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Influence of Organic Dye Ligands on the Photocatalytic Reduction of Copper Ions in Aqueous Solution Using UV-Nano TIO_2 System

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Abstract

This study investigates the influence of some organic dyes on the photocatalytic reduction of Cu (II) ions in aqueous solution. The dyes of interest were Eosin red, Eriochrome black T, Bromothymol blue and Malachite green. Slurry photoreactor design, with nano-sized titanium dioxide photocatalysts, and illuminated by a 15 W UV light, was utilized. Results showed that the percentage reduction of Cu (II) ions altered from 44.7% (without dye) to 25.7% (with ER), 60.7% (with EBT), 15.2% (with BTB) and 17.8% (with MG) after 60 minutes reaction time at pH 5. This implies that EBT enhanced Cu (II) ions reduction while the other three dyes inhibited the photoreduction process. The kinetic study indicated that the photo-reduction of Cu (II) ions followed the pseudo-first-order kinetics, with the exception of Cu-MG reduction which gave the best correlation values in zeroth-order plot. Statistical analysis was carried out with the ANOVA, Dunnetts post-hoc and Tukeys post-hoc multiple comparison tests. Tukeys post-hoc multiple comparison test was effected to determine the pair of Cu (II) ions with significant difference in mean values while Dunnetts post-hoc was effected to compare the measured values with the initial values. Photoreduction of Cu (II) ions were considered significant at P< 0.05 and 95% confidence interval.

Keywords: Photoreduction; Photocatalyst; Titanium dioxide; Dyes; Statistical analysis; Kinetics.

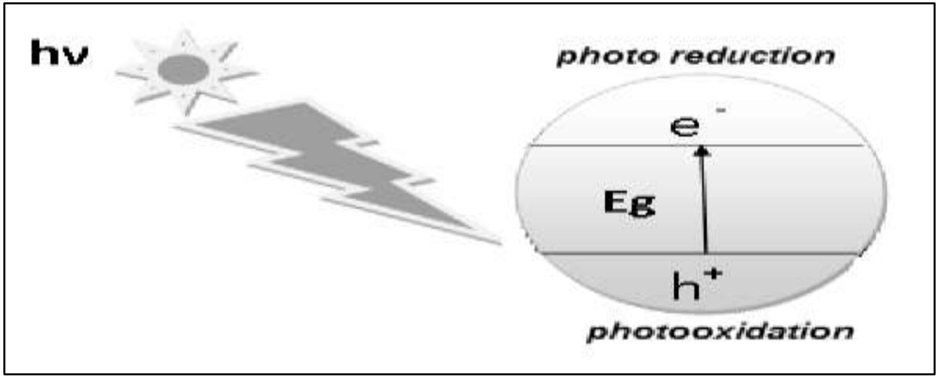
1. Introduction

Incidence of heavy metal accumulation in fish, sediments and other elements of the aquatic ecosystems has been reported globally [1-3]. These toxic heavy metals entering into aquatic environment are adsorbed onto particulate matter, although they can form free metal ions and soluble complexes that are easily available for uptake by biological organisms [4]. Industrial effluents and wastewater contain significant amounts of heavy metals such as nickel, lead, cadmium, arsenic, copper, mercury, zinc and chromium, which have deleterious effects on the environment. Wastewater pollution is unique because it contains different classes of contaminants; therefore, its cleanup poses a pertinent challenge. However, photocatalysis has been found to be very efficient in the treatment of wastewater. The application of photocatalysis in the degradation of numerous organic and inorganic contaminants has been reported in several literature [5-10]. Photocatalysis is an efficient substitute for non-destructive methods (like biosorption), by employing advanced oxidation process (AOPs) in the degradation of organic pollutants. It also possesses the capacity to simultaneously reduce inorganic metal ions into less toxic species. Ekwere, *et al.* [11] has stated that nanotitanium dioxide – UV system was used to achieve the photoreduction of Cu^{2+}, Pb^{2+} and Cd^{2+} ions in their aqueous solution with varying reduction efficiencies; Ma, *et al.* [12] also reported the photoreduction of Cr^{6+} to Cr^{3+} ions using the UV/TiO_2 System.

