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Degradation of paraquat herbicide using hybrid AOP process: statistical optimization, kinetic study, and estimation of electrical energy consumption

Azam Ghavi^{1*}, Ghadamali Bagherian¹ and Hadi Rezaei-Vahidian²

Abstract

Background: This work studied the performance of UV/PS/TiO₂NPs and UV/PI/TiO₂NPs as hybrid advanced oxidation processes for degradation of paraquat in aqueous solution, because this very toxic herbicide is used third most widely.

Results: The effects of several factors such as UV irradiation, initial oxidant concentration, TiO₂ nanoparticles dosage, and pH on the degradation efficiency were investigated. The process optimization was performed by the central composite design as a tool of response surface methodology for 30 mgL⁻¹ of the herbicide initial concentration at 25 °C and 40 min of degradation process. Based on the results, a degradation efficiency of 77% and 90% were obtained for the UV/PS/TiO₂NPs and UV/PI/TiO₂NPs processes, respectively, in the optimum conditions. The mineralization efficiency of the paraquat solution using UV/PS/TiO₂NPs and UV/PI/TiO₂NPs processes are about 32% and 55%, respectively, after 40 min. The kinetic studies show that both processes follow a pseudo-first-order kinetic model, and the kinetic constants are 0.0299 min⁻¹ for the PS process and 0.0604 min⁻¹ for the PI process. The electrical energy consumption was estimated to be about 481.60 kWhm⁻³ for the PS process and 238.41 kWhm⁻³ for the PI process.

Conclusions: The degradation and mineralization efficiency of the paraquat solution using the UV/PI/TiO₂NPs process was more than that of the UV/PS/TiO₂NPs process at the optimum conditions after 40 min.

Keywords: Hybrid advanced oxidation processes, Periodate oxidations, Persulfate oxidations, Paraquat degradation, Mineralization, Response surface methodology, Kinetic study

Background

Paraquat (PQ) is a non-selective contact herbicide used to control or suppress a broad spectrum of emerged weeds. It is the most toxic herbicide, and the third most widely used in the world [1]. The United States Environmental Protection Agency (USEPA) has classified paraquat dichloride as a restricted-use pesticide due to its highly acute toxicity to animals and people from intentional or inadvertent exposure with acute oral toxicity

of 4,4-bipyridyl with an LD₅₀ value of 40–200 mg/kg of body weight. It has life-threatening effects on the gastrointestinal tract, kidneys, liver, heart, and other organs [2, 3].

In the recent years, advanced oxidation processes (AOPs) have been intensively studied as the most environmentally friendly and promising techniques for the degradation of recalcitrant organic pollutants in water by powerful oxidants, especially hydroxyl radicals and superoxide radicals [4–10].

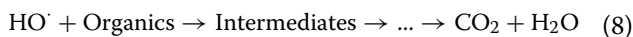
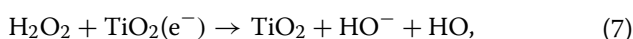
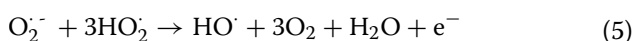
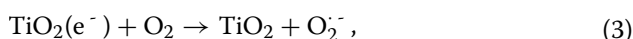
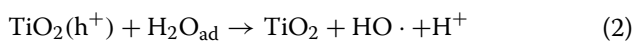
Heterogeneous photocatalytic degradation in the presence of the nanostructure catalysts has attained good efficiencies in the degradation of organic compounds among

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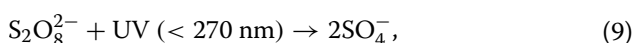
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the various AOPs [11–18]. In the photocatalytic activity process, the photoelectrons in the conduction band and highly oxidative holes in the valence band are produced, where a reaction occurs with the adsorbed water to form the highly reactive hydroxyl radicals according to Eqs. 1–8 [19].

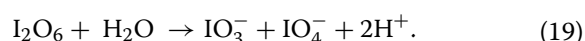
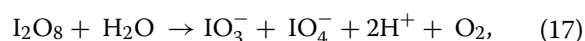
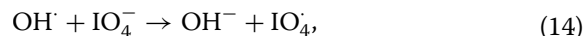
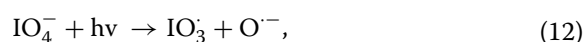


As another powerful AOP method, inorganic oxidants such as ClO_3^- , BrO_3^- , H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, and IO_4^- are used for the removal and mineralization of various organic pollutants from aqueous solutions. They produce different highly reactive radicals and in the hybridizing oxidation processes they have synergistic effect which gives better results in comparison to the individual processes [20–24]. They have enhanced the rate of UV-induced decomposition of organic pollutants in the presence of photocatalysis. This enhancement is as a result of the reduction of electron/hole recombination because of the reaction of activated electron by active oxidant such as $\text{S}_2\text{O}_8^{2-}$ and IO_4^- [25–27].

