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Tilia Platyphyllos Extract Assisted Green Synthesis of CuO/TiO_2 Nanocomposite: Application as a Reusable Catalyst for the Reduction of Organic Dyes in Water

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Abstract

In this paper, CuO nanoparticles are synthesized using *Tilia platyphyllos* extract as reducing and stabilizing agents and $TiO_2$are prepared via facile sol-gel method as an ideal support. FT-IR spectroscopy, UV-Vis spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy (FE-SEM), Energy Dispersive X-ray Spectroscopy (EDS), and Transmission Electron Microscopy (TEM) were used to characterize TiO_2, CuONPs, and CuO/ TiO_2 nanocomposite. The catalytic activity of the CuO/ TiO_2 nanocomposite was investigated for the reduction of Methyl Orange (MO), and Methylene Blue (MB) at room temperature. CuO/ TiO_2 nanocomposite can was found to be a highly active catalyst. In addition, it was found that CuO/ TiO_2 nanocomposite can be recovered and reused several times without significant loss for its catalytic activity.

Keywords: *TiO_2, CuO/ TiO_2 nanocomposite, Tilia platyphyllos, $NaBH_4$, Organic dyes.*

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Introduction

Azo dyes are widely used in numerous industries. These substances are some of the most important sources of environmental pollutants and the majority of the dyes are hazardous to aquatic organisms. However, they are stable in the environment and are hardly biodegradable, except in the presence of a catalyst. Dyes containing effluents are generally treated by chemical, physicochemical and biological methods. Nevertheless, some of these techniques are usually expensive and sluggish. Therefore, the use of highly efficient and environmentally friendly methods for the degradation of these pollutants from the environment should be explored [1-4].Metal nanoparticles (MNPs) catalysts play an important part in the overall catalytic performance which studied by researchers in the past decades. The application of MNPs as heterogeneous catalysts is highly beneficial because of their large surface [5-10].Nevertheless, there are disadvantages associated with MNPs such as difficulty of quantitative separation from the reaction mixture, impossibility to recycle, and agglomeration [5-11]. To overcome these problems, MNPs have recently been supported on solid supports such as zeolites to form composite catalysts [8, 10].TiO_2 NPs are inorganic compounds widely applied as efficient supports for the immobilization of the MNPs given their exceptional opto-electronic properties, low synthesis cost, environmentally friendliness and highly versatile device fabrication [7–10]. To date, several methods have been employed for the synthesis of TiO_2 nanostructure. Among the various chemical techniques, sol-gel process is a promising method owing to the notable advantages of high purity, good homogeneity, low temperature synthetic conditions, low equipment cost and easily controlled reaction parameters [12, 13].

Hence, in this work, we reported a facile sol-gel method to synthesize selected support (TiO_2)using starch as an important, naturally abundant organic polymer for controlling the morphology of nanostructure and preventing agglomeration of samples [13, 14].According to literature, several physical and chemical methods have been applied in the preparation of MNPs. However, these methods are extremely costly and also involve application of hazardous chemicals such as hydrazine and N,N-dimethylformamide, all of which are highly reactive and have potential environmental and biological risks. Therefore, biological methods have recently become popular due to their many advantages of including low cost, no requirement of expensive and toxic capping agents or stabilizers, economic feasibility, moderate reaction conditions and simplicity [15]. It is found that the extracts of living organisms act both as reducing and capping agents in the synthesis of nanoparticles. Several plants have been successfully used for efficient and rapid extracellular synthesis of MNPs [3- 15]. The biosynthesis of CuO NPs using *Tilia platyphyllos* extract has not so far been reported. *Tilia platyphyllos* (Figure 1)is widely spread throughout Europe, North America, and Asia. *Tilia platyphyllos* is a large deciduous tree *Tilia platyphyllos* grows in Baluchestan, Bandar-abbas and north parts of Iran. Flowers and flowering branches of this tree are used in Iranian traditional medicine. *Tilia platyphyllos*, is used as diaphoretic, appetizer, diuretic, expectorant, antispasmodic and sedative in phytotherapy. It has been also used for the treatment of cough, nervous tension, migraine, insomnia, and different types of spasms in traditional medicine [16- 18].Accordingly, phenolic compounds such as flavonoids and phenol carbonic acids constitute one of the most important groups in *Tilia platyphyllos.Tilia platyphyllos* is a biennial herbaceous plant commonly known as evening Primroses with a well-established status in pharmaceutical, medicinal, cosmetic, and nutritional applications.

Figure 1. Image of *Tilia platyphyllos.*

Recently, researchers have been focused on the synthesis of metal or metal oxide NPs using plant extracts. Herein, an environmentally friendly, clean and non-toxic method is reported for the first time for the green synthesis of CuO/ TiO_2 nanocomposite using *Tilia platyphyllos* in the absence of any stabilizer or surfactant. The CuO/ TiO_2 nanocomposite catalytic activity in the reduction of MO and MB using aqueous $NaBH_4$ has also been studied.

