



## **PHOTOCATALYTIC OXIDATION OF THIOSULPHATE ION IN PRESENCE OF AMMONIUM PHOSPHOMOLYBDATE**

**MAHENDRA CHAUDHARY<sup>\*</sup>, RAMESHWER AMETA<sup>a</sup> and  
SURESH C. AMETA<sup>b</sup>**

Department of Chemistry, Singhania University, Pachheri-Bari, JHUNJHUNU – 333515 (Raj.) INDIA

<sup>a</sup>Department of Chemistry, S. M. B. Govt. College, NATHDWARA – 313301 (Raj.) INDIA

<sup>b</sup>Department of Chemistry, Pacific University, Debari, UDAIPUR – 313024 (Raj.) INDIA

### **ABSTRACT**

Photocatalytic oxidation of thiosulphate over ammonium phosphomolybdate powder was carried out. The progress of reaction was observed volumetrically. The effect of variation of different parameters like pH, concentration of thiosulphate ion, amount of photocatalyst, light intensity, particle size etc. on the rate of photocatalytic oxidation was observed. A tentative mechanism for this reaction has been proposed.

**Key words:** Photocatalytic, Ammonium phosphomolybdate, Thiosulphate.

### **INTRODUCTION**

Metallurgical industries based on sulphur containing ores throw a lot of sulphur containing ions in effluents. These ions include sulphite, sulphates, thiosulphate, thionites etc. Normally, a lime treatment is given to remove these ions, but only sulphate ion is removed predominantly. Rest other ions are either not removed or if these are removed, then only partially. This industrial effluent is filtered to remove precipitated CaSO<sub>4</sub>. The other ions are slowly air oxidised or degraded to form sulphate ions; thus, increasing the acidity of underground water in areas around that particular industrial set-up. The increased acidic behaviour of water will make the land infertile and will not permit any crop to grow in that area. Not only this, the water can not be used for any other useful purpose. Thus, there is a pressing demand to develop alternate suitable methods to oxidize these problem creating ions to sulphate ions in a relatively shorter period so that it can be removed alongwith existing sulphate by lime treatment. Photocatalysis seems to be a step towards the solution to this problem.

---

\* Author for correspondence; Email: kashwa12@yahoo.co.in

Tanaka<sup>1</sup> has reported that photocatalytic materials are useful in either mineralizing or eliminating the polluting materials from the environment. It has been used by Pelizzetti et al.<sup>2</sup> for degradation of pesticides like atrazine. Hermann et al.<sup>3</sup> and Ameta et al.<sup>4</sup> reported heterogeneous photocatalysis as an emerging technology for waste water treatment. It may also prove useful in recovery for some transition metals from industrial effluents. The photocatalytic activity of titanium and cobalt oxides for the degradation of methyl orange has been investigated by Sun et al.<sup>5</sup> Das et al.<sup>6</sup> carried out photocatalytic degradation of waste water pollutants like polynuclear aromatic hydrocarbons using TiO<sub>2</sub>. Osawa and Sunakani<sup>7</sup> reported photocatalytic degradation of some polymer like polyurethane and polyvinyl chloride (PVC). Terzian and Serpone<sup>8</sup> also carried out heterogeneous photocatalysed mineralization of xylenol over titanium dioxide. Chhabra et al.<sup>9</sup> observed the effect of addition of sodium bicarbonate/carbonate on the rate of photobleaching of methylene blue over CdS powder. Waki et al.<sup>10</sup> reported such a process for some nitrogen containing pollutants at TiO<sub>2</sub>/H<sub>2</sub>O interfaces. Tanaka<sup>11</sup> observed photocatalytic degradation of some sulphonated aromatics in aqueous TiO<sub>2</sub> suspension whereas Ahmed and Attia<sup>12</sup> used certain aerogel materials for photocatalytic detoxification of cyanide in waste waters. Prevot et al.<sup>13</sup> investigated the effect of bio-based chemicals from urban wastes on the photodegradation of azo dyes. CdS supported on a solid surface was used as a photocatalyst by deMayo et al.<sup>14</sup> while Green and Mills<sup>15</sup> have carried out kinetic studies of photoinduced electron transfer reaction sensitized by colloidal CdS. Recently, Sachdeva et al.<sup>16</sup> used ammonium phosphomolybdate for photocatalytic bleaching of fast green. Although a lot of work has been carried out by different workers from time to time, but negligible attention has been paid to use ammonium phosphomolybdate as a photocatalyst. The present study describes the photocatalytic oxidation of thiosulphate ion to sulphate ion over ammonium phosphomolybdate.

