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Elimination of malachite green by modified Fenton like process. Application of Box Behnken design

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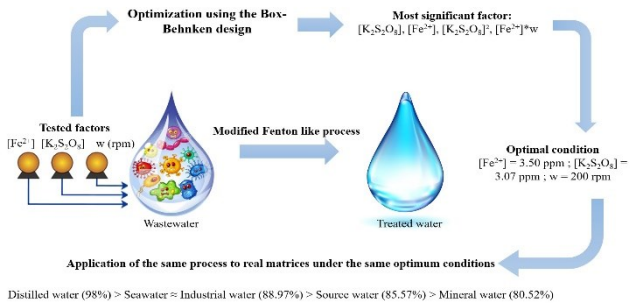
Graphical abstract



Abstract

The aim of this work was to investigate an advanced oxidation process for removing malachite green from aqueous solutions using a modified Fenton-like process. An experimental Box-Behnken design was applied to determine the optimal conditions by examining the effects of catalyst concentration ($[Fe^{2+}]$), oxidant concentration ($[K_2S_2O_8]$), and stirring speed. The analysis of variance (ANOVA) indicated that oxidant concentration was the most significant factor, with a p-value of 0.001, while catalyst concentration, the quadratic term of the oxidant, and the interaction between catalyst concentration and stirring speed were also significant. The optimal conditions for maximum dye removal were found to be a catalyst concentration of 3.5 ppm, an oxidant concentration of 3.07 ppm, and a stirring speed of 200 rpm, achieving a theoretical degradation yield of 100% and an experimental yield of 98%. This agreement validates the model and the importance of the optimized parameters. Additionally, degradation kinetics studies in various natural waters revealed that oxidation efficiency followed this order: Distilled water (98%) > Seawater ≈ Industrial water (88.97%) > Source water (85.57%) > Mineral water (80.52%).

Keywords: Modified Fenton oxidation, Water treatment, Box-Behnken design, Homogeneous catalysis optimization, degradation kinetics, real matrix.

1. Introduction

With the growth of humanity, science, and technology, our world is reaching new horizons, but the cost we'll be paying soon is bound to be too high. Environmental disorder, with a major pollution problem, is among the consequences of this rapid growth. Apart from other needs, the water demand has increased enormously with the agricultural, industrial, and domestic sectors consuming 70, 22, and 8% of the available freshwater respectively, resulting in large quantities of wastewater containing several pollutants (Gupt *et al.* 2009, Ali Akbar *et al.* 2017, Karimipour *et al.* 2021, Azizpour *et al.* 2024). Once dissolved in water, they can be difficult to treat, as dyes have a synthetic origin and a complex molecular structure that makes them more stable and difficult to biodegrade (Forgacs *et al.* 2004, Rai *et al.* 2005, Jalilzadeh *et al.* 2014, Shobirynia *et al.* 2024, Brati *et al.* 2024). They can therefore be a risk factor for our health and a nuisance for our environment, and it is necessary to limit these pollutants as much as possible by setting up a suitable treatment method, such as a decolorization unit.

There are several physical, chemical, and biological methods for treating and decolorizing polluted effluents, such as coagulation and flocculation (Wu *et al.* 2015, Lee *et al.*2006, Zonoozi *et al.*2009, Zahrim *et al.* 2013, Souhaimi *et al.* 2011), membrane filtration (Jiraratananon *et al.* 2000, Koyuncu *et al.* 2002), chemical oxidation (Liu et al 2006, Ghodbane *et al.* 2014, Shokri *et al.* 2020, Nemati *et al.* 2024), extraction (Bendebane *et al.* 2016), ozonation (Lee *et al.* 2006, Baban et al 2010), ion exchange and electrochemical methods (Soloman et al 2009, Bahadir *et al.* 2008), and adsorption, etc. (Rangabhashiyam *et al.* 2013, Gashtasbi *et al.* 2017, Bendebane *et al.* 2021).

In recent decades, much research has focused on a new class of oxidation techniques for dyes.

This work is mainly based on the application of the modified Fenten-like process experimental design, the aim of which is to improve dye removal efficiency.

Indeed, we first studied the oxidation of malachite green by the modified Fenton-like process ($K_2S_2O_8/SO_4^{-\circ}$ system) by showing the influence of some experimental parameters on the degradation yield.

