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SOLAR LIGHT ASSISTED REDUCTION OF AQUEOUS COPPER(II) IONS USING ZINC OXIDE PHOTOCATALYST

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Abstract: This study investigates the solar light assisted photocatalytic reduction of aqueous copper(II) ions using zinc oxide particles as a cost-effective and eco-friendly photocatalyst. The effect of various process parameters like initial Cu(II) concentration, pH of solution, ZnO doses, light intensities, amount of hole scavenger (methanol) and chelating agents have been studied. It has been observed that reduction of Cu(II) increases with increase in pH, but at higher pH, precipitation of copper ions take place.

The photocatalytic reduction process follows pseudo first order kinetics and increase in initial concentration from 200 to 2000 mg.L^{-1}, the rate of reaction decreases from 0.0059 to 0.0015 min^{-1}. With increase in light intensity and ZnO doses the rate of reduction process also increases. The presence of methanol might act as scavenger for holes, by suppressing electron-hole recombination enhance the photocatalytic reduction of Cu(II) ion by electrons. It has been also observed that the presence of chelating agents such as disodium ethylene diamine tetraacetic acid, trisodium citrate and sodium, potassium tartrate adversely affects the reduction process. These findings demonstrate that solar driven ZnO photocatalysis is a highly promising, low-cost, and sustainable approach for the efficient removal of copper from industrial wastewater.

Index Terms **-** Cu(II), photoreduction, ZnO, chelating agents.

I. INTRODUCTION

India's total consumption of refined copper in 2024 is around 8.44 lakh tonnes. Copper demand in India is expected to grow due to increased thrust of Government of India towards renewable energy and major infrastructure which accounting for 43% of copper use. The automotive and consumer durables sectors, each contributing 11% and 12% respectively, which will drive the demand of copper in the country. Copper is essential to EV technology and its supporting infrastructure, the projected demand for copper due to electric vehicles is expected to increase by 1.7 million tonnes by 2032 [1]. A distinctive combination of properties, including excellent conductivity (both electrical and thermal), as well as elevated corrosion resistance, makes Cu suitable for a wide range of applications [2].

Copper(II) was selected as a representative heavy metal ion due to its widespread occurrence in natural and anthropogenic environments. It is continuously introduced into ecosystems through industrial discharge from processes such as electroplating, mining, metal finishing, and the production of pesticides and fertilizers. These activities often lead to the contamination of aquatic systems, where Cu(II) can enter the food chain and pose significant health risks to humans and other organisms. Excessive levels of Cu(II) in the environment are associated with severe ecological and health hazards. In humans, prolonged or

high-level exposure to copper ions can lead to adverse effects such as severe headaches, kidney damage, nausea, hypoglycemia, and disorders like Wilson's disease and Menkes syndrome. Given these detrimental effects, it is crucial to develop effective methods for the removal of Cu^{2+} from contaminated environments to mitigate its negative impacts on both ecosystems and public health [3-5]. The World Health Organization (WHO) establishes that the maximum limit of the concentrations of copper ions in drinking water should not exceed 2 $mg.L^{-1}$. In view of the toxic effects of copper, it must be removed from wastewater before it can be discharged.

Due to extensive use of copper and copper containing salts in various industries, several conventional separation processes have been employed to remove it from aqueous solutions. These processes include precipitation and membrane filtration [6], ion exchange [7], electrochemical techniques [8] and solvent extraction [9]. In recent years, sorption has gained considerable interest as a promising route to remove and recover Cu from solutions [10]. It is considered one of the most effective and extensively studied approaches in water remediation and hydrometallurgical processes. Among materials investigated for sorption purposes, graphene-based materials, including graphene oxide, have demonstrated significant potential in removing metal contaminants from water [11, 12].

Conventional wastewater treatment processes such as chemical precipitation (as hydroxide or sulfide), ion exchange, reverse osmosis, adsorption, electro winning etc. have several limitations and drawbacks. They may require pretreatment, their by-products often considered hazardous and their disposal is costly. In industry chemical precipitation is by far the widely used process to remove metal ions. However presence of chelating agents such as ethylene diamine tetracetic acid, nitrolotriacetic acid, citrate, tartarate may make the precipitation process ineffective. Due to high buffer capacity provided by these chelating agents, excessive amount of chemicals are required for alkaline neutralization [13, 14]. Copper is usually discharged with chelating agents from electroless Cu(II) plating for printed circuit boards [15, 16].