## EXPERIMENTAL

Photocatalytic oxidation of sodium thiosulphate was observed by taking 0.12 M solution in a 100 mL beaker and 0.20 g ammonium phosphomolybdate was added to it. Then this solution was exposed to light by a 200 W tungsten lamp (Light intensity = 22.0 mW cm<sup>-2</sup>). 5 mL of this solution was taken out and transferred to a conical flask containing 5 mL of 0.06 M iodine solution and 5 mL of 2N HCl. The solution was diluted with 50 mL of water. The excess of iodine was then titrated against previously standardized sodium thiosulphate solution ( $7.75 \times 10^{-2}$  M) using starch as an indicator. It was observed that consumption of sodium thiosulphate solution increases with increasing time of irradiation. From the titre value ( $V_1$ ), the volume of unreacted sodium thiosulphate was determined<sup>17</sup> by subtracting it from value of required volume of sodium thiosulphate to consume complete iodine (7.75 mL). The results are given in Table 1.



presence of isopropanol. It indicates that hydroxyl radical  $\cdot\text{OH}$  is not an active oxidising species in this case, rather it is produced as a side product. This is possible, if  $\text{HO}_2\cdot$  radical is considered as an active species responsible for oxidation of thiosulphate. It is further substantiated by the fact that the reaction rate is higher in lower pH range. The generation of  $\text{HO}_2\cdot$  radical involving superoxide anion radical ( $\text{O}_2^{\cdot-}$ ) as an intermediate may be considered as follows :



**Table 2: Effect of pH**

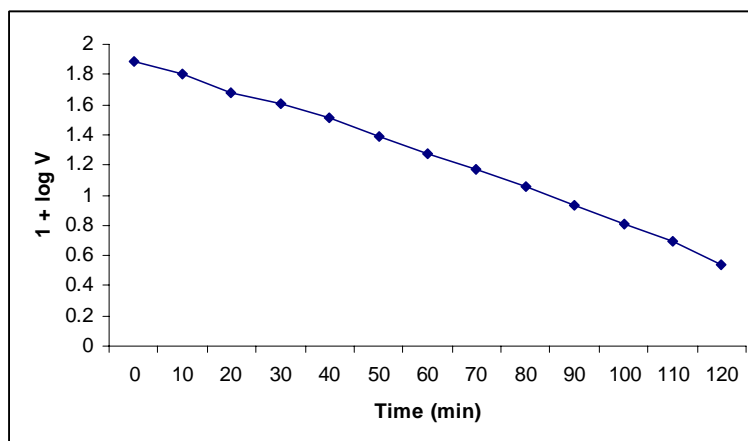
Ammonium phosphomolybdate = 0.20 g    Light intensity = 22.0 mW cm<sup>-2</sup>  
 [Sodium thiosulphate] = 0.12 M

pH	k x 10 <sup>4</sup> (sec <sup>-1</sup> )
4.5	1.80
4.8	2.02
5.0	2.13
5.2	2.44
5.5	2.78
5.8	3.00
6.0	3.21
6.2	3.45
6.5	3.88
6.8	3.50
7.0	3.27
7.2	3.09
7.5	2.92
7.8	2.68
8.0	2.41

### Effect of particle size of photocatalyst

The effect of particle size on the rate of photocatalytic oxidation was also investigated by varying the size of particles of semiconductor. The observations are tabulated in Table 3. Particle size of ammonium phosphomolybdate was kept between 0.8 to 4.0  $\mu\text{m}$ . As indicated

form the data in the table that the rate of photocatalytic oxidation of thiosulphate ions increases with the decrease in particle size of semiconductor. The increase in the rate may be explained on the basis of the increased surface area of the photocatalyst as the particle size was reduced. The increase in surface area of the semiconductor will be four times on reducing the particle size to its half. This should increase the rate of reaction four times, but it was never achieved. This irregularity may be attributed to the fact that the surface area exposed to light will not increase to the extent as expected theoretically.



**Fig. 1: A Typical run**

**Table 3: Effect of particle size**

Ammonium phosphomolybdate = 0.20 g      Light intensity = 22.0 mW cm<sup>-2</sup>  
 [Sodium thiosulphate] = 0.12 M                      pH = 6.5

Particle size (μm)	k x 10 <sup>4</sup> (sec <sup>-1</sup> )
0.8	3.88
1.6	3.54
2.4	3.14
3.2	2.61
4.0	2.15

#### **Effect of sodium thiosulphate concentration**

The effect of variation of sodium thiosulphate concentration on the rate of its photocatalytic oxidation was studied by taking different concentrations of sodium thiosulphate, keeping all other factors identical. The results obtained are summarized in Table 4.

**Table 4: Effect of sodium thiosulphate concentration**

Ammonium phosphomolybdate = 0.20 g      Light intensity = 22.0 mW cm<sup>-2</sup>  
 pH = 6.5

[Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ] x 10 <sup>2</sup> M	k x 10 <sup>4</sup> (sec <sup>-1</sup> )
4.25	1.47
5.00	1.93
6.25	2.22
8.33	2.68
10.08	3.14
12.00	3.88
14.00	3.26
16.50	2.98
18.25	2.10
20.00	1.53

It is evident from the results that as the concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was increased, the rate of photocatalytic oxidation of thiosulphate to sulphate ion increases up to [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>] = 0.12 M; but on further increase, a decrease in the rate of reaction was observed. It may be explained on the basis that as the concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> increases, more S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions are available for oxidation and hence, an enhancement in the rate was observed. On the other hand, a decrease in the rate of photocatalytic oxidation was observed with increasing concentration of sodium thiosulphate, where more thiosulphate ions are available to hinder the movement of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions towards the semiconductor surface in a desired time limit.

