

PHOTOCATALYTIC OXIDATION OF SULPHITE ION OVER AMMONIUM PHOSPHOMOLYBDATE POWDER

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ABSTRACT

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

Key words: Photocatalytic, Ammonium phosphomolybdate, Sulphite, Oxidation.

INTRODUCTION

Metallurgical industries based on pyrite ores throw a lot of sulphur containing ions in their effluents. These ions include sulphite, sulphate, thiosulphate, thionites etc. A lime treatment is commonly given to remove these ions, but only sulphate ion is removed predominantly. Rest other ions are partially removed. Then industrial effluent is filtered to remove precipitated CaSO₄. Some 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 acidic behaviour of water will make the land infertile and will not permit any crop to grow in that area. Thus, there is a pressing demand to develop alternate suitable methods to oxidize these 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.

Tanaka¹ has observed that photocatalysis is useful in either mineralizing or eliminating the polluting materials from the environment. Photocatalysis has been used by Pelizzetti et al.² for degradation of atrazine. Hermann et al.³ and Ameta et al.⁴ reported photocatalysis as an emerging technology for waste water treatment. It may also prove useful in removal and recovery for some transition metals from industrial effluents. The photocatalytic activity of titanium and cobalt oxides has been used for the degradation of methyl orange by Sun et al.⁵ Das et al.⁶ carried out photocatalytic degradation of waste water pollutants like polynuclear aromatic hydrocarbons over TiO₂ powder. Osawa and Sunakani⁷ carried out photocatalytic degradation of some polymer like polyurethane and polyvinyl chloride (PVC). Terzian and Serpone⁸ also carried out heterogeneous photocatalysed mineralization of xylenol over titanium dioxide. Chhabra et al.⁹ investigated the effect of

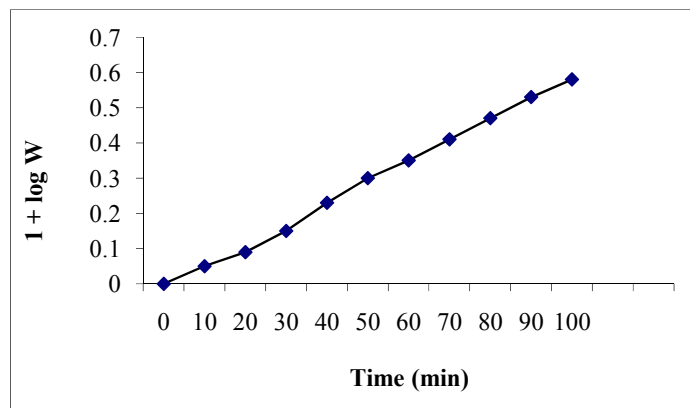


Fig. 1: A Typical run

Effect of pH

The photocatalytic oxidation of sodium sulphite is likely to be affected with a change in the pH of the medium and therefore, the rate of photocatalytic oxidation of sodium sulphite was investigated in the pH range (4.5 to 8.0). The results are reported in Table 2.

Table 2: Effect of pH

Ammonium phosphomolybdate = 0.20 g Light intensity = 50.0 mW cm⁻²
 [Sodium sulphite] = 0.22 M

| pH | k x 10 ⁴ (sec ⁻¹) |
|-----|--|
| 4.5 | 1.21 |
| 4.8 | 1.46 |
| 5.0 | 1.67 |
| 5.2 | 1.89 |
| 5.5 | 2.02 |
| 5.8 | 2.10 |
| 6.0 | 2.38 |
| 6.2 | 2.07 |
| 6.5 | 1.94 |
| 6.8 | 1.87 |
| 7.0 | 1.72 |
| 7.2 | 1.64 |
| 7.5 | 1.53 |
| 7.8 | 1.41 |
| 8.0 | 1.20 |

It has been observed that rate of photocatalytic oxidation of sodium sulphite increases with increase in pH reaching a maximum at pH = 6.0; a further increase in pH again decreases the rate of degradation. The reaction was also carried out in the presence of hydroxyl radical scavenger isopropanol and it was observed that the reaction rate is adversely affected in presence of isopropanol. It indicates that hydroxyl radical $\cdot\text{OH}$ is the active oxidising species in this case.

