Enhanced reactivity of the CuO-Fe₂O₃ intimate heterojunction for the oxidation of quinoline yellow dye (E104)

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Abstract
This research work describes the degradation of quinoline yellow (QY) in aqueous solutions by the heterogeneous Fenton and photo-Fenton processes in the presence of CuO/Fe₂O₃ photocatalyst. CuO/Fe₂O₃ derived from LDH structure was synthesized by the co-precipitation method. The physiochemical characteristics of CuO/Fe₂O₃ were described by XRD, TEM/SEM, BET surface area, and FTIR techniques. The effects of pH, H₂O₂ concentration, dye concentration, catalyst dose, reaction temperature, and reusability of catalyst on the QY decolorization efficiency were studied. The results indicated that a complete removal of QY was achieved within 150 min, when the H₂O₂ and QY concentrations were 27.6 mM and 100 mg/L, respectively. The rate constants for QY removal by the heterogeneous Fenton system were calculated, and the experimental data were found to fit the pseudo-first order model. Under optimal conditions, the rate constants were, respectively, 0.02032 and 0.01715 min⁻¹ for the photo-Fenton and Fenton systems; this means that the addition of light has not a noticeable effect.

Keywords Quinoline yellow · CuO/Fe₂O₃ · Intimate heterojunction · Hydrogen peroxide · Heterogeneous catalysis

Introduction
A wide variety of colors from natural and synthetic origin are added to food products in order to make them more aesthetic to consumers and to restore their original appearance, lost during the production process. However, most dyes obtained from natural sources are unstable and can easily degrade during food processing. On the other hand, the dyes of synthetic origin are widely used, not only because of their stability, but also because of their very low production cost compared to those of natural origin (Saleh et al. 2016; Yamjala et al. 2016). Therefore, It is difficult to remove the synthetic dyes from the industrial effluent, because they are stable to light and heat, and biologically non-degradable.

The presence of dyes in aqueous ecosystems decreases photosynthesis by preventing the penetration of light into deeper layer by deteriorating the quality of the water and reducing the solubility of the gas. In addition, the dyes and/or their degradation products can be toxic to flora and fauna (Bhatia, 2007; Abdul Rahman et al. 2018). Hence, the conventional methods used in sewage treatment, such as the primary and secondary treatment systems, are unsuitable. Therefore, it is necessary to use tertiary treatment to remove them (Nassar and Magdy 1997). Advanced oxidation processes (AOPs), like Fenton and photo-Fenton processes, could be a good technique to treat and eliminate dyes. These processes appear to have the capacity to completely decolorize and partially mineralize the textile industry dyes in a short reaction time (Lucas and Peres, 2006).

The heterogeneous catalyst process in the advanced oxidation process (AOP) is used for degradation of organic pollutants; among the catalysts used are: metallic oxides such as α-MnO₂ (Zhang et al. 2012), β-Fe₂O₃ (Zhang et al. 2019), CoO, CuO (Shen et al. 2015), NiO (Huo et al. 2020), ZnO (Miao et al., 2013) …, the mixed metal oxides to improve
the catalytic reactivity (Deutschmann et al. 2009; Bousalah et al. 2021) and the heterosystems (Mohaghegh et al., 2014; Mohaghegh et al., 2015; Tasviri et al., 2016; Faraji et al., 2018). Recently, many researchers have focused on the utilization of iron oxide material due to their being environmentally friendly, easily obtainable, and for their high surface reactivity and magnetic properties (Boudjemaa et al., 2009; Boudjemaa and Trari, 2010). It is demonstrated that iron combined with copper to obtain a mixed oxide improved their photocatalytic properties, compared to the iron oxide (Sun et al. 2020).