The activity of a photocatalyt in the reduction of metal ions can be summarized as follows [13, 14]:

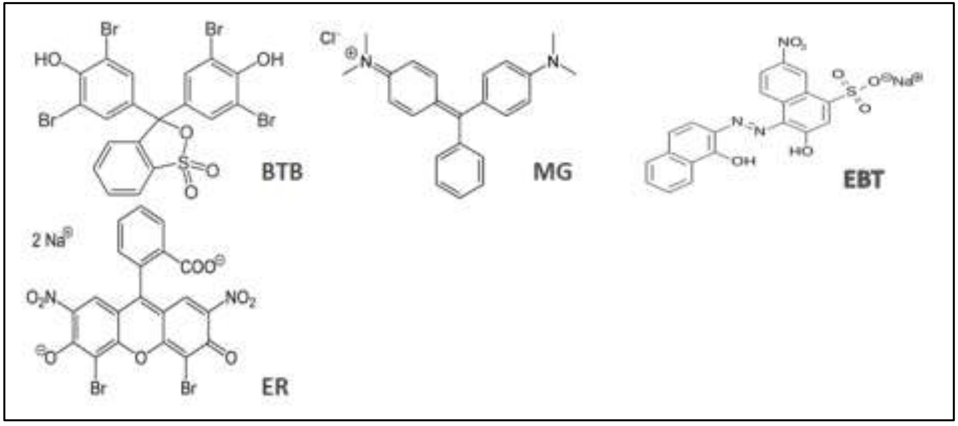
- Photocatalyst is irradiated with photons of energy with the same or more than the band gap energy of PC, exiting electrons from the valence band (VB) to conduction band (CB), leading to the creation of holes in VB (fig. 1)
  $PC + hv \rightarrow e_{CB}^{-} + h_{VB}^{+}$ ……………………………………… (1)
- Metal ions are reduced by the electrons, found on the conduction band, to the metal zerovalent state.
  $M^{+} + e^{-} \rightarrow M_{(s)}$ ……………………………………………………. (2)

Fig-1. Activation of a photocatalyst to generate holes and electrons by a photon



A study by Longli, *et al.* [15] revealed a significant synergistic effect between the photoreduction of Cu (II) and oxidation of organic ligands. However, Chaudhary, *et al.* [16] observed a contradictory result to that reported by Longli, *et al.* [15], stating that in mixed wastewater streams, the presence of metal ions can inhibit the mineralization of organic contaminants as well as hinder the efficiency of recovery of the metal because of the presence of organic species. Samarghandi, *et al.* [17], also outlined the photoreduction of Pb^{2+} and Cd^{2+} with phenol in aqueous solution using photocatalysts. Accordingly, this study aims to investigate the influence of some organic dyes, namely, Eosin red (ER), Eriochrome black T (EBT), Bromothymol Blue (BTB) and Malachite Green (MG), on the photocatalytic reduction of Cu (II) ions.

Fig-2. The structures of four dyes used in the study



2. Materials and Methods

The titanium dioxide utilized is a nano-particle with 20 nm particle size (fig 3), and consists of 80 % anatase phase/ 20 % rutile phase. The nano titanium dioxide has a white powdery appearance, with a solid surface area (SSA) of 20 – 45 m^2/g, bulk density of 0.46 g/ml and pH 6.0. Its loss of weight on drying is 0.48% while the loss of weight on ignition is 0.99%. The nanotitanium dioxide's purity is ≥99% and other elements present in trace amounts are shown in table 1. The nano titanium dioxide particle is a crystalline solid as depicted by the X-ray Diffraction (XRD) Pattern (fig 3). All analysis of the nano-TiO_2 powder was carried out by the vendor, US Research Nanomaterials Inc. Texas, USA.