Undergoing photolysis or thermolysis in an aqueous solution, persulfate (PS) is decomposed to generate the reactive radicals (Eqs. 9–11) [28, 29].



Periodate (PI), as an inorganic oxidant, can oxidize a wide range of organic compounds quickly due to the generation of highly reactive radicals and non-radical intermediates under photolysis in an aqueous solution (Eqs. 12–19) [28–30].



AOPs have limitations. In general, one of the main limitations of AOPs is that they cannot be used for effluents with high pollutant content due to their high cost. Also, in the AOP methods, the safety aspects of using UV light should be considered in the design of the process and the relevant reactors, which is one of the limitations of process operating. Cantavenera et al. [31] investigated the photocatalytic degradation of PQ in the presence of polycrystalline TiO_2 Degussa P25 irradiated by near-UV light. They observed an increase of both degradation and mineralization rates after an induction time of 45–60 min and the complete photocatalytic mineralization of PQ (20 mgL^{-1}) after 3 h of irradiation using 0.4 g l^{-1} of catalyst at natural pH [31] such that both time and catalyst amount used were high. Ignace et al. [32] studied the photocatalytic degradation of PQ in a fixed bed photoreactor under UV irradiation at 368 nm. This contained β -SiC alveolar foams coated with TiO_2 P25. The results showed that under optimal operating conditions at natural pH=6.7, [PQ]=10 mgL^{-1} , and flow (26 mL/min), degradation and mineralization obtained about 43% and 27% respectively, after about 70 min [32] and these results are low. Zahedi et al. [33] studied the photocatalytic degradation of paraquat herbicide in the presence TiO_2 nanostructure thin films under visible and sunlight irradiation using continuous flow photoreactor. The results indicated that at optimum pH 5.8, maximum decomposition of 84.39% in 5 h occurred under visible irradiation with initial concentration of 10 mgL^{-1} and the amount of photocatalyst of 30.8 g [33] such that both time and used catalyst amount were high.

The aim of this work is comparative study of the performance of UV/PS/ TiO_2 NPs and UV/PI/ TiO_2 NPs as hybrid AOPs and synergistic effect of these hybrid processes for degradation of the paraquat herbicide in aqueous

solution. The process was modeled and optimized by response surface methodology (RSM). Also, the kinetic and the electrical energy consumption were assessed. So far, researchers have not studied the electrical energy consumption for the hybrid photocatalytic/periodate and persulfate process of paraquat herbicide and, this assessment have been performed in this work for the first time.

Methods

Materials and instruments

A standard solution of PQ (42%) with the chemical name of 1,1dimethyl-4,4-bipyridinium dichloride, whose molecular structure is shown in the Additional file 1: Figure S1, was prepared from the Golsam Chemicals Company. Anatase TiO₂ nanopowder (purity: >99%, APS: 10–25 nm, SSA: 200–240 m²g⁻¹, color: white) was supplied from the US Research Company as a photocatalyst; its TEM and XRD analysis results are shown in Additional file 1: Figs. S2 and S3. Sodium periodate and sodium persulfate were used as the oxidants. Hydrochloric acid (2N) and sodium hydroxide (2N) were used to adjust the solution pH, and in all the experiments, deionized water was utilized to prepare the solutions. All the chemicals used were Merck and Fluka products.

The concentration of PQ was measured by a UV–visible spectrophotometer (Double-beam Rally UV-2601). The total organic carbon (TOC) analysis was carried out using a multi-N/C 3100 (Germany) instrument.

Photochemical reactor

A UVC lamp (Philips, 150 W and $\lambda_{\max} = 254$ nm) was used as the light source fixed into the quartz tube and located in the center of the reactor. A cylindrical Pyrex container with a volume of 500 mL, which was equipped with a cooling jacket to control the temperature, was used as the reactor vessel. The reactor content was stirred by a magnetic stirrer. A schematic representation of the photoreactor is shown in Fig. 1.

Procedure

In each run of the process, 400 mL of the PQ solution with the desired initial concentration and pH value was transferred into the reactor. A certain amount of the TiO₂ nanopowder and the inorganic oxidant was added, and after mixing well the UV lamp was switched on to initiate the process. At regular time intervals, the samples were withdrawn, and the degradation studies were carried out by measuring the absorbance at $\lambda_{\max} = 258$ nm that corresponded to C=C bands in the pyridinium ring with the help of a UV–visible spectrophotometer (Fig. 2) [34]. Also the mineralization study was carried out by measuring the TOC of the samples (Additional file 1: Fig. S5).

