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Introduction

Praise be to Allah, who has guided and enabled us to publish the eleventh issue of the ***Gharyan Journal of Technology***. We thank Him for this blessing. As we promised from the very beginning with the release of the first issue in 2016, we have continued our commitment to maintaining the journal's credibility by upholding academic integrity and relying on reviewers with sufficient expertise in their fields. This ensures that the works published in the journal are characterized by rigor and scientific methodology, without favoritism, bias, or leniency in publishing studies that lack scientific and research value. Although we receive a larger number of submissions, we publish only a limited number of research papers in each issue because many are declined by reviewers for not meeting scientific standards. We look forward to ensuring that the published studies contribute to offering proposals and developing effective solutions to the challenges faced by institutions such as companies, factories, hospitals, and other sectors.

Nations strive for progress and for attaining distinguished status through achieving growth, economic advancement, and a decent quality of life for their people. Scientific research is one of the most important means of reaching that noble goal. By employing research in innovative applications that serve humanity in general, this objective can be fulfilled. Developed countries allocate significant portions of their financial resources toward achieving this aim.

We fully recognize that working in peer-reviewed scientific journals is a demanding task, especially under the circumstances our country in particular—and the world in general—are experiencing. However, we accepted this challenge with full confidence that Allah will support us as we endeavor to present valuable work that benefits researchers, specialists, and interested readers. Our aim is for the journal to be one of the scientific platforms for researchers in a world witnessing an intense race in the realms of civilization, science, research, and technology. We strive diligently to carve out a worthy place for the journal, benefiting from the experiences of those who preceded us in this long path. With God's permission, we hope that upcoming issues will be of even higher quality and that our journal will achieve an impact factor that reflects the value of the research it publishes. What further strengthens our determination and confidence is that the ***Gharyan Journal of Technology*** is issued by a well-established academic institution more than thirty years old, distinguished by its graduates who have joined numerous institutions across the country and have presented a positive image of the educational institution that prepared them.

The eleventh issue of the ***Gharyan Journal of Technology*** contains numerous research papers and scientific articles characterized by creativity and diversity, contributed by researchers from various educational institutions.

The Editorial Board renews its welcome to all researchers and contributors wishing to participate with scientific papers and innovative research in your journal, the ***Gharyan Journal of Technology***, which seeks to achieve distinction among peer-reviewed scientific journals. We open the door to your suggestions, remarks, and constructive criticism, believing that such feedback is the best way to develop the journal, enhance its scientific value, and support its continuity.

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Influence of Reactive Chemical Ions on the Solar-Induced Oxidative Degradation of Chlorophenols in Water

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الملخص:

تعدّ مركبات الكلوروفينول من الملوثات الثابتة في الأنظمة المائية نظرًا لمقاومتها القوية للتحلل البيولوجي الطبيعي، وسميتها العالية، وقدرتها على توليد نواتج ثانوية ضارة. من بين هذه المركبات العضوية، يُعدّ الكلوروفينول وثنائي كلوروفينول من الملوثات ذات الأهمية في مياه الصرف الصناعي. ركزت هذه الدراسة على تحلل هذه الملوثات تحت ضوء الشمس، سواءً بشكل فردي أو كخليط ثنائي، في وجود أيونات الحديد و مُحفّز ضوئي و هو TiO_2 بالإضافة إلى كمية صغيرة من أيونات النحاس. أظهرت النتائج أن هذه الأيونات عززت التحلل بشكل ملحوظ مقارنةً بالإشعاع الشمسي المباشر وحده بحيث اختُزل الحديديك بسرعة إلى حديدوز، مما حافظ على الدورة التحفيزية وسهّل الإنتاج المستمر لأنواع الأكسجين التفاعلية (ROS). تم تحديد العديد من المركبات الوسيطة الناتجة من هذه الأكسدة، بما في ذلك الفينول، و2–كلوروكاتيكول، إلى جانب كميات صغيرة من البنزوكوينون في المراحل اللاحقة. كانت أقصى نسبة تحلل تم الحصول عليها باستخدام أيونات الحديدوز هي 95% و 87% لمركبي الكلوروفينول وثنائي كلوروفينول على التوالي. تُسلّط هذه النتائج الضوء على مسارات إزالة الكلور التدريجية والدور الرئيسي للحديدوز في الحفاظ على النشاط. وبشكل عام، أظهرت الدراسة إمكانات التحفيز الضوئي الشمسي بمساعدة الحديد كاستراتيجية فعالة ومنخفضة التكلفة لمعالجة المياه الملوثة بالكلوروفينول.

