A Green Synthesis of Iron/Copper Nanoparticles as a Catalytic of Fenton-like Reactions for Removal of Orange G Dye

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Abstract:

This research paper studies the use of an environmentally and not expensive method to degrade Orange G dye (OG) from the aqueous solution, where the extract of ficus leaves has been used to fabricate the green bimetallic iron/copper nanoparticles (G-Fe/Cu-NPs). The fabricated G-Fe/Cu-NPs were characterized utilizing electron microscopy, BET, atomic force microscopy, energy dispersive spectroscopy, Fourier-transform infrared spectroscopy and zeta potential. The rounded and shaped as like spherical nanoparticles were found for G-Fe/Cu-NPs with the size ranged 32-59 nm and the surface area was 4.452 m²/g. Then the resultant nanoparticles were utilized as a Fenton-like oxidation catalyst. The degradation efficiency of OG dye highly depends on H₂O₂ concentration (1.7-5.28 mM), catalyst dose (0.4-1.6 g/L), pH (2-7), initial OG concentration (25-75 mg/L), and temperature (20-50 ºC). Batch experiments showed that 94.8 % of 50 mg/L of OG dye was removed within the optimum peroxide concentration, dose, pH and temperature which were 3.52 mM, 1 g/L, 3, and 40ºC respectively along with 30 min contact time. The results of kinetic models showed that OG removal followed the second-order model. Finally, the thermodynamic study of reaction was also examined and concluded to endothermic reaction with 29.725 kJ/mol activation energy.

Keywords: Fenton-like, Green synthesis, Iron/copper nanoparticles, Kinetics, Orange G dye.

Introduction:

Globally, dyes are produced up to thousands of tons yearly and used by many industries such as textile, leather, and printing. However, the release of these materials into effluent water impacts the ecosystem and causes pollution due to entering some risky elements in their production 1. Further, dyes harm the esthetic of water, prevent absorption of sunlight, and photosynthesis 2. Some literature confirmed that the azo structure contains benzene rings and the increase of these rings leads to rising toxicity 3. Orange G dye (OG) is one of the common synthetic azo dyes, it is easily dissolved in water and has been used to color textile products such as wool and silk. On the other hand, OG is a highly toxic anionic dye, the hazardous of this dye can be imputed to the azo group which is existing in its structure, furthermore, direct exposure to OG dye can impact the human digestive or respiratory 4. Therefore, various methods and technologies have been used for treating dyes in wastewater. In the last few decades, the removal of dyes was accomplished using classical methods such as sedimentation and equalization 5. Recently, various technologies and techniques have been used for treating wastewater polluted with dyes including adsorption, chemical coagulation, ions exchange, membrane separation, photocatalysis and electrocoagulation 6, however, these technologies have their drawbacks represented by the formation of undesirable intermediates, expensive, and restricted in some applications 7. In the most recent decade, advanced oxidation technologies (AOTs) have emerged as potential alternative techniques to eliminate the organic contaminants derived from industrial effluents, these techniques provided a significant solution for removing the wastewater dyes and have the ability to treat the components that are resistant to traditional treatment technologies and without
generating secondary wastes \(^8\). The AOTs are performed by the activation of hydrogen peroxide \((\text{H}_2\text{O}_2)\) and produced highly reactive and non-selective species like hydroxyl radicals \((\cdot\text{OH})\), these compounds have the capability to oxidize the organic pollutants existing at high concentrations \(^9\), \(^10\). Among the ATOs treatment methods, Fenton’s reagent has taken major attention due to the simplicity and eco-friendly of this method, it depends on the reaction between \(\text{Fe}^{2+}\) ions and \(\text{H}_2\text{O}_2\) for producing very reactive compounds named hydroxyl radicals \(^11\). However, there are some limitations with using \(\text{Fe}^{2+}\) ions related either by ferrous precipitation at the low pH or \(\cdot\text{OH}\) scavenging for using a high concentration of \(\text{H}_2\text{O}_2\), thereby, the \(\text{Fe}^{2+}\) replaced by zero-valent iron (ZVI) nanoparticles which have proved a good catalyst to overcome the drawbacks. Therefore, the Fenton-like reactions are promising good techniques for the degradation of complex organic pollutants \(^12\).

Different methods are used to synthesize ZVI such as the physical method that includes milling, vacuum sputtering, and thermal decomposition. Moreover, the chemical method uses borohydride \((\text{NaBH}_4)\) as a reduction agent. These two methods may need a piece of sophisticated equipment, difficult conditions to control during the experiment, long procedures, and toxic capping agents. Therefore, the biological method is a promising technique to overcome these problems while achieving a safe and suitable procedure to synthesize nanoparticles, treatment technology from plant extract and microorganisms which have been used as an alternative to physical and chemical methods \(^13\). The biological synthesis using leaf extract of plants is shown to be a more promising technique due to economic feasibility and are not complex synthetic procedures. Plant leaves contain an extremely large amount of both capping and reducing agents like flavonoids, polyphenols, and other reducing components that have the ability to reduce the salts to zero-valent and prevent them from agglomeration. The abundance of plants that do not have chemicals with bad side effects, non-toxic, have high efficiency and are not expensive, have been approved to be used in synthesizing green nanoparticles which are going to be utilized in treating wastewater \(^14\), \(^15\). One of the most abundant evergreens in several Asian countries and the United States is the ficus tree. It belongs to the Moraceae family and can grow up to 30 meters in its normal habitat \(^16\). Ficus contains numerous bioactive compounds such as phenolic, flavonoids, alkaloids and tannins. These components are critical to the creation of ficus-zero valent iron nanoparticles \((\text{F-Fe}^0)\) because they do not have negative or toxic side effects. They are also biodegradable, environmentally safe, and can act as capping and reducing agents \(^17\). Although iron nanoparticles \((\text{Fe-NPs})\) has become widely used as a promising metal in treatment processes for the removal of various environmental contaminants \(^18\), the reactivity of \((\text{Fe-NPs})\) may be impacted by the development of an oxide layer around particle surfaces \(^19\). To prevent this reaction, bimetal has been widely used to protect nanoparticles from oxidizing by adding a second catalyst such as \(\text{Cu}, \text{Pt}, \text{Pd}, \text{Ni}\) to \(\text{Fe-NPs}\) \(^19\). The mutual effect of two metals improves the properties of nanoparticles over the use of just one metal (monometallic); therefore, bimetallic nanoparticles have become of great interest to researchers \(^20\), \(^21\). Due to the economically and safely uses of copper compared to \(\text{Pd}\), \(\text{Ni}\), it has been used for coating the catalyst to enhance the rate of decolourization \(^19\). The novel idea of removing \(\text{OG}\) by using a catalyst of bimetallic \(\text{Fe/Cu}\) nanoparticles synthesized by ficus leaves can be ascribed to the significance of using green chemistry methods that represent an alternative environmentally and not expensive ways, furthermore, the bimetallic catalyst of nanoparticles is more effective than mono-metal in the removal of various contaminants \(^22\).

In this study, green synthesis of iron/copper nanoparticles \((\text{G-Fe/Cu-NPs})\) was prepared using the extract of the ficus plant. Then the effects of experimental factors such as concentration of \(\text{H}_2\text{O}_2\), pH, the initial concentration of dye, temperature, and the dose of catalyst on the degradation of anionic Orange G dye using Fenton-like reactions have been investigated.

