



## Kinetic Study and Process Optimization of Dye Degradation in Aqueous Solutions Using Advanced Oxidation Processes

Soraya Zuberiwala

Department of Computer Science and Engineering, Aurora Metropolitan Institute of Technology, Philippines  
soraya.zuberiwala@amit-ph.edu

| Peer Review Information                                                                                                                                                                                                                                        | Abstract                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
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| <p><i>Submission: 11 Jan 2017</i><br/> <i>Revision: 26 Feb 2017</i><br/> <i>Acceptance: 05 March 2017</i></p> <p><b>Keywords</b></p> <p><i>Advanced oxidation processes, Methyl Orange, Photo-Fenton, Reaction kinetics, Response surface methodology.</i></p> | <p>Advanced oxidation processes (AOPs) are effective for degrading persistent dye molecules because they generate highly reactive radical species, particularly hydroxyl radicals, that attack chromophoric groups and aromatic structures. This methodology paper proposes an integrated kinetic and statistical framework for degrading Methyl Orange (MO) in aqueous solution using UV irradiation, UV/H<sub>2</sub>O<sub>2</sub>, Fenton and photo-Fenton oxidation, followed by optimization of the most efficient system. The experimental design uses a central composite design within response surface methodology to quantify the effects of initial pH, ferrous-ion dosage and hydrogen-peroxide dosage while holding temperature, mixing and irradiation intensity constant. Dye concentration is monitored by UV-Vis spectrophotometry and mineralization is evaluated by chemical oxygen demand (COD). Kinetic data are examined using pseudo-first-order and pseudo-second-order expressions, and the optimized conditions are verified through confirmation experiments. An illustrative dataset, included only to demonstrate analysis and interpretation, indicates the expected superiority of photo-Fenton oxidation and the importance of acidic pH and balanced Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> doses. The proposed approach integrates kinetic constants, half-life, percentage decolorization, COD reduction, analysis of variance and response-surface optimization into a reproducible procedure suitable for laboratory studies of dye-containing wastewater.</p> |

### Introduction

Synthetic dyes released from textile, printing, leather and related industries are difficult to remove because many contain stable aromatic rings, azo bonds and auxochromic groups that resist conventional biological treatment. Even when color disappears, partially oxidized intermediates may remain and continue contributing to chemical oxygen demand. Advanced oxidation processes are designed to overcome this limitation by producing strongly oxidizing transient species in situ. Oturan and Aaron (2014) described AOPs as a broad family of water-treatment methods in which hydroxyl-radical chemistry is exploited for the destruction

of persistent organic contaminants. For dye treatment, commonly investigated routes include Fenton oxidation, photo-Fenton oxidation, UV/H<sub>2</sub>O<sub>2</sub>, heterogeneous photocatalysis, ozonation and persulfate-assisted oxidation.

Among these methods, Fenton chemistry is attractive because Fe<sup>2+</sup> activates H<sub>2</sub>O<sub>2</sub> to form hydroxyl radicals under mild conditions. Light-assisted Fenton systems can further improve radical generation by photoreducing Fe<sup>3+</sup> to Fe<sup>2+</sup> and photolyzing iron-hydroxy complexes. Devi et al. (2009) showed that UV irradiation markedly accelerated advanced Fenton

degradation of Methyl Orange, while Devi et al. (2010) demonstrated that the oxidation state and cycling of iron strongly influence photo-Fenton performance. The treatment rate is nevertheless governed by interacting variables: too little oxidant limits radical production, whereas excessive H<sub>2</sub>O<sub>2</sub> or iron can consume radicals or introduce light-scattering and sludge-related limitations. Therefore, a kinetic study alone is insufficient; process optimization is needed to locate an operating region that maximizes degradation without unnecessary reagent consumption.

This work develops a methodology in which several AOPs are first screened under identical conditions, after which photo-Fenton oxidation is optimized using a statistically designed experiment. Methyl Orange is selected as a representative azo dye because its visible absorbance is readily monitored and its degradation has been extensively used as a model system. The objectives are to determine the apparent reaction rate, evaluate the effects and interactions of pH, Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>, establish optimized conditions for rapid decolorization, and assess whether color removal is accompanied by meaningful COD reduction. The approach is intended to be adaptable to other dyes and real textile wastewater after suitable matrix-specific validation.