Photocatalytic method provides an excellent alternate for removing and chemically reducing metal ions from metal bearing wastewater and prevents the problems associated with conventional methods. Several studies have used ZnO for the removal of toxic pollutants, such as Cr(VI), Ni(II), Pb(II) [17-21]. However, few studies have focused on the removal of Cu(II) [22, 23]. The removal of Cu(II), Cd (II) and Pb(II) cations by ZnO particles encapsulated in hollow microspheres are more efficient than commercial ZnO particles reported by Wang et al., [24]. Highly Efficient removal of Cu(II) ions from acidic aqueous solution using ZnO nanoparticles has been reported by Leiva et. al., [25]. Joshi et al., [26] reported the utilization of polypyrrole/ZnO nanocomposite in the adsorptive removal of Cu^{2+}, Pb^{2+} and Cd^{2+} ions from Wastewater. Nalva et. al., [27] reported synthesis of zinc oxide nanoparticles by simple solution based approach, these nanoparticles were used as an adsorbent for the removal of Cu(II) ions from aqueous solution.

This paper reports the detail investigation of solar light induced photocatalytic reduction of Cu(II) from aqueous solution by suspended ZnO particles in presence and absence of chelating agents.

II. MATERIALS AND METHODS

2.1 Materials

The chemicals $CuSO_4.5H_2O$, methanol, di sodium salt of ethylene diamine tetra acetic acid, tri sodium citrate, sodium potassium tartrate, KI, $Na_2S_2O_3$, NaOH, HCl, starch and ZnO used in present investigation were of analytical grade, procured from Loba Cheme, E.Merk and Qualigens (Mumbai).

2.2 Batch Experiments

Batch experiments were conducted for optimization of process parameters like, pH, contact time, initial concentration of Cu(II) solution, ZnO dose and amount of hole scavenger (methanol). The batch experiments were also conducted to study the effect of light, light intensity and chelating agents on photo reduction of Cu(II) on ZnO. The solutions of Cu(II) of different concentration were prepared by dissolving desired amount of $CuSO_4.5H_2O$ in distilled water. The photocatalytic experiments were conducted by

adding predetermined amount of ZnO particles in Cu(II) solution, ZnO particles were dispersed in solution by stirring at 200 rpm. The concentration of Cu(II) was determined by iodometric titration [28]. The percentage removal of Cu(II) ions was calculated using equation (1).

$$\% \, Removal = \frac{Co - Ct}{Co} * 100 \quad \ldots\ldots\ldots\ldots (1)$$

Where, C_0 and C_t were the concentration of Cu(II) ions at the initial and time t, respectively.

The effect of pH on photocatalytic reduction of Cu(II) was studied in the pH range 2 to 4.5. The experiments were conducted using 100 ml solution of 500 $mg.L^{-1}$ Cu(II) solution with 0.5, 1.0, 2.0, 3.0 and 5.0 $g.L^{-1}$ ZnO catalyst at various pH. The pH of the solution was adjusted by 0.1 N HCl, and 0.1 N NaOH using digital pH meter (Equiptronics model-EQ 610). The illumination of the above solutions was carried out for 150 minutes under tungsten lamp (200 W). It is difficult to study the reduction process of higher pH because above pH 4.5 the precipitation of Cu(II) observed.

The effect of contact time was studied with 300 ml of 500 $mg.L^{-1}$ Cu(II) solution in presence of 1.0 $g.L^{-1}$ ZnO at pH 3. The experiments were conducted at various conditions like, with catalyst in dark, illumination under sunlight and tungsten lamp with catalyst. The supernant were separated at definite time interval and residual concentration of Cu(II) was determined as mention above. These experiments were conducted in order to examine, whether the removal of Cu(II) is light induced or simple adsorption on ZnO take place.