**Materials and Methods:**

**Chemical and reagents**

The purity of all chemicals utilized was high \((99.9\%)\), ficus leaves were collected from the University of Baghdad, Iraq. \(\text{OG}\) was purchased from Central Drug House (BDH) Company, and Table 1 shows the properties of this dye. Ferrous sulfate heptahydrate \((\text{FeSO}_4\cdot7\text{H}_2\text{O})\) was purchased from BDH company and copper sulfate pentahydrate \((\text{CuSO}_4\cdot5\text{H}_2\text{O})\) was purchased from Fluka AG company. The change of \(\text{pH}\) was adjusted using \(1.0\ M\ \text{H}_2\text{SO}_4\) and \(1.0\ M\ \text{NaOH}\) solutions. The wavelength \(\lambda_{\text{max}}\) was specified using a UV/VIS spectrophotometer.
Table 1. Physicochemical characteristics of orange G dye (OG).

| Properties of (OG) dye | Molecular structure |
|------------------------|---------------------|
| Molecular formula      | C_{16}H_{10}N_{2}Na_{2}O_{7}S_{2} |
| Molecular weight (g/mole) | 452.37 |
| Solubility in water   | Soluble in water    |
| Maximum wavelength (nm) | 478 |

Catalyst Preparation

The G-Fe/Cu-NPs was prepared following the same procedures showed in the previous study [23], with some modifications as follows:

**Step 1:** Fresh ficus leaves were washed several times using tap water, and then washed with distilled water to eliminate any impurities or dust, followed by drying in an oven at 60 °C. Additionally, they were cut using mortar and pestle into small pieces with sifting using a 2.5mm sieve.

**Step 2:** The ficus leaf extract is prepared in 150 ml of deionized water with 20 g of ficus leaf pieces which were then boiled at 70 °C for 20 min and then filtered using filter paper to remove suspended ficus particles. Finally, the filtrate is refrigerated at 4 °C until used as a reducing and capping agent.

**Step 3:** A solution of 1.494 g of FeSO_{4}.7H_{2}O and 0.7g of CuSO_{4}.5H_{2}O salts were dissolved in 100 ml of deionized water. After the salts had completely dissolved, the filtration process using a filter paper was followed to remove any impurities. To develop the synthesis of G-Fe/Cu-NPs, 100 ml of extract from step 2 was added dropwise to the 100 ml of Fe (II) / Cu (II) mixture. After several drops of ficus extract were added, the mixture’s color changed gradually from yellow, brown, and finally to black indicating the metals equivalent were reduced to zero-valent and the formation of G-Fe/Cu-NPs completed. The remaining ficus extract is added to accelerate the reduction. In addition, the mixture is stirred continuously at 300 rpm by using a magnetic stirrer for 15 min. The black precipitate of G-Fe/Cu-NPs nanoparticles was separated by vacuum filtration using filter paper and immediately washing process was involved using distilled water three times, followed by rinsing with absolute ethanol. The washing and rinsing processes are important steps in the synthesis because they prevent the fast oxidation of nanoparticles. The G-Fe/Cu-NPs were then dried overnight at ambient temperature and then ground by mortar and pestle to a fine powder. Fig. 1 illustrates the green synthesis of G-Fe/Cu-NPs.

Analytical Methods

Before starting the experiments, a calibration curve for standard OG solution was done to locate the maximum wavelength (\(\lambda_{\text{max}}\)) of dye and the equation that joined the absorbance with concentration. Thus, the \(\lambda_{\text{max}}\) of OG was found to be 478 nm as shown in Fig.2.

According to the below formula the removal efficiency (RE) was calculated:

\[
RE = \frac{C_0 - C_t}{C_0} \times 100 \quad ...1
\]

Where the \(C_0\) is the initial concentrations and \(C_t\) is the OG concentration at time t.
Batch Fenton-like Experiments

In Fenton-like processes, the experiments would be carried out to evaluate the OG removal efficiency. A working solution of 50 mg/L of OG was prepared by dissolving 0.05 g of dye in 1 L deionized water, followed by adjusting pH by using 1.0 (by 1.0 M H₂SO₄ and 1.0 M NaOH) before adding G-Fe/Cu-NPs and H₂O₂. Some operating parameters were changed including hydrogen peroxide concentrations ranged (1.7-5.28 mmol/L), G-Fe/Cu-NPs dosage ranged (0.4–1.6 g/L), pH ranging from (2-7), the range of initial OG concentrations were (25–75 mg/L), contact time interval up to 120 min, the temperature ranged from (20-50 °C), and coexisting NaCl from (0.5 – 50 g). A particular amount of G-Fe/Cu-NPs was supplemented to the OG solution followed by mixing for 1 minute to homogenize the catalyst, after that, the H₂O₂ at a certain concentration was added and agitated at 300 rpm using a magnetic hot plate. The parameters were optimized separately by maintaining all operating conditions constant except for the one that wants to optimize. During each run, 10 ml samples were taken at a regular time and mixed with prepared 200 μL of 1M Na₂SO₃ in the vial, then they were analyzed by UV/VIS spectrophotometer after filtering them using 0.22 μm membrane filter. The purpose of adding Na₂SO₃ is just to quench the reaction 8. The removal efficiency was measured using Eq. 1.

Mechanism of Reaction

The possible mechanism of the reaction between iron/copper nanoparticles and hydrogen peroxide can be expressed by approaching the hydrogen peroxide to the nanoparticle and reacts with these particles, followed by oxidizing the zero-valent iron/copper to form Fe³⁺ and Cu⁺ where the electrons of iron and copper nanoparticles transferred from NPs to H₂O₂, as a result, the iron/copper ions are activated by hydrogen peroxide, thereby, to generating •OH as illustrated by the following equations 24:

\[
\begin{align*}
\text{Fe}^{0} + \text{H}_{2}\text{O}_{2} + \text{H}^+ &\rightarrow \text{Fe}^{2+} + 2\text{H}_{2}\text{O} \quad \text{... 2} \\
2\text{Cu}^{0} + \text{H}_{2}\text{O}_{2} + \text{H}^+ &\rightarrow 2\text{Cu}^{2+} + 2\text{H}_{2}\text{O} \quad \text{... 3} \\
\text{Fe}^{2+} + \text{H}_{2}\text{O}_{2} &\rightarrow \text{Fe}^{3+} + \text{H}^+ + \text{OH}^- \quad \text{... 4} \\
\text{Fe}^{3+} + \text{H}_{2}\text{O} &\rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{•O}_2\text{H} \quad \text{... 5} \\
\text{Cu}^{+} + \text{H}_{2}\text{O}_{2} &\rightarrow \text{Cu}^{2+} + \text{•OH} + \text{OH}^- \quad \text{... 6} \\
\text{Cu}^{2+} + \text{H}_{2}\text{O}_{2} &\rightarrow \text{Cu}^+ + \text{H}^+ + \text{•O}_2\text{H} \quad \text{... 7}
\end{align*}
\]

In the electrochemical regard, the presence of copper ions contributes to reducing Fe³⁺ to Fe²⁺ (Eq. 8) due to variance in potential between Fe²⁺/Fe³⁺ (0.77V) and Cu²⁺/Cu⁺ (0.17V). This reaction is very important in improving the decomposition of H₂O₂ and accelerates the pollutants degradation process. Therefore, the •OH formation and the oxidative process kinetics are highly developed in the presence of bimetallic iron/copper as a catalyst 24.