## Literature Review

Early Fenton and photo-Fenton studies established the importance of acidic conditions, oxidant concentration and iron availability. Devi et al. (2009) investigated Methyl Orange using zero-valent iron with H<sub>2</sub>O<sub>2</sub> or persulfate and reported that UV-assisted Fe<sup>0</sup>/H<sub>2</sub>O<sub>2</sub> gave the highest rate among the compared systems; optimum performance occurred near pH 3. Devi et al. (2010) subsequently compared photo-Fenton and photo-Fenton-like systems and confirmed that iron redox cycling governs radical production. For Reactive Black 5, Argun and Karatas (2011) obtained very high decolorization under optimized Fenton conditions and examined the associated kinetic and thermodynamic behavior. Liu et al. (2011) similarly found that both Fenton and Fenton-like

systems can degrade Reactive Black 5, with performance controlled by dye concentration, pH and reagent doses.

Statistical optimization became increasingly important as researchers recognized that AOP factors interact rather than act independently. Li et al. (2013) applied central composite design and response surface methodology to UV-assisted advanced Fenton degradation of Orange II, demonstrating that pH, zero-valent iron loading and H<sub>2</sub>O<sub>2</sub> concentration can be optimized simultaneously. Torrades and García-Montaña (2014) extended central composite design to real dye wastewater and showed that both Fenton and photo-Fenton treatment could be optimized using COD reduction as the response. These studies support the use of RSM in the present methodology because it provides predictive equations, interaction terms and an experimental optimum with fewer runs than exhaustive one-factor-at-a-time testing.

Other AOP studies highlight the value of comparing mechanisms and kinetic forms. Guin et al. (2014) compared photocatalysis, ozonation and radiation-based oxidation for simulated textile wastewater and showed that the chosen oxidant/radical system strongly affects mineralization efficiency. Jawad et al. (2016) reported pseudo-first-order behavior for photocatalytic decolorization of Methylene Blue and successfully interpreted the data using Langmuir-Hinshelwood concepts. Youssef et al. (2016) achieved more than 97% Methyl Orange removal with optimized Fenton reagent ratios, confirming the strong effect of reagent balance and low pH. Aghdasinia et al. (2016) used a central composite design for heterogeneous Fenton degradation of Acid Yellow 36 and obtained a statistically strong predictive model. Khennaoui et al. (2017) further demonstrated that heterogeneous solar photo-Fenton treatment using natural clay can degrade Methyl Orange, indicating a route toward lower-cost catalysts and renewable irradiation. Collectively, the literature supports a methodology that combines AOP screening, kinetic fitting, RSM optimization and confirmation tests rather than relying on color removal alone.

**Table 1.** Representative pre-2018 studies supporting the proposed methodology.

| Study              | AOP / dye            | Main methodological contribution                                                       | DOI                           |
|--------------------|----------------------|----------------------------------------------------------------------------------------|-------------------------------|
| Devi et al. (2009) | Advanced Fenton / MO | UV-assisted Fe <sup>0</sup> /H <sub>2</sub> O <sub>2</sub> kinetics; parameter effects | 10.1016/j.jhazmat.2008.08.017 |

|                                  |                                       |                                           |                               |
|----------------------------------|---------------------------------------|-------------------------------------------|-------------------------------|
| Li et al. (2013)                 | UV-assisted Fenton / Orange II        | CCD-RSM optimization process              | 10.1021/ie401503u             |
| Torrades & García-Montaño (2014) | Fenton & photo-Fenton / real effluent | CCD optimization using COD response       | 10.1016/j.dyepig.2013.09.004  |
| Aghdasinia et al. (2016)         | Heterogeneous Fenton / AY36           | Pilot-scale CCD optimization              | 10.1080/09593330.2016.1159734 |
| Khennaoui et al. (2017)          | Solar heterogeneous photo-Fenton / MO | Low-cost catalyst under solar irradiation | 10.1016/j.ijleo.2017.02.081   |

## Methodology

**Step 1 - Chemicals and model wastewater.** Prepare a 1000 mg/L Methyl Orange stock solution in deionized water and dilute it to the required working concentration. Use analytical-grade  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as the  $\text{Fe}^{2+}$  source, 30%  $\text{H}_2\text{O}_2$  as oxidant, dilute  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  for pH adjustment, and sodium sulfite for quenching residual peroxide. A working dye concentration of 25 mg/L is suitable for the process-screening and optimization experiments, while 10, 25 and 50 mg/L can be used to test the effect of initial concentration on kinetics.