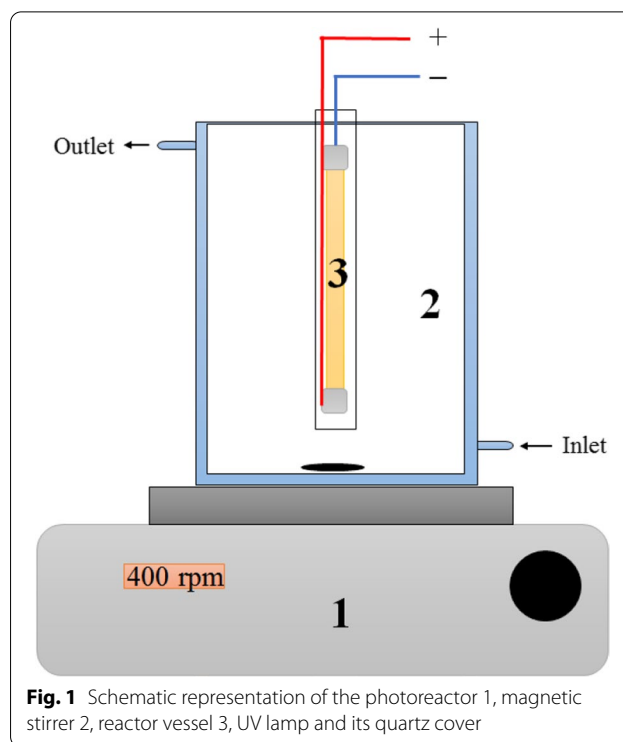


Fig. 1 Schematic representation of the photoreactor 1, magnetic stirrer 2, reactor vessel 3, UV lamp and its quartz cover

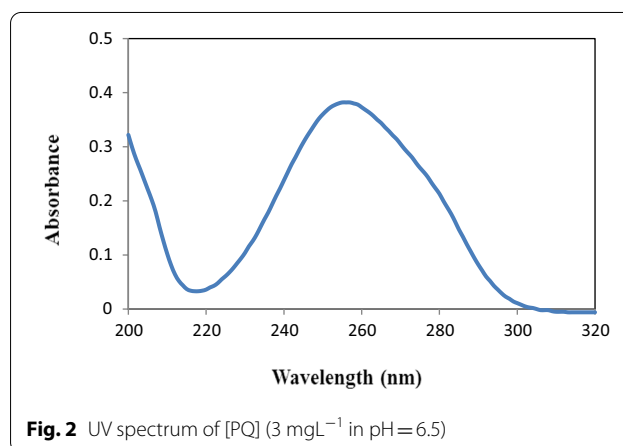


Fig. 2 UV spectrum of [PQ] (3 mgL⁻¹ in pH=6.5)

The percentages of degradation and mineralization were calculated according to the following equations:

$$\% \text{ Degradation} = \frac{C_0 - C_i}{C_0} \times 100, \quad (20)$$

where C_0 and C_i are the concentrations of PQ before and after treatment.

$$\% \text{ Mineralization} = \frac{\text{TOC}_{\text{initial}} - \text{TOC}_t}{\text{TOC}_{\text{initial}}} \times 100\%, \quad (21)$$

where TOC_t is the TOC at time ' t ' [34].

Design of experiments

The effects of various experimental parameters on the efficiency of the degradation processes and their optimum values were studied using the central composite design (CCD) as one of the important tools of the RSM [35]. RSM is one of the useful mathematical and statistical methods for analyzing the relation between several independent variables [36].

CCD was used to optimize the values of the significant variables and obtain the best quantitative response. Also, it reduced the effects of the uncontrolled variables [37].

The total number of experiments (N) could be determined as follows [38, 39]:

$$N = 2^k + 2k + N_0, \quad (22)$$

where k , 2^k , $2k$, and N_0 are the number of factors, the terms of cubic points, the axial points, and the center points, respectively.

Thus CCD is able to model and optimize the related operational factors of AOPs and can specify the possible interaction between them [38].

In this work, the three important factors initial pH, TiO₂NPs dosage, and inorganic oxidant concentration were optimized based on the obtained degradation efficiency (DE) of PQ as the response via the CCD method.

