5.0 General Introduction

Synthesis and application of magnetic nanoparticles (MNPs) have achieved significant importance in the field of catalysis in recent years and have efficiently been employed in many popular industrially important reactions e.g. Suzuki-Miyaura, Heck and Sonogashira couplings, hydrogenation, hydroformylation, Friedel-Crafts acylation etc. There are also a number of examples of using these magnetic nanocomposites in photocatalytic degradation reactions with promising results.

Wastewater containing organic pollutants, such as dyes, may bring about serious environmental problems if directly discharged into waters. The release of those colored waste- waters in the environment is a considerable source of non aesthetic pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater [1-4]. There are various technological systems such as adsorption [5], biodegradation [6] and chemical methods [7] which are mostly used for wastewater treatment. The use of homogeneous catalyst for wastewater treatment suffers the disadvantage of recovery and reusability and may result in secondary pollution by discharging immobilized metal ion into water [8-12]. Due to the stability of modern dyes, conventional biological treatment methods for industrial wastewater are ineffective resulting often in an intensively colored discharge
from the treatment facilities. Therefore, the use of heterogeneous photocatalyst has been appeared as a promising destructive technology leading to total mineralization of most organic pollutants [13-17]. Recently, several semiconductors photocatalysts such as TiO$_2$ [18-21 44-47], CdS [22] and ZnO [23, 24], ZnS [25-28] have been developed for degradation of organic pollutants in water under UV-irradiation. Coupled semiconductors e.g. WO$_3$/WS$_2$ [29] have also been widely employed for removal of many organic and inorganic pollutants from air or aquatic environment. Use of semiconductor particles as photocatalyst has also been found in other areas such as solar energy conversion, organic synthesis and prebiotic chemistry [30, 31]. Photoreductions, which require at least a net two electron transfer [32, 33], is hitherto carried out by using noble metal deposited semiconductors. Irradiation of semiconductors with photon energies equal to or larger than their band gap generate electron-hole ($e^-/h^+$) pairs. Hence, following irradiation the semiconductors act as either electron or hole donors, which then take part in photo-reduction and photo-oxidation reactions respectively and initiate the oxidation and reduction processes to decompose the organic wastes. If visible light can excite the dye molecules, the electron transfer then occurs from the excited dye molecules (sensitized) into the conduction band of the semiconductor. For UV excitation the reverse is usually the case.

Photocatalytic process has many advantages over other methods for waste water treatment. It is environmentally friendly, capable of performing at room temperature and it can treat organic pollutants in extremely low concentrations. However, the use of nanoparticles as photocatalysts can have some added advantages such as large volume
to area ratio, high ultraviolet (UV) absorption, and long life-span etc. [34]. One of the serious drawbacks of suspended photo-nano-catalysts lie in that they tend to agglomerate in aqueous solution, hinder the penetration of lights. Moreover, they are pertinent to be lost because separation and recovery of nanoparticles is difficult. Although different approaches were made to recover the catalyst by various immobilization techniques, the efficiency of the photocatalyst is lowered because of the reduction of the effective surface area of the catalyst. Therefore, the need of magnetic cored nanocomposites (NCs) has been highly realized to resolve this difficulty so that efficiency of nanocatalyst can be enhanced in a greater way. Amongst various magnetic materials, the Fe₃O₄, BaFe₂O₄, NiFe₂O₄, γ-Fe₂O₃ have been used as core material in making composites with other catalysts which can be separated by using magnetic field from the reaction medium.

This chapter addresses the synthesis and application of two core-shell magnetic nanocomposites: CoFe₂O₄-Cr₂O₃-SiO₂ and CoFe₂O₄-ZnS. Section I deals with the synthesis and application of CoFe₂O₄-Cr₂O₃-SiO₂ core-shell magnetic nanocomposite in methylene blue degradation and Section II discusses the synthesis and application of CoFe₂O₄-ZnS core-shell nanocomposite in methyl orange degradation.

We wish to use CoFe₂O₄ magnetic nanoparticles as core material in making magnetic nanocomposites which could act as photocatalyst in degradation of dye in wastewater.
CHAPTER-V SECTION-I

Use of a novel CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ fluorescent magnetic nanocomposite for photocatalytic degradation of Methylene blue
5.1.1 Introduction

Methylene blue is a heterocyclic aromatic compound which has been widely used as organic dye in textile and other industries. It is an important redox indicator in analytical chemistry. Besides, it has many other applications i.e. in photosensitizing to generate peroxide, staining bio-molecules, treatment of carbon monoxide and cyanide poisoning and some medicinal uses [35].

Magnetic nanocomposites are emerging as a new type of functional material due to their multidirectional potential in comparison to the single-component counterparts which have in various technological applications [36-39]. Among various nanocomposites, iron oxides based nanostructures have been extensively studied and they give multifunctional properties in combination with other materials [40-43]. In general, the magnetic nanocomposites with transition metal or their oxides have been used in catalytic reactions which retain high reactivity and display facile separation from the reaction media.
5.1.2 Review of Literature

There several heterogeneous photocatalysts which have been efficiently utilized for degradation of methylene dye in water. In general, TiO$_2$ semiconductor is used for degradation of this dye under solar energy or UV irradiation [44, 45].

V. Ramaswamy et al. developed nanocrystalline particles of pure anatase-TiO$_2$ which showed photocatalytic activity in both UV and visible region [46].

Photocatalytic activities of ZnO nanoparticles were investigated by measuring the photocatalytic degradation of methylene blue in aqueous solution under the illumination of UV light [47].

The degradation of methylene blue dye was evaluated for a series of in situ generated TiO$_2$ resulting from the impregnation of TiCl$_4$ into a series of NaA zeolites. The catalytic activity was comparable to that exhibited by commercial P-25 under UV light exposition [49].