الكلمات المفتاحية : الكلوروفينولات ، الأكسدة ، أيونات الحديد ، الحفاز الضوئي ، معالجة المياه .

Abstract

Chlorophenolic compounds are persistent pollutants in aquatic systems due to their strong resistance to natural biodegradation, high toxicity, and potential to generate harmful byproducts. Among them, chlorophenol and dichlorophenol are considered priority contaminants in industrial wastewater. This study examined their degradation under solar light, both individually and as a binary mixture, in the presence of iron ions and photocatalyst TiO_2 as well as small quantity of cupper ions. The results showed that iron significantly enhanced degradation compared to direct solar irradiation alone. Under sunlight, Ferric was rapidly reduced to ferrous, maintaining the catalytic cycle and facilitating continuous production of reactive oxygen species (ROS). Several intermediates, including phenol, and 2-chlorocatechol, were identified, along with small amounts of benzoquinone in later stages. The maximum degradation efficiencies of 95% (chlorophenol) and 87% (dichlorophenol) using ferrous ions within 120 minutes were achieved. These findings highlight the progressive dechlorination pathways and the central role of ferrous in sustaining activity. Overall, the study demonstrates the promise of iron-assisted solar photocatalysis as an efficient and low-cost strategy for treating water contaminated with chlorophenols.

Key words, chlorophenols, oxidation, iron ions, solar photocatalytic, water treatment.

1. **Introduction**

Chlorophenols constitute an important group of halogenated aromatic compounds that are widely distributed in aquatic environments due to both industrial activities and disinfection practices. These compounds are considered highly toxic, non-biodegradable, and persistent, thereby posing serious threats to public health and ecological systems (Field & Sierra-Alvarez, 2008). Their stability and resistance to microbial degradation stem largely from the strong carbon–chlorine (C–Cl) bond, which not only extend their environmental half-life but also enhances their bioaccumulation potential. The toxicological profile of chlorophenols includes mutagenic, carcinogenic, and endocrine-disrupting effects, underscoring the urgency of developing efficient methods for their removal from contaminated waters (Olaniran & Igbinosa, 2021).

Among these compounds, chlorophenol and dichlorophenol have been identified as priority pollutants by regulatory agencies due to their widespread industrial use and high toxicity. The European Union and the United States Environmental Protection Agency (USEPA) classify chlorophenol as a hazardous substance, while dichlorophenol has been listed on the USEPA’s inventory of toxic pollutants since 1976 (USEPA, 1976; European Commission, 2001). Industrially, these compounds are applied in the synthesis of dyes, pesticides, pharmaceuticals, resins, and antiseptics, as well as in petroleum refining (Gomes et al., 2019). Their extensive utilization has resulted in their frequent detection in wastewater effluents, surface waters, and, in some cases, groundwater sources. This persistence, coupled with their toxicity, necessitates the development of cost-effective and sustainable treatment technologies.

Conventional biological and chemical treatment methods, although widely applied for organic pollutant removal, are often insufficient for chlorophenols due to their recalcitrant nature and inhibitory effects on microbial consortia (Luo et al., 2022). Consequently, advanced oxidation processes (AOPs) have been increasingly explored as alternative treatment methods. AOPs rely on the generation of highly reactive oxygen species (ROS), particularly hydroxyl radicals (•OH), which possess oxidation potentials high enough to non-selectively degrade a wide range of organic pollutants, ultimately leading to mineralization into carbon dioxide, water, and inorganic ions (Glaze et al., 1987). Among various AOPs, photocatalysis based on titanium dioxide (TiO_2) has attracted considerable attention owing to its chemical stability, strong oxidative capacity, non-toxicity, and relatively low operational cost (Fujishima & Honda, 1972; Chong et al., 2010).

Traditional photocatalytic systems have primarily employed ultraviolet (UV) irradiation to activate TiO_2. While effective, the reliance on UV light significantly increases energy costs and restricts large-scale applications. In contrast, substituting solar irradiation for artificial UV sources offers an environmentally sustainable and economically attractive alternative, particularly in regions with high solar irradiance (Malato et al., 2009). However, a major limitation of solar photocatalysis is the rapid recombination of photogenerated electron–hole pairs, which drastically reduces the quantum efficiency of the process. Thus, strategies to suppress recombination and enhance ROS generation are crucial to improving overall photocatalytic performance.