The reactions of persulfate ions with various inorganic compounds have been extensively studied (Ivanov et al

2000), and sulfate radicals are more powerful oxidants than hydroxyl and the thermodynamics of transition metal-oxidant coupling (Anipistakis *et al.* 2003, Anipistakis *et al.* 2004), as they are more selective for oxidation (electron transfer). Hydroxyl radicals can also react rapidly through hydrogen elimination and addition, a fact also highlighted by our observation. secondly, we describe the oxidation kinetics of malachite green in a real matrix using different types of water.

2. Materials and methods

2.1. Materials

Malachite green ($C_{52}H_{56}N_4O_{12}$), Iron (II) sulfate heptahydrate (purity 99%, $FeSO_4 .7H_2O$), and sulfuric acid (purity 96-98%, H_2SO_4) were purchased from Sigma Aldrich, Potassium persulfate (purity 30%, $K_2S_2O_8$) was purchased from Biochem Chemopharma. All the solutions used in the experiments were prepared with distilled water at pH was regulated using H_2SO_4 (1 M).

2.2. Experimental procedures and analysis

The study of the degradation of malachite green by potassium persulfate ($K_2S_2O_8$) was carried out in a discontinuous, perfectly stirred and thermostated reactor shown in **Figure 1.**

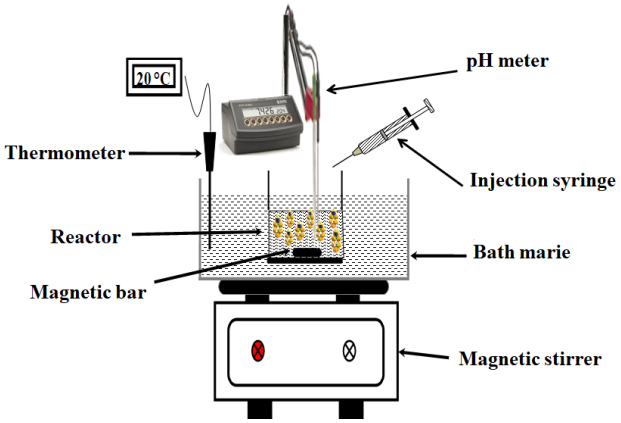


Figure 1. Experimental set-up

The reactor is first charged with 100 mL of a 10 ppm solution of malachite green. The pH of the reaction medium is adjusted to 3 using a few drops of sulfuric acid (H_2SO_4, 98% purity). The solution is then stirred for several minutes to ensure optimum homogenization. Subsequently, a determined volume of $FeSO_4$ solution is added, followed by the introduction of a volume of $K_2S_2O_8$ solution at the specified concentration. The mixture thus prepared is subjected to controlled stirring by a magnetic stirrer, at the prescribed speed as indicated in **Table 1**, while maintaining the system temperature at 20°C. The oxidation reaction starts as soon as the oxidant is added. To monitor reaction kinetics, a sample is taken after one hour of reaction. The samples are then analyzed by UV-visible spectrophotometry to quantify the species in solution. The malachite green removal yield is then calculated from the following equation:

$$Y(\%) = \left[1 - \frac{[MG]_f}{[MG]_0}\right] \times 100 \quad (1)$$

Where: $[MG]_0$ the initial concentration of dye (mg/L) ; $[VM]_f$ the final concentration (at equilibrium) of dye (mg/L) ; Y (%): removal efficiency of MG.

In this study, operating conditions were optimized to maximize the degradation yield of malachite green dye by applying response surface methodology (RSM), using a Box-Behnken design (BBD). Three independent variables were selected for the study: catalyst concentration [Fe^{2+}], oxidant concentration [$K_2S_2O_8$], and stirring speed, while the other operating parameters were kept constant.

The persulfate ion ($S_2O_8^{2-}$) was used as the main oxidant, being one of the strongest oxidizing agents in aqueous solution, with a standard potential of 2.01 V/ENH. This potential, which is higher than that of hydrogen peroxide (H_2O_2, E°=1.78 V/ENH), gives the persulfate increased efficacy. However, to optimize its effectiveness, persulfate must be activated in the presence of catalysts, leading to the formation of the sulfate radical ($SO_4^{\cdot-}$), an even more powerful oxidant with a high oxidation potential (E° = 2.6 V/ENH) (Liang *et al.* 2003, Liang *et al.* 2008, Zhao *et al.* 2013).

Table 1 summarizes the factors studied and their respective levels. Statistical analysis of the experimental data was carried out using MINITAB 18 software.

