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Photocatalytic Degradation of Metronidazole in Aqueous Solutions by Copper oxide nanoparticles

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Abstract

CuO has been synthesized in the nano-sized (10-15 nm) and examined as a photocatalyst for degradation of metronidazole in its aqueous solution. The removal studies were performed in the absence of light and under the effect of UV-radiation. The influences of various operational parameters such as catalyst dose, drug concentration, and time of exposure on percentage photodegradation of metronidazole were investigated. The experimental results revealed that the photodegradation of metronidazole increased with increasing CuO dose and exposure time, while decreasing with increase initial concentration of metronidazole. The maximum degradation efficiency (85.0%) occurred after about 120 min of irradiation. The degradation rate followed first order kinetics with a rate constant of 0.0198 min^{-1}.

1. Introduction

Antibiotics are organic compounds effective against bacterial infections, certain fungal infections and some kinds of parasites. Hazardous drugs are often prepared and administered to human and animal patients in hospitals, outpatient centers, physician's offices, veterinary hospitals and veterinary clinics. Generally, pharmaceuticals reach waterways through the discharge of wastewaters and effluents on environment, which often are not properly treated.

Several alternatives to eliminate pharmaceutical compounds in water have been considered. These include reverse osmosis [1], adsorption onto activated carbons [2], ozonation [3], advanced oxidation processes, such as the Fenton or photo-Fenton system [4], ultrasound [5], peroxidation combined with UV light [6], photocatalysis using TiO_2 [7] or advanced oxidation hybrid processes [8]. Advanced oxidation processes (AOPs), are based on the production and use of hydroxyl radicals, which are strong oxidizing species that react with most organic contaminants [9].

The majority of pharmaceuticals are photo-active having the ablility to absorb light as because their structures generally contain aromatic rings, heteroatoms, and other functional groups that enable them to absorb UV and visible radiation (direct photolysis) or to react with photosensitizing species (indirect photolysis) [10].

The photodegradation of metronidazole was studied by direct absorption of UV radiation [11]. Because the use of nanoparticles technology may be a promising approach for antibiotic wastewater treatment, a great attention is focused on the potential of many types of nano materials for water treatment. The removal of metronidazole in aqueous solution by nanoscale particles was investigated by several methods. Zero-valent iron nanoparticles have been used for removal of metronidazole from aqueous solution by applying Fenton reaction [12]. Zero-valent iron [13] and also zero-valent nickel and zinc oxide [14] were used in their nano-scale size as effective materials for metronidazole removal from wastewater by either adsorption or photodegradation.

Metronidazole (2-(2-methyl-5-nitro-1H-imidazol-1-yl) ethanol), is an antibiotic used in the treatment of infections caused by a wide range of anaerobic bacteria, protozoa and bacteroides, including trichomoniasis, amoebiasis, vaginosis and gingivitis [15]. In this study the degradation of metronidazole using copper oxide nanoparticles was examined. Operating factors such as initial drug concentration, photocatalyst dosage, and photocatalysis time were investigated in order to evaluate the extent of mineralization.

2. Materials and Methods

2.1. Preparation of Copper oxide nanoparticles

CuO nano powder was prepared by Sol-Gel method [16]. An aqueous solution of $CuCl_2.6H_2O$ (0.2 M) was placed in a clean round bottom flask. 1 ml of glacial acetic acid was added to above aqueous solution and heated to 100 ºC with constant stirring. 8 M NaOH was then added to the heated solution till pH reached 7. The color of the solution turned to black and a large amount of black precipitate was formed immediately. The solution was centrifuged and washed several times with deionized water. The obtained precipitate was dried in air for 24 h.

2.2. Reagents

Metronidazole Fig. 1 was obtained as a pure substance from Copper chloride, NaOH, and glacial acetic acid were of analytical grade and purchased from Sigma–Aldrich and used without further purification. Double distilled water was used throughout all experiments.

