



PHOTOCATALYTIC REDUCTION OF SILVER (I) TO METALLIC SILVER OVER SrWO₄

JAGDISH CHANDRA SHARMA, JAYANT GANDHI, AJAY SHARMA^a, NIVEDITA GUPTA^b and SHIPRA BHARDWAJ*

Department of Chemistry, Maharana Pratap Govt. P. G. College,
CHITTORGARH – 312001 (Raj.) INDIA

^aDepartment of Chemistry, Govt. P. G. College, Sirohi, SIROHI (Raj.) INDIA

^bDepartment of Chemistry, J. D. B. Govt. Girls College, KOTA (Raj.) INDIA

ABSTRACT

In present work, an attempt has been made for photocatalytic removal of Ag (I) from its aqueous solution. The photoreduction of Ag⁺ ions at the surface of SrWO₄ has been investigated. The progress of reaction was observed by atomic absorption spectrophotometrically (AAS). The effect of variation of different parameters like pH, concentration of silver (I), amount of photocatalyst, light intensity etc. on the rate of reaction was observed. A tentative mechanism for this reaction has been proposed.

Key words: Photocatalyst, Reduction, Silver (I), Semiconductor, Strontium tungstate

INTRODUCTION

A potential and very attractive practical application of light driven photocatalytic reduction is the deposition of environmentally harmful toxic metals on the surface of semiconductor and recovery of noble metals from industrial waste effluents. It is well-known that Hg (II), Pb (II), Cd (II), Ni (II) and Cr (VI) are much toxic among the metal ions present in the waste water. Discharges containing silver, in particular are strictly controlled because it is a valuable natural resource of finite supply, high cost and hence its release into the environment is strictly regulated.

The photocatalytic reduction of a variety of dissolved metal ions in TiO₂ suspensions has been investigated¹. Photocatalytic reduction of chromium in aqueous solution by Fe³⁺ doped TiO₂ nanoparticles were carried out by Thakare and Jugele².

* Author for correspondence; E-Mail : sidsidsmart@yahoo.co.in; Sharma_jagdish84@yahoo.com

Troupis et al.³ studied the photocatalytic reduction and recovery of copper by polyoxometallates. Photocatalytic reduction of environmental pollutant Cr (VI) over some semiconductors under UV/visible light illumination was reported by Khalil et al.⁴ while Reiche et al.⁵ investigated the photoreduction of Cu (II) in TiO₂ suspensions.

Effects of bismuth vanadate and anthraquinone dye on the photodegradation of polycarbonate are discovered by Saron et al.⁶ Verma et al.⁷ carried out the photocatalytic reduction of nickel from waste water using iron (III) oxide. Photocatalytic removal of Ni (II) from aqueous solutions using ultraviolet irradiated TiO₂ was also studied by Lin and Rajeshwar⁸. Whereas Wang and Zhuang⁹ investigated photocatalytic reduction of pollutant Hg (II) ions on doped WO₃ dispersion.

Marine animals show mark diversity in tolerance to silver. Fish and lower organisms are susceptible to silver poisoning. It is a cumulative poison and chronic ingestion can cause a permanent discoloration of skins in humans. Concentrations in the range of 0.4 to 1 mg / L caused pathological changes in the kidneys, liver and spleen of rats. Toxic effects on fish in fresh water have been observed at concentration as low as 0.17µg / L. In the present paper, the photoreduction of Ag⁺ ion over SrWO₄ powder has been reported.

EXPERIMENTAL

Semiconducting powder SrWO₄ was prepared via precipitation reaction between SrCl₂ and Na₂WO₄¹⁰. The precipitate was washed with distilled water a number of times and dried. Stock solution of silver nitrate was prepared in doubly distilled water. The photocatalytic reduction of silver nitrate was observed by taking 100 mL solution (4.20 ppm) in a 150 mL beaker and 0.30 g of strontium tungstate was added to it. Irradiation was carried out by keeping whole assembly exposed to a 1000 W halogen lamp (Okano, Light intensity 54.0 mWcm⁻²). The intensity of light at various distances from the lamp was measured with the help of a solarimeter (Surya Mapi Model CEL201). 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 solutions. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals using Atomic Absorption Spectrophotometer (Varian AA240FS Model).