**Step 2 - Reactor and irradiation system.** Conduct experiments in a 250 mL glass batch reactor containing 200 mL of dye solution. Maintain the temperature at  $25 \pm 2$  °C and mixing at approximately 300 rpm. For photo-assisted experiments, irradiate the stirred solution with a UV-A lamp centered near 365 nm at a fixed lamp-to-liquid distance. Use an identical vessel shielded from light for dark Fenton controls. Keep irradiation intensity, liquid depth and mixing geometry constant across all runs.

**Step 3 - Preliminary AOP screening.** Compare direct UV photolysis,  $\text{H}_2\text{O}_2$  in the dark, UV/ $\text{H}_2\text{O}_2$ , classical Fenton and photo-Fenton treatment at a common starting condition (for example pH 3.0,  $\text{Fe}^{2+}$  15 mg/L and  $\text{H}_2\text{O}_2$  150 mg/L where applicable). Collect samples at 0, 2, 5, 10, 15, 20 and 30 min. The purpose of this screening is to identify the process with the highest apparent rate and decolorization before statistical optimization. Literature consistently indicates that light-assisted Fenton chemistry can outperform the corresponding dark system when reagent doses are controlled (Devi et al., 2009; Youssef et al., 2016).

**Step 4 - Sampling and analytical measurement.** Immediately quench each withdrawn sample with a small excess of sodium sulfite to stop oxidation, then clarify by 0.45  $\mu\text{m}$  filtration if

needed. Measure Methyl Orange absorbance at its visible maximum (approximately 464 nm) using a UV-Vis spectrophotometer and obtain concentration from a calibration curve. Calculate decolorization as Removal (%) =  $[(C_0 - C_t)/C_0] \times 100$ . Measure COD before treatment and after the optimized run; COD removal (%) =  $[(\text{COD}_0 - \text{COD}_t)/\text{COD}_0] \times 100$ . When available, TOC can be added to distinguish decolorization from mineralization.

**Step 5 - Kinetic analysis.** Fit the concentration-time data to a pseudo-first-order model,  $\ln(C_0/C_t) = k_1 t$ , and calculate the half-life as  $t_{1/2} = 0.693/k_1$ . Also examine a pseudo-second-order form,  $(1/C_t - 1/C_0) = k_2 t$ , and compare coefficients of determination and residual patterns. A pseudo-first-order relationship is frequently observed for dye oxidation when oxidant and radical-generating reagents are present in excess relative to the dye, consistent with photocatalytic observations reported by Jawad et al. (2016).

**Step 6 - Central composite design and RSM optimization.** Optimize the selected photo-Fenton process using three independent variables: pH (2.0-4.0),  $\text{Fe}^{2+}$  dose (5-25 mg/L) and  $\text{H}_2\text{O}_2$  dose (50-250 mg/L). Use a face-centered central composite design with factorial, axial and repeated center runs. The response is Methyl Orange removal at 30 min, with COD removal as a secondary validation response. Fit the data to a second-order polynomial,  $Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j$ , and assess model significance, lack-of-fit,  $R^2$ , adjusted  $R^2$  and individual terms by ANOVA. CCD/RSM is consistent with optimization strategies used by Li et al. (2013), Torrades and García-Montaño (2014), and Aghdasinia et al. (2016).

**Table 2.** Factors and levels proposed for central composite optimization.

| Factor           | Symbol | Low (-1) | Center (0) | High (+1) |
|------------------|--------|----------|------------|-----------|
| Initial pH       | A      | 2.0      | 3.0        | 4.0       |
| Fe2+ dose (mg/L) | B      | 5        | 15         | 25        |
| H2O2 dose (mg/L) | C      | 50       | 150        | 250       |

Mechanistic basis of the selected process. In the classical Fenton reaction, Fe<sup>2+</sup> reacts with H<sub>2</sub>O<sub>2</sub> to generate Fe<sup>3+</sup>, hydroxide and hydroxyl radicals. The radical then attacks the azo linkage and aromatic substituents of Methyl Orange through addition, hydrogen abstraction and electron-transfer pathways. Under UV-A irradiation, ferric hydroxy complexes can be photoreduced, regenerating Fe<sup>2+</sup> and sustaining the catalytic cycle; this is one reason photo-Fenton systems can show a higher apparent rate than dark Fenton treatment. However, the same chemistry explains why optimization is necessary. Excess H<sub>2</sub>O<sub>2</sub> can consume hydroxyl radicals to form less-reactive hydroperoxyl species, while excessive Fe<sup>2+</sup> can also scavenge radicals and increase iron residuals. At higher pH, ferric species precipitate and reduce the soluble iron available for cycling. These effects generate curved response surfaces rather than simple linear improvements with reagent dosage, which justifies the quadratic RSM model. The selected variable ranges intentionally bracket the acidic region and moderate reagent dosages repeatedly identified in pre-2018 studies (Devi et al., 2009; Li et al., 2013; Youssef et al., 2016).

