Photocatalytic Degradation Studies of Textile Industrial Effluent Using Nano Tungstate

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ABSTRACT

Untreated dye effluents from the textile industries and other industries such as paper, paint etc., poses a serious threat to the environment which creates enormous health hazards to the living beings. Tremendous efforts are been made by the researchers for an amicable solution for this serious issue. Semiconductor based photocatalysis has emerged as a prominent technology for decolorization of dye pollutants due to appreciable photocatalytic properties, especially binary semiconductor oxides such as ZnO, TiO₂, Cu₂O etc. However, further quest in enhancing the catalytic properties led to exploration of the ternary oxides. Therein, in this project, we have prepared nanostructured ternary tungstate i.e FeWO₄ by hydrothermal method with help of hydrazine hydrate as mineralizing agent. The prepared compound was characterized by Power-X-ray diffraction for structural analysis and Scanning electron microscope (SEM) for morphology and size analysis. The characterizations revealed pure nanocrystalline FeWO₄ was formed. Photocatalytic studies using prepared FeWO₄ were carried for Methylene Blue (MB) as model dye pollutant and the results were summarized. 

Index terms : Textile effluent, Nano tungstate FeWO₄, Scanning electron microscope, Model dye Methylene blue.

1. INTRODUCTION

1.1 WATER POLLUTION BY TEXTILE INDUSTRIES

Color the earth beautiful and kill it with sweet poison!! The art of color application to enhance our self appearance and the world around us has been known to man since time immemorial. Historical records of the use of natural dyes extracted from vegetables, fruits, flowers, certain insects and fish dating back to 3500 BC have been found. Color is the main attraction of any fabric. No matter how excellent its constitution, if unsuitably colored it is bound to be a failure as a commercial product. Fabric was earlier being dyed with natural dyes. These however gave a limited and a dull range of colors. Besides, they showed low color fastness when exposed to washing and sunlight. As a result they needed a mordant to form a dye complex to fix the fiber and dye together thus making the dyers' work tedious. The discovery of synthetic dyes by W. H. Perkins in 1856 has provided a wide range of dyes that are color fast and come in a wider color range and brighter shades. As a result “dye application” has become a massive industry today.

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1.2 CAUSES OF WATER POLLUTION BY TEXTILE INDUSTRIES
The industry is using more than 8000 chemicals. Many of these chemicals are poisonous and damaging to human health directly or indirectly. Large quantities of water are required for textile processing, dyeing and printing. The daily water consumption of an average sized textile mill having a production of about 8000 kg of fabric per day is about 1.6 million liters. 16% of this is consumed in dyeing and 8% in printing. Specific water consumption for dyeing varies from 30 - 50 liters per kg of cloth depending on the type of dye used. The overall water consumption of yarn dyeing is about 60 liters per kg of yarn. Dyeing section contributes to 15% - 20% of the total waste water. It takes about 500 gallons of water to produce enough fabric to cover one sofa. The World Bank estimates that 17 to 20 percent of industrial water pollution comes from textile dyeing and finishing treatment given to fabric. Some 72 toxic chemicals have been identified in water solely from textile dyeing, 30 of which cannot be removed. This represents an appalling environmental problem for the clothing and textile manufacturers.

1.3 EFFECT OF WATER POLLUTION
Textile effluent is a cause of significant amount of environmental degradation and human illnesses. About 40 percent of globally used colorants contain organically bound chlorine a known carcinogen. All the organic materials present in the wastewater from a textile industry are of great concern in water treatment because they react with many disinfectants especially chlorine. Chemicals evaporate into the air we breathe or are absorbed through our skin and show up as allergic reactions and may cause harm to children even before birth.

1.4 TREATMENT OF EFFLUENT FROM TEXTILE INDUSTRY
Effluent treatment methods can be classified into physical, chemical and biological methods; (Table 1.2). Exclusive treatment by one of these three methods has proved to be insufficient in removing color and other effluent from textile industry wastewater. While some dyes are difficult to biodegrade few, particularly the hydrolyzed reactive and certain acidic dyes are not readily absorbed by active sludge; hence they escape treatment. Combination of various effluent treatment methods can remove more than 85% of unwanted matter.