Table 1. Factors and domains studied.

Factors	Units	Levels		
		Low (-1)	Medium (0)	High (+1)
[Fe2+]	ppm	2	3.5	5
[K2S2O8]	ppm	2	6	10
W	rpm	200	300	400

3. Results and Discussion

3.1. Results

In the first part of this article, the removal of malachite green (MG) was studied from aqueous solutions prepared with distilled water, using the Box-Behnken design (BBD). The matrix presented in **Table 2** combines the three factors varying according to this experimental design.

3.1.1. ANOVA

Table 3 of the analysis of variance shows that the oxidant [$K_2S_2O_8$] is a highly significant parameter for the degradation of malachite green, with a probability value of 0.001. The catalyst [Fe^{2+}], the oxidant squared ([$K_2S_2O_8$])^2 and the interaction [Fe^{2+}]*w are also significant for the degradation of MG, with a probability value of 0.001. The catalyst [Fe^{2+}], the oxidant squared ([$K_2S_2O_8$])^2 and the interaction [Fe^{2+}]*w are also significant for MG degradation, with P values of 0.024, 0.019 and 0.038 respectively.

Table 2. Experiment matrix for MG degradation

Try	$[Fe^{2+}]$(ppm)	$[K_2S_2O_8]$ (ppm)	w(rpm)	$Y_{exp.}$(%)	$Y_{th.}$ (%)
1	3.5	6	30	96.02	96.12
2	3.5	10	40	96.57	90.39
3	2.0	2	30	48.00	54.98
4	3.5	2	20	40.71	46.88
5	3.5	6	30	96.15	96.13
6	2.0	6	20	96.27	83.11
7	3.5	2	40	38.82	28.33
8	5.0	6	20	93.29	89.78
9	2.0	6	40	97.00	100
10	3.5	10	20	96.39	100
11	5.0	2	30	9.88	7.22
12	5.0	10	30	94.75	87.76
13	3.5	6	30	96.21	96.13
14	2.0	10	30	93.84	96.50
15	5.0	6	40	24.17	37.33

Table 3. ANOVA results according to Box-Behnken design

Source	DL	P value
Model	9	0.011
Linear	3	0.003
$[Fe^{2+}]$	1	0.024
$[K_2S_2O_8]$	1	0.001
w	1	0.104
Square	3	0.061
$[Fe^{2+}]*[Fe^{2+}]$	1	0.113
$[K_2S_2O_8]*[K_2S_2O_8]$	1	0.019
w*w	1	0.400
2-factor interaction	3	0.109
$[Fe^{2+}]*[K_2S_2O_8]$	1	0.179
$[Fe^{2+}]$*w	1	0.038
$[K_2S_2O_8]$*w	1	0.937
Error	5	
Inadequacy of fit	3	0.000
Pure error	2	
Total	14	

Table 4. Box-Behnken coefficients

Termes	Coeff	Coef ErT	T value	P value
Constant	96.13	7.21	13.34	0.000
$[Fe^{2+}]$	-14.13	4.41	-3.20	**0.024**
$[K_2S_2O_8]$	30.52	4.41	6.91	**0.001**
W	-8.76	4.41	-1.98	0.104
$[Fe^{2+}]*[Fe^{2+}]$	-12.47	6.50	-1.92	0.113
$[K_2S_2O_8]*[K_2S_2O_8]$	-22.03	6.50	-3.39	**0.019**
w*w	-5.97	6.50	-0.92	0.400
$[Fe^{2+}]*[K_2S_2O_8]$	9.76	6.24	1.56	0.179
$[Fe^{2+}]$*w	-17.46	6.24	-2.80	**0.038**
$[K_2S_2O_8]$*w	0.52	6.24	0.08	0.937

According to **Table 4**, the factors that positively influence malachite green degradation are the oxidant, the [Fe^{2+}]*[$K_2S_2O_8$] interaction, and the [$K_2S_2O_8$]*w interaction. On the other hand, the other factors studied have a negative effect on this phenomenon

3.1.2. Histogram of residual values

Figure 2 shows the histogram of residual values for the degadation yield of malachite green. From this figure, we can see that the histogram follows a bell-shaped curve. This means that the residual values are almost normally distributed. We can also see that the histogram values are highly symmetrical, so the residual values are probably normally distributed.