However, mixed oxides CuO/Fe2O3 are largely investigated to improve the material reactivity, the example of the dye photodegradation (Alp et al. 2019; Sukma Hayati and Ratnawulan, 2019; Pan et al. 2013), the thermal decomposition of ammonium perchlorate (Hao et al. 2019; Wang et al. 2019), the catalytic decomposition of H2O2 (Amin et al. 2016), the CO removal and oxidation (Lamai et al., 2016), the n-hexane oxidation (Cao et al. 2008), and the CO removal and oxidation (Todorova et al. 2021) and the heterosystems (Mohaghegh et al., 2014; Tasviri et al., 2016; Faraji et al., 2018). Recently, many researchers have focused on the utilization of iron oxide material due to their being environmentally friendly, easily obtainable, and for their high surface reactivity and magnetic properties (Boudjemaa et al., 2009; Boudjemaa and Trari, 2010). It is demonstrated that iron combined with copper to obtain a mixed oxide improved their photocatalytic properties, compared to the iron oxide (Sun et al. 2020).

Quinoline yellow (QY) named also: E104, CI Food Yellow 13, C.I. 47005 is a quinophthalone dye composed of a mixture of disulfonates (80%), monosulfonates (15%), and trisulfonates (7%) as sodium salts. QY with a formula of C18H9NNa2O8S2 is obtained by the sulfonation of 2-(2-quinolyl)-1, 3 indandione. QY is a yellow powder or granule, soluble in water, sparingly soluble in ethanol. It is not permitted as food colorant in the US (Socaciu 2008). The QY is one of the most widely dye used in the food coloration (Damant 2011). It is well utilized in drug and cosmetic industries (Güray et al., 2020), jellies, caramels, processed seafood (e.g., ca2004 viar), lipsticks, hair products, colognes, liquors, and a wide range of medications (Macioszek and Kononowicz 2004). QY is well exploited as a synthetic coloring agent in food and drink products, as well as in cosmetics (Khan et al. 2020), for dyeing wool, silk, and nylon (Björkner and Niklasson 1983). However, Björkner and Niklasson demonstrated that QY can cause dermatitis and allergic reactions in some individuals (Björkner and Niklasson 1983). Moreover, the QY exhibits genotoxicity which leads to both damage to human DNA if metabolized or absorbed through the skin (Macioszek and Kononowicz 2004; Zhao et al. 2011; Drumond Chequer et al., 2014) and increased hyperactivity in children aged 8 to 9 years (McCann et al. 2007). For these reasons, the employ of QY in foods and medicines has been excluded in some countries, as Australia, USA, Norway, and Japan (Macioszek and Kononowicz 2004; Roy et al. 2018), but it is still utilized in many countries around the world.

Several processes have been suggested for the removal of QY from wastewater, including simultaneous ultrasound-assisted using zinc oxide nanoparticle loaded on activated carbon (ZnO–NP–AC) (Karimi et al. 2019), the photocatalytic degradation using Ag3PO4, TiO2, and ZnO photocatalysts (Regulsk et al. 2016; Gupta et al. 2012; Salem et al., 2009), the ultrafiltration technique by polymeric membranes (Popa et al. 2017), the adsorption and the desorption studies (Gupta et al. 2005), removal from solutions and sludge by using polyelectrolytes and polyelectrolyte–surfactant complexes (Petzold and Schwarz 2006), and in the electrochemical sensor based on carbon nanotube–modified electrode (Zhao et al. 2011).

The aim of the present work focused on the study of the catalytic performance of CuO/Fe2O3 via the removal of food dye. Herein, we synthesized the intimate heterojunction CuO/Fe2O3 and further investigated the catalytic activity for heterogeneous Fenton and photo-Fenton. The catalytic reactivity was evaluated by the degradation of Quinoline yellow (QY), widely used in the food industries. The effects of operating parameters including the pH, H2O2 concentration, dye concentration, catalyst dose and its reuse, the irradiation, and the temperature on the degradation kinetics were also reported and discussed.