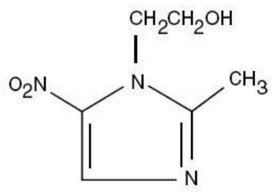

Fig 1**:** Chemical structure of metronidazole

2.3. Experimental procedures

The batch experiments of metronidazole degradation were performed in a 250 ml glass beaker, where a total of 100 ml of metronidazole solution was used. The solution inside the beaker was exposed vertically to 15 W UV-254 lamp mercury (0000) at a fixed height (20 cm) as shown in Fig. 2. After the irradiation time, samples were withdrawn from the beaker and quickly analyzed. Another set of experiments were performed in dark to study the effect of adsorption efficiency only.

Metronidazole concentration was quantified by an Aquamate V4.60 UV spectrophotometer (Thermo Scientific, USA) using for the quantification the wavelengths of 318.5 nm.

The amount of the drug adsorbed per unit mass of the CuO was evaluated by using following equations:

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (1)$$

Where, C_0 is the initial metal ion concentration, and C_e is the analyte concentration at equilibrium and V is the volume of metal ion solution in milliliters, W is the mass of adsorbent in grams. The percent of drug removal was evaluated from the equation:

$$\%\text{Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

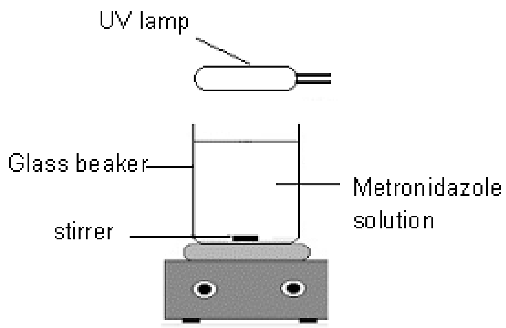

Fig 2: Schematic diagram of the photocatalytic system

3. Results and discussion

3.1. Characterization of copper oxide nanoparticles

The particle size and morphology of the prepared nanoparticles particle were observed with transmission electron microscope (TEM, Hitachi VP-SEM S-3400N, Germany), the particle size was from 10-15 nm Fig. 3.