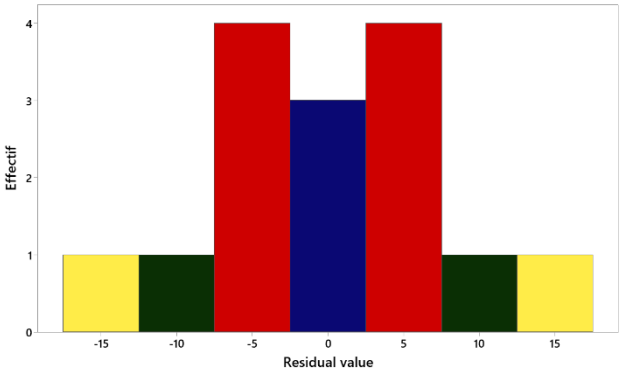


Figure 2. Histogram of residual values for Malachite Green degradation yield

3.1.3. Main effects of the factors

From Figure 3, a decrease in dye degradation yield was observed as a function of increasing Fe(II) concentration as well as increasing stirring speed. For the [Fe^{2+}] catalyst, the yield decreased from 83.78% at 2 ppm to 55.52% at 5 ppm. Similarly, agitation speed reduces yield, from 81.66% at 200 rpm to 64.14% at 400 rpm. On the other hand, increasing oxidant concentration has a positive effect on malachite green degradation yield. This improvement is significant, with yields rising from 34.35% at 10 ppm to 85.58% at 30 ppm, reaching 95.39% at 50 ppm oxidant.

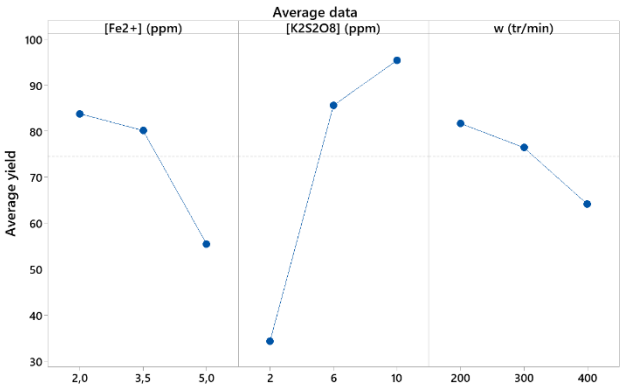


Figure 3. Main effects of the factors studied on the degradation yield of MG

Figure 4 shows the interaction effects on the degradation yield of Malachite Green. The strong interactions obtained between:

- At 6 ppm oxidant between 2 and 3.5ppm catalyst.
- At 250 rpm between 2 and 3.5 ppm of [Fe2+].
- At 350 rpm between 2 and 3.5 ppm of [Fe2+].
- At 300 rpm, between 6 and 10 ppm of oxidant.

Weak interactions are also observed between:

- At 10 ppm of oxidant between the three concentrations of [Fe2+].
- At 200 rpm between 2 and 5ppm of [Fe2+].
- At 200 rpm between 6 and 10ppm [K2S2O8].

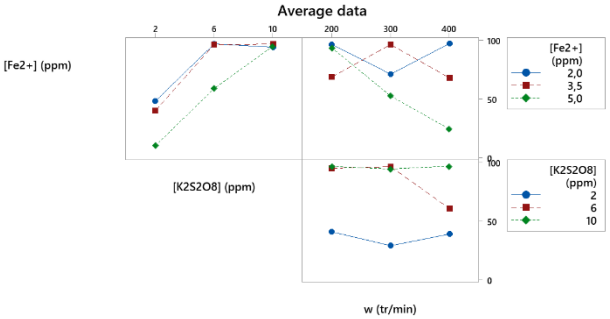


Figure 4. Interaction effects of the factors studied.

3.1.4. Pareto diagram

The Pareto diagram is used to evaluate the value and importance of effects. This diagram presents the absolute value of the effects of factors and includes a reference line on the graph. According to **Figure 5**, any effect that exceeds this reference line can be considered significant. The terms identified as significant are oxidant concentration [$K_2S_2O_8$], iron concentration [Fe^{2+}], the oxidant quadratic term ([$K_2S_2O_8$])^2, and the interaction between iron and stirring rate [Fe^{2+}]*w. This confirms the results obtained previously.

