Original Article

Highly efficient photocatalytic performance of Cu$_2$O@TiO$_2$ nanocomposite: influence of various inorganic oxidants and inorganic anions

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**Abstract**

This work offers the facile synthesis of Cu$_2$O@TiO$_2$ nanocomposites by solid state reaction towards the elimination of Acid-Red 8 (AR8) dye as a target pollutant model through the photocatalytic oxidation system. Another goal is to assess the capacity of various inorganic oxidants that act as alternative electron acceptor for Cu$_2$O@TiO$_2$ mediated photocatalytic oxidation. The prepared nanocomposite was analyzed by various analysis instruments, and their photocatalytic performance was systemically assessed with respect to the removal of AR8 dye. Upon irradiation, compared to pure Cu$_2$O and pure TiO$_2$ alone, the Cu$_2$O@TiO$_2$ has exhibited a higher photocatalytic performance which show that the combining TiO$_2$ (n-type) with Cu$_2$O (p-type) has been improved the electron mobility and subsequently decreasing the rate of electron-hole recombination. A kinetic study is confirmed that the degradation of AR8 has been obeyed the pseudo-first-order model. The perfection of the photocatalytic activity is achieved by using various inorganic oxidants such as; H$_2$O$_2$, Na$_2$S$_2$O$_8$, and NaIO$_4$ so as to produce an electron scavenger. Also, the apparent rate constant (k$_{app}$) and apparent quantum yield (Q$_{app}$) are higher for all oxidants than without oxidants, while is lower in terms of electrical energy per order ($E_0$) and half-life time ($t_{0.5}$). Periodate ion has considered the most efficient oxidant when compared with other oxidants for enhancing the photocatalytic activity via the formation of various reactive oxygen species. The degradation efficiency of these catalytic systems could be arranged in an ascending order: Cu$_2$O@TiO$_2$/NaIO$_4$ > Cu$_2$O@TiO$_2$/Na$_2$S$_2$O$_8$ > Cu$_2$O@TiO$_2$/H$_2$O$_2$ > Cu$_2$O > TiO$_2$.

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1. Introduction

Recently, the shortage of water is becoming more severe problem due to an environmental pollution, rapid industrial growth, uncontrolled groundwater progress and reducing the water resources. Hence, the fixing of these problems and
cleaning of wastewater are urgently vital [1,2]. In the recent decades, there are enormous application of the dyes in many industries, especially in textile, chemical, pharmaceutical, food, and cosmetics industries which is the main involvement of the generation and growth of hazardous and toxic chemicals like amines and cyanides [3].

There is great battery in the removal of dye-containing wastewater by conventional methods like biological treatment [4], coagulation-flocculation [5], anodic oxidation [6], electrocoagulation [7], ozonation [8], reverse osmosis [9], and adsorption [10]. All of these techniques suffer from one or more limitation, and none of them is able to completely remove dyes from wastewater. The target of complete mineralization of organic toxic dyes is being established by advanced oxidation processes (AOPs) in order to respond to the progressive growth of the water pollution. Among them, heterogeneous photocatalysis is esteemed a motivating technique with today’s challenging demands especially for clean water technology [11,12].

Nanostructured TiO2 is considered as a well-known photocatalyst for the highly efficient performance for decomposition of textile pollutants in water [13]. The destruction of organic pollutants by titania in the presence of suitable light is as a result of production of hydroxyl radical, very strong oxidant, that are the key of using the photocatalyst for oxidation of organic molecules. Also, there were many efforts for improving the photocatalytic activity by combination with other oxidants [14]. Great challenges have been made in order to improve the performance of titania, mainly joint with other semiconductor, regardless the excellent prospect of efficient photocatalytic mineralization of toxic dyes in water [15].

Sensitization of n-type such as; TiO2 with p-type such as; Cu2O is an effective path for fabrication TiO2 based photocatalyst with extended absorption and subsequently improved the photocatalytic activity. This is due to the low band gap of Cu2O (Eg = 1.9–2.2 eV) and the formation of heterostructure between TiO2 and Cu2O that helps the separation and transportation of the photo induced charge carriers in Cu2O@TiO2 hetero junction nanocomposite, and hence declines the opportunity of recombination and improves the photocatalytic properties [16]. Also, the synergistic effect between TiO2 and Cu2O is very important for improving the charge separation and leads to much higher photocatalytic activity than pure TiO2 and Cu2O [17,18].