Results

Experimental design

To design the experiments, the effective operational parameters such as the PS and PI concentrations, initial pH, and TiO₂NPs dosage were considered to be optimized by the DOE software. Next, by introducing the parameters and their levels to the DOE software, 20 tests were designed to be done for both processes. The tests were performed, and their correlated DE was calculated and introduced to the software as a response. The range of the variables companion with the designed experiments for the UV/PS/TiO₂NPs and UV/PI/TiO₂NPs processes are shown in Tables 1 and 2, respectively.

After the regression analysis of the data, a second-order polynomial equation was suggested by the software to predict the response of the processes of UV/PS/TiO₂NPs and UV/PI/TiO₂NPs.

The significance of the model and its terms was evaluated by the analysis of variance (ANOVA) such that the p values less than 0.05 and greater than 0.10 indicated that the model terms were significant and not significant, respectively. The terms TiO₂NPs, pH², PS, and PS × pH in the PS process, and the terms PI², pH², and TiO₂NPs in the PI process were significant. The ANOVA output for the reduced quadratic models (Eqs. 23 and 24) is demonstrated in Tables 3 and 4 for the UV/PS/TiO₂NPs and UV/PI/TiO₂NPs processes, respectively. The model

F value of 110.37 and the p value < 0.0001 for the UV/PS/TiO₂NPs process, and the F value of 41.12 and the p value < 0.0001 for the UV/PI/TiO₂NPs process imply that the models are significant.

$$\begin{aligned} \%DE = & 9.01321 + 0.13468 \text{ PS} + 4.99923 \text{ pH} \\ & + 0.02698 \text{ TiO}_2\text{NPs} - 0.00459 \text{ PS} \\ & \times \text{pH} - 0.25118 \text{ pH}^2, \end{aligned} \quad (23)$$

$$\begin{aligned} \%DE = & -64.83410 + 1.08949 \text{ PI} + 20.05376 \text{ pH} \\ & + 0.12196 \text{ TiO}_2\text{NPs} - 0.00434 \text{ PI}^2 \\ & - 1.35832 \text{ pH}^2. \end{aligned} \quad (24)$$

The "Pred R -Squared" of 0.93 and "Adj R -Squared" of 0.97 represent that the model predicts the response as well, and the "Adeq Precision" of 38.26 indicates an adequate signal-to-noise ratio (a ratio greater than 4 is desirable). The R^2 of 0.97 implies that the model can predict the UV/PS/TiO₂NPs process performance. Also in the case of the UV/PI/TiO₂NPs process, the "Pred R -Squared", "Adj R -Squared", and "Adeq Precision" were 0.78, 0.91, and 19.73, respectively. The R^2 of 0.94 implies that the model can predict the UV/PI/TiO₂NPs process performance. The adequacy of the models was graphically evaluated and approved by the diagnostic plots (Additional file 1: Fig. S6a, b).

Discussion

The effects of the operational factors on the process were assessed by the 3D surface graphs. Figures 3 and 4 show the variation in the degradation efficiency as a function of the initial pH, the dose of TiO₂NPs, and the oxidant dosage (PS and PI), while the PQ initial concentration is 30 mgL⁻¹ in all tests. Figure 3 shows that the efficiency of the PI process at the neutral condition is more than that for the alkaline and acidic conditions, and it decreases intensity at the acidic condition, while the activity of PS is independent of the pH variations. Figure 4 shows that the degradation efficiency is increased by increasing the PI, PS, and TiO₂NPs concentrations for both processes at a constant pH. This increase is very intensive for PI due to the production of more radicals (Eqs. 12–19). Thus PI is a stronger and more active oxidizer.

The operational parameters were numerically optimized based on the models (Eqs. 23 and 24) using the related numerical facilities of the applied software. For this aim, the goals of the three variables and the model response were set at "in the range" and "maximizing", respectively. The desirability ramps for the numerical optimization of the UV/PS/TiO₂ NPs and UV/PI/TiO₂ NPs processes are shown in the Additional file 1: Figs. S7 and S8. For the PS process, in the optimum conditions

Table 1 Range of the variables and the designed experiments as well as the corresponding responses for the PS process ([PQ] = 30 mgL⁻¹, T = 25 °C)

Variables	Range and level				
	- α	-1	0	+1	+ α
A: S ₂ O ₈ ²⁻ (mg L ⁻¹)	64.77	150	275	400	485.22
B: pH	2.29	4	6.5	9	10.70
C: TiO ₂ (mg L ⁻¹)	15.91	50	100	150	184.09

