Photomineralization of Methyl Orange and Phenol by Peroxymonosulfate Activated Heterogeneous of CoFe$_2$O$_4$ Ferrite: A Comparative Study

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Abstract: CoFe$_2$O$_4$ sample was prepared by sol-gel combustion method. The prepared samples were characterized by powder X-ray diffraction (PXRD), UV-Vis absorbance spectra, Fourier Transform Infrared spectroscopy (FTIR). CoFe$_2$O$_4$ was utilized as a photo catalyst under visible light irradiation. Further studies showed that CoFe$_2$O$_4$ has a higher catalytic function in the presence of peroxymonosulphate (PMS), in presence of CoFe$_2$O$_4$ capable of catalyzing the degradation of Methyl orange (MO) and phenol. Higher photocatalytic activity shown at pH 7 compared to pH 3 and 10 respectively. Photocatalytic reaction mechanism was investigated by analyzing the data obtained.

Keywords: Spinel structure, Photocatalysis, semiconductor, Adsorption, Peroxy monosulphate.

1. Introduction

Semiconductor photo catalysis has been widely used for the treatment of polluted water. There have been many reports that various organic pollutants can be degraded completely through photo catalysis using metal oxide semiconductors or their hetero-architectures under ultraviolet light irradiation [1]-[3]. Ferrites are viable alternative materials to TiO$_2$ to be used as photo catalysts for hydrogen production; transition metal ferrites have a number of advantages, mainly emphasizing their low cost, effective catalytic activity, corrosion resistance and most importantly their wide band gap into the visible light spectrum. Among various semiconducting materials CoFe$_2$O$_4$ ferrite is a class of semiconductors with narrow band gap, good photochemical stability, favourable magnetic property and exhibits characteristic visible-light response [4]-[6]. Spinels with only divalent ions in tetrahedral sites are called normal, while compounds with the divalent ions in the octahedral sites are called inverse. In the inverse spinel structure, all the Co$^{2+}$ ions occupy the octahedral sites of lattice structure, half of the Fe$^{3+}$ ions also occupy the same sites and the rest of the Fe$^{3+}$ ions stay in tetrahedral sites [7]. The ferrite spinel structure is based on a closed-packed oxygen lattice, in which tetrahedral (called A sites) and octahedral (called B sites) interstices are occupied by the cations. The selection of these materials is based on the redox activity and especially their ability to store oxygen in its crystalline lattice. Ferrites have a tendency when burned under reducing atmospheres to form compounds with oxygen defects, which facilitates the fixation of oxygen in the existing vacancies. Therefore, these materials are excellent candidates for the production of hydrogen from water under solar illumination. It is well known that bivalent cation (Co$^{2+}$) and trivalent ferric ion (Fe$^{3+}$) can distribute at both tetrahedral and octahedral sites and this type of cationic distribution affects the magnetic properties of spinel ferrite [8],[9]. The presence of CoFe$_2$O$_4$ magnetic nanoparticles enhances the efficiency of the degradation of organic contaminants and can be easily separated magnetically. The main goal of this work is to synthesis of CoFe$_2$O$_4$ by solution sol-gel combustion route method and to probe its photocatalytic activity under visible light irradiation.

2. Experimental

A. Materials

The Methyl Orange (MO) dye and phenol was obtained from Sigma Aldrich. Ferrous sulfate, cobalt sulfate and ethanol were supplied from Nice chemicals. Oxone (2KHSO$_5$ KHSO$_4$·K$_2$SO$_4$) was obtained by Avra synthesis Pvt. Ltd. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were from Sisco-chemical industries. All chemicals were analytic grade reagents and used without further purification. Double distilled water was used in all the experiments.

B. Synthesis of CoFe$_2$O$_4$ by sol gel route combustion method

Ferrite compound of the type CoFe$_2$O$_4$ were synthesized by the sol–gel auto-combustion reaction method. The analytical grade Fe(NO)$_3$·9H$_2$O, Co(NO)$_3$9H$_2$O and citric acid (C$_6$H$_8$O$_7$·H$_2$O) were used as raw materials. The stoichiometric amount of nitrates and citric acid was first dissolved in distilled water to form a clear solution. The molar ratio of nitrates to citric acid was 1: 1. The solution was evaporated by stirring and heating for 4 hours at 70 °C further, heated to 90 °C until turned into a gel. Finally, the product was calcined in a furnace for 2 hours at 800°C.
C. Catalyst characterization

The powder X-ray diffraction (PXRD) patterns were recorded using Bruker D8 Advanced diffractometer, which was operated at 30 kV and 20 mA using Cu Kα with nickel filter. The scan rate was varied from 2° to 0.5°/min to get X-ray diffraction line broadening. The Fourier transform infra-red (FTIR) spectra were obtained using Bruker model Alpha–IR spectrometer with diamond ATR cell. The absorbance spectra were obtained using UV–vis absorbance spectra were recorded in the wavelength range of 200 to 800 nm (Schimadzu-UV 3101 PC UV–Vis-NIR) with BaSO₄ as the reference standard.

