

# Treatment of Sulfide Waste In Tannery Industry By Spinel Photocatalyst

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**ABSTRACT-** *The discharge of sulfide containing wastewater from tannery industries into natural streams and rivers poses several problems. Sulfides are toxic to aquatic life, damage the environment's aesthetic nature, and are difficult to treat by conventional methods. The present work investigated the degradation of sulfide by photocatalysis using ZnFe<sub>2</sub>O<sub>4</sub> spinel catalyst. ZnFe<sub>2</sub>O<sub>4</sub> was prepared by the chemical co-precipitation method, and their surface area, morphology, crystal structure, composition, and bandgap energy were analyzed by BET, SEM, XRD, EDS, and UV-DRS. The effect of operational variables such as control conditions, catalyst dosage, pH, irradiation time, catalyst reuse, and solar light intensity was investigated. The maximum degradation of sulfide was achieved at optimum conditions of catalyst dose of 240 mg/L, pH=9.8, and irradiation time =180 min for tannery wastewater, respectively. Kinetic analyses indicated that photocatalytic degradation rate followed the first-order model.*

**Keywords:** *Sulphides, photocatalysis, ZnFe<sub>2</sub>O<sub>4</sub>, degradation*

## I. INTRODUCTION

The Leather industry is one of the oldest and fastest-growing industries in India. More than 3000 tanneries throughout the country with an annual processing capacity of 7 lakh tonnes of hides and skins. Tannery industrial processes are considered one of the most polluting industrial activities globally (Amparo Bes-Pia et al., 2011). Sulfide degradation from tannery effluents has been the target of great attention in the last few years, not only because of its toxicity but only mainly due to its aesthetic effect, even at lower concentrations, compared to many other chemicals found in wastewater (Mannucci et al. 2010). Because of sulfide's recalcitrant nature, conventional biological treatment processes are ineffective, and adsorption and coagulation practices result in secondary pollution (Sayers 1997).

The heterogeneous photocatalytic oxidation process developed in the 1970s is of special interest, especially when solar light is used. The photocatalytic degradation of sulfides is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation, electrons are promoted from the valence band to

the conduction band, and an electron-hole pair is produced (equation 1).



Where  $e^{-}\text{ cb}$  and  $h^{+}\text{ vb}$  are the electrons in the conduction band and the valence band's electron valency, both these entities can migrate to the catalyst surface, where they can enter redox reaction with other species present on the In surface.

This reaction prevents the combination of the electron and the hole produced in the first step.

OH and O<sub>2</sub><sup>•</sup> can react with the sulphides to form other species and is thus responsible for the degradation of sulphides. Among various metal oxide

photocatalyst, ZnFe<sub>2</sub>O<sub>4</sub> has proved to be the most suitable photocatalyst for treating sulfide and sulfite waste stream because of its chemical inertness, oxidizing power, non-toxicity, and long term stability against photo and chemical corrosion.

Photocatalysis using spinel photocatalyst ZnFe<sub>2</sub>O<sub>4</sub> constitutes one of the emerging technologies due to its high catalytic efficiency. Jun Chen et al. (2007) reported 92% sulphide degradation efficiency of industrial wastewater at pH=13, catalyst dose=100mg/L and contact time= 240min using spinel photocatalyst. The degradation efficiency of 90% within 180 minutes of sulfide wastewater was reported by Saadi et al.(2009) at pH=13.96, catalyst concentration=250mg/L. The degradation efficiency of 96% of sulfide and sulfite waste stream was reported by Jianhui Yan et al. (2009) at pH=8, catalyst dose=0.6g/L.

The photocatalytic activity of ZnFe<sub>2</sub>O<sub>4</sub> was reported to be higher than FeCr<sub>2</sub>O<sub>4</sub> spinel photocatalyst in the degradation of sulfide (Jun Chen et al., 2007) and sulfite (Trari et al., 2010).

Photocatalysis may be defined as the acceleration of a photoreaction by the presence of a catalyst. ZnFe<sub>2</sub>O<sub>4</sub> was used as a catalyst because of its high level of photoconductivity and low toxicity.