Runs	Factors			DE (%)	
	S ₂ O ₈ ²⁻ (mgL ⁻¹)	pH	TiO ₂ (mgL ⁻¹)	(Exp.)	(Pred.)
	1	150.0	4.0	50.0	44.8
2	275.0	6.5	100.0	64.0	62.4
3	150.0	9.0	150.0	53.3	51.7
4	275.0	6.5	100.0	62.7	62.4
5	400.0	9.0	50.0	72.0	72.4
6	275.0	6.5	100.0	63.5	62.4
7	485.2	6.5	100.0	83.2	84.5
8	150.0	4.0	150.0	49.3	46.5
9	150.0	9.0	50.0	47.2	49.0
10	275.0	10.7	100.0	61.9	60.0
11	275.0	2.3	100.0	53.1	56.0
12	64.80	6.5	100.0	36.5	40.4
13	275.0	6.5	100.0	62.7	62.4
14	275.0	6.5	184.1	62.4	64.7
15	275.0	6.5	100.0	64.0	62.4
16	400.0	9.0	150.0	73.1	75.1
17	400.0	4.0	50.0	73.1	72.9
18	275.0	6.5	100.0	62.7	62.4
19	275.0	6.5	15.9	60.8	60.2
20	400.0	4.0	150.0	77.1	75.6

of [PS] = 400 mgL⁻¹, [TiO₂NPs] = 150 mgL⁻¹, and [pH]_{in} = 6.3, the predicted DE is about 77%. Also DE for the PI process is about 90% in the optimum conditions of [PI] = 90 mgL⁻¹, [TiO₂NPs] = 125 mgL⁻¹, and [pH]_{in} = 6. To assess the accuracy of the model prediction, under the supposed values of the parameters, the photocatalytic degradation efficiency empirically reached 90% (i.e., 0% error) for the PI process and 83% (i.e., 6% error) for the PS process. Comparison of the several studies on degradation of paraquat by AOPs is presented in Table 5. Considering the table, it can be concluded that UV/PI/TiO₂NPs and UV/PS/TiO₂NPs processes (this study) have a good ability to remove paraquat, rather than other studies.

The degradation kinetic of PQ was assessed under the optimum conditions for both processes based on pseudo-first-order equation as follows:

$$\ln \frac{PQ_0}{PQ_t} = kt, \quad (25)$$

where [PQ]₀, [PQ]_t, k , and t are the initial and at any time concentrations of the PQ, first-order kinetic constant, and process time, respectively.

The linear relationship between the investigated results for both the PS and PI processes shows that they follow the first-order kinetics; the fitting is shown in Fig. 5. Plotting the variation in the logarithmic concentration ratio versus the irradiation time forms a straight line with a slope equal to k_{app} . The kinetic constant was 0.0299 min⁻¹.

Mineralization is the process of complete oxidative degradation of an organic compound and the relevant intermediates to CO₂, H₂O, and other mineral oxides [25, 42]. For detection of the degradation of PQ, the UV-visible spectrophotometry analysis is used, and to

Table 2 Range of the variables and the designed experiments as well as the corresponding responses for the PI process ([PQ] = 30 mgL⁻¹, T = 25 °C)

Variables	Range and level				
	-α	-1	0	+1	+α
A: IO ₄ ⁻ (mg L ⁻¹)	110.45	30	60	90	9.54
B: pH	2.29	4	6.5	9	10.70
C: TiO ₂ (mg L ⁻¹)	15.91	50	100	150	184.09

Runs	Factors			DE (%)	
	IO ₄ ⁻ (mg L ⁻¹)	pH	(mg L ⁻¹)	(Exp.)	(Pred.)
1	90.00	9.00	50.00	76.61	74.62
2	60.00	6.50	100.00	69.90	70.07
3	110.45	6.50	100.00	86.56	87.71
4	30.00	9.00	150.00	45.70	52.70
5	60.00	6.50	184.90	77.42	80.32
6	60.00	2.29	100.00	25.53	35.98
7	60.00	6.50	100.00	70.43	70.07
8	60.00	10.70	100.00	69.62	62.64
9	90.00	4.00	50.00	68.82	62.64
10	60.00	6.50	15.91	56.18	59.81
11	30.00	4.00	150.00	47.58	40.72
12	30.00	4.00	50.00	36.56	28.52
13	9.54	6.50	100.00	25.54	30.33
14	60.00	6.50	100.00	69.89	70.07
15	90.00	4.00	150.00	82.79	74.84
16	60.00	6.50	100.00	69.62	70.07
17	60.00	6.50	100.00	69.35	70.07
18	60.00	6.50	100.00	70.43	70.07
19	30.00	9.00	50.00	44.09	40.50
20	90.00	9.00	150.00	84.14	86.82

Table 3 ANOVA for the response surface reduced quadratic model for the PS process