Many research groups concerned with the fabrication of Cu2O@TiO2 in order to make a progress in the destruction of organic contaminants from water. The photocatalytic activity of TiO2/zeolite (TZ) was improved the photocatalytic degradation of bisphenol A(BPA) by adding Cu2O [19]. Mixed oxides of Cu2O-TiO2 was synthesized on a copper substrate for reduction of 2,2',4,4'-tetrabromodiphenyl ether (BDE47) [20]. Also, the morphology is significant factor for enhancing the photocatalytic activity. The Cu2O@TiO2 heterostructure hollow spheres (Cu2O/TiO2 HS) for removal of Rhodamine B as a result of design the heterojunction between TiO2 and Cu2O [21]. The degradation of reactive blue 49 (RB 49) dye is observed by using 4 wt.% Cu2O-CuO/TiO2 catalyst [22].

do, there is no studies concerning the various inorganic oxidants using Cu2O@TiO2 as a photocatalyst for destruction of toxic dyes in an aqueous solution. Herein, it is in those perspectives as mentioned above, the goal of this work is to (i) synthesize Cu2O@TiO2 nanocomposites by solid-state reaction, which may perform as a photocatalyst for removal of AR8 dye under UV irradiation; (ii) study the influence of adding various oxidants like H2O2, Na2S2O8 and NaIO4 suspended systems for improving the photocatalytic activity; and (iii) investigate the quantum yield and electrical energy per order with addition of various oxidants.

2. Materials and methods

2.1. Materials

TiO2 (Degussa P25) was supplied from Degussa Cooperation, Germany. CuCl2·2H2O, NaOH and glucose were purchased from Aldrich chemicals, Germany. Acid Red 8 (AR8) (anionic dye) with molecular formula C18H12N2Na2O7S2, molecular weight of 480.42 g/mol, and λ max 508 nm was purchased from Fluka, Germany. All oxidants such as sodium periodate (NaIO4), hydrogen peroxide (H2O2, 30% w/v), and sodium persulphate (Na2S2O8) were obtained from Fisher Scientific, Germany.

2.2. Synthesis of Cu2O and Cu2O@TiO2

Nano Cu2O was fabricated by co-precipitation method. Cu2O@TiO2 nanocomposite was prepared by two steps; one by synthesis of Cu2O nanoparticles, followed by adding it (10 wt.% of Cu2O) to Degussa P-25 (90 wt.% of TiO2) for synthesis of Cu2O@TiO2 by solid state reaction. The powders have been mixed uniformly and formed fine powder by grinding 2 h. The resultant powders have been calcined at 500 °C for 3 h in a muffle furnace. The overall procedure for synthesis of nanocomposite is presented in Fig. 1.

2.3. Physicochemical characterization

The physicochemical properties of the synthesized Cu2O@TiO2 nanocomposite was observed by scanning electron microscope (SEM, JEOL, Model JSM-6360 LA, Japan) [Prior to the investigation, the samples were coated with gold using sputtering coater (model: S 150 B, Edwards High Vacuum Ltd., England)], and joint it with Energy Dispersive X-ray (EDX), X-ray diffraction (XRD, Bruker, D8 ADVANCE, Germany) [Cu(Kα) radiations of wavelength (λ = 1.5406 A°) generated at 40 K, 40 mA], and Fourier Transform Infrared spectrophotometer (FTIR, Shimadzu-8400, Japan) [IR spectra were taken from the test samples, pressed into KBr-supported discs and scanned in the wavelength range from 400 to 4000 cm−1].