The rate kinetic study was carried out by monitoring the reduction process for 4 hours. The residual concentration of Cu(II) was determined at definite time interval. The process parameters like initial Cu(II) concentration, hole scavenger (methanol), light intensities, photocatalyst dose and chelating agent have been studied for their effect on rate constants of photocatalytic reduction of Cu(II) ions. The effect of initial Cu(II) concentration was studied with 300 ml 200 to 2000 $mg.L^{-1}$ solution and 1.0 $g.L^{-1}$ ZnO and at pH 3. The assembly was kept in afternoon sunlight and the solutions were stirred manually for 4 hrs.

The effect of light intensities was studied using tungsten lamp as source of light. Changing the distance between the assembly and lamp varied the intensity of light that was measured by digital illuminance meter (Model TES-1332). The experiments were conducted at various light intensities in the range 1100- 6800 lux with 300 ml 500 $mg.L^{-1}$ Cu(II) solution and 1.0 $g.L^{-1}$ ZnO. The effect of hole scavenger was studied with 300 ml of 500 $mg.L^{-1}$ Cu(II) solution in 500 ml beakers to which 1.0 $g.L^{-1}$ ZnO was added along with 0, 0.05, 0.5 and 1.0 % (volume) of methanol. All the four beakers were kept in afternoon sunlight for 4 hours. After definite time interval the supernants were separated and used to find out residual Cu(II) concentration. The catalyst concentration was varied in the range 1.0 to 5.0 $g.L^{-1}$ to study the effect of catalyst dose. In 500 ml beakers, 300 ml of 500 $mg.L^{-1}$ Cu(II) solution was taken to which 1.0, 2.0, 3.0, 5.0 $g.L^{-1}$ ZnO was added along with 0.05 % (volume) methanol. The assembly was illuminated under sunlight for 4 hours.

The chelating agents like disodium ethylene diamine tetraacetic acid, trisodium citrate, and sodium potassium tartrate were examined for their effects on rate constants of photocatalytic reduction of Cu(II) ions in aqueous solution. The aqueous solutions of chelated Cu(II) were prepared as mention above. The experiments were conducted in four 500 ml beaker in which 300 ml solution of chelated Cu(II) was taken to which 1.0 $g.L^{-1}$ ZnO added and the assembly was illuminated for 4 hours in afternoon sunlight. The analysis of Cu(II) was carried out after refluxing the supernant for 30 minutes to which 5 ml (1:1) concentration HCl-HNO_3 was added. This treatment for supernant was necessary otherwise in chelated form of Cu(II) cannot be analysed by iodometric titration.

Beside the above, the effect of photocatalyst dose was also studied on photo reduction of Cu(II) in presence of chelating agents. In 250 ml beaker 100 ml solution of Cu(II) organic complexes was taken to which various concentration of ZnO ranging from 0.25 to 5.0 $mg.L^{-1}$ was added and illuminated in afternoon sunlight for 4 hrs.

III. RESULTS AND DISCUSSION

The results obtained from batch experiments conducted for photo reductive deposition of Cu(II) ions from aqueous solution on ZnO particles were discussed below:

3.1 Effect of pH

The experiments were carried out to study the adsorption behavior of Cu(II) on 1.0 to 5.0 $g.L^{-1}$ ZnO dose in pH range 2 to 4.5 (Figure 1). Above pH 4.5 precipitation of Cu(II) was observed. Amount of Cu(II) adsorbed on ZnO particles increases with increase in pH as well as catalyst dose. As the catalyst dose increases, the available surface area and adsorption sites increases results in increase in adsorption. The pH dependency of adsorption can be explained on the basis that in highly acidic pH range the catalyst surface become positively charged therefore there is electrostatic repulsion between Cu(II) ions and catalyst surface. But as pH increases the adsorption increases due to decrease in positive charge on catalyst surface.