Fig-3. (A) SEM image of the nano-TiO_2 particles. (B) XRD pattern of TiO_2

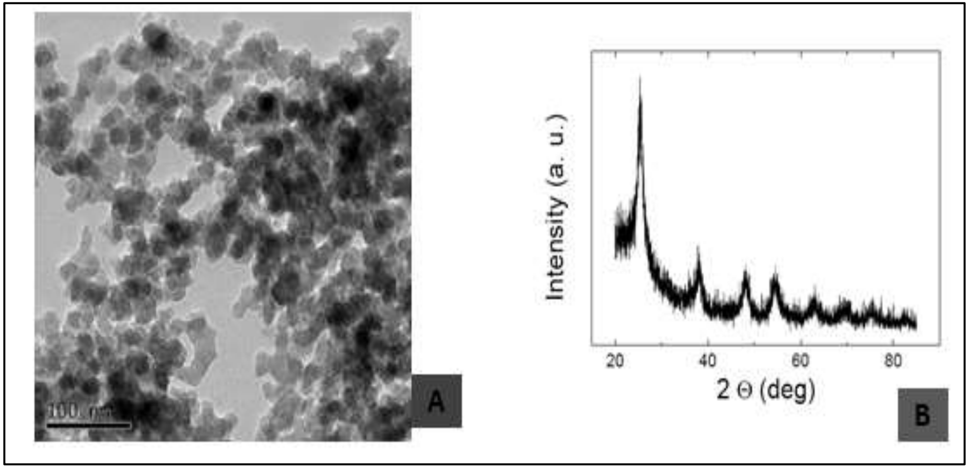


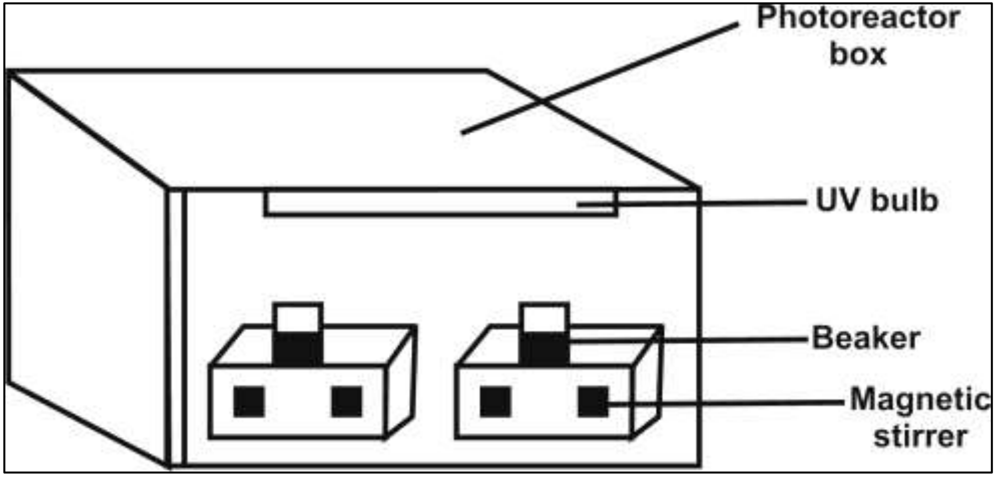
Table-1. Titanium Oxide Nanoparticles (TiO_2) Certificate of Analysis (www.*us-nano.com)*

TiO_2	Al	Mg	Si	Ca	S	Nb
≥99%	≤17 ppm	≤65 ppm	≤120 ppm	≤75 ppm	≤130 ppm	≤80 ppm

2.1. The Ultraviolet - nano Titanium Dioxide System

Photoreactor: A box was fabricated, with outer dimensions of 68 cm × 31 cm × 33 cm, corresponding to length, width and height respectively. The inner dimension of the photo-reactor box was 65.8 cm (length), 29.2 cm (width) and 31 cm (height). The interior of the box was completely painted black to screen out reflected light. Furthermore, it was completely sealed to avoid stray light from outside. A 15W UV bulb (T8 15 W UVC) with wavelength of 254 nm was placed inside the photo-reactor box. The UV bulb was a germicidal lamp (soda lime glass) and contains mercury at low pressure. Two magnetic stirrers were placed inside the photo-reactor box to facilitate the continuous stirring of the sample during photo-degradation experiment.