In this study, photocatalytic degradation of sulfide using ZnFe<sub>2</sub>O<sub>4</sub> spinel photocatalyst was investigated.

## MATERIALS AND METHODS

Zinc nitrate, Ferric nitrate, and HCl used in this study were purchased from Merck Chemical Associates, Chennai. The photocatalytic activity was carried out in a 5L photoreactor of 20cmx20cmx15cm dimensions. The photocatalytic



experiment was carried out in the reactor of 5L capacity. One liter of sulfide wastewater was used, and it was purged with nitrogen gas for 30 minutes. The sketch of the experimental set-up used in the study was shown in Fig 1. ZnFe<sub>2</sub>O<sub>4</sub> spinel was used as a catalyst. Experiments were done with an initial sulfide concentration of 168mg/L and in the absence of ZnFe<sub>2</sub>O<sub>4</sub> and sunlight individually. The effect of operating variables like catalyst dose, pH, irradiation time, dark adsorption, direct photolysis, catalyst reuse, and light intensity was studied. Degradation of sulfide was measured by the titration method. The efficiency of sulfide degradation was calculated

$$\text{Efficiency} = \frac{C_0 - C_1}{C_0} \quad (4)$$

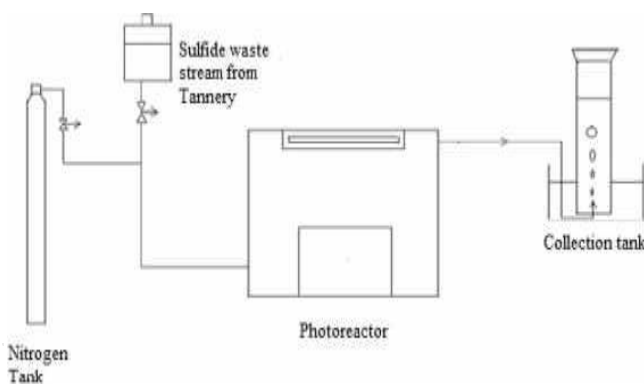
using equation 4.

Where C<sub>0</sub> is the initial sulfide concentration (mg/L) and C<sub>1</sub> is the final sulfide concentration (mg/L) at a given time.

Photooxidation can be fitted reasonably well by an exponential decay curve suggesting a pseudo-first-order reaction with respect to sulfide concentration.

The kinetic pathway of sulfide degradation is expressed by equation 5.

$$-Dc / dt = kt \quad (5)$$



**Fig 1: Experimental set-up for photocatalysis**

K is the reaction apparent rate constant l/min; and t, the exposure time (min). This equation after integration with initial condition

$$\ln = \frac{C_1}{C_0} - kt \quad (6)$$

C<sub>1</sub>=C<sub>0</sub> for t=0, leads to equation 6.

ZnFe<sub>2</sub>O<sub>4</sub> spinel powder was prepared by the co-precipitation method and characterized by SEM, UV-DRS, EDS, and XRD. The powder X-ray diffraction patterns of as-synthesized and claimed samples were recorded on a Siemens D5005 diffract meter using CuK $\alpha$  ( $\lambda=0.154\text{nm}$ ) radiation.

The diffract grams were recorded in the 2 $\theta$  range and a step time of 10s. The effect of catalyst dosage on sulfide degradation was studied in 80-400 mg/L for 180 minutes. The effect of pH on sulfide degradation for 168 mg/L of sulfide was studied at an optimum catalyst dosage of 240 mg/L for a contact time of 180 minutes. To study the effect of

## RESULTS and DISCUSSION

### Effect of control conditions

Dark adsorption experiments (ZnFe<sub>2</sub>O<sub>4</sub> dosage: 240 mg/L), photolytic experiments (absence of ZnFe<sub>2</sub>O<sub>4</sub>) were conducted for a tannery wastewater sample of 168 mg/L of sulfide concentration at the actual pH for 180 minutes. No significant degradation was observed in dark adsorption and photolytic conditions (Fig. 2)

