Investigating the Performance of UV/PS/Tio2nps and UV/PI/Tio2nps Processes on Paraquat Herbicide Degradation in Aqueous Media: Statistical Optimization, Kinetic Study, and Estimation of Electrical Energy Consumption

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Research

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

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**Investigating the performance of UV/PS/TiO₂NPs and
UV/PI/TiO₂NPs processes on paraquat herbicide degradation in
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estimation of electrical energy consumption**

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27

28 **Abstract**

29 **Background:** In this work, the performance of UV/PS/TiO₂NPs and UV/PI/TiO₂NPs as
30 hybrid advanced oxidation processes for degradation of the herbicide paraquat in aqueous
31 solution is studied.

32 **Results:** The effects of several factors such as the UV irradiation, initial oxidant
33 concentration, TiO₂ nanoparticles dosage, and pH on the degradation efficiency are
34 investigated. The process optimization is performed by the central composite design and the
35 response surface methodology for 30 mg L⁻¹ of the herbicide at 25 °C and 40 min. Based on
36 the results, a degradation efficiency of 77 % and 90 % have been obtained for the
37 UV/PS/TiO₂NPs and UV/PI/TiO₂NPs processes respectively, in the optimum conditions. The
38 mineralization efficiency of the paraquat solution using UV/PS/TiO₂NPs and UV/PI/TiO₂NPs
39 processes are about 32 % and 55%, respectively, after 40 min. The kinetic studies show that
40 both processes follow a pseudo-first-order kinetic model, and the kinetic constants are 0.0299
41 min⁻¹ for the PS process and 0.0604 min⁻¹ for the PI process. The electrical energy
42 consumption has been estimated to be about 481.60 kWh/m³ for the PS process and 238.41
43 kWh/m³ for the PI process.

44 **Conclusions:** The degradation and mineralization efficiency of the paraquat solution using
45 UV/PI/TiO₂NPs process are more than UV/PS/TiO₂NPs process in the optimum conditions
46 after 40 min.

47 **Keyword:** Hybrid advanced oxidation processes; Periodate oxidations; Persulfate oxidations;
48 Paraquat degradation; Mineralization; Response surface methodology; Kinetic study.

49 **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 one 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 the 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, the advanced oxidation processes (AOPs) have been intensively studied as the most environmental 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 photo-catalytic degradation in the presence of the nanostructure catalysts has attained good efficiencies in the degradation of organic compounds among the various AOPs [11,12]. Heterogeneous photo-catalysis involves the use of a suspension of a semiconductor powder (usually transition metal oxides) as a catalyst for AOPs. The process is photo-induced, and requires irradiation for the activation of the catalyst [13-16]. For example, the metal-oxide nanoparticles of TiO₂ (TiO₂NPs) have been extensively utilized in the photo-catalytic oxidation processes due to the high photo-catalytic activity and non-toxic properties [17-20]. In the photo-catalytic activity process, the photo-electrons 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 [21].

79 Thus the heterogeneous photo-catalysis technique is particularly considered due to its
80 ability to completely oxidize many organic compounds without the formation of hazardous
81 by-products [22-24].

82 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
83 and mineralization of various organic pollutants from aqueous solutions due to the synergistic
84 effect in different highly reactive radicals in the hybridizing photo-oxidation process of
85 various inorganic oxidants, and are having better results in comparison to the individual
86 processes [25-29]. They have enhanced the rate of UV-induced decomposition of organic
87 pollutants in the presence of photo-catalysis. This enhancement is as a result of the scavenging the
88 active species radicals, such as hydroxyl radicals, and holes by the inorganic ions. [30,31] Inorganic
89 oxidants can be activated by ultrasonic waves, heating, and UV irradiation, and also can be
90 chemically activated using Fe^0 , Fe^{2+} , Zn^{2+} , etc. [32,33].

91 Undergoing photolysis or thermolysis in an aqueous solution, $\text{S}_2\text{O}_8^{2-}$ is decomposed to
92 generate the reactive radicals (Eqs. 9-11) [34,45].

Periodate, 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) [36,37].

