Full Length Article

Sono–incorporation of CuO nanoparticles on the surface and into the mesoporous hexatitanate layers: Enhanced Fenton-like activity in degradation of orange–G at its neutral pH

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In this work, for the first time, CuO/Ti₆O₁₃ mesoporous nanocomposite was synthesized by direct intercalation of CuO nanoparticles into hexatitanate layers in the presence of ultrasound. In fact mesoporous potassium hexatitanate with high pore size (44.94 nm) was used as a support. CuO nanoparticles were grown into the titanate pores which caused formation of ultra small CuO with uniform size and high surface area. In fact, titanate is considered as a substrate for better dispersion and nucleation of the CuO nanoparticles which prevented the agglomeration and overgrowth of guest molecules. The prepared sample was characterized by XRD, FE–SEM, TEM, UV–Vis spectra, N₂ adsorption–desorption, Raman spectra and FT-IR techniques. The product was used as a heterogeneous Fenton-like catalyst for the degradation of Orange G (OG). The effect of important parameters, including pH, H₂O₂ addition rate and catalyst loading on the decolorization of OG were investigated. Based on the results, CuO/Ti₆O₁₃ catalyst exhibited high catalytic activity for OG degradation in aqueous solution at neutral pH of the dye. Moreover, breaking of H₂O₂ during the catalytic reaction was monitored by spectroscopic method. The results confirmed the decomposition of H₂O₂ to produce *OH which is the main active species for the degradation of OG.

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1. Introduction

Recently, the removing of toxic and non-biodegradable industrial wastewaters using Advanced Oxidation Processes (AOPs) have been widely studied due to their high efficiency in oxidizing a wide range of compounds that are otherwise difficult to degrade. Among the various AOPs, the Fenton type is considered as the most attractive treatment owing to its high efficiency, low cost, ease application, the lack of toxicity of the reagents and because they do not require complicated equipment or reagents for being applied [1,2]. The Fenton system uses ferrous iron (catalyst acting) to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing and non-selective ability to degrade a variety of organic compounds [2]. However, the application of Fenton reaction has limited due to the narrow working pH range (acidic pH), requiring much effort for separation and low recovery of catalyst [3]. Several approaches have been suggested to improve the performance of Fenton reactions like using the heterogeneous catalysts based on the benefits of easy separation and catalyst recovery [4]. One of the effective strategy to solve these problems is possibility of using supports for metal ions such as zeolite [5], silica [6], resins and activated carbon [7] to prepare novel heterogeneous Fenton catalysts for catalytic activation of H₂O₂. Obviously, low catalytic activation at high pH values were shown in most of heterogeneous Fenton catalysts that often depend on using ultrasound, UV irradiation or ferrous ions for accelerating in reaction [8]. Therefore the development of the heterogeneous Fenton catalysts with high activity in wide working pH range, is considered as one of the most important goal in designing the new catalysts.

Up to now, a series of titanates with tunnel or layered crystal structures with exclusive properties such as commercial availability, high thermal resistivity, chemical durability, high surface area and dispersibility have been used in many application such as ion-exchange materials, reinforcements, heat insulators, catalysts and photocatalysts [9]. Among them potassium hexatitanate (K₂Ti₆O₁₃) with tunnel structure has attracted growing attention owing to the low cost, high chemical and thermal stability and potential applications in reinforced plastics and metals and cat-
alytic activity [10]. One of the advantages of these compounds is that their material properties maybe capable for doping or intercalating with transition metal ions as a supported heterogeneous catalysts. The combination of a large and accessible surface area with modifications by metal oxide catalysts such as CuO can also lead to the melioration in catalytic performance [11]. One of the main factor for good catalytic performance is the nature of support. It has been reported that the supported heterogeneous catalyst with CuO-based nanoparticles has an acceptable catalytic behavior due to the high surface area, uniform mesoporosity, stability and high-dispersibility [12]. Besides that, some tactics are necessary to prevent the oxidation of metallic copper and the agglomeration of nanoparticles as well as copper nanoparticles must be bonded strongly enough to the support in order to avoid leaching processes [13]. It seems that preparing the heterogeneous catalyst with copper nanoparticles could be consider the effective solution to overcome these problems.