Experimental

Instruments and reagents

Highly pure chemical reagents were purchased from Merck and Aldrich Chemical Companies. Characterization of the products was carried out by comparison of their physical and spectral data with those of authentic samples. A Nicolet 370 FT/IR spectrophotometer (Thermo Nicolet, USA) was used to record FT-IR spectra using pressed KBr pellets. A Shimadzu UV-2500 double beam spectrophotometer was used to record UV-visible spectra in the wavelength range of 200-700 nm.

A Cam scan MV2300) was used to perform Scanning Electron Microscopy (SEM). EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM was used to determine the measured chemical composition of the prepared nanostructures. The sample shapes and sizes were identified by Transmission Electron Microscopy (TEM) using a Zeiss-EM10C operating at an accelerating voltage of 80 kV.A Philips model X'Pert Pro diffractometer was used to carry out X-ray Diffraction (XRD) measurements using Cu Kα radiation (λ=1.5418Å) at a scanning rate of 2 °/min in the 2θ range of 10-80˚.

Preparation of TiO_2 sol

Yellow-colored TiO_2 sol was prepared at room temperature in 3 steps:

Step 1) solution **I**: First, 0.2 g starch was dispersed in 50 mL of absolute ethanol and stirred for 10 min using a homogenizer. TTIP was then added to the solution (at a molar ratio of 1: 9) and stirring was continued for 15 min.

Step 2) solution **II**: Acetic acid and deionized water were added to absolute ethanol (at a molar ratio of 6: 1: 10).

Step 3) solution **II** was added dropwise into solution **I** and the resulting solution was vigorously stirred for 15 min. to obtain a yellow transparent sol.

Then, the obtained transparent colloidal suspension was sonicated for 30 min and aged to allow a gel to form. The sample was dried in an oven at 50 ºC and ultimately calcinated at 500 ºC for 3 hours.

Preparation of Tilia platyphyllos extract

10 g of dried powdered *Tilia platyphyllos* were extracted using 100 mL of 70% (V/V) ethanol solution at 70°C for 45 min, after cooling mixture to room temperature, the extract of *Tilia platyphyllos* was centrifuged at6500 rpm and the supernatant was separated by filtration.

Preparation of the CuO NPs using the extract of the Tilia platyphyllos

In a typical CuO NPs synthesis, 10 mL of 5 mM $CuCl_2{\cdot}2H_2O$ solution was added to 30 mL of extract of the *Tilia platyphyllos* at 80 °C and vigorously shaken. The mixture became dark during the heating process after 5 min.; showing the formation of Cu NPs. The solution of NPs was then centrifuged at 6500 rpm for 30 min to completely precipitate Cu NPs, which were then washed several times with ethanol to remove possible impurities and air dried for 24 h at 70 °C in an oven and placed in a furnace at 350 °C for 2 h.

Preparation of the CuO/ TiO_2 nanocomposite using the extract of the Tilia platyphyllos

To synthesize CuO NPs/TiO_2, all the steps were similar to those for CuO NPs, but 1 g $TiO_2$was added to *Tilia platyphyllos* extract solution in the first step.

Reduction of MO and MB by CuO/ TiO_2 nanocomposite

CuO/ TiO_2 nanocomposite catalytic activity was evaluated by the degradation of an aqueous solution of 10 ppm MB in a typical reduction experiment. First, 25 mL of freshly prepared aqueous $NaBH_4$ was added to 25 mL of Mo or MB aqueous solution (10 ppm). Then, different amounts of catalyst was added and the resulting mixture stirred at room temperature until the solution was colorless, which indicated the completion of the reaction. However, the progress of the reaction was monitored by UV-Vis spectroscopy. Finally, after the reaction was complete, the catalyst was simply separated by brief centrifugation, washed several times with distilled water and the process was repeated to investigate the recyclability of the catalyst.

Results and discussion

Characterization of Tilia platyphyllos extract and CuO NPs

The UV-Vis analysis of *Tilia platyphyllos* extract was performed to demonstrate the presence of polyphenolics as antioxidant sources in the green synthesis of nanoparticles and results are shown in Figure 2.According to the UV spectrum of *Tilia platyphyllos* extract, the bands at around 283 and 332 nm are assigned to the $\pi \rightarrow \pi^*$ transitions, which can be attributed to the presence of polyphenolics as antioxidants for green synthesis of nanoparticles [18, 19].The UV-Vis spectra of synthesized CuO NPs are shown in Figure 3.The bands centered in the range of 250–300 nm in the UV–Vis spectrum of CuO NPs suggest the formation of CuO NPs [20, 21].