<table>
<thead>
<tr>
<th>Physical</th>
<th>Chemical</th>
<th>Biological</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedimentation</td>
<td>Neutralization</td>
<td>Stabilization</td>
</tr>
<tr>
<td>Filtration</td>
<td>Reduction</td>
<td>Aerated Lagoons</td>
</tr>
<tr>
<td>Floatation</td>
<td>Oxidation</td>
<td>Trickling Filters</td>
</tr>
<tr>
<td>Foam Fractionation</td>
<td>Catalysis</td>
<td>Activated Sludge</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Ion Exchange</td>
<td>Anerobic Digestion</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>Electrolysis</td>
<td>Fungal Treatment</td>
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<tr>
<td>Solvent Extraction</td>
<td>-</td>
<td>Flocculation</td>
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<tr>
<td>Ionization Radiation</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Adsorption</td>
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<td>Incineration</td>
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<td>Distillation</td>
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<td>-</td>
</tr>
<tr>
<td>Membrane Treatment</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1.5 PHOTOCATALYST METHOD
Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals: •OH) able to undergo secondary reactions. Its practical application was made possible by the discover of water electrolysis by means of titanium dioxide (TiO₂).

1.5.1 MECHANISM OF PHOTOCATALYSIS
When photo catalyst Iron Tungstate (FeWO₄) absorb ultraviolet radiation from sunlight or illuminate light source, it will produce pair of electron and hole. The electron of the valence band of fewo₄ become excited when illuminated by light. The excess energy of this excited electron promoted the electron to the conduction band of the FeWO₄ therefore creating the negative electron (e−) and positive hole (h+) pair. This stage is referred as the semiconductor’s photo-excitation state. The energy difference between the valence band and the conduction band is known as the band gap. The positive hole of FeWO₄ break apart the water molecule to form hydrogen gas and
hydroxyl radical. The negative electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. Wavelength of the light necessary for photo-excitation is \( \frac{1240}{3.3} \text{ev} = 375.7\text{nm} \)

### 1.6 FeWO\(_4\) STRUCTURE

- **Phase Label(s):** WFeO\(_4\)
- **Classification by Properties:** antiferromagnet AFM
- **Mineral Name(s):** ferberite
- **Pearson Symbol:** \( mP12 \)
- **Space Group:** 13
- **Phase Prototype:** MgWO\(_4\)

#### 1.6.1 CHARACTERISTIC OF FEWO\(_4\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Color</strong></td>
<td>Black, dark brown in transmitted</td>
</tr>
<tr>
<td><strong>Crystal habit</strong></td>
<td>Bladed crystals; massive</td>
</tr>
<tr>
<td><strong>Twinning</strong></td>
<td>Contact or interpenetrant or</td>
</tr>
<tr>
<td><strong>Cleavage</strong></td>
<td>Perfect on {010}; partings on</td>
</tr>
<tr>
<td><strong>Fracture</strong></td>
<td>Uneven</td>
</tr>
<tr>
<td><strong>Tenacity</strong></td>
<td>Brittle</td>
</tr>
<tr>
<td><strong>Mohs</strong></td>
<td>4–4.5</td>
</tr>
<tr>
<td><strong>Luster</strong></td>
<td>Submetallic to metallic</td>
</tr>
<tr>
<td><strong>Streak</strong></td>
<td>Brownish black</td>
</tr>
<tr>
<td><strong>Diaphaneity</strong></td>
<td>Nearly to entirely opaque</td>
</tr>
<tr>
<td><strong>Specific gravity</strong></td>
<td>7.58</td>
</tr>
</tbody>
</table>

#### Optical properties
- Biaxial (+)

#### Refractive index
- \( n_\alpha = 2.255 \)
- \( n_\beta = 2.305 \)
- \( n_\gamma = 2.414 \)

#### Birefringence
- \( \delta = 0.159 \)

#### 2V angle
- Measured: 66°

#### Other
- Slightly magnetic

### 1.7 PREPARATION OF NANO CATALYST

Following are the chemical methods widely used to prepare nano catalyst.

1. chemical precipitation.
2. Sol-Gel Technique
3. hydrothermal synthesis.

### 1.8 Hydrothermal synthesis

It includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows if a steel tube is used. There are autoclaves made out of thick walled glass, which can be used up to 300°C and 10 bar.
1.9 PROPERTIES OF NANOMATERIALS

1.9.1 Physical Properties of Nanomaterials.

1. Nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably reduced lattice constants, due to a huge fraction of surface atoms in the total amount of atoms.

2. Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form.

3. Optical properties of nanomaterials can be significantly different from bulk crystals. For example, the optical absorption peak of a semiconductor nanoparticle shifts to a short wavelength, due to an increased band gap.

4. Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, electrical conductivity of nanomaterials could also be enhanced appreciably, due to the better ordering in microstructure, e.g. in polymeric fibrils.

1.9.2 Chemical properties of nanomaterials.

1. The preponderance of surface is a major reason for the change in behaviour of materials at the nanoscale. As up to half of all the atoms in nanoparticles are surface atoms, properties such as electrical transport are no longer determined by solid-state bulk phenomenon.

2. The atoms in nanomaterials have a higher average energy than atoms in longer structures, because of the larger proportion of surface atoms. For example, catalytic materials have a greater chemical activity per atom of exposed surface as the catalyst is reduced in size at the nanoscale.

3. Defects and impurities may be attracted to surfaces and interfaces, and interactions between particles at those small dimensions can depend on the structure and nature of chemical bonding at the surface.

4. Molecular monolayers may be used to change or control surface properties and to mediate the interaction between nanoparticles.

2. INSTRUMENTATION:

2.1 Structural characterization - Powder X-Ray Diffraction

The crystallographic nature of a sample very well influences its electrical and optical properties. X-ray
diffraction (XRD) studies are generally used for structural analysis. The advantage of the technique is that it discloses the presence of a substance, as that substance actually exists in the sample and not in terms of its constituent chemical elements. Hence, diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis the diffraction method has the advantage that it is usually much faster, requires only very small quantity of sample and is non-destructive.

In the present study X-ray diffraction analyses were performed using a Philips X’Pert vertical goniometer with Bragg–Brentano geometry. Nickel-filtered Cu Kα radiation and a step-by-step technique were employed (steps of 0.05° 2θ), with collection times of 10s/step. The size of the crystallites was evaluated by Scherer method.

2.2 Morphological analysis - Scanning Electron Microscope (SEM)
Surface morphology and particle size plays a vital role on properties; the characterization tools used to study about the surface of the prepared TCO material is described below.

3. EXPERIMENTAL WORK
3.1 Preparation of FeWO₄ by hydrothermal method with support of hydrazine hydrate
0.1 M of Na₂WO₄, 3H₂O and FeCl₂ solutions were prepared using double distilled water. 20 ml of the each stock solution was mixed along with 20 ml of Hydrazine hydrate. The mixed solution was taken in 80ml Teflon lined hydrothermal bomb. The hydrothermal bomb was heated to 170 °C for 6 hrs in the muffle furnace.

Pictorial image- illustrate the preparation of FeWO₄

3.2 Photocatalytic studies
Photocatalytic activity for the prepared FeWO₄ was carried out in the open space expose to sunlight for Methylene Blue (MB) as a model dye pollutant. In this experiment, 25 mg of FeWO₄ was suspended in 250ml of 25 ppm Methylene Blue solution. The suspension was magnetically stirred in the dark for 30 min to attain adsorption-desorption equilibrium.
Then the suspension was placed in the sun light. During photocatalysis process approximately 5 ml of dye solution was withdrawn at regular irradiation interval of time. And quantified the MB dye in the solution by recording the absorbance using the UV-vis spectrophotometer.

The efficiency of the CFO catalyst degrading the MB dye under UV irradiation was calculated using the equation:

\[
\% \text{ Degradation} = \frac{(C_0 - C_t)}{C_0} \times 100, \text{ Where, } C_0 = \text{initial absorbance and } C_t = \text{absorbance at time ‘t’}.
\]

3.3 Photo-Fenton studies

Photo-Fenton studies were done to have increased dye degradation. In this experiment, 25 mg of FeWO₄ was mixed with 2ml of H₂O₂ and the mixture was suspended in 250ml of 25 ppm Methylene Blue solution. The suspension was magnetically stirred in the dark for 30 min to attain adsorption-desorption equilibrium. Then the suspension was placed in the sun light. During photocatalysis process approximately 5 ml of dye solution was withdrawn at regular irradiation interval of time. And quantified the MB dye in the solution by recording the absorbance using the UV-vis spectrophotometer and percentage of degradation was calculated.

3.3.1 Powder X-Ray diffraction

Prepared compound was characterized by Powder – X-ray diffraction to study the phase of the compound. XRD was recorded using BRUKER D2 Phaser with Cu Kα radiation (\(\lambda=0.15418\) nm). Figure shows the recorded XRD pattern of the hydrothermal method prepared FeWO₄ compound. The red line are the diffraction pattern of the standard data (International Centre for Diffraction Data - card No. 71-2390) of the FeWO₄ and the blue lines are the XRD data of the recorded pattern.