In this paper, we have synthesized and characterized the CuO nanoparticles into the layers and on the surface of K$_2$Ti$_6$O$_{13}$ by sonochemical method for the first time. Ultrasonic irradiation leads to cavitation process, including the formation, growth and sudden collapse of microbubbles. Their collapse in less than a microsecond producing the local extreme temperature and pressure conditions [14]. We utilized these extreme conditions to direct exchanging the potassium ion (between titane layers) with copper ions (in solution) and finally obtain CuO/Ti$_6$O$_{13}$ nanocomposite in a facile reaction. The CuO/Ti$_6$O$_{13}$ intercalated nanocomposites were applied as highly active catalyst for Orange G dye (OG) degradation in aqueous solution at neutral pH of dye by using H$_2$O$_2$ as a green oxidant (Fenton-like reaction). To our best knowledge, the use of CuO/Ti$_6$O$_{13}$ as a Fenton-like catalyst has not been reported. Furthermore, the decomposition of H$_2$O$_2$ during the catalytic process was monitored by spectrophotometric method. The conditions of the process were optimized by varying the concentration of catalyst and H$_2$O$_2$ content in order to minimize the quantity of reagents and so the cost of the process. In addition, it was shown the possibility of reusing the catalyst without significant loss of its catalytic capacity.

2. Experimental

2.1. Chemicals

All reagents used in this work were analytical grade and used without any further purification. Tetrabutyl titanate (Ti(O-Bu)$_4$), potassium hydroxide (KOH) and stearic acid (CH$_3$(CH$_2$)$_{15}$CO$_2$H) were purchased from Merck. Copper Sulfate (CuSO$_4$·5H$_2$O), sodium thiosulfate (Na$_2$S$_2$O$_3$), Orange G (C$_{10}$H$_{10}$N$_2$Na$_2$O$_7$S$_2$) and sodium hydroxide (NaOH) were from sigma Aldrich. Hydrogen peroxide (30\% wt) was supplied from Merck.

2.2. Preparation of host precursor

The host K$_2$Ti$_6$O$_{13}$ was prepared according to the method presented in our previous work [15]. Briefly, the procedure is described as follows: an appropriate amount of stearic acid was melted at 120 °C while the saturated solution of KOH was added. After addition of Ti(O-Bu)$_4$, the mixture sonicated for 30 min (ultrasonic amplitude 40\%). Finally, the ignition of solution was done at 300 °C in furnace and then calcined at 750 °C.

2.3. Preparation of nanocomposite (CuO/Ti$_6$O$_{13}$)

The as-prepared potassium hexatitanate nanoparticles (0.2 g) was added to 0.2 M copper sulfate solution and sonicated for 1.5 h at room temperature (ultrasonic amplitude 60\%). Then the 0.2 M NaOH and Na$_2$S$_2$O$_3$ solutions were added to mixture at the same time and sonication was continued at 70 °C for 30 min until the color of mixture turned to black. Na$_2$S$_2$O$_3$ was added to reduce the Cu (II) in CuSO$_4$ at first stage and produce the Cu$_2$O. Then with increasing the time and temperature Cu$_2$O turned to CuO nanoparticles. After that the product was centrifuged, washed with deionized water and ethanol, dried under vacuum for 24 h at 60 °C.