\[
\Delta E^0 = 0.6 \text{ V} \quad \text{... 8}
\]

Results and Discussion:

Characterization of G-Fe/Cu-NPs

Some techniques are utilized to prove the chemical classification, structure, size, and surface area of nanoparticles. The morphology, topography, and average size of these nanoparticles were characterized by a scanning electron microscopy (SEM) model. The EDAX technique is a confirmatory method used to ensure the identification and chemical classification of each particle, the EDAX detector and SEM model was (TESCAN MIRA 3, Czech Republic). In addition, AFM characterization is very helpful for determining the morphology of nanoparticle surfaces, it measures the contact force between the tip and surface, the model of AFM test which was tested on the G-Fe/Cu-NPs is (TT-2, USA). Furthermore, the XRD system is also utilized to investigate the crystallinity of the materials. The major picks using the XRD system can accurately
determine the crystalline nature of nanoparticles, the XRD test was already applied on the nanoparticles using (Philips X’pert diffractometer) model. In addition, FT-IR spectroscopy is widely used to confirm the structure of unidentified compounds, as well as to determine the functional group of numerous materials, especially for biomaterials, and (Shimadzu, Japan) was the FT-IR spectroscopy model in this work. The BET technique determines the specific surface area, the size radius of average pore, average porosity radius, and pore volume of nanoparticles, the G-Fe/Cu-NPs subjected to the BET test by the device model (TriStar II Plus Version 2.03, USA). At last, zeta potential is widely used to inspect the potential stability of the colloid nanoparticles. The high positive or negative zeta potential for colloids tends to be stable electrically while low zeta potential for colloids is flocculated or coagulated.

As a result, the variations in the color of the solution from yellow, brown, and then to black indicate the reduction process happened and formation of G-Fe/Cu-NPs, as well as the variation in the pH before and after the reduction process, where the pH of the ficus extract was 5.42 and the pH of the mixture after reduction was 3.24. As a result, along the reduction route, the pH of the solution declines and goes to the higher acidic range.

The scanning electron microscopy (SEM) images showed that the synthesized G-Fe/Cu-NPs were porous and shaped like spherical with diameters ranging from 32-59 nm (Fig. 3a and Fig.3b). Additionally, the porous and hollows in the nanoparticles improve dye removal. Moreover, the size variation of NPs created was due to the variation of the local concentration of the fucus extract which was responsible to reduce the metal ions.

The Energy Dispersive Spectroscopy (EDAX) of nanoparticles presented in Fig. 4b contains further information about the synthesis of G-Fe/Cu-NPs, where the place of atomic distribution and chemical composition of the catalyst was demonstrated by the intense peaks of Fe, Cu, C, and O, 5.51 wt%, 3.33 wt%, 48.67 wt%, and 42.49 wt%, respectively. The finding of adjoint elements such as C and O signals resulted mainly from the fucus extracts that contain organic compounds such as C and O molecules which play a major role in the reduction and stabilizing process of G-Fe/Cu-NPs.

According to the atomic force microscopy (AFM) images of G-Fe/Cu-NPs, the high rough surface through hills and valleys shape with a nano-rough texture and homogenous of nanoparticles can be seen in Fig. 4 which indicates the amorphous and granular shape of G-Fe/Cu-NPs. This roughness enhances the capability of the surface of the nanoparticles to absorb dye ions. Furthermore, the average size distribution of G-Fe/Cu-NPs tested by AFM ranged between (7.5-23 nm).
The FT-IR for preparing G-Fe/Cu-NPs is taken in the band range 400-4000 cm\(^{-1}\) to ensure the functional group of these nanoparticles as depicted in Fig. 5, the O-H stretching vibrations illustrated in the band between 3220-3430 cm\(^{-1}\) belong to polyphenol compounds which play an important role in reducing the Fe/Cu metals and then synthesis of bimetallic nanoparticles \(^{15}\). The amide group in the prepared nanoparticles can be noticed at band 1614 cm\(^{-1}\) which indicate the presence of flavonoids, polyphenols and proteins in ficus leaf, these compounds attribute to reduce the formation of G-Fe/Cu-NPs \(^{16}\).

The C=C sequences at 1446 cm\(^{-1}\) are attributed to the aromatic ring, while the bands at 1396 and 1244 cm\(^{-1}\) is related to C-OH bending, respectively \(^{26}\). The band observed at 823 cm\(^{-1}\) is related to the (Fe-O-Fe) stretching, and the vibration broadband ranged between 549-403 cm\(^{-1}\) could be assigned as Fe/Cu nanoparticles \(^{27}\). The peaks ranged from 1174 to 1070 cm\(^{-1}\) are caused by the carbonyl groups (C=O-C) stretching, these groups have the capability to prevent nanoparticles agglomeration by producing capping agents \(^{28}\). The phenolic compounds of ficus leaf extract adsorbed on the prepared nanoparticles are confirmed by the mentioned peaks. Furthermore, these phenolic compounds provide more stability to the nanoparticles when they were adsorbed on the surface of particles and act as a capping agent \(^{29}\). As a result, the FT-IR analysis proved the ability of the ficus leaf for doing the stabilizing and reducing functions for G-Fe/Cu-NPs.

The XRD curve of synthesized nanoparticles is revealed in Fig. 6 which is not including any sharp peaks indicating there is no crystal structure in this case, even with a wide range of diffraction peaks (from 20°-25°). The above result proves that the bimetallic G-Fe/Cu-NPs prepared by the green method are amorphous \(^{30}\). The XRD result is in agreement with what had been concluded by \(^{31, 30}\).
Effect of Parameters on the Degradation efficiency of OG dye

Effect of H2O2 Concentration

The existence of proper amounts of H2O2 in a satisfied concentration is a crucial matter in the Fenton-like reactions for generating the highly active \('\text{OH}\) radicals \(^{12}\), therefore, the influence of H2O2 concentrations was investigated. Initially, one experiment was carried out by adding a certain amount of H2O2 without adding any amounts of the catalyst to examine if any reaction may be observed between OG solution with \(\text{H}_2\text{O}_2\), and the result showed not. The concentration of \(\text{H}_2\text{O}_2\) was changed in the range 1.7-5.28 mmol/L by keeping the rest of the experimental factors constant (G-Fe/Cu-NPs dosage 0.4 g/L, pH 4, initial OG concentration 50 mg/L, temperature 30°C, and agitation speed 300rpm). The results showed that the removal rates of OG were 30.9, 47.1, 72.8, 65.9, and 56.6 % for concentrations 1.7, 2.64, 3.52, 4.4, and 5.28 mmol/L respectively, at 120 min period time. As illustrated in Fig. 8, the efficiency increased with increasing \(\text{H}_2\text{O}_2\) from 1.7 to 3.52 mmol/L and this was attributed to more production of very reactive \('\text{OH}\) radicals.

Nevertheless, it can be noticed that with the continuous rising of \(\text{H}_2\text{O}_2\) concentration (as in 4.4 and 5.28 mmol/L) the removal efficiency decreased. The diminish of efficiency, in this case, can be explained by recombination of \('\text{OH}\) with \(\text{H}_2\text{O}_2\) that led to gradually reducing the number of \('\text{OH}\) radicals in the solution and replaced with less reactive \(\text{HO}_2\) \(^{7}\) as illustrated in the following equation:

\[ \text{H}_2\text{O}_2 + \text{'OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^{'} \]  

Figure 6. X-Ray diffraction (XRD) of G-Fe/Cu-NPs sample.