Fig-4. Schematic diagram of the photoreactor design



Light intensity of UV light source: Intensity of a light source is a function of the number of photons within it per unit time. The UV light intensity on the sample in photoreactor is given as;

$$Light\ Intensity\ = \frac{Power\ of\ bulb\ (W)}{4\pi r^2}$$

where power of bulb is 15W, r is the distance from the bulb to the sample solution in the photoreactor = 0.095m. Thus, the light intensity on the sample = 15 / 4 × 3.14 × $(0.095)^2$ = 132.33 Wm^{-2}

Total Energy of light source: Mathematically, Power is given as Energy per time; invariably Watts (W) can be translated as Joules per second. This implies that Energy can be calculated from Power and time as follows;

$$Total\ Energy\ produced\ by\ light\ source\ (Joules) =$$
$$Power\ of\ light\ source\ (Watts) \times time\ of\ irradiation\ (seconds)\ .$$

Table-2. Energy of 15 W UV bulb at different irradiation times

Time(mins)	20	30	40	60	90	100
Energy (KJ)	18	27	36	54	81	90

Energy of one photon of light: Light exists in discrete particles called photons. The amount of photons produced by a light source correlates with the intensity of light beam from the light source. Also, energy of a photon of light is directly proportional to the frequency of light and inversely proportional to its wavelength. Thus, mathematically it is given as;

$$Energy\ of\ a\ photon\ of\ light\ = hf\ = h\frac{c}{\lambda}$$

where h is 6.626 × 10^{34} Js, c is 2.998 × 10^8 ms^{-1}, λ is the wavelength of the UV light = 254 × 10^{-9} m. Thus, the energy of one photon released by the UV light source is (6.626 × 10^{-34} Js × 2.998 × 10^8 ms^{-1})/254 × 10^{-9} m = 7.82 × 10^{-19} J

Number of photons generated by light source: The number of photons generated by the light source was determined through the mathematical formula,

$$No.of\ Photons\ = \frac{Total\ Energy}{Energy\ of\ one\ photon}$$

Table-3. Number of photons generated at different irradiation times

Time (mins)	20	30	40	60	90	100
No. of photons ($\times 10^{22}$)	2.3	3.45	4.6	6.91	10.36	11.5

2.2. Preparation of Dye/ Cu (ii) ions Solution

50 mg (0.207 moles) of $Cu(NO_3).3H_2O$ salt was introduced into a 500 ml volumetric flask. 30 ppm ER solution was added to the 250 ml mark using a measuring cylinder, to obtain 200 ppm Cu^{2+} and 30 ppm ER mixture. The procedure outlined above was repeated for EBT, BTB and MG to obtain the mixture of 200 ppm Cu^{2+} ions and 30 ppm EBT, BTB, MG respectively.

2.3. Procedure

50 ml of 30 ppm dye/ 200 ppm of $Cu(N0_3)_2.3H_2O$ aqueous mixture was measured into a 100 ml beaker and TiO_2 (0.2 g) was added to it. This mixture was stirred with a magnetic stirrer continuously while being irradiated with a 15 W UV light in the photoreactor. The investigation was carried out at various reaction times of 0, 30, 60 and 90 minutes respectively and at a pH of 5. Reduction of Cu (II) ions was monitored with an Atomic Absorption Spectrophotometer (bulk scientific model 210VGP-variable giant pulse). Percentage reduction of Cu (II) ions was calculated using the formula,

$$Reduction\ (\%) = \frac{Co\ - Ct}{Co} \times 100$$

where C_O is the initial metal ion concentration, C_t is the final metal ion concentration at time, t.

3. Results and Discussion

Fig-5. Influence of the presence of dye molecules on the photoreduction of Cu (II) ions (Reaction conditions: initial metal ion conc. 200ppm, dye conc. 30ppm, cat. dose 4g/l, pH 5)