2.4. Characterization and equipments

The crystalline structure of potassium hexatitanate and CuO/Ti$_6$O$_{13}$ was identified by XRD and the patterns were collected on a diffractometer (PHILIPS PW1800). Diffraction patterns were obtained within the range of 20 = 5–60° with Cu Kα radiation and a step size of 0.04°. The size and morphology were determined with FESEM (Mira 3-3XMU) and TEM (CM120-Philips). The FTIR measurements were carried out with a spectrometer (Thermo Nicolet-Avatar 370) at room temperature in KBr pellets. The concentration of K\(^+\) and Cu\(^{2+}\) ions during the intercalation process were examined by atomic absorption spectrophotometry (AAS, Varian, spectra-110880/220-Australia Pty Ltd.). The absorption spectrum of OG and its derivatives were measured using a UV-Vis spectrophotometer (Unico 2800). The Bruyana-Emmet-Teller (BET) surface area was estimated on an (TriStar II 3020, Micromeritics-USA) BET surface area analyzer from the adsorption branch in the relative pressure of p/p$_0$= 0.07–0.14. Pore size distribution was obtained following the Barrett-Joyner-Halender method. The pore volume and average pore diameters were measured according to the nitrogen adsorption volumes at the relative pressure of 0.99. Raman spectrum was obtained at room temperature using a HANDHELD Raman analyzer. The ultrasonic irradiation was applied with equipment operating at 20 kHz (Branson Digital Sonifier, W-450 D).

2.5. Catalytic activity

The catalytic activities of as-prepared CuO/Ti$_6$O$_{13}$ nanocomposite were investigated using the aqueous solution of OG. The typical catalytic reaction was done at room temperature in a Pyrex glass vessel containing 30 mL OG with neutral pH (30 mg L$^{-1}$). A 0.65 mL of hydrogen peroxide (H$_2$O$_2$ 30\% wt) was added dropwise to the mixture of 0.04 g of CuO/Ti$_6$O$_{13}$ nanocatalyst in dye solution. The mixture was allowed for 15 min to complete degradation of the dye. After various interval times, 5 mL of solution was withdrawn, centrifuged and the spectrum of UV–visible absorption was recorded. In order to measure the COD during the catalytic degradation over the different interval times, the reaction solution was mixed with 1 mL NaOH (0.1 M) for 15 min to eliminate the residual H$_2$O$_2$. Then the solution was filtered and used for COD measurement.

3. Results and discussion

3.1. Characterization of CuO/Ti$_6$O$_{13}$ nanocomposites

The X-ray diffraction patterns of K$_2$Ti$_6$O$_{13}$ before and after intercalating with CuO were shown in Fig. 1(a). Compared with potassium hexatitanate, CuO/Ti$_6$O$_{13}$ nanocomposite could keep the typical titane crystal structure after incorporation of CuO nanoparticles into the titane layers except for the decrease in peak intensity related to first intense peak. In contrast with the standard diffraction patterns for CuO (JCPDS 045-0937), the diffraction peaks at 2θ = 35.5°, 38.7° and 48.7° for CuO/Ti$_6$O$_{13}$ nanocomposites were allocated to that of monoclinic CuO crystals [16]. In addition, the small peaks in XRD pattern located at (2θ = 12–18°) most probably are related to potassium titanium oxide phases (K$_2$Ti$_6$O$_{13}$, K$_2$Ti$_3$O$_5$ and KTi$_6$O$_{16}$). According to Fig. 1(b), the main peaks correspond to (200) of CuO/Ti$_6$O$_{13}$ shifted
TEM analysis was used in order to investigate the morphology of the synthesized CuO/Ti$_6$O$_{13}$ nanocomposites. Fig. 4 shows the TEM images of CuO/Ti$_6$O$_{13}$ nanocomposite. It is obviously seen that during the intercalation process, the nanobelt morphology and crystalline form of K$_2$Ti$_6$O$_{13}$ remain unchanged. The darker contrast on the surface and between the titanate layers are related to CuO nanoparticles. In fact, TEM image showed the substrate effect of titanate for growth and deposition of uniform and tiny CuO nanoparticles on the host surface. CuO nanoparticles were intercalated between the layers and uniformly deposited on the surface of titanate.

FT-IR technique can be used as an important method for investigating of the substructure of layered materials and for demonstrating the conformational changes after the guest molecules intercalate into the layered compound. FT-IR spectra of K$_2$Ti$_6$O$_{13}$ and CuO/Ti$_6$O$_{13}$ are illustrated in Fig. 5(a) and (b), respectively. Absorption bands around 482–518 cm$^{-1}$ and 694–783 cm$^{-1}$ are related to O–Ti–O bending vibrations and Ti–O stretching of TiO$_6$ octahedral groups. Furthermore, FTIR spectra show a peak around 940 cm$^{-1}$ for the prepared titanate sample, which is expected for Ti=O group \[17\].

