Synthesis and Characterization of CuO/SnO₂ Nanocomposite for Catalytic Reduction of *p*-Nitrophenol

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A simple room temperature synthesis of CuO nanostructures was developed over SnO₂ for the catalytic reduction of *p*-nitrophenol. The prepared nanocomposite shows remarkable efficiency in reducing *p*-nitrophenol displaying an apparent rate constant of 0.3026 and 1.4763 min^{-1}, which was approximately 1.3 and 7.3 times higher than that achieved by the CuO and SnO₂ counterparts, respectively. This study paves the way for exploring the potential of metal oxide composite materials as highly effective catalysts for *p*-nitrophenol reduction.

Keywords: Metal oxides, Nanocomposites, Catalysis, Nitrophenol, Reduction.

INTRODUCTION

The substantial rise in environmental concerns, especially water pollution, has largely been attributed to the swift industrialization witnessed in recent times [1]. Nitrophenol, a widely used materials in pharmaceutical and textile industries is a major contaminant of water bodies. The current situation needs efficient water treatment methods to eliminate harmful pollutants or transform them into less toxic compounds before releasing them into water bodies. Among different methods for degradation of organic pollutants like chemical oxidation, coagulation photocatalytic reduction, *etc.* catalytic reduction is the best way owing to its high selectivity, low cost and efficiency [2]. The development of low-cost catalysts is essential for effective water treatments.

p-Aminophenol holds significant value as a pharmaceutical intermediate in the production of paracetamol, a commonly used pain relieving and fever-reducing medication. Traditionally, *p*-aminophenol is synthesized through multi-step processes involving iron-acid reduction of either *p*-nitrochlorobenzene or *p*-nitrophenol. The primary drawback of iron-acid reduction is the production of a substantial quantity of Fe–FeO sludge, leading to significant environmental pollution concerns [3]. The conversion of *p*-nitrophenol to *p*-aminophenol using catalytic reduction is a simple and cost-effective way. Among different

catalyst metal oxides gets much attention owing to its low cost, low toxicity and high efficiency [4,5]. CuO and SnO₂ are two main metal oxides that can be successfully utilized as a catalyst [6]. Moreover, the synergistic effect of these materials can improve the overall performance. Therefore, this work explored the combined effect of this catalyst, which is prepared through simple two-step process.

EXPERIMENTAL

Copper(II) sulphate pentahydrate (≥ 99%), sodium hydroxide pellets and *p*-nitrophenol was purchased from Sisco Research Laboratories Pvt. Ltd., India. Stannous chloride dihydrate (≥ 99.99%) and ammonia solution (25%) was purchased from Merck Ltd., India. All the chemicals were used as received and the double distilled water was used for all the experimental works.

Synthesis of SnO₂: SnO₂ nanoparticles were synthesized using a simple co-precipitation method. A 0.5 M SnCl₂·2H₂O was stirred for 1 h at room temperature. To keep the pH at 9, 5% aqueous NH₃ solution was added dropwise and the mixture was agitated for 1 h. For nucleation, precipitate developed and was left at room temperature for 24 h. It was filtered and washed continuously with double-distilled water and ethanol. The precipitate was then dried at 80 ℃ for 4 h and annealed at 600 ℃ to obtain crystalline SnO₂.

Synthesis of SnO$_2$/CuO nanocomposite: A facile room temperature precipitation method was employed to synthesize SnO$_2$/CuO nanocomposite. In brief, 100 mg of SnO$_2$ nanoparticles was dissolved in 100 mL of 0.05 M CuSO$_4$·5H$_2$O and sonicated for 5 min followed by the addition of 125 mL of 0.125 M NaOH into the mixture dropwise. After 3 h of magnetic stirring, the obtained product was allowed to settle at room temperature for 12 h and then filtered, washed with double distilled water and ethanol several times. The final product was then dried at 80 ℃ for 4 h in a hot air oven to obtain SnO$_2$/CuO nanocomposite. Bare CuO was synthesized without the addition of SnO$_2$.