One promising approach to address this challenge involves the incorporation of transition metal ions, which can act as electron scavengers, redox mediators, or co-catalysts. Among these, iron ions (Fe^{2+}/Fe^{3+}) are especially attractive due to their low cost, natural abundance, and environmentally benign nature compared with other transition metals (Pignatello et al., 2006). Iron-based systems also provide the advantage of operating under the principles of photo-Fenton chemistry, wherein Fe^{3+} undergoes photoreduction to Fe^{2+} under irradiation, thereby sustaining the catalytic cycle and promoting continuous radical generation (De Laat & Gallard, 1999). Previous studies have demonstrated that Fe^{3+} ions enhance the degradation efficiency of chlorophenols and accelerate the mineralization process (Nogueira & Jardim, 1998). Nevertheless, the precise mechanistic roles of Fe^{2+} and Fe^{3+} remain a subject of debate. While Fe^{2+} is known to participate directly in Fenton-like reactions with oxidants such as hydrogen peroxide, Fe^{3+} plays a dual role by both accepting electrons and being photoreduced under irradiation (Gogate & Pandit, 2004). This interplay between the two oxidation states of iron necessitates further systematic investigation to clarify their contributions under solar-driven photocatalytic conditions.

In this context, the present study focuses on the solar photocatalytic degradation of chlorophenol and dichlorophenol, investigated both individually and as binary mixtures, in the presence of Fe^{2+} and Fe^{3+} ions. Particular attention is devoted to identifying the key intermediates formed during the degradation pathways, elucidating the mechanistic contributions of iron ions, and assessing their role in sustaining photocatalytic activity. The findings are expected to contribute to a deeper understanding of iron-assisted solar photocatalysis and to provide valuable insights for the development of cost-effective and sustainable treatment strategies for chlorophenol-contaminated waters.

2. Materials and Methods

2.1 Materials

High-purity samples of chlorophenol, dichlorophenol, hydroquinone, 4-chlorocatechol, phenol, and benzoquinone were obtained from Sigma-Aldrich. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were used as iron sources. The photocatalyst TiO_2 (P25, 80% anatase, 20% rutile, 21 nm particle size) was purchased from Acros Organics. Hydrochloric acid was used to adjust pH, and deionized ultrapure water was employed for all solutions.

2.2 Photocatalytic Experiments

Experiments involved degrading a combined mixture (100 mg/L of each chlorophenol) under solar simulation using TiO_2 with added Fe^{2+} or Fe^{3+}. A 1 L suspension was prepared in a Pyrex reactor and irradiated with a solar simulator (1,000 mW/cm^2). Prior to irradiation, the suspension was stirred in the dark for 30 minutes to establish adsorption equilibrium. Aliquots were collected at intervals, filtered, and analyzed by high-performance liquid chromatography (HPLC) to determine compound concentrations. Degradation efficiency was calculated from initial and remaining concentrations. COD and iron concentrations were also measured periodically.

2.3 Analytical Methods

HPLC analysis with a UV-visible detector and C18 column was used to quantify chlorophenols and intermediates. COD was determined with a Hach spectrophotometer using standard digestion procedures. Iron ion concentrations were monitored via the phenanthroline method.

3. Results and Discussion

3.1 Effect of Chemical Ions

Photocatalytic degradation was more effective under acidic conditions (pH 3). For Fe^{2+}, the optimal concentration was 10 mg/L, achieving degradation efficiencies of 95% (chlorophenol) and 87% (dichlorophenol) within 120 minutes. Higher concentrations led to reduced efficiency due to increased electron-hole recombination. Figure 1.