The peaks located at 1647 and 3300 cm$^{-1}$ are attributed to the bending and stretching vibrations of adsorbed water molecules which remained after intercalation. Incorporation of CuO nanoparticles between the potassium hexatitanate appeared a series of changes on the FT-IR spectra of intercalated sample. The shifts in peak positions and changes in the intensity were observed as a consequence of incorporation. The absorption bands between 480 and 971 cm$^{-1}$ in nanocomposite became sharper and stronger than that of K$_2$Ti$_6$O$_{13}$ sample and shifted to lower wavenumbers, indicating a smaller distortion of the structure after the guest particles intercalation \[18\]. The characteristic peak at around 530 cm$^{-1}$ which corresponding to the Cu–O stretching vibration mode can be assigned to the monoclinic phase of CuO \[19,20\]. Moreover, the weak peak appeared at 1368 cm$^{-1}$ corresponding to the bond between the metal atom (Cu) and oxygen from TiO$_6$ layers of host (Cu$^{2+}$–O$^2$–Stretching) \[21\].

The bands which emerged in around 3568 cm$^{-1}$ and 3332 cm$^{-1}$ were attributed to the stretching modes of OH groups and the stretching vibrations of interlayer water contents, respectively.

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>O (%)</th>
<th>Ti (%)</th>
<th>K (%)</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$Ti$<em>6$O$</em>{13}$</td>
<td>57.83</td>
<td>15.96</td>
<td>26.21</td>
<td>0.00</td>
</tr>
<tr>
<td>CuO/Ti$<em>6$O$</em>{13}$</td>
<td>68.25</td>
<td>15.60</td>
<td>5.72</td>
<td>10.43</td>
</tr>
</tbody>
</table>

Fig. 6 shows Raman spectra of the CuO/Ti$_6$O$_{13}$ sample. The spectrum has four peaks located at around 490, 640, 1050 and 1650 cm$^{-1}$. The bands located at 490 and 640 cm$^{-1}$, relating to CuO nanoparticles, corresponds to the $A_g$ and $B_{1g}$ mode of the crystal. These bands could demonstrate the high crystallinity and purity of the intercalated CuO nanoparticles. The peak appeared at 1050 cm$^{-1}$ assign to $B_{2g}$ peak of CuO. Besides that the band at about 1050 cm$^{-1}$ could represent the stretching vibration of the short Ti–O bonds in distorted TiO$_6$ unit.

To determine the optical property of the prepared CuO/Ti$_6$O$_{13}$ nanocomposite, the optical absorption experiment was studied by UV–vis spectroscopy. As shown in Fig. 7, the strong absorption peak of K$_2$Ti$_6$O$_{13}$ Sample in the UV region at about 250–350 nm was observed, relating to characteristic band for the TiO$_6$ nanosheets. CuO nanoparticles have a broad absorption peak around 285 nm to 400 nm. After incorporating the CuO into the titanate layers, the broad absorption band from 250 to 550 nm was also presented. Such phenomena would be attributed to the coexistence of CuO and titanate nanoparticles.

