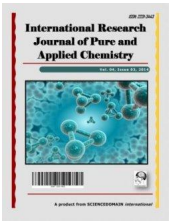

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Micro-strip Coating Method for Improved Photocatalytic Performance of ZnO through Bimetal Coupling with AgCu

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Authors' contributions

This work was carried out in collaboration between all authors. Authors HSA and AIO designed the study, performed the analysis, managed the literature search and wrote the first and came up with the draft of the manuscript. Author JY revised the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The bimetal coupling of Ag and Cu into the matrix of ZnO semiconductor was successfully achieved using microwave irradiation technique under very low synthetic temperature and power of 120^0C and 240 Watt, respectively. In order to determine the phase, structural, morphological and elemental composition of the synthesized nano-composite powder, some solid state characterizations such as Transmission electron microscopy (TEM), Field Emission Scanning Electron Microscope (FESEM), X-ray Diffraction (XRD) and Energy Dispersed X-ray (EDX) were employed. The energy band gaps of the nano-composites were estimated from adsorption data obtained from UV-Vis-NIR spectroscopy. Elemental compositions were also confirmed through the XRF analysis result. The Photo-degradation efficiency of the synthesized AgCu-ZnO nano-composite was evaluated using the micro strip coating method with Nitrobenzene as the model organic pollutant. Maximum absorption time obtained was 30 minutes and 0.75 g as maximum mass load. The efficiency of the MW-synthesized nano-composite was found to be 98.83% after 2 hrs which is higher as compared with commercial ZnO, metal coupled Ag-ZnO and Cu-ZnO.

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1. INTRODUCTION

The surface modification of any semiconductor with any noble metal is to improve its sensing and catalytic properties. Noble metal deposition onto the surface of semiconductor nano-composites is considered an effective method for the improvement of photo-catalytic efficiency through the influence of indirect interfacial charge transfer process. Ag and Cu being noble metals can effectively act as electron scavengers and store them as well. The role of metal in photo-catalysis can be explained by the understanding of photo induced interaction of interfacial charge transfer processes [1,2].

Extent of electron-hole recombination can be minimized by intensity of light luminescence. ZnO absorption of light at suitable wavelength can result in promotion of electrons from valence band to conduction band, thus, leading to the formation of hydroxyl radicals which can eventually degrade the adsorbed pollutants on the surface of the photo-catalyst.

The development of simpler, fast, efficient and low cost methods for the complete destruction of persistent organic waste water pollutant has become very necessary due to the rapid industrialization and globalization of most developing countries. Photo-degradation has been considered as one of the most promising techniques used for the complete demineralization of most persistent organic pollutants found in many industrial effluents. Nitrobenzene [NB] an aqueous pale yellow in appearance and poisonous aromatic organic waste water pollutant with bitter almond odor mostly used as aniline precursor chemical in the manufacture of textiles, pesticides, rubber materials pharmaceutical and cosmetics, is considered to be highly toxic organic pollutant that is easily absorbed in to the human body when inhaled or contacted through skin and causes sickness such as, headache, general body weakness, vertigo and sometimes vomiting [3].

Due to this reason, nitrobenzene [NB] was chosen as the model organic pollutant in the present study. Hence the effective removal of this organic waste water pollutant is recently becoming both economic and environmental problem [4,5]. Though, various methods both physical and chemical processes have been developed in order to remove these pollutants such as; coagulation method, precipitation, ultra filtration, air stripping, adsorption using light activated carbon, UV-irradiated degradation and reverse osmosis [6,7,8]. However, only UV-irradiated degradation was found to degrade NB with optimum efficiency of nitrobenzene residue as low as 8.8% achieved which is still considered insufficient and highly expensive. While all the other aforementioned existing water treatment processes and pollutant removal methods have a major drawback in the sense that they only end up transforming the pollutants into different phase instead of destroying them completely, and eventually may lead to more severe pollution (secondary pollution). Therefore it becomes necessary to develop methods of treatments that can lead to the complete destruction of the pollutants from industrial discharged waste water [9].

Micro-strip inductor and capacitor as a detector does not require complex circuit, cost effective and can be designed in the form of wireless detector or sensor. It is also a passive device and requires no power supply (on sensor) to operate. Therefore micro-strip detector can be utilized as temperature detector, pressure sensor and for personal monitoring of concentration such as dyes.