2.4. Evaluation of the photocatalytic activity

The photocatalytic performance of the prepared Cu2O@TiO2 nanocomposite was used to evaluate the removal efficiency of AR8 dye in an aqueous solution using batch slurry photoreactor. The contents (TiO2/dye, Cu2O/dye, Cu2O@TiO2 dye and Cu2O@TiO2/dye/oxidant) of the glass container were agitated by a magnetic stirrer and kept purged with air (rate 3000 ml min−1). The dye solution was agitated with photocat-
3. Results and discussion

3.1. Formation pathway of Cu$_2$O@TiO$_2$ nanocomposite

In this work, Cu$_2$O@TiO$_2$ nanocomposite was prepared by two steps. Cu$_2$O nanoparticles were firstly prepared using co-precipitation method, and then Cu$_2$O nanoparticles were deposited on the inside and outside surface of TiO$_2$ by solid-state reaction, yielding the Cu$_2$O@TiO$_2$ nanocomposite (Fig. 1).

Firstly, Cu$^{2+}$ ions and solvent were firstly mixed to form blue solution. Then, the addition of NaOH and glucose that supports the reduction of Cu$^{2+}$ to Cu$^{+}$ ions. The addition of glucose during the synthesis of Cu$_2$O associates to reduce the rate of agglomeration and also improve the homogeneity and the distribution of this particles with small grain size [23]. After increase the temperature from room temperature to 70 °C, a large number of Cu$_2$O were formed at short time. Secondly, Cu$_2$O was added to Degussa P-25, the ions of Cu$^{+}$ may be diffused and adsorbed on the surface of TiO$_2$ as well as absorbed into the interstitial space in TiO$_2$ at high calcination temperature, yielding Cu$_2$O@TiO$_2$ nanocomposite because TiO$_2$ is used as a substrate with associated of low amount of Cu$_2$O (10 wt.%) [19, 24].

3.2. Characterization of Cu$_2$O@TiO$_2$ nanocomposite

Fig. 2 (a) shows the SEM of the prepared Cu$_2$O@TiO$_2$ nanocomposite with high homogeneity and uniformity of aggregated semi-spherical shape. The average diameter of grain size of 56 nm. The EDX of the prepared Cu$_2$O@TiO$_2$ nanocomposite stated that the existence of considerable amounts of Cu, Ti, and O which confirmed that the successful fabrication of high purity of Cu$_2$O@TiO$_2$ nanocomposite were noticed by the existence of the distinctive energy peaks for Ti and Cu without any impurities (Fig. 2b). The spectrum shows the strong Ti signal at about 4.5 eV and a weak signal at about 0.45 eV with atomic percentage of 39.25%. Also, a weak signal at about 0.45 eV for oxygen was detected with atomic percentage of 48.52%. The two weak signals at about 0.94 and 8.04 eV for copper were detected with atomic percentage of 12.23%.

Fig. 2 (c) shows the XRD pattern of the fabricated Cu$_2$O@TiO$_2$ nanocomposite which displays the diffraction peaks at 2θ = 25.23, 27.31, 35.42, 36.02, 37.82, 38.66, 47.97, 48.73, 54.04, 55.05 and 62.61, which match to anatase and rutile titania (JCPDS card No 021-1272 and 021-1276), respectively and also pure cubic Cu$_2$O (JCPDS 99-0041) [25, 26]. Compared to Degussa P-25 TiO$_2$, Cu$_2$O@TiO$_2$ nanocomposite has three additional XRD peaks that located at 36.02, 62.61, and 73.54 which fits to the (111), (220) and (311) and ascribed to cuprite phase as well as stated that Cu$_2$O are really found on the surface of the P25 TiO$_2$ [16]. It is indicated that the combination of Cu$_2$O in the crystal structure of TiO$_2$ which has not any effect on the structure of Degussa P-25 and this structure is preserved. These findings are demonstrated that a two-phase composition of TiO$_2$ and Cu$_2$O exist in the Cu$_2$O@TiO$_2$ heterostructure.

The FTIR spectrum of Cu$_2$O@TiO$_2$ nanocomposite (Fig. 2d) shows a band at 3471 cm$^{-1}$, which is distinctive of the non-hydrogen bonded surface hydroxyl groups. Also, the peak observed at 1638 cm$^{-1}$ is ascribed to the bending mode of the adsorbed water [27]. The characteristic vibration band of the
inorganic Cu—O has been detected at 378 cm⁻¹ whereas the representative band of the inorganic Ti—O has been observed at 587 cm⁻¹ [16].