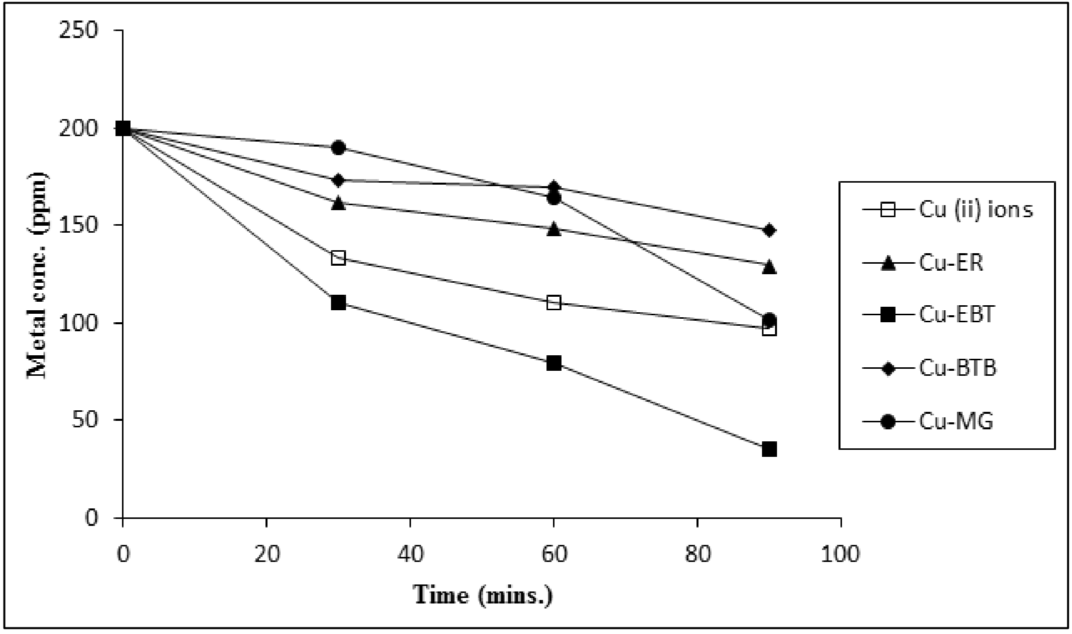
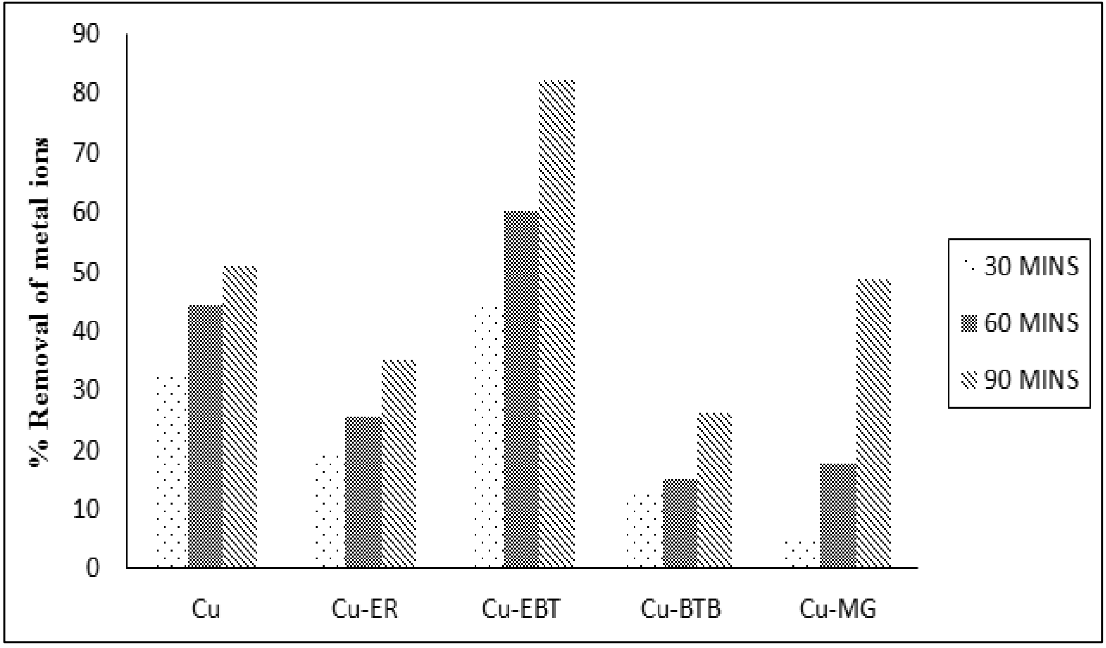


Fig-6. Influence of the presence of dye molecules on % removal of Cu (II) ions from their solution (Reaction conditions: initial metal ion conc. 200ppm, dye conc. 30ppm, cat. dose 4g/l, pH 5)