### Effect of catalyst dosage

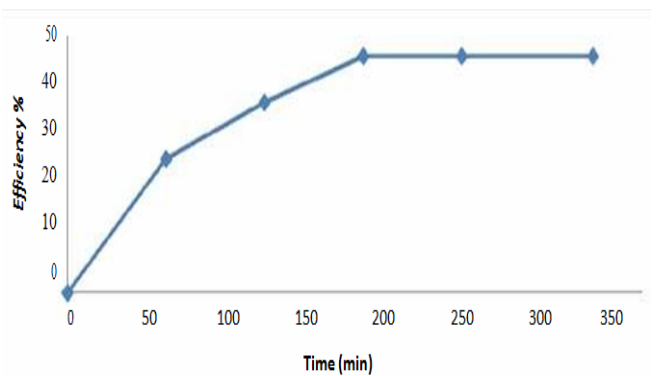
Maximum sulfide degradation was achieved for a catalyst dosage of 240 mg/L for tannery wastewater sample (Fig. 3)

### Effect of pH

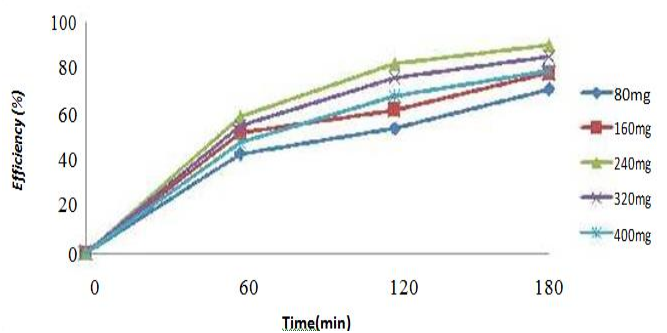
Fig.4 shows the effect of pH on sulfide degradation for sulfide wastewater samples. The maximum sulfide degradation efficiency of the sulfide wastewater sample was observed at pH 9.8.

### Effect of contact time

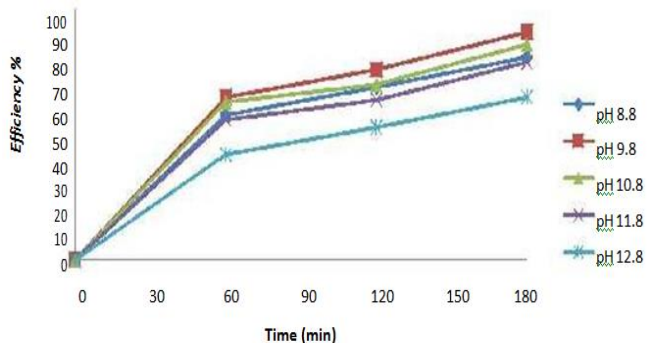
Fig. 5 shows the effect of irradiation time on



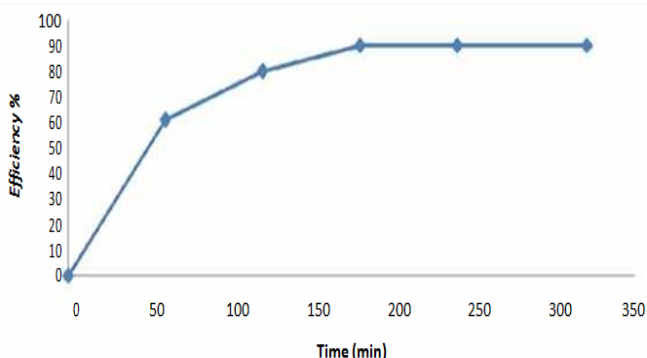
**Fig.2: Effect of control conditions on sulfide degradation**