Table 2 shows the results of G-Fe/Cu-NPs surface area obtained by the BET technique. In this analysis, the pore size for G-Fe/Cu-NPs was 40.4 nm which can be classified as mesopore according to the classification of the IUPAC that categorized the pore size as macropore ( >50 nm), mesopore (2 to 50 nm), super-micropore (0.7 to 2 nm) and ultra-micropore ( <0.7 nm). Thus, as the catalytic performance is highly dependent on accessible pore channels due to their benefits for the diffusion of material, these sizes of pores provide more stability by acting as a shielding agent to prevent the harsh reaction conditions of the nanoparticles’ active sites \(^{27}\).

![Figure 6. X-Ray diffraction (XRD) of G-Fe/Cu-NPs sample.](image)

**Figure 6. X-Ray diffraction (XRD) of G-Fe/Cu-NPs sample.**

**Table 2. BET parameters for G-Fe/Cu-NPs**

| Parameter       | Value  |
|-----------------|--------|
| BET (m\(^2\)/g) | 4.452  |
| Pore size (nm)  | 40.4   |
| Pore volume (cm\(^3\)/g) | 0.0108 |

Figure 7. Zeta potential analysis for sample of G-Fe/Cu-NPs.

The high values of zeta potential provide the stability to nanoparticles for resisting the aggregation, while the small potential leads to flocculate. As shown in Fig. 7, a high negative value at (-51.47 mV) was obtained from zeta analysis provides good stability of G-Fe/Cu-NPs, this stability derives from existing phenolic compounds in the ficus leaf extract \(^{17}\).

![Figure 7. Zeta potential analysis for sample of G-Fe/Cu-NPs.](image)

**Figure 7. Zeta potential analysis for sample of G-Fe/Cu-NPs.**

![Figure 8. Effect of H2O2 concentration at the dose of G-Fe/Cu-NPs, initial OG concentration, pH, temperature, and agitation rate were 0.4g/L, 50 mg/L, 4, 30°C, and 300 rpm.](image)

**Figure 8. Effect of H\(_2\)O\(_2\) concentration at the dose of G-Fe/Cu-NPs, initial OG concentration, pH, temperature, and agitation rate were 0.4g/L, 50 mg/L, 4, 30°C, and 300 rpm.**

In general, the removal efficiency of OG increases with increasing as the hydrogen peroxide...
concentration till reaching critical concentration and then the removal drops down. However, the excess of H₂O₂ of more than critical concentration would lead to a phenomenon known as a scavenging effect where the removal of dye decreases. Therefore, the H₂O₂ amount of 3.52 mmol/L was selected as the optimum concentration for subsequent experiments. This result was in agreement with a previous conclusion of removal Acid Black 1 reported by 33.

**Effect of Catalyst Doses**

The catalytic activity of the G-Fe/Cu-NPs prepared by ficus leaves extract was also studied. Therefore, a set of experiments was carried out by changing the dosage of nanoparticles in the range 0.4-1.6 g/L with maintaining the rest of operating conditions as H₂O₂ concentration, pH, initial OG concentration, temperature, and agitation speed at 3.52 mmol/L, 4, 50 mg/L, 30°C, and 300 rpm respectively. Accordingly, the removal rates of OG were 86.5, 87.6, 91.6, 83.7, and 69.3 % for doses 0.4, 0.7, 1.0, 1.3, and 1.6 g/L respectively, at 120 min period time. Fig. 9 clearly shows that the removal efficiency of OG increased with the rising amount of G Fe/Cu-NPs up to a certain dose, thereby the performance decreased with a higher catalyst amount indicating the uselessness of adding more quantities than the critical limit. The reason was related to the presence of ficus polyphenols compounds surrounded the catalyst surface, these compounds may be discharged to a working solution and reacted with 'OH radicals 8. On the other hand, the low amount of G-Fe/Cu-NPs led to a decrease in the removal performance of OG due to the low 'OH radicals’ concentration at this catalyst dose 34. Hence, the optimum catalyst dosage for the current study was 1 g/L. Similar behaviour in the removal of malachite green was found by 35.

**Effect of pH**

In the Fenton-like process, the removal of organic pollutants is highly influenced by pH value, due to its impact on the catalyst performance, stability of H₂O₂, and the generation of very reactive 'OH radicals. Fig. 10 demonstrates the OG removal efficiency at various pH 2, 3, 4, 5, and 7 along with 120 min, whereas the other experimental factors were kept constant. The OG removal efficiencies were 76.1, 92.5, 91.6, 17.3, and 9.3 % respectively. The results revealed that the removal efficiency of OG was decreased with raising the pH of the solution, and the best removal performance of OG was at pH 3. The explanation of this behavior belongs to the Fenton-like mechanism and production of 'OH, where the reaction between Fe⁶ with H₂O₂ is enhanced at the low pH values through the ions exchange to generating Fe³⁺ as the ions surrounded the surface of catalyst that in turn react with H₂O₂ and producing free radicals 'OH. In addition, the high acidic medium at the pH below 3 led to provide excessive amounts of H⁺ ions which, in turn, contributed to reducing the number of very reactive 'OH and therefore decreasing the degradation efficiency 36. The reduction of 'OH leads to the inability of converting Fe³⁺ to Fe²⁺ efficiently 37. Furthermore, the ferrous ions and hydrogen peroxide are unstable at higher pH values (above 4), therefore, the catalyst would be precipitated and generate complex byproducts (ferric hydroxocomplexes) which thereby leads to decomposition of the H₂O₂ and lowering the removal efficiency 38. Notably, the removal of OG dye at these higher pH values was conducted by coagulation or sorption, not the oxidation process 39, 38. Several studies have reported the same conclusion such as 40 and 41.

![Figure 9](image9.png)  
**Figure 9.** Effect of G-Fe/Cu-NPs dosage at H₂O₂ concentration, initial OG concentration, pH, temperature, and agitation rate were 3.52 mmol/L, 50 mg/L, 4, 30°C, and 300 rpm.

![Figure 10](image10.png)  
**Figure 10.** Effect of pH at G-Fe/Cu-NPs dosage, H₂O₂ concentration, initial concentration, temperature, and agitation rate were 1.0 g/L, 3.52 mmol/L, 50 mg/L, 30°C, and 300 rpm.
Effect of Initial OG Concentration

Generally, the degradation rate is a function of the initial concentration of dye, which makes it a crucial parameter to be considered for effective Fenton-like. Thus, several OG concentrations of 25, 35, 50, 65, and 75 mg/L were used to investigate the impact of these concentrations on degradation efficiency. The other experimental factors were fixed (G-Fe/Cu-NPs=1.0 g/L, pH=3.0, temperature=30 °C, agitation speed=300 rpm) and removal rates were 97%, 93.8%, 92.5%, 85%, and 76.3% respectively. Therefore, it is concluded along the 30 min of reactions that the removal efficiency of OG decreased from 94.4% to 75.5 as the increase of dye concentration from 25 to 75 mg/L thereby led to lowering the concentration of radicals Fig. 11. As a result, the degradation of OG diminishes with increases in the dye concentrations, which indicated that the production and scavengers of high reactive •OH could be affected by the higher dye concentration, where the •OH radicals scavenging effects occur slightly when the dye concentration rising without exceeding the optimum •OH radicals value 41. Therefore, this study selected 50 mg/L as the optimum initial concentration. Similar results were reported by 11.