The photo-catalyst base film is known to be efficient in absorbing metal ion due to the presence of large number of hydroxyl radicals used during photo catalytic recombination for for adsorption of light. For example Surface Plasmon Resonance (SPR) spectroscopy was observed to improve the detection of heavy metal ion tremendously. Although the use of photo catalyst to degrade organic pollutant is not new, until now there is no report on the use of micro-strip incorporated with catalyst film as photo-catalyst in waste water treatment. Photo-catalyst can easily bind with metal ions to produce better dielectric constant required for adsorption.

2. METHODOLOGY

2.1 Microwave Synthesis of Bimetal AgCu-ZnO Nano-composite Powder

11 gram of Zn $(CH_3OO)_2.2H_2O$ was dissolved in 100 ml deionised water and was agitated for 15 minutes and then it was finally transferred into a Teflon reaction vessel were it was irradiated in the Microwave oven operating at 120°C and 240

Watt for 15 minutes. 2.532 grams of $AgNO_3$ was dissolved into 60 ml deionised water and then added into the zinc solution in a 250 ml conical flask and agitated for 5 mins. Then 2.532 grams of $Cu(NO_3)2.2H_2O$ was also dissolved into 60 ml deionised water and then added into the zinc solution containing the $AgNO_3$ solution in a 250 ml conical flask and agitated for 5mins, 0.146 grams of EDTA which act as the complexing agent was dissolved in 20 ml deionised water and was added into the mixture Once EDTA was added to the mixture of Silver and copper zinc solution, the solution was irradiated at 90°C and 240 Watt for 15 minutes. The mixture was allowed to cool and filtered. All the filtrates were dried in the oven at 60°C for 8 hours and stored in a dark air tight bottled. The irradiated solution was then removed from the microwave and allowed to cool down naturally. After which two separate layers of condensate and water were formed and was separated by microfiltration, filtrate was washed several times with ethanol absolute and deionised water. The obtained crystallite sample was further dried in the oven for 6 hrs at temperature of 60°C.

2.2 Immobilization of Bimetal AgCu-ZnO Nano-Composite Powder on to Micro Strip

In order to overcome the limitations experienced by earlier reports such as uneven surface coating, a special rectangular thick solid glass with thickness of $0.2\,\mathrm{cm}$ was used and a hole was drilled at the upper edge of one side of the slid which was used to tie with a thin plastic string for easy handling. First chitosan solution was prepared by dissolving 0.8 g of chitosan flakes into 100 ml of $1\%(w/v)$ acetic acid and stirred for 24 hours. The solution was then mixed the synthesized nano-powder already dissolved in de-ionized water and then coated on to the sterilized slid. The coated slid was then allowed to dry for 12 hours in an oven operating at very low power, which was further applied for the degradation process.

2.3 Photo-Degradation Procedure

In order to determine the adsorption ability of the of synthesized photocatalysts, 0.75 g each of the micro strip coated sample was immersed completely in 20 ppm nitrobenzene in 100 ml beaker and the reaction process was conducted in a dark closed air tight reaction chamber. An aliquot of the sample was withdrawn at a time interval of 15 minutes for 2 hours and filtered.

Finally, the procedure was carried out by immersing the coated strip into 100 ml of pollutant and stirred in the dark for 45 minutes to attain physical molecular absorption equilibrium. Light was then switched on and at specific time intervals of 15 minutes sample aliquot was withdrawn from bulk solution up to 120 minutes, and filtered through $0.45\,\mu m$ PTFE filters. Concentration of nitrobenzene was determined by measuring the absorption intensity at its maximum absorbance wavelength of $\lambda = 378\,\mathrm{nm}$ using UV-Visible spectro-photometer (Shimadzu, UV-1650 pc) with 1 cm path length spectrometric quartz cell, and calculated from the calibration curve. The photo-degradation percentage of the pollutant in the waste water was calculated as follows;

$$\text{Photodegradation}\,\% = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where C_0 = Initial concentration of nitrobenzene, C_t = concentration of nitrobenzene after time (*t*) of photo irradiation. All the photo-degradation experiments are carried out in triplets.

