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Photocatalytic Reduction of Copper(II) over Semiconducting Powder

VIJAY VERMA, ANIL DESAI and V.R. DWIVEDI*
Department of Chemistry, M.L. Sukhadia University, Udaipur-313 002, India

Photocatalytic reduction of copper(II) over semiconducting iron(III) oxide was carried out. The progress of reaction was observed spectrophotometrically. The effect of variation of different parameters like pH, concentration of copper(II), amount of photocatalyst, particle size, light intensity, etc. on the rate of photocatalytic reduction was observed. A tentative mechanism for this reduction has been proposed.

Key Words: Photocatalytic, Reduction, Copper(II), Semiconducting, Powder

INTRODUCTION

Various industrial effluents contain a number of metal ions, which are toxic to aquatic life at higher levels. Efforts are being made to remove these pollutants from aquatic environment. The photocatalytic treatment of such effluents holds promising results and, therefore, the present study was undertaken.

Wang and Zhuang[1] have investigated photocatalytic reduction of pollutant Hg(II) ions on doped WO_3 dispersion. Photocatalytic reduction and immobilization of Cr(VI) at TiO_2 in aqueous basic media has been reported by Lin *et al.*[2] Horvath *et al.*[3] observed photocatalytic self-generation reaction in Hg(II) reduction *via* photochemical reactions of Hg(I) cations, whereas photoreduction of iron(III) in marine mineral aerosol solutions has been reported by Zhu *et al.*[4] Inel and Ertek[5] observed photocatalytic deposition of Bi(III) ions on titania powder.

Heterogeneous photocatalytic oxidation of Mn(II) over TiO_2 has been reported by Lozano *et al.*[6] while photocatalytic reduction of the environmental pollutant Cr(VI) over CdS powder under visible light illumination has been observed by Wang *et al.*[7] Recently, photocatalytic degradation of the environmental pollutant Cr(VI) over stannic oxide powder has been reported by Dangi[8]. Osunda and Huntsman[9] have investigated photoreduction of manganese oxides in sea water.

Photocatalytic reduction of Cr(VI) over cadmium sulphide, zinc sulphide and titanium dioxide has been reported by Domenech and Munoz[10]. They also used zinc oxide for this purpose later on. Deposition of platinum on to CdS in aqueous suspension under ultra-violet illumination has also been investigated by the same group[11]. Photocatalytic reduction of Hg(II) and Cu(II) ions[12,13] in illuminated aqueous suspension of ZnO powder has also been reported. Mollers *et al.*[14] discussed photocatalytic deposition of noble metals.

Copper is essential for normal biological activities in human being. Its main source is chlor-alkali, electroplating industry, paints and dyes, petroleum refinery, fertilisers, mining and metallurgy, explosives, etc. Copper is present in several

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**Address for correspondence*: 29, Subhash Nagar, Udaipur-313 001, India.

industrial wastes causing toxic effects at higher concentrations. The present study describes the photocatalytic reduction of Cu(II) in water over Fe_2O_3 powder.

EXPERIMENTAL

Copper sulphate (E. Merck) and iron(III) oxide (Reidel) were used in the present investigation. Stock solution of copper sulphate was prepared in doubly distilled water. The photocatalytic reduction of copper sulphate was observed by taking 100 mL solution (2.40 ppm) in a 150 mL beaker and 0.3 g of iron(III) oxide was added to it. Irradiation was carried out keeping the whole assembly exposed to a 1000 W halogen lamp (Okana, light intensity 54.0 mW cm^{-2}). The intensity of light at various distances from the lamp was measured with the help of a solarimeter (Surya Mapi Model CEL 201). A water filter was used to cut out thermal radiations. The pH of the solution was measured with a digital pH meter (Systronics Model 324). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solution. The necessary condition for the correct measurement of the optical density is that the solution must be free from semiconductor particles and impurity; a centrifuge (REMI-1258) was used to remove these species.

The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals using atomic absorption spectrophotometer (Phillips PU 9200).