Characterization: The XRD patterns of the samples were examined using a Bruker D8 advance X-ray powder diffractometer equipped with Cu$K\alpha$ radiation (λ = 1.5406 Å). Diffuse reflectance spectra were recorded with UV-visible spectrometer (Shimadzu, UV-2600). For the investigation of surface morphology and elemental composition, a scanning electron microscope (FEI Quanta FEG 200) was used. Thermo-Scientific Nicolet iS50 instrument was used to record FTIR spectrum.

Catalytic studies: The ability of SnO$_2$/CuO nanocomposite to catalyze the conversion of *p*-nitrophenol to *p*-aminophenol was evaluated using a spectrophotometric approach. In this technique, approximately 1 mg of catalyst was introduced into 3 mL solution containing 0.1 mM *p*-nitrophenol. Subsequently, 0.2 mL of NaBH$_4$ (0.2 M) was added and then the UV-visible spectra of the reaction mixture were monitored at various time points.

RESULTS AND DISCUSSION

The powder XRD pattern was used to analyze the structure and phase purity of the prepared samples. Fig. 1 shows the XRD diffractograms of CuO, SnO$_2$ and SnO$_2$/CuO nanocomposite. These are consistent with JCPDS card file Nos. 00-902-4580 (CuO) and 000-100-0062 (SnO$_2$). The sharp and well defined peaks confirmed the crystalline nature of the prepared sample [2,6]. In SnO$_2$/CuO nanocomposite, the finished structure retains its integrity by incorporating two or more constituent materials that possess notably distinct physical and chemical characteristics, yet remain separate and identifiable. Moreover, in SnO$_2$/CuO nanocomposite, the diffraction peaks of indivi-dual components are present, validating the successful formation of the composite. The absence of other impurity peaks confirms the high purity of the prepared samples.

From the FTIR spectra (Fig. 2), CuO shows two major peaks at 496 cm^{-1} and 614 cm^{-1} belonging to the characteristic vibrations of Cu–O bond, revealing the formation of CuO nanostructure [7], while the main characteristics IR features of SnO$_2$ appear at 462.38 and 596.1 cm^{-1} assigned to O–Sn–O and Sn–O stretching vibrations, respectively [8]. The SnO$_2$/CuO nanocomposite exhibits merged peaks between 481 and 600 cm^{-1}, indicating a potential interaction between CuO and SnO$_2$.

Diffuse reflectance spectral study in the UV-visible region was conducted to estimate the optical band gap of the prepared sample (Fig. 3). The Kubelka-Munk theory is used for the analysis of diffuse reflectance spectra obtained from weakly
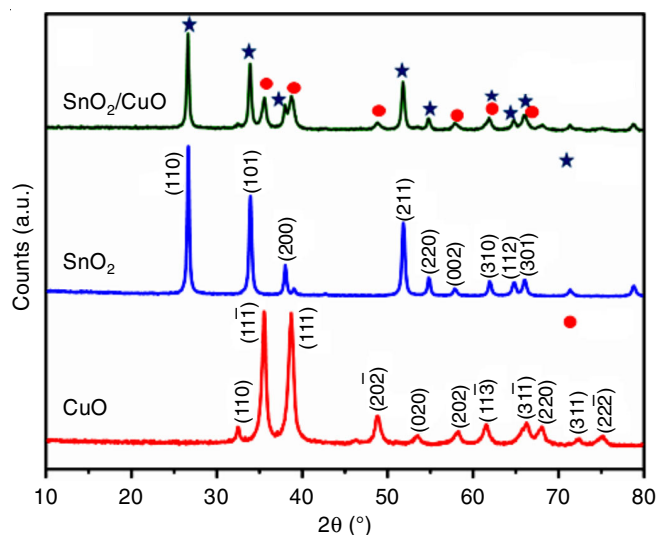