Fig. 1. a) XRD patterns of K$_2$Ti$_6$O$_{13}$ and CuO/Ti$_6$O$_{13}$, b) Changes in interlayer spacing and peak positions in host and intercalated samples.
In this study, intercalation of CuO nanoparticles between the titanate layers was done through ion-exchanging process under ultrasound irradiation. According to structural nature of potassium hexatitanate, potassium ions were located into the interlayer space of K$_2$Ti$_6$O$_{13}$ [22]. It was expected that during the incorporation process, the K$^+$ ions were exchanged with Cu$^{2+}$ ions via ultrasonic shock waves and bubble oscillating between layers, presenting in solution [15]. In order to illustrate proposed process, in each half an hour period a certain amount of sonicated solution was separated and tested by atomic absorption spectrophotometer for measuring the released K$^+$ ions and remained Cu$^{2+}$ ions in solution. As shown in Fig. 8, with increasing the time of sonication, the amount of remained K$^+$ ions between the interlayer of titanate were decreased. On the other hand, with extended in ultrasound irradiation time the amount of residual Cu$^{2+}$ ions in solution were remarkably declined. In fact, the K$^+$ ions, presenting between K$_2$Ti$_6$O$_{13}$ layers, were replaced with Cu$^{2+}$ ions in solution during the intercalation process. Furthermore, after ion exchanging during the limited time with direct intercalation without pretreatment process, only 22% of K$^+$ ions remained between the titanate layers. Each two K$^+$ were exchanged with one Cu$^{2+}$ between layers. Some Cu$^{2+}$ ions attached to the surface by electrostatic attraction between the Cu$^{2+}$ and TiO$_6$$^{2-}$ layers. After formation of CuO nanoparticles
Fig. 4. TEM images of CuO/Ti6O13 nanocomposite.

Fig. 5. FTIR spectra of a) K2Ti6O13, b) CuO/Ti6O13.

Fig. 6. Raman spectrum of CuO/Ti6O13.

between layers and on the surface, the remained K⁺ and unreacted Cu²⁺ ions can be neutralized with negative layers of titanates.

The nitrogen adsorption/desorption isotherms and the pore size distributions of the sample CuO/Ti6O13 are shown in Figs. 9 and 10, respectively. The type IV isotherms with small H3 hysteresis loop was observed for the intercalated sample, demonstrating the presence of the dominate mesoporous (2–50 nm) structures [23], that was further proved by the pore size distribution (Fig. 10). The specific surface area, pore volume and pore size of CuO/Ti6O13 were determined to be 6.93 m² g⁻¹, 0.03 cm³ g⁻¹ and 44.94 nm, respectively. The hysteresis loop of the CuO/Ti6O13 sample closes at relative pressures P/P₀ = 0.44. This suggests the presence of large pores as also found out via enlarging the pore size into 44.94 nm [24]. The low specific surface area and pore volume with high pore size in composite might reveal the well incorporation of CuO nanoparticles in the hexatitanate pores. In fact, titanate is considered as a substrate for better dispersion and nucleation of the CuO.

Fig. 7. UV–vis absorption spectra of sono-synthesized samples.

Fig. 8. Amounts of remained K⁺ ions between titanate layers and Cu²⁺ ions in solution during the intercalation process.
nanoparticles which prevented the agglomeration and overgrowth of guest molecules [25]. Very small CuO nanoparticles was uniformly deposited over the entire region of the titanate and into the substrate pores, caused a reduction in the substrate surface area.