**Fig.3: Effect of catalyst dosage on sulfide degradation**



**Fig.4: Effect of pH on sulfide degradation**

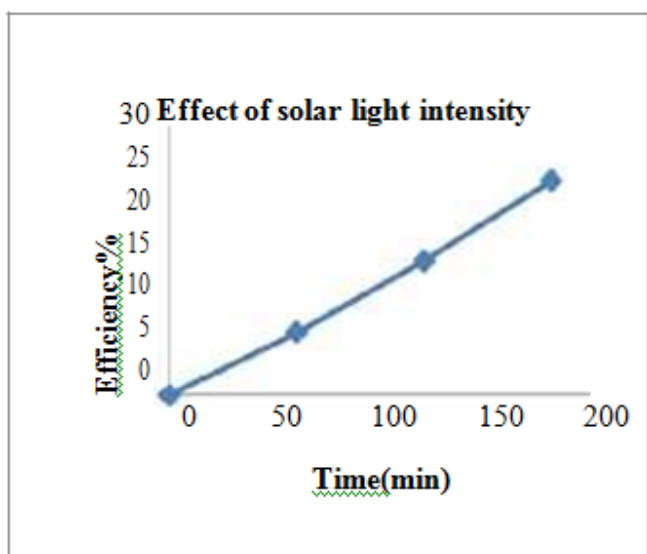


**Fig.5: Effect of irradiation time on sulfide degradation**

sulfide degradation for sulfide wastewater sample. Maximum sulfide degradation was achieved for a contact time of 180 minutes at optimum conditions of pH and catalyst dosage.

Effect of solar light intensity

The results of the effect of solar light intensity are shown in Fig.6. With the increase in solar UV light for wastewater samples, maximum sulfide degradation of 26% occurred.



**Fig.6: Effect of solar light intensity**

**CONCLUSION**

This study has shown that the spinel photocatalyst ZnFe<sub>2</sub>O<sub>4</sub> was very effective in the degradation of sulfide. The negligible effect of dark adsorption indicated that the reaction followed the photocatalytic process, and it is reported that the photocatalytic process does not need to occur at the catalyst surface based on the assumption that the reactive hydroxyl radicals and other oxidizing species could diffuse into solution bulk to react with organic pollutants (Arsalan et al., 2001)

The dosage of ZnFe<sub>2</sub>O<sub>4</sub> plays an important role in the photocatalytic degradation of sulfide. The increase in catalyst dosage beyond the optimum level (240 mg/L) decreases sulfides due to an increase of turbidity, reducing the light transmission through the solution. Similar findings have been reported in the treatment of sulfide (Saadi et al., 2005), sulfite, and sulfide wastewaters (Jimmy Bangun et al., 1998 ).

The effect of pH on the photocatalytic degradation process is still very much unresolved. In the present study, the percentage of degradation increased with an increase in pH in the alkaline conditions and then decreased beyond the optimum level. Similar findings were observed in the treatment of tannery effluent (Theodora Papadom et al., 2007), and sulfide solution (Linkous et al., 2005), and also in acid orange 20 (Ioannis poulios et al., 2007). It was observed that the rate of degradation increased with an increase in pH. Beyond the optimum pH level, the rate of

degradation gets reduced due to  $e^-/h^+$  recombination. Similar findings were observed in the treatment of sulfide solution using FeC<sub>2</sub>O<sub>4</sub> as the catalyst at optimum pH of 11. Theodora papadom (2007) also made a similar observation in treating tannery effluent using TiO<sub>2</sub> as the catalyst. No photo activity has been observed below pH7 and this indicates that the free S<sup>2-</sup> ions are determining species. The photoactivity was the peak at pH 9 and decreased with decreasing pH. As the pH decreases, the mixture is protonated and the proportion of the positively charged surface increases. The catalyst surface becomes negatively charged, thus preventing the negatively charged hydroxide anion from adsorbing onto the surface and reducing degradation. A similar observation on the effect of pH on the photocatalytic reaction has been reported for degradation of acid orange 20 using TiO<sub>2</sub> as catalyst (Ioannis Poullos et al. 2007).

In general, the photocatalytic process is observed to be a function of light intensity. In the present study, it was observed that the increase in the intensity of solar UV light increased the efficiency of sulfide degradation. In the photocatalytic degradation of sulfide using TiO<sub>2</sub>, Kansal et al. (2008) have also observed a significant increase in reaction rate as the flux increased. In the photocatalytic degradation of dichloroacetic acid (DCA) in a solar pilot plant, the rate was linear concerning light intensity (0-40

W/m<sup>2</sup>) under similar experimental conditions. The results suggest that solar light irradiation could be a feasible technique for reducing sulfide wastewater and could be a cost-effective technique for industrial-scale application.

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