The simultaneous oxidation and reduction of dye molecules and Cu^{2+} ions respectively, was carried out in order to investigate the effect of the presence of dye molecules on the photoreduction of Cu^{2+} ions in solution. A mixture of 200 ppm of Cu^{2+} ions and 30 ppm dye solution was prepared, the solution was then placed in the photocatalytic reactor and photoreduction of the Cu^{2+} ions was investigated. Figs. 5 and 6 indicate that only Cu^{2+} – EBT mixture showed an enhanced photoreduction of the Cu^{2+} ions. After 60 minutes reaction time and pH of 5, the photoreduction of Cu^{2+} ions increased from 44.7% in the absence of dye molecule to 60.25%, in the presence of dye molecule; after 90 minutes, reduction increased from 51.21% to 82.3% without and with dye molecule respectively. However, this was not the case for other Cu^{2+} ion - dye mixture, since the presence of the other dye molecules inhibited the reduction of Cu^{2+} ions in their solution. After 90 minutes reaction time, the photoreduction percentage of Cu^{2+} ions decreased from 51.2% (without dye) to 5.21% (with ER), 26.32% (with BTB) and 48.97% (with MG). Chaudhary, *et al.* [16], opined that in mixed wastewater, the reduction in metal recovery efficiency is as a result of the formation of complexes between the organic species and the metal ions in solution. Thus, the photoreduction inhibition observed in Cu-ER, Cu-BTB and Cu-MG may be due to the formation of complexes with these dye molecules, thereby preventing the reduction of the metal ions by the electrons on the conduction band of the TiO_2 photocatalyst under UV light.

3.1. Statistical Analyses

Table-4. Photoreduction of Cu (ii) ions in the presence of dye molecules (Dunnetts post hoc comparison)

Sample	Initial conc. (ppm)	30 mins (Mean conc. ± SD)	60 mins (Mean conc. ± SD)	90 mins (Mean conc. ± SD)
Cu^{2+} ions	200	133.4±0.29*	110.46±0.06*	97.60±0.21*
Cu-ER	200	133.4±0.29*	148.76±0.04*	129.58±0.03*
Cu-EBT	200	110.28±0.02*	79.33±0.01*	35.44±0.01*
Cu-BTB	200	173.79±0.00*	169.99±0.04*	147.35±0.02*
Cu-MG	200	190.50±0.52*	164.40±0.02*	102.06±0.02*
ANOVA (p		0.00	0.00	0.00

* = significant at $P<0.05$, when the conc.at different reaction times were compared against initial conc.

Table-5. Turkeys Post Hoc Multiple Comparisons on Photoreduction of Cu (ii) ions in the presence of Dye Molecules (initial metal ion conc., 200 ppm, pH 5)

Reaction time (mins)	Metal ion (I)	Metal ion (J)	Mean Difference (I-J)	SEM	P-value
30 mins	Cu-ER	Cu-EBT	51.19	0.21	0.00
		Cu-BTB	-12.32	0.21	0.00
		Cu-MG	-29.03	0.21	0.00
	Cu-EBT	Cu-BTB	-63.51	0.21	0.00
		Cu-MG	-80.22	0.21	0.00
	Cu-BTB	Cu-MG	-16.71	0.21	0.00
60 mins	Cu-ER	Cu-EBT	69.43	0.02	0.00
		Cu-BTB	-20.90	0.02	0.00
		Cu-MG	-15.64	0.02	0.00
	Cu-EBT	Cu-BTB	-90.33	0.02	0.00
		Cu-MG	-85.06	0.02	0.00
	Cu-BTB	Cu-MG	5.26	0.02	0.00
90 mins	Cu-ER	Cu-EBT	94.14	0.02	0.00
		Cu-BTB	-17.77	0.02	0.00
		Cu-MG	27.52	0.02	0.00
	Cu-EBT	Cu-BTB	-111.91	0.02	0.00
		Cu-MG	-66.62	0.02	0.00
	Cu-BTB	Cu-MG	45.29	0.02	0.00