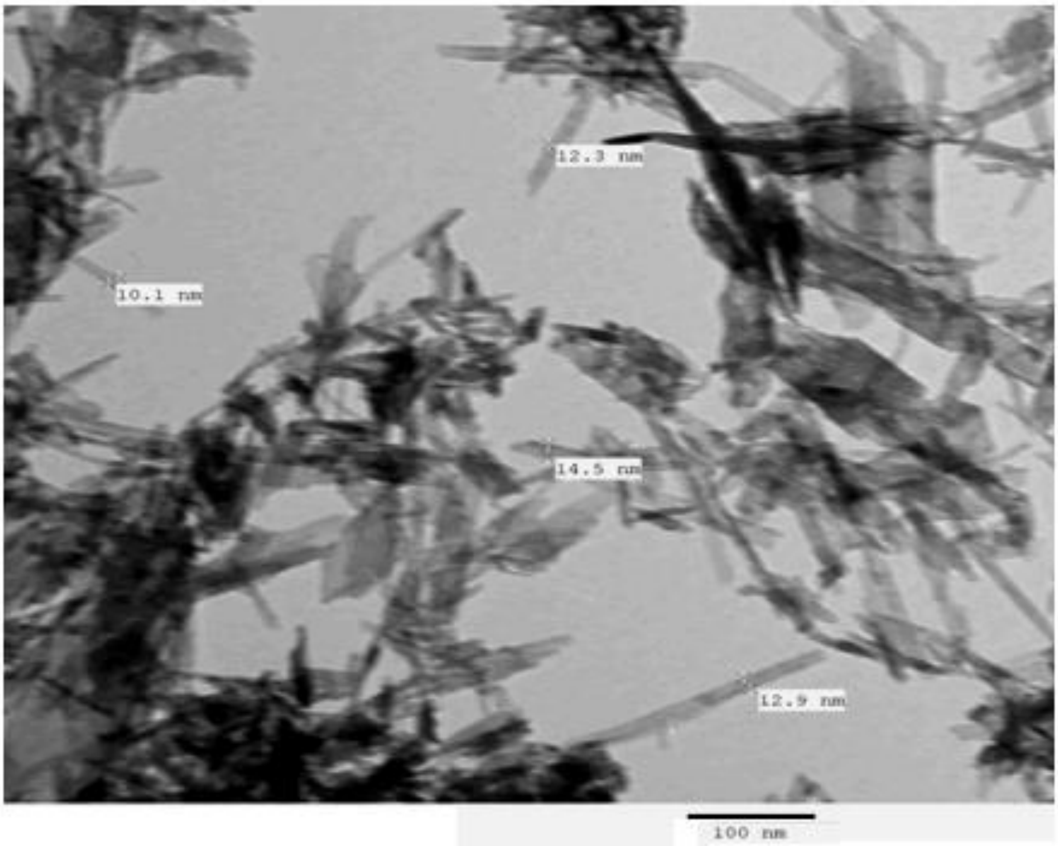

Fig 3: TEM image of nano CuO nanoparticles

3.2. Adsorption experiments

The adsorption experiments were performed in dark using 100 ml aqueous solution of metronidazole of different concentrations (1-8 mg/L) at 25 ◦C. Each solution was loaded with 0.01 g CuO and its pH was maintained at 2. This pH was chosen as the optimum pH as solubility studies of metronidazole indicated that it has its high solubility around pH 2.0 [17]. As shown in Fig. 4, the percent removal of metronidazole by adsorption is greatly affected by the initial concentration of the drug. Previous studies have reported the dependency of the adsorption efficiency on the initial concentration of the adsorbed species [18,19].

The lower uptake at higher concentration results from increased ratio of initial adsorption number of species of the adsorbate to the available surface area. For a given adsorbent dose the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration [20].

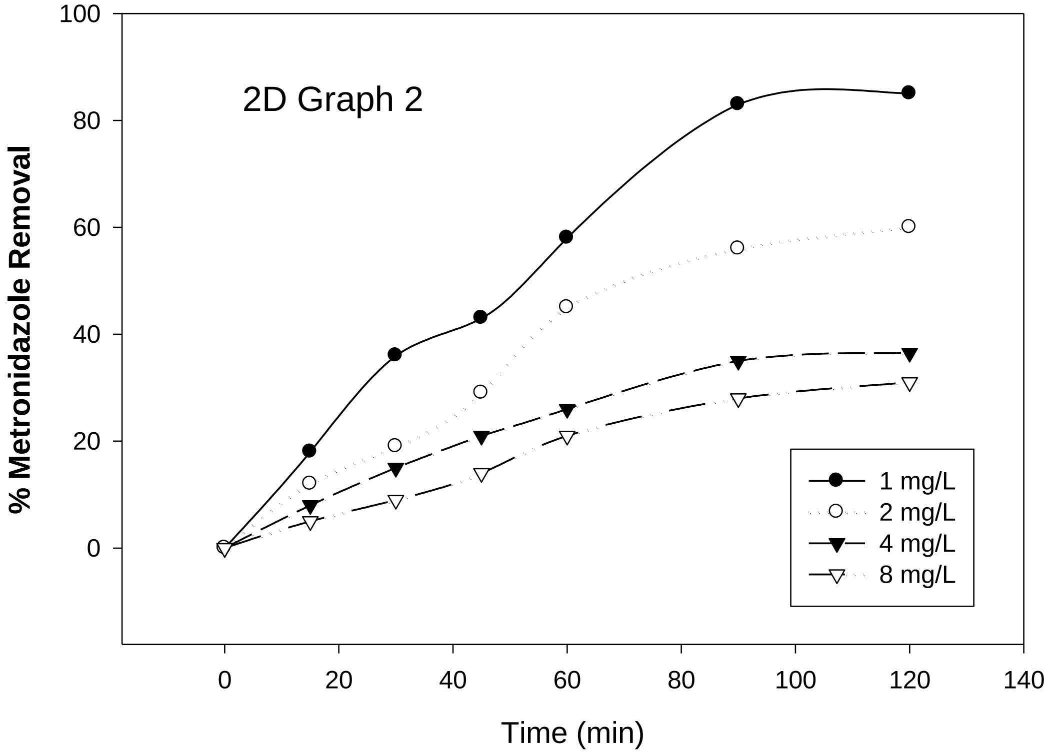

Fig 4: Effect of initial concentration of metronidazole on percent removal

3.2.1. Adsorption isotherms

Adsorption isotherm indicates a graphical representation of the relationship between the amount adsorbed by a unit weight of adsorbent and that of adsorbate remaining in a test solution at a constant temperature under equilibrium condition. This represintation gives the information about the distribution of adsorbed solute between the liquid and solid phases at various equilibrium concentrations [21]. Two adsorption isotherms were applied to the adsorption process; namely: Langmuir and Freundlich isotherms.