**Experimental**

**Analytical reagents**

All chemicals and reagents; tartrazine (high purity biological stain), iron(III) nitrate nonahydrate (Fe(NO3)3·9H2O, 98%, Panreac), copper(II) nitrate hexahydrate (Cu(NO3)2·3H2O, 99%, Merck), hydrogen peroxide (H2O2, 30%, VWR Chemicals), hydrochloric acid (HCl, 37%, Analar Normaour VWR Prolabo Chemicals), and sodium hydroxide (NaOH, 85–100%, Biochim Chimo pharma) were used without any purification.

**Catalyst preparation**

The CuO/Fe2O3 composite was synthesized by co-precipitation method. Five grams Cu(NO3)2, 6H2O, and 4.18 g Fe(NO3)3, 9H2O (initial atomic ratio Cu2+/Fe3+ = 2:1) were dissolved into 50 mL distilled water. Then, the obtained mixture was added dropwise to NaOH (1N) under vigorous stirring at room temperature until the pH at ~10 by adjusting the flow of this solution. The suspension, thus obtained, was kept at 60 °C for 15 h. The precipitate formed was filtered and washed with deionized water until pH ~7 of the filtrate and then dried at 70 °C for 24 h. Finally, the obtained precursor was calcined at a constant heating rate of 5 °C min−1 up to 600 °C for 4 h to produce the CuO/Fe2O3.
Characterization techniques

The chemical composition and scanning electron microscopy (SEM) of the material were determined by EDX FEI QUANTA F Environmental apparatus equipped with a backscatter detector (BSE) at 15 kV. The crystallization phase of the sample obtained was studied using powder X-ray diffraction (PXRD). The analysis was carried out in a Siemens D-5000 diffractometer with a monochromator, using CuKα radiation (λ = 0.154056 nm) over a range of 5–70° (2θ), with step of 0.05° and 28 by step. The infrared spectra were obtained using a FTIR spectrophotometer (Alpha Bruker FTIR). Sample was prepared by mixing the powdered solids with potassium bromide, KBr (the blank) in 15:85 ratio to get transparent pellet auto supported on the different solids at 10 ton pressure. The infrared spectrum was recorded both over the wave number range from 4000 to 400 cm⁻¹. The textural characteristics, such as BET specific area, pore volume, and average pore diameter (BJH method) were determined using conventional nitrogen adsorption/desorption method at −196 °C in a Micromeritics Tristar 3000. Prior to nitrogen adsorption, the sample was outgassed for 8 h at 250 °C to evacuate the physically adsorbed moisture. Scanning electron microscopy (SEM) experiment was performed with a Zeiss Supra 55 VP FEG microscope with an accelerating voltage of 30 kV. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2000EX-II instrument at an accelerating voltage of 120 Kv; the sample was dispersed in ethanol, and carbon-coated copper grids were used as the sample holder. The zeta potential was measured by the use of 0.1 g of the prepared material in 100 mL of distilled water. The sample was transferred to a zeta cell and measured at 25 °C with an applied voltage of 150 V using a Zeta Sizer. The suspensions must be kept in constant stirring, at room temperature, for 48 h, in order to determine the final pH. The pH of each (values between 2 and 12) by adding NaOH or HCl solution (0.1 M); 0.15 g was added to the adsorbent. The suspensions must be kept in constant stirring, at room temperature, for 48 h, in order to determine the final pH. The suspensions were collected in each 15 min and analysis by a UV/visible spectrometer (T60 UV/Vis, PG. Instruments) at 413 nm.

