was then added dropwise to the prepared solution. The final solution was magnetically stirred for 300 min. Then, the color changed from white to yellow in the solution. The Ag₃PO₄/TiO₂ nanocomposites were then filtered and washed with ethanol and water and dried at 60 °C for 12 h. The photocatalyst was prepared and then was used for photocatalytic reaction and characterization (Taheri et al. 2017).

**Characterization of Ag₃PO₄/TiO₂ nanocomposite**

In order to characterize the physicochemical properties of the Ag₃PO₄/TiO₂ nanocomposite, the X-ray diffraction (XRD) pattern technique was applied. XRD analysis was employed to investigate the existence of Ag, phosphate, and TiO₂ nanoparticles in this structure. The crystalline size of Ag₃PO₄/TiO₂ nanocomposite was calculated...
applying the Debye–Scherer relation given in Equation (7)

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(7)

where D is the crystalline size (nm), \( \lambda \) is the wave-length of the X-ray radiation, \( \theta \) is the diffraction angle, K is the Scherer constant (0.94), and \( \beta \) is the full width at half maximum (FWHM) of main intensity peak (Orooji et al. 2020).

Field emission scanning electron microscopy (FESEM) images were obtained by using a sigma vp scanning electron microscope equipped with an Energy Dispersive Spectrometer (EDS) for the determination of the elemental compounds distribution, surface morphology, and size of the nanoparticles.

### Photocatalytic degradation procedures

One factor at a time was used to obtain the optimized conditions. The type and value of operational parameters in the degradation of 2,4-D are presented in Table 2. During our photocatalytic experiment, 100 ml of the solution containing the desired concentration of 2,4-D was loaded in the open glass reactor under continuous stirring. The appropriate amount of photocatalyst was dispersed to the solution and was magnetically stirred for 15 min in the fully dark environment to ensure adsorption/desorption equilibrium. Then, a 300 W xenon (ozone free) lamp with a UV cut off filter (\( \lambda < 420 \) nm) was turned on. After that, 2 ml samples were filtered with a syringe filter and analyzed with HPLC.

### Analytical methods

HPLC was employed to monitor the concentration of 2,4-D. The separation was achieved on a C18 (OD) column. The mobile phase consisted of 80:20 UPW: acetonitrile eluted at 0.8 ml/min and 30 °C, while the injection volume was 20 μl. Detection was achieved through a UV detector. The limit of detection (LOD) and limit of quantification (LOQ) for 2,4-D are 15 and 50 μg/L, respectively. The excitation wavelength was 280 nm. Under these conditions, the retention time was 2.45 min. The 2,4-D removal efficiency was calculated with Equation (8)

\[ \text{Removal Efficiency(\%)} = \frac{C_0 - C_e}{C_0} \times 100 \]  

(8)

where \( C_0 \) demonstrates initial concentration of 2,4-D (mg/L), \( C_e \) denotes residual concentration of 2,4-D (mg/L) after degradation. Also, the adsorption capacity of 2,4-D by Ag₃PO₄/TiO₂ was calculated according to the following equation (Mazloomi et al. 2019; Zakeri et al. 2021).

\[ q_e \text{ (mg/g)} = \frac{(C_i - C_e) \times V}{M} \]  

(9)

where \( q_e \) is the amount of 2,4-D adsorbed per mass unit of photocatalyst in milligrams per gram, \( C_i \) and \( C_e \) are the initial and equilibrium concentration of 2,4-D (mg/L), respectively. V is the volume of the solution (L), and M is the amount of nanoparticle used (g).

### Reaction kinetics

Equations (10) and (11) show the reaction kinetics equation (Gu et al. 2015; Jaafarzadeh et al. 2017). Where \( C_t \) and \( C_0 \) are herbicide concentrations at t and zero times, respectively, \( k \) is the degradation rate constant (min⁻¹).

\[ \frac{d[2, 4 - D]}{dt} = k[2, 4 - D] \]  

(10)

\[ \ln \frac{C_0}{C_t} = kt \]  

(11)

The pseudo-first-order and pseudo-second-order kinetic model equations for 2,4-D degradation by Ag₃PO₄/TiO₂ are represented as follows (Sharifi et al. 2019; Tapouk et al. 2020).