3. RESULTS AND DISCUSSION

3.1 Structural Morphology and Phase Study

Rod-like nano-crystals with hexagonal ends connecting with each other forming multi-linked rods were observed in Fig. 1a. The high magnified FESEM images revealed homogeneous diameter over the entire particles with both metals Ag and Cu well attached on the surface of the ZnO nano-rods without agglomeration. Finally it was observed that synthesized nano-composite was covered by small particles with particle sizes about 50 nm. Hence, the particles might lead to surface area increment thus, may enhance their light absorption which is of great importance in photo-catalysis.

Fig. 1b shows that the powders obtained from the microwave preparation typically contain hexagonal ZnO which is in accordance with International Centre for Diffraction Data

(Reference Code: 98-004-0985). And also exhibits a typical pattern for the face-centred-cubic Ag metal which is consistent with values of (Ref Code: 98-008-4046) and face-centred-Anorthic Cu metal which is consistent with (Ref Code: 98-011-5831). There were no extra peaks observed showing the purity and crystalline nature of the sample.

The average crystallite sizes (D) of the nanocomposite is 38.67 nm as estimated using the Sherrer's equation utilizing the data obtained from XRD PAnalytical instrument.

$D = \frac{k\lambda}{BCos\theta}$ Where λ=wave length 1.54 Å, K= constant 0.94, B= FWHM at 2θ.

3.2 Elemental Composition

EDX obtained from the FESEM shows that the composition of the selected areas of the MW as-synthesized nano-composite contains only pure elements of Zn, Ag, Cu and O as observed from Fig. 2a this confirms the purity of the sample. Extra bands observed where confirmed to be due to equipment vibration. The spectra peaks were observed $Zn_{L\alpha 1,2}$ at $1.00\,\mathrm{KeV}$, Kα$_1$ at $8.60\,\mathrm{KeV}$ and Kβ$_1$ at $9.60\,\mathrm{KeV}$. This indicates that the coupling of the metals into the matrix of the ZnO semiconductor did not affect the structural and morphological properties of the actual ZnO material.

TEM images of the MW-synthesized nano-composite shown in Fig. 2b revealed all the particles having sizes below 100 nm in diameter which is in agreement with the estimated average crystallite sizes from the XRD results.

3.3 Optical Study using UV-VIS-NIR Spectroscopy

UV-VIS-NIR spectrophotometer was used to measure the absorbance of the as-synthesized nanocomposite at room temperature in the wavelength range 220-800 nm and band gap absorbance edge was found to appear at 378 nm which is within the visible region. The band gap energy which is the photon energy at which transition between absorption and non absorbing behaviour takes place is determined as $2.85\,\mathrm{eV}$ through linear fitting of the sample absorption spectrum edge using the Kubelka Munk plot analysis which is the transition region. As observed in Fig. 3.

