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Enhanced Photocatalytic Efficiency of Microwave Synthesized Cu/ZnO Nanocomposite

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Abstract
The use of visible light for the Photodegradation and mineralization of the pollutant nitrobenzene was successfully achieved using microwave synthesized coupled Cu/ZnO nanocomposite as photocatalyst by applying the dispersion method. Photocatalytic efficiency of the synthesized photocatalyst was evaluated by studying different variable conditions such as amount of photocatalyst loading, pollutant (Nitrobenzene) concentration and the reusability. Optimization study revealed that 86.7% of nitrobenzene was removed by 0.25 g/L photocatalyst at nitrobenzene concentration of 20 ppm. Mineralization of the pollutant recorded using the UV-Vis spectrophotometer shows that during 2hrs of irradiation period 86.7% degradation efficiency was obtained and 76% of the total organic carbon is removed from the solution.

Keywords: Cu/ZnO, Photodegradation, Microwave, Metal coupling, Nitrobenzene

1. Introduction
Though various semiconductor photo-catalysts have been used, ZnO nanomaterial has received much attention due to its chemical and thermal stability, non-toxicity, high catalytic efficiency and low cost [1]. The major advantages of ZnO over other semiconductor nanocomposites is its absorption ability of great portion of the solar spectrum, thus, able to remove many organic pollutants in an aqueous solution under visible light irradiation[2].
Significant efforts have been made to retard the recombination of the photo-excited electron-hole pairs and enhance photo-catalysis by coupling the photocatalyst with other materials such as semi-conductors and metal such as Au/ZnO, Pd/ZnO, CuO-ZnO and Ag/ZnO. Comparing Au, Pd, Ag and Cu, Cu is less expensive and has become priority for further investigation [3, 4 &5]

Methodology
Photodegradation procedure
The photodegradation of nitrobenzene was performed in a closed and sealed batch photo reactor equipped with Philips lamp (23 Watt) as light source. Air pump was used to increase oxygen access, eliminate effect of lamp's heat and fluidize the catalyst at the rate of approximately 10m^3/hr. The solution was magnetically stirred at 190 rpm to maintain the homogeneity of the solution throughout the reaction period. Prior to time of experiment, the Philip lamp was turned on for about 5 mins in order to warm up for constant output supply. The photocatalytic degradation was carried by suspending 0.5 g photocatalyst in 1000 mL of nitrobenzene solution and stirred in the dark for 45 min to attain absorption equilibrium, before switching on the light. At specific time intervals, sample aliquot was withdrawn from bulk solution and filtered through 0.45µm PTFE filters. The residual concentration of nitrobenzene was determined at its maximum absorbance wavelength of λ_{max} = 267 nm using UV-Visible spectrophotometer (Shimadzu, UV-1650 PC). The photodegradation percentage was calculated as follows:

$$\text{Photodegradation \%} = \left[\frac{C_t - C_0}{C_0}\right] \times 100$$

Where $\boldsymbol{C_0}$ = Initial concentration of nitrobenzene, $\boldsymbol{C_t}$ = concentration of nitrobenzene after time $\boldsymbol{t}$ of photo-irradiation. All the photodegradation experiments for carried out in triplets.

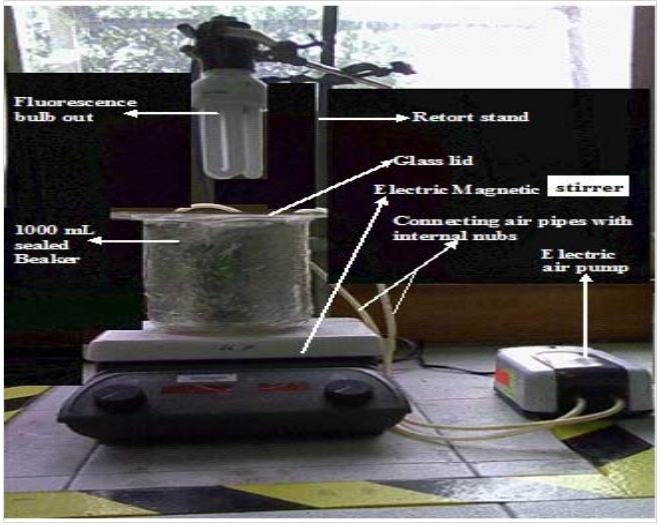


Fig 1: Experimental set up for Nitrobenzene photodegradation

TOC Measurement

TOC measurement is a valuable environmental analytical technique which is required in waste water, municipal water systems and industries for process control and regulation of levels of organic discharge. TOC is also used for protection of important and vital systems by monitoring the process of water quality and raw material feedstock. In this analysis, approximately 30 mL of the nitrobenzene solution was placed in glass vial. The TOC measurement of the samples was made using Shimadzu Total Organic Carbon (TOC) Analyzer which is combined with ASI-V automated sampler.