![XRD pattern](image)

XRD pattern of hydrothermal method prepared FeWO₄.

Recorded XRD pattern well match with the standard data which confirms pure FeWO₄ formed. Crystallite size for the prepared compound of Copper iron oxide and Copper Chromium oxides were calculated using Scherrer equation, Crystallite size = \(0.9 \lambda / B \cos \theta\) Where B – Full width half maximum of the peak, \(\theta\) is the angle of the diffracted peak. Crystallite sizes were calculated as 70 – 90 nm.

4. RESULTS AND DISCUSSIONS:

4.1 Powder X-Ray diffraction

Prepared compound was characterized by Powder – X-ray diffraction to study the phase of the
4.2 Morphological studies - Scanning Electron Microscope

Scanning electron micrograph of the FeWO₄ the SEM micrograms of prepared FeWO₄. The particles were crystallized in rod shape morphology of the length and breadth in the range of 1 - 2 μm and 200 – 300 nm. respectively.

4.3 Photocatalytic activity

The MB solution drawn at different time during the photo- Fenton studies of FeWO₄ in the exposure of visible light. The picture clearly shows the decrease in the colour of the dye.

Time-dependent UV–Visible absorption spectra for the photodegradation of MB in the presence of FeWO₄ catalyst

Time-dependent UV–Visible absorption spectra for the photodegradation of MB in the presence of H₂O₂ & FeWO₄ (Fenton)

MB degradation results in the presence of FeWO₄ and H₂O₂ - FeWO₄ (Fenton studies) respectively. The intensity of MB absorption peak at 662 nm wavelength is observed significantly decreased with increase in the visible light illumination time with the presence of the FeWO₄ catalyst and FeWO₄ plus H₂O₂ (Fenton). The concentration of the dye at different time is proportional to the absorbance of the dye solution. Therefore, exponential nature of absorbance vs. time (C/Co vs. t) plot confirms the first order kinetics of the reaction.

Plots of C/Co versus irradiation time for the photo degradation of Methylene Blue

Dye degradation reaction was also carried out in the dark condition in the presence of catalysts which observed that there is no marginal change in the concentration of MB dye even after 30 min.
4.4 Mechanism of Photocatalysis

The justifiable photocatalytic degradation mechanism of MB as a model dye mediated by FeWO4 is explained below. The illumination of visible light on FeWO4 having greater energy than the band gap of FeWO4 generates the electron – hole pair i.e electrons in the conduction band (eCB- ) and holes (hVB+) in the valence band. Holes (hVB+) in the valence band could form the reactive hydroxyl radical (OH) while oxygen produces the superoxide radical by accepting an electron. These free radicals possess high chemical activity. The MB dye is decomposed through oxidation by OH radical and O. -2 radicals.

\[
\text{FeWO}_4 + h\nu \rightarrow \text{eCB}^- + \text{hVB}^+ \\
\text{hVB}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \cdot \text{OH} \\
\text{eCB}^- + \text{O}_2 \rightarrow \text{O}^- -2 \\
\text{O}^- + \cdot \text{OH} + \text{MB} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

4.5 Mechanism of Photo-Fenton studies

Fe²⁺ present in the FeWO₄ is oxidized by hydrogen peroxide to iron(III), forming a hydroxyl radical and a hydroxide ion in the process. Iron(III) is then reduced back to iron(II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical and a proton.

The net effect is a disproportionate of hydrogen peroxide to create two different oxygen-radical species, with water (H⁺ + OH⁻) as a byproduct. These free radicals possess high chemical activity. The MB dye is decomposed through oxidation by OH radical and O. -2 radicals.

\[
\text{Fe}^{2+} (\text{FeWO}_4) + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{HO}^- + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} (\text{FeWO}_4) + \cdot \text{HOO}^- + \text{H}^+ \\
\cdot \text{OH} + \text{MB} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

5. CONCLUSION

We have prepared pure nanocrystalline FeWO₄ catalyst by hydrothermal method using hydrazine hydrate as mineralizing agent. The prepared compound was characterized by powder X-ray diffraction and Scanning electron microscope for structural and morphological analysis. Photocatalytic dye degradation and Photo-Fenton studies were carried using prepared FeWO₄ catalyst to assay the catalytic effect. Photo-Fenton studies shown effective degradation of methylene Blue dye due to more number of hydroxyl radicals in created in the

6. REFERENCES