3.3. Photocatalysis of acid red 8 dye

3.3.1. Degradation kinetics

The decomposition kinetics of AR8 dye by TiO₂, Cu₂O, and its composite Cu₂O@TiO₂ were assessed by following the Langmuir-Hinshelwood model [11]. When the chemical concentration C₀ is millimolar solution the integrated form of Eq. (2) be an apparent first order equation.

\[ \ln(C_0/C) = k_{app}t \]  

(2)

Where, \( k_{app} \) represents the apparent first order rate constant, \( C_0 \) and \( C \) are concentration before and photocatalytic reaction, respectively. The half-life time (\( t^{0.5} \)) of the first order reaction is the time required for the reactants to be degraded to the half of their \( C_0 \). The relationship between \( t^{0.5} \) and \( k_{app} \) is given by Eq. (3).

\[ t^{0.5} = 0.693/k_{app} \]  

(3)

3.3.2. Comparison between TiO₂, Cu₂O and its composite Cu₂O@TiO₂

The decomposition of AR8 dye as an organic contaminant model has been achieved by photocatalytic performance using TiO₂ P-25, Cu₂O and it surface modified Cu₂O@TiO₂ nanocomposite as photocatalysts at room temperature. The destruction of AR8 dye was assessed by reducing the \( C_0 \) at \( \lambda_{max} \) 508 nm due to the azo bond (N=N). The AR8 dye was completely degraded at around 90 min with obeyed the pseudo-first-order kinetic models (Figure not shown). In Table 1, the decomposition rate follows the order Cu₂O@TiO₂ > Cu₂O > TiO₂. The rate of removal by pure Cu₂O was higher than that of pure TiO₂ which may be due to the low band gap of Cu₂O. The most effective catalytic system is obtained by using combined Cu₂O@TiO₂ system which can be ascribed to the more efficient separation of photoinduced electron-hole (e⁻/h⁺) pairs, and also improve the surface-active sites in composite [17,20,29].

3.3.3. Influence of various oxidation processes on the degradation by addition of electron acceptors

One of the significant drawbacks of the photocatalysis is the electron-hole recombination which signifies the major energy-wasting step and subsequently leads to the reduction of the quantum yield. So, the deferring of electron-hole recombination by addition of irreversible electron acceptors in
order to increase the rate of photocatalysis, especially in high concentration of toxic dyes. The observed drastically accelerated the decomposition were attributed to the improving the electron scavenging from the added inorganic oxidants. The merits of adding electron acceptors is to avoid the recombination via (i) increase the number of trapped electrons; (ii) generation of more radicals and other oxidizing species; (iii) increasing the oxidation rate of the intermediate compounds and (iv) avoiding the problems of low oxygen concentration [28–30]. Hence, various concentrations of oxidants (H₂O₂, Na₂S₂O₅ and NaIIO₄) were added to the AR8 dye solution in the presence of the combined Cu₂O@TiO₂ system that illustrated in Fig. 3. The introduction of inorganic oxidants is utilized for enhancing the rate of degradation of AR8 dye through better scavenge the ejected electrons of TiO₂ and hence the survival time h⁺ at Cu₂O will be higher and subsequently reacts effectively with AR8 dye. The effect of the concentration of various oxidants is described well as follows:

(a) H₂O₂

The UV/Cu₂O@TiO₂/H₂O₂ system is used to trap the electrons at conduction band and formation of more •OH radicals from generation for superoxide anion radicals (•O₂⁻) and homolytic cleavage of bonds of two hydroxyl groups during the photolysis, which enhancing the rate of photocatalytic reaction. H₂O₂ is used as an electron acceptor than oxygen in other mechanisms and subsequently the rate of recombination will decrease [11]. Also, H₂O₂ is more electrophilic than O₂ that result from two hydrogen atoms bonded to oxygen atoms (H–O–O–H).