#### Effect of amount of photocatalyst

The effect of variation in the amount of photocatalyst on the rate of photocatalytic oxidation of thiosulphate ion was also observed. The results are reported in Table 5. The rate of photocatalytic oxidation of sodium thiosulphate increases with increase in the amount of semiconductor. However, the increase in the rate was observed only up to a certain amount of the photocatalyst (0.20 g) will not affect the rate of reaction appreciably.

This variation can be attributed to the fact that initially, the amount of the semiconductor was not enough so as to cover the lower surface of the reaction vessel. As the amount of the semiconductor was increased, the surface area exposed to light also increases

and as a result, higher rate values are obtained. After a certain value (0.20 g) i.e., when the bottom surface of the reaction vessel was completely covered, an optimum rate was observed and therefore, a plateau was obtained. Any further increase in the amount of photocatalyst will only increase the thickness of the layer of photocatalyst already formed at the bottom of the vessel and not its surface area. Hence, the rate of reaction will remain unaffected by the addition of the photocatalyst above a certain range. This was further confirmed by taking reaction vessels of different dimensions. The point of saturation is shifted to higher side for larger vessels. A reverse trend was observed for smaller vessels, where it is shifted to lower side.

**Table 5: Effect of amount of photocatalyst**

[Sodium thiosulphate] = 0.12 M

Light intensity = 22.0 mW cm<sup>-2</sup>

pH = 6.5

Amount of photocatalyst (g)	k x 10 <sup>4</sup> (sec <sup>-1</sup> )
0.02	1.72
0.05	2.01
0.08	2.44
0.10	2.81
0.12	3.12
0.15	3.64
0.20	3.88
0.22	3.82
0.24	3.81
0.26	3.79

### Effect of light intensity

The effect of variation of light intensity on the photocatalytic oxidation of sodium thiosulphate was also investigated and the observations are given in Table 6. It was observed that an increase in the light intensity adds to the photocatalytic activity of ammonium phosphomolybdate. This may be due to the fact that more photons will be available for excitation on increasing the light intensity and in turn, more electron-hole pairs will be generated in the semiconductor. Therefore, an enhanced rate of photocatalytic oxidation was observed.





(present in solution) to give superoxide anion radical. An addition of proton to this anion radical will give rise to formation of  $\text{HO}_2^\bullet$  radicals, which in turn then oxidizes thiosulphate to sulphate ions. Hydroxyl radical may be obtained as the side product, which may accept an electron from the conduction band and a proton from the medium to give water molecules.

## REFERENCES

1. K. Tanaka, Kogyo Yosh., **332**, 2 (1986)
2. E. Petizzetti, C. Minero, E. Pramauro, M. Barbini, V. Mairina and M. Tosata, Chem. Industr., **69**, 88 (1987).
3. J. M. Herrmann, C. Gullard and P. Pichat, Catal. Today, 17 (1993).
4. Rakshit Ameta, Anil Kumar, P. B. Punjabi and Suresh C. Ameta, Advanced Oxidation Processes : Basics and Applications, in Waste Water Treatment : Advanced Technologies, Taylor & Francis, (in Press).
5. C. G. Sun, L. Tao and M. L. Fan, Catal. Lett., **129**, 26 (2009).
6. S. Das, M. Muneer and K. R. Gopal Das, J. Photochem. Photobiol., **77A**, 83 (1994).
7. Z. Ozawa and T. Sunakani, Polymer Degradation & Stability, **150**, 61 (1994)
8. R. Terzian and N. Serpone, J. Photochem. Photobiol., **89A**, 163 (1995).
9. N. Chhabra, R. Ameta, J. Verdia and S. C. Ameta, J. Indian Chem. Soc., **80**, 687 (2003).
10. K. Waki, L. X. Wang, K. Wang, K. Nohara and H. Hidada, J. Mol. Catal., **95**, 53 (1995).
11. K. Tanaka, J. Photochem. Photobiol., **85A**, 187 (1995).
12. M. S. Ahmed and Y. A. Attia, J. Non-crystalline Solids, **186**, 402 (1995).
13. A. B. Prevot, D. Fabbri and E. Pramauro, J. Photochem. Photobiol., **209A**, 224 (2010).
14. P. Denmayo, K. Muthuramu and K. W. Wun, Catal. Lett., **10**, 71 (1991).
15. A. Green and A. Mills, J. Photochem. Photobiol., **64A**, 211 (1992).
16. D. Sachdeva, B. Parashar, S. Bharadwaj, P. B. Punjabi and V. K. Sharma, Int. J. Chem. Sci., **8(2)**, 1321 (2010).
17. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3<sup>rd</sup> Ed., ELBS, London, (1961) p. 370.