RESULTS AND DISCUSSION

The photocatalytic reduction of copper sulphate was observed at wavelength 324.8 nm; the results of a typical run are given in Table-1 and represented graphically in Fig. 1. It has been observed that a plot of log (concentration) *vs.* time is linear, which indicates that this photocatalytic reduction follows pseudo first order kinetics. The rate constant of this reaction was calculated from the relation

$$k = 2.303 \times \text{slope}$$

TABLE-1
TYPICAL RUN

[Copper sulphate] = 2.40 ppm, Intensity of light = 54.0 m Wcm^{-2}, Temperature = 303 K, pH = 4.5, Fe_2O_3 = 0.3 g

Time (min)	Concentration (C) (ppm)	1 + log C
0	2.400	1.3802
30	1.800	1.2552
60	1.280	1.1072
90	1.000	1.0000
120	0.763	0.8825
150	0.545	0.7363
180	0.407	0.6096
210	0.301	0.4785
240	0.220	0.3424
270	0.151	0.1789

$k = 1.62 \times 10^{-4}\ sec^{-1}$.

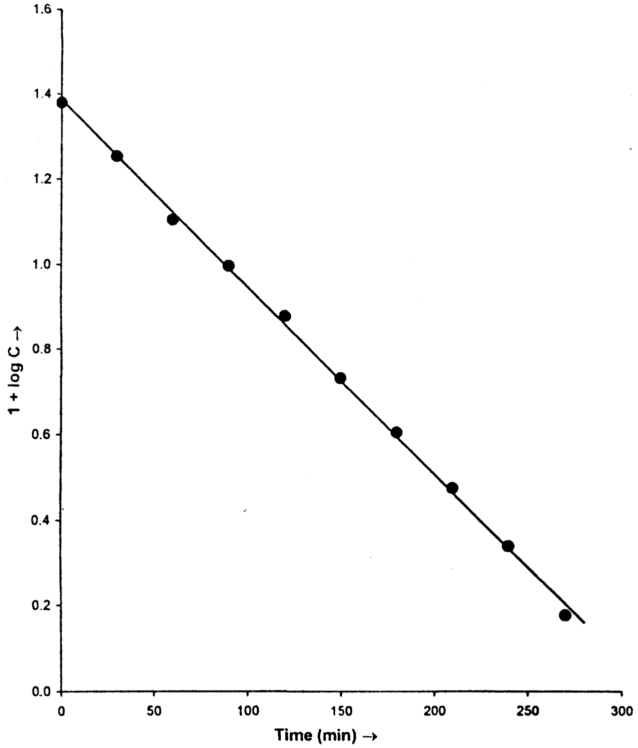

Fig. 1. A typical run

Effect of pH: Photocatalytic reduction of copper(II) may be affected by the pH values and, therefore, the effect of pH on this photocatalytic reaction has been investigated. The results are reported in Table-2.

TABLE-2
EFFECT OF pH

[Copper sulphate] = 2.40 ppm, Fe_2O_3 = 0.3 g,
Intensity of light = 54.0 mW cm^{-2}, Temperature = 303 K

pH	$k \times 10^4$ (sec^{-1})
2.0	0.67
2.5	0.82
3.0	1.00
3.5	1.17
4.0	1.43
4.5	1.62
5.0	1.49
5.5	1.37
6.0	1.20
6.5	1.06

It has been observed that this reaction proceeds smoothly in acidic range up to pH = 6.5, above which precipitation of copper was obtained, even under ordinary conditions and, therefore, the effect of variation was observed in the pH range for

2.0 to 6.5. The reaction rate was found to increase as the pH was increased and an optimum value was obtained for pH = 4.5. This pH dependence can be explained on the basis that the hole can generate H^+ ions in solution from water whereas these protons are utilised by dissolved oxygen (in solution).

$$2H^+ + H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+ \tag{1}$$

$$2H^+ + O_2 \text{ (in solution)} + 2e^- \longrightarrow H_2O_2 \tag{2}$$

These two reactions counter balance each other to a particular extent. Now it is known that the processes at the semiconductor-electrolytic interface depend on the surface properties of the semiconductor[15]. Therefore, the surface charge on the semiconductor will play a major role in deciding the fate of this photocatalytic reaction, because it controls the driving force for electron transfer[16–18]. This surface charge depends on the pH of the solution being positive in acidic media and negative in alkaline media. The pH, where the net charge on the surface of the semiconductor is zero, is called the point of zero charge (PZC).[15] It corresponds to the point, where no charge of pH is observed after adding the semiconductor[19].