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  

(12)

\[ t/q_t = 1/k_2 q_e^2 + t/q_e \]  

(13)

According to these equations, the \( q_e \) and \( q_t \) parameters are the adsorption capacity at the equilibrium time and time t (mg/g), respectively. Also, \( k_1 \) and \( k_2 \) are the adsorption rate constant (min⁻¹) in pseudo-first-order (Dehghani

| Operational parameters in degradation of 2,4-D |
|-----------------------------------------------|
| 2,4-D concentration (mg/L) | Catalyst dosage (g/L) | Time (min) | pH |
|---------------------------|----------------------|-----------|----|
| 10                        | 0.1                  | –         | 3  |
| 20                        | 0.5                  | 30        | 5  |
| 30                        | 1                    | 60        | 7  |
| 40                        | 1.5                  | 90        | 9  |
| 50                        | 2                    | 120       | 11 |
| –                         | 3                    | –         | –  |
et al. 2019) and pseudo-second-order (Zhang et al. 2015) kinetic model equations.

Thermodynamic studies

In order to study the thermodynamics of the adsorption process, the thermodynamic parameters, including changes in enthalpy (ΔH°), changes in entropy (ΔS°), and Gibb’s free energy (ΔG°), were obtained using the following equations (Dehghania et al. 2020).

\[
\Delta G° = -RT \ln(q_m/C_e) \quad (14)
\]

\[
\Delta G° = \Delta H° - T(\Delta S°) \quad (15)
\]

\[
\log\left(q_m/C_e\right) = \left(\Delta S°/2.303R\right) + \left(-\Delta H°/2.303R\right) \quad (16)
\]

In this equation, R represents the global constant of gases (8.314 J/mol.K) and T is the temperature in Kelvin. To determine the enthalpy (ΔH°) and entropy (ΔS°) parameters, Ln (q_m/C_e) vs. 1/T was plotted. Where m is the photocatalyst dosage (g/L), q_e was the amount of 2,4-D adsorbed per unit mass of the photocatalyst (mg/g), and C_e was the equilibrium concentration of 2,4-D (mg/L).

RESULTS AND DISCUSSION

Characterization of the synthesized photocatalysts

The XRD patterns of Ag₃PO₄/TiO₂ composite photocatalyst (Figure 2) showed a remarkable peak at 25.3°, which could be indexed to the (101) plane of TiO₂ (P25). For the Ag₃PO₄/TiO₂, except the peak at 25.3° indexed to the (101) plane of TiO₂(P25), further peaks at 2θ values of 20.93°, 29.78°, 33.39°, 36.68°, 47.94°, 52.85°, 55.19° and 57.64° could be indexed to the (110), (200), (210), (310), (222), (320), and (321) crystal planes of Ag₃PO₄. According to the figure it is clear that the structure of Ag₃PO₄ is cube-shaped and TiO₂ particles are composed of anatase phase. The sharp and strong XRD peaks demonstrate the extremely crystallized structure of Ag₃PO₄/TiO₂ nanoparticles. These results affirmed that Ag₃PO₄/TiO₂ particles had been successfully synthesized and Ag₃PO₄ nanoparticles have been perfectly placed on the surface of the TiO₂. This pattern showed complete integrity without impurities.

The morphology of the synthesized samples evaluated in Figure 3. The presence of Ag₃PO₄ nanoparticles on TiO₂ surface are confirmed by the FESEM-EDS analysis. Figures 3

![Figure 2](image_url) | XRD pattern of Ag₃PO₄/TiO₂, Ag₃O₄: ■ and TiO₂: □.
and 4 show the FESEM images and the EDS spectrum of the synthesized Ag₃PO₄/TiO₂ heterostructure photocatalyst. As observed in these images, the synthesized Ag₃PO₄/TiO₂ consists of agglomerations of spherical shape nanoparticles. The energy dispersive X-ray spectrum (EDS) analysis of this photocatalyst proves the existence of Ag, Ti, P, and O elements. Moreover, the particle size appears to be less than 81 nm.