Results and Discussion

Optimization

The photodegradation efficiency of the microwave synthesized Cu/ZnO nanocomposite semiconductor photocatalyst material has been investigated under visible light and its properties such as structural, morphological, particle size, elemental compositions, molecular vibrational study and optical studies were determined and reported in our earlier work[6]. Experimental results obtained showed the optimum effective catalyst load as 0.25g/L Fig. 1a which is capable of removing up to 86.7% of nitrobenzene effectively within 2 hours as illustrated in Fig 1b. Thus the degradation process can be observed to follow the first order Langmuir-Hinshelwood reaction kinetics Fig. 2d. With maximum efficiency achieved at very low catalyst load of 0.25 g and pollutant concentration of 20 ppm Fig. 2c. The observed efficiency can probably be as a result of low recombination of photogenerated charge carriers resulting from efficient charge transfer between the semiconductor ZnO and the metal Cu.

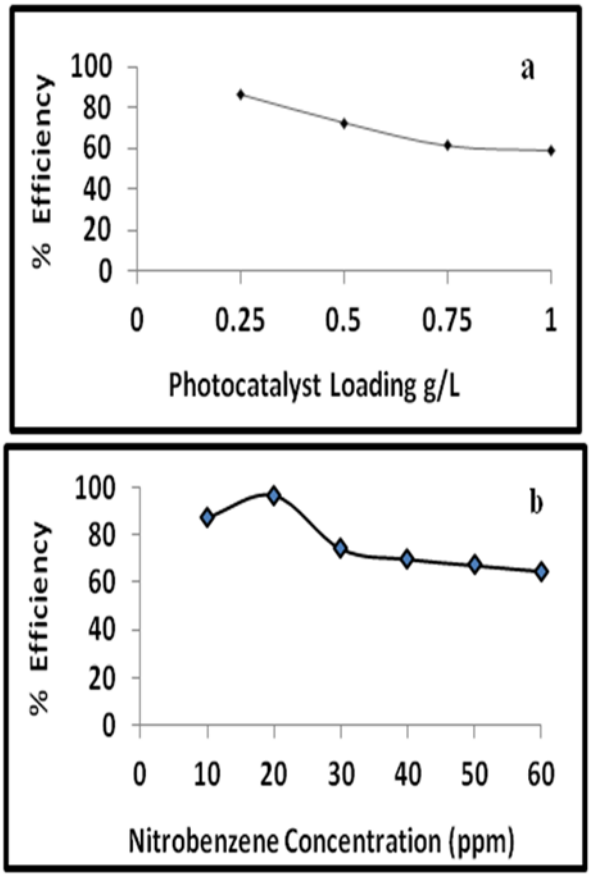


Fig 2 (a&b): Effect of (**a**) photocatalyst loading, and (**b**) concentration on photodegradation efficiency. Condition: Conc. = 20-70ppm, Mass load =0.25-1 g/L and pH=7.43 for the period of 2hrs.

Rate and Order Determination

The plot of Photocatalytic degradation rate with concentration of nitrobenzene at optimum value of 20 ppm tends to exhibit quadratic linear behaviour as observed from Fig. 2c. The rate shows nonlinear function with nitrobenzene concentration (C *nitrobenzene*). This observed behaviour may best be attributed to the catalyst surface interaction with the nitrobenzene concentration since a mechanistic photocatalytic study over photocatalyst surface usually involves a single constituent (model organic pollutant) at a given time, thus effect of pollutant concentration on the photodegradation rate of the molecules in the organic pollutant can simply be described by pseudo-first-order reaction kinetics expressed in terms of Langmuir-Hinshelwood (L-H) model, adjusted in order to accommodate reactions that occur at the solid-liquid interface. Due to the surface area dependency of the L-H model, the dependency of rate on concentration of substrate can be expressed as follows:

$$r = -\frac{dc}{dt} = Kr\theta = \frac{KrKC}{1+KC} \quad (1)$$

r = reaction rate and is said to be proportional to the fraction of the substrate surface of the organic pollutant (q), Kr = Reaction rate constant, C= Concentration of organic substrate (pollutant), and K= Langmuir absorption constant. The maximum substrate concentration in the present study was observed to be low thus; the first-order rate constant for the reaction can further be expressed as:

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

Where ko is expressed in (min¡1) which is equivalent to krK. By rearranging and integrating equation 4.8, a typical pseudo-first-order equation can be obtained as follows:

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

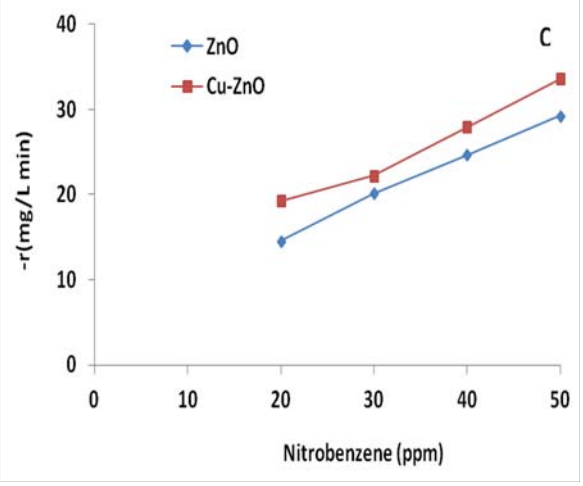
In order to determine the photocatalytic activity of the photocatalysts, the rate constant (ko) is chosen to be the basic kinetic parameter since it is independent on the dark adsorption period and remaining solution concentration. Therefore, the rate constant would serve as a description and comparison in the reaction system for the photocatalytic reaction rate. These rate constant for the first-order reaction kinetic is used for the linear fitting of the experimental data as shown in Fig. 1c as follows:

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

C=Concentration of the remaining Nitrobenzene in the solution at a given irradiation time t, Co= initial concentration of nitrobenzene at time t = 0. The plot of the variations of $In\frac{C_0}{C}$ as function of time is shown in Fig. 2d. And the K_0 value according to the straight line was obtained and presented in Table 1.

Table 1: Rate constant determined at various concentrations of NB

$Concentration(ppm)$	$K_0(\min)^{-1}$	R^2	*Rate*
20	5.0×10^{-3}	0.979	-0.01
40	2.5×10^{-4}	0.972	-0.001
60	1.7×10^{-4}	0.990	-0.01
80	1.25×10^{-4}	0.893	-0.01
100	1.0×10^{-5}	0.805	-0.001



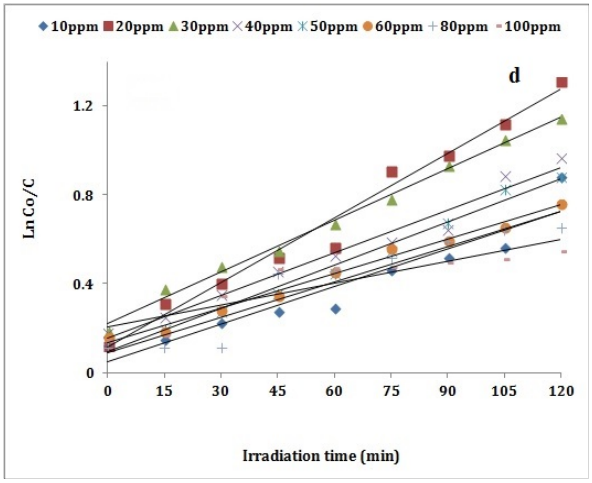


Fig 2 (c & d): (**c**) Rate constants (r), and (**d**) Logarithmic plot of In Co/C Versus Reaction time (t, min) Condition; 20-70ppm and pH=7.43, for the period of 2hrs.