The value of point of zero charge can be lower if anions are adsorbed on the surface of the semiconductor[20]. Reverse may be true, if cations are adsorbed. The data available indicate that the photocatalytic degradation of copper sulphate proceeds smoothly, when the surface is slightly positively charged as the reaction rate is maximum at pH = 4.5. It may also be concluded that for pH > 4.5 equation (2) starts dominating the equation (1), so that there will be an additional decrease in the amount of H^+ ions and hence the decrease in rate of photocatalytic degradation of Cu(II) species. The reduction of Cu(II) to its lower oxidation states will also adversly affect the value of PZC and thus it will add to the lowering in the rate of the reaction.

Effect of Copper(II) Concentration: The effect of the concentration of copper sulphate on the rate of photocatalytic reduction was observed, by keeping all other factors identical. The range of concentration investigated in the present case is 2.40–10.30 ppm. The results are reported in Table-3.

TABLE -3
EFFECT OF COPPER(II) CONCENTRATION

pH = 4.5, Fe_2O_3 = 0.3 g, Intensity of light = 54.0 mW cm^{-2}, Temperature = 303 K

[Copper sulphate] (ppm)	k × 104 (sec^{-1})
2.40	1.62
3.36	1.43
4.32	1.28
5.28	1.12
6.24	0.98
7.20	0.83
8.20	0.73
9.22	0.63
10.30	0.45

It was observed that as the concentration of copper sulphate was increased, there was a decrease in the rate of the reaction. This may be explained on the ground that at larger concentrations the coloured solution of copper ions will absorb the major portion of the incident light or, in other words, it may act like a filter, so it will not permit the desired light intensity to fall on the semiconductor powder and hence a decrease in the rate of photocatalytic reaction was observed.

Effect of Amount of Photocatalyst: The effect of amount of photocatalyst on the rate of photocatalytic reduction of copper(II) was also observed by taking different amounts of semiconductor, keeping all other factors identical. The results are reported in Table-4.

TABLE-4
EFFECT OF AMOUNT OF PHOTOCATALYST

[Copper sulphate] = 2.40 ppm, pH = 4.5,
Intensity of light = 54.0 mW cm^{-2}, Temperature = 303 K

[Fe_2O_3] (g)	k × 10^4 (sec^{-1})
0.10	1.01
0.15	1.12
0.20	1.26
0.25	1.41
0.30	1.62
0.35	1.62
0.40	1.61
0.45	1.62
0.50	1.63
0.55	1.62
0.60	1.62

As evident from the data given in Table-4, the rate of photocatalytic reduction of Cu(II) increases with increasing the amount of photocatalyst. After a certain amount of semiconductor, the rate of photocatalytic degradation became constant. In the present investigations, this value of k was obtained for 0.30 g of the semiconductor. Any further increase in the amount of semiconductor showed no increase in the rate of the reaction. It indicates that there is a limiting value of the amount of semiconductor above which any increase in its amount will not affect the reaction rate appreciably. It may be considered like a saturation point.

This observation may be explained on the basis that as the amount of semiconductor was increased, more particles are available for excitation and there is a greater possibility of electron-hole pair generation on exposure to light. This will result into a corresponding increase in the rate of photocatalytic removal of copper (II). After a certain value is reached (0.30 g), the bottom of the reaction vessel is almost covered and now any addition of semiconductor will not increase the exposed surface area, rather it will only add to the thickness of the layer of semiconductor at the bottom of the reaction vessel. Hence a saturation like behaviour was observed.