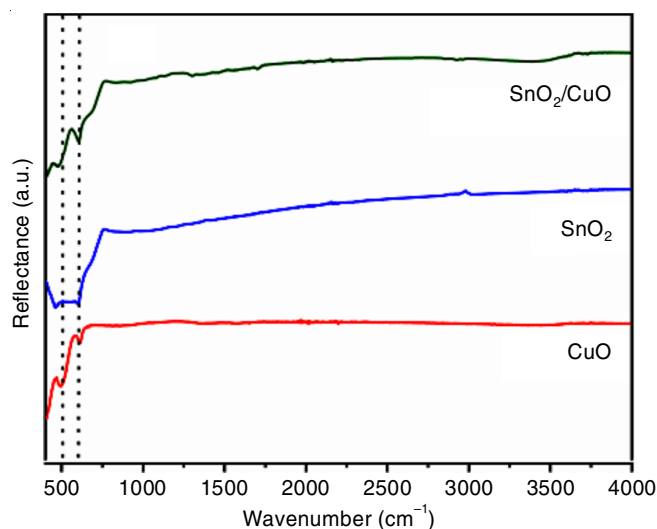Fig. 1. XRD spectra of SnO$_2$, CuO and SnO$_2$/CuO nanocomposite

Fig. 2. FTIR spectra of SnO$_2$, CuO and SnO$_2$/CuO nanocomposite

absorbing samples. The Kubelka-Munk function is obtained from eqn. 1 [9]:

$$F(R) = \frac{(1-R)^2}{2R} \qquad (1)$$

where R is the measured reflectance. The band gap of the prepared sample was calculated by plotting a graph of $[F(R)h\nu]^{0.5}$ *vs.* energy (hν) (Fig. 4). The band gap of SnO$_2$, CuO and CuO/SnO$_2$ nanocomposite were found to be 3.32, 1.30 and 1.4 eV, respectively.

The SEM image of SnO$_2$ nanoparticles (Fig. 5a) exhibits spherical morphology with almost uniform sized particles whereas individual CuO particles (Fig. 5b) show flake-like morphology. But in the SnO$_2$/CuO nanocomposite (Fig. 5c), the flakes are grown over the spherical structure of SnO$_2$ nanoparticles.

The catalytic activity of synthesized metal oxide and their nano composites were analyzed by selecting, the reduction of nitrophenol in presence of NaBH$_4$ as a basic reaction. *p*-Nitrophenol was converted to *p*-aminophenol due to the transfer of
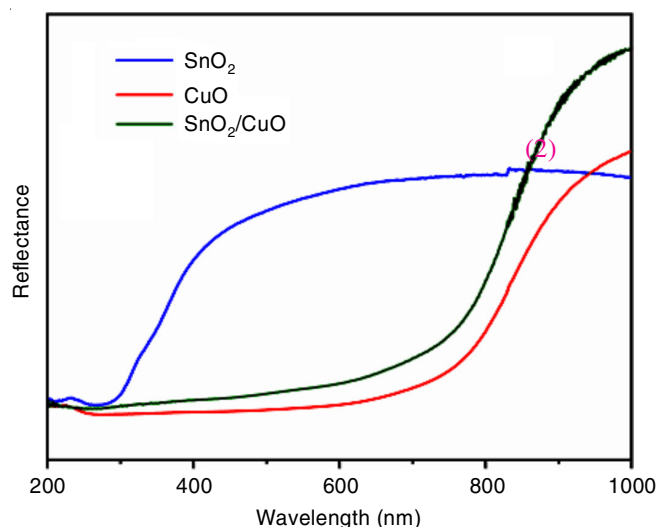
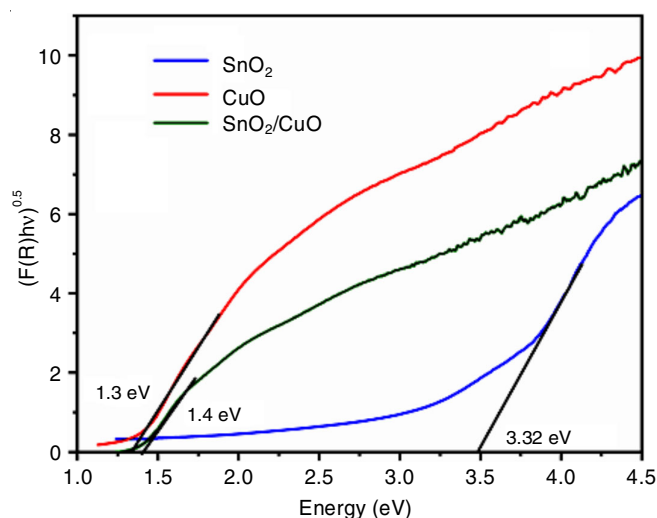Fig. 3.   Diffuse reflectance (DR) spectra of SnO₂, CuO and SnO₂/CuO nanocomposite