N. Shimizu et al. reported the degradation of methylene blue by the irradiation of ultrasound onto TiO$_2$ in aqueous solution [50].

P. Z. Araujo and his co-workers developed a crystalline titanosilicate Quantum-Confined semiconductor which was efficiently used for photodegradation of methylene blue [51].

Photodegradation of methylene blue was also carried out by the treatment of UV/H$_2$O$_2$ under UV light [52].
Magnetic nanoparticle catalysts have many advantages over other heterogenous or homogenous catalyst in view of their high catalytic activity, high catalyst loading capacity, high dispersion and stability, and most importantly catalyst separation and recycling [53-55]

The nanostructure magnetic materials, such as iron oxide/SiO₂ [56], iron oxide/Au(Ag) [57-59], Fe₃O₄/quantum dot (CdSe, CdTe) [60-62], and Fe₃O₄/TiO₂ [63-66] have been successfully prepared by various methods.

Recently, ferrite magnetic nanoparticles have received significant importance in various technological fields including photo-catalysis [67-69]. Among these, cobalt ferrite (CoFe₂O₄) draws more attention due to their high thermal and chemical stability, structural stability, tunable size and magnetic properties[70] which make it a good candidate as catalyst carrier or support along with other potential applications such as high-density magnetic storage, spintronic devices and for the fabrication of sensors for biomedical applications and hyperthermia [71-73].

5.1.3 Present Work

Objective

There are many reports for the use of nanoparticles or their composites as photocatalyst for the degradation of organic pollutants in wastewater. However, investigation on photocatalyst based on magnetic nanoparticles or composites is very limited. In recent years, iron oxide (Fe₃O₄ or γ-Fe₂O₃) magnetic nanoparticles have been
used as magnetic core material with other catalyst for various organic transformations. Chromium oxide (Cr$_2$O$_3$) on the other hand is an important material since it has a high melting temperature, is resistance to oxidation and exhibits interesting optical, electrical and magnetic properties [74, 75].

The objective of the present investigation is to synthesize a new magnetic nanocomposite based on CoFe$_2$O$_4$ magnetic core with multifunctional properties which is stable chemically or thermally compared to the commonly used core material e.g. Fe$_3$O$_4$ or $\gamma$-Fe$_2$O$_3$. We intend to make a composite material using CoFe$_2$O$_4$ magnetic nanoparticle and Cr$_2$O$_3$. Magnetically CoFe$_2$O$_4$-Cr$_2$O$_3$ is a two-phase exchanged coupled system consisting of a ferromagnet (CoFe$_2$O$_4$) biased by an antiferromagnet (Cr$_2$O$_3$). Literature search reveals that such systems with ferro-antiferromagnetic coupling have been extensively studied in light of magnetoresistive read-head applications [76, 77].

We would like to carry out the catalytic activity of the nanocomposite by measuring degradation of methylene blue (Fig. 5.1.1) in aqueous solution under illumination of UV light.

![Methylene Blue Structure]

**Fig. 5.1.1** Structure of methylene blue
5.1.4 Result and Discussion

We used the coated SiO₂ layer over CoFe₂O₄-Cr₂O₃ NC for the photocatalytic reaction. The pure magnetic nanocomposites may not be very useful in practical application as they are likely to form large aggregation and their magnetic properties change readily or the active sites may detach from the core when they are exposed in the reaction. The coated SiO₂ layer overcomes these difficulties and hence the CoFe₂O₄-Cr₂O₃-SiO₂ NC was used for the photocatalysis (Scheme 5.1.1).

![Preparation of CoFe₂O₄ nanoparticle: CoCl₂·6H₂O + 2FeCl₃ + 8NaOH → CoFe₂O₄ + 8NaCl + 10H₂O](image)

**Scheme 5.1.1** Schematic representation of CoFe₂O₄-Cr₂O₃-SiO₂ NC synthesis

**Structural analysis**

**Fig.5.1.2a** shows the XRD of the CoFe₂O₄-Cr₂O₃ nanocomposite. The diffraction peaks and relative intensities of the pattern match well with the cubic spinel structure of CoFe₂O₄ (JCPDS—International center diffraction data, PDF cards 3-864 and 22-1086) and of Cr₂O₃ (JCPDS—International center diffraction data, PDF cards 06-0504). The crystallite size (D) of the nano-particle was determined using the Scherer
formulae [78] on the (311) peak of CoFe$_2$O$_4$ was found to be 30 nm. The IR spectra of the material (Figure 5.1.2b) shows peaks at 611, 938, 1037, 1180, 1338 and 1586 cm$^{-1}$ corresponding to CoFe$_2$O$_4$ and the peaks at 575, 624, 923, 1155, 1528 and 1638 cm$^{-1}$ corresponding to CoFe$_2$O$_4$-Cr$_2$O$_3$. The peak obtained at 611 cm$^{-1}$ in the CoFe$_2$O$_4$ samples is attributed to Fe-O or Co-O bond [79]. In the CoFe$_2$O$_4$ -Cr$_2$O$_3$ samples the peak at 575 corresponds to Cr-O bond [80].

![Fig. 5.1.2](image)

Fig. 5.1.2 (a) XRD pattern and (b) FT-IR spectra of the as-prepared CoFe$_2$O$_4$-Cr$_2$O$_3$ particles.
**TEM and EDX analysis**

The structural composition and crystallinity of the cobalt ferrite nanoparticles was further examined using TEM. **Fig. 5.1.3** shows the TEM image of the cobalt-ferrite nanocrystals deposited on a carbon-coated copper grid. A TEM image of the CoFe$_2$O$_4$-Cr$_2$O$_3$ nanoparticle is shown in **Fig. 5.1.3a** and **Fig. 5.1.3b** shows the TEM image of the CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ nanocomposite. The SAED pattern (**Fig. 5.1.3d**) obtained from TEM showed CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$, with the rings corresponding to reflections from the planes of CoFe$_2$O$_4$, Cr$_2$O$_3$ and SiO$_2$. The average size of the nanoparticles from the TEM analysis (**Fig. 5.1.3a-b**) was found to be 30 ± 5 nm.