Source	Sum of squares	df	Mean square	F-value	p-value prob > F
Model	2443.11	5	488.62	110.37	< 0.0001
A- S ₂ O ₈ ²⁻	2346.59	1	2346.59	530.06	< 0.0001
B- pH	19.06	1	19.06	4.30	0.0569
C- TiO ₂	24.86	1	24.86	5.61	0.0327
AB	16.44	1	16.44	3.71	0.0746
B ²	36.17	1	36.17	8.17	0.0126
Residual	61.98	14	4.43		
Lack-of-fit	59.79	9	6.64	15.15	0.0040
Pure error	2.19	5	0.44		
Cor Total	2505.09	19			

Table 4 ANOVA for the response surface reduced quadratic model for the PI process

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F
Model	6168.64	5	1233.73	41.12	< 0.0001
A- IO ₄ ⁻	3977.48	1	3977.48	132.57	< 0.0001
B- pH	489.86	1	489.86	16.33	0.0012
C- TiO ₂	507.83	1	507.83	16.93	0.0011
A ²	221.91	1	221.91	7.40	0.0166
B ²	1048.98	1	1048.98	34.96	< 0.0001
Residual	420.03	14	30.00		
Lack-of-fit	418.49	9	46.50	150.81	< 0.0001
Pure error	1.54	5	0.31		
Cor Total	6588.67	19			