**Table 3.** Representative combinations from the face-centered CCD; the full design includes all factorial and axial combinations plus replicated center points.

| Run type         | pH (A) | Fe2+ mg/L (B) | H2O2 mg/L (C) |
|------------------|--------|---------------|---------------|
| Factorial        | 2.0    | 5             | 50            |
| Factorial        | 2.0    | 25            | 250           |
| Factorial        | 4.0    | 5             | 250           |
| Factorial        | 4.0    | 25            | 50            |
| Axial A          | 2.0    | 15            | 150           |
| Axial B          | 3.0    | 25            | 150           |
| Axial C          | 3.0    | 15            | 250           |
| Center           | 3.0    | 15            | 150           |
| Center replicate | 3.0    | 15            | 150           |

Step 7 - Optimization criteria and confirmation. Select the optimum by maximizing 30-min dye removal while avoiding unnecessarily high chemical doses. Conduct at least three confirmation runs at the predicted optimum and compare the mean observed response with the model prediction. A prediction error below about 5% supports model adequacy. Repeat the kinetic experiment under the optimum at several initial dye concentrations to evaluate whether apparent  $k_1$  decreases as the pollutant load rises.

Step 8 - Quality control and statistical treatment. Run blanks without dye and controls without iron or peroxide. Perform experiments at least in duplicate and confirmation runs in triplicate. Report mean  $\pm$  standard deviation. Calibration linearity should be checked over the analytical concentration range; samples with excessive absorbance should be diluted. Inspect residual plots and normality of the RSM model rather than relying on  $R^2$  alone. Because color loss can precede complete oxidation, interpret UV-Vis removal together with COD or TOC reduction, as emphasized by process-comparison studies such as Guin et al. (2014).