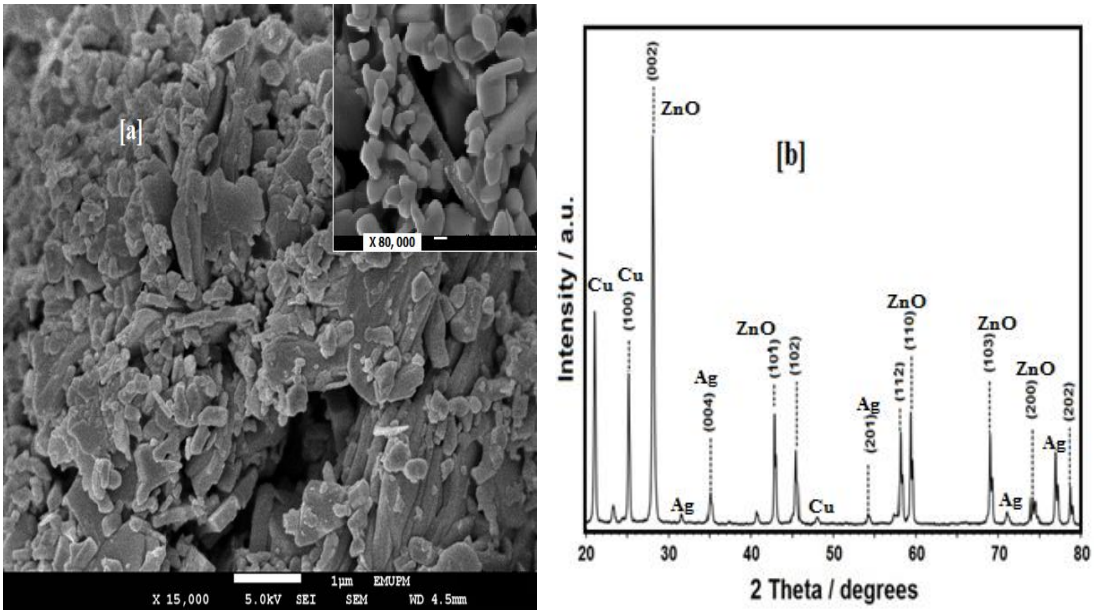


Fig. 1(a). Low and high magnified FESEM image and (b) XRD spectra of microwave synthesized AgCu/ZnO nano-composite before immobilization

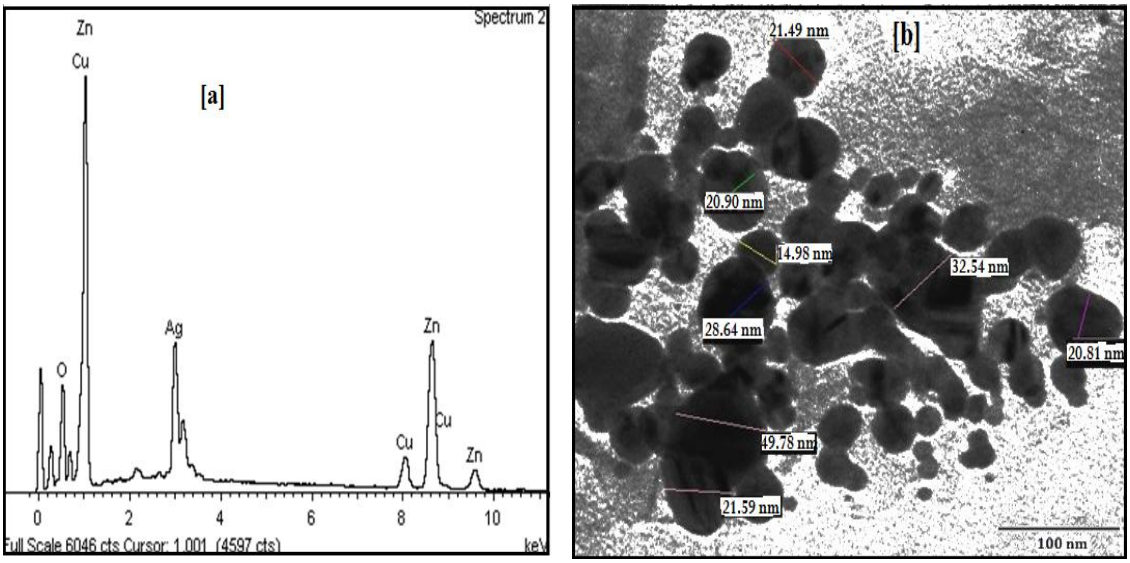


Fig. 2(a). EDX spectra and (b) TEM image of AgCu/ZnO nanocomposite magnified at 42,000m