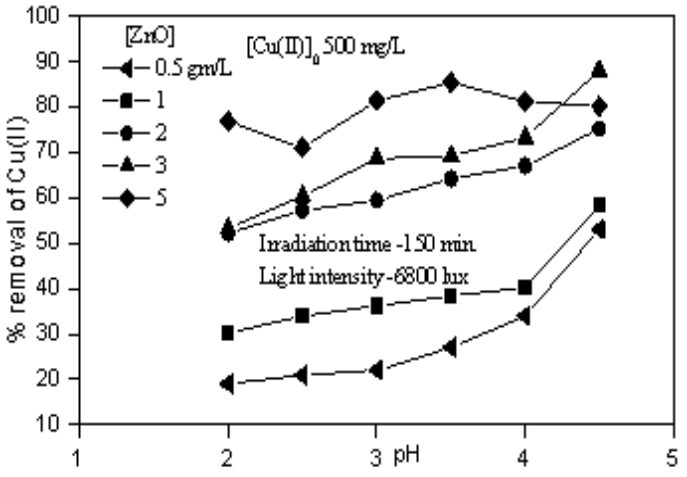

Figure 1. Effect of pH on % removal of Cu(II) by various ZnO doses.

3.2 Effect of different illumination conditions

The experiments were conducted in dark, sunlight and under tungsten lamp, in order to examine whether the Cu(II) removal is either light assisted or by adsorption (Figure 2). It has been observed that in dark, there was insignificant removal of Cu(II), this may be due to adsorption of metal ions on ZnO particles. While in case of sunlight irradiation maximum removal was observed as compared to irradiation under tungsten lamp. These observation are indicating that the removal was light assisted. Therefore further the experiments were carried out under sunlight irradiation. The reduction of Cu(II) was confirmed by change in white colored ZnO particles to brown. On the basis of these observations, the possible mechanism for photo reduction can be proposed as follows:

The band gap of Zinc Oxide (ZnO) is 3.37 electron-volts (eV) at room temperature, classifying it as a wide-band-gap semiconductor. Electrons need at least 3.37 eV of energy to jump from the valence band to the conduction band. When semiconductor exposed to photon having energy equal to or greater than band gap energy, electron-holes pairs are generated. The possible mechanism of Cu(II) reduction by ZnO is as follows:

$$ZnO \xrightarrow{h\nu} e^- CB + h^+ VB$$

$$h^+ VB + H_2O \longrightarrow 1/2\ O_2 + 2H^+$$

$$2H^+ + O_2 + 2\ e^- \longrightarrow H_2O_2$$

(Dissolved)

$$Cu^{2+} + 2e^- \longrightarrow Cu^0$$

Where, e^-CB - electrons in conduction band

$h^+ VB$ - holes in valence band

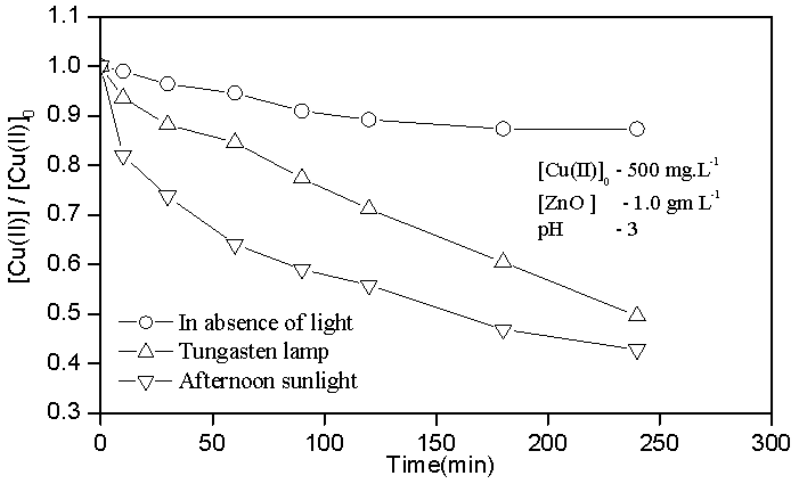

Figure 2. Effect of different illumination conditions on concentration of Cu(II) with time.

3.3 Effect of contact time and initial Cu(II) concentration

By varying the initial Cu(II) concentration in the range 200 to 2000 mg.L^{-1} at pH 3, catalyst concentration l.0 g.L^{-1}, the effect of contact time and initial concentration was studied and presented in figure 3. It can be clearly seen from the figure 3 that the percentage removal increases with increase in the contact time till equilibrium was attained. The percentage removal decreases with increases in initial concentration. As initial concentration increases from 200 to 2000 mg.L^{-1} the percentage removal decreases from 80.5 to 28.2. The initial faster removal rate of Cu(II) was due to the availability of a larger number of active adsorption sites during the initial period of contact and thereafter the removal is slow. In the adsorption process, initially the Cu(II) encountered boundary layer effect and then diffused from boundary layer to surface of metal oxides, finally they diffused into porous structure, therefore higher concentration solution takes relatively longer time to reach equilibrium.