RESULTS AND DISCUSSION

The photocatalytic reduction of AgNO_3 was observed by AAS at wavelength 328.1 nm. The results of a typical run are given in Table 1 and represented graphically in Fig. 1. It has been observed that plot of $\log(\text{concentration})$ vs. time was linear, which indicates that this photocatalytic reduction follows pseudo-first order kinetics. The rate constants were calculated by the expression-

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

Table 1. A typical run

| [Silver nitrate] = 4.20 ppm | | Temperature = 302 K | | |
|---|---|--|------------|-----------|
| pH = 6.0 | | SrWO ₄ = 0.30 g | | |
| Intensity of light = 54.0 mWcm ⁻² | | $\lambda_{\text{max}} = 328.1 \text{ nm}$ | | |
| Time (min.) | Concentration in dark [C ¹] (ppm) | Concentration in presence of light [C] (ppm) | 1 + log C' | 1 + log C |
| 0 | 4.20 | 4.20 | 1.6232 | 1.6232 |
| 30 | 3.94 | 3.52 | 1.5955 | 1.5465 |
| 60 | 3.64 | 2.85 | 1.5611 | 1.4548 |
| 90 | 3.44 | 2.30 | 1.5366 | 1.3617 |
| 120 | 3.30 | 1.87 | 1.5185 | 1.2718 |
| 150 | 3.32 | 1.62 | 1.5211 | 1.2095 |
| 180 | 3.21 | 1.29 | 1.5065 | 1.1106 |
| 210 | 2.93 | 1.12 | 1.4661 | 1.0492 |
| 240 | 2.84 | 0.87 | 1.4533 | 0.9395 |
| 270 | 2.78 | 0.70 | 1.4440 | 0.8451 |
| 300 | 2.72 | 0.58 | 1.4346 | 0.7634 |
| K' = 2.36 x 10 ⁻⁵ (sec ⁻¹); k = 1.10 x 10 ⁻⁴ (sec ⁻¹) | | | | |

As expressed in Table 1, the rate constants are $2.36 \times 10^{-5} \text{ (sec}^{-1}\text{)}$ and $1.10 \times 10^{-4} \text{ (sec}^{-1}\text{)}$ in dark and in presence of light, respectively. Thus, the rate of removal in presence

of light is about five times greater than the adsorption process alone. This enhancement indicates that it is a photocatalytic process.

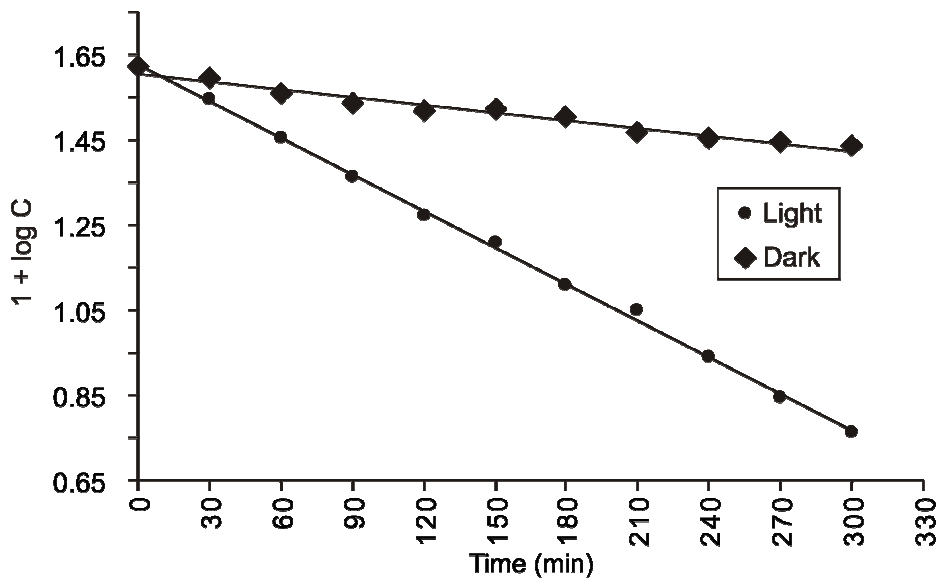
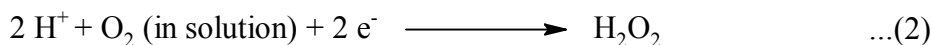
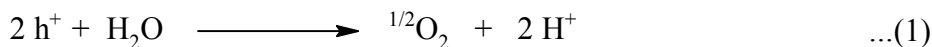