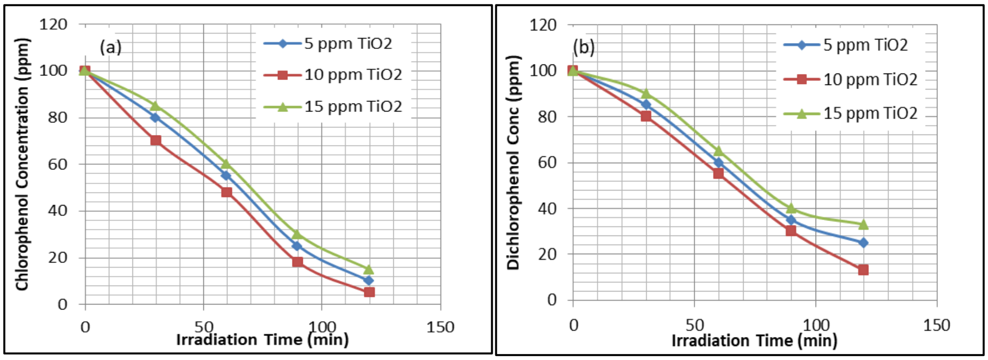

Figure 1 Influence of (Fe^{+2}) on the oxidation of (a) chlorophenol and (b) dichlorophenol

For Fe^{3+}, the best performance was at 13 mg/L, yielding efficiencies of 80% (chlorophenol) and 70% (dichlorophenol). Thus, both ions significantly enhanced degradation, though Fe^{2+} showed slightly higher activity Figure 2.

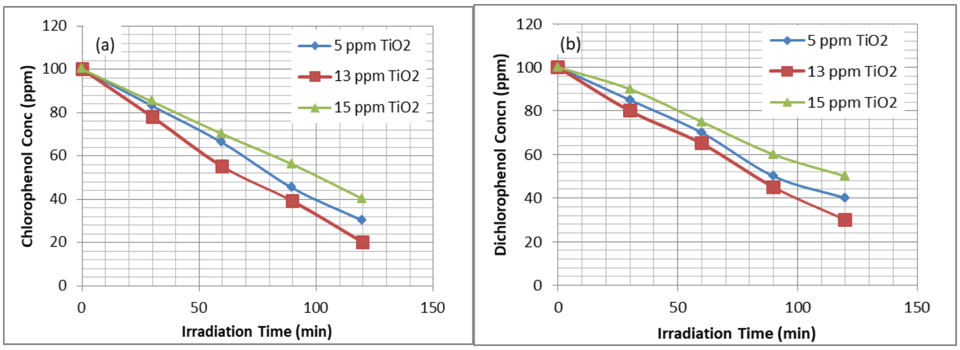

Figure 2 Effect (Fe^{+3}) on the oxidation of (a) chlorophenol and (b) dichlorophenol

This result should be clarified by the fact that the recombination of the e^-/h^+ pairs increases at high metal ion doses, leading to reduce d hydroxyl radicals (•OH) (Arslan et al. 2000).

3.2 Degradation Pathways and Intermediates

At optimal ion concentrations, three primary intermediates were detected: phenol, and 2-chlorocatechol, with traces of benzoquinone. These intermediates reached peak concentrations around 60 minutes and degraded within 120 minutes. Compared to earlier work without added iron, degradation times were shortened by nearly half. The mechanism suggests that Fe^{2+} accelerates degradation by capturing photogenerated electrons and reacting with hydrogen peroxide to produce hydroxyl radicals, whereas Fe^{3+} produces radicals through slower pathways Figure 3.

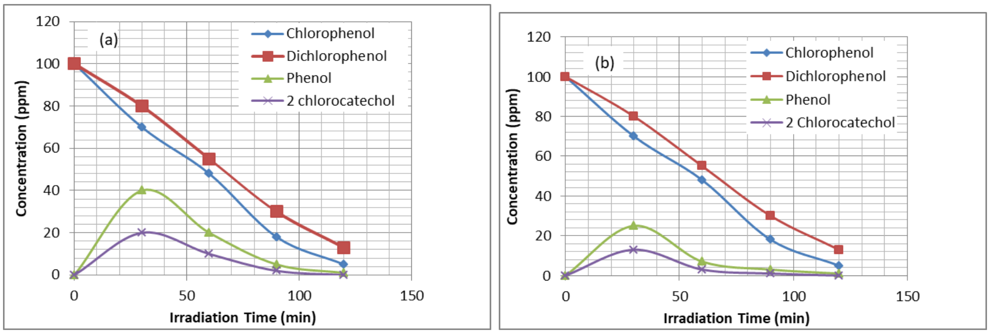

Figure 3 Concentration profiles of the combined mixture of 100 mg/L of both chlorophenol and dichlorophenol with optimal values of (a) Fe^{+2} = 10 ppm and (b) Fe^{+3} = 13 ppm.

