5.1. Introduction

A large number of organic substances are introduced into the water system from various sources such as industrial effluents, agricultural runoffs and chemical spills. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of major concern to societies and regulation authorities around the world. Steps must be taken for recycling the wastewater of the various industries as water shortage has now become a key symbol of protest around the world and is seen as the most serious social and political issue of this generation.

Fig. 5.1: Dye effluent from industrial waste

Among the various organic pollutants dyes released from textile industries are of major concern. Dyes are the substances that when applied to a substrate provide color by a process that alters, at least temporarily, any crystal structure of the colored substances [1,2]. The first evidence of the use of colorant materials by man goes as far as 15000-9000 BC in the walls of the Altamira cave in Spain. The drawings were performed with inorganic pigments like soot, manganese oxide, hematite and ochre. Historically, dyes
originated from animal sources (molluscs) are very significant although presently they have no relevance.

The textile dyeing industry has been in existence for over 4000 years. In ancient times dyes were obtained from natural sources and not everyone could possess colored fabrics. It is estimated that over 10,000 different dyes and pigments are used industrially and over $7 \times 10^5$ tons of synthetic dyes are annually produced worldwide [3,4]. Color waste water is one of the pollution which released from the textile industries and has become an issue of curiosity during the last few years. Because of the toxicity of the dyes more often the colored wastewater from the textile industries also decreases the visibility of the receiving waters. The presence of dyes in the aquatic bodies leads to an aesthetic problem and can have an unenthusiastic impact on public health [5].

Dyes are classified into different classes according to their application and chemical structure. They are composed of a group of atoms known as chromophores, responsible for the dye color. These chromophore containing centers are based on diverse functional groups, such as azo, anthraquinone, methine, nitro, arilmethane, carbonyl and others. In addition, electrons withdrawing or donating substituents which intensify the color of the chromophores are denominated as auxochromes [6]. Out of different classes of dyes, azo dyes constitute the largest group of colorants widely used in various fields and technologies like textiles, leather, plastics, paper, laser liquid crystalline displays and ink jet printers [7-8]. They are also used in food drug and photochemical production [9].

The azo dyes have the general structure $R-N=N-R'$, where $R$ and $R'$ are alkyl, aryl or heterocyclic radicals. Most of them are prepared by the condensation of azo compounds with hydroxyl, aldehydes or ketones. There are several bidentate azo dyes in which the phenolic $-\text{OH}$ group and azo nitrogen are present in such a way that they form six membered ring with metal ions [10]. They are extensively used in large quantities in textile industries as compare to other dyes because of the ease and cost-effectiveness of their synthesis, stability, fixatives and the diversity of colors available in comparison to natural dyes [11,12]. But after the cleavage of azo dyes aromatic amines are released which is carcinogenic in nature. The azo dye, $p$-dimethylaminobenzene ($p$-DAB), caused cytotoxic and genotoxic effects in the chromosome aberrations test, micronucleus test and mitotic index in bone marrow cells and spermatozoids of rats [13]. Aromatic amines
formation takes place with the intestinal microflora and by liver azoreductases on the oral exposure of azo dyes by humans. These amines may have carcinogenic properties [14]. The dyes also effect photosynthetic activity of plants and have detrimental effects to health, such as skin and eye irritation [15]. Therefore, degradation of these dyes is very important before discharging them into the environment.

In order to eliminate these dyes from the industrial effluent chemical methods (reduction, oxidation, ion exchange, complexometric methods), physical methods (coagulation, reverse osmosis, membrane filtration) and biological methods (aerobic, anaerobic) have been used [16]. However, there are still some limitations for the wide applications of these methods because of the technical difficulties or high cost, less efficiency, limited applicability and generation of sludge leading to secondary pollution [17,18]. The advanced oxidation process (AOP) is a potential alternative to treat textile waste water and is based on the generation of powerful oxidizing species, i.e. hydroxyl radical (OH·) [19]. Different AOP are reported in literature such as Fenton reaction [20], ozonation [21], sonopho-tocatalysis [22], electrochemical oxidation [23] and heterogeneous photocatalysis [24]. Among the various AOP method reported in literature for the treatment of textile wastewater, Fenton’s process is of significant importance.