Fig. 4. Calculated band gaps of SnO₂, CuO and SnO₂/CuO nanocomposite

electrons from NaBH₄ to *p*-nitrophenol. However, the reaction is possible under thermodynamic condition but kinetically unfavourable because of the repelling nature of NaBH₄ and nitrophenolate ion. However, the present investigation has shown that the synthesized CuO/SnO₂ nanocomposite may address this drawback by providing reactant molecules with an improved surface for electron transfer.

Mechanism: The mechanism related to the reduction of nitrophenol to aminophenol is shown in Fig. 6. The mechanism entails the adsorption of *p*-nitrophenol and NaBH₄ and a series of electron and H⁺ transfer occurs through the surface of nano-catalyst. Initially, the interaction between *p*-nitrophenol and NaBH₄ produces the nitrophenolate ion, which then changes to unstable nitrosophenol. The unstable intermediate quickly converts to *p*-hydroxyl nitrophenol and in the final step, *p*-aminophenol is formed. The final stage was identified as the rate determining step in the whole reduction process [2].

The progress of the reaction was assessed using UV-visible absorption spectrophotometer. In the presence of NaBH₄, the aqueous solution of *p*-nitrophenol shows a characteristic red shift from 317to 400 nm as a result of formation of nitropheno-late ion [3]. But the intensity of peak at 400 nm persists for a long time, indicating the necessity of catalyst to speed up the reduction process. After the introduction of CuO/SnO₂ nano-composite, the intensity of nitrophenolate ion decreased with time, at the same time a new peak was formed at 300 nm. The new peak corresponds to *p*-aminophenol and the reaction was completed within 6 min (Fig. 7a). The current study shows that, as compared to the nanocomposite, the reduction using individual CuO and SnO₂ nanoparticles takes significantly longer time and are less effective. The synergistic action of individual nanoparticles results in the excellent catalytic activity of nanocomposites. The *p*-nitrophenol reduction with CuO ended in 12 min while it took 30 min for SnO₂ nano-particle (Fig. 7b-c).

The present work reports 97% conversion efficiency of nanocomposite (Fig. 8a) and the efficiency was calculated from eqn. 2:

$$\text{Reduction (\%)} = \frac{C_o - C_t}{C_o} \times 100$$

However, with CuO particles the conversion efficiency was 99% which is slightly greater than nanocomposite, but the time required for the same is as high as CuO-SnO₂ (Fig. 8b). While, bare SnO₂ nanoparticles exhibited 95% efficiency which is displayed in Fig. 8c.