3.2. Catalytic performance of CuO/Ti6O13 nanocomposite

3.2.1. Methods of H2O2 addition

Obviously, heterogeneous Fenton-like catalyst can accelerate the decomposition of H2O2 into active radicals which responsible for the enhanced degradation of water pollutants [3]. In catalytic system using CuO/Ti6O13 and H2O2 for OG degradation, the addition method of H2O2 had a significant effect on the efficiency of OG removal. Two methods of addition were examined in catalytic Fenton-like system. Fig. 11 shows the efficiency of OG degradation when H2O2 was added in one step or gradually. In one step addition of hydrogen peroxide at first into the medium containing OG dye and catalyst, the OG concentration was reduced to 86% of the initial value after 15 min stirring. On the other hand, with the drop-wise addition of H2O2 during the catalytic process, the best result was obtained for 1 drop/min. In this case, 100% of OG removed in 15 min. According to Fig. 11, the removal of OG dye was done in the shorter time in the condition of 1 drop addition of H2O2 in every min. The difference between sudden and gradual addition can be related to the catalyst ability for decomposition of specified amounts of H2O2 during the time of addition. In one step addition, a large amount of H2O2 was added to the dye solution and the catalyst caused fast decomposition of partial amount of hydrogen peroxide and dye removal. The fast removal of dye can be observed from the steep plunge at the beginning. Over the time, the slop of OG degradation diagram became lower in comparison with initial time of addition. Furthermore, in the initial period of time, a large amount of *OH was created at dye solution so the chance of reaction between *OH radical and H2O2 instead of OG molecules was increased. H2O2 was generated under the scavenging reaction of *OH with H2O2 which was much less reactive than hydroxyl radicals, and did not contribute to the degradation of OG [26,27]. On the other hand, in the case of drop-wise addition of hydrogen peroxide during the catalytic process, the slope of diagram was increased gradually at defined intervals. In fact, with drop wise addition of H2O2, the trace and fresh amount of hydrogen peroxide with a high potential to react, was available for catalyst in each interval time and catalytic degradation of H2O2 to create *OH and dye removal were done more efficiently. In addition, the possibility of reaction between generated hydroxyl radicals and OG molecules was increased due to the gradual enlargement of *OH in the solution. Therefore, the next experiments were conducted by drop-wise addition of H2O2 during the process.

3.2.2. Catalyst loading, amount of H2O2, and removal time

In the Fenton-like systems, catalyst dosage has a strong influence in oxidative removal of compounds. The effect of the CuO/Ti6O13 catalyst dosage on the amount of H2O2 required for complete removal of OG and degradation time was shown in Fig. 12. In order to evaluate these parameters, different catalyst dosage were exposed to OG solution under stirring while H2O2 added drop-wise to the solution until the degradation was completed. It was observed that the OG degradation rate enhanced with an
increase addition of CuO/Ti6O13, the time of complete degradation was about 75, 36, 25, 15 and 14 min for 0.01, 0.02, 0.03, 0.04 and 0.05 g catalyst dosage, respectively. Moreover, the amount of H2O2, requiring for complete removal of OG, was significantly decreased with increasing the catalyst dosage. The results showed that the degradation of the OG was remarkably influenced by the increasing amount of active sites, which remained unsaturated during the Fenton-like reaction for H2O2 decomposition and more generated of active •OH radicals [28]. However, at higher dosage (>0.04 g), there was no considerably change in removing time of the dye and amount of H2O2. Therefore, the optimum dosage of catalyst was chosen (0.04 g) for the rest of experiments.

3.2.3. Effect of initial pH

It is well known that the surface charge of catalyst was influenced by solution pH, which persuaded the decomposition of hydrogen peroxide to produce hydroxyl radicals and affected the removal of contaminant [29]. Fig. 13 indicates the effect of initial pH on the removal of OG. About 100% of OG was degraded in 15 min at neutral pH of dye (pH = 6), whereas the degradation efficiency were 84%, 88%, 93% and 95% after 15 min at pH 10, 8, 2.5 and 4, respectively. Unlike the classic Fenton reaction, the degradation efficiency reduced with decreasing pH. This may be related to the adsorption capacity of the catalyst at various pH values that directly associated with catalytic activity [3]. The point of zero charge (pZC) of CuO/Ti6O13 catalyst was evaluated by salt addition method [30] and it is equal to 6.95 based on Fig. S2 (Supplementary materials). Accordingly, the catalyst surface was positively charged at neutral pH of dye and the surface charge density enlarged with increasing pH. The lower adsorption capacity of OG at higher pH (>6.95) can be attributed to the electrostatic repulsion between the catalyst surface and OG (anionic dye). Thus the OG dye molecules in aqueous solution can be degraded in bulk solution with •OH. Due to the repulsion between the catalyst surface and dye, it was slowly disintegrated through the fast decomposition of H2O2 at high basic condition [31]. In addition, the adsorption and decomposition of OG at lower pH (2.5 and 4) were slightly declined. The above results suggests that more •OH could be formed at near neutral pH value in CuO/Ti6O13 catalyzed Fenton-like reaction which was responsible for degradation of adsorbed dye molecules. Thus, it is not essential to pre-adjust the solution pH during the catalytic reaction.