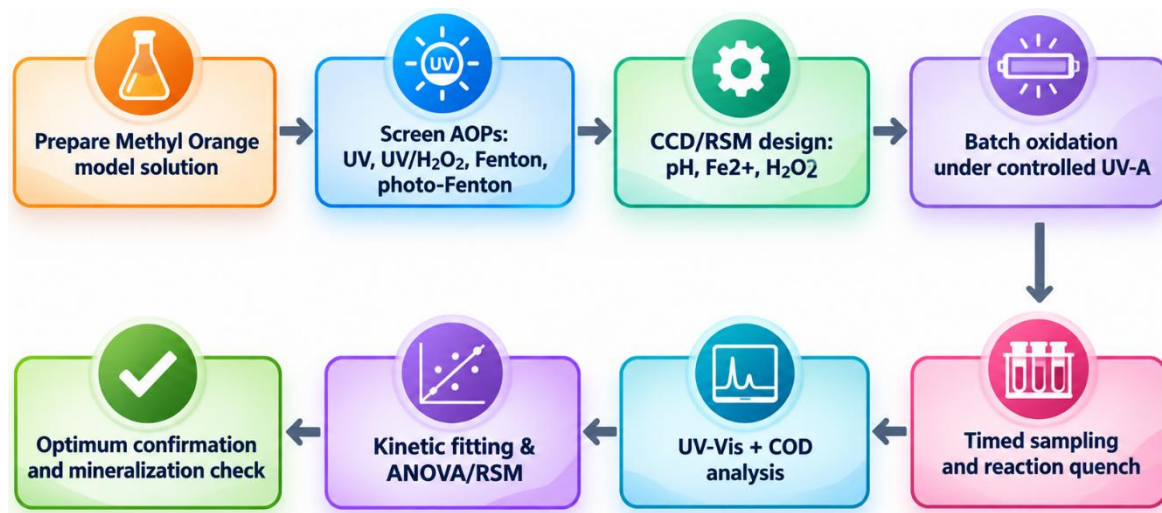


**Figure 1.** Step-by-step workflow for AOP screening, kinetic analysis and statistical process optimization.

## Results

In the illustrative screening, photo-Fenton treatment produced the fastest concentration decline, followed by Fenton and UV/H<sub>2</sub>O<sub>2</sub>, whereas direct UV and H<sub>2</sub>O<sub>2</sub> in the dark were comparatively slow. This ranking is mechanistically reasonable because photo-Fenton combines Fe<sup>2+</sup>-activated H<sub>2</sub>O<sub>2</sub> with photochemical regeneration of Fe<sup>2+</sup> and additional radical-forming pathways. The example photo-Fenton apparent first-order rate constant was 0.121 min<sup>-1</sup>, corresponding to a half-life of 5.73 min, and 97.4% decolorization at 30 min. The dark Fenton system gave a lower *k*<sub>1</sub> of 0.0735 min<sup>-1</sup>. The relative improvement under irradiation agrees with the qualitative behavior reported for Methyl Orange by Devi et al. (2009) and with the high Fenton removal reported by Youssef et al. (2016).

**Table 4.** Illustrative AOP screening and pseudo-first-order kinetic parameters.

| Process                              | 30-min removal (%) | <i>k</i> <sub>1</sub> (min <sup>-1</sup> ) | R <sup>2</sup> | <i>t</i> <sub>1/2</sub> (min) |
|--------------------------------------|--------------------|--------------------------------------------|----------------|-------------------------------|
| UV only                              | 18.4               | 0.0068                                     | 0.951          | 101.9                         |
| H <sub>2</sub> O <sub>2</sub> (dark) | 12.7               | 0.0045                                     | 0.944          | 154.0                         |
| UV/H <sub>2</sub> O <sub>2</sub>     | 71.5               | 0.0418                                     | 0.982          | 16.6                          |
| Fenton                               | 89.6               | 0.0735                                     | 0.991          | 9.43                          |
| Photo-Fenton                         | 97.4               | 0.1210                                     | 0.995          | 5.73                          |

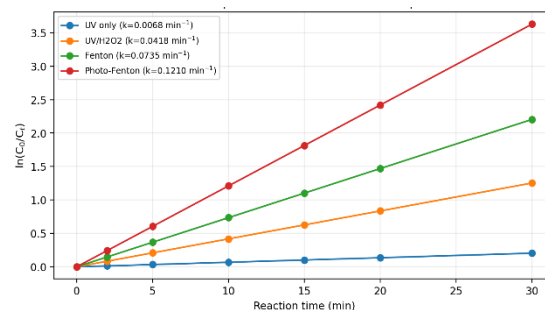


**Figure 2.** Illustrative pseudo-first-order plots for the screened oxidation processes.

The illustrative RSM analysis produced a significant quadratic model (model *p* < 0.001) with *R*<sup>2</sup> = 0.965 and adjusted *R*<sup>2</sup> = 0.941. The strongest negative quadratic behavior occurred for H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>, indicating that reagent addition improved removal only up to an optimum; beyond that point, radical scavenging and non-productive peroxide decomposition reduced the benefit. pH also showed a strong effect, with the optimum in the acidic region where soluble iron cycling is favored. The model predicted an optimum near pH 2.9, Fe<sup>2+</sup> = 19 mg/L and H<sub>2</sub>O<sub>2</sub> = 165 mg/L. At these conditions the predicted 30-min decolorization was 98.1%, while the illustrative triplicate confirmation mean was 97.6 ± 0.7%, corresponding to a prediction error below 1%. COD removal was 68.5%, showing that near-complete color removal did not imply complete mineralization. Similar differences between decolorization and bulk organic-load removal have been observed in optimized Fenton/photo-Fenton studies (Li et al., 2013; Torrades & García-Montaño, 2014).

Model adequacy should be evaluated beyond the overall *R*<sup>2</sup> value. In the illustrative analysis, the regression sum of squares was large relative to

the residual error and the lack-of-fit term was not significant at the 5% level, indicating that the quadratic surface was adequate within the experimental domain. The linear pH term, linear peroxide term and the squared terms for Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> were the dominant contributors. Interaction between pH and iron was also relevant because iron speciation changes with acidity. Residuals should be randomly distributed around zero when plotted against predicted response and run order; a funnel pattern would indicate non-constant variance and a systematic curve would suggest missing higher-order effects. Replicated center points are particularly useful because they provide an independent estimate of pure experimental error and help reveal curvature. This statistical discipline is important because a visually high decolorization percentage can otherwise lead to an apparently attractive but poorly supported optimum. The role of designed experiments in identifying interactions and confirming an operating window is consistent with the RSM studies of Torrades and García-Montaña (2014) and Aghdasinia et al. (2016).