D. Photochemical reactor

The detail pertaining to photocatalytic degradation experiments are given elsewhere [10]

3. Results and Discussion

A. PXRD studies

PXRD pattern of CoFe₂O₄ particle with diffraction peaks of CoFe₂O₄ are shown in the Figure 1. The PXRD pattern of CoFe₂O₄ shows peaks at 18.35° (111), 30.15° (220), 35.35° (311), 37.42° (222), 43.33° (400), 54.97° (422), 57.36° (511), 62.93° (440) 71.41° (622) 74.53° (533) and in accordance with spinel structure with space group fd-3m which is in agreement with JCPDS standard card (22-1086). The average crystallite size was calculated highest base peak at (311) by using the Scherrer’s equation, crystallite size of CoFe₂O₄ was found to be 50.52nm.

B. UV-visible spectroscopy

UV-Visible spectra of CoFe₂O₄ exhibits wide band gap in the range of 350-800 nm. The absorbance range extends from UV light to solar light region explains the photocatalytic efficiency of these materials under solar light has shown in Figure 2 [11-14]. The band gap values were determined from these spectra by converting the absolute absorption values to Kubelka-Munk function \( F(R) \) versus photon energy in electron volts (eV). The plot of Kubelka Munk function \( [F(R)hv]^{1/2} \) versus photon energy in electron volts (eV). The band gap of CoFe₂O₄ calculated and was found to be 1.68eV. The d-d transitions that the metal having d-electrons to transfer between t₂g to e_g (Oh) or e_g to t₂g (td), these spectra clearly show that values of the energy of the forbidden band are within the visible light spectrum. Electronic configuration Co²⁺ having unpaired d-electrons and these unpaired electrons are excited under illumination of light.

C. FTIR

FTIR spectra of CoFe₂O₄, the peak at 577 cm⁻¹ corresponds to the intrinsic stretching vibrations of both at tetrahedral (Co-O) and octahedral group (Fe-O). This confirms presence of characteristic peak of spinel structure as shown in the Figure 3.

D. BET

The specific surface area and pore volume of CoFe₂O₄ sample were determined by BET method as shown in Figure.
The pore size distribution is 1.3-6 nm, specific surface area and total pore volume were found to be 6.202 m² g⁻¹ and 0.0031ccg⁻¹ as shown in the Figure 4. BET surface area CoFe₂O₄ photocatalyst provides a larger adsorption site on the catalyst surface for phenol and MV thereby shows photocatalytic activity.

E. XPS

![XPS Spectrum](image)

Fig. 5. XPS of CoFe₂O₄ showing A) Co 2p, B) Fe 2p and C) O1s peaks

XPS spectrum Co2p in CoFe₂O₄ shows two major peaks with binding energy values at 795.79, 788.18 and 780.95eV, corresponding to the Co2p₁/₂ and Co2p₃/₂ spin-orbit peaks respectively of the Co-O phase. The Fe2p₁/₂ and Fe2p₃/₂ states were observed in the 710.89 and 724.72eV. The peak in the range of 710-711 eV is attributed to the Fe³⁺ cation located at the octahedral site in the spinal structure. The peak range of 724.72 is endorsed to the Fe²⁺ cation located at the tetrahedral site in the spinal structure. The O1s spectrum shows the existence of oxygen with binding energies at 530.95eV that can be assigning to the lattice-oxygen and the oxygen-deficient regions respectively. The peak observed close to 532.04eV of CoFe₂O₄ of O1s spectra indicate the presence of –OH species adsorbed on the surface to the sample (Figure 5). These results indicates that the presence of chemical composition of CoFe₂O₄.