**Fig. 5.1.3** TEM images of (a) CoFe$_2$O$_4$-Cr$_2$O$_3$ and (b) CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ nanocomposite; (c) HRTEM images of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ nanocomposite and (d) SAED pattern of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ nanocomposite.
The EDX analysis (Fig. 5.1.4) in TEM measurement gave the elemental distribution (atomic percent) in the CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ NC as: Co = 5.9%, Fe = 11.6%, Cr = 11%, O = 54%, Si = 17.5%. Thus the Fe/Co ratio in the nanocomposite by EDX was found to be 1.9 which is close to the atomic ratio in the CoFe$_2$O$_4$ along with contributions from Cr, O and Si without any impurity.

![EDX spectra of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ NC](image)

**Fig. 5.1.4** EDX spectra of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ NC

*Magnetic Properties*

It is well known that the magnetic properties of CoFe$_2$O$_4$ depend on the chemical nature of Co, as the Fe$^{3+}$ in the structure are evenly distributed in the tetrahedral and octahedral interstices within the structure and are antiferromagnetic coupled. Such coupling cancels the moment contribution from Fe$^{3+}$ and the moment contribution is solely dependent on Co$^{2+}$ [81]. The incorporation of antiferromagnetic Cr$_2$O$_3$ and SiO$_2$ in the Co-Fe-O matrix may cause changes in the magnetic properties of the material. M-H loop was taken at room temperature with a maximum applied field of ± 2T. From the hysteresis loop, saturation magnetization, coercivity and retentivity
values were extracted. Fig. 5.1.5 shows that the prepared CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ particles are ferromagnetic at room temperature with saturation magnetization of 5.1 emu$^{-1}$ and coercivity of 482 Oe.

![M-H loops of CoFe$_2$O$_4$, CoFe$_2$O$_4$-Cr$_2$O$_3$ and CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$](image)

**Fig. 5.1.5** M-H loops of CoFe$_2$O$_4$, CoFe$_2$O$_4$-Cr$_2$O$_3$ and CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$

Nanaocomposite

It can be seen from Table 5.1.1 that incorporation of Cr$_2$O$_3$ and SiO$_2$ in the Co-Fe-O matrix has very little effect on the coercivity; however the magnetisation and the retentivity decrease rapidly. Therefore by controlling the quantity Cr$_2$O$_3$ and SiO$_2$ in the Co-Fe-O matrix magnetic properties of the nanocomposite can be tailored to suite different applications.
Table 5.1.1 Effect of the incorporation of antiferromagnetic Cr$_2$O$_3$ and SiO$_2$ into the Co-Fe-O matrix on its magnetic properties

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Coercivity (Oe)</th>
<th>Magnetisation/mass (emu/gm)</th>
<th>Retentivity (emu/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>539</td>
<td>64.97</td>
<td>17.49</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$-Cr$_2$O$_3$</td>
<td>529</td>
<td>24.74</td>
<td>6.62</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$</td>
<td>482</td>
<td>5.10</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Spectral Analysis

We have performed room temperature optical absorption and photoluminescence to show the optical properties of the nanocomposite over its individual component (Cr$_2$O$_3$). Fig.5.1.6 (a-d) shows the UV-vis absorption and fluorescence emission spectra of the CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ particles dispersed in water.

Fig. 5.1.6 (a–b) Absorption and (c-d) Fluorescence spectra and (e) aqueous dispersion of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ NC
The sharp peak at 200 nm of the UV-visible spectra indicated that the colloids are well dispersed. The spectrum showed two absorption bands at around 270 nm and 370 nm which are due to the presence of Cr$_2$O$_3$ in the sample. In the case of as synthesized Cr$_2$O$_3$, two peaks at 274 and 373 nm were observed and a slight blue shift was noticed in CoFe$_2$O$_4$-Cr$_2$O$_3$ sample as compared to pure Cr$_2$O$_3$. The band gap corresponding to the absorption bands was calculated by plotting $(\alpha h\nu)^2$ vs $h\nu$ (Fig. 5.1.6b) using the relation [82].

$$ah\nu = \text{const} \ (h\nu-E_g)^n, \quad \text{---(1)}$$

The value of $\alpha$ is obtained from the equation [83]

$$\alpha = 2.3026 \left( \frac{A}{t} \right)^{\frac{1}{n}}, \quad \text{---(2)}$$

Where $A$ is the absorption and $t$ is the thickness of the sample.

The extrapolation (Fig. 5.1.6b) of the straight line to $\alpha^2 = 0$ give the value of band gap energy. To further investigate absorption bands, the fluorescent properties of the nanoparticles are measured using a steady state time resolved spectrofluorometer at a wavelength of 260-360 nm for excitation scans and 350-600 nm for emission scans. We did not observe any prominent fluorescence peak for the as-prepared CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ nanoparticles (Fig. 5.1.6d). However, when the sample was annealed at 1000 °C, a broad band at 460 nm appeared in the fluorescence spectrum, (Fig. 5.1.6c). This was attributed to lattice defects, such as interval atoms, displacement atoms and line defects resulting from grain boundary diffusion between CoFe$_2$O$_4$ and Cr$_2$O$_3$. The presence of defects in the nanocomposite is also supported by the HRTEM images of the sample.
Such lattice defects are responsible for the luminescent properties of the nanocomposite [84].