The kinetic studies of nanocomposites revealed that the reduction follows a pseudo-first order kinetics. The rate of the reaction is independent of the concentration of NaBH₄, since the concentration of NaBH₄ was higher than that of nitrophenol in this procedure. Therefore, it is proposed that the concen-
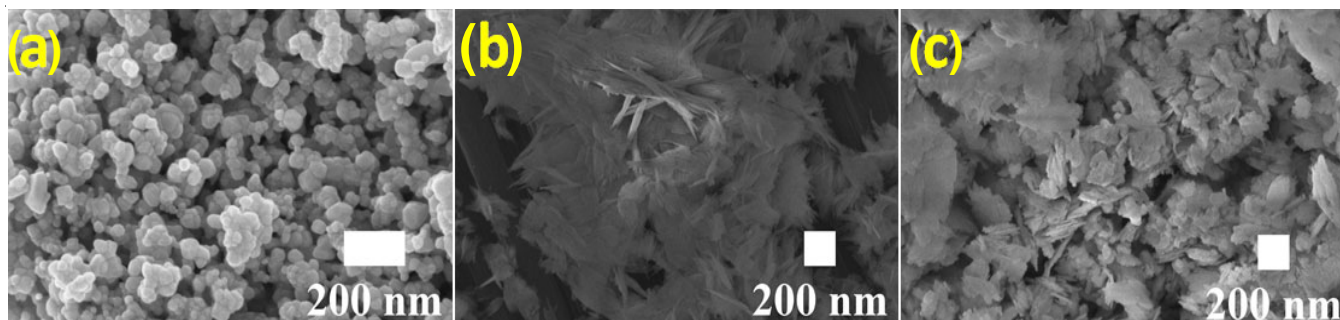