3.2.1.1. Langmuir isotherm model

This model describes the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. This model assumes that there is no interaction between molecules adsorbed on neighboring sites [22]. Based upon these assumptions, Langmuir represented the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (3)$$

where, C_e is the concentration at equilibrium (mg/L), q_e is the adsorption capacity at equilibrium in mg/g, Q_0 is the theoretical maximum adsorption capacity and K_L is the Langmuir adsorption constant (L/mg). The linear plot of C_e/q_e vs C_e shows that adsorption follows the Langmuir adsorption model Fig. 5a. The values of q_e and K_L can be calculated Table (1) from the slope and intercept of the plot, respectively.

3.2.1.2. Freundlich isotherm model

The Freundlich isotherm model The Freundlich equilibrium isotherm equation is an empirical equation used for the description of multilayer adsorption with interaction between adsorbed molecules. The Freundlich equation implies that adsorption energy exponentially decreases on the finishing point of adsorptional centres of an adsorbent:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is the Freundlich isotherm constant $mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}, and n represents the adsorption intensity. The plot of ln C_e versus ln q_e gives a straight line Fig. 5b with slope 1/n and intercept ln K_F. The data obtained from Freundlich isotherm are shown in Table 1.

Table 1: Langmuir and Freundlich parameters of adsorption of metronidazole on CuO nanopsrticles

Langmuir isotherm			Freundlich isotherm		
Q_0 (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
25.90	1.078	0.9055	1.313	3.67	0.9529

As seen, the regression correlation coefficient calculated for Freundlich model (R^2=0.9529) is higher than that of Langmuir model (R^2 = 0.9055). This indicates that the Freundlich model is more suitable for describing the sorption of metronidazole compared to Langmuir model.