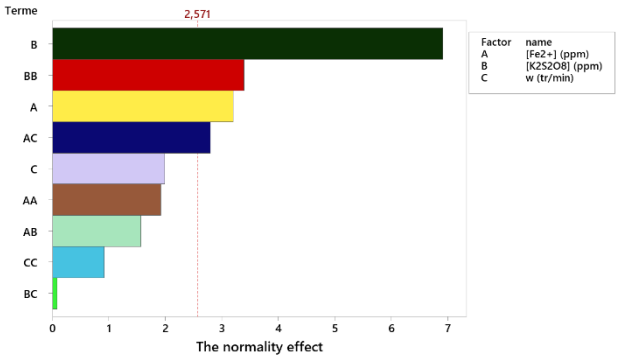


Figure 5. Pareto diagram for MG degradation

3.1.5. Mathematical model

The mathematical model is second-order and relates the degradation yield of MG to the various factors, their squares, and their interaction.

The regression of the response in coded units as a function of all terms is represented by equation 2, and in uncoded units by equation 3.

Regression equation in coded units

$$Y(\%) = -147.4 + 54.6 \times [Fe^{2+}] + 3.62 \times [K_2S_2O_8] + 6.70 \times w - 5.54 \times [Fe^{2+}]^2 - 0.0551 \times [K_2S_2O_8]^2 - 0.0597 \times w^2 + 0.325 \times [Fe^{2+}] \times [K_2S_2O_8] - 1.164 \times [Fe^{2+}] \times w + 0.0026 \times [K_2S_2O_8 \times] w \quad (3)$$

Regression equation in uncoded units

$$Y(\%) = 96.13 - 14.13 \times [Fe^{2+}] + 30.52 \times [K_2S_2O_8] - 8.76 \times w - 12.47 \times [Fe^{2+}]^2 - 22.03 \times [K_2S_2O_8]^2 - 5.97 \times w^2 + 9.76 \times [Fe^{2+}] \times [K_2S_2O_8] - 17.46 \times [Fe^{2+}] \times w + 0.52 \times [K_2S_2O_8] \times w \quad (4)$$

3.1.6. Response surfaces

Minitab18 allows us to plot response and contour surfaces by varying two factors simultaneously and setting the third at different levels (min, medium, and max). The surface and contour figures show that MG degradation yields are very good (around 100%). The zone of best yields is obtained at an oxidant concentration between 5.5-10ppm and throughout the range of Fe^{2+} concentration at a minimum level for the stirring speed (200rpm) (**Figure 6)**.

The response surface is concave and slightly inclined.

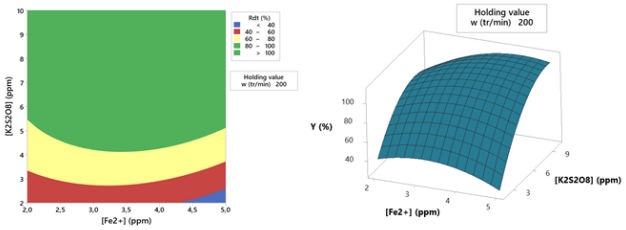


Figure 6. Contour and response surfaces of Y as a function of $[Fe^{2+}]$-$[K_2S_2O_8]$ at 200 rpm

Figure 7 shows MG degradation efficiency's response and contour surfaces by varying $[Fe^{2+}]$ and w at 6 ppm for $[K_2S_2O_8]$.

It can be seen that total degradation of the pollutant was obtained, and the zone of good yields is located in the middle of the chosen domain in inclined form (blue contour).

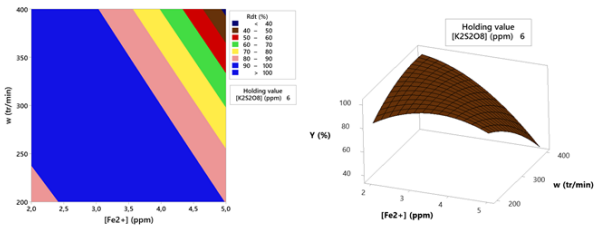


Figure 7. Contour and response surfaces of Y as a function of $[Fe^{2+}]$-w at 6ppm $[K_2S_2O_8]$

3.1.7. Optimization

The main objective was to identify the optimum operating conditions for achieving complete degradation of MG. A constraint was imposed on the selected factors.

After several optimizations, the optimum conditions are summarized in **Table 5**. The results of these optimizations were used to determine the ideal values for each factor influencing the process, as well as the theoretical maximum value for malachite green (MG) degradation efficiency (**Figure 8**).