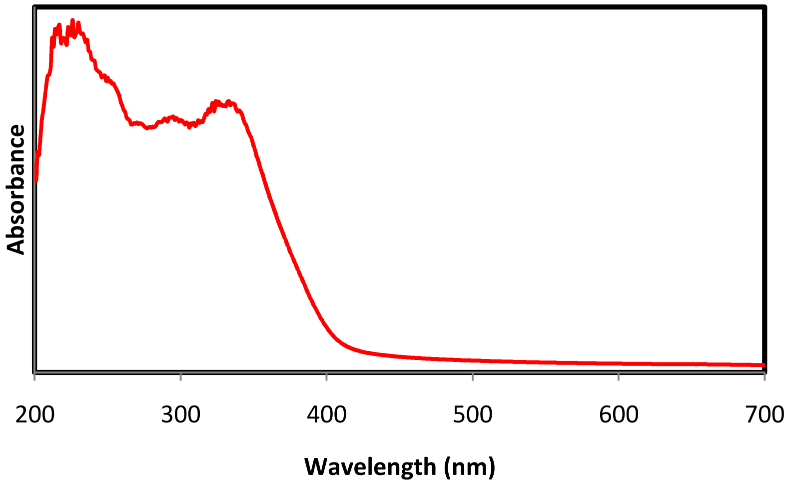


Figure 2. UV-Vis spectra of *Tilia platyphyllos* extract.

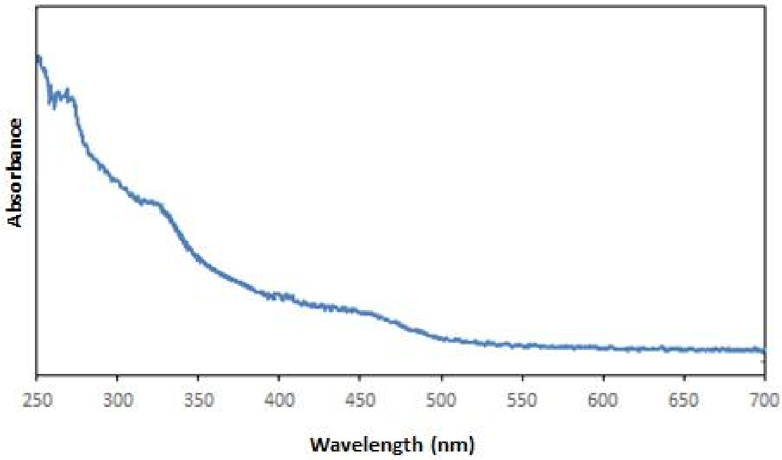


Figure 3. UV-Vis spectra ofthe green synthesized CuONPs using *Tilia platyphyllos* extract.

In order to determine the functional groups of *Tilia platyphyllos* extract and nanoparticles synthesized using this extract, FT–IR analysis was carried out and results are shown in Figure 4.

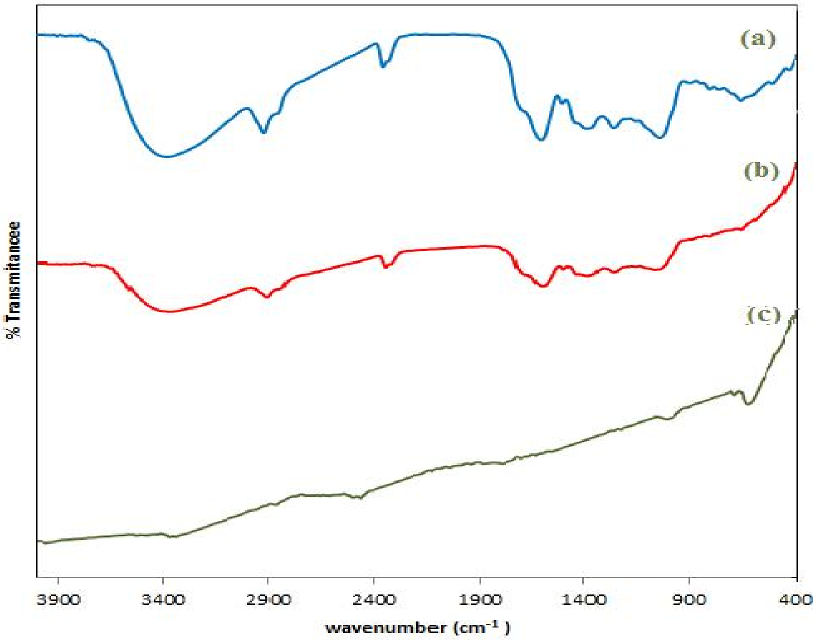


Figure 4. FT-IR spectra of Tilia platyphyllos extract (a), green synthesized Cu NPs using Tilia platyphyllos extract (b) and CuO NPs.