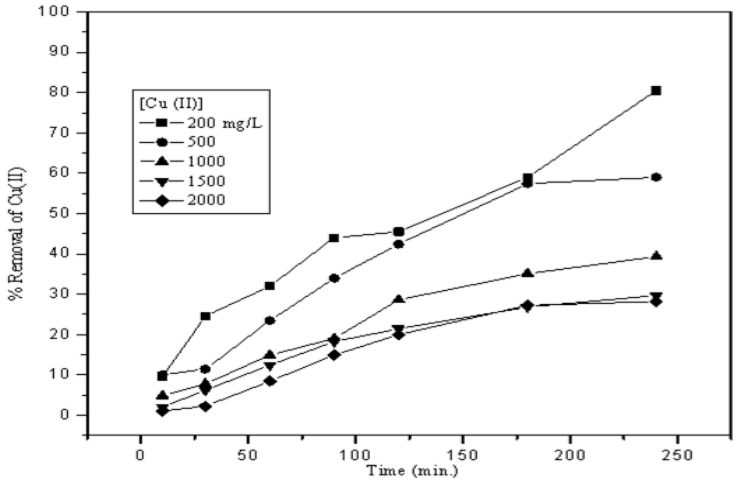

Figure 3. Effect of contact time and initial concentration of Cu(II) on % removal.

3.4 Effect of hole scavenger

In order to enhance the photocatalytic reduction of metal ions, organic acids and alcohols were reported to be added in aqueous solution to serve as hole scavenger to inhibit the electron-hole recombination [29-31]. But the information regarding the effect of these organics on kinetics of photocatalytic reduction of Cu(II) is scarce. In this study, methanol is used as hole scavenger. It was observed from figure 4, that concentration of Cu(II) decreases with increase in amount of methanol. It has been observed that increase in methanol concentration from 0.05 to 1 vol. % the rate of reduction increases from 0.0036 to 0.0044 min^{-1} (Table 1). When methanol was added in to photo reduction system the possibility of capture of electrons by Cu(II) can by promoted while the part of hole can be scavenged by methanol and photocatalytic reduction rate increases. But no significant increase was observed at higher amount of hole scavenger, therefore further experiments were carried out with addition of 0.05 vol. %

methanol. It has also been observed that in presence of hole scavenger white colored ZnO particles become dual gray colored after adsorption of Cu(II) and then gradually changed in to brown during photocatalytic reduction process.

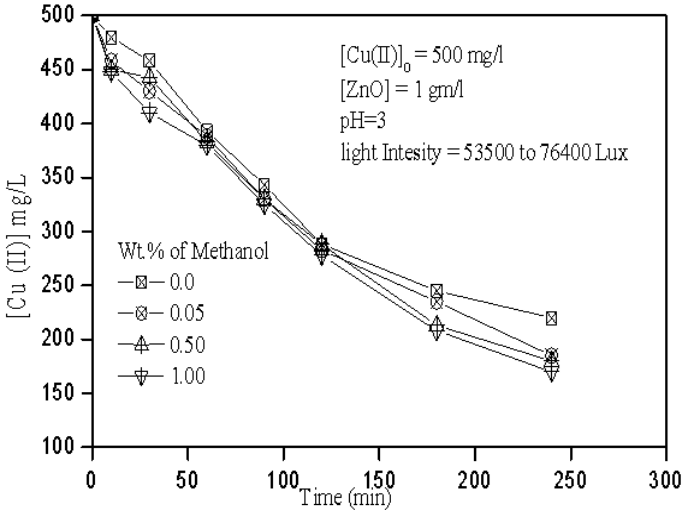

Figure 4. Effect of amount hole scavenger on concentration of Cu(II) with time.