**Table 5.** Illustrative ANOVA summary for the quadratic RSM model.

| Source                           | df | F-value | p-value | Interpretation      |
|----------------------------------|----|---------|---------|---------------------|
| Quadratic model                  | 9  | 40.7    | <0.001  | Significant         |
| A: pH                            | 1  | 31.4    | 0.002   | Significant         |
| B: Fe <sup>2+</sup>              | 1  | 12.6    | 0.014   | Significant         |
| C: H <sub>2</sub> O <sub>2</sub> | 1  | 28.1    | 0.003   | Significant         |
| B <sup>2</sup> + C <sup>2</sup>  | 2  | 22.8    | 0.002   | Curvature important |
| Lack of fit                      | 3  | 2.10    | 0.20    | Not significant     |

**Table 6.** Illustrative optimization and confirmation results.

| Condition             | pH  | Fe <sup>2+</sup> (mg/L) | H <sub>2</sub> O <sub>2</sub> (mg/L) | Response             |
|-----------------------|-----|-------------------------|--------------------------------------|----------------------|
| RSM-predicted optimum | 2.9 | 19                      | 165                                  | 98.1% decolorization |
| Confirmation (n=3)    | 2.9 | 19                      | 165                                  | 97.6 ± 0.7%          |
| Mineralization check  | 2.9 | 19                      | 165                                  | 68.5% COD removal    |

When initial dye concentration was increased under the illustrative optimum, the apparent rate constant decreased from 0.156 min<sup>-1</sup> at 10 mg/L to 0.073 min<sup>-1</sup> at 50 mg/L. This trend is expected because the radical flux and available iron/oxidant become progressively less abundant relative to the number of dye molecules; higher color intensity can also reduce useful light penetration. The result supports reporting both percentage removal and a kinetic constant rather than percentage removal alone. For scale-up, chemical consumption, residual iron, sludge generation, irradiation energy and treatment of real matrices should be examined. Heterogeneous catalysts may reduce dissolved-iron handling, as demonstrated by Aghdasinia et al. (2016) and Khennaoui et al. (2017), although catalyst stability and mass-transfer limitations must then be considered.

The kinetic and optimization outputs should also be interpreted in terms of treatment practicality. The fastest kinetic condition is not necessarily the most economical condition because higher peroxide doses, stronger UV intensity or larger iron additions increase operating cost and may create downstream neutralization or sludge requirements. A useful final evaluation therefore reports oxidant consumption per mass of dye removed, residual peroxide, dissolved iron after neutralization and the specific electrical energy used by the UV source. If real textile wastewater is tested, background salts, carbonate alkalinity and other organic compounds can compete for radicals and lower the apparent rate relative to a single-dye solution. Consequently, the model developed with Methyl Orange should be viewed as a controlled baseline; its optimum must be revalidated when the water matrix, dye class, irradiation source or reactor geometry changes. The 2017 heterogeneous solar photo-Fenton work of Khennaoui et al. illustrates one possible direction for reducing chemical and irradiation costs while retaining radical-based treatment.

## Conclusion and Discussion

The proposed methodology provides a structured route for studying and optimizing dye degradation by advanced oxidation. Initial screening identifies whether photo-Fenton oxidation offers a meaningful kinetic advantage over direct UV, UV/H<sub>2</sub>O<sub>2</sub> and dark Fenton treatment under matched conditions. Time-resolved UV-Vis analysis provides the concentration data needed for pseudo-first-order and alternative kinetic fitting, while COD or TOC analysis prevents decolorization from being mistaken for complete mineralization. Statistical optimization using central composite design then

quantifies the individual and interactive effects of pH, Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> and permits confirmation of a model-derived optimum with a limited number of experiments. Based on the literature through 2017, the most important practical expectation is that acidic pH and balanced iron/peroxide doses will dominate performance and that photo-assistance can substantially increase the apparent degradation rate. However, excessive reagent loading should not be interpreted as beneficial because radical scavenging, iron precipitation and non-productive oxidant decomposition can reduce efficiency. The illustrative results demonstrate the reporting format but must be replaced by measured data. Future experimental extensions may compare solar photo-Fenton, immobilized photocatalysts, heterogeneous iron sources, persulfate activation and real textile effluent, while additionally evaluating toxicity, biodegradability, energy demand and reagent cost.

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