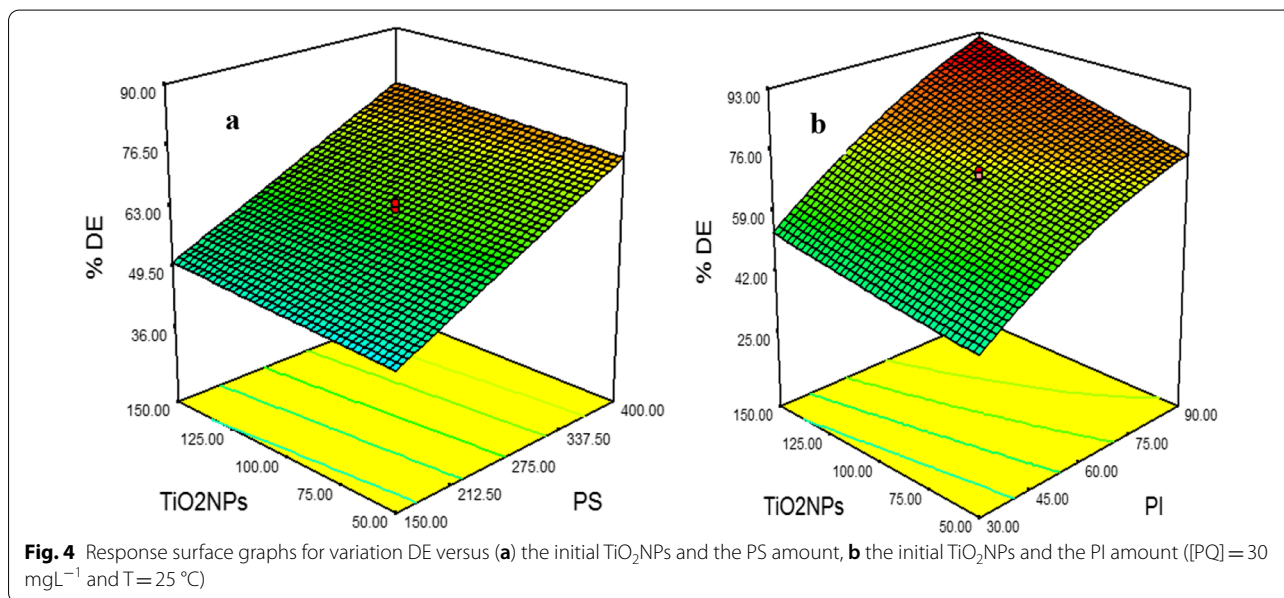
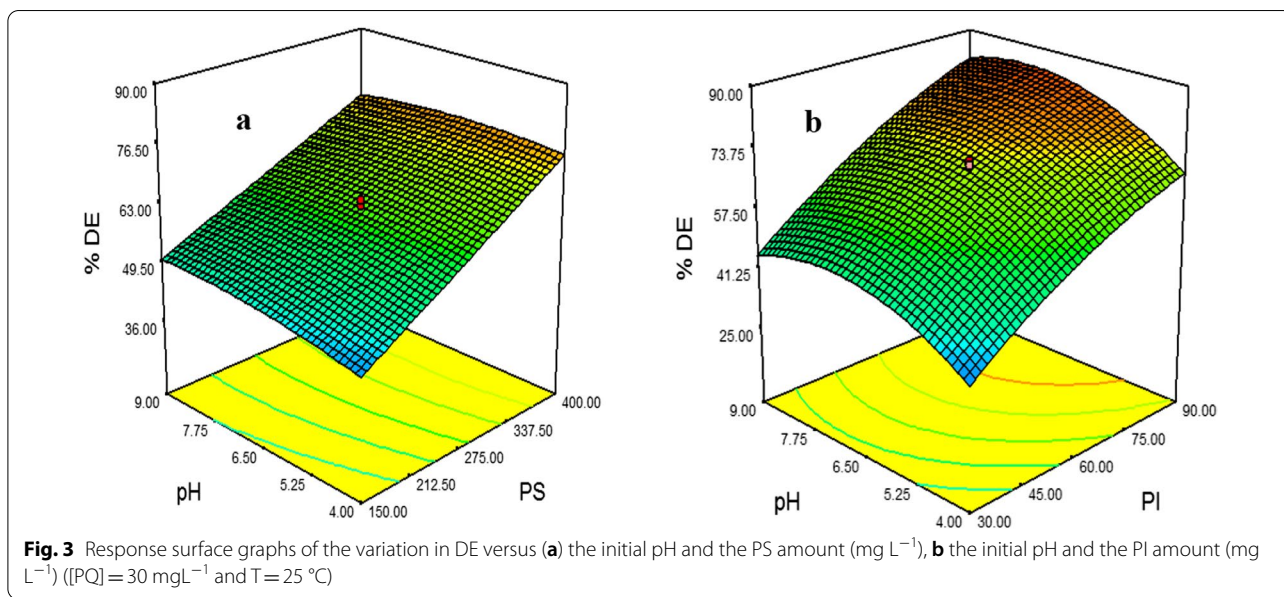
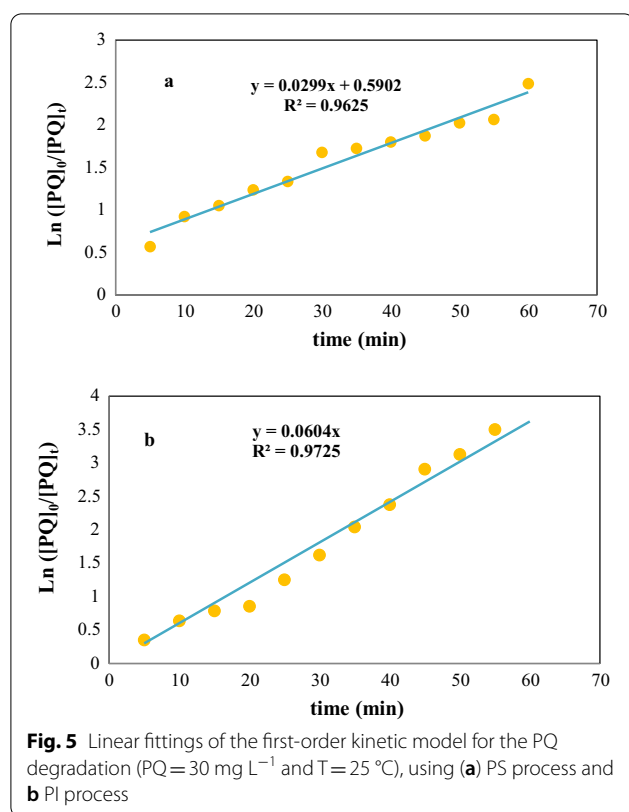


Table 5 Comparison of the several studies' results on degradation and mineralization of PQ by AOPs

Optimum conditions						%DE	%Min	Refs.
Concentration of PQ (mg L^{-1})	initial pH	Oxidant amount (mg L^{-1})	Amount catalyst (g L^{-1})	Radiation time (min)	Temperature ($^\circ\text{C}$)			
20	3	$[\text{H}_2\text{O}_2] = 425$	$[\text{C-Fe}] = 1$	720	25	90	100	[40]
10	6.7	–	$[\text{TiO}_2 \text{ P25}/ \beta\text{-SiC}] = 3$	70	20	43	27	[32]
10	6	–	$[\text{TiO}_2/\text{RH-SiO}_2] = 2$	120	25	90	–	[41]
10	5.8	–	$[\text{TiO}_2] = 0.35$	300	25	84	–	[33]
30	6	$[\text{PI}] = 90$	$[\text{TiO}_2] = 125$	40	25	90	55	This study
30	6.3	$[\text{PS}] = 400$	$[\text{TiO}_2] = 150$	40	25	77	32	This study