Peaks at 3400–3500, 1680, 1435, 2925, and 1050–1270 cm^{-1} are observed in FT–IR spectrum of *Tilia platyphyllos* extract (Fig. 4a), which are related to the free OH in molecule and OH group forming hydrogen bonds, carbonyl group (C=O), stretching C=C aromatic ring, C-Hand C–OH stretching vibrations, respectively. These peaks suggest the presence of flavonoid and phenolic acids in the *Tilia platyphyllos* extract, which are probably responsible for the reduction of metal ions and for the formation of nanoparticles [9, 18]. The positions of observed peaks in the FT–IR spectrum of Cu NPs synthesized using *Tilia platyphyllos* extract (Fig. 4b) are similar to the corresponding peaks in the FT–IR spectrum of *Tilia platyphyllos* extract, confirming that the organic compounds in *Tilia platyphyllos* extract are absorbed on the surfaceof Cu NPs by π-electron interaction [10, 22- 24]. The spectrum in Fig. 4ccorresponds to the CuO NPs that were produced from placing Cu NPs for 2 hat 350 °C. The peak in 400–600 cm^{-1}range is associated with Cu–O bond.

Characterization of $TiO_2$and CuO/ TiO_2 nanocomposite

The characterization of functional groups of TiO_2 and the CuO/ TiO_2 nanocomposite samples was carried out using Fourier transform infrared (FTIR) spectroscopy at room temperature in the range of 400–4000 cm^{-1} and the results are shown in Figure 5.

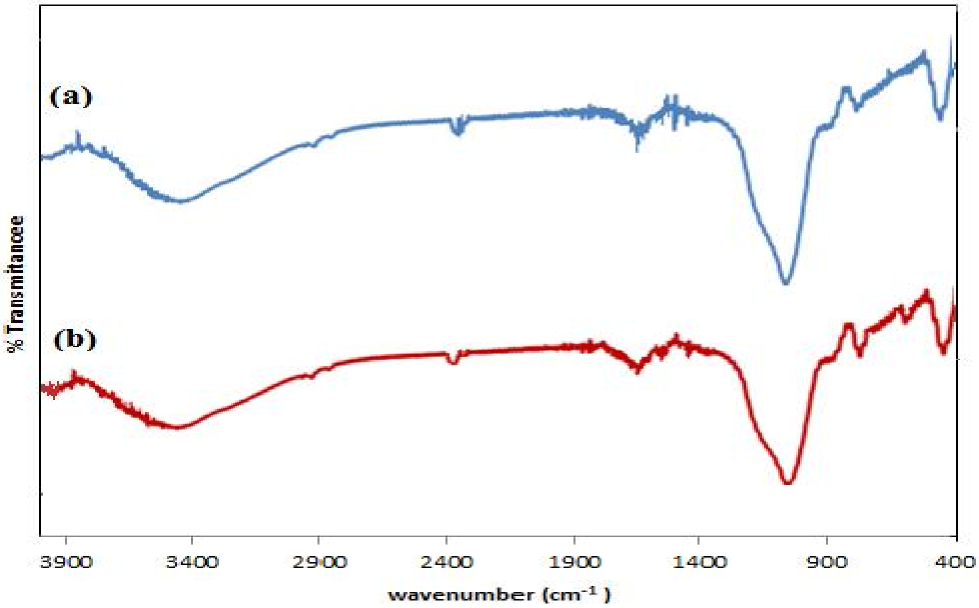


Figure 5. FT-IR spectra of TiO_2 (a) and CuO/ TiO_2 nanocomposite.

FTIR spectra of TiO_2 (Figure 5a) and CuO/TiO_2 nanocomposite (Figure 5b) samples show that no changes occur in the functional groups following CuO immobilization on TiO_2. According to these results, in all samples, the absorption bands at 920 and 860 cm^{-1} originate from the Ti-O stretching vibration and Ti-O-Ti linkage vibration, respectively [13, 14]. Moreover, the bands at 1117 cm^{-1} in the samples can be assigned to asymmetric stretching vibration of the Ti-O bonds [13, 14, 25]. The peak at 602 cm^{-1} can be assigned to symmetric stretching vibration of the Ti-O-Ti group. The peaks at 400 and 1400 cm^{-1} were attributed to the vibration mode of Ti-O bond and those at 1240, 1160 and 1080 cm^{-1} should be due to the Ti-OH bond [25-30]. In addition, the Cu–O bond witch appears in the range of 400–550 cm^{-1}, overlaps up TiO_2peaks in this range.

Phase investigation and the crystalline structures of TiO_2 and CuO/ TiO_2 nanocomposite samples were investigated by X-ray diffraction (XRD) measurements and the results are presented in Figure 6.