Effect of pH

The effect pH of the nitrobenzene solution on the photocatalytic performance of the synthesized Cu/ZnO photocatalysts was tested and results obtained are shown in Fig. 3a.The pH was found to significantly affect the photocatalytic activity of the photocatalyst and the optimal pH was observed at pH range of 5-7 where the percent of nitrobenzene photodegradation increased from 53.23 to 72.87% Fig. 3a. But as pH increases above 7.43, the Photodegradation% efficiency was found to decrease.

Therefore, the effect of pH of Nitrobenzene on the photocatalytic activity of the synthesized Cu/ZnO photocatalysts can be explained from the point charge basis of the ZnO where the interfacial charge-transfer tends to be affected by changing the pH of the pollutant thus shifting the redox-potentials of both the valence and conduction bands [7]. At the surface of the ZnO, the photocatalyst is said to be positively charged at lower pH while at higher pH values it becomes negatively charged. Nitrobenzene being a cationic organic compound favors its high adsorption at high pH on the surface of the photocatalyst resulting in higher percentage photodegradation performance under the neutral and basic conditions.

Though at high pH, the actual stability of the photocatalyst might not be necessarily guaranteed due to alkaline dissolution [2, 7 & 8].

Total Organic Carbon (TOC) Analysis

After Photodegradation measurement, total organic and inorganic carbons removal ability of the samples was determined (TOC & TIC) using TOC analyzer. The total organic carbon (TOC), usually measured in ppm or mg/L, is the sum concentration measurement of all organic carbon atoms in the molecule of a given water sample that are covalently bonded. It does not specifically identify organic contaminants, but identifies the presence of any organic contaminant by detecting the presence of all carbon bearing molecules, regardless of the molecular make-up. The TOC value is obtained by subtracting the inorganic carbon (IC) from the total carbon (TC) (TC-IC=TOC) Fig. 3b

Based on the present study, the microwave irradiation technique can be regarded as an effective method for the synthesis of Cu/ZnO nanocomposite photo catalyst. The photodegradation efficiency of the synthesized nanocomposites was evaluated by employing nitrobenzene as a model organic pollutant and the maximum absorption time was found to be 45 mins with 0.25 g/L as maximum mass load after 2 hours of photodegradation period.

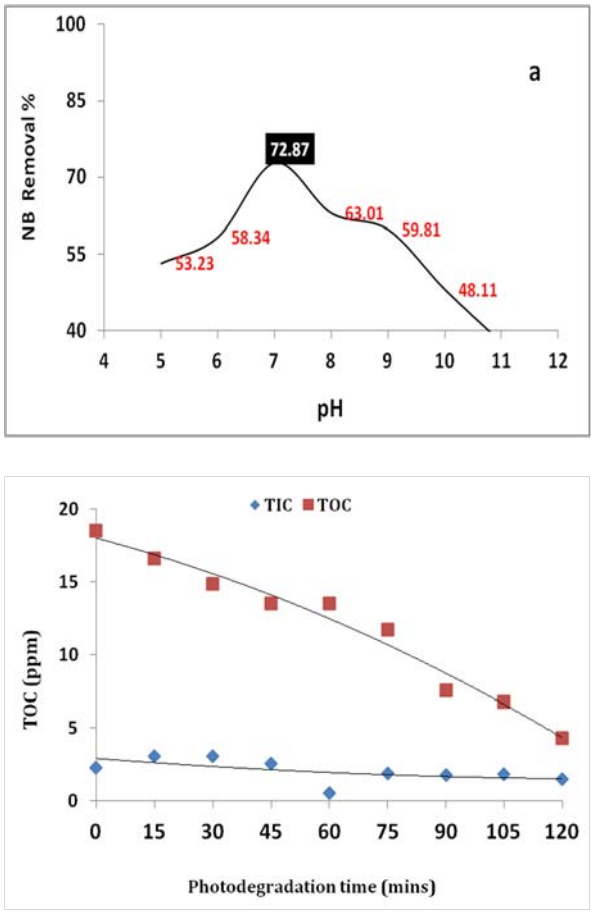


Fig 3: (**a**) Effect of pH of solution on NB photodegradation; (**b**) Amount of TOC and TIC during nitrobenzene photo-degradation under visible light irradiation. Reaction condition; Conc. = 20 ppm, pH = 5-11, time =2 hrs.

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