Effect of solution pH

The pH of a solution plays a key role in the photocatalytic degradation of an organic pollutant from aqueous solutions. In this work, the effect of solution pH in the range of 3–11 was investigated on the photocatalytic process efficiency for 2,4-D degradation. These experiments were conducted at initial 2,4-D concentration of 20 mg/mL, catalyst dosage of 0.5 g/L during 30 min. The temperature was maintained at 25°C with a magnetic stirrer equipped with a thermostat. Figure 5 shows the efficiency of the photocatalytic degradation under several pH values. According to the results, the photocatalytic degradation efficiency of 2,4-D increased with decreasing pH. The maximum photocatalytic degradation efficiency of 2,4-D was obtained at pH = 3 (acidic pH). This can be related to P_Ka of the 2,4-D herbicide and pH_{pzc} of the photocatalyst. The P_Ka factor for the 2,4-D herbicide is 2.64 (Tang et al. 2015). Above this pH, the herbicide exists in the anion form. On the other hand, pH_{pzc} for TiO₂ and Ag₃PO₄ nanoparticles has been reported to be 6.9 and 6.55, respectively (Gaya & Abdullah 2008). The surface charge of the photocatalyst is positive at a lower pH than pH_{pzc} (acidic pH). Therefore, the pH should be lower than the pH_{pzc} and higher than the pollutant P_Ka.
because the electrostatic interaction between the pollutant anions and the positive surface charge of the catalyst increase. In acidic conditions (lower than pH_{zpc}), the photocatalyst surface is positively charged and can adsorb negative charge from 2,4-D molecules. Therefore, the photocatalyst performance increased with decreasing pH \cite{Orooji2020}. A similar result of the effect of solution pH on the 2,4-D degradation was reported earlier by Singh et al. \cite{Singh2004}.

**Effect of catalyst dosage**

The effect of the amount of catalyst in the limited area of 0.1–3 g/L was examined on the photocatalyst performance for 2,4-D degradation under the following conditions, pH = 3, initial 2,4-D concentration = 20 mg/L at a temperature of 25 °C during 30 minutes. The results, as shown in Figure 6, demonstrated that the photocatalytic efficiency of Ag_{3}PO_{4}/TiO_{2} increased with increasing catalyst amount from 0.1 to 1 g/L. This can be attributed to the increase in the surface area and active sites available in the photocatalyst for photocatalytic degradation of the pollutant. After 1 g/L, excessive amounts of catalyst reduced the degradation efficiency. This is due to the additional increase in catalyst amounts, which leads to the agglomeration of catalyst nanoparticles, decrease in the active sites on catalyst surface, prevention of light penetration (Chun et al. 2000; Singh & Muneer 2004; Gaya & Abdullah 2008), and eventually reduction in the removal efficiency.

**Effect of contact time**

The results of investigating the effect of contact time on 2,4-D removal with Ag_{3}PO_{4}/TiO_{2} under visible light are shown in Figure 7. In this diagram, the increase of removal efficiency is clearly seen with increasing contact time. By increasing the contact time to 60 minutes, the removal efficiency increases with a relatively steep slope, which can be due to the presence of unsaturated active sites on the outside surface of the nanocomposite. After this time, the trend of
removal efficiency was approximately constant, which can be ignored. Therefore, 60 minutes was considered as the optimum contact time.

The optimum contact time of 2,4-D removal was considered 90 minutes with MIEX resin in Diang et al. (2012) study and 60 minutes in Dehghani et al. (2014) study by using modified granular activated carbon. In the study conducted by Tang et al. (2015), the maximum contact time for removal of 2,4-D with a concentration above 100 mg/L from the solution was 5 minutes. This may be due to the high tendency of 2,4-D for the carboxyl groups that exist on the Fe/OMC nanoparticles. The reason for the difference in equilibrium time in different studies can be attributed to the type of nanoparticles that were used for the removal of 2,4-D and the difference in the initial concentrations of the desired contaminant.