To deep the illustration of into the effective reactivity of H₂O₂/ Cu₂O@TiO₂ system on the decomposition of AR8 dye was studied at various concentration of H₂O₂ in Fig. 3 (a). It has been stated that the enhanced photo-destruction rate with increasing the dose of H₂O₂. Also, the kₚ was increased from 182 × 10⁻⁴ to 1834 × 10⁻⁴ min⁻¹ when the concentration of H₂O₂ was ranged from 2 × 10⁻³ to 45 × 10⁻² M (Table 1). The effect of rate determining species is expressed by a power law relation

\[
k_{\text{app}} = K[H₂O₂]^n \tag{4}
\]

Where k₂ and K are the apparent and the true rate constants, respectively. The n is the order of the photocatalytic reaction. From Fig. 3 (b), the value of n was 0.4 (Table 1). The rate of AR8 dye degradation using UV/Cu₂O@TiO₂/H₂O₂ system is better when compared to UV/Cu₂O@TiO₂ alone. This may be ascribed to (i) trap of the photogenerated conduction band electrons of Cu₂O@TiO₂ by H₂O₂, which is more efficient than trapping by O₂, according to the following reaction [31].

\[
H₂O₂ + e^−(ch) → •OH + H₂O \tag{5}
\]

(ii) generate other oxidizing species (•OH), which can contribute to the oxidative decay process; and (iii) after illumination, substantial photolysis of the H₂O₂ would produce more hydroxyl radicals (Eq. 6) [32].

\[
H₂O₂ + hν → 2•OH \tag{6}
\]

In summary, the increasing the H₂O₂ concentrations leads to an increase in both electron scavenging action, and hydroxyl radicals, which oxidize the dye and lead to a higher rate of decomposition.

(b) Peroxydisulphate ions S₂O₈²⁻

Fig. 3 (c) displays the influence of adding S₂O₈²⁻ to combined Cu₂O@TiO₂ system on the destruction of AR8 dye. It was found that the rate of removal was enhanced with the addition of a low concentration of the S₂O₈²⁻ (1 × 10⁻³ M) to UV/Cu₂O@TiO₂ system. According to a first-order model for dye destruction, it has been found that the enhanced photodegradation rate is result from the increasing the concentration of S₂O₈²⁻. Also, the kₚ was increased from 302 × 10⁻⁴ to 3651 × 10⁻⁴ min⁻¹ when the concentration of

<table>
<thead>
<tr>
<th>Catalytic system</th>
<th>Concentration of oxidant (M)</th>
<th>kₚ (min⁻¹)</th>
<th>t½ (min)</th>
<th>Apparent reaction order (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/Cu₂O</td>
<td>–</td>
<td>124 × 10⁻⁴</td>
<td>5.6</td>
<td>–</td>
</tr>
<tr>
<td>UV/TiO₂</td>
<td></td>
<td>84.0 × 10⁻⁴</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>UV/Cu₂O@TiO₂</td>
<td></td>
<td>150 × 10⁻⁴</td>
<td>4.6</td>
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<tr>
<td>UV/Cu₂O@TiO₂/H₂O₂</td>
<td>2 × 10⁻³</td>
<td>182 × 10⁻⁴</td>
<td>3.8</td>
<td>0.4</td>
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<td></td>
<td>4 × 10⁻³</td>
<td>278 × 10⁻⁴</td>
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</tr>
<tr>
<td></td>
<td>12 × 10⁻³</td>
<td>375 × 10⁻⁴</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14 × 10⁻²</td>
<td>531 × 10⁻⁴</td>
<td>1.3</td>
<td></td>
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<tr>
<td></td>
<td>28 × 10⁻²</td>
<td>1257 × 10⁻⁴</td>
<td>0.6</td>
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</tr>
<tr>
<td></td>
<td>45 × 10⁻²</td>
<td>1834 × 10⁻⁴</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>UV/Cu₂O@TiO₂/S₂O₈⁵⁻</td>
<td>1 × 10⁻³</td>
<td>302 × 10⁻⁴</td>
<td>2.3</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2 × 10⁻³</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>4 × 10⁻³</td>
<td>983 × 10⁻⁴</td>
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<tr>
<td>UO</td>
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<td>3651 × 10⁻⁴</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>UV/Cu₂O@TiO₂/I₂⁻</td>
<td>4.0 × 10⁻⁴</td>
<td>1297 × 10⁻⁴</td>
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<tr>
<td></td>
<td>7.4 × 10⁻⁴</td>
<td>2001 × 10⁻⁴</td>
<td>0.30</td>
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<tr>
<td></td>
<td>1.0 × 10⁻³</td>
<td>2846 × 10⁻⁴</td>
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<td>21 × 10⁻³</td>
<td>3664 × 10⁻⁴</td>
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</tr>
<tr>
<td></td>
<td>48 × 10⁻³</td>
<td>4881 × 10⁻⁴</td>
<td>0.14</td>
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<td></td>
<td>11 × 10⁻²</td>
<td>7229 × 10⁻⁴</td>
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Table 1 – Collective data of apparent rate constants, half-life times, and reaction orders for degradation of AR8 dye [conc. of catalyst 0.1 g/l].
Fig. 3 – (a, c, e) Change of ln (C/C₀) with time at different concentrations of H₂O₂, S₂O₈²⁻, and IO₄⁻, respectively, and (b, d, f) Change of ln kₐₚₚ (min⁻¹) with ln [H₂O₂], ln [S₂O₈²⁻], and ln [IO₄⁻], respectively.
Table 2 – Collective data of apparent rate constants, electrical energy per order and apparent quantum yield for degradation of acid red 8 dye [conc. of catalyst 0.1 g/l].