3.5 Effect of photocatalyst doses

It has been observed that the photocatalytic reduction of Cu(II) increases with increase in catalyst dose. The percentage removal increases from 63 to 91, when catalyst dose increases from 1.0 to 5.0 $g.L^{-1}$. The rate of reduction increases from 0.0039 to 0.0093 min^{-1} (Table 1). This increase in rate can be explained on the basis that as the catalyst dose increases more ZnO particles are available for photo excitation and possibility of generation of electron hole pair will be higher on exposure to sunlight, results in to the corresponding increase in the rate of reduction of Cu(II). It was observed from Figure 5, that concentration of Cu(II) decreases with increase in ZnO dosages.

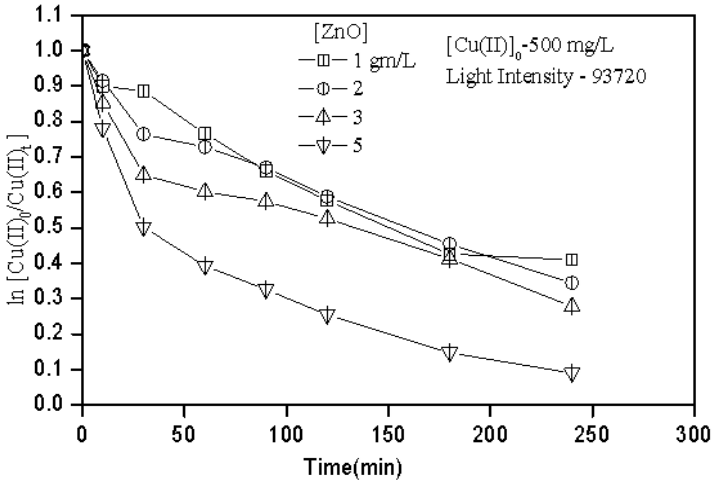

Figure 5. Effect of ZnO dose on concentration of Cu(II) with time.

3.6 Effect of light intensity

By varying the distance between photo reduction system and light source the effect of light intensity has been studied. It was observed from figure 6, that concentration of Cu(II) decreases with increase in light intensity. It has been observed that as the intensity of light increases from 1100-6300 lux, the reduction rate increase from 0.0018 to 0.0027 min^{-1} (Table 1). Similar results have been reported by Desai et al. [32] for reduction of Pb(II) over MnO_2. This increase in the rate can be explain on the basis that more electron-hole pair generated due to an increased number of photons striking on ZnO particles at high intensity of light. Now more electrons are available from chemical reduction of Cu(II) in solution.

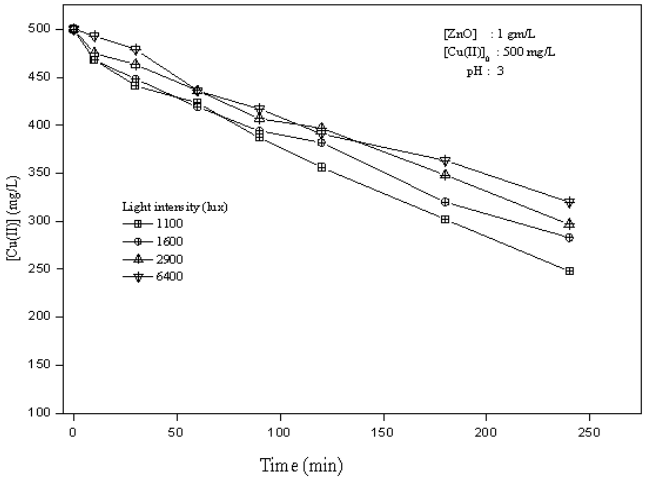

Figure 6. Effect of light intensity on concentration of Cu(II) with time.

3.7 Effect of chelating agents

It was evident from figure 7 that the presences of chelating agents seriously affect the Cu(II) reduction. The rate constant for reduction in absence of chelating agent was found to be 0.0039 min^{-1}. But in presence of disodium ethylene diamine tetra acetic acid, trisodium citrate, sodium, potasium tartarate, the rate constant was found to be 8.98×10^{-4}, 7.8×10^{-4}, 1.7×10^{-3} min^{-1} respectively (Table 1). This is due to the chelation of Cu(II), which restrict the adsorption on ZnO surface. But as the photocatalysis proceed the decomposition of complex takes place and simultaneously Cu(II) undergoes reduction. As the photo reduction proceeds, there is formation brown colored precipitate at the bottom of the vessel, which covered the photocatalyst, this results in decrease in the rate constant. It has also been observed (Figure 8) that as the catalyst dose increases the percent reduction of Cu(II) also increases albeit Cu(II) present in chelated form. This observation indicates that even though there is presence of chelating agent in Cu(II) bearing wastewater it can be treated successfully by photocatalytic technique.