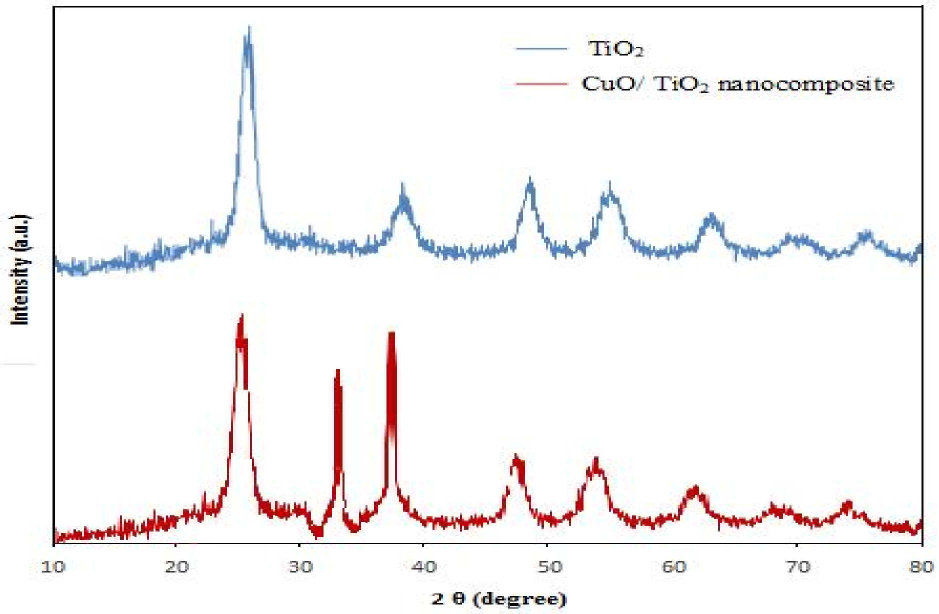


Figure 6. XRD pattern of TiO_2 and CuO/ TiO_2 nanocomposite.

The diffraction patterns of TiO_2 sample is in good agreement with JCPDS card of TiO_2 (No. 01-04-0477). XRD pattern of samples can be indexed to that of tetragonal anatase structure phase (the base peak in the range of $20<2\theta<30$ is an evidence of anatase phase). Moreover, diffraction peaks at 25.3°, 37.8°, 48.2°, 55.1°, 62.9°, and 70.5°are assigned to the characteristic anatase phase and those at 27.5°, 36.2°, 41.5°, 45.2°, 54.5°, 57°, and 69.5° are assigned to the characteristic rutile phase [29, 30]. Based on the above results, XRD patterns of the TiO_2 sample showed that the anatase phase is dominant. Figure 6 shows the XRD pattern of CuO NPs/TiO2. The diffraction peaks at 35.39°, 38.77°, 48.85°, and 61.69°, assigned to face centered cubic structure of CuO NPs with a monoclinic phase, are observed in the XRD pattern (ICSD- 087-122). The synthetic CuO NPs are crystalline in nature as verified by the XRD pattern [10, 21, 31].In order to investigation of the size and morphologies of TiO_2 and CuO/TiO_2 nanocomposite, scanning electron microscopy (SEM) analysis was employed. Fig. 7 shows the typical FE-SEM image of the samples.

These images indicate that TiO_2 and the CuO/ TiO_2 nanocomposite show spherical morphology with diameters of less than 30 nm with very narrow diameter distributions. It should be also noted that, theCuO particles are deposited on the surface of TiO_2without being incorporated in TiO_2.

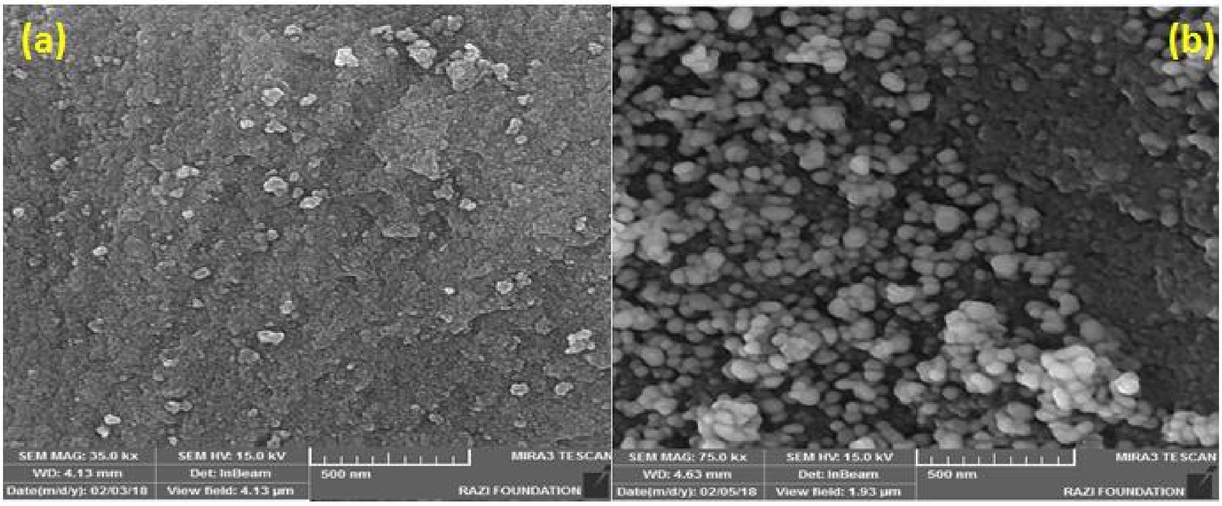


Figure 7. FE-SEM image of TiO_2(a), and CuO/ TiO_2 nanocomposite (b).