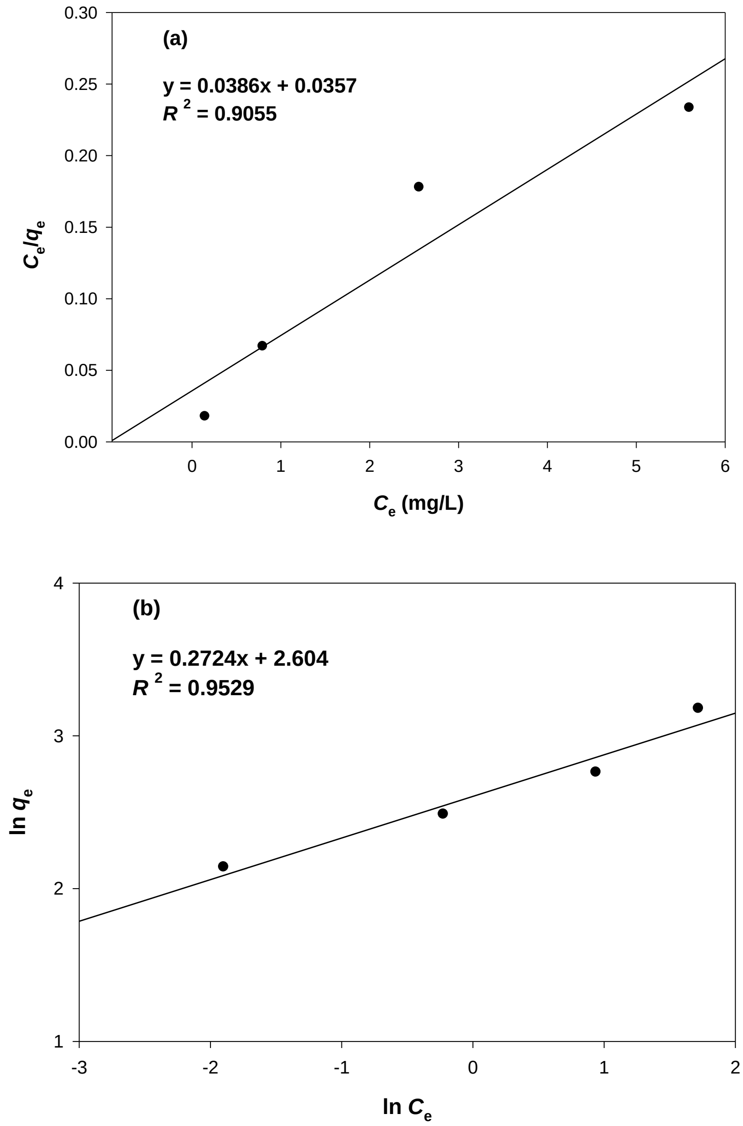

Fig 5: Plots of (a) Langmuir and (b) Freundlich isotherm models for adsorption of metronidazole on CuO nanoparticles.

3.2. Irradiation experiments

As the photocatalytic mechanism suggests, both the photocatalyst and a light source are necessary for the degradation reaction to occur, experiments were conducted for the removal of metronidazole from aqueous solution in the presence of

CuO nanoparticles alone and under the influence of UV radiation and in the precence of both Fig. 6. As shown in the figure, maximum removal (97%) for initial metronidazole concentration of 1 mg/L occurred in presence of CuO (0.1 g/L) nanoparticles under the effect of UV radiation.

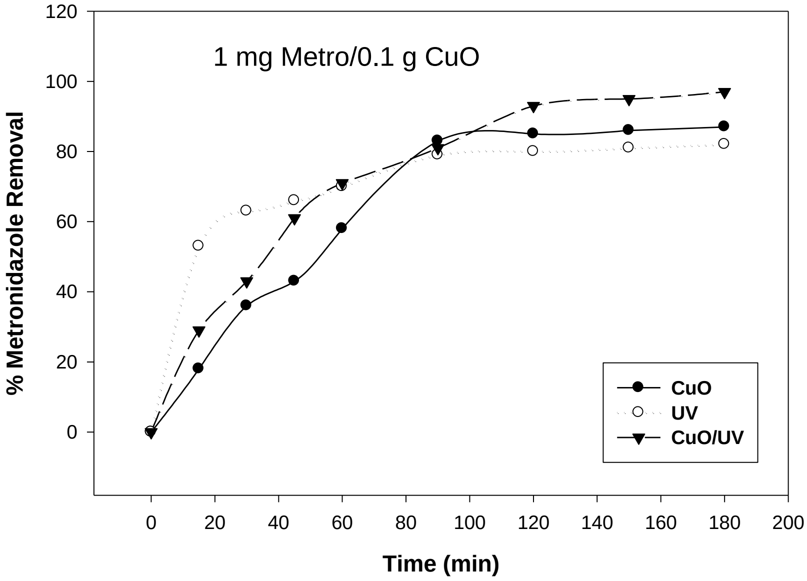

Fig 6: Effect of degradation time of Metronidazole on CuO

3.2.1. Effect of CuO nanoparticles loading

The effect of photocatalyst concentration on the degradation rate of metronidazole has been investigated during exposure to UV light by employing different doses of CuO nanoparticles varying from 0.05 to 0.3 g/L for 1 mg/L drug. It is observed that the initial rate increases with the increase in catalyst concentration, becomes maximum and remains almost constant thereafter after about 120 min as shown in Fig. 7. The optimum catalyst concentration for the degradation of metronidazole is 0.2 g/L. The influence of photocatalyst dosage on the degradation of metronidazole can be explained in terms of the active sites on the CuO surface available for photocatalytic degradation and the penetration of UV light into the nanoparticles suspension. As the dosage of photocatalyst was increased, an increase in the active surface area of CuO was obtained. When the CuO dosage was overdose, a shielding effect of excess particles occurred owing to an increase in the turbidity of the CuO suspension [23]. Hence further addition of catalyst does not lead to the enhancement of the degradation rate.