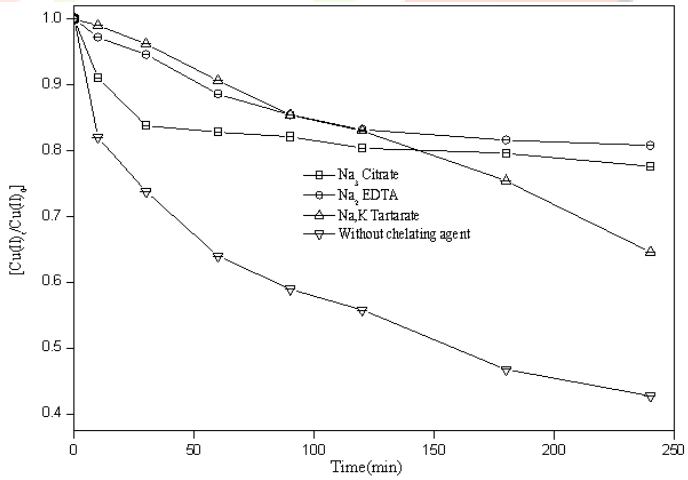

Figure 7. Effect of chelating agents on concentration of Cu(II) with time.

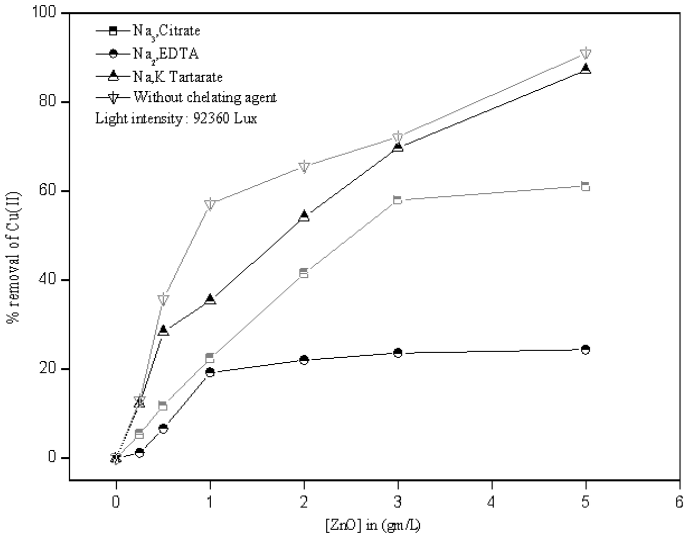

Figure 8. Effect of ZnO dose on concentration of Cu(II) in the form of chelates.

3.8 Pseudo first order kinetics

The rate constant for photocatalytic reduction of Cu(II) was calculated by following Langmuir-Hinshelwood equation, which is reduced to pseudo first order rate equation (2).

$$\ln [Cu(II)_0 / Cu(II)_t] = k_{red} * t \quad \ldots\ldots\ldots\ldots (2)$$

The pseudo first order kinetic plots for various initial Cu(II) concentration were represented in figure 9. It has been evident from table 1, that the rate of reduction decreases from 0.0095 to 0.0015 min^{-1} with increase in concentration from 200 to 2000 $mg.L^{-1}$.

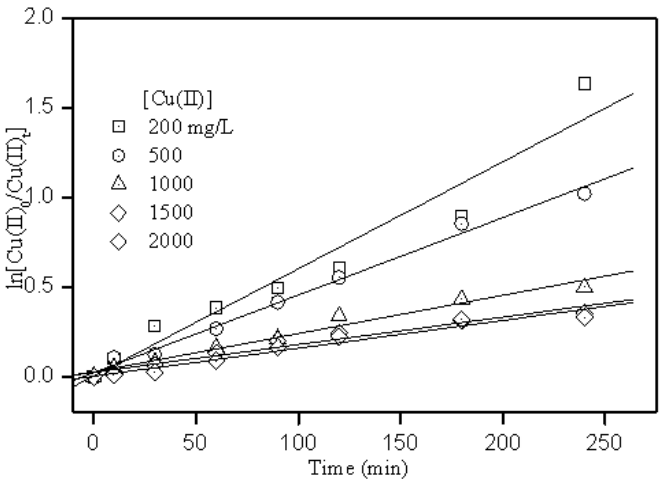

Figure 9. Pseudo first order kinetics plots for photoreduction of Cu(II)