Fig. 5. SEM images of (a) SnO₂, (b) CuO and (c) SnO₂-CuO nanocomposite
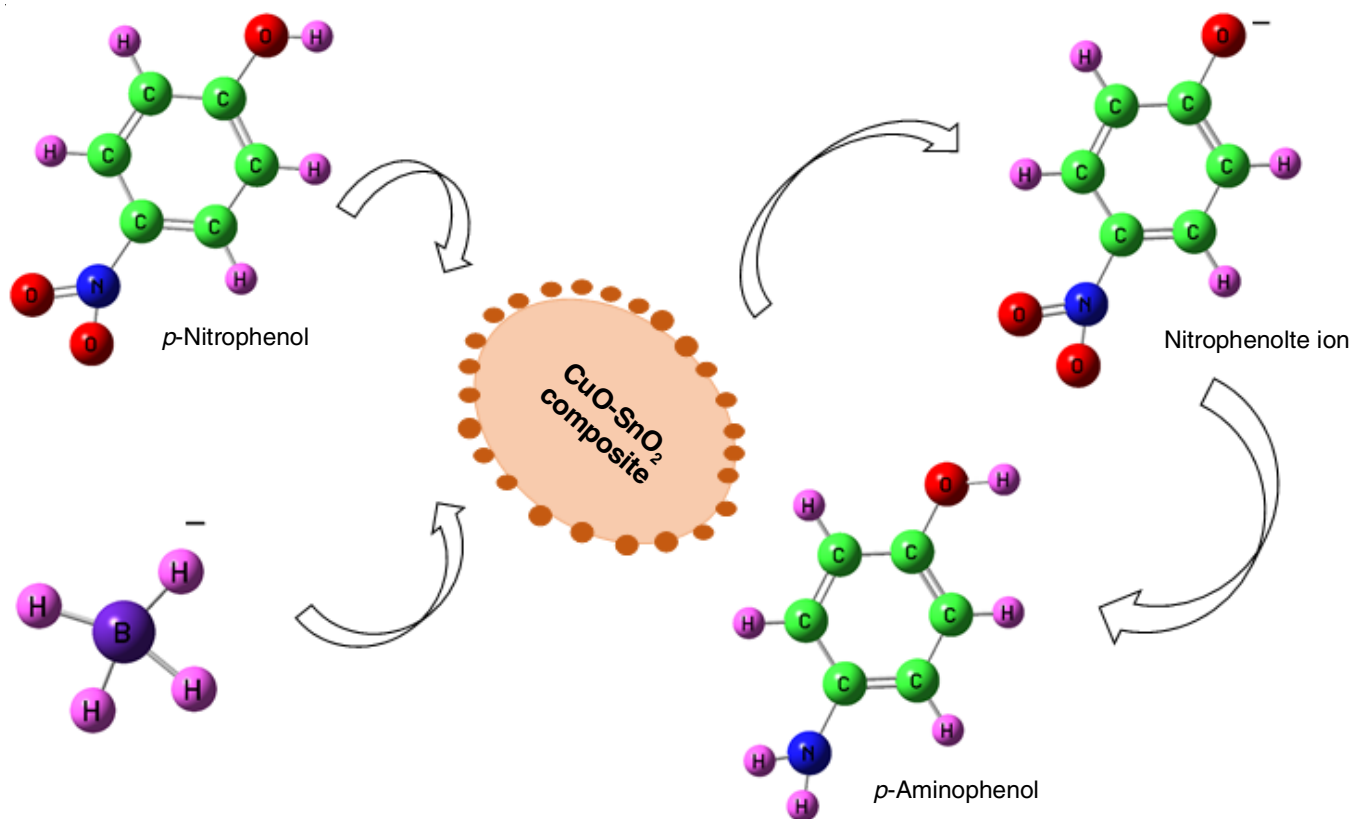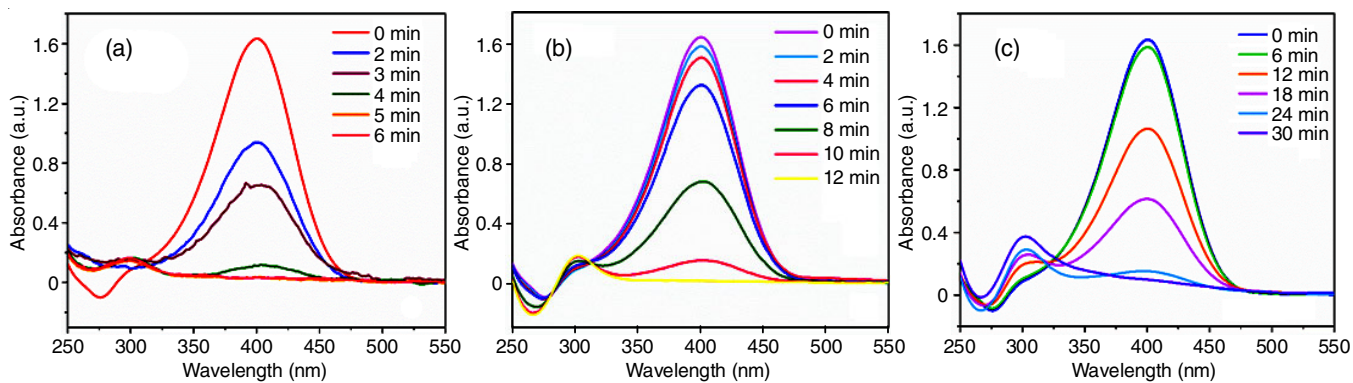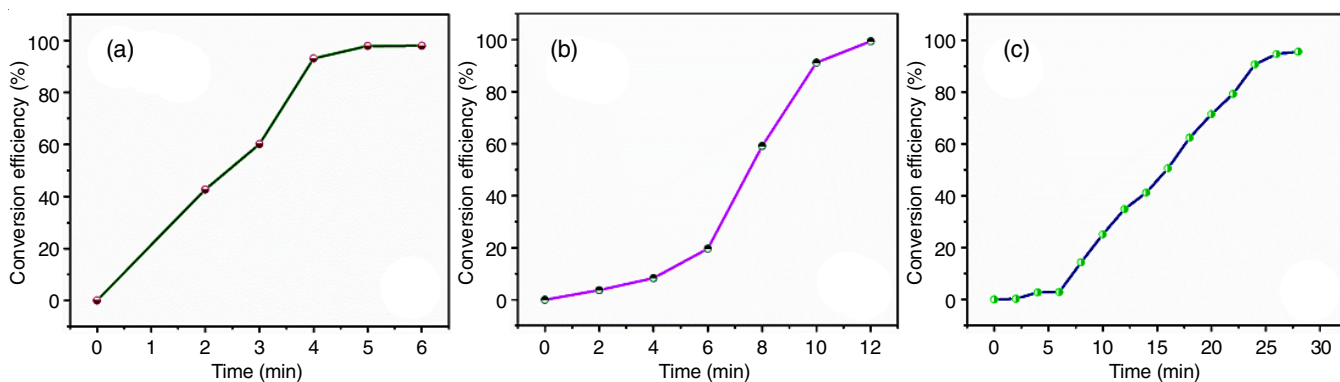
Fig. 6. Schematic showing the mechanism of nitrophenol reduction