Figure 12. Effect of presence NaCl on the removal OG at catalyst dose, H2O2 concentration, initial OG concentration, pH, temperature, and agitation rate were 1.0 g/L, 3.52 mmol/L, 50 mg/L, 3, 30°C, and 300 rpm.

Effect of Inorganic Salts

As a matter of fact, the real wastewater commonly contains amounts of inorganic salts such as NaCl which may impact the performance of dye degradation through the heterogeneous Fenton process. Therefore, various concentrations of NaCl were used to investigate the influence of the presence of these salts on OG dye degradation. Based on this purpose, 0.5, 10, and 50 g/L were introduced with maintaining the experimental conditions constant (G-Fe/Cu-NPs=1.0 g/L, H2O2=3.52 mmol/L, pH=3, initial concentration=50 mg/L, temperature=30°C). As shown in Fig. 12, the removal of OG efficiencies for the above NaCl concentration were 90%, 85.5%, and 77.5 respectively. It should be noted that the removal efficiency under the same conditions and without the presence of NaCl was 92.5%.

It was obvious that the presence of Cl− anion had a negative impact on the OG removal performance, and this effect is directly proportional to increasing the concentrations of these compounds. The decrease in the rate performance was attributed to the accumulation of Cl− anion on the G-Fe/Cu-NPs surface which led to blocking the active sites on this surface, another reason may belong to OH radicals scavenging by the effect of Cl− anion 42 according to the below equation:

\[ \text{Cl}^- + \cdot\text{OH} \rightarrow \text{Cl}^- + \text{OH}^- \]

The same behaviour of removal of sulfanilic acid azochromotrop dye by the Fenton process was reported by 43.

Effect of Temperature

Temperature plays an important role in dye degradation via a Fenton-like process. Therefore, further experiments were carried out to examine various temperature effects on the OG degradation by heterogeneous Fenton-like reaction. For this purpose, different temperatures (20, 30, 40, and 50 °C) were used with maintaining the other experimental conditions fixed (H2O2 = 3.52 mmol/L, catalyst dose =1.0 g/L, pH =3, initial OG concentration=50 mg/L, agitation speed =300 rpm). The results revealed that the removal efficiencies for the studied temperature were 87.2%, 92.5%, 95.3%, and 90.3% respectively at the end of 120 min as shown in Fig. 13. It can be notified that the raising in temperature led initially to improving the removal performance, moreover, the removal
efficiency of dye increased during the first 10 min from 72.7 to 92.1% for the temperature range of 20 to 50 °C. Therefore, the increase of removal performance was attributed to an increase in the rate of production of high reactive \(^{•}\)OH radicals \(^{44}\), where rising in the temperature could be led to motivate hydrogen peroxide and react efficiently with G-Fe/Cu-NPs which thereby growing the rate product of hydroxyl radicals \(^{45}\). Besides, the rate of \(^{•}\)OH radical and OG dye interactions was enhanced by the increasing temperature resulting in rapid degradation \(^{35}\). Anyway, it was evident that the rate of color removal at the end of 120 min diminished from 92.1 to 90.3% by the cause of decomposition of hydrogen peroxide at 50 °C reaction temperature \(^{8}\). These results agree with research papers published for the Fenton-like degradation of methylene blue \(^{46}\).

![Graph](image-url)  
**Figure 13.** Effect of temperature on the removal OG at G-Fe/Cu-NPs dosage, \(\text{H}_2\text{O}_2\) concentration, initial OG concentration, pH, and agitation rate were 1.0 g/L, 3.52 mmol/L, 50 mg/L, 3, and 300 rpm.

**Kinetic of degradation OG by Fenton-like reactions**

The kinetic models are used to analyze the degradation rate of pollutants. The mechanism of \(^{•}\)OH radical-mediated is the major function of the Fenton process for degradation of dye, where the reaction between catalyst and hydrogen peroxide can produce \(^{•}\)OH radicals which thereby attack the compounds of dye \(^{47}\). Hence, Fenton-like kinetics models were engaged to estimate the decolorization data, including the zero-order, first-order, and second-order \(^{41}\). Moreover, the Fenton-like process includes many-step reactions which made it a complex process \(^{48}\). Therefore, the removal kinetics of OG by the Fenton-like was investigated at the varying period time 0-30 min with experimental conditions such as concentration in the range of (25-75 mg/L), \(\text{H}_2\text{O}_2\) concentration of (1.7-5.28 mmol/L), a dosage of nanoparticles (0.4 - 1.6 g/L), initial pH (2 - 7), temperature (20 - 50°C), and co-existing NaCl (0.5 - 50 g/L) respectively for each factor. In order to investigate the above kinetics, Table 3 shows the kinetic equations were used:

| Model         | Equation               | Parameters                  |
|---------------|------------------------|-----------------------------|
| Zero-order    | \(C_t = C_o - k_st\)   | \(k_s\): zero-order rate constant (M/min). |
|               | \(t: \text{time (min)}\) |                             |
| First-order   | \(\ln C_t = ln C_o - k_1 t\) | \(k_1\): first-order rate constant (min\(^{-1}\)). |
| Second-order  | \(\frac{1}{C_t} - \frac{1}{C_o} = k_2 t\) | \(k_2\): second-order rate constant (g/mg.min). |

The value of \(k_0\) can be calculated from the slope of \(C_t\) against \(t\), the values of these parameters with the regression coefficient were inserted in Table 4. Obviously, the values regression coefficient \(R^2\) for all studied parameters of this model were not high enough indicating that they are poorly fitted with the zero-order model. On the other hand, the value of \(k_1\) can be obtained from the slope of the natural logarithm of \(C_t\) versus \(t\). As illustrated in Table 4 that the first-order was not fitted of degradation OG by the Fenton-like process due to had low values of \(R^2\). For the second-order kinetic model, the value of \(k_2\) can be calculated from the slope of \(1/C_t\) versus \(t\) graph. It can be seen from Table 4 that the linear fitting value of the regression coefficient \(R^2\) for the second order is higher than those for zero-order and first-order, which indicates that second-order kinetic model is a fitted model for OG kinetic degradation by the Fenton-like process catalyzed by G-Fe/Cu-NPs. Further, Fig. 14 shows the second-order kinetics for all studied parameters.
Figure 14. Second-order kinetic model for (a) initial OG concentration, (b) $H_2O_2$ concentration, (c) G-Fe/Cu-NPs doses, (d) pH, (e) temperature, and (f) co-existing inorganic salts.

Moreover, Table 4 shows that the increase of initial OG concentration from (25 to 75 mg/L) led to a decrease in the rate constant (0.166 to 0.007 M$^{-1}$.min$^{-1}$) attributed to lowering the hydroxyl radicals. Besides, when the amount of $H_2O_2$ was raised off (1.7 to 3.52 mmol/L) the removal of OG increased and that ascribed to increase the •OH. In contrast, the excess amount of peroxide (from 3.52 to 5.28 mmol/L) led to a decrease in the rate constant for the reason of •OH scavenging. Additionally, the high amount of catalyst resulted in an increase in the degradation rate due to increasing the concentration of •OH. Otherwise, high G-Fe/Cu-NPs concentrations resulted in a decrease in the degradation rate, this was attributed to scavenging the •OH by the high amount of Fe$^{3+}$ 44. Furthermore, the $k_2$ increased with increasing the temperature due to enhancing the reaction between G-Fe/Cu-NPs and $H_2O_2$ at the higher temperature thereby more formation of •OH. Otherwise, because of the thermal decomposition of $H_2O_2$, the rate of degradation was decreased at a temperature higher than 313K.