Table 5. Optimization results for malachite green

Factors	$[Fe^{2+}]$ ppm	$[K_2S_2O_8]$ ppm	W rpm	Y_{th} (%)	d
Opt.	3.5	3.07	200	100	1,00

These results show that the optimum conditions for the complete degradation of MV are a $[Fe^{2+}]$ concentration of 3.5 ppm, a $[K_2S_2O_8]$ concentration of 3.07 ppm, and a stirring speed of 200 rpm. Under these conditions, a theoretical degradation yield of 100% was achieved.

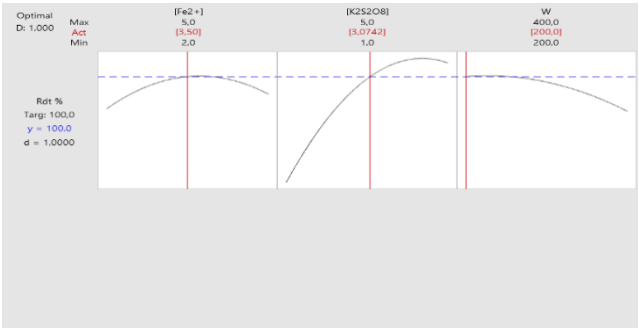


Figure 8. Optimization diagram for MG degradation

The theoretical model predicts a degradation efficiency of 100% for these optimized values. A verification test was carried out twice under the same experimental conditions to validate these optimum conditions. The experimental results showed an average yield of 98%, confirming the accuracy of the theoretical model. These results indicate that the model is adequate to represent the degradation process under the optimized conditions.

3.2. Discussion

Persulfate concentration $S_2O_4^{2-}$ plays a crucial role in the degradation system $S_2O_4^{2-}/Fe^{2+}$. The persulfate anion can be activated, either by thermal conditions or by chemical catalysts such as transition metal ions, to generate a powerful oxidant, the sulfate free radical (SO_4^{-}). This radical is extremely reactive and actively participates in the degradation of organic pollutants (Rastogi *et al.* 2008, Zhang *et al.* 2011, Li *et al.* 2014, Wang *et al.* 2017)

The impact of free radicals and transition metal ions Fe^{2+} on the degradation process has been widely studied. An increase in persulfate concentration promotes the formation of additional sulfate radicals, accelerating the degradation rate of methyl green (MG). This observation is in line with previous studies, which show that higher persulfate concentrations lead to faster MG degradation (Sun *et al.* 2011, Ho *et al.* 2012, Yu *et al.* 2013).

In addition, sulfate radicals formed by persulfate activation can initiate complex chain reactions involving radical transfer. These reactions contribute to more efficient contaminant degradation. The dynamics of these chain reactions and their impact on degradation rates are influenced by persulfate concentration and the presence of transition metal ions, which modulate the production and

consumption of free radicals (Yang *et al.* 2012, Li et al 2012, Kim *et al.* 2013).

The study also revealed that the presence of transition metal ions, such as iron, not only catalyzes the generation of sulfate radicals, but can also influence their stability and reactivity. The specific mechanisms by which these metal ions influence MG degradation merit further investigation to optimize reaction conditions and improve the efficiency of persulfate-based degradation systems (Lee *et al.* 2012, Ding *et al.* 2014, Liu *et al.* 2015).

The sulfate radicals formed by adding the catalyst can trigger a series of radical transfer chain reactions (Rastogi *et al.* 2009, Bennedsen *et al.* 2012, Fang *et al.*2023).

$$SO_4^{-} + H_2O \rightarrow HSO_4^{-} + OH$$

$$SO_4^{-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+}$$

$$S_2O_4^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} + SO_4^{-}$$

$$2SO_4^{-} \rightarrow S_2O_8^{2-}$$

3.3. Kinetics of malachite green degradation in a real matrix

In order to investigate the kinetics of malachite green degradation in different natural environments, various experiments were carried out at room temperature under a stirring speed of around 300 rpm for 1h. The physicochemical characteristics of the waters used are shown in **Table 6**. The concentrations are in ppm.