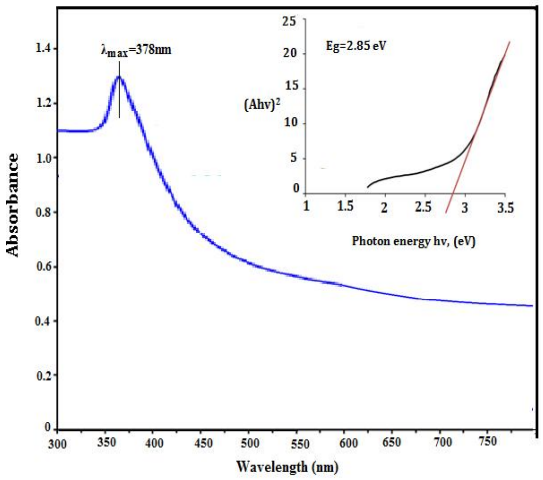


Fig. 3. Energy band gap and absorption energy of AgCu/ZnO nano-composite

3.4 Optimization Study

The determination of the optimum photo-catalyst loading is of utmost importance when conducting any type of heterogeneous photo-catalytic reaction in order to avoid excessive usage. The effect of photo-catalyst loading in the photo-degradation efficiency of nitrobenzene was tested as shown in Fig. 4a. Obtained results revealed an increase in photo-degradation efficiency up to 98.83% by increasing the mass load from $0.25\,gL^{-1}$ to $0.75\,gL^{-1}$ before declining down with further increase in mass load from $0.75\,gL^{-1}$ to $1.0\,gL^{-1}$. While Fig. 4b reveals a decrease in the photo-degradation percentage of nitrobenzene as concentration was increased. This could be due to the active sites of the photo-catalyst being covered with the nitrobenzene at higher concentration and it's intermediate as a result of the photo-degradation process leading to reduction in $e^- - h^+$ generation and consequently causes reduction in photo-degradation efficiency [10]. Another possibility may be at constant photo-catalyst mass, the amount of ^{-}OH and O_2^{-2} species formed at the surface of the photo-catalyst tend to be constant, at constant photo-catalyst mass, illumination time and light intensity. Thereby, the relative ratio of the species attacking nitrobenzene decrease with increasing concentration of nitrobenzene which leads to decrease in photo-degradation percentage (for photo-generated h^+ can be another responsible factor for the decrease in photo-degradation rate [11]. Similar results were observed by Pannee et al . [12], Pardeshi and Patil [13].

The increase in concentration of a substrate can result in the generation of reaction intermediates capable of absorbing at Photo-catalyst surface. However the gradual diffusion of these generated intermediates can lead to complete active sites deactivation of the photocatalysts which can reduce the overall photo-degradation rate.

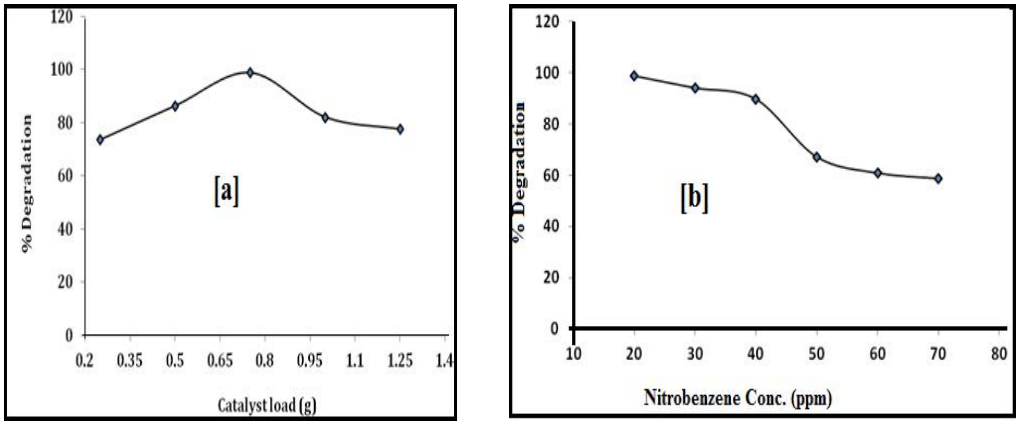


Fig. 4. Effect of (a) catalyst mass loading (b) [NB] photodegradation efficiency of AgCu/ZnO. Experimental condition: $[AgCu/ZnO] = 0.75\ gL^{-1}$ **, pH=7.43**

3.5 Kinetics of Photo-catalytic Mechanism of the Nitrobenzene

The total number of photo-catalytic active site at lower pollutant concentration may not be a limiting factor at lower nitrobenzene concentration since the photo-degradation rate is proportional to the nitrobenzene concentration which is in accordance to the pseudo-first-order reaction kinetics of the Langmuir-Hinshelwood model (L-H model).

$$r = -\frac{dc}{dt} = Kr\,\theta = \frac{KrKC}{1 + KC} = K_0 C \qquad (2)$$

Where K_0 is expressed in ($\min^{-1}$) which is equivalent to krK. By rearranging and integrating equation 2, a typical pseudo-first-order equation can be obtained as follows:

$$C = C_0 e^{-K_0 t} \qquad (3)$$

In order to determine the photo-catalytic activity of the photocatalysts, the rate constant (K_0) is chosen to be the basic kinetic parameter since it is independent on the dark adsorption period and remaining solution concentration.