In recent years, magnetic nano-ferrites have emerged as potential tool for heterogeneous catalysis in various chemical reactions. Ferrites offer enhanced catalytic activities compared to the corresponding single component metal oxides. This is because metal oxides are susceptible to acid and alkali attacks. Ferrites, however, are chemically more stable and are resistant towards such substances [25-34]. These are also used in the reactions which are addressing environmental concerns [35-38] and those involving degradation of organic pollutants and harmful dyes [39-42]. Magnetic ferrite catalysts are preferred materials for heterogeneous catalysis because these are magnetically separable; therefore, these can be easily removed from reaction medium [43,44]. In addition, these can be reused many times without any significant loss of catalytic activity [45,46]. Therefore, it would not be wrong to mention that ferrites have been emerging as forefront materials in the field of heterogeneous catalysis.

The magnetic nano-ferrite materials exhibit catalytic activity owing to the presence of transition metal ions which are stable in more than one oxidation states. Due
to this reason, the constituent metal ion/ions undergo a cyclic electron transfer process, enabling ferrites to exhibit catalytic activity. In addition, the catalytic activity of spinel ferrites is influenced by various other factors like particle size, redox properties of metal ions and their distribution among the tetrahedral (A) and octahedral (B) co-ordination sites. In general, the transition metal ions occupying A- sites are catalytically inactive; consequently, the catalytic activity is crucially related to the metal cations on B-sites. This is due to the fact that the metal ions present at B-sites are placed at sufficiently large distances from each other, so that the reactant molecule can interact with B-cations [47].

5.2. Literature on ferrites catalysts for the degradation of organic pollutants

Many researchers have reported the degradation of dye with pure ferrites [48-59]. Jadhav et al. [48] studied the effect of sintering on photo catalytic degradation of methyl orange (MO) using zinc ferrite. The authors concluded that the photo catalytic activity decreased with increase in the sintering temperature due to the decrease in the surface area resulting from the increased crystallite size. Sun et al. [49] prepared ZnFe$_2$O$_4$ octahedra nano-crystal of 10nm particle size via a hydrothermal method. The prepared nano crystal showed good photo catalytic activity for the degradation of Rhodamine B (RhB) under solar light. Shahid et al. [50] investigated the photo catalytic degradation of methylene blue (MB) using MgFe$_2$O$_4$ under visible light irradiation. The authors reported 95 % of dye was decomposed in 50 minutes. The authors also mentioned that the photo catalytic activity increased with increase in surface area. Li et al. [51] synthesized spinel zinc ferrite nanospheres of 212 nm diameter using solvothermal route and concluded that the hydroxyl radicals played an important role in the photo catalytic reaction. Albuquerque et al. [52] explored the structural and catalytic properties of Co, Cu and Ni spinel ferrites. The authors stated that Cu ferrite had best catalytic performance in methylene blue oxidation as compared to that of other ferrites. Baldrian et al. [53] utilized magnetic mixed iron oxides (MO: Fe$_2$O$_3$; M: Fe, Co, Cu, Mn) for the decolorization of synthetic dyes. The authors reported that FeO.Fe$_2$O showed best catalytic performance. They also mentioned that fastest decomposition proceeded during the first hour of the reaction. Mahmoodi [54] carried out degradation of reactive dyes using ZnFe$_2$O$_4$ in the presence of hydrogen peroxide (H$_2$O$_2$). The authors reported that the photo degradation
rate was slow in the absence of H$_2$O$_2$. Harish et al. [55] investigated the photo-catalytic degradation of methylene blue under solar light radiation at different calcination temperatures using CdFe$_2$O$_4$ as a nano-catalyst. The authors stated that the cadmium ferrite calcined at 600$^\circ$C exhibited a high photocatalytic activity, excellent recyclability, durability properties and a good efficiency under solar light irradiation. Photo-catalytic efficiency of CuFe$_2$O$_4$ supported on clinoptilolite in the decolorization of acid red 206 aqueous solutions was investigated by Ghomi and Ashayeri [56]. Photo-catalytic degradation of the methylene blue using cubic copper ferrite powder prepared from the industrial waste has been investigated by Rashad et al. [57]. The authors mentioned that the 95.9 % of dye was degraded due to high surface area 118.4 m$^2$/g of the catalyst.