Results and discussion

Characterization

The stoichiometry of the synthesized Cu/Fe was verified by the SEM/EDX analysis. The molar fraction of the cations Cu²⁺/Fe³⁺ in the sheet is reported in Table 1. As can be seen, the Cu²⁺/Fe³⁺ atomic ratio was similar to that expected. The PXRD pattern of Cu/Fe is shown in Fig. 1. The typical peaks indexed with 2θ approximately at 35°, 38°, 48°, 53°, 58°, 61°, and 66°, which were attributed to CuO phase (JCPDS 89-2529) whereas those at 2θ = 24°, 33°, 41°, 56°, 63°, and 68° indicate the presence of Fe₂O₃ (JCPDS 89-0595). The FTIR spectrum of CuO/Fe₂O₃ shows absorption bands at 3428 and 1647 cm⁻¹ ascribed to the O–H stretching mode (νO–H) and to the HOH deformation mode (δH–O–H), respectively (Ohnishi et al. 2007) (Fig. 2). Also, bands located at 2924 and 2850 cm⁻¹ are attributed to H₂O-NO₃ bridging vibration (Hajibeygi et al., 2017). The bands at 475 cm⁻¹ was ascribed to CuO vibration, whereas that at 578 cm⁻¹ corresponding to the Fe³⁺ and O²⁻ bonds stretching in the FeO₄ tetrahedron (Hao et al. 2015). The adsorption–desorption isotherms of the CuO/Fe₂O₃ is presented in Fig. 3. According to the International Union of Pure and Applied Chemistry classification, the sample exhibited type IV adsorption isotherms with a hysteresis loop in the relative pressure region around 0.4–0.9, which is characteristic of mesoporous materials (Sing et al., 1985). The BET specific surface areas and the pore diameter calculated by the Barrett–Joyner–Halenda (BJH) theory were listed in Table 1. The morphology of the CuO/Fe₂O₃ was revealed by SEM (Fig. 4a). The CuO/Fe₂O₃ sample consists of many irregular spherical grains of different colors; these observations confirm the formation of a mixed oxide CuO/Fe₂O₃. TEM image of the CuO/Fe₂O₃ is shown in Fig. 4b; it is observed

Fenton experiments

The degradation tests of the QY (E104) were performed during a series of experiments in batch method at temperature of 20 °C. In this oxidation tests, 100 ml of QY (100 mg/L) was maintained under continuous stirring (250 rpm); hydrogen peroxide was injected simultaneously with the material. This latter step was considered as t₀ (time zero). The samples

Table 1 Chemical composition and textural properties of Cu/Fe sample

| Sample           | Cu-Fe-LDH |
|------------------|-----------|
| Theoretical ratio Cu²⁺/Fe³⁺ | 2         |
| Cu²⁺/Fe³⁺ molar ratio  | 1.80      |
| BET surface area (cm²/g)   | 9         |
| Langmuir surface area (m²/g) | 13        |
| BJH pore volume (cm³/g)    | 0.022     |
| BJH pore size (nm)         | 12        |
| Crystallite size (nm)      | 23.18     |
that CuO/Fe$_2$O$_3$ is composed by two different morphology particles, where several Fe$_2$O$_3$ hexagonal morphology can be observed on and around the CuO spherical structure. For the zeta potential (ZP), the average (over five measurements) was (−38.96 mV), which may indicate the presence of a negative charge on the surface of CuO/Fe$_2$O$_3$. A negative surface charge favors the adsorption of cationic and basic dyes, which can be explained by the increased electrostatic attraction force (Guedes et al. 2009). The pH$_{PZC}$ of the material is 9 (Fig. 5). This makes its charge positive for a lower pH and negative for a higher pH.

**Optimization of QY removal**

**Effect of pH**

Heterogeneous Fenton oxidation is one of the advanced oxidation processes which has gained widespread acceptance for higher removal efficiency of pollutants under wide range of pH compared to homogeneous reactions (Atalay and Ersöz, 2016). The catalytic degradation of QY (100 ml, 100 ppm), in the presence of [H$_2$O$_2$]$_0$ = 27.6 mM, and using CuO/Fe$_2$O$_3$ (0.01 g/L) was studied by varying pH in the
range (3–10). The pH value affects the oxidation of organic substances both directly and indirectly. The Fenton reaction is strongly pH dependent. The pH value influences the generation of HO° and thus the oxidation efficiency (Behnajady et al. 2007). The results illustrated in Fig. 6 indicate that the degradation of QY is significantly influenced by the pH of the solution, and the process is more efficient in acid medium. The pH = 3 shows the best rate of dye removal (100%) after 150 min of reaction may be due to the substantial production of HO° (Khataee and Pakdehi 2014; Bousalah et al., 2019). Thus, the results clearly show that the extent and efficiency of the degradation of QY decreases with the increase in the pH value (i.e., 80.5, 64.2, 56.8, and 55.2% for pH = 5, 6.5, 8, and 10, respectively) leading to the decomposition of H₂O₂ (Eq. (1)) (Szpyrkowicz et al. 2001). On the other hand, the oxidation rate decreases due to the decrease of HO° (Hameed and Lee 2009).