The fluorescent efficiency of the nanocomposite was measured using quinine sulphate ($\Phi_R = 0.55$) [85] in 0.1 mol L$^{-1}$ H$_2$SO$_4$ solution as a standard using the relationship [86]:

$$\Phi = \Phi_R \frac{\text{Int} \ A_R n^2}{\text{Int}_R A n_R^2}$$

Where $\Phi$ is the quantum yield, Int is the area under the emission peak (on a wavelength scale), $A$ is absorbance at the excitation wavelength of 372 nm, and $n$ is the refractive index of the sample (we have taken the value of $n_R = 1.338$ [87], $n = 1.34639$ [87], $\Phi_R = 0.55$ [76]. The subscript R denotes the respective values of the reference substance.

The fluorescence spectrum of the solutions was recorded in a 20 mm fluorescence cuvette of constant slit width. In order to minimize reabsorption effects, absorbances at 0.1 above the excitation wavelength (at 372 nm) were used [88]. The quantum yield of the FMNP sample was found to be 0.0354 (Fig. 5.1.7).

![Fluorescence spectrum](image)

**Fig. 5.1.7** Quantum yield from fluorescence spectra of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ NC.
The combination of nanoscale dimensions, high band gap energy, ferromagnetic properties and fluorescence for this nanocomposite has prompted us for photocatalytic application.

**Photocatalytic activity**

To demonstrate the potential application of the fluorescence magnetic nanocomposite (FMNC) for removal of organic pollutants from wastewater we examined their photocatalytic activity in degradation of methylene blue (MB) as a model reaction.

![Graph showing UV-Vis spectra](image)

**Fig. 5.1.8** UV-Vis spectra in (a) 200-800 nm, (b) 450-750 nm region of MB degradation by CoFe_2O_4-Cr_2O_3-SiO_2 NC

The catalytic performance was tested under UV lamp at ambient temperature and Fig. **Fig. 5.1.8** shows the absorption spectra of the aqueous solution of MB exposed to UV
light for various time periods. The typical absorption peak at 664 nm gradually diminished with increasing the UV exposure time and almost completely disappeared after 120 min, suggesting the nearly complete degradation of MB by the FMNC. It was observed that the degradation of MB was faster initially (almost 51% in 15 min) and decreased thereafter. A typical run without UV-irradiation confirmed that there is no photo-degradation taking place, except adsorption of small amount of MB on the samples. A typical run without UV-irradiation by stirring the reaction mixture in dark for 120 min confirms that photo-oxidation does no take place in absence of UV light (spectral line b in Fig.5.1.8). We checked the catalytic performance of the CoFe$_2$O$_4$-Cr$_2$O$_3$ before coating with SiO$_2$ and the result is shown in Fig. 5.1.9.

![UV-Vis spectra of MB degradation by CoFe$_2$O$_4$-Cr$_2$O$_3$ NC](image)

**Fig. 5.1.9 UV-Vis spectra of MB degradation by CoFe$_2$O$_4$-Cr$_2$O$_3$ NC**

Between CoFe$_2$O$_4$-Cr$_2$O$_3$ and CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ samples, the later shows almost complete degradation of MB in 120 min. after UV irradiation whereas there is only 10% decrease in the concentration of MB to initial state in the former within the
same duration. There is a steady decrease in the concentration of MB to initial state for the CoFe₂O₄-Cr₂O₃-SiO₂ NC after first 15 min and it took nearly 120 min for 90% photo-oxidation of MB. The enhanced photocatalytic activity of CoFe₂O₄-Cr₂O₃-SiO₂ compared to CoFe₂O₄-Cr₂O₃ is due to the surface coating of SiO₂. The SiO₂ forms a complete membrane round the surface of CoFe₂O₄-Cr₂O₃ nanoparticles, which might serve as an effective polar surface and make complete dispersibility of the nanocomposite in water and hence more exposed to UV radiation. In addition, the SiO₂ layer is uv-transparent and porous which allow the organic molecule to come into contact with the active layer through its pores. Therefore, the coating of SiO₂ is necessary not only to prevent self-degradation but also promote efficient dispersion of nanoparticle in solution and thus accounts for high photocatalytic activity of the coated nanocomposite (CoFe₂O₄-Cr₂O₃-SiO₂) as compared to the uncoated nanocomposite (CoFe₂O₄-Cr₂O₃). Thus the SiO₂ coating plays a vital role in degradation processes of methylene blue solution. Besides this, the observed high photocatalytic activity of the FMNC may be attributed to (a) remarkably high band gap energy (4eV) and (b) small particle size which is associated with high surface area.

In photocatalytic degradation of organic compounds by semiconductors, a dopant such as Cr₂O₃ ion may act as an electron trap or hole trap which in turn prolong the lifetime of the generated charge carriers, resulting in enhanced photocatalytic activity. Recently, the composite material of TiO₂ semiconductor with CoFe₂O₄ as magnetic core has been reported to be a useful photocatalyst for degradation of organic contaminants in water [89]. However, no one has addressed the Cr₂O₃ associated with
magnetic core such as Fe₃O₄ or CoFe₂O₄ making the nanocomposite as photocatalyst till date that can be separated by the action of an external magnet. On the other hand, the FMNCs can be synthesized easily with better control of size, shape and magnetic property, and well separated from the media by applying external magnetic field after the reaction.

It has been examined that pure CoFe₂O₄ nanoparticles can hardly degrade MB solution, but exhibit good magnetism. Pure Cr₂O₃ shows very low photocatalytic activity [90] and antiferromagnetism. Hence, it is highly necessary to choose appropriate molar ratios of Cr₂O₃ to CoFe₂O₄ in order to sustain effective photocatalytic as well as magnetism for easy magnetic separation.