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 μm . As indicated from the data in the table that the rate of photocatalytic oxidation of sulphite 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.

Table 3: Effect of particle size

| Ammonium phosphomolybdate = 0.20 g Light intensity = 50.0 mW cm ⁻² [Sodium sulphite] = 0.22 M pH = 6.0 | |
|--|--------------------------------------|
| Particle size (μm) | $k \times 10^4$ (sec ⁻¹) |
| 0.8 | 2.38 |
| 1.6 | 2.05 |
| 2.4 | 1.96 |
| 3.2 | 1.84 |
| 4.0 | 1.60 |

Effect of sodium sulphite concentration

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

Table 4: Effect of sodium sulphite concentration

| Ammonium phosphomolybdate = 0.20 g Light intensity = 50.0 mW cm ⁻² pH = 6.0 | |
|--|--------------------------------------|
| [NaSO ₃] x 10 ² M | $k \times 10^4$ (sec ⁻¹) |
| 6.25 | 1.06 |
| 8.33 | 1.23 |
| 10.08 | 1.41 |
| 12.00 | 1.67 |
| 14.50 | 1.83 |
| 16.00 | 1.96 |
| 18.14 | 2.22 |
| 22.00 | 2.38 |
| 24.25 | 2.03 |
| 26.42 | 1.64 |

It is evident from the results that as the concentration of Na₂SO₃ was increased, the rate of photocatalytic oxidation of sulphite to sulphate ion increases up to [Na₂SO₃] = 0.22 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_2SO_3 increases, more SO_3^{2-} 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 sulphite, where more sulphite ions are available to hinder the movement of SO_3^{2-} 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 sulphite ion was also observed. The results are reported in Table 5. The rate of photocatalytic oxidation of sodium sulphite 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); thereafter it 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 exposed 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 sulphite] = 0.22 M Light intensity = 50.0 mW cm^{-2}
pH = 6.0

| Amount of photocatalyst (g) | k x 10 ⁴ (sec ⁻¹) |
|-----------------------------|--|
| 0.02 | 1.12 |
| 0.05 | 1.26 |
| 0.08 | 1.53 |
| 0.10 | 1.74 |
| 0.12 | 2.00 |
| 0.15 | 2.16 |
| 0.20 | 2.38 |
| 0.22 | 2.36 |
| 0.24 | 2.38 |
| 0.26 | 2.37 |

Effect of light intensity

The effect of variation of light intensity on the photocatalytic oxidation of sodium sulphite 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.

Table 6: Effect of light intensity

| Ammonium phosphomolybdate = 0.20 g | | pH = 6.0 |
|--|--|----------|
| [Sodium sulphite] = 0.22 M | | |
| Light intensity (mW cm ⁻²) | k x 10 ⁴ (sec ⁻¹) | |
| 5.0 | 1.22 | |
| 10.0 | 1.41 | |
| 20.0 | 1.62 | |
| 30.0 | 1.83 | |
| 40.0 | 2.10 | |
| 50.0 | 2.38 | |
| 60.0 | 2.72 | |
| 70.0 | 3.04 | |

Mechanism

Sulphite ions are slowly air oxidised to sulphate ions and it takes a considerable longer time. A comparative study indicated that the rate of air oxidation of SO₃²⁻ ions under ordinary conditions is quite low (3.02 x 10⁻⁷ sec⁻¹) as compared to the rate of photocatalytic oxidation of SO₃²⁻ ions, which is 2.38 x 10⁻⁴ sec⁻¹.

It has been confirmed earlier that the active oxidising species in this case is OH radical and hence, a tentative mechanism may be proposed for photocatalytic oxidation of sulphite ions to sulphate ion as follows :



The semiconductor (SC) is excited to SC* on exposure to light, which generates an electron-hole pair. The hole from the valence band is accepted by hydroxyl ions to generate hydroxyl radicals, which in turn oxidizes sulphite to sulphate ions

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