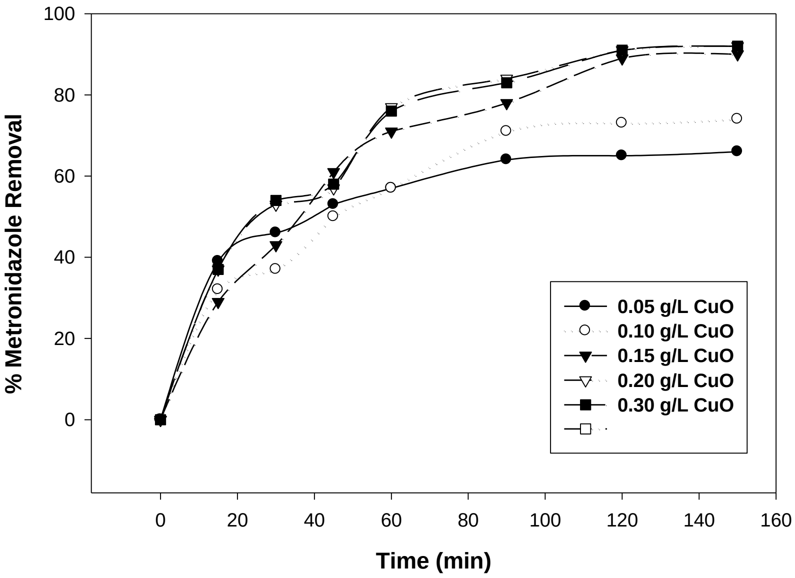

Fig 7: Effect of CuO dose on metronidazole photodegradation

3.2.2. Effect of initial metronidazole concentration

Initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. The influence of initial analyte concentration on the photocatalytic degradation of metronidazole is illustrated in Fig. 8. The examined range of the initial metronidazole concentration was varied from 1 to 8 mg/L. As the concentration increases, the degradation efficiency reduces. The possible reason is that, as the initial concentration of the drug increased, more drug molecules are adsorbed onto the surface of CuO. But the adsorbed drug molecules are not degraded immediately because the intensity of the light and the catalyst amount is constant. Also with an increase in the drug concentration, the concentration of unadsorbed dye in the solution increases leading to lesser penetration of light through the solution on to the surface of CuO thereby decreasing the degradation efficiency [24]. Previous studies have reported the dependency of the photocatalytic oxidation rate on the concentration of water contaminants [25-27].

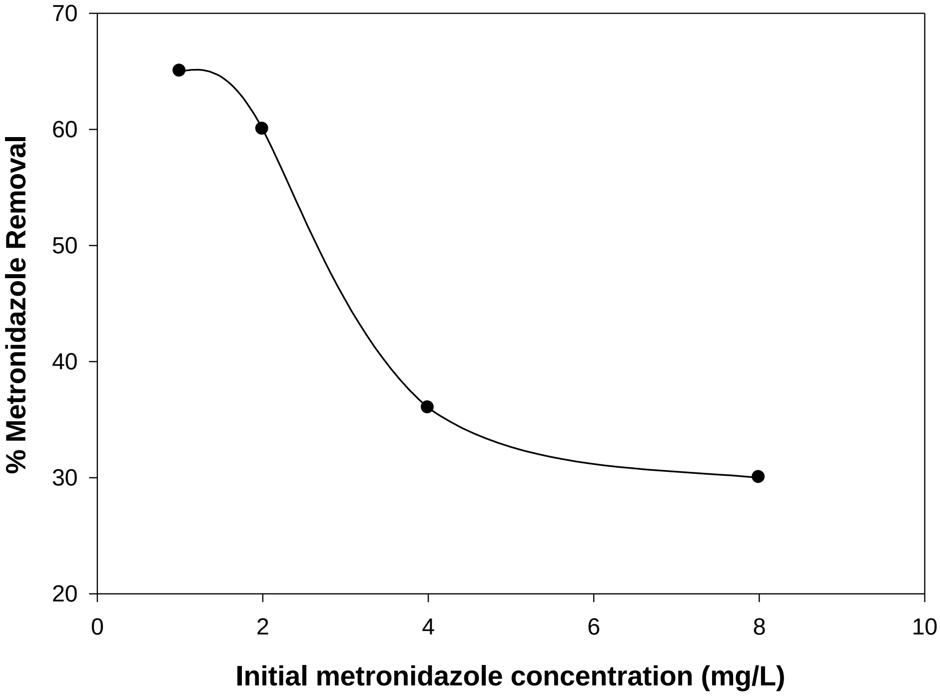

Fig 8: Effect of initial metronidazole concentration of percent removal

3.2.3. Effect of initial metronidazole concentration

The degradation rate is calculated by the following equation [28]:

$$\text{photodegradation rate} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (5)$$

where C_0 is the initial concentration at 0 min and C_t is the concentration at time t.