In conclusion, the kinetic behaviors of degradation OG followed two stages, the first one was fast degradation due to the reaction between hydrogen peroxide and ferrous ions, while the second stage is the slow progress of decolorization which can be attributed to accumulation of ferrous ions and decline their activity 49. Furthermore, Table 4 demonstrates that the second-order kinetic was the best fitted for OG degradation as evident from the higher values of correlation coefficient ($R^2$). The same result had been concluded by 50.
Table 4. The kinetics parameters for the Fenton-like reactions of the degradation OG.

| Parameter | RE% after 30 min | RE% after 120 min | Zero-order | First-order | Second-order |
|-----------|------------------|-------------------|------------|-------------|-------------|
| Initial OG Concentration (mg/L) | | | | | |
| 25 | 94.4 | 97 | 0.066 | 0.447 | 0.076 | 0.668 | 0.166 | 0.941 |
| 35 | 93.0 | 93.8 | 0.15 | 0.526 | 0.075 | 0.792 | 0.066 | 0.986 |
| 50 | 90.2 | 92.5 | 0.233 | 0.566 | 0.067 | 0.803 | 0.028 | 0.977 |
| 65 | 82 | 85 | 0.529 | 0.717 | 0.054 | 0.877 | 0.0122 | 0.978 |
| 75 | 75.5 | 76.3 | 0.327 | 0.738 | 0.044 | 0.872 | 0.007 | 0.952 |
| Average R² | | | | | |
| 1.7 | 50.9 | 53.5 | 0.134 | 0.52 | 0.017 | 0.576 | 0.002 | 0.641 |
| 2.64 | 61.7 | 67.7 | 0.148 | 0.561 | 0.025 | 0.655 | 0.004 | 0.762 |
| Initial H₂O₂ Concentration (mmol/L) | | | | | |
| 3.52 | 85.1 | 86.5 | 0.236 | 0.754 | 0.059 | 0.935 | 0.019 | 0.933 |
| 4.4 | 71 | 77.6 | 0.19 | 0.602 | 0.034 | 0.728 | 0.007 | 0.851 |
| 5.28 | 69.9 | 75.8 | 0.193 | 0.63 | 0.033 | 0.768 | 0.007 | 0.875 |
| G-Fe/Cu-NPs Doses (g/L) | | | | | |
| 0.4 | 85.1 | 86.5 | 0.236 | 0.754 | 0.059 | 0.935 | 0.019 | 0.933 |
| 0.7 | 84.2 | 87.6 | 0.228 | 0.718 | 0.054 | 0.921 | 0.016 | 0.976 |
| 1.0 | 89.8 | 91.6 | 0.234 | 0.674 | 0.068 | 0.921 | 0.012 | 0.975 |
| 1.3 | 80.7 | 83.8 | 0.258 | 0.72 | 0.048 | 0.906 | 0.011 | 0.982 |
| 1.6 | 63.5 | 69.3 | 0.17 | 0.88 | 0.03 | 0.952 | 0.006 | 0.962 |
| Average R² | | | | | |
| Initial pH | | | | | |
| 2 | 73.4 | 76.1 | 0.17 | 0.521 | 0.0334 | 0.639 | 0.008 | 0.784 |
| 3 | 90.2 | 92.5 | 0.233 | 0.566 | 0.067 | 0.803 | 0.028 | 0.978 |
| 4 | 89.8 | 91.6 | 0.234 | 0.674 | 0.068 | 0.921 | 0.028 | 0.975 |
| 5 | 14.6 | 17.3 | 0.042 | 0.851 | 0.004 | 0.867 | 0.0005 | 0.881 |
| 7 | 7.3 | 9.3 | 0.024 | 0.945 | 0.002 | 0.95 | 0.096 | 0.951 |
| Average R² | | | | | |
| 20 | 86.5 | 87.3 | 0.252 | 0.739 | 0.061 | 0.943 | 0.019 | 0.979 |
| Temperature (°C) | | | | | |
| 30 | 90.2 | 92.5 | 0.233 | 0.566 | 0.067 | 0.803 | 0.028 | 0.977 |
| 40 | 94.8 | 95.3 | 0.243 | 0.543 | 0.087 | 0.854 | 0.058 | 0.995 |
| 50 | 94.7 | 90.3 | 0.22 | 0.47 | 0.078 | 0.718 | 0.052 | 0.964 |
| Average R² | | | | | |
| 0 | 94.8 | 95.3 | 0.243 | 0.543 | 0.087 | 0.854 | 0.058 | 0.995 |
| NaCl (g/L) | | | | | |
| 0.1 | 90.2 | 92.5 | 0.235 | 0.577 | 0.069 | 0.773 | 0.03 | 0.865 |
| 10 | 94.8 | 95.3 | 0.208 | 0.636 | 0.054 | 0.828 | 0.018 | 0.95 |
| 50 | 94.7 | 90.3 | 0.182 | 0.674 | 0.033 | 0.804 | 0.006 | 0.916 |
| Average R² | | | | | |
| 6.07 | 0.814 | 0.931 |

**Thermodynamic of OG Degradation by Fenton-like Reactions**

The degradation of OG via heterogeneous Fenton-like reaction a catalytic by G-Fe/Cu-NPs was investigated at various temperatures (293, 303, 313, and 323 K) to determine the reaction spontaneity and the nature of the reaction. These properties of the OG degradation process can be found from the thermodynamic parameters of standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) that calculated by Eyring equation 31:

\[
\ln \left( \frac{k}{T} \right) = \left[ \ln \left( \frac{k_B}{h} \right) + \left( \frac{\Delta S^o}{R} \right) \right] - \frac{\Delta H^o}{R} \cdot \frac{1}{T} + ... 11
\]

Where \( k \) is the rate controls the reaction 51, \( T \) is the absolute temperature (K), \( k_B \) is the constant of Boltzman (1.3806 \times 10^{-23} \text{ J/K}), \( R \) is a general constant for gases (8.314 J/mol.K), and \( h \) is the Plank’s constant (6.0026 \times 10^{-34} \text{ J.s}).

Hence, \( \Delta S^o \) and \( \Delta H^o \) can be obtained through the intercept and slope of graph \( \ln(k/T) \) versus \( 1/T \) of Eyring equation as depicted in Fig. 15a, thereby \( \Delta G^o \) would be found from the below equation:

\[
\Delta G^o = \Delta H^o - T \Delta S^o \quad ... 12
\]

Furthermore, the activation energy can be obtained from the Arrhenius equation shown below

\[
\ln k = \ln A - \frac{E_a}{RT} \quad ... 13
\]
Where $E_a$ is the activation energy (kJ/mol), and $A$ is the Arrhenius constant (J/mol/K). $E_a$ represents the slope of plot between ln$k$ versus 1/T as shown in Fig. 15b.

In the current case, the rate constant of second-order ($k_2$) is the rate controls of the reaction. Therefore, the thermodynamic parameters of OG degradation are illustrated in Table 5.