Moreover, the elemental mapping images are also showed in Figure 8, which demonstrate that the CuO NPs are dispersed on the surface of TiO_2.

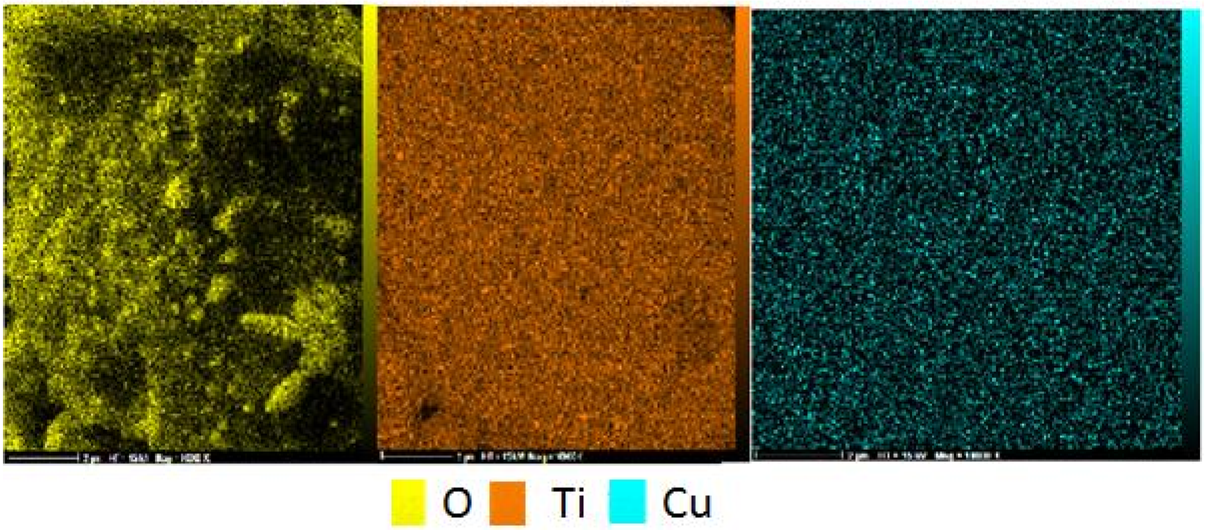


Figure 8. Elemental mapping of CuO/ TiO_2 nanocomposite.

EDS spectroscopy was used to characterize the elemental composition of CuO/ TiO_2 nanocomposite (Figure 9). EDS spectroscopy confirms the presence of Ti, O, and Cu elements in the CuO/TiO_2 nanocomposite.

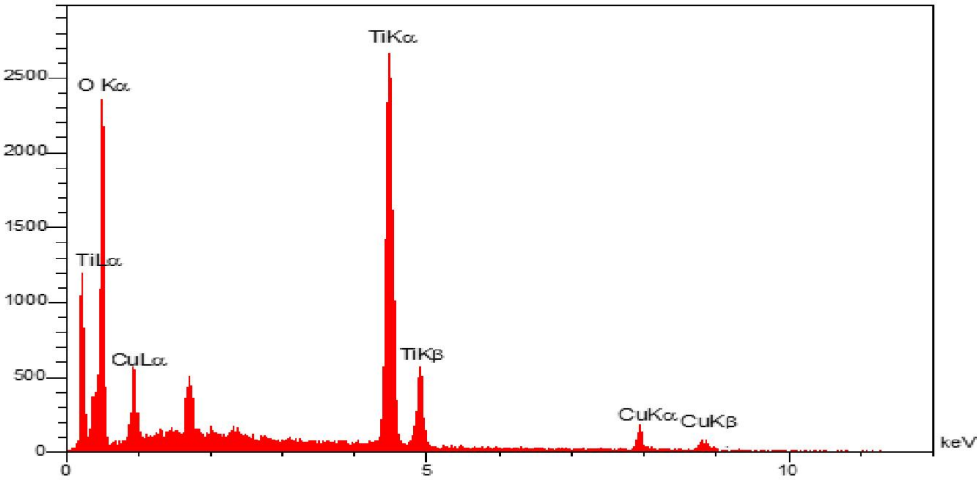


Figure 9. EDS spectrum of CuO/ TiO_2 nanocomposite.

Furthermore, the morphology and size of CuO/ TiO_2 nanocomposite was studied by Transmission Electron Microscopy (TEM). Figure 10 shows TEM images of CuO/ TiO_2 nanocomposite. The CuO NPs appear as dark dots over the surface ofTiO_2. The TEM micrographs show that CuO NPs are spherical with a narrow size distribution with an average diameter of less than 30 nm.