Kinetics

The kinetics of disappearance of methylene blue is illustrated in Fig. 5.1.10.

![Fig. 5.1.10 First-order representation of decomposition of MB by CoFe₂O₄-Cr₂O₃SiO₂NC vs. time.](image)
The results show that the photocatalytic degradation of methylene blue can be described by the first order kinetic model which can be expressed as follows.

\[ \ln\left(\frac{C_0}{C}\right) = kt \quad (1) \]

where \( C_0 \) is the initial MB concentration, and \( C \) is the concentration at a certain time, \( k \) is reaction rate constant, and \( t \) is time. \( C_0/C \) can be substituted by \( A_0/A \) for the reason that the concentration is basically directly proportional to the absorbency.

The plots of the concentration data gave a straight line. The apparent first order linear transforms are given in Fig. 5.1.11. The slope yield apparent rate constants of 0.025 min\(^{-1}\). The experimental results were well supported to the reported data for photocatalytic decomposition of MB aqueous solution [91-95].

![First-order kinetics for MB degradation under UV-irradiation](image)

**Fig. 5.1.11** First-order kinetics for MB degradation under UV-irradiation

*Recyclability of the photocatalyst*
The recyclability of the photocatalyst was further investigated by separating the nanocomposite by external magnet. The recycled nanocomposite was further utilized to photodegradation of fresh methylene blue solution as presented in Fig. 5.1.12.

**Fig. 5.1.12** Photocatalytic degradation of MB in three catalytic cycles.

**Fig. 5.1.13** shows the fluorescence emission spectra of the recycled nanocomposite in the reaction medium in three consecutive cycles. It may be noted that the observed fluorescence is due to the formation of defect created by deficiency of Cr-ions in Cr₂O₃ in high temperature annealing during preparation of CoFe₂O₄-Cr₂O₃ NC.

**Fig. 5.1.13** Fluorescence emission spectra of the reaction mixture in three repeated cycles of Photocatalysis
The photocatalytic activity of the recycled nanocomposite had no significant loss after three cycles which reveal that the magnetically separable photocatalyst is stable and effective for the removal of organic pollutants in water. Moreover, the fluorescence property remains unaltered in repeated photocatalytic cycles and hence accounts for its fluorescence stability.

We applied this nanocomposite as photocatalyst for degradation methylene blue dye in water. The UV absorption spectra as well as the fluorescence emission spectra of the nano composites did not show any significant changes in position and intensity during photo degradation measurement which shows the stability of the nanoparticles during catalysis.

5.1.5 Conclusion

We have prepared the SiO₂-coated CoFe₂O₄-Cr₂O₃ nanocomposite which exhibit high photo-catalytic efficiency toward the oxidation of organic pollutant in aqueous solution under UV-irradiation. The associated magnetic activity of the ferrite core allows easy separation of the photo-catalyst after the photo-catalysis and recyclability. These results suggest that the CoFe₂O₄-Cr₂O₃-SiO₂ NC is a suitable photo-catalyst for potential applications in organic waste removal from water. Future works is in progress to prepare a CoFe₂O₄-Cr₂O₃-SiO₂ NC in appropriate molar ratio of the composite materials to be used as photo-catalyst under visible light.
5.1.6. Experimental Procedure

Synthesis of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ FMNC

CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ FMNCs have been synthesized by a combined sonochemical and co-precipitation technique. The synthesis was achieved in three successive steps (a-c). Initially uncapped CoFe$_2$O$_4$ was synthesized which was then coated with Cr$_2$O$_3$. Subsequent treatment of the CoFe$_2$O$_4$-Cr$_2$O$_3$ nanoparticles with trietylorthosilicate produced the CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ magnetic nanocomposites which on further heat treatment furnished its fluorescence properties. The procedure is described below.

(a) Synthesis of CoFe$_2$O$_4$ nanoparticle by co-precipitation

First step of the synthesis is the formation of uncapped cobalt ferrite nanoparticles. The synthesis of CoFe$_2$O$_4$ MNPs was made by ultrasonication assisted co-precipitation method as described in Chapter 3, Section-I.

(b) Synthesis of CoFe$_2$O$_4$-Cr$_2$O$_3$ NC

Coating of a layer of Cr$_2$O$_3$ on the surface of the CoFe$_2$O$_4$ nanoparticle was achieved by premixing a dispersion of CoFe$_2$O$_4$ nanoparticle in deionised water with appropriate molar ratios of Cr(CH$_3$COO)$_3$.H$_2$O in a round bottom flask and placed in a ultrasonic bath. An aqueous solution of NaOH was added to the mixture in the presence of ultrasonic irradiation (frequency 40 KHz at 40 KW). Prior to mixing, all these four solutions were degassed by sonication for 30 min. The temperature of the sonicator bath
was raised up to 60 °C and the mixture was further sonicated for 30 min in air atmosphere. The brown precipitate formation was observed during that time. The reaction mixture was centrifuged (10000 rpm) at ambient temperature for 15 min. The brown precipitate was then separated, washed with copious amount of distilled water, ethanol and kept overnight in an incubator at 60 °C for ageing. The precipitate was further dried in oven at 100 °C for 1 h and subsequently kept under high vacuum (10⁻² bar) for one hour. Finally, the particles were taken in 50 ml of dry ethanol and subjected to successive sonication (30 min) and centrifugation (15 min) repeatedly till a brown colored solution appears. The precipitate was separated, dried and held at 1000°C in a muffle furnace for 10 h to obtain a fine black powder. Energy dispersive X-ray spectroscopy (EDX) analysis at this point showed excellent agreement between expected and observed values of the constituent elements and therefore confirms the formation of CoFe₂O₄-Cr₂O₃.