Controlled synthesis of mono-disperse CoFe$_2$O$_4$ nanoparticles by the phase transfer method and their catalytic activity on MB discoloration with H$_2$O$_2$ have been studied by Feng et al. [58]. The authors concluded that the CoFe$_2$O$_4$ nanoparticles exhibited excellent catalytic performance in the oxidation of MB dye. Sun et al. [59] reported the enhanced photo-catalytic activity of sponge–like ZnFe$_2$O$_4$ synthesized by solution combustion method. The authors concluded that the ZnFe$_2$O$_4$ showed higher photo catalytic activity for the degradation of RhB under visible light irradiation.

Various researchers have reported on dye degradation using composites of ferrites. Fu et al. [60] studied the degradation of methylene blue (MB), Rhodamine B (RhB), methyl orange (MO), active black BL-G and active red RGB under visible-light irradiation using composite of CoFe$_2$O$_4$ nanoparticles with graphene. The authors concluded that the photo activity increased which was ascribed to the reduction of graphene oxide. Nano-crystalline CoFe$_2$O$_4$ embedded on one dimensional ZnO prepared by sono-chemical route were used for the photo-catalytic degradation of phenolphthalein under UV irradiation. The authors observed enhancement of photo catalytic activity due to the formation of a hetero-junction at the interface of CoFe$_2$O$_4$ and ZnO [61]. Mishra et al. [62] synthesized CoFe$_2$O$_4$–Fe$_3$O$_4$ magnetic nano-composites (MNCs) by hydrothermal process and reported that the MNCs degrade 93% of MO in 5 hours of UV irradiation. The authors also reported that the coercivity increased from 500 Oe to 6800 Oe with decrease in temperature to 20 K. Xie et al. [63] utilized composite ZnFe$_2$O$_4$/SrFe$_{12}$O$_{19}$ for the degradation of MB and reported that more than 70% of dye was degraded when the
composite was reused for four times. Senapati et al. [64] used CoFe$_2$O$_4$-Cr$_2$O$_3$-SiO$_2$ fluorescent magnetic nanocomposite for the degradation of MB and reported that catalyst could be recycled without appreciable loss in activity.

Limited literature is available on the dye degradation using substituted ferrites. The removal of RhB by Co$_x$Fe$_{3-x}$O$_4$ magnetic nanoparticles activated Oxone was performed by Su et al. [65]. The authors reported that removal performance increased with increase in the cobalt content in the catalyst. The authors also mentioned that 80% of the dye was degraded within 60 min even after the Co$_x$Fe$_{3-x}$O$_4$ was used for the fourth time. Fan et al. [66] studied the photo-catalytic degradation of MB under visible light irritation with cobalt doped zinc ferrite (Zn$_{1-x}$Co$_x$Fe$_2$O$_4$). The authors concluded that the photo catalytic activity for the degradation of MB dye was increased with increase in cobalt concentration which was mainly attributed to decrease in band gap with increase in cobalt ion concentration. Nano-crystalline Cd$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.0, 0.3, 0.7 and 1.0) were synthesized by co precipitation method and it was found that the cadmium substitution enhanced the catalytic activity of zinc ferrite [67]. Hankare et al. [68] explored the photo catalytic degradation of Rose Bengal in visible light with Cr substituted MnFe$_2$O$_4$ ferrospinel. The authors showed that the photo catalytic activity efficiency towards degradation of Rose Bengal solution increased with increase in Cr ion concentration. Borhan et al. [69] examined the effect of Al$^{3+}$ substituted zinc ferrite on photo catalytic degradation of Orange I azo dye. The authors observed that Orange I azo dye removal efficiency was maximum when the Al$^{3+}$ and Fe$^{3+}$ were present in equimolar amounts. Various transition metal cations like Pb$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Bi$^{3+}$, Cd$^{2+}$, Mg$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ enhance the exchange capacity and rate of the reaction towards the degradation of dye [70,71].