**Table 5. Thermodynamic parameters for the removal of OG.**

| Parameter         | Value       |
|-------------------|-------------|
| $\Delta G^\circ$ (kJ/mol) | 84.03       |
| $\Delta H^\circ$ (kJ/mol)  | 27.168      |
| $\Delta S^\circ$ (J/mol.K) | -185        |
| $E_a$ (kJ/mol)  | 29.725      |
| $A$              | $3.97 \times 10^3$ |

The results for different studied temperatures illustrate that the Gibbs free energy $\Delta G^\circ$ had a positive value and lied in the range 81.259 - 86.8 kJ/mol (the average was 84.03 kJ/mol), thus confirms the nonspontaneous reaction nature, on the other hand, the positive value obtained for $\Delta H^\circ$ (27.168 kJ/mol) indicated that process of degradation OG via Fenton-like was an endothermic process, in addition, the value of $(\Delta S^\circ)$ was negative (-184.6 J/mol.K) which indicated the endergonic process. This result is consistent with the previous study of pretreated pulping effluent by the Fenton-like process reported by 52. Moreover, the Fenton-like reaction needed not high energy barrier as revealed from the value of $E_a$ (29.725 kJ/mol) this value of energy agreed with the research article studied by 34.

**Conclusion:**

In this work, Iron/copper nanoparticles are prepared by green synthesis using the extracts of ficus leaves and applied for the processing of orange G dye from wastewater. The good stable, amorphous, rounded and shaped as spherical of G-Fe/Cu-NPs are found with the size ranged 32-59 nm and the surface area was 4.452 m$^2$/g. The maximum degradation efficiency of OG is 94.8% in the first 30 min and reaches 95.3% at the final 120 min contact time. It is found that the best value of the heterogeneous Fenton parameters such as hydrogen peroxide concentration, G-Fe/Cu-NPs dose, pH, initial OG concentration, and the temperature is 3.52 mmol/L, 1 g/L, 7, 50 mg/L, and 40 $^\circ$C respectively. The kinetic study exhibits that the degradation of OG by Fenton-like reactions catalyzed by G-Fe/Cu-NPs fit the second-order kinetic model. Also, the reaction thermodynamic parameters clarify the non-spontaneity nature, endothermic process, and endergonic process. Finally, the value of activation energy (29.725 kJ/mol) illustrates that the Fenton-like reaction need not be as a high energy barrier.

**Authors’ declaration:**

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in Ministry of Science and Technology.

**Authors' contributions statement:**

A.K. H. has designed the experiments and corrected the manuscript, M. A. A. has supervised the work, critically revised the manuscript, and proved the manuscript, and I. M. L. has collected...
the data, analyzed/interpreted the results, and drafted the manuscript.