Table 6. Characteristics of waters used

	Ca2+	Mg2+	K+	Na+	HCO_3^-	SO_4^{2-}	NO_3^-	NO_2^-	Cl-	dry residue at180°C	pH
1	99	24	2.1	15.8	265	68	15	<0.02	72	380	7.20
2	72	27	2	11	336	11	20.20	<0.01	21	475	7.28
3	0.01	0.006	3.05	0.004	0.23	/	0.02	<0.01	0.23	1.51	6.20
4	430	1.45	400	12	160	3.1	2.00	<0.01	21	38	8.00

(1) natural mineral water (ifri); (2) Source water; (3) industrial water; (4) seawater.

It should be noted that the industrial water used in this study is desalinated water, intended for the cooling circuits of the Fertial complex, and was used as the actual matrix. In addition, the spring water used in this part of the work was collected from a mountain at Séraidi, near Annaba. This water was stored in a container at a temperature of 4°C (**Figure 9**).

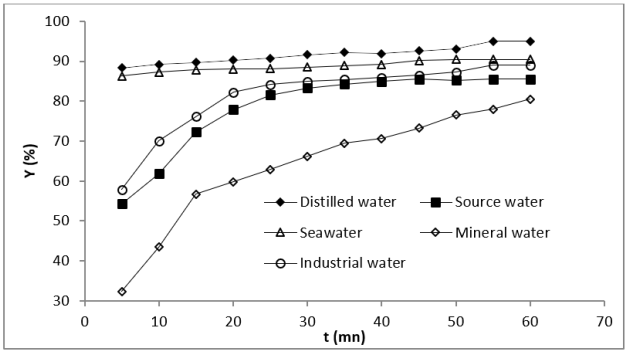


Figure 9. Effect of real matrix on degradation efficiency of malachite green

It was found that yields vary according to the physicochemical characteristics of each type of water. Distilled water, which is free of ions and impurities, allows a maximum degradation of 98% due to the absence of interference with sulfate radicals (Huang *et al.* 2020). In contrast, seawater and industrial water show similar efficiencies of 88.97%, due to their high concentration of chloride ions (Cl^-) and conductivity, which can influence the reactivity of sulfate radicals and alter the efficiency of the degradation process (Smith *et al.* 2018). Source water, with a yield of 85.57%, has high concentrations of bicarbonates and calcium, which can interact with the radicals or malachite green, reducing the rate of degradation (Johnson *et al.* 2019). Finally, natural mineral water, with the lowest yield of 80.52%, contains a high concentration of various ions, such as calcium and magnesium, as well as a significant dry residue, which can complex the radicals or neutralize their action (Williams *et al.* 2019). These variations can be explained by the influence of the specific physicochemical characteristics of each medium on the effectiveness of sulfate radicals in the degradation process of malachite green.

4. Conclusion

In order to eliminate malachite green from aqueous solutions, an advanced oxidation process was investigated. The experimental Box-Behnken design was used to determine the optimum operating conditions for improving the percentage of dye removal using a modified Fenton-like process. In fact, the three factors studied were: catalyst concentration [Fe^{2+}], oxidant concentration [$K_2S_2O_8$] and stirring speed. The results of the analysis of variance (ANOVA) showed that oxidant concentration [$K_2S_2O_8$] was the most significant parameter for malachite green degradation, with a probability value (p-value) of 0.001. In addition, catalyst concentration [Fe^{2+}], the oxidant quadratic term [$K_2S_2O_8$]², and the interaction between catalyst concentration and stirring speed [Fe^{2+}] * W were also identified as significant, with p-values of 0.024, 0.019 and 0.038 respectively.

Based on these results, the optimum conditions for malachite green removal were determined to be a catalyst concentration of 3.5 ppm, an oxidant concentration of 3.07 ppm, and a stirring speed of 200 rpm. These conditions enable a theoretical degradation yield of 100% to be achieved, while experimental tests showed a yield of 98%. This agreement confirms not only the effectiveness of the

model used to represent the degradation process under the optimized conditions, but also that the parameters identified play a crucial role in the almost complete removal of the dye. Indeed, the experimental results show that the optimized conditions achieve a yield close to that predicted theoretically, thus validating the importance of the optimized parameters in the degradation process.

Furthermore, in order to investigate the degradation kinetics of malachite green in different natural media, experiments were carried out at room temperature, with a stirring speed of 300 rpm for 1 hour. The results showed that malachite green oxidation follows the following order:

distilled water (98%) > seawater ≈ industrial water (88.97%) > source water (85.57%) > mineral water (80.52%).

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Conflict of Interest

The authors have no conflicts of interest to disclose

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