From the above discussion it is clear that ferrites have been used in the photo catalytic degradation of textile dyes in Fenton process. However, the use of substituted spinel ferrites for the degradation of dye has been studied to a very limited extent. Therefore, through this study, an attempt has been made to explore the photo catalytic activity of different metal ion substituted Co-Cu-Zn ferrites nano ferrites for the degradation of methyl orange dye. Methyl orange, 4-[4-(dimethylamino) phenylazo]
benzene sulfonic acid, is an azo dye that forms orange crystals as shown in Fig. 5.2 and is commonly used as an acid-base indicator, due to the fact that its anion form is yellow and its acid form is red:

![Methyl orange dye structure](image)

**Fig.5.2:** (a) Structure of Methyl orange dye (MO) (b) MO dye powder.

### 5.3. History of Fenton process

The hydrogen peroxide oxidation in the presence of iron was firstly reported by Henry John Horstman Fenton in 1894 referred as “Fenton reagent” [72]. Fenton reagent is defined as a mixture of hydrogen peroxide and ferrous ions (H$_2$O$_2$+Fe$^{2+}$). The process is based on the formation of reactive oxidizing species i.e •OH, which efficiently degrade the pollutants of the wastewater stream. This reaction mechanism was proposed (with Joseph Weiss) in Professor Haber’s final paper published in 1934 [73]. The efficiency of the Fenton reaction mainly depends on H$_2$O$_2$ concentration, Fe$^{2+}$/H$_2$O$_2$ ratio, pH and reaction time. Also, initial concentration of the pollutant and its character as well as temperature, have a substantial influence on final efficiency. The Fenton reagent is used extensively because of its simplicity: the components are commonly available and there is no need for special equipment. Fenton reagent is an attractive oxidative tool for degradation of various contaminating compounds without the formation of toxic by-products because iron is very abundant and nontoxic element and hydrogen peroxide is easy to handle and environmentally safe [74]. Fenton’s process involves following steps [75]:

\[
\begin{align*}
    Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^- + OH^- \\
    Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + HOO^- + H^+ \\
    Fe^{2+} + OH^- & \rightarrow Fe^{3+} + OH^- 
\end{align*}
\]

\[
\begin{align*}
    k_1 &= 76 \, M^{-1} \, S^{-1} \\
    k_2 &= 0.02 \, M^{-1} \, S^{-1} \\
    k_3 &= 3 \times 10^8 \, M^{-1} \, S^{-1}
\end{align*}
\]
Fe(II) and Fe(III) are representative for all species present in solution in each respective oxidation state. The hydroxyl radical formed in reaction (1) can react with organic compounds by H abstraction or addition to alkenes, alkynes or aromatic rings. In technical applications, iron is usually used in much lower concentration than hydrogen peroxide (catalytic Fenton systems) in order to avoid the formation of large amounts of iron sludge. Furthermore, the scavenging of OH• by Fe(II) (Eq. (4)) is reduced when iron is applied in catalytic concentrations. Since the recycling of Fe(III)/Fe(II) by reaction (2) is several orders of magnitude slower than reaction (1), it is considered as the rate limiting step of the reaction chain in catalytic Fenton systems.

5.4. Photo-catalytic activity evaluation:

Photo-catalytic activity of all the magnetic nano-particles was evaluated by measuring the degradation of methyl orange (MO) in the aqueous solution under visible light irradiation. The experimental setup for the photo degradation experiment is shown in Scheme 1. A 400 W visible lamp was employed as light source. For each experiment, 0.05 g of photo-catalyst was dispersed in 100 ml of 10 mg/l MO aqueous solution. The pH of the dye solution was adjusted at 3 by adding sulphuric acid solution. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure the adsorption-desorption equilibrium between MO aqueous solution and the photo-catalyst. The solution was exposed to visible light under stirring after addition of 0.1 ml of 30% H₂O₂. At given time intervals, 3 ml of aliquots were withdrawn and centrifuged to remove ferrite particles. The concentration of MO in aqueous solution was determined with the help of UV-Vis spectrophotometer. Photo catalytic activity of all the prepared magnetic nanoferrites (MNPs) evaluated by degradation of MO in aqueous solution. The
absorption spectra of Co$_{0.6}$Zn$_{0.4}$Cu$_{0.2}$M$_x$Fe$_{1.8-x}$O$_4$ annealed at 1000°C was obtained using the UV-Vis spectrophotometer. The solution of methyl orange shows bands at 463 nm. The absorption peak at 463 nm decreased considerably throughout the irradiation time which indicated the degradation of MO. Percentage of the dye degraded was calculated by using equation [76]:

\[
\% \text{ degradation} = \left( \frac{C_o - C_t}{C_o} \right) \times 100
\]

where $C_o$ is initial MO concentration and $C_t$ is the concentration of MO at time $t$. Photo catalytic activity of all the ferrite compositions (Co$_{0.6}$Zn$_{0.4}$Cu$_{0.2}$M$_x$Fe$_{1.8-x}$O$_4=0.2, 0.4, 0.6$ and $0.8$) annealed at 1000 °C was also evaluated.

5.5. Result and Discussion

5.5.1. Determination of OH$^-$ radical:

To determine the formation of hydroxyl radicals (OH$^-$) in the photo catalytic reaction solution, terephthalic acid photoluminescence (TAPL) probing technique has been used. This is a very sensitive and reliable technique for the detection of hydroxyl
radicals. In this experiment, the alkaline solution of terephthalic acid (TA) (1x 10^{-4} M) in 0.1M in aqueous NaOH, having ferrite catalyst was irradiated with UV-Visible light. Sample was withdrawn from the reaction mixture after 10 min of irradiation and centrifuged to separate catalyst particles. TA reacts with OH\(^-\) to produce highly fluorescent 2-hydroxyterephthalic acid. As shown in Fig.5.3 the product of TA hydroxylation gave a peak at 425 nm with excitation at a wavelength of 315 nm monitored using Perkin Elmer LS 55 Fluorescence Spectrometer. The intensity of the PL signal at 425 nm of 2-hydroxyterephthalic acid was in proportion to the amount of hydroxyl radicals produced in water.

Fig. 5.3: Fluorescence spectra of Co_{0.6}Zn_{0.4}Cu_{0.2}Mn_{0.8}Fe_{1.0}O_4 (a) Terephthalic acid and (b) 2-hydroxyterephthalic acid.

5.5.2. Control experiments

Fig.5.4 illustrates the data of different control experiments in the presence of nanoferrites samples annealed at 1000 °C for 2h.
Fig. 5.4: Control experiments for the degradation of MO in the presence of typical Co$_{0.6}$Zn$_{0.4}$Cu$_{0.2}$Mn$_{0.8}$Fe$_{1.0}$O$_4$ ferrite. The reaction conditions are (a) MO+light (b) MO+H$_2$O$_2$+dark (c) MO+H$_2$O$_2$+light (d) MO +ferrite+dark (e) MO +ferrite+light (f) MO +ferrite+H$_2$O$_2$+dark (g) MO +ferrite+H$_2$O$_2$+light.

From the graphs it is clear that negligible dye was degraded both in a direct photolytic process under mercury lamp as well as in the absence of ferrite (MO + H$_2$O$_2$ only). The dye degradation efficiency was very less even in the absence of H$_2$O$_2$ (MO + ferrite only) both in dark and under light. The removal efficiency was enhanced when Fenton’s reagent was generated. However the rate of reaction was significantly enhanced to 99% when reaction was done in the presence of light. Similar trend was found for all the other substituted nano ferrites.

5.5.3. CATALYTIC ACTIVITY OF SUBSTITUTED COBALT ZINC FERRITES:

(i) Catalysis by chromium substituted Co-Cu-Zn ferrite (Co$_{0.6}$Zn$_{0.4}$Cu$_{0.2}$Cr$_x$Fe$_{1.8-x}$O$_4$=0.2, 0.4, 0.6 and 0.8) annealed at 1000 °C
The catalytic activity of chromium substituted Co-Cu-Zn ferrite is shown in Fig. 5.5.