References:
1. Rosly NZ, Abdullah AH, Ahmad Kamarudin M, Ashari SE, Alang Ahmad SA. Adsorption of Methylene Blue Dye by Calix[6]Arene-Modified Lead Sulphide (Pbs): Optimisation Using Response Surface Methodology. Int J Environ Res Public Health. 2021; 18(2), 379. doi:10.3390/ijerph18020397.
2. Cai Z, Sun Y, Liu W, Pan F, Sun P, Fu J. An overview of nanomaterials applied for removing dyes from wastewater. Environ Sci Pollut Res. 2017; 24(19): 15882–15904.
3. Gičević A, Hindija L, Karačić A. Toxicity of azo dyes in pharmaceutical industry. Springer International Publishing: IFMBE Proc. 2020; 73(1): 581–587.
4. Imam SS, Muhammad AI, Babamale HF, Zango ZU. Removal of Orange G Dye from Aqueous Solution by Adsorption: A Short Review. J Environ Treat Tech. 2021; 9(1): 318–327.
5. Katheresan V, Kansedo J, Lau SY. Efficiency of various recent wastewater dye removal methods: A review. J Environ Chem Eng. 2018; 6(4):4676–4697.
6. Atiya MA, M-Ridha MJ, Saheb MA. Removal of aniline blue from textile wastewater using electrocoagulation with the application of the response surface approach. Iraqi J. Sci. 2020; 61(11): 2797–2811.
7. Önal ES, Yatkin T, Ergüt M, Özer A. Green Synthesis of Iron Nanoparticles by Aqueous Extract of Eriobotrya japonica Leaves as a Heterogeneous Fenton-like Catalyst: Degradation of Basic Red 46. Int. J Chem Eng Appl. 2017; 8(5): 327–333.
8. Hassan AK, Al-Kindi GY, Ghanim D. Green synthesis of bentonite-supported iron nanoparticles as a heterogeneous Fenton-like catalyst: Kinetics of decolorization of reactive blue 238 dye. Water Sci Eng. 2020; 13(4): 286–298.
9. AL-Saade K, Al- Saida S, Juad H. Degradation of Brilliant Green by Using a bentonite Clay- Based Fe Nano Composite Film as a Heterogeneous Photo-Fenton Catalyst. Baghdad Sci J. 2016; 13(3): 524–530.
10. Wang D, Zou J, Cai H, Huang Y, Li F, Cheng Q. Effective degradation of Orange G and Rhodamine B by alkali-activated hydrogen peroxide: roles of HO 2− and O 2.−. Environ. Sci. Pollut. Res. 2019; 26(2): 1445–1454.
11. Li R, Gao Y, Jin X, Chen Z, Megharaj M, Naidu R. Fenton-like oxidation of 2,4-DCP in aqueous solution using iron-based nanoparticles as the heterogeneous catalyst. J Colloid Interface Sci. 2015; 438(1): 87–93.
12. Pasinszki T, Krebsz M. Synthesis and application of zero-valent iron nanoparticles in water treatment, environmental remediation, catalysis, and their biological effects. Nanomaterials. 2020; 10(5): 917 doi:10.3390/nano10050917.
606–617.
26. Mohamed EA. Green synthesis of copper & copper oxide nanoparticles using the extract of seedless dates. Heliyon. 2020; 6(1): e03123. doi:10.1016/j.heliyon.2019.e03123.
27. Elahiemeh N, Zemati BA, Elhamophy A. Synthesis of a magnetic-based yolk-shell nano-reactor: A new class of monofunctional catalyst by CuO-nanoparticles and its application as a highly effective and green catalyst for A3 coupling reaction. Arab J Chem. 2020; 13(1): 3372–3382.
28. Khajjish M, Duvald A, Mehralian M, Ebrahimii AA, Khorsavi. Removal of reactive black 5 dye using zero valent iron nanoparticles produced by a novel green synthesis method. Pigment Resin Technol. 2020; 49(3): 215–221.
29. Nasrollahzadeh M, Sajadi SM, Khalaj M. Green synthesis of copper nanoparticles using aqueous extract of the leaves of Euphorbia esula L and their catalytic activity for ligand-free Ullmann-coupling reaction and reduction of 4-nitrophenol. Rsc Adv. 2014; 4(88): 47313–47318.
30. Shaker Ardakani L, Aiman AM, Taghizadeh S. Green synthesis of iron-based nanoparticles using Chlorophyllum comosum leaf extract: methyl orange dye degradation and antimicrobial properties. Heliyon. 2021; 7(2): e06159. doi:10.1016/j.heliyon.2021.e06159.
31. Wang X, Jiang C, Hou B, Wang Y, Hao C, Wu J. Carbon composite lignin-based adsorbents for the adsorption of dyes. Chemosphere. 2018; 206(17): 587–596.
32. Kuang Y, Wang Q, Chen Z, Megharaj M, Naidu R. Heterogeneous Fenton-like oxidation of monochlorobenzene using green synthesis of iron nanoparticles. J Colloid Interface Sci. 2013; 410(2): 67–73.
33. Kakavandi B, Takdastan A, Pourfadakari S, Ahmadmoozam M, Jorfi S. Heterocatalytic degradation of organic compounds using nanoscale zero-valent iron supported on kaolinite: Mechanism, kinetic and feasibility studies. J Taiwan Inst Chem. Eng. 2019; 96(3): 329–340.
34. Giwa ARA, Bello IA, Olabintan AB, Bello OS, Saleh TA. Kinetic and thermodynamic studies of fenton oxidative decolorization of methylene blue. Heliyon. 2020; 6(8): e04454. doi:10.1016/j.heliyon.2020.e04454.
35. N, Benamor A, Nasser MS, Ba-Abbad MM, El-Naas MH, Mohammad AW. Effective Heterogeneous Fenton-Like degradation of Malachite Green Dye Using the Core-Shell Fe3O4@SiO2 Nano-Catalyst. ChemistrySelect. 2021; 6(4): 865–875.
36. Sukla Baidya K, Kumar U. Adsorption of brilliant green dye from aqueous solution onto chemically modified areca nut husk. South African J Chem Eng. 2021; 35(1): 33–43.
37. Nadeem N, Zahid M, Tabasum A, Mansha A, Jilani A, Bhatti IA et al. Degradation of reactive dye using heterogeneous photo-Fenton catalysts: ZnFe2O4 and GO-ZnFe2O4 composite. Mater Res Express. 2020; 7(1): 015519 doi:10.1088/2053-1591/ab66ee.
38. Park JH, Wang JJ, Xiao R, Tafti N, DeLaune RD, Seo DC. Degradation of Orange G by Fenton-like reaction with Fe-impregnated biochar catalyst. Bioreason Techol 2018; 249(3): 368–376.
39. Xavier S, Gandhimathi R, Nidheesh PV, Ramesh ST. Comparison of homogeneous and heterogeneous Fenton processes for the removal of reactive dye Magenta MB from aqueous solution. Desalin Water Treat. 2015; 53(1): 109–118.
40. Bao C, Zhang H, Zhou L, Shao Y, Ma J, Wu Q. Preparation of copper doped magnetic porous carbon for removal of methylene blue by a heterogeneous Fenton-like reaction. Rsc Adv. 2015; 5(88): 72423–72432.
41. Ergüt M, Özer A. Heterogeneous Fenton-like decolorization of Procion Red MX-5B with iron-alginate gel beads as an effective catalyst. The Glas. 2019; 13(4): 297–304.
42. Ahmad ARD, Imam SS, Oh W Da, Adnan R. Fe3O4-Zeolite hybrid material as hetero-fenton catalyst for enhanced degradation of aqueous ofloxacin solution. Catalysts. 2020; 10(11): 1–19.
43. Hassan AK, Rahman MM, Chattopadhay G, Naidu R. Kinetic of the degradation of sulfanilic acid azochromotrop (SPADNS) by Fenton process coupled with ultrasonic irradiation or L-cysteine acceleration. Environ Technol Innov. 2019; 15(3): 100380 doi:10.1016/j.eti.2019.100380.
44. Hashemian S. Fenton-like oxidation of malachite green solutions: Kinetic and thermodynamic study. J Chem. 2013; 2013(4): 1–7 doi:10.1155/2013/809318.
45. Hussain S, Aneggi E, Goi D. Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: a review. Environ. Chem. Lett. 2021; 19(3): 2405–2424.
46. Durgut M, Kaya Ş, AŞÇi Y. Using Iron-Containing Metal Oxide as Catalyst for Heterogeneous Fenton Process in Textile Industry Wastewater. J ESOGU Engin Arch Fac. 2021, 29(1), 110–117.
47. Liang X, Zhong Y, He H, Yuan P, Zhu J, Zhu S et al. The application of chromium substituted magnetite as heterogeneous Fenton catalyst for the degradation of aqueous cationic and anionic dyes. Chem Eng J. 2012; 191(10): 177–184.
48. Emami F, Tehrani-Bagha AR, Gharanjig K, Menger FM. Kinetic study of the factors controlling Fenton-promoted destruction of a non-biodegradable dye. Desalination. 2010; 257(1-3): 124–128.
49. Santana CS, Ramos MDN, Vellioso CCV, Aguiar A. Kinetic evaluation of dye decolorization by fenton processes in the presence of 3-hydroxyanthranilic acid. Int. J. Environ. Res. Public Health. 2019; 16(9): 1602 doi:10.3390/ijerph16091602.
50. Yousef NA, Shaban SA, Ibrahim FA, Mahmoud AS. Degradation of methyl orange using Fenton catalytic reaction. Egypt J Pet. 2016; 25(3): 317–321.
51. El Haddad ME, Regti A, Laamari MR, Mamouni R, Saffaj N. Use of fenton reagent as advanced oxidative process for removing textile dyes from aqueous solutions. J Mater Environ Sci. 2014; 5(3): 667–674.
52. Lal K, Garg A. Utilization of dissolved iron as
catalyst during Fenton-like oxidation of pretreated pulping effluent. Process Saf. Environ Prot. 2017;

الخلاصة:
وتدرس هذه الورقة البحثية استخدام طريقة صديقة للبيئة وغير مكلفة لإزالة الصبغة البرتقالية (OG) من المحلول المائي، حيث تم استخدام مستخلص أوراق شجرة الفيكس لغرض التخليق الأخضر لجسيمات الحديد/نحاس ثنائية الفلز النانوية (G-Fe/Cu-NPs) بعد أن تم تحضيرها باستخدام مجهز القوة الذرية، مطياف إلكتروني، مطيافية الأشعة تحت الحمراء، وMJ. أظهرت التجربة التشخيص بأن شكل G-Fe/Cu-NPs كان مستدير شبه كروي ويتراوح الحجم بين 14-21 نانومتر بينما كانت مساحتها السطحية 24.2.2 متر²/غم. فيما بعد اُستخدمت الجسيمات النانوية الناتجة كعامل مساعد في تفاعلات الأكسدة الشبيهة بالفنتون. حيث أن كفاءة تحلل صبغة OG (العتمد 12.1%) لم تتأثر بشكل كبير عند تركيز الهيدروجين بيروكسايد (9.1-2.4 مللي مولاري)، كمية العامل المساعد (1.2-9.1 غم/لتر)، درجة الحامضية (4-1)، تركيز OG الابتدائي (42-12 ملغم/لتر) ودرجة الحرارة (21-41 درجة مئوية). أظهرت التجربة عند الظروف المثلى للهيدروجين بيروكسايد، كمية العامل المساعد، درجة الحامضية، ودرجة الحرارة التي كانت 1.2 مللي مولار، 9 غم/لتر، 1، و 21 درجة مئوية على التوالي خلال زمن مداره 30 دقيقة. أيضاً أظهرت النتائج دراسة التفاعل الحراري بأن ازالة صبغة OG تتبع نموذج حركي من الدرجة الثانية. أخيراً، تم دراسة الديناميكية الحرارية لتفاعل وخلصنا إلى أن التفاعل ماصاً للحرارة ولله طاقة تنشيط مقدارها 41.142 كيلوجول/مول.

الكلمات الإفتتاحية: شبيهة بالفنتون، التخليق الأخضر، جسيمات الحديد/نحاس النانوية، الحركة، الصبغة البرتقالية