(c) Surface modification of CoFe₂O₄-Cr₂O₃ nanoparticle by SiO₂

The third synthesis step involves silica coating on the as prepared CoFe₂O₄-Cr₂O₃ nanoparticle surface by hydrolysis of tetraethyl orthosilicate (TEOS) [94]. The CoFe₂O₄-Cr₂O₃ nanoparticles (0.2 g) were dispersed in to a mixture of ethanol (20 ml), water (9 ml) and ammonia (25%, 0.5 ml) under ultrasonication and then TEOS (0.5 ml) was added into the mixture. After 3 h, the precipitate was isolated by centrifugation and washed with ethanol and water several times and dried at 80°C under vacuum for 2 h.
Photocatalytic degradation

0.02 g of CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ FMNC were dispersed in to 1x10$^{-5}$ M MB aqueous solution (50 mL) by ultrasonication for 10 min and the obtained dispersion was kept in dark with stirring for 30 min to reach the absorption-desorption equilibrium. Then, the dispersion was placed in a 200 mL cylindrical quartz tube with stirring facility and kept under UV irradiation (12 mW, major wavelength 400 nm). Sampling per 15 minute and separating dispersed particles by external magnet, we measured the UV-Vis absorption of the clarified solution at the wavelength from 200 nm to 800 nm. Finally, photocatalytic degradation percentage of MB was calculated using Eq. (1)

$$\text{Degradation (％)} = \left( \frac{A_0 - A}{A_0} \right) \times 100$$

where, $A_0$ and $A$ are the UV-Vis absorption of original and sampled solutions, respectively.
Use of CoFe$_2$O$_4$-ZnS nanocomposites for photocatalytic degradation of Methyl orange
5.2.1 Introduction

The core-shell magnetic nanocomposites with the combined properties of core and the shell have attracted immense importance to researchers' because of their unique physicochemical properties and great potential applications in broad disciplines e.g. electronics, photonics, biotechnology and catalysis. The core-shell structures possess the ability to be surface modified with different charges, functions or reactive species which render enhanced stability and compatibility to the surrounding environment with the possibility to design and develop new core-shell composites. With respect to these properties, the design and synthesis of various core-shell magnetic nanocomposites based on ferrite magnetic core are important research subject. Among ferrite nanoparticles, magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) have been widely used for both catalyst supports and biomedical applications [93].

5.2.2 Review of Literature

The nano-size photocatalysts which have the quality of high surface area, high UV absorption and long life-span have been broadly used in degradation of organic pollutants in water [94-96]. The photocatalytic efficiency of semiconductors can be enhanced by doping with other metal ions such as Mn, Ni, Cu, Pd.
Recently, S. Suslick et al have developed a nanostructured Ni$^{2+}$ doped ZnS catalyst for photocatalytic application [97].

G. Zhang et al. have reported the synthesis of CoFe$_2$O$_4$-ZnO nanocomposite with multiple properties [98]. Very recently, H. A. J. L. Mourão et al. have reported the synthesis of CoFe$_2$O$_4$-TiO$_2$ nano-composite and used for photodegradation of dye in water [99].

5.2.3 Present Work

Objective

Among various semiconductor photocatalyst employed, ZnS has served as one of the most efficient catalysts due to its large bandgap energy (3.6 eV) for degradation of water pollutants, reduction of heavy metals and water-splitting for H$_2$ evolution [89, 100-102].

It is noteworthy that while preparing magnetic nanocomposite, complete dispersion of the magnetic cores is very much necessary in order to have full coating of the nanoparticles. Moreover, the core materials such as Fe$_3$O$_4$ or γ-Fe$_2$O$_3$ are not chemically or thermally stable [103, 104]. Therefore, a new synthesis strategy is desirable to develop a stable magnetic core with easy dispersion for effective surface coating in nano scale dimension. Cobalt ferrite is well known to have large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and a
mechanical hardness [105], which makes it a good candidate as core material for the fabrication of nano-composite.

However, core-shell structure of CoFe₂O₄-ZnS with photocatalytic activity and magnetism has never been reported. Therefore, we wish to combine CoFe₂O₄ and ZnS with effective coating layer making the core-shell nanocomposite for photodegradation of organic contaminants in waste-water and performing the magnetic separation of the photocatalyst from the reaction medium.

We intend to prepare the core-shell magnetic nanocomposite of CoFe₂O₄-ZnS by co-precipitation method under ultrasonic irradiation and examine its photocatalytic efficiency in methyl orange (MO) (Fig. 5.2.1) degradation in aqueous medium.

![Fig. 5.2.1 Structure of methyl orange](image)

### 5.2.4 Result and Discussion

**Crystalline structure of the core-shell CoFe₂O₄-ZnS**

The Powder X-ray diffraction (XRD) measurement was carried out for the ZnS nanoparticles and CoFe₂O₄-ZnS NC to characterize the phase and crystallization. Fig. 5.2.2 shows the XRD patterns of the as-synthesized CoFe₂O₄-ZnS nanocomposite and ZnS nanoparticles. From Fig. 5.2.2a, it can be seen that pure ZnS nanoparticles have been prepared and the diffraction peaks is very broad, which implies that the particle
size is very small. The diffraction pattern of as synthesized CoFe$_2$O$_4$-ZnS particles in Fig. 1(b) shows that all the peaks are in good agreement with the spinel structure (JCPDS Cards 3-864 and 22-1086) [109, 110] known from CoFe$_2$O$_4$ crystal meaning its high crystallization which has also contribution from ZnS NPs.