The rate constant values for dye degradation for all the catalysts were calculated using first order rate equation [29]:

$$ln\frac{C_0}{C_t} = kt \qquad (6)$$

where, k is the first order rate constant.

A plot of $\ln(C_0/C_t)$ versus time represents a straight line, and the slope is equal to the apparent first order rate constant. Fig. 9 shows the plot depicting linear relationship between $\ln(C_o/C_t)$ and time and from the slope of the graph, rate constant value was calculated and was found to be 0.0198 min^{-1}. The decrease in photocatalytic efficiency can be explained by the fact that transition metal ions substituted in CuO lattice act as recombination centers for electron holes [30]. This results in reduced hydroxyl radicals generated in the system. So there is decrease in catalytic efficiency with doping.

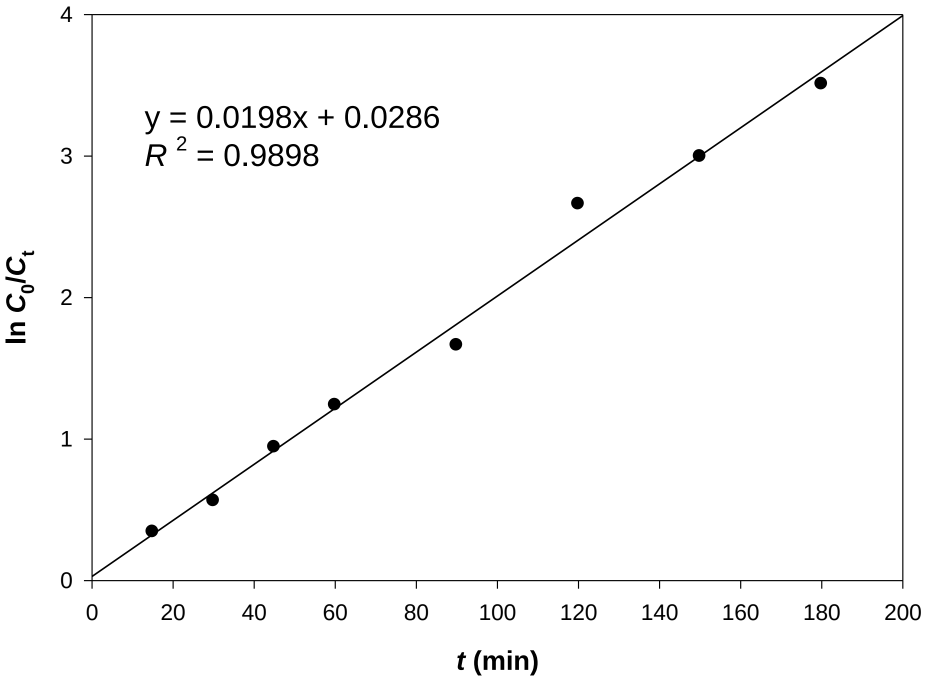

Fig 9: Plot of ln (C_o/C_t) vs. time for the degradation of metronidazole (1 mg/L) using CuO (0.1 g/L) as a photocatalyst

4. Conclusion

Heterogeneous photocatalysis using CuO nanoparticles as photocatalyst was proven to be an effective method for the degradation of metronidazole in its aqueous solution. The experimental results demonstrated that increasing the substrate concentration, light exposure period, and CuO dosage in an appropriate range contributed to the photocatalytic degradation of metronidazole. The removal of the drug by adsorption on CuO nanoparticles was found to follow Fresundlich isotherm model. The rate of photodegradation follows first order with a rate constant 0.0198 min^{-1}.

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