3.2.4. Role of catalyst, H2O2 and catalyst + H2O2 in OG degradation

In order to compare the effective degradation of OG under different conditions, some control experiments containing catalyst, H2O2 and catalyst + H2O2 were carried out and the UV–vis spectra are shown in Fig. 14. According to Fig. 14(a), in the presence of catalyst alone, dye adsorbed on the catalyst surface and the structure little changed. But this adsorption was weak so with passing the time partial amount of adsorbed OG molecules came back to the dye solution (desorbed) and the intensity of each peaks of absorption spectra continuously increased. Meanwhile, the OG was hardly decolorized after 15 min by H2O2 in the absence of catalyst (Fig. 14b). Based on Fig. 14(c), when catalyst and H2O2 were added to the dye solution, the peaks related to dye chromophore and naphthalene group were shifted and then completely removed after 15 min. It should be noted that H2O2 absorption peak (185–300 nm) covered the peak located at lower wavelengths (300 nm<), so the effect of catalyst with H2O2 on the cleavage of benzene rings cannot be followed by UV–vis spectrum. The results revealed that the improved removal of OG in the presence of catalyst and H2O2 can be attributed to the heterogeneous Fenton-like process.

3.2.5. Comparison of catalytic efficiency

In order to compare the catalytic efficiency of different samples, the degradation of OG was evaluated with K2Ti6O13, CuO and CuO/Ti6O13 as catalyst and H2O2 as an oxidant and the results are shown in Fig. S3 (Supplementary materials). For catalytic degradation of OG on K2Ti6O13, dye molecules could only adsorb on the titanate surface without degradation. In the case of CuO, OG dye can be degraded through the Heterogeneous Fenton-like reaction. In comparison, the catalytic degradation of OG dye by CuO/Ti6O13 was greater than guest and host lonely. This is due to the effect of titanate as substrate in preparation of tiny and uniform CuO nanoparticles without agglomeration.

3.2.6. Catalyst stability and reusability

Fig. S4 (Supplementary materials) indicates the removal percentage of OG by the recoverable CuO/Ti6O13 catalyst in the several successive cycles. All experiments were performed with 0.04 g catalyst and 0.65 mL H2O2 for 15 min. After each run, the used catalyst was collected by centrifuge, washed with distilled water, dried and followed by adding fresh solution of OG and H2O2 for another catalytic run. The results show the slight decrease in the efficiency of OG decolorization after three consecutive cycles, proving the good reusability of catalyst. The insignificant reduction of catalyst activity may be related to the loss of the catalyst during the washing and filtering. Besides that, the recycle CuO/Ti6O13 can confirm the relative stability of the catalyst.

3.2.7. H2O2 degradation

To facilitate investigations of hydrogen peroxide destruction during the catalytic removal of OG, a convenient spectroscopic method was used for determining the residual hydrogen peroxide concentration [32]. The method is based on the reaction of H2O2 with vanadium pentoxide in sulfuric acid solution to form a red-brown colored peroxovanadate complex with maximum absorption at 454 nm. To monitor the H2O2 decomposition during the catalytic reaction, an appropriate amount of solution containing H2O2 was separated at given interval times, added to acidic vanadium pentoxide solution and finally the absorption spectrum for each solution was recorded. Fig. 15 shows the UV–vis absorption spectra of the colored complex in the wavelength range of 350–700 nm. As shown in Fig. 15, the H2O2 which presented at solution was hardly degraded in the absence of catalyst. On the other hands, based on Fig. 16, the absorbance at 454 nm was decreased with increasing the contact time of H2O2 and catalyst and finally eliminated. Obviously, the H2O2 was catalytically degraded during the OG removal by CuO/Ti6O13 nanocatalyst in order to produce the active hydroxyl radicals.
3.2.8. COD measurement

To characterize quantitatively the mineralization of OG during the catalytic degradation in the solution, the chemical oxygen demand (COD) is used. According to Fig. 17, the amount of COD was determined by standard acid dichromate method [33]. The determined COD for initial OG (30 mg/L) at time zero was about 90 mg/L. After addition of H$_2$O$_2$ and catalyst to the dye solution, the COD value decreased with increasing the time of reaction. The COD was totally disappeared in 30 min and the dye in solution was completely mineralized in the heterogeneous Fenton-like process. On the other hand, the Fenton-like degradation efficiency is slightly higher than the COD removal efficiency. This may be related to some intermediates which formed during the mineralization of OG on the surface and in the solution.