The aim of this work is comparative study of the performance of UV/PS/TiO₂NPs and UV/PI/TiO₂NPs as hybrid AOPs for degradation of the paraquat herbicide in aqueous solution and conversion to water, carbon dioxide, and mineral salts. The process was modeled and optimized by the response surface methodology (RSM). Also the kinetic and the electrical cost estimation were assessed.

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 Supplementary information Figure1, was prepared from the Golsam chemicals Company. Anatase TiO₂ nanopowder (purity: > 99%, APS: 10-25 nm, SSA: 200-240 m²/g, color: white) was supplied

from the US Research Company as a photo-catalyst; its TEM and XRD analysis results are shown in the Supplementary information (Figure 2 and 3). Sodium periodate (PI) and sodium persulfate (PS) were used as the oxidants. Hydrochloric acid and sodium hydroxide 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 the 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.

Photo-chemical 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 photo-reactor is shown in Figure 1.

Figure 1. Schematic representation of the photo-reactor 1, magnetic stirrer 2, reactor vessel 3, UV lamp and its quartz cover.

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 Nano-powder and the inorganic oxidant was added, and after well-mixing, 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 $\lambda_{\text{max}} = 258 \text{ nm}$ that corresponded to C=C bands in the pyridinium ring with the help of a UV-visible spectrophotometer (Figure 2) [38]. Also the mineralization study was carried out by measuring the TOC of the samples (Supplementary information Figure 4).

Figure 2. UV spectrum of [PQ] (3 ppm).

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' [38].

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 [39]. RSM is one of the useful mathematical and statistical methods for analyzing the relation between several independent variables [40].

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 [41].

The total number of experiments (N) could be determined as follows [42,43]:

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

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 [42].

In this work, the three important factors initial pH, TiO_2NPs 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

In order 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.

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

Variables	Range and level				
	$-\alpha$	-1	0	$+1$	$+\alpha$
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

Design matrix					
Runs	Factors			DE (%)	
	S ₂ O ₈ ²⁻ (mg L ⁻¹)	pH	TiO ₂ (mg L ⁻¹)	(Exp.)	(Pred.)
1	150.0	4.0	50.0	44.8	43.8
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

181

182 **Table 2. Range of the variables and the designed experiments as well as the corresponding responses for**
183 **the PI process ([PQ] = 30 mg L⁻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
Design matrix					
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

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.

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

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

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			

202

203

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			

204

205 The "Pred R-Squared" of 0.93 and "Adj R-Squared" of 0.97 represent that the model
206 predicts the response as well, and the "Adeq Precision" of 38.26 indicates an adequate signal-
207 to-noise (a ratio greater than 4 is desirable). The R² of 0.97 implies that the model can predict
208 the UV/PS/TiO₂NPs process performance. Also in the case of the UV/PI/TiO₂NPs process,
209 the "Pred R-Squared", "Adj R-Squared", and "Adeq Precision" were 0.78, 0.91, and 19.73,
210 respectively. The R² of 0.94 implies that the model can predict the UV/PI/TiO₂NPs process
211 performance. The adequacy of the models was graphically evaluated and approved by the
212 diagnostic plots (Supplementary information Figure 5a,b).

Discussion

The effects of the operational factors on the process were assessed by the 3D surface graphs. Figure 3 and 4 show the variation in the degradation efficiency as a function of the initial pH, the dose of TiO_2NPs , 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 intensitly at the acidic condition, while the activity of PS is independent from the pH variations. Figure 4 shows that the degradation efficiency is increased by increasing the PI, PS, and TiO_2NPs 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.

Figure 3. Response surface graphs of the variation in DE versus (a) the initial pH and the PS amount (mg L^{-1}), (b) the initial pH and the PI amount (mg L^{-1}) ($[\text{PQ}] = 30 \text{ mg L}^{-1}$ and $T = 25^\circ \text{C}$).

Figure 4. Response surface graphs of the variation in DE versus (a) the initial pH and the PS amount, (b) the initial pH and the PI amount ([PQ] = 30 mg L⁻¹ and T = 25 °C).