\[
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\]  

(1)

The pHzc of CuO/Fe₂O₃ is 9, makes its charge positive for lower pH values and negative for higher pH values. The QY molecule is anionic (its mobile ion is Na⁺ in basic medium and

Fig. 4 SEM and TEM images of CuO/Fe₂O₃

Fig. 5 The pHzc of the material

Fig. 6 Effect of pH value on the degradation of dye: \([\text{Dye}]_0 = 100\ \text{mg/L}, \ [\text{H}_2\text{O}_2]_0 = 27.6\ \text{mM}, 0.01\ \text{g of catalyst}, \ \text{and } T = 20\ \text{°C}\)
H⁺ in acidic medium). For the pH below 9, there is an attraction between the catalyst and dye, thus promoting the catalytic action due to the fact that the electrostatic repulsion-attraction between the catalysts and the dyes improves the degradation rate.

**Effect of hydrogen peroxide concentration**

The effect of the oxidizing agent dose on the catalytic oxidation process was investigated by varying the H₂O₂ concentrations from 9.2 to 55.2 mM under the following conditions: [Dye]₀ = 100 mg/L, pH = 3, catalyst amount = 0.01 g, and at T = 20 °C. The results regrouped in Fig. 7 show a great influence of the H₂O₂ concentration on the process catalyzed by CuO/Fe₂O₃. At the beginning of the reaction, the discoloration increases with H₂O₂ dose may be due to the formation of more radicals, in agreement with literatures results (Hameed & Lee 2009; Sohrabi et al. 2014). But above 36.8 mM, the effect of H₂O₂ is not significant. So, after 150 min of reaction, the removal rates were 97.86, 100, 100, and 100% for the H₂O₂ concentrations of 27.6, 36.8, 46, and 55.2 mM, respectively. This difference may be due to the fact that with a higher concentration of H₂O₂, the degradation of °OH will have occurred (Aravindhan et al. 2006; Ramirez et al. 2007; Hameed and Lee 2009).

However, the higher concentrations of H₂O₂ in the presence of additional HO° leads to the formation of less reactive hydroperoxyl radicals (HO₂°) and thereby decrease the yield of the dye degradation (Eqs. (2) and (3)) (Najjar et al. 2007; Hameed and Lee 2009).

\[
\text{H}_2\text{O}_2 + \text{HO}° \rightarrow \text{HO}_2° + \text{H}_2\text{O} \quad (2)
\]

\[
\text{HO}_2° + \text{HO}° \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (3)
\]

**Effect of QY concentration**

The effect of the initial concentration of QY on the degradation rate was studied by varying the initial concentration of QY from 10 to 100 mg/L under the following operating conditions: pH = 3, [H₂O₂]₀ = 27.6 mM, catalyst amount = 0.01 g at T = 20 °C. The results reveal that the increase of QY concentration decreases the removal efficiency (Fig. 8). Thus after 60 min of reaction, the discoloration rates are total for the concentration of 10 and 30 mg/L, whereas the rates decreased to 87.15, 64.7, 61.8, and 53.5% for QY concentrations of 50, 70, 80, and 100 mg/L.