3.3 COD Reduction

To monitor the total removal efficiency of the combined mixture, Chemical oxygen demand (COD) was continuously measured during the course of the reaction.

analysis showed significant reductions, though complete COD removal was not achieved, indicating the presence of undetected intermediates. Maximum COD reductions were 88% (Fe^{2+}) and 79% (Fe^{3+}) after 240 minutes Figure 4.

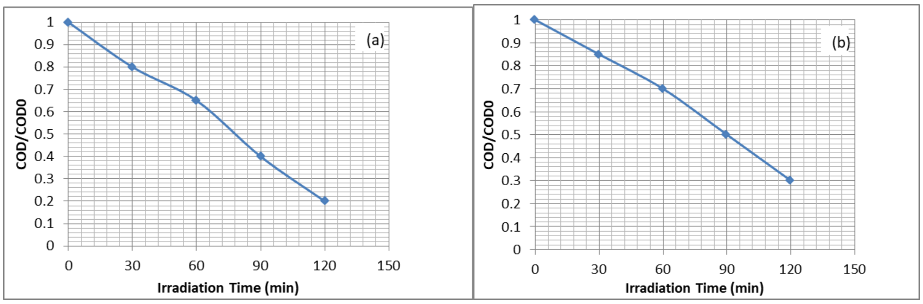

Figure 4 COD reduction of the combined mixture of 100 ppm of both chlorophenol and dichlorophenol with the optimum values of (a) Fe^{+2} = 10 mg/L and (b) Fe^{+3} = 13 mg/L.

The low reduction rate during the first 60 min of the solar irradiation might be attributed to the formed intermediates (HQ, Ph, 4-cCat) that make the solution rich in organic compounds.

3.4 Iron Concentration Behavior

Fe^{2+} concentrations declined steadily during irradiation, with partial conversion to Fe^{3+} due to reactions with hydroxyl radicals and hydrogen peroxide Equation1.

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^{-} \quad (1)$$

It can be noticed that most Fe^{3+} ions rapidly reduced to Fe^{2+} under solar irradiation, highlighting the dominant role of Fe^{2+} in the degradation process Equation 2.

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (2)$$

Despite different initial oxidation states, both ions ultimately contributed similarly to pollutant breakdown Figure 5.

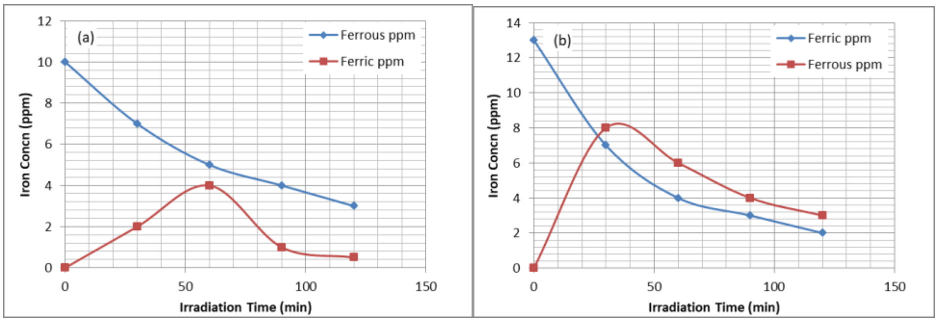

Figure 5 Iron concentrations during solar photocatalytic degradation of the combined mixture of 50 mg/L of both chlorophenol and dichlorophenol (a) Fe^{2+} (b) Fe^{3+} .

4. Conclusion

This study has confirmed that both ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions play a significant role in enhancing the solar photocatalytic degradation of chlorophenolic mixtures. Although both species improved pollutant removal, Fe^{2+} demonstrated marginally superior performance, largely due to its direct involvement in generating reactive oxygen species through Fenton-like reactions. The rapid photoreduction of Fe^{3+} to Fe^{2+} under irradiation further supports the central role of Fe^{2+} in sustaining catalytic activity. The detection of hydroquinone, phenol, and 4-chlorocatechol as intermediates, alongside COD measurements, suggests that while degradation was effective, complete mineralization was not fully achieved, and some by-products persisted. Importantly, the low residual iron concentrations indicate that catalyst recovery and reuse are feasible, enhancing the sustainability of the process. These findings highlight the promise of iron-assisted solar photocatalysis as a cost-effective water treatment strategy, while emphasizing the need for future research on affordable iron sources and by-product toxicity.

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