<table>
<thead>
<tr>
<th>Catalytic system</th>
<th>Concentration of oxidant (M)</th>
<th>(k_{\text{app}}) (min(^{-1}))</th>
<th>(E_{\text{EO}}) (kWh/m(^3))</th>
<th>(Q_{\text{app}}) % (mol/Einstein)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/Cu(_2)O</td>
<td>2 × 10(^{-3})</td>
<td>124 × 10(^{-4})</td>
<td>526.3</td>
<td>1.07</td>
</tr>
<tr>
<td>UV/TiO(_2)</td>
<td>4 × 10(^{-3})</td>
<td>182 × 10(^{-4})</td>
<td>357.1</td>
<td>1.58</td>
</tr>
<tr>
<td>UV/Cu(_2)O@TiO(_2)/H(_2)O(_2)</td>
<td>1 × 10(^{-3})</td>
<td>1834 × 10(^{-4})</td>
<td>36</td>
<td>16.0</td>
</tr>
</tbody>
</table>

\(S_2\)O\(_2\)^{2−}\) was ranged from \(1 \times 10^{-3}\) to \(8 \times 10^{-3}\) M (Table 1). The complete decomposition of the dye in a short time (20 min) at conc. \(8 \times 10^{-3}\) M of \(S_2\)O\(_2\)^{2−}\). The rate order of photocatalytic reaction with respect to \(S_2\)O\(_2\)^{2−}, which was obtained from Fig. 3(d), was found to be 1.2 (Table 1).

The addition of \(S_2\)O\(_2\)^{2−}\) ions could have increased the photocatalytic performance due to the interaction with light and its interaction with Cu\(_2\)O@TiO\(_2\). The photolysis of persulphate leads to the formation of sulphate radicals whose redox potential 2.5–3.1 V/NHE is higher than that of \(S_2\)O\(_2\)^{2−}\) ions (1.96 V/NHE) [32]. The \(S_2\)O\(_2\)^{2−}\) anions can trap the electrons that formed from the conduction band of Cu\(_2\)O@TiO\(_2\) more than the electrons from \(O_2\), and thus formed other oxidant SO\(_4\)^{•−}\) (Eq. 7) [33].

\[
S_2\text{O}_2^{2−} + \text{e}^{−}(\text{cb}) \rightarrow \text{SO}_4^{2−} + \text{SO}_4^{•−}
\]

(7)

Upon irradiation, the SO\(_4\)^{•−}\) is also generated and can contribute in the photocatalytic reaction with water for formation of \(\cdot\)OH, according to Eqs. (8 and 9).

\[
S_2\text{O}_8^{2−} + \text{hv} \rightarrow 2\text{SO}_4^{•−}
\]

(8)

\[
\text{SO}_4^{•−} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{SO}_4^{2−} + \text{H}^+
\]

(9)

So, the increased concentrations of \(S_2\)O\(_2\)^{2−}\) have increased the trapping of the electrons from the conduction bands of Cu\(_2\)O@TiO\(_2\) and the production of SO\(_4\)^{•−}\) and \(\cdot\)OH. These two factors are responsible for higher rate of photodecomposition of AR8 dye.