Fig. 1: A typical run

Effect of pH

The effect of pH on the rate of reduction of Ag (I) was studied in the pH range 2.5-7.5. The data are presented graphically in Fig. 2.

It was observed that rate of reduction increases with an increase in pH. After attaining a maximum value (pH 6.0) rate decreases on increasing pH further. The optimum value was obtained at pH = 6.0. It has been established that surface properties of semiconductor are responsible for photocatalytic process¹¹. The hole generated by semiconductor generates H⁺ ions in the solution from water. These protons are utilized by dissolved oxygen in solution.



These two reactions counter balance each other to a particular extent. The surface charge on the semiconductor-electrolyte interface will play a major role in deciding the fate of this

photocatalytic reduction^{11,12}. The surface charge on semiconductor is responsible for transfer of electrons to Ag (I) converting it into Ag (0)¹³. The surface charge on semiconductor favors the reduction, it is positive. This surface charge depends on the pH of the solution being positive in acidic media and negative in alkaline media. After a particular pH, net charge on semiconductor surface becomes zero and it is called point of zero discharge (PZC)¹⁴.

[Silver nitrate] = 4.20 ppm

Temperature = 302 K

SrWO₄ = 0.30 g

λ_{\max} = 328.1 nm

Intensity of light = 54.0 mWcm⁻²

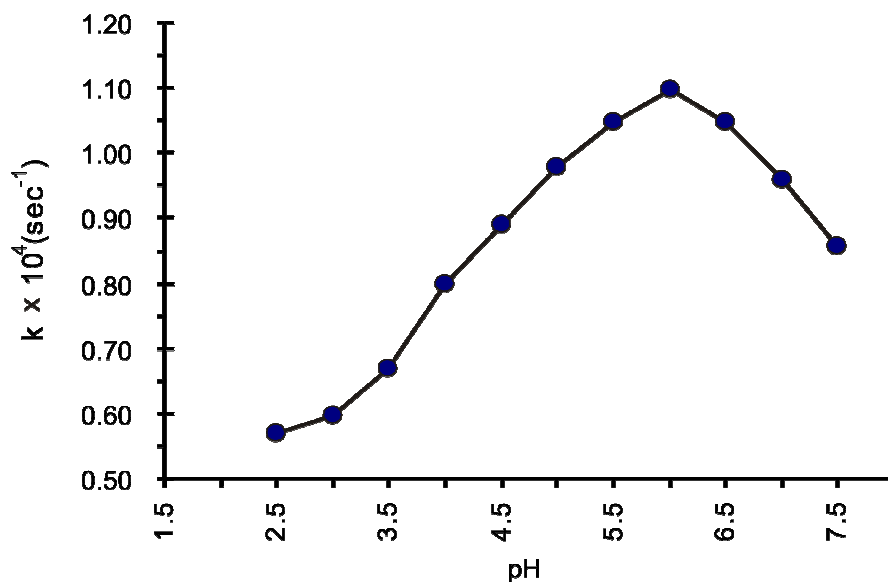


Fig. 2: Effect of pH

It seems that when the pH of the solution is low then reaction (1) dominates and reduction of Ag (I) takes place. As the pH was raised, the reaction (2) starts dominating the reaction (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 Ag (I) was observed. The reduction of Ag (I) to its lower oxidation state will also adversely affect the value of PZC and thus, it will add to the lowering in the rate of reaction.