Furthermore, according to the full width at half maximum (FWHM) of (311) reflections, the average size of the crystalline particles for the primary CoFe$_2$O$_4$ is calculated to be 30±2 nm based on the Debye-Scherrer formula [78]. These results reveal that the nanocomposites are composed of cubic-structured CoFe$_2$O$_4$ and ZnS nanoparticles.

**Morphology and structure of core-shell CoFe$_2$O$_4$-ZnS**

Fig. 5.2.3 (a) shows the FESEM image of CoFe$_2$O$_4$-ZnS nanocomposites at the magnification of 150 KX which shows the uniform size distribution of nanoparticles with almost spherical morphology. The EDX of the sample is shown in Fig. 5.2.3 (b)
**Fig. 5.2.3** (a) FE-SEM and (b) EDX spectra of CoFe$_2$O$_4$-ZnS NCs

The TEM micrographs of the ZnS and CoFe$_2$O$_4$ NPs with their corresponding diffraction patterns (inset) are presented at the scale of 50 nm and 2 nm$^{-1}$ respectively in **Fig. 5.2.4**

**Fig. 5.2.4** TEM image of (a) ZnS NPs (inset b is SAED), and (c) CoFe$_2$O$_4$-ZnS NC (inset d is SAED).

**Fig. 5.2.4a** shows the representative TEM image of the ZnS nanoparticles which are in uniform size and measured to be around 5-10 nm. The inset (b) is the corresponding diffraction pattern (SAED) pattern, exhibiting crystalline nature of ZnS NPs. The TEM image of CoFe$_2$O$_4$-ZnS NC shows a clear core-shell nanostructure
where the black particles of CoFe$_2$O$_4$ are shielded by white ZnS particles. The sizes of the nanocomposites were found to be in the range of 20-30 nm which is roughly closed to the average size resulted from the Debye-Scherrer formula.

The as-synthesized nanocomposites were further characterized using micro Raman spectroscopy.

![Raman spectra of CoFe$_2$O$_4$-ZnS NC](image)

**Fig. 5.2.5** Raman spectra of (a) CoFe$_2$O$_4$ nanoparticles (b) CoFe$_2$O$_4$-ZnS NC and inset is of ZnS NPs (*Raman scattering peaks from ZnS NPs*)

Raman spectroscopy is a useful tool for investigating nanoparticles and its surrounding media [111]. The core-shell structure of CoFe$_2$O$_4$-ZnS which was shown by XRD pattern and TEM images can be evaluated by micro-Raman spectroscopy. The inset in Fig. 5.2.5 shows the Raman spectra of ZnS nanoparticles with the characteristic peaks of for the nanoparticles around at 258 and 345 cm$^{-1}$ which shows the cubic structure [112]. The CoFe$_2$O$_4$ shows five Raman active modes (A$_g$ + E$_g$ + 3E$_{2g}$) [113-115]. Three modes of CoFe$_2$O$_4$ 458 cm$^{-1}$, 600 cm$^{-1}$ and 665 cm$^{-1}$ can be seen in Fig. 5.2.5 (b) along with the 258 cm$^{-1}$ and 345 cm$^{-1}$ modes from ZnS nanoparticles. There are no significant shifts in the bands in Raman spectra is occurred and shifting arise
when substitution occurs [116]. In this case, there is no substitution in the CoFe$_2$O$_4$-ZnS nanocomposites and thus by combining Raman analysis, XRD and TEM results, we can conclude that core-shell structure of CoFe$_2$O$_4$-ZnS nanocomposites has been effectively synthesized.

**Magnetic properties of the core-shell nanocomposites**

The magnetic properties of as-synthesized CoFe$_2$O$_4$-ZnS nanocomposite with CoFe$_2$O$_4$ nanoparticles were studied by examining magnetic hysteresis loops (M-H) (Fig. 5.2.6) measured in a VSM at room temperature.

![Magnetic hysteresis loops](image)

**Fig. 5.2.6** Magnetic hysteresis loops for (a) CoFe$_2$O$_4$ MNPs and (b) CoFe$_2$O$_4$-ZnS NC

The M-H loop of CoFe$_2$O$_4$-ZnS NC indicates its ferromagnetic behavior at room temperature where the coercivity (Hc) and the saturation magnetization (Ms) were found to be 1.2 Oe (1.6 kOe for CoFe$_2$O$_4$) and (18 emug$^{-1}$ for CoFe$_2$O$_4$) respectively.

**Spectral analysis**

The UV-Vis spectrum of as synthesized colloidal solution of CoFe$_2$O$_4$-ZnS shows absorption bands at around 280 nm. The band-gap energy, $E_g$ corresponding to
the absorption band was determined from the absorbance spectra, where a steep increase in the absorption is observed due to the band-band transition using the general relation.

$$(\alpha \nu)^n = B(E - E_g)$$

Where $B$ is a constant related to the effective masses of charge carriers associated with valance and conduction bans, $E_g$ the band-gap energy, $E = h\nu$ the photon energy, and $n=1/2$ or 2, depending on whether the transition is indirect or direct, respectively. The intersection of the slope of $(\alpha \nu)^2$ vs $h\nu$ curve on the X-axis gives band-gap energy of the sample. The Tauc plot [117] for the CoFe$_2$O$_4$-ZnS nanocomposite is depicted in the inset in Fig. 5.2.7 and the bandgap energy was found to be 3.0 eV.