The operational parameters were optimized numerically based on the proposed reduced 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 Supplementary information Figure 6 and 7. For the PS process, in the optimum conditions of [PS] = 400 mg L⁻¹, [TiO₂NPs] = 150 mg L⁻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 mg L⁻¹, [TiO₂NPs] = 125 mg L⁻¹, and [pH]_{in} = 6. To assess the accuracy of the model prediction, under the supposed values of the parameters, the photo-catalytic 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.

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

optimum conditions						%D E	%Mi n	Ref.
Concentration of PQ (mg L ⁻¹)	initial pH	Oxidant amount (mg L ⁻¹)	Amount catalyst (g L ⁻¹)	Radiation time (min)	Temperature (°C)			
20	3	[H ₂ O ₂]=425	[C-Fe]=1	720	25	90	100	[44]
10	6.7	-	[TiO ₂ P25/β-SiC]=3	70	20	43	27	[45]
10	6	-	[TiO ₂ /RH-SiO ₂]=2	120	25	90	-	[46]
10	5.8		[TiO ₂]=0.35	300	25	84		[47]
30	6	[PI]=90	[TiO ₂]=125	40	25	90	55	This study
30	6.3	[PS]=400	[TiO ₂]=150	40	25	77	32	This study

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

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

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 Figure 5. Plotting the

254 variation in the logarithmic concentration ratio versus the irradiation time forms a straight
 255 line with a slope equal to k_{app} . The kinetic constant was 0.0299 min^{-1} .

Figure 5. Linear fittings of the first-order kinetic model for the PQ degradation (PQ = 30 mg L^{-1} and T = 25°C) a) PS process and b) PI process.

256

Mineralization is the process of complete oxidative degradation of an organic compound and the relevant intermediates to CO₂, H₂O, and other mineral oxides [48,49]. For detection of the degradation of PQ, the UV-visible spectrophotometry analysis is used, and to investigate the mineralization, the total organic carbon (TOC) test should be used. This test was performed on the PQ solution treated by the photo-catalytic process under the optimum conditions. The TOC results showed that the photo-catalytic processes of UV/PS/ TiO₂NPs and UV/PI/TiO₂NPs were able to mineralize the PQ solution about 32% and 55%, respectively, after 40 min.

The electrical energy consumption (EEC) is one of the important criteria in the photo-chemical 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 1 order of magnitude (i.e. 90% degradation) in 1 m³ of contaminated water, and can be calculated as follows [50]:

$$EEC = \frac{1000 \text{ p t}}{60 \text{ V} \log\left(\frac{[PQ]_0}{[PQ]}\right)} \quad (26)$$

where P is the electrical power (kW) of the light source in the photo-chemical 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 photo-catalytic process, the constant ratio of log([PQ]₀/[PQ])/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 photo-catalytic 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 kWh/m³ for the PS process and 238.41 kWh/m³ for the PI process after 60 min.

Conclusions

In this work, a photo-catalytic 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. Concisely, the following outstanding conclusions could be drawn from this work.

- A reduced second-order equation could model the photo-catalytic degradation efficiency as a function of the initial pH, PQ, the PS and PI concentrations, and the TiO₂NPs dosage.
- The operating parameters were optimized based on the models as follow: the initial pH = 6.3, [PS] = 400 mg/L and [TiO₂NPs] = 150 mg/L for the PS process; and the initial pH = 6, [PI] = 90 mg/L, and [TiO₂NPs] = 125 mg/L 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 photo-catalytic 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 and, 47.5% and 57% after 80 min for the UV/PS/TiO₂NPs and UV/PI/TiO₂NPs processes, respectively.

- The electrical energy consumption for the performance of the photo-catalytic process at the optimum conditions after 60 min were calculated as 481.60 kWh/m³ for the UV/PS/TiO₂NPs process and 238.41 kWh/m³ for the UV/PI/TiO₂NPs process.
- Based on the results obtained, PI is a stronger, more active, and economical oxidizer than PS.

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.

Ethical Approval and Consent to Participate: Not applicable

Consent to Publish: Not applicable

Author's contributions

Dr. Ghadamali Bagherian: supervision and finalization of the manuscript, Dr. Hadi Rezaei Vahidian: advisor and design of experiments, Mis Azam Ghavi: 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.

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Competing interest

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

Data availability

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

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