Effect of silver (I) concentration

In the present study, the concentration of silver nitrate was varied between range

1.90-9.00 ppm. The effect of change in concentration of Ag (I) on the rate of reaction was also observed, keeping all other factors identical. The results are reported in Fig. 3

| | |
|--|---|
| pH = 6.0 | Temperature = 302 K |
| SrWO ₄ = 0.30 g | $\lambda_{\text{max}} = 328.1 \text{ nm}$ |
| Intensity of light = 54.0 mWcm ⁻² | |

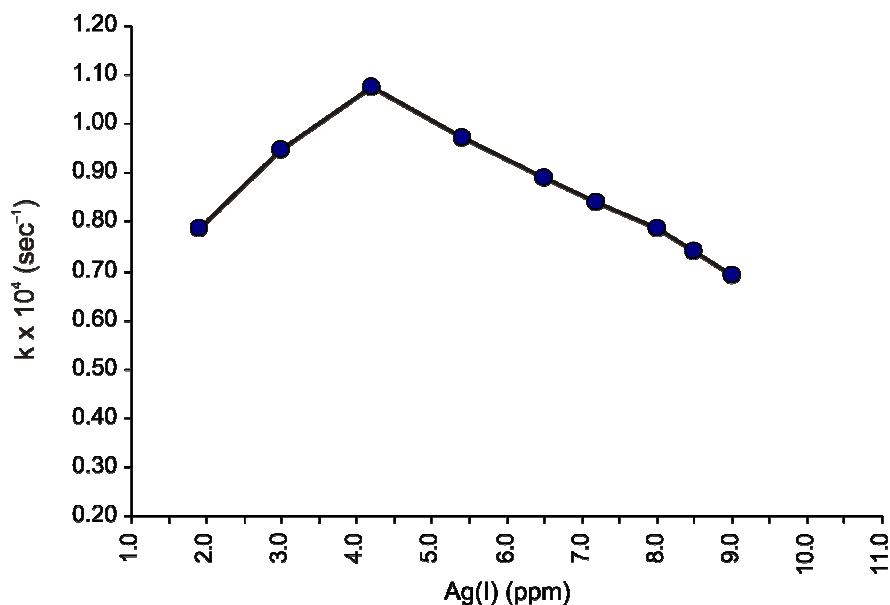


Fig. 3: Effect of silver nitrate concentration

It was observed that as the concentration of silver nitrate increases, the rate of reaction also increases. After attaining a maximum value (4.20 ppm), a decrease in the rate of reaction was observed. This may be explained on the ground that at larger concentrations, the movement of silver ions towards semiconductor surface will be hindered, which will not permit silver ions to reach the desired site within the limited time domain and hence, a decrease in the rate of photocatalytic reaction was observed

Effect of amount of SrWO₄

The effect of amount of photocatalyst on the rate of photocatalytic reduction of silver (I) was observed by taking different amounts of semiconductor. The results are shown in Fig. 4.