SEM = Standard Error of Mean Difference, * = significant at $P< 0.05$

Dunetts post hoc test (table 4) showed that the concentration of Cu (II) ions, in the presence of dye molecules, was significantly reduced from an initial concentration of 200 ppm through photoreduction. The ANOVA at different reaction times of 30, 60 and 100 minutes was 0.00, indicating that significant photoreduction of Cu (II) ions was achieved, while the mean standard deviation (S.D) ranged from 0.00 in Cu-BTB to 0.52 in Cu-MG; the low mean S.D values highlights result and instrumental accuracy. Tukeys post hoc multiple comparisons showed that Cu-ER (I) or Cu-EBT (I) gave negative mean difference (I – J) values when compared to other Cu-BTB (J) or Cu-MG (J). This implies that the photoreduction of Cu (II) ions in the presence of ER or EBT was higher when compared to the photoreduction of Cu (II) ions in the presence of BTB or MG. Comparing Cu-ER (I) and Cu-EBT (J) gave positive values of mean difference (I – J), implying that the photoreduction of Cu in the presence of EBT is higher when ER is present. Standard Error of Mean Difference (SEM) values ranged from 0.02 – 0.21 while P-values were 0.00

3.2. Kinetics of Cu (ii) ions Photoreduction

Fig-7. Photoreduction kinetics for Cu (II) ions in the presence of dye molecules (Reaction conditions: initial Cu (II) ions conc. 200 ppm, dye conc. 30 ppm, cat. dose 4g/l, pH 5, 15W UV light, nano TiO_2 PC)

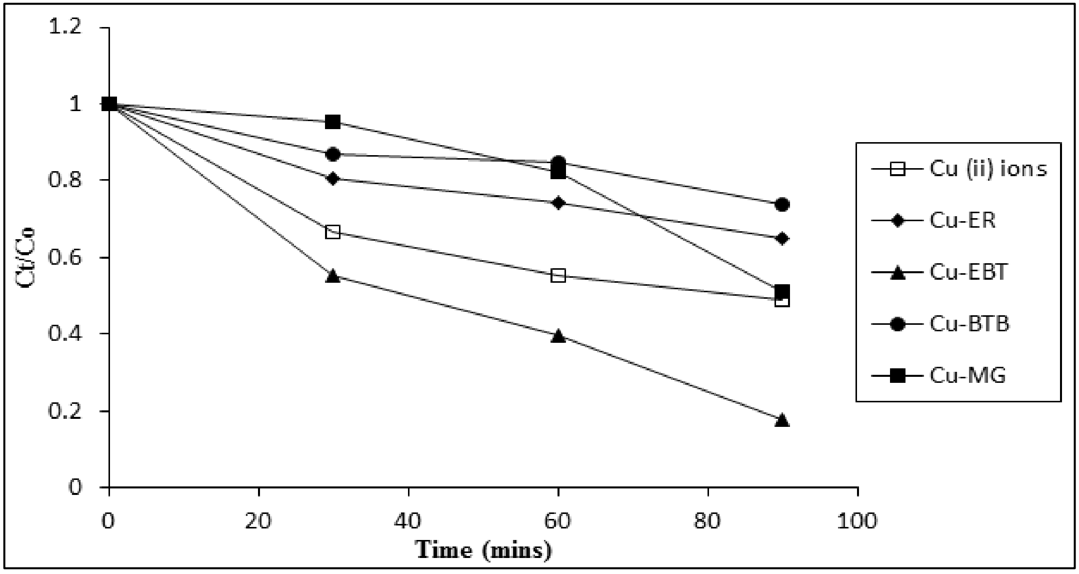


Fig-8. Pseudo-first-order kinetics plot for the photoreduction of Cu (II) ions in the presence of dye molecules (Reaction conditions: initial Cu (II) ions conc. 200 ppm, dye conc. 30 ppm, cat. dose 4g/l, pH 5, 15W UV light, nano TiO_2 PC)