**Fig. 5.2.7** UV-Vis absorption spectrum of CoFe$_2$O$_4$-ZnS NC and inset (b) is the Tauc plot of the UV-Vis data for the calculation of band-gap energy.
Photocatalysis of methyl orange

The photocatalytic activity of the NC has been tested by degrading methyl orange (MO) solution under UV illumination (main wave length 400 nm, 12 mW) at different time intervals and shown in Fig. 5.2.8. The magnetic composite shows high photocatalytic activity for the degradation of methyl orange in water. The UV-Vis measurement shows that the concentration of methyl orange decreased to 54% after reacted for 10 min comparing the original concentration, and the maximum removal capacity of the photocatalysis reached about 90% in 20 min which is much shorter time period than any other reported degradation period of methyl orange. We observed that the photocatalyst can be easily separated by applying an external magnetic field while maintaining their photocatalytic activity during at least three cycles of use.

Fig. 5.2.8 UV-Vis absorption spectra of MO degradation by CoFe$_2$O$_4$-ZnS NC
5.2.5 Conclusion

In conclusion, we have fabricated the CoFe$_2$O$_4$-ZnS core-shell nanostructures on the surface of primary CoFe$_2$O$_4$ NPs which shows high efficiency in photocatalytic degradation of methyl orange. The magnetic separation of the photocatalyst provides a convenient method for removing and recycling of the magnetized species by applying an appropriate magnetic field suggesting as one of the promising candidates for photocatalytic treatment of waste-water.
5.2.6 Experimental Section

The cobalt ferrite nanoparticles were synthesized following the method as described in Chapter 3, Section-I except using 1:1 adduct of oleic acid-dodecylamine. Then, ZnS nanoparticles were prepared and poured into the dispersion of CoFe$_2$O$_4$ nanoparticle in the reaction medium, forming CoFe$_2$O$_4$-ZnS core-shell nanocomposites.

Synthesis of CoFe$_2$O$_4$-ZnS nanocomposite

(a) Synthesis of ZnS nanoparticles

Prior to coating of ZnS nanoparticles to CoFe$_2$O$_4$ surface, ZnS nanoparticles were synthesized by slightly modified method reported by N. Saravananet et al. [118]. A solution of 0.1 M zinc chloride, 0.1 M sulphur powder, 5 M NaOH in 100 mL deionised distilled water was ultrasonicated for 2 h at 80 °C. The product was then separated by centrifugation at 14000 rpm, washed several times with distilled deionised water, dried under vacuum and characterized.

(b) Synthesis of CoFe$_2$O$_4$-ZnS nanocomposite

The optimal concentration of Co$^{2+}$, Fe$^{3+}$ and a mixed surfactant (total concentration of oleic acid/dodecylamine, designated as [OA + DA] was [Co$^{2+}$] = 0.2 M, [Fe$^{3+}$] = 0.4 M, and [OA + DA] = 4M. In a typical procedure, absolute ethanol (20 mL) was mixed with 1:1 adduct of oleic acid and dodecylamine under magnetic stirring for 15 min to form homogeneous solution I.

In the next step, a solution of CoCl$_2$·6H$_2$O (1g, 4.2 mmol) in distilled water (50 mL) was mixed with a solution of FeCl$_3$ (1.5 g, 9.3 mmol) in distilled water (50 mL) in
a two-neck 200 mL flat bottom flask and kept under ultrasonication for 30 min in argon atmosphere. Then this mixture was added drop wise to solution I under magnetic stirring. The whole mixture was kept in a ultrasonic bath and an aqueous KOH solution (3M, 25 mL) was added drop wise under argon atmosphere with continuous ultrasonic irradiation (frequency 40 KHz and power of 40 KW). The temperature of the sonicator bath was raised up to 60 °C and the mixture was further sonicated for 1h till the formation of black particles was observed. Thereafter the reaction was cooled to room temperature and the product was collected by centrifugation (20000 rpm) at ambient temperature. The separated oleic acid-dodecyl amine coated CoFe$_2$O$_4$ nanoparticles were washed several times with distilled water and finally with ethanol to get rid of excess surfactants as confirmed by EDX analysis. Then a specific amount of ZnS NPs dispersion in de-ionized water was added to the dispersion of oleic acid-dodecyl amine coated CoFe$_2$O$_4$ NPs in de-ionized water under vigorous sonication for 1h. The precipitates were further washed with ethanol (4 times) so as to remove excess ZnS particles in the final product. Finally, the precipitate was dried at 400 °C under nitrogen purging for 6 hours to obtain the CoFe$_2$O$_4$-ZnS core-shell structure. The dried CoFe$_2$O$_4$-ZnS NCs were kept under vacuum till further use. The as synthesized nanocomposite could be easily redispersed in aqueous medium.
Measurement of photocatalytic activities

The photocatalytic activity of the magnetic nanocomposite for degradation of methyl orange (MO) in aqueous solution was studied. The experiment was carried out in a 200 mL quartz glass vessel. The obtained core-shell CoFe$_2$O$_4$-ZnS-NC-2 (0.02g) was placed into the tubular quartz vessel containing 100 mL of 1x10$^{-5}$ M MO aqueous solutions and mixed by ultrasonication for 10 min. Then the mixture was stirred in dark to obtain absorption/desorption equilibrium until the concentration of MO was constant. The mixture was then illuminated with a UV lamp (12 mW, main wavelength of 400 nm) which was put into the bottom of the quartz vessel and with continuous stirring. After the reaction, a definite amount of sample was withdrawn at different time interval and the nanoparticles were separated by using an external magnet. Then, absorption spectra of the samples were obtained through a wavelength scan from 300 to 600 nm on a UV-vis spectrophotometer. The percentage of photocatalytic degradation of MO was calculated using Eq. (1)

$$\text{Degradation} \, (\%) = \left( \frac{A_0 - A}{A_0} \right) \times 100$$  \hspace{1cm} (1)

Where, $A_0$ is the initial absorbance of MO before degradation and $A$ is the absorbance after time $t$. 
5.3 References


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