[Silver nitrate] = 4.20 ppm

Temperature = 302 K

pH = 6.0

$\lambda_{\max} = 328.1 \text{ nm}$

Intensity of light = 54.0 mWcm^{-2}

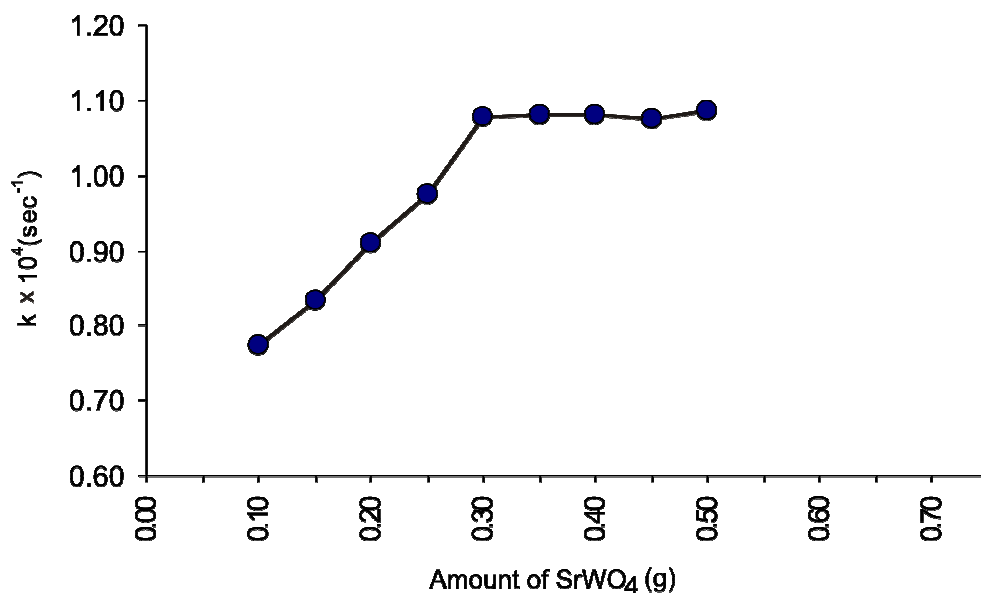


Fig. 4: Effect of amount of photocatalyst

It has been observed that the rate of photocatalytic reduction of Ag (I) increases with increasing the amount of photocatalyst. After a certain amount of semiconductor (0.30 g), the rate of photocatalytic degradation becomes almost constant as any further increase in amount of semiconductor showed no reasonable increase in the rate of reaction.

It can 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 results into a corresponding increase in the rate of reaction. After a certain amount of the semiconductor (0.30 g), the bottom of the reaction vessel is almost covered and now, any addition of semiconductor does not increase the exposed surface area, rather it only adds to the thickness of the layer of semiconductor at the bottom of the reaction vessel. Hence, a saturation like behavior was observed. It was confirmed by the fact that as the vessel size was changed, value of k for such saturation point also changes and as solution was stirred, then also, the rate increases. It may be due to increase in the number of particles exposed to light.

Effect of light intensity

The intensity of light reaching to the semiconductor was varied by placing the reaction vessel at different distances from the lamp. The results are presented graphically in Fig. 5.

| | |
|-----------------------------|-------------------------------------|
| [Silver nitrate] = 4.20 ppm | Temperature = 302 K |
| pH = 6.0 | $\lambda_{\max} = 328.1 \text{ nm}$ |
| SrWO ₄ = 0.30 g | |