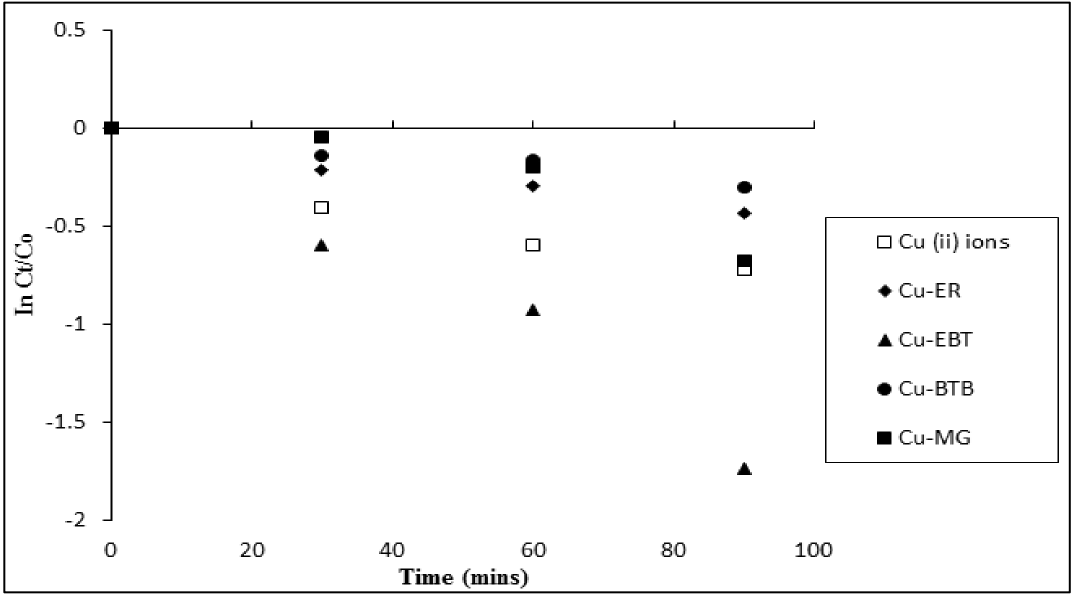


Table-6. Pseudo-first-order Plot Parameter for Cu (ii) ions Photoreduction in the presence of Dye

Sample	R^2 values	Equation of 1^0 kinetic plot	K_1 ($mins^{-1}$)
Cu (without dye)	0.929	y = -0.0078x – 0.078	0.0078
Cu + ER	0.968	y = -0.0046x – 0.0284	0.0046
Cu + EBT	0.975	y = -0.0184x + 0.0155	0.0184
Cu + BTB	0.944	y = -0.0031 – 0.0115	0.0031
Cu + MG	0.829	y = -0.0072x + 0.0955	0.0072

Table-7. Comparison of the Zeroth(0^0), First (1^0) and Second order (2^0) Kinetic Plot Parameters for Cu-MG

Sample	K_0($ppmmin^{-1}$)/R^2 values	K_1(min^{-1})/R^2 values	K_2($ppm^{-1}min^{-1}$)/R^2 values
Cu + MG	1.6066/0.877	0.0072/0.828	0.000/0.78

The correlation values R^2, for the reduction of Cu (II) ions in the presence of dye molecules correspond to a pseudo-first-order kinetics except with MG, which comparatively gave a best fit in the zeroth order plot (table 7). The rate constant, k_1 for the reduction of Cu (II) ions in the presence of dye molecules are given as: Cu-ER (0.0046 min^{-1}), Cu-EBT (0.0184 min^{-1}) and Cu-BTB (0.0031 min^{-1}). It is observed that only Cu-EBT gave a higher first-order photoreduction rate constant value than the rate constant value of Cu (ii) ions reduction in the absence of dye molecule (0.0078 min^{-1}).

4. Conclusion

The photocatalytic reduction of Cu (II) ions was successfully achieved with the UV-titanium dioxide system utilized in this study. It was observed that ER, BTB and MG inhibited the photoreduction of Cu (II) ions while EBT enhanced the photoreduction. The inhibition action may be due to the formation of complexes between the Cu (II) ions and the organic dye ligands, thereby, decreasing the photoreduction activity on the metal ions. However, there is need for further characterization of the ligand - copper ions complex to adequately explain the inhibition or enhancing property of the ligands on the photoreduction process. Kinetic study revealed that the photoreduction of Cu (II) ions largely follow the pseudo-first-order kinetics, except for Cu-MG which showed a zeroth-order kinetics.

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