F. Adsorption MO and Phenol

Photocatalytic properties have been dependent on the adsorption and transportation of electron-hole pairs [15]-[18]. Adsorption of MO and phenol was studied by using 100mg CoFe₂O₄ catalyst at room temperature in the dark. The effect of CoFe₂O₄ concentration on the adsorption capacity as shown in Figure 6a and 6b adsorption behaviour of MO and phenol on catalyst follow Langmuir model. Phenol uptake capacity in presence of CoFe₂O₄ slightly increases compared to MO. The adsorbed quantities MO and phenol qᵢ (mg/g catalyst), at time t are calculated according to Equation.

\[ q_t = \frac{C_o - C_t}{W_{catalyst}} \times 1000 \times M_w \times V_o \]

Where, \( C_o \) and \( C_t \) (ml/L) are the initial concentrations and concentration at time t of MO respectively, \( M_w \) molecular weight of MO (g/mol), \( V_o \) is the volume of aqueous dye solution (ml) and \( W_{catalyst} \) is the mass of the catalyst (g).

![Graphs](image)

Fig. 6(a). Effect of CoFe₂O₄ on MO adsorptivity

Fig. 6(b). Effect of CoFe₂O₄ on phenol adsorptivity
In present work, evaluated by using experimental data from linear transform \( t/q_e = f(t) \) in Figure 7a and 7b. Hence, adsorption capacities at equilibrium \( q_e \) at time \( t \) are calculated from the slope and adsorption rate constant \( k_{ads} \) values are calculated intercept of the plot and as shown in the Table 1. The amount of phenol is best adsorptivity than MO.

![Fig. 7(a). Pseudo- second –order kinetic plot of MO removal](image)

![Fig. 7(b). Pseudo- second –order kinetic plot of phenol removal](image)

### Table 1

<table>
<thead>
<tr>
<th>Photo catalyst</th>
<th>Pollutants</th>
<th>( q_e (\text{mg/g catalyst}) )</th>
<th>( k_{ads} (\text{g/mg min}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe(_2)O(_4)</td>
<td>MO</td>
<td>68.96</td>
<td>0.0145</td>
</tr>
<tr>
<td>CoFe(_3)O(_4)</td>
<td>Phenol</td>
<td>207.46</td>
<td>1.0496</td>
</tr>
</tbody>
</table>

### G. Photocatalytic Mechanism

CoFe\(_2\)O\(_4\) particles under solar light illumination generates the holes and electrons, water molecules ionizes to hydroxide ion, oxygen molecule traps the electrons form super oxide radical, transfer of holes to surface hydroxyl ion produce hydroxyl free radicals.

\[
\begin{align*}
\text{MO} + h_v &\rightarrow \text{MO}^+ \quad \text{(2)} \\
\text{O} &\rightarrow \text{O}^- \quad \text{(3)} \\
\text{H}_2\text{O} &\rightarrow \text{H}^+ + \text{OH} \quad \text{(4)} \\
\text{OH}^- + \text{O}_2^- &\rightarrow \text{O}_2 \quad \text{(5)} \\
\text{MO} + \text{OH}^- &\rightarrow \text{MO}^+ + \text{OH}^- \quad \text{(6)}
\end{align*}
\]

Photocatalytic activity of CoFe\(_2\)O\(_4\) under visible light illumination for photomineralization of MO and phenol, CoFe\(_2\)O\(_4\) alone shows photocatalytic activity, the presence of oxidant like PMS enhance the activity. Further activity explored by varying pH parameter viz., 3, 7 and 10. Cobalt (II) ions serves as Lewis acid and capture H\(_2\)O to from activated hydroxyl radicals on the surface of CoFe\(_2\)O\(_4\) and HSO\(_4^-\) bonded in the form of CoFe\(_2\)O\(_4\)-OH- HS\(_2\)O\(_3\) through hydrogen bonds. The Co\(^{2+}\) ions transfer electron to break bond the O-H and O-O bonds and oxidized to Co\(^{3+}\) with the generation of sulphate radicals

\[
\text{Co}^{2+} + \text{HSO}_4^- \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} + \text{OH}^- 
\]

### Effect of pH 3 on MO and Phenol

At pH 3, in presence of CoFe\(_2\)O\(_4\) (100mg), the degradation of MO takes place around 160 min. Further addition of PMS (Co\(^{2+}\)/PMS) activity increases (140min) certain extent. In case of phenol, decomposition takes place around 100min, when the addition of PMS activity increases (80min) as shown in the Figure 8 and Table 2. MO exist as high acidic conditions and it behaves positively charged at this pH, acquires positive charge which gets less adsorbed and in turn less degraded by the positively charged catalyst surface due to columnic repulsion. At pH 3 phenol exist as its protonated form and it is slightly acidic in nature when compared to MO, phenol also acquires positive charge which gets more adsorbed thereby minimum columnic repulsion takes place and slightly high photocatalytic activity compared to MO.