Fig. 7. UV-Visible absorption spectra of nitrophenol at various time intervals with (a) CuO-SnO₂, (b) CuO and (c) SnO₂

Fig. 8. Percentage of degradation of nitrophenol with (a) CuO-SnO₂, (b) CuO and (c) SnO₂
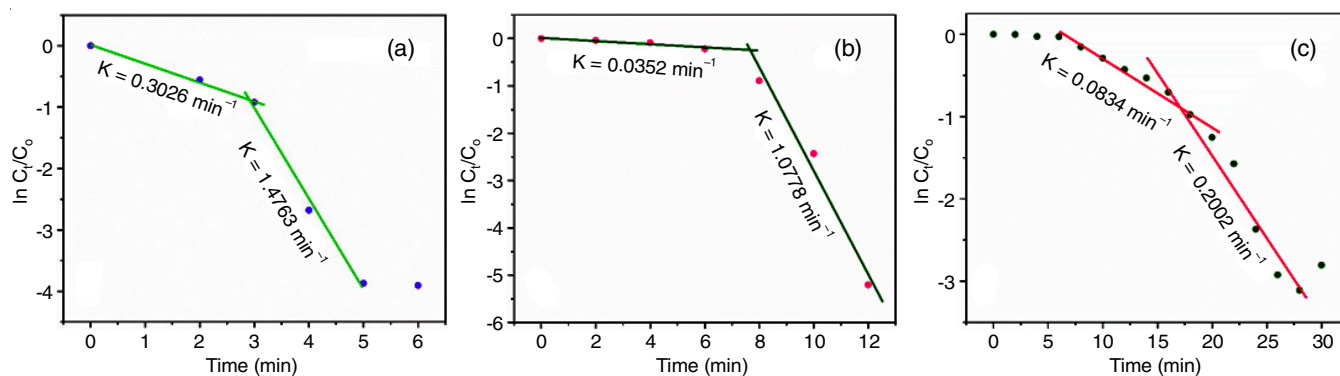
Fig. 9. Plot of ln C_t/C_o *vs.* time using (a) CuO-SnO$_2$, (b) CuO and (c) SnO$_2$

tration of NaBH$_4$ remains constant during the reaction. Hence, the pseudo-first order equation was used to determine the rate constant [10].

$$\ln\left(\frac{C_t}{C_o}\right) = -kt \qquad (3)$$

where C_o and C_t are the concentration of nitrophenol at the initial phase and different time intervals, respectively, k is the rate constant and t is the time. Fig. 9a described the linear variation of ln C_t/C_o with time, which also confirmed the pseudo-first order nature of the reduction process. The lower rate constant (k = 0.3026 min^{-1}) at the beginning is due to the rearrangement and reorganization of reactant molecules which needs some time. After that, the reaction followed with higher rate constant (k = 1.4763 min^{-1}). Similarly, the similar pattern was observed bare CuO and SnO$_2$ nanoparticles also (Fig. 9b-c).

Conclusion

A cost-effective method for the synthesis of SnO$_2$/CuO nanocomposite is discussed. The synergistic effect of the individual components acts highly effective catalyst for reducing *p*-nitrophenol under mild reaction conditions. The conversion efficiency of composite was found to be 97%. With a short span of time and with a minimum amount of catalyst, the composite exhibit high catalytic ability.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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