(c) Periodate ion IO\(_4\)^{−}\)

Oxyhalogens have atom of oxygen and another atom of halogen as a central atom. The difference in polarization between oxygen and halogen leads to the capturing of the ejected electron. The effect of oxyhalogen system is extremely based on the differences in the electronegativity and the atomic radius of the halogen [34]. The electropositive halo-}

The increasing of the atomic radius leads to the decreasing of the electronegativity that result from capturing the ejected electron by halogen. Hence, the atomic radius of I has higher than that of Cl or Br and it has more bonded with oxygen than Cl or Br, and the ability of electrons over photocatalyst will be higher. So, the UV/Cu\(_2\)O@TiO\(_2\)/IO\(_4\)^{−}\) is the best system for decomposition of AR8 dye by the oxyhalogen oxidant.

Fig. 3(e) shows the influence of addition of various concentration of periodate ions to UV/Cu\(_2\)O@TiO\(_2\) system on the destruction of AR8 dye. The addition of very low concentrations of IO\(_4\)^{−} (4.0 × 10\(^{-5}\) M) to Cu\(_2\)O@TiO\(_2\) has resulted in a higher decomposition rate than UV/Cu\(_2\)O@TiO\(_2\) only. Also, when increasing the concentration of the periodate to \(11 \times 10^{-3}\) M has resulted in dye destruction after the shortest time (18 min). According to the IO\(_4\)^{−}, The reaction rate order is 0.2 (Fig. 3(f) and Table 1). The scavenging of the electrons by Cu\(_2\)O@TiO\(_2\)/IO\(_4\)^{−}\) system leads to the improvement of the photocatalytic decomposition of AR8 dye, which is more efficient than trapping with O\(_2\) or \(S_2\)O\(_2\)^{2−}\) as follows [35];

\[
\text{IO}_4^{−} + 8\text{e}^{−}(\text{cb}) + 8\text{H}^{+} \rightarrow 4\text{H}_2\text{O} + \text{I}^{−}
\]

(10)

Also, upon irradiation, the photolytic decomposition of the IO\(_4\)^{−}, involves the formation of a number of highly reactive radical- and non-radical intermediates (IO\(_3\)^{•−}, \(\cdot\)OH, \(\cdot\)O and IO\(_4\)^{−}) (Eqs. 11–13) as follows [35];

\[
\text{IO}_4^{−} + \text{hv} \rightarrow \text{IO}_3^{•−} + \text{O}^{•−}
\]

(11)

\[
\text{O}^{•−} + \text{H}^{+} \rightarrow \cdot\text{OH}
\]

(12)

\[
\cdot\text{OH} + \text{IO}_4^{−} \rightarrow \text{OH}^{−} + \text{IO}_4^{•−}
\]

(13)

These intermediates are responsible for the enhancing the decomposition of organic compounds [32]. Increasing the con-
centration of IO$_4^-$, the number of available h$^+_\mathrm{VB}$ is increased and their long lifetime would be beneficial for the decomposition of AR8 dye (Fig. 3e). This may be due to the trapping of the electrons in conduction bands of combined Cu$_2$O@TiO$_2$ system and also the production of highly reactive oxygen species such as IO$_4^-$, O$^•_2$, O$_3$, •OH and IO$_4^•$. This led to a higher rate of degradation [32,35].