3.2.9. Verification of the proposed mechanism

It is broadly accepted that the decomposition of hydrogen peroxide into the active radicals (mostly *OH) can be accelerated by
heterogeneous Fenton-like catalysts [3]. The Fenton-like reaction can be represented by Eqs. (1) and (2) [34].

\[ \text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + \cdot \text{HO}_2 + \text{H}^+ \]  

(1)

\[ \text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HO}^- + \cdot \text{HO}^+ + \text{Cu}^{2+} \]  

(2)

In order to understand the degradation mechanism, three different types of radical scavengers like isopropyl alcohol (IPA), sodium fluoride (NaF) and potassium iodide (KI) were introduced to predict the role of the active species in CuO/TiO$_2$-H$_2$O$_2$ system. The role of total OH radicals both in bulk (\(\cdot \text{OH}_{\text{free}}\)) and on the catalyst surface (\(\cdot \text{OH}_{\text{ads}}\)) in decomposition of OG could be found from the quenching effects of radical inhibitors. Fig. 18 shows the effect of adding the various \(\cdot \text{OH}\) scavenger on decolorization of OG. As can be seen from Fig. 18, addition of IPA (60 mM) as a scavenger especially \(\cdot \text{OH}_{\text{free}}\) had a trace impact on OG degradation which confirm that only little \(\cdot \text{OH}_{\text{free}}\) was participated in the reaction. When 60 mM KI and NaF were used as scavenger for the \(\cdot \text{OH}_{\text{ads}}\), the number of oxidizing species available at the surface of the catalyst and decolorization rate of OG were remarkably declined. Obviously, iodide ions and fluoride could react with adsorbed hydroxyl radicals on the catalyst surface and thereby reduced the number of available \(\cdot \text{OH}_{\text{ads}}\) which were responsible for dye decomposition [35]. These evidences distinctly illustrated that although all \(\cdot \text{OH}_{\text{ads}}\) and \(\cdot \text{OH}_{\text{free}}\) radicals were produced in the CuO/TiO$_2$-H$_2$O$_2$ catalytic reaction, only the adsorbed hydroxyl radical on the CuO/TiO$_2$ surface was the major reactive species responsible for the catalytic degradation of OG. In fact, during the catalytic degradation of OG dye by Fenton-like system, dye molecules could adsorb on the surface of catalyst while H$_2$O$_2$ was degraded to the \(\cdot \text{OH}\). After that adsorbed OG molecules reacted by \(\cdot \text{OH}_{\text{ads}}\) and was turned to smaller molecules. These process continued until the complete decomposition of OG.

4. Conclusions

CuO nanoparticles were successfully incorporated into the titanate layer pores via facile ultrasound method and used for the first time as heterogeneous Fenton-like catalyst for the decolorization of the azo dye OG. The results showed that the CuO/TiO$_2$ exhibited high catalytic activity for the Fenton-like degradation of OG in aqueous solution at neutral pH. Designing the experiments with various scavengers demonstrated that \(\cdot \text{OH}_{\text{ads}}\) played the crucial role in the degradation process. The adsorption of OG on the CuO/TiO$_2$ surface accelerated its reaction with \(\cdot \text{OH}\) produced on the catalyst surface. The experiments about the reuse of the catalyst indicated that the CuO/TiO$_2$ was stable and can be used in successive cycles. This study provides an efficient pathway for preparing the heterogeneous Fenton-like catalysts, using in CuO/TiO$_2$-H$_2$O$_2$ system, which consider as a promising process for the treatment of dye wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2016.12.079.

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