investigate the mineralization, the total organic carbon (TOC) test should be used. This test was performed on the PQ solution treated by the photocatalytic process under the optimum conditions. The TOC results showed that the photocatalytic processes of UV/PS/TiO₂NPs and UV/PI/TiO₂NPs were able to mineralize the PQ solution about 32% and 55%, respectively, after 40 min. To confirm the ability of the process to remove more TOC, the process continued by adding 90 mgL⁻¹ of periodate and 400 mgL⁻¹ persulfate for up to 120 min, so that the amount of TOC removal reached to 64 and 82% for UV/PS/TiO₂NPs and UV/PI/TiO₂NPs, respectively.

The electrical energy consumption (EEC) is one of the important criteria in the photochemical process. The figure of merit is the electrical energy per order, defined as the number of kWh of electrical energy required for reducing the concentration of a pollutant by one order of magnitude (i.e., 90% degradation) in 1 m³ of contaminated water and can be calculated as follows [43]:

$$EEC = \frac{1000Pt}{60 V \log\left(\frac{[PQ]_0}{[PQ]_t}\right)}, \quad (26)$$

where P is the electrical power (kW) of the light source in the photochemical system, V is the volume (L) of the treated solution, and t is the irradiation time (min).

According to the first-order kinetic for the photocatalytic process, the constant ratio of $\log([PQ]_0/[PQ]_t)/t$ represents the rate constant, k (in unit of min⁻¹), and therefore, Eq. 26 can be re-written as follows:

$$EEC = \frac{38.4 \times P}{V \times k}. \quad (27)$$

Hence, under the optimum conditions of the photocatalytic PS and PI processes and considering the rate constant of 0.0299 min⁻¹ for the PS process and the rate constant of 0.0604 min⁻¹ for the PI process, 150 W light source, and 0.4 L of treated PQ solution, EEC was calculated as 481.60 kWhm⁻³ for the PS process and 238.41 kWhm⁻³ for the PI process after 60 min.

Conclusions

In this work, a photocatalytic process was applied using the TiO₂NPs, and the PS and PI oxidizers to degrade PQ as a highly toxic herbicide. The experiments were designed based on the CCD method, and also the processes were modeled. The operating parameters were optimized based on the models as follows: the initial pH = 6.3, [PS] = 400 mgL⁻¹ and [TiO₂NPs] = 150 mgL⁻¹ for the PS process; and the initial pH = 6, [PI] = 90 mgL⁻¹, and [TiO₂NPs] = 125 mgL⁻¹ for the PI process. Under the optimized conditions, the models predicted the efficiency of about 77% for the UV/PS/TiO₂ process and 90% for the UV/PI/TiO₂NPs process; they were confirmed empirically with only 6% and 0% errors, respectively. The photocatalytic PQ degradation for both processes was well fitted by a pseudo-first-order kinetic model with a rate constant of 0.0299 min⁻¹ for the UV/PS/TiO₂NPs process and a rate constant of 0.0604 min⁻¹ for the UV/PI/TiO₂NPs process. Under the optimum conditions, the PQ molecules were mineralized for about 32% and 55% after 40 min for the UV/PS/TiO₂NPs and UV/PI/TiO₂NPs processes, respectively. The electrical energy consumption for the performance of the photocatalytic process at the optimum conditions after 60 min were calculated as 481.60 kWhm⁻³ for the UV/PS/TiO₂NPs process and 238.41 kWhm⁻³ for the UV/PI/TiO₂NPs process. Based on the results obtained, PI is a stronger, more active, and economical oxidizer than PS. The main result of this work compared to other works is to achieve proper efficiency with less oxidant consumption.

Abbreviations

PQ: Paraquat; AOPs: Advanced oxidation processes; TiO₂NPs: Nanoparticles of TiO₂; RSM: Response surface methodology; PI: Sodium periodate; PS: Sodium persulfate; TOC: Total organic carbon; CCD: Central composite design; DE: Degradation efficiency; Min: Mineralization; EEC: Electrical energy consumption.

Supplementary Information

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Additional file 1. Degradation of paraquat herbicide using hybrid AOP process: statistical optimization, kinetic study, and estimation of electrical energy consumption.

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Authors' contributions

GB: supervision and finalization of the manuscript, HRV: advisor and design of experiments, AG: doing the experiment and writing the original draft of the manuscript. It is confirmed that the manuscript has been read and approved by all named authors and is confirmed that the order of authors listed in the manuscript has been approved by all of authors. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that there is no conflict of interest associated with this publication.

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