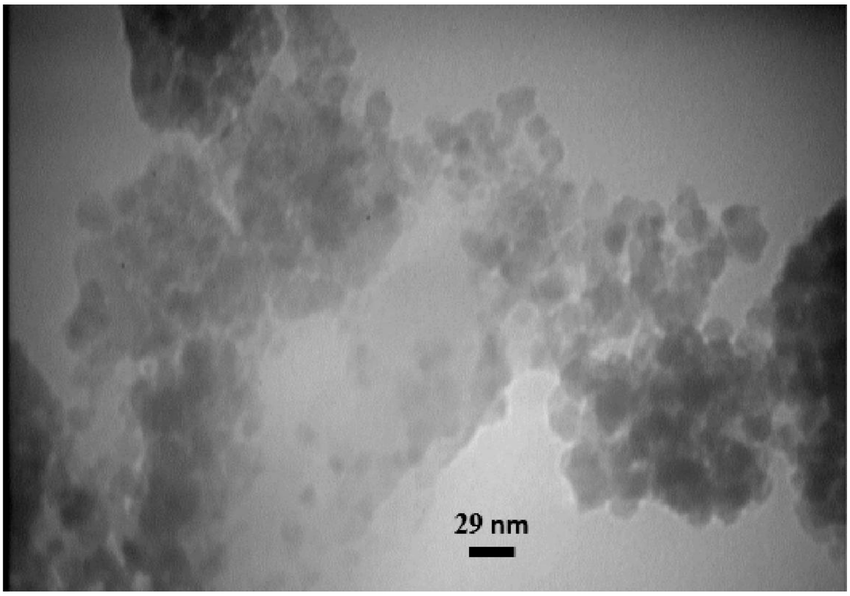


Figure 10.TEM image ofCuO/ TiO_2 nanocomposite.

Evaluation of the catalytic activity of CuO/ TiO_2 nanocomposite through the reduction of MO and MB

Having characterized the catalysts, the catalytic activity of the CuO/ TiO_2 nanocomposite was examined in the reduction of MO and MB in water at room temperature. The progress of the reaction was monitored by recording UV-Vis spectroscopy as a function of time, as illustrated in Figure 11.

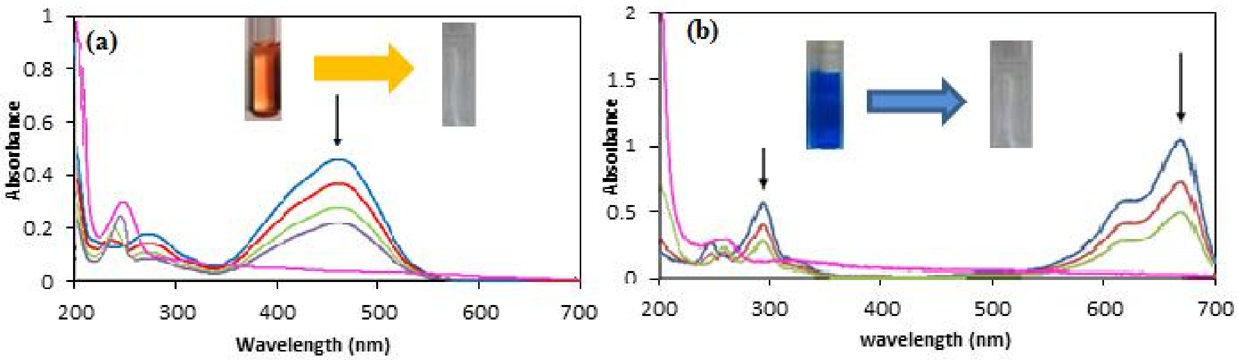


Figure 11. The UV-Vis spectra of MO (a) and MB (b) aqueous solution in the presence of catalyst.

As observed in the UV-Vis spectra, MO and MB in water solution exhibit peaks at 465and 663 nm, respectively, which disappear when reduction of dyes is complete. Firstly, the reduction of 10 ppm MO and MB dyes (25 mL) using 10 mg of TiO_2 in the presence of 25 mL of $NaBH_4$ (5.3×10^{-3} M) was examined. However, after 150 min, no changes were observed. Moreover, the reduction of 10 ppm MO and MB dyes (25 mL) using 10 mg of CuO NPs in the presence of 25 mL of $NaBH_4$ (5.3×10^{-3} M) was examined. Reduction of MO and MB using 10.0 mg of CuONPS was complete within 38 and 37, min respectively. Finally, in order to illuminate the effect of the TiO_2 as a support, constant amounts of $NaBH_4$ and different amounts of CuO/ TiO_2 nanocomposite catalyst were then applied in the catalytic reduction of MO or MB dyes which completion times are shown in Figure 12.Based on the results, CuO/ TiO_2 nanocomposite shows the shortest time forthe reduction of MO and MB in comparison with CuO NPs. Hence it is confirmed thatTiO_2 as a support play a pivotal role on prevents the agglomeration of CuO NPs and increases catalyst surface area.