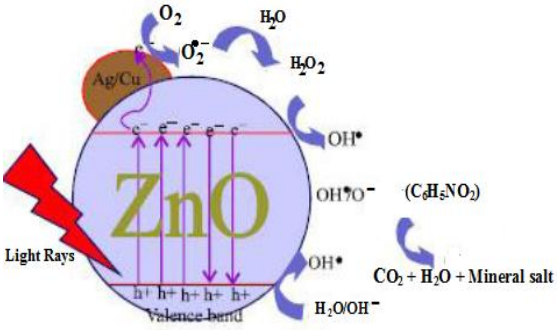
$$In\,\frac{C_0}{C} = KrKt = K_0 t \qquad (4)$$

C= remaining [NB] in the solution at a given irradiation time t, C*o*= initial [NB] at time t = 0.

Thus, the rate constant serves as a comparing description for the photo-catalytic reaction rate in the reaction system. These rate constant for the first-order reaction kinetic is used for the linear fitting of the experimental data as shown in Fig. 5a the plot of the variations of $In\frac{C_0}{C}$ as function of time. And the K_0 value according to the straight line was obtained as 1.7×10^{-4} with $R^2 = 0.999$ at the rate of -0.01 and the total amount of nitrobenzene removed at this rate as shown in Fig. 5b.

3.6 Photo-catalytic Mechanism of (Ag/Cu) Coupled ZnO with NB

The photocatalytic mechanism of Ag/Cu coupled ZnO nano-composites for organic pollutant nitrobenzene can be proposed as follows:



Schematic diagram illustrating Mechanism for photo-catalytic process of Ag/Cu coupled ZnO nano-composite for nitrobenzene under visible light irradiation.

$$ZnO + hv \rightarrow e_{CB}^{-} + h_{VB}^{+} \qquad (I)$$

$V_o^{**} + e_{CB}^- \rightarrow V_o^*$ (II)

$V_o^* + O_2 \rightarrow V_o^{**} + O_2^{\cdot-}$ (III)

Ag $\rightarrow Ag^{2+} + 2(e_{CB}^-)$ (IV)

$Ag^{2+} + 2(e_{CB}^-) \rightarrow$ Ag (V)

$OH^- + h_{VB}^+ \rightarrow {}^{\cdot}OH$ (VI)

$O_2^{\cdot-} + H_2O \rightarrow H_2O_2$ (VII)

$H_2O_2 + e_{CB}^- \rightarrow 2{}^{\cdot}OH$ (VIII)

$OH/O_2^{\cdot-}$ + Nitrobenzene ($C_6H_5NO_2$) $\rightarrow CO_2 + H_2O$ + (Mineral salts (IX)

3.7 TOC Removal and Reusability

The TOC removal capability of bimetal AgCu-ZnO nano-composite to remove both the total organic and inorganic carbon present in nitrobenzene was determined to be 92% at catalyst dosage of $0.75 gL^{-1}$ and 20ppm NB concentration at neutral pH as illustrated in Fig. 6a.

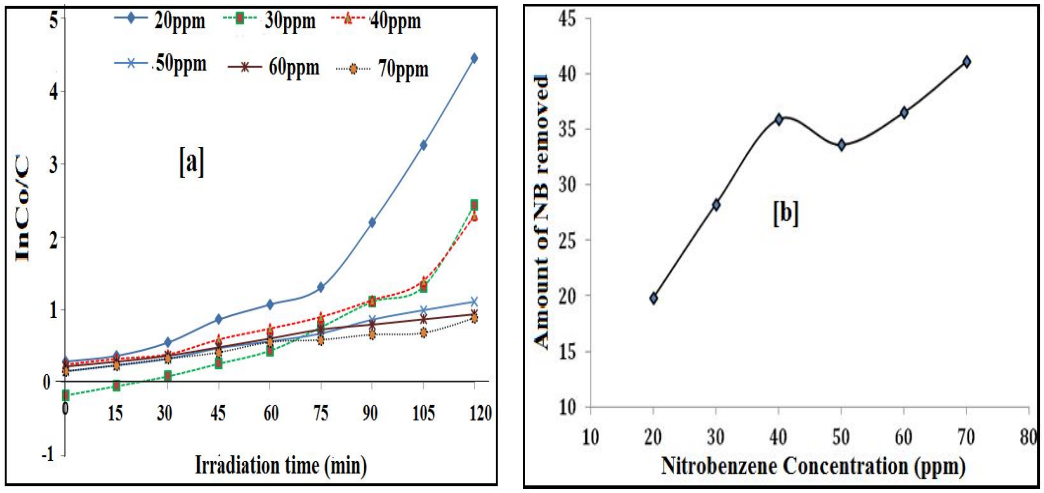


Fig. 5(a). Linear plot of ln Co/C Versus Reaction time (min) (b) Amount of nitrobenzene removed by AgCu/ZnO. Condition: $[NB] = 10 - 80$ ppm $pH = 7.43$, $Tempt = 25^o C$ $[AgCu/ZnO] = 0.75\ gL^{-1}$