It was further confirmed by using vessels of different dimensions where the saturation point was shifted to higher values for larger vessels and show a downward shift for smaller vessels. It was further supported by the observation that this point shifts to higher side, when the solution was stirred. This increase is due to the greater probability of each particle to be exposed in all directions, which was otherwise not possible in an unstirred solution.

Effect of Light Intensity: The effect of light intensity on the rate of photocatalytic reduction of Cu(Il) has been observed by varying the distance between the exposed surface of the photocatalyst and the source. The results are reported in Table-5.

TABLE-5
EFFECT OF LIGHT INTENSITY

[Copper sulphate] = 2.40 ppm, pH = 4.5,
Fe_2O_3 = 0.3 g, Temperature = 303 K

Intensity of light (mW cm^{-2})	$k \times 10^4$ (sec^{-1})
9.0	0.72
14.0	0.85
19.0	0.91
24.0	1.04
29.0	1.13
34.0	1.25
39.0	1.32
44.0	1.44
49.0	1.52
54.0	1.62

It has been observed that the rate of photocatalytic reaction increases with increasing the light intensity. It may be attributed to the fact that more electron-hole pairs will be generated due to an increased number of photons striking the semiconductor surface with an increase in the intensity of light. Now more electrons will be available for reducing the substrate and hence the rate of photocatalytic reaction will be enhanced.

Effect of Particle Size: The effect of particle size on the rate of photocatalytic reduction of Cu(II) was also investigated by taking semiconductor particles of different sizes. The obseivations are reported in Table-6.

Particle size of the photocatalyst was kept between 38.0 to 130.0 μm. As evident from the experimental data given in Table-6, there was a decrease in the rate of photocatalytic removal of Cu(II) as the particle size of the semiconductor was increased. This decrease in the rate may be explained on the basis that as the particle size was increased, there was a corresponding decrease in the surface area. The decrease in surface area will be about four times by increasing the size of the particle to its double. This four-fold decrease in area should decrease the rate to it one-fourth, but was never observed. This may be due to the fact that the exposed surface area may not decrease to that extent as predicted theoretically.

TABLE-6
EFFECT OF PARTICLE SIZE

[Copper sulphate] = 2.40 ppm, pH = 4.5,
Intensity of light = 54.0 mW cm^{-2}, Fe_2O_3 = 0.3 g, Temperature = 303 K

Particle size (μm)	$k \times 10^4$ (sec^{-1})
38.0	1.62
50.0	1.26
75.0	1.06
100.0	0.92
130.0	0.76

Mechanism

On the basis of the observed experimental data, the following tentative mechanism has been proposed for the photocatalytic reduction of copper(II).

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB) \quad (3)$$

$$2h^+ + H_2O \longrightarrow 1/2O_2 + 2H^+ \quad (4)$$

$$2H^+ + O_2 \text{ (in solution)} + 2e^- \longrightarrow H_2O_2 \quad (5)$$

$$Cu(II) + 2e^- \longrightarrow Cu \quad (6)$$

In the first step, the semiconductor is excited by the adsorption of light of an appropriate wavelength. An electron from the valence band of the semiconductor will jump into its conduction band, thus leaving behind a hole. This hole may be utilised by the water molecules to generate oxygen and H^+ ions. These H^+ ions and dissolved oxygen in solution can be reduced by two electrons to form hydrogen peroxide, which may slowly degrade. In the last step, copper(II) may accept two electrons from the conduction band of the semiconductor and will be reduced to its metallic state. This reduction of Cu(II) to Cu is also clearly indicated by light reddish brown coloured deposit on the semiconductor. This observation is similar to the results obtained earlier in case of TiO_2 and WO_3 powder[21].

Photocatalytic reduction of metal ions from their higher oxidation states to lower oxidation states will not only make the industrial effluents less toxic, but, in some cases, it will provide an easier method to recover these metals, where some metallic deposits were observed on semiconducting particulate systems. So the photocatalytic system will help us in the treatmet of industrial wastewater containing metal ions on one hand and make this method commercially viable from the recovery point of view, on the other.

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