The rate constant decreases with increasing dye concentration, i.e., values of 0.0504, 0.04108, 0.02731, 0.02541, 0.02185, and 0.02016 min⁻¹, respectively for 10, 30, 50, 70, 80, and 100 mg/L. This behavior is one of the characteristics of advanced oxidation processes (Daneshrav et al. 2008). The increase of QY concentration would decrease the probability of the reaction between QY molecules and °OH (Zhang et al. 2009). So, the amount of reactive radicals is not enough to oxidize the excessive concentration of QY due to the constant rate of the reactive species formed during the reaction (Dulman et al. 2012; Khataee and Pakdehi 2014).

**Effect of the catalyst dose and its reuse**

To clarify the role of the catalyst in the degradation of QY by heterogeneous Fenton, the experiments were carried out to study the variations in the rate of discoloration at different concentrations of the catalyst, (0–0.4 g/L) under the following experimental conditions: 100 mg/L dye, [H₂O₂]₀ = 27.6 mM, pH = 3, and T = 20 °C. The results show that the degradation of QY is strongly dependent on the dose of catalyst (Fig. 9). The degradation of QY
was very slow in the absence of the catalyst; only 13.2% of reaction efficiency was obtained after 60 min. Nevertheless, an increase to 34.6% is achieved when 0.05 g/L of catalyst was added, thus demonstrating the vital role of the catalyst in the rapid formation of HO° promoted by its surface. Further increase of the catalyst dose from 0.1 to 0.4 g/L could greatly increase the QY degradation efficiency from 53.5 to 68.1% after 60 min of reaction. The improved degradation rate may be due to the increased availability of the active sites, which increases the number of QY molecules adsorbed and subsequently degraded (Song et al. 2008; Szeto et al. 2014; Sun et al. 2018; Bousalah et al. 2019; Hamza et al. 2020; Bousalah et al. 2021). The kinetic study shows that the degradation of the dye by oxidation with H₂O₂ catalyzed by our catalyst follows the pseudo-first order (Table 2). The degradation rate constant increases from 0.00222 to 0.02066 min⁻¹, when the catalyst dose passed from 0 to 0.4 g/L.

The stability of the catalyst was studied by the reuse of the same sample for three successive times and before each reuse; the catalyst was washed with deionized water and dried at 100 °C. The results show that the rate of QY removal decreases slightly between the first and third cycles (Fig. 10). At 150 min, the degradation efficiency obtained for the first, second, and the third cycles was 100, 95.7, and 93.6%, respectively.

![Fig. 9](image1.png) Effect of the catalyst dose: 100 mg/L of dye (), [H₂O₂]₀ = 27.6 mM, pH = 3, and T = 20 °C

| Catalyst rate (g/L) | 0    | 0.05 | 0.1  | 0.2  | 0.3  | 0.4  |
|---------------------|------|------|------|------|------|------|
| R²                  | 0.9991 | 0.9236 | 0.9273 | 0.9319 | 0.9407 | 0.9523 |
| K (min⁻¹)           | 0.0022 | 0.0118 | 0.0168 | 0.0177 | 0.0192 | 0.0206 |

The effect of the temperature was studied in the range of 20–40 °C. The results demonstrated that the removal efficiency of QY was accelerated by a rise in temperature (Fig. 11). So, the efficiency increased from 53.5 to 100% with increasing temperature up to 40 °C, which improved the generation rate of °OH, and therefore enhancing the decolorization of QY (Ertugay and Acar 2017; Sun et al. 2009), indicating that the catalytic degradation of QY is an endothermic process. This may be due to the facilitated interaction of the catalysts with H₂O₂ to yield ROS (reactive oxygen species) HO° and the accelerated molecular diffusion at higher reaction temperatures (Sun et al. 2018). The high temperature leads to an increase in the rate of reaction between H₂O₂ and any form of ferrous/ferric ion, thus increasing the rate of generation of oxidizing species such as HO° radical or high valence iron species (Chen and Zhu 2007; Daud et al. 2010).

### Kinetic model for the removal of QY

The oxidation of QY in the presence of CuO/Fe₂O₃ for the various temperatures studied follows a pseudo first-order model; and it can be described by the following relation (Eq. (4)):

![Fig. 10](image2.png) Reusability test of catalyst (reaction conditions: 100 mg/L of dye, [H₂O₂]₀ = 27.6 mM, pH = 3, T = 20 °C, in 240 min)
where \( C \), \( t \), and \( K_{\text{app}} \) are, respectively, QY concentration, time, and apparent rate constant.