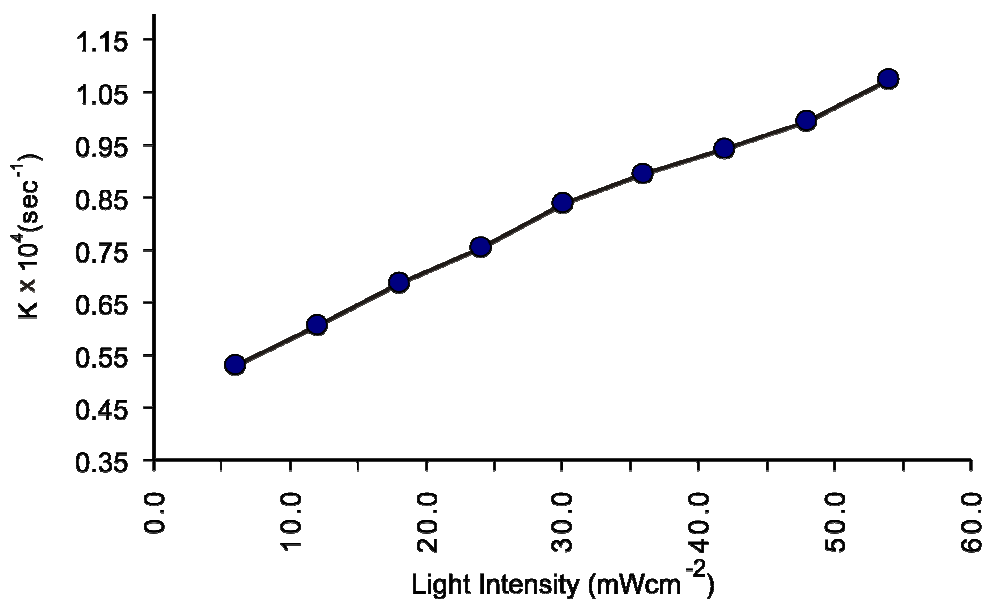


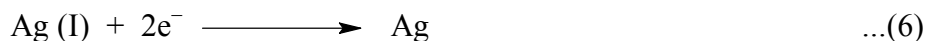
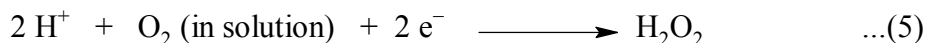
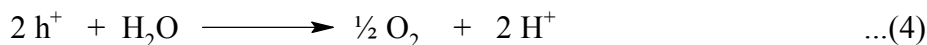
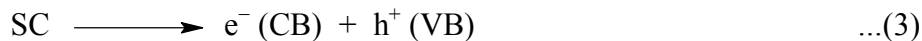
Fig. 5: Effect of light intensity

It has been observed that the rate of photocatalytic reaction increases with increasing 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. Therefore, more electrons will be available for reduction; thus, resulting into an increase in rate of reaction.

MECHANISM

On the basis of the observed experimental data, the following tentative mechanism

has been proposed for the photocatalytic reduction of silver metal ion.



In the first step, semiconductor is excited by absorbing the 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 utilized 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, silver (I) may accept an electron from the conduction band of semiconductor and will be reduced to its metallic state. This reduction of Ag (I) is clearly indicated by silvery grey deposit on the semiconductor surface.

CONCLUSION

The photocatalysis appears to be a promising technology for the removal of heavy metal ions from waste water. This method is also applicable at ppm level of metal contaminants, which will not only make the industrial effluents less toxic, but it provides an effective way to recover such metals.

ACKNOWLEDGMENT

We are grateful to M/s. Hindusthan Zinc Limited, Process control laboratory to provide instrumental facility and Prof. Suresh C. Ameta, Deptt. of Chemistry, M. L. Sukhadia University, Udaipur for his invaluable suggestions.

REFERENCES

1. Michael R. Prairie, Lindsey R. Evans, Bertha M. Stange and Sheryi L. Martinez, *Environ. Sci. Technol.*, **27**, 1776 (1999).
2. Sanjay R. Thakare and R. N. Jugele, *Indian J. Chem.*, **42A**, 513, (2003).

3. A. Troupis, A. Hiskia and E. Papaconstantinou, *Environ. Sci. Technol.*, **36**, 5355 (2002).
4. L. B. Khalil, W. E. Mourad and M. W. Rophael, *Appl. Catal. B, Environ.*, **17**, 267 (1998).
5. H. Reiche, W. W. Dunn and A. J. Bard, *J. Phys. Chem.*, **83**, 2248 (1979).
6. C. Saron, M. I. Felisberti, F. Zulli and M. Giordano, *J. Braz. Chem. Soc.*, **18**, 900 (2007).
7. V. Verma, M. Mehta, V. R. Dwivedi and S. C. Ameta, *Chem. Environ Res.*, **9**, 315- (2000).
8. Wen-Yuan Lin and Krishnan Rajeshwar, *J. Electrochem. Soc.*, **144**, 2751 (1997).
9. Z. H. Wang and Q. X. Zhuang, *J. Photochem. Photobiol.*, **75A**, 105, (1993).
10. X. Zhao, Y. Cheung, X. Zhang, Dickon H. L. Ng and Yu Jaguar, *J. Am. Ceramic Soc.*, **89**, 2960 (2006).
11. D. Duonghong, J. Ramsdev and M. Gratzel, *J. Am. Chem. Soc.*, **104**, 2977 (1982).
12. G. T. Brown, J. R. Darwent and P. Fletcher, *J. Am. Chem. Soc.*, **107**, 6446 (1985).
13. J. Moser and M. Gratzel, *J. Am. Chem. Soc.*, **106**, 6557 (1984).
14. S. R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, Plenum Press, New York, (1980).

Accepted : 23.03.2008