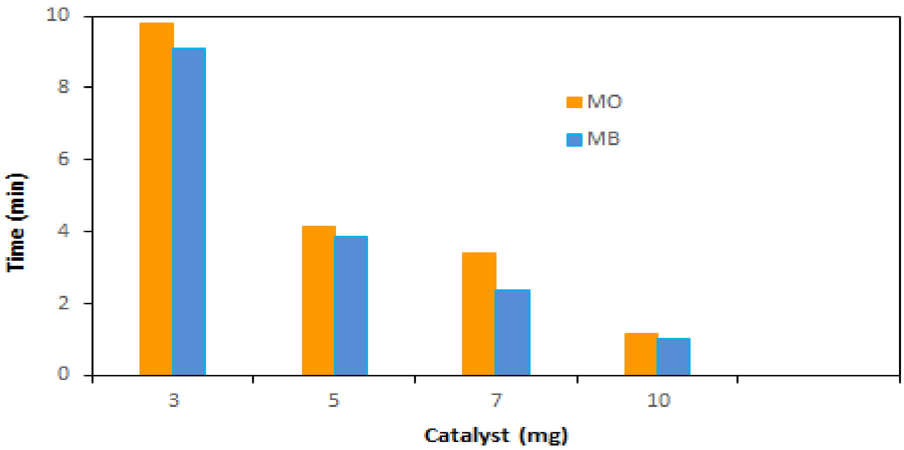


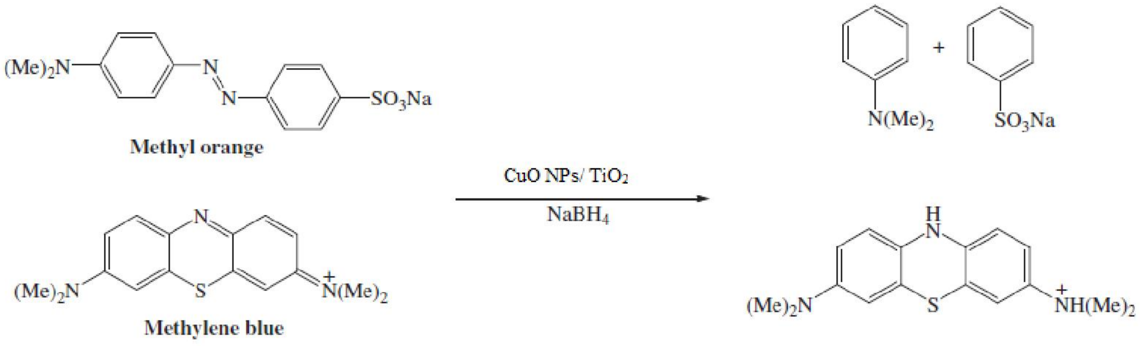
Figure 12. Competition time for the reduction of Mo and MB (10 ppm) using $NaBH_4$(5.3×10^{-3} M) and different amountsofCuO/ TiO_2 nanocomposite.

It was reasonable to conclude thatthe following steps are assumed to be involved in this reaction:

(I)Adsorption of $NaBH_4$onto the surface of the catalyst and formation of metal hydride;

(II)Adsorption of MO or MB onto the surface of the catalyst;

(III)Reduction of MO or MB and desorption in order to create a free space for the reaction to continue. The mechanism of the catalytic reduction and degradation of dyes with CuO/TiO2 nanocomposite shown in scheme 1.



Scheme 1. Mechanism of the catalytic reduction and degradation of MO and MB using CuO/ TiO_2 nanocomposite.

Evaluation of the recyclability of the catalyst

It is worth noting that reusability of the heterogeneous catalysts, which makes them useful for industrial applications, is one of their advantages. The recyclability of CuO/ TiO_2 nanocomposite in this study in the reduction of MO and MB with $NaBH_4$ was investigated. After each cycle, CuO/ TiO_2 nanocomposite can be easily separated by mild centrifugation, washing with distilled water and drying. The catalyst was reused at least five times for 100% reduction of MO and MB without significant loss of catalytic activity. Little decrease of efficiency was observed after the 5th cycle.

Conclusion

In this article,theCuO NPs and CuO/TiO_2 nanocomposite were synthesized using *Tilia platyphyllos* extract as reducing and stabilizing agent. CuO/ TiO_2 nanocomposite was utilized in the reduction of MO and MB in water at temperature. Results revealed that CuO/ TiO_2 nanocomposite had the high catalytic activity on the reduction of MO and MB. Moreover, recycling results confirm that the catalyst can be recycled at least five times in the reduction of MO and MB with almost no loss of catalytic activity. On the other hand, this work showed many remarkable advantages, including:

- The use of plant extract as an economic, low cost and effective reducing and stabilizing agent

-Very fast and clean synthesis without the use of toxic, hazardous and dangerous compounds or surfactants

- The synthesized catalyst is stable and could be easily recovered and reused.

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