3.3.4. Quantum efficiency of photocatalytic reaction

The quantification of heterogenous catalysis can be determined by the estimation of quantum yield, which may be defined as the rate at which reactant molecules disappear or product molecules are formed, divided by the number of photons absorbed per unit time. With dispersed catalysts, a large fraction of the incident light is either reflected or scattered and not absorbed by the dye solution. There does not usually exist any possibility to determine experimentally the amount of light absorbed by the photocatalyst. In order to bypass the difficulty of determining quantum yields in heterogeneous photocatalysis, another parameter often reported is the apparent quantum yield (Q$_{\text{app}}$) which defined as shown in Eq. (14) [36,37]

$$\text{Apparent quantum yield (Q}_{\text{app}, \text{mol/Einstein}}) = \frac{\text{Rate of disappearance of reactant molecules}}{\text{Rate of incident photons inside reactor cell}} = k_{\text{app}} C_0 / I \quad (14)$$

Where $k_{\text{app}}$ is the apparent first-order rate constant, $C_0$ is the initial dye concentration and $I$ is the total intensity of incident photons entering the reactor cell. It was observed from Table 2 that Q$_{\text{app}}$ for UV/Cu$_2$O@TiO$_2$/IO$_4^-$-system is higher than those for UV/Cu$_2$O@TiO$_2$/H$_2$O$_2$ and UV/Cu$_2$O@TiO$_2$/S$_2$O$_8^{2-}$-systems. This may be due to the higher activity of peroxide when compared to hydrogen peroxide and persulfate as obtained in the previous studies [33,36].

3.3.5. Figure of merit

Nowadays, the economic study of each process is a significant factor which it includes the major fraction of operating cost. Hence, it is necessary to study the electrical energy consumption of the AOPs under experimental conditions. The electrical energy per order ($E_{\text{EO}}$) is an informative factor for the photocatalytic degradation because it obeys the first order kinetic model [6]. The figures of merit $E_{\text{EO}}$ allows for a rapid determination of the electrical energy cost and they indicate the total power required. For comparative purpose, the treatment efficiencies for the different processes are evaluated through the $E_{\text{EO}}$ values. The $E_{\text{EO}}$ is defined as the number of kWh of electrical energy required to reduce the concentration of pollutant by one order of magnitude (90%) in 1 m$^3$ of contaminated water. Considering first-order degradation kinetics, the UV doses were calculated for all AOPs using Eq. (15) [38]. From the UV doses, the simplest form of the estimation of $E_{\text{EO}}$ can also be calculated using Eq. (16) [37].

$$\text{UVDose} = \frac{[\text{Lamppower(kW)} \times \text{Time(h)} \times 1000]}{[\text{Treated volume(L)}]}$$

$$\text{Fig. 4 - Change of log (Co/C) with UV dose for degradation of AR8 dye using 0.1 gm of Cu$_2$O@TiO$_2$ with different concentrations of (a) H$_2$O$_2$, (b) S$_2$O$_8^{2-}$, and (c) IO$_4^-$, respectively.}$$
4. Conclusions

In summary, we revealed that the facile and proficient approach for the fabrication of CuO@TiO$_2$ nanocomposite via a solid-state approach. The formation of this composite was revealed by SEM-EDX, XRD, and FT-IR. The combined CuO@TiO$_2$ heterojunction system exhibited much higher photocatalytic activity than that of pristine CuO and TiO$_2$. This is due to the transfer of electrons from CuO to the conduction band of TiO$_2$ is concurrently with the photogenerated holes at the valence band of CuO, which facilitates the electron and hole separation and improves the photocatalytic activity of CuO@TiO$_2$ heterojunction nanocomposite. It was found that the heterogeneous photocatalytic degradation, under UV illumination, using the following order: CuO@TiO$_2$/NaIO$_3$ > CuO@TiO$_2$/Na$_2$S$_2$O$_8$ > CuO@TiO$_2$/H$_2$O$_2$ > CuO@TiO$_2$. The photocatalytic activity enhancement was attributed to the various reactive oxygen species like *OH and IO$_4^-$. The higher decolorization and quantum efficiency and lower energy per order and energy consumption of combined CuO@TiO$_2$ system with oxidants than bare CuO@TiO$_2$. The combination of CuO@TiO$_2$ nanocomposite with various oxidants may bring a new insight into highly efficient photocatalytic applications in the future.

Conflicts of interest

The authors declare no conflicts of interest.

References