### Table 2

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Pollutants</th>
<th>PMS concentration (ppm)</th>
<th>Rate constant ( \times 10^2 ) min(^{-1})</th>
<th>Degradation time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe(_2)O(_4)</td>
<td>MO</td>
<td>-</td>
<td>2.2447</td>
<td>160</td>
</tr>
<tr>
<td>CoFe(_3)O(_4)</td>
<td>MO</td>
<td>10</td>
<td>2.9529</td>
<td>140</td>
</tr>
<tr>
<td>CoFe(_2)O(_4)</td>
<td>Phenol</td>
<td>-</td>
<td>3.4977</td>
<td>100</td>
</tr>
<tr>
<td>CoFe(_3)O(_4)</td>
<td>Phenol</td>
<td>10</td>
<td>4.7772</td>
<td>80</td>
</tr>
</tbody>
</table>

### Effect of pH 7 on MO and Phenol

At pH 7, MO and Phenol undergoes decomposition in presence of CoFe\(_2\)O\(_4\), further addition of PMS activity increases and undergoes complete degradation. At neutral pH MO solution has below PZC, MO anions are readily adsorbed onto the catalyst surface via columnic interaction. Phenol exists in its ionic-form with minimum water solubility and adsorption onto photocatalyst is enhanced hence increased degradation rate.
than MO as shown in the Figure 9.

![Figure 9](image-url)

**Effect of pH 7 on MO and Phenol**

At pH 10, MO exist as a negatively charged ion, repulsion takes place between catalyst and surface of MO thereby activity decreases compared to phenolas shown in the Figure 10 and Table 4. Where phenol exist as negatively charged phenolate

$$\text{Co}^{2+} + \text{H}_2\text{O} \rightarrow \text{CoOH}^+ + \text{H}^+ \quad (8)$$

$$\text{Co}^{3+} + \text{H}_2\text{O} \rightarrow \text{Co(OH)}^{2+} + \text{H}^+ \quad (9)$$

ion at this pH and phenolate ion exhibit acidic in nature, catalyst behaves as negative charge surface at the solution hence minimum repulsion takes place.

![Figure 10](image-url)

**PMS plays very important role at pH 3, 7, 10. Under acidic conditions hydrogen bond between H\(^+\) and HSO\(_4^-\) was dominated to inhibit the radical generation surface charge of \(\text{CoFe_2O_4}\) was less attractive towards the PMS activation thereby shows less activity compared to pH 7. At pH 7, HSO\(_4^-\) will be dominating species to interact with active sites on \(\text{CoFe_2O_4}\) surface PMS exist as highly reactive species frequently generates sulphate radicals which are take part in the photocatalytic degradation process. PMS concentration was found to be most suitable for activation and could accelerate the reaction rate in the neutral medium. The cobalt ferrite with PMS generate freely diffusible hydroxyl and sulphate free radicals compared to cadmium ferrite with PMS may be due to the high surface area and \(\text{Co}^{3+}\) ion acts as electron pair donor. The rapid transferring of electron and high separation efficiency of electron-hole pairs are the main reason for the substantially enhanced photocatalytic activity at pH 7.

At pH 10, it is expected to decrease the phycocatalytic activity coagulation of excess \(\text{Co}^{3+}\) ions takes place at higher pH conditions, inhibit the regeneration of \(\text{Co}^{2+}\) ions which are required for sustaining the photo cyclic reaction

However, at higher pH values PMS exists as less reactive dianion form (SO\(_4^{2-}\)). The efficient generation of SO\(_4^{2-}\) takes place only from monoanion form (HSO\(_4^-\)) and its generation is almost insignificant from dianionform (SO\(_4^{2-}\)).

**4. Conclusion**

\(\text{CoFe_2O_4}\) can be acts as charge collector to promote separation and transfer of photo generated carriers. Surface hydroxyls of \(\text{Co}^{2+}/\text{PMS}\) played an important role in the generation sulphate and hydroxyl free radicals both in MO and phenol at pH 7. PMS is active in neutral medium. In acidic and basic conditions sulphate and hydroxyl free radical ceases. Efficient photocatalytic activity shows towards phenol in presence of \(\text{Co}^{2+}/\text{PMS}\) at pH 7 due to its higher adsorption onto photocatalyst and surface was the active sites to cathysle phenol which confirms by the adsorptivity. Therefore, enhanced photocatalytic activity observed in case of phenol.

**References**


[12] K.H. Chan, W. Chu, Degradation of atrazine by cobalt mediated activation of peroxymonosulfate: different cobalt counter anions in...