The linear plots of \( \ln \left( \frac{C_0}{C} \right) \) versus time are plotted, and \( K_{\text{app}} \) was determined from the slopes (Fig. 12). The result shows that the dye removal by oxidation with \( \text{H}_2\text{O}_2 \) catalyzed by \( \text{CuO}/\text{Fe}_2\text{O}_3 \) follows a pseudo-first order. The apparent rate constants \( K_{\text{app}} \) and the coefficient of determination \( R^2 \) at different temperatures are regrouped in Table 3. The apparent activation energy of QY removal by \( \text{H}_2\text{O}_2 \) in the presence of \( \text{CuO}/\text{Fe}_2\text{O}_3 \) is calculated from the linear form of the Arrhenius equation (Eq. 5)

\[
\ln K_{\text{app}} = \ln K_0 - \frac{E_a}{RT}
\]  

where \( K_0 \) is the pre-exponential factor, and \( E_a \) is the apparent activation energy (\( \text{J} \, \text{mol}^{-1} \)); \( R \) is the ideal gas constant (8.314 \( \text{J} \, \text{mol}^{-1} \, \text{K}^{-1} \)); \( T \) is the reaction absolute temperature

**Fig. 11** Temperature of effect on the reaction efficiency: 100 mg/L of dye, \([\text{H}_2\text{O}_2]_0 = 27.6 \text{ mM}, \text{pH} = 3\), and 0.01 g of catalyst

**Fig. 12** \( \ln \left( \frac{C_0}{C} \right) \) versus time (\( t \)) under conditions: 100 mg/L of dye, \([\text{H}_2\text{O}_2]_0 = 27.6 \text{ mM}, \text{pH} = 3\), and 0.01 g of catalyst

\[
-d\frac{C}{dt} = K_{\text{app}} C
\]  

**Fig. 13** Validation of Arrhenius law for the degradation of quinoline yellow by hydrogen peroxide in the presence of CuO/Fe\(_2\)O\(_3\)

**Fig. 14** Comparative study of the degradation of the dye by Fenton and photo-Fenton systems under optimal conditions: \([\text{Dye}]_0 = 100 \text{ mg/L}, [\text{H}_2\text{O}_2]_0 = 27.6 \text{ mM}, 0.01 \text{ g of catalyst, and } T = 20 \text{ °C}\)

---

**Table 3** Apparent rate constants \( K_{\text{app}} \) and coefficient of determination \( R^2 \) of dye degradation by hydrogen peroxide at different temperatures

| \( T \)(°K) | \( K \)(min\(^{-1}\)) | \( R^2 \) |
|---|---|---|
| 293 | 0.0172 | 0.9335 |
| 298 | 0.0199 | 0.9021 |
| 303 | 0.0227 | 0.9187 |
| 308 | 0.0329 | 0.9387 |
| 313 | 0.0441 | 0.9969 |
(K). After plotting ln Kapp as a function of 1/T (Fig. 13), the value of the apparent activation energy was determined from the slope of regression line. The apparent activation energy of catalytic decomposition of QY is 36.36 kJ/mol. The value of the activation energy confirms that the oxidation mechanism of QY is radical (Yeddou et al. 2010; Bousalah et al. 2021).