**Effect of initial 2,4-D concentration**

The effect of initial concentration of 2,4-D in the range of 10–50 mg/L was evaluated on the photocatalyst efficiency under the given conditions, pH = 3, catalyst dosage = 1 g/L at a temperature of 25 °C during 60 minutes. As shown in Figure 8, the photocatalyst efficiency decreased with increasing 2,4-D concentration. These results are obviously related to occupying the empty active site from the photocatalyst, catalyst surface becomes saturated and inactivated eventually, therefore, less degradation efficiency is achieved (Arana et al. 2004). The results of Orooji et al. (2020) study are consistent with the present study.

**Photocatalytic activity**

Ag₃PO₄/TiO₂ composite under visible light represented high photocatalytic activity in the degradation of 2,4-D. Figure 9 shows the results of the photocatalytic activity of TiO₂, Ag₃PO₄ and Ag₃PO₄/TiO₂ composite with and without visible light for 2,4-D degradation. As shown in the Figure 9, titanium dioxide had a low removal efficiency because titanium dioxide is active only in the presence of UV light radiation due to its wide band gap (3.2eV). The Ag₃PO₄ substantially increased the photocatalytic degradation activity of Ag₃PO₄/TiO₂, which indicates the existence of a synergistic effect between silver and titanium phosphate nanoparticles. Furthermore, degradation activity of Ag₃PO₄/TiO₂ composite investigated in the presence of visible light compared with the absence of visible light irradiation. The results showed the photocatalytic degradation activity of Ag₃PO₄/TiO₂ composite under visible light irradiation was much greater than Ag₃PO₄/TiO₂ composite without light, which can be attributed to the photo generated active species, this subject denoting the role of light irradiation.

A number of studies have been performed on 2,4-D removal with a variety of catalysts. For example, it has been reported that 83% degradation of 100 mg/L 2,4-D can be achieved in 240 min with novel TiO₂@MgFe₂O₄ core@shell, using 0.05 g of catalyst per liter of solution (Huy et al. 2017). Mn-doped with ZnO/Graphene has also been tested, degrading 66.2% of 25 mg/L 2,4-D adding 2 g/L catalyst (Ebrahimi et al. 2020). TiO₂/clinoptilolite/UV
system achieved 58% degradation of 6 mg/L 2,4-D using 0.4 g/L catalyst (Mehrabadi & Faghihian 2018). ZnFe2O4 catalyst achieved 97.84% removal of 10 mg/L 2,4-D using 0.3 g/L catalyst (Zaghloul et al. 2020).

Reusability of photocatalyst

One of the most critical issues for practical applications in photocatalytic processes is the investigation of the long term stability and reusability of photocatalysts in photocatalytic degradation processes. To evaluate the reuse of the photocatalyst, 1 g/L of Ag3PO4/TiO2 photocatalyst was added to 10 mg/L 2,4-D in 100 ml of aqueous solution under the visible light for five consecutive cycles. After each step, the catalyst was centrifuged, washed with water and ethanol, and dried in the oven at a temperature of 60 °C; the catalyst was used again for degradation purposes. As shown in Figure 10, the efficiency of degradation of 2,4-D decreased slightly from 98.4% to 96.1% after five cycles; this may be related to the inactivation of some Ag3PO4/TiO2 photocatalyst (Xin et al. 2016). It could be concluded that recycling of Ag3PO4/TiO2 show high efficiency for 2,4-D removal. This is consistent with the Liu et al. (2019) study.