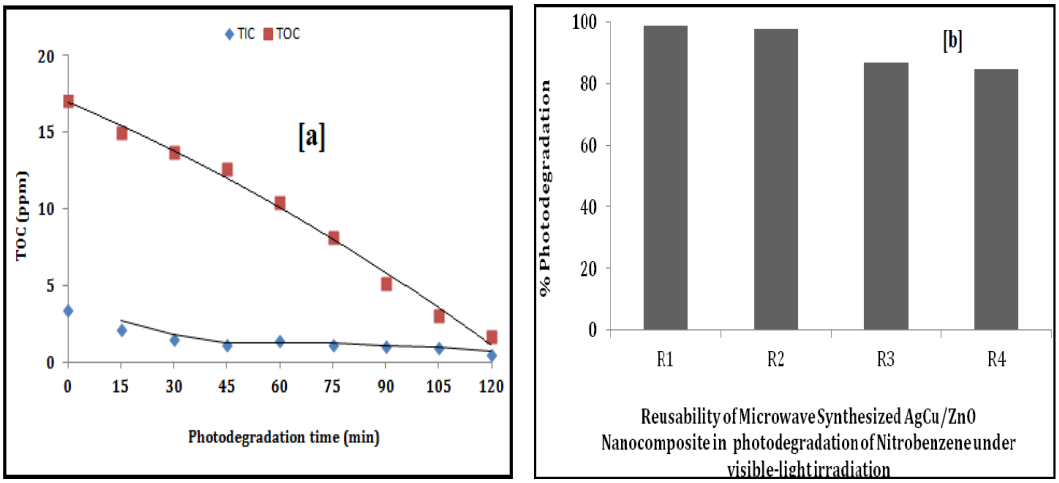


Fig. 6(a). Total Organic Carbon Removal Ability; (b) Reusability of AgCu-ZnO in degradation of NB. R1-R4 are the slides reused cycles. Experimental Condition: [NB]= 20 ppm, pH=7.43, $[AgCu/ZnO] = 0.75\ gL^{-1}$**, t=2 hrs**

The reusability of the sample was investigated by keeping all parameters constant such as irradiation time, pH of solution, catalyst load and concentration of nitrobenzene. After every usage, the catalyst was micro-filtered from the reaction mixture, rinsed several times with de-ionized water and dried at 60°C in the oven for 6hrs. The dried recovered catalyst was then reused 3 times for the degradation process as previously conducted before the reduction in performance was observed at the fourth time and this could be as a result of the photocatalysts being shielded by the nitrobenzene through coverage of the active sites on its surface, thus causing instability of the catalyst as more and more active sites tend to be covered by the nitrobenzene. Result obtained is shown in Fig. 6b were no significant drop in efficiency was observed from round 1-2 (R1-R2). But little decrease was observed from R2-R4. This confirms the reusability as-synthesized sample.

4. CONCLUSION

Based on the present study, the microwave irradiation technique can be regarded as an effective method for the preparation of bimetal coupling of ZnO. It was also observed that MW-irradiation technique has the ability to bind the metals (Ag and Cu) composites into the matrix of a semiconductor ZnO without affecting the structural and morphological properties of the material. The technique increases the catalysts performance through optical character enhancement by reducing its energy band gap and promoting its adsorption capability towards the visible spectral region. The synthesized nano-composite showed hexagonal wurtzite ZnO crystallite structure with crystalline sizes below 50 nm .The photo-degradation efficiency of the synthesized nano-composite was evaluated by employing nitrobenzene as a model organic pollutant. Maximum adsorption time was found to be 30 minutes with $0.75\ gL^{-1}$ as maximum mass load with the highest efficiency of 98.83% reached after 2 hours of photo degradation period and the reusability of the photo-catalyst was investigated and was found to be stable and decreased after the third round.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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