This may be due to the fact that at higher Cu(II) concentration the entire surface of ZnO was covered by Cu(II) ions, which inhibits the activation of photocatalyst. It could be due to diminished penetration depth of sunlight at higher concentration, which can slow the excitation of semiconductor, ultimately the rate of reduction decreases.

The data obtained from the study of effect of hole scavenger concentration (Vol. %), ZnO dose ($g.L^{-1}$), light intensity (lux), chelating agents was also subjected for pseudo first order kinetics analysis, the corresponding rate constants were summarized in table 1.

Table 1. The values of rate constant for Cu(II) reduction at various experimental conditions.

Experimental Conditions	**Concentration of Cu(II)**	**K_{red} (min^{-1})**	**Correlation Coefficient (r)**	**S.D.**
Initial Concentration of Cu(II) ($mg.L^{-1}$)	200	0.0095	0.9731	0.1295
	500	0.0039	0.9842	0.065
	1000	0.0021	0.9875	0.0313
	1500	0.0015	0.9768	0.0308
	2000	0.0015	0.9776	0.0307
Hole Scavenger Concentration (Vol. %)	**Volume % of Methanol**	K_{red} (min^{-1})	Correlation Coefficient (r)	S.D.
	0	0.0036	0.9862	0.0561
	0.05	0.0040	0.9972	0.028
	0.5	0.0043	0.9959	0.0357
	1	0.0044	0.9968	0.0324
ZnO dose ($g.L^{-1}$)	**Concentration of ZnO**	K_{red} (min^{-1})	Correlation Coefficient (r)	S.D.
	1.0	0.0039	0.9842	0.065
	2.0	0.0041	0.9926	0.0465
	3.0	0.0045	0.9719	0.1017
	5.0	0.0093	0.9869	0.1406
Light intensity (lux)	**Light Intensity**	K_{red} (min^{-1})	Correlation Coefficient (r)	S.D.
	1100	0.0018	0.9962	0.0146
	1600	0.0020	0.9953	0.018
	2900	0.0022	0.9952	0.0203
	6300	0.0027	0.9969	0.0197
Chelating Agents	**Chelating Agents**	K_{red} (min^{-1})	Correlation Coefficient (r)	S.D.
	-	0.0039	0.9842	0.065
	Na_2 EDTA	0.000898	0.9204	0.035
	Na_3 Citrate	0.000782	0.7952	0.0547
	Na, K tartrate	0.0017	0.9947	0.0166

IV. CONCLUSIONS

The findings of this study demonstrate that ZnO serves as a highly efficient photocatalyst for the removal and reductive recovery of Cu(II) ions from aqueous solutions under solar illumination. The efficiency of the photocatalytic process is deeply dependent on key operational parameters, including solution pH, initial metal ion concentration, contact time, light intensity, catalyst dosage, and the concentration of the sacrificial hole scavenger. Mechanistically, the reduction process obeys pseudo-first-order kinetics.

Increasing the ZnO dosage significantly accelerated the pseudo-first-order rate constant of photoreduction of Cu(II). Increasing the light intensity enhanced the photo-reduction rate, highlighting the system's strong dependence on photon flux. Furthermore, the addition of methanol as a sacrificial hole scavenger effectively suppressed electron-hole recombination, thereby making photogenerated

conduction-band electrons more available to accelerate Cu(II) reduction. A crucial finding of this research is that while the presence of chelating agents generally impedes the process, increasing the catalyst dosage successfully drives a high percentage of Cu(II) reduction even when the copper is completely bound in chelated forms. Consequently, this study demonstrates that solar assisted ZnO photocatalysis is viable, and highly promising technology for the remediation of complex, heavy metal bearing industrial wastewaters.

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