Reaction kinetics

In the present study, the kinetics of 2,4-D degradation by Ag3PO4/TiO2 was investigated using two common models, pseudo-first-order and pseudo-second-order kinetic models (Figures 11 and 12). The values of the kinetic parameters are shown in Table 3. Figure 11 demonstrates that the degradation rate of 2,4-D conformed with pseudo-first-order kinetic model. Hence, the high value of correlation coefficient (R² = 0.9908) approved that the data were matched well with pseudo-first-order kinetic for 2,4-D degradation. Moreover, Sandeep et al. (2018), Meenakshi et al. (Meenakshi & Sivasamy 2018) have reported the same results regarding that photocatalytic degradation of 2,4-D by TiO2 and zinc oxide nanorods respectively, followed the first-order kinetics.

Thermodynamic study

Figure 13 shows Ln (qem/Ce) diagram versus 1/T. Slope and y-intercept of this diagram were used to determine the values of ΔH° and ΔS°. According to Table 4, we observed
that the values of $\Delta H$ and $\Delta S$ were 75.581 kJ/mol and 0.289 kJ/mol K, respectively. The positive $\Delta H$ value confirmed that the reaction was endothermic in nature. The positive $\Delta S$ value showed a high tendency to adsorb 2,4-D to the catalyst and therefore high degradation efficiency. The values of $\Delta G$ were obtained at temperatures of 293.15 K, 303.15 K, and 313.15 K equal to $-9.189$ kJ/mol, $-12.084$ kJ/mol, and $-14.975$ kJ/mol, respectively (Figure 14). The negative value of $\Delta G$ demonstrated the feasibility and automatic nature of the process (Dehghania et al. 2020). Also in the Nejati et al. study on the 2,4-D removal from aqueous solution by Cu-Fe-layered double hydroxide, $\Delta S$, $\Delta H$ and $\Delta G$ values were obtained as positive, negative and negative respectively (Nejati et al. 2013).

**CONCLUSION**

In this work, a novel Ag$_3$PO$_4$/TiO$_2$ heterostructure photocatalyst was successfully prepared via in-situ deposition of Ag$_3$PO$_4$ nanoparticles onto TiO$_2$ (P25) and was applied under the visible light for degradation 2,4-D from aqueous solution. The operation parameters on the degradation efficiency were evaluated by one-factor-at-a-time (OFAT) method. The results showed that the maximum degradation efficiency of 2,4-D was attained at the optimum condition of the process ($\text{pH} = 3$, catalyst dosage = 1 g/L, contact time = 60 min, initial 2,4-D concentration = 10 mg/L). 2,4-D degradation efficiency with Ag$_3$PO$_4$/TiO$_2$ photocatalyst reached 96.1% from 98.4% after 5 cycles. The results demonstrated that the photocatalytic process by using Ag$_3$PO$_4$/TiO$_2$ nanoparticles in the presence of visible light have a relatively

| Table 3 | Kinetic parameters |
|---|---|
| Kinetic models | Equation | $R^2$ | $K$ |
| Pseudo-first-order | $\ln \left( q_e - q_t \right) = \ln q_e - k_1 t$ | 0.994 | 0.028 (min$^{-1}$) |
| Pseudo-second-order | $t/q_t = 1/k_2 q_e^2 + t/q_e$ | 0.853 | 0.052 (g/mg.min) |

**Table 4 | Thermodynamic parameters for 2,4-D degradation**

| Temperature (K) | $\Delta G$ (kJ/mol) | $\Delta S$ (kJ/mol K) | $\Delta H$ (kJ/mol) |
|---|---|---|---|
| 293.15 | $-9.189$ | $0.289$ | $75.581$ |
| 303.15 | $-12.084$ | | |
| 313.15 | $-14.975$ | | |

**Figure 13 | Plot of $\ln \left( q_{em}/C_e \right)$ vs $1/T$ for 2.4-D degradation.**

**Figure 14 | $\Delta G$ values at different temperatures.**
good efficiency in removing 2,4-D. Ag₃PO₄/TiO₂ can be used as a reusable photocatalyst for degradation of such toxins from polluted water and wastewater.

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CONFLICT OF INTEREST

We declare that we have no conflicts of interest.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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