**Photo-Fenton degradation**

Figure 14 presents the decoloration efficiency of QY as a function of time under two different systems, Fenton and photo-Fenton. The irradiation source used for the photo-Fenton was a tungsten lamp (200 W). The results reveal a significant increase in the rate and the time of discoloration. The total degradation (100%) was recorded after 105 and 135 min for photo-Fenton and Fenton process, respectively with rate constants of 0.02032 and 0.01715 min⁻¹. In the photo-Fenton, the additional sources of °OH should be considered: through photolysis of H₂O₂ (Eq. (6)), through reduction of Fe³⁺ ions under UV light (Eq. (7)), and through the reduction of Cu²⁺ ions under UV light (Eq. (8)) (Peternel et al. 2007). However, as it has been observed the presence of CuO plays an important role in the photo-Fenton process. This result can be explained by the activation of CuO in the presence of light to generate the pair electron-hole and contribute to the degradation of QY by a photo-Fenton mechanism (Taufik and Saleh 2016).

\[
\begin{align*}
H_2O_2 + \nu & \rightarrow HO^\circ + HO^\circ \\
Fe^{3+} + H_2O + \nu & \rightarrow Fe^{2+} + HO^\circ + H^+
\end{align*}
\]  

(6) (7)

\[
Cu^{2+} + \nu \rightarrow Cu^+
\]  

(8)

**Oxidative degradation mechanism “heterogeneous Fenton-like”**

On the basis of all the experimental results and references of the previous work, we have proposed a possible mechanism of heterogeneous Fenton-type reaction in the presence of CuO/Fe₂O₃/H₂O₂ system (see Eqs. (9)–(16)). H₂O₂ molecules absorbed on the inner surface of CuO/Fe₂O₃ can reduce Fe³⁺ to Fe²⁺ ions, according to the Fenton-type process, and the formed Fe²⁺ ions can react with Cu²⁺ ions to generate Cu⁺ and Fe²⁺ ions (Eqs. (9) and (10)) (Li et al., 2017). Thus, Cu⁺ and Fe³⁺ ions react with other H₂O₂ molecules to promote the generation of highly active HO° for dye degradation (Eqs. (11) and (12)) (Li et al., 2017). These equations explain the exceptional performance of the heterojunction due to the presence of Cu and Fe as two catalytically active sites that can generate larger amounts of the HO° radicals responsible for dye degradation. On the other hand, the excess of H₂O₂ can react with Cu²⁺/Fe³⁺ ions to form Cu²⁺–H₂O₂ and Fe³⁺–H₂O₂ complexes and generate HO₂° (Eqs. (13) and (14)) (Jin et al. 2017). These equations can explain that the further increase of H₂O₂ dosage leads to the production of HO₂° radicals, which are less active than HO° radicals.

\[
\begin{align*}
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + H^+ + HO_2^\circ \\
Fe^{2+} + Cu^{2+} & \rightarrow Fe^{3+} + Cu^+
\end{align*}
\]  

(9) (10)

\[
Cu^{2+} + H_2O_2 \rightarrow Cu^{2+} + OH^- + HO^o
\]  

(11)

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^o
\]  

(12)

\[
Fe^{4+} - O - O - Fe^{3+} + 2H_2O_2 \rightarrow Fe^{3+} - O - O - Fe^{3+} + 2H_2O_2 + 2H^+
\]  

(13)

\[
Cu^{2+} - O - O - Cu^{2+} + 2H_2O_2 \rightarrow Cu^{2+} - O - O - Cu^{2+} + 2H_2O_2 + 2H^+
\]  

(14)

**Conclusion**

CuO/Fe₂O₃ heterojunction was prepared by a simple co-precipitated process and examined by different analytical techniques. It was found to be a low-cost and efficient catalyst for Fenton and Fenton-like oxidation reaction, especially for the degradation of QY in aqueous solution. In the optimum condition of: 27.6 mM of H₂O₂ and 100 mg/L of dye, pH = 3, and 0.01 g of the catalyst at 20 °C, the decolorization efficiency of 53.5 and 100% was achieved within 60 and 150 min of the reaction. The kinetics study indicated that the decolorization kinetics of QY followed the first-order kinetics. Most importantly, the regeneration of the heterojunction is quite easy and has an excellent recyclability (93.6 %), even after three consecutive cycles. The apparent activation energy Ea, for the decolorization of QY by Fenton oxidation was determined to be 36.36 kJ mol⁻¹.

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