From the Fig. 5.5 it can be concluded that the dye degradation increased with increase in chromium concentration and follows the order $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Cr}_{x}\text{Fe}_{1.8-x}\text{O}_4 > \text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Cr}_{0.6}\text{Fe}_{1.8-x}\text{O}_4 > \text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Cr}_{0.4}\text{Fe}_{1.8-x}\text{O}_4 > \text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Cr}_{0.2}\text{Fe}_{1.8-x}\text{O}_4$. With the substitution of Fe$^{3+}$ with Cr$^{3+}$ in cobalt-zinc ferrite, the surface barrier becomes higher and the space charge region becomes narrower. This variation occurred because Fe$^{3+}$ ions substitution by Cr$^{3+}$ ions limits the Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ electronic exchange, thus a variable number of electron exchanges are free to interact with the large electrical field. This increases the probability that electrons reach the surface barrier, resulting in a decrease in the space charge polarization. The electron hole pairs within the region are
efficiently separated by the large electric field before recombination which led to the higher photo catalytic activity [77]. As indicated by the previous research [78], the positive effect of Cr originates from the substitution of Cr$^{3+}$ in octahedral sites that can decompose H$_2$O$_2$ to create \textquoteleft OH and improve the electron transfer to produce Fe$^{2+}$ during the reaction, thus improve the degradation.

(ii) Catalysis by manganese substituted Cobalt zinc ferrite

\textit{(Co$_{0.6}$Zn$_{0.4}$Cu$_{0.2}$Mn$_x$Fe$_{1.8}$O$_4$)=0.2, 0.4, 0.6 and 0.8) annealed at 1000 °C}

The dye degradation activity of MO dye with Mn$^{3+}$ substitution Co-Cu-Zn ferrite is shown in Fig. 5.6. From the Fig. 5.6 it was observed that the manganese substituted cobalt zinc nano ferrites exhibited a larger catalytic activity as compared to other substituted nano ferrite samples.

Fig. 5.6: Change in absorption with time of methyl orange solution in the presence of Co$_{0.6}$Zn$_{0.4}$Cu$_{0.2}$Mn$_x$Fe$_{1.8}$O$_4$ annealed at1000 °C.
The catalytic activity increased with increase in manganese substitution. The increase might be attributed to the ability of manganese to itself participate in the cyclic electron transfer process. In the case of Mn$^{3+}$ ion substituted compounds, the dye was completely degraded in 40 min. The Mn$^{3+}$ ions also have octahedral site preference. Costa et al. [79] reported that species at the octahedral site in the magnetite strongly affects the reactivity towards H$_2$O$_2$. Other reason of dye degradation is that Mn$^{3+}$ ion (1.51V) has higher reduction potential as compared to that of Fe$^{3+}$ ions (0.77V) which endorse the reduction of Mn$^{3+}$ ions and produce Mn$^{2+}$ ions which again continue the catalytic cycle of H$_2$O$_2$ decomposition. Similar results were reported by Sahoo et al. [80]. The authors concluded that the mesoporous MnFe$_2$O$_4$ nano composites was a useful catalyst for the MO dye degradation. Doping of the manganese and iron ions into TiO$_2$ nanoparticles significantly enhanced the overall photo catalytic activity for MB degradation under visible light irradiation as reported by Zhang and Zeng [81].

(iii) **Catalysis by cobalt substituted Cobalt zinc ferrite (Co$_{0.6}$Zn$_{0.4}$Cu$_{0.2}$Co$_x$Fe$_{1.8-x}$O$_4=0.2, 0.4, 0.6 and 0.8) annealed at 1000 °C**

Photo catalytic activity of cobalt substituted cobalt zinc ferrite samples annealed at 1000 °C is shown in Fig. 5.7. The increase in the catalytic activity with increasing concentration of Co$^{3+}$ ion may be attributed to the substitution of trivalent iron ions with divalent cobalt ions in the octahedral site, which might have led to the development of oxygen vacancies on the surface of catalyst, thereby, increasing their degradation capacity. Cobalt preference for the octahedral B site was also reported earlier [82].
Fig. 5.7: Change in absorption with time of methyl orange solution in the presence of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Co}_x\text{Fe}_{1.8-x}\text{O}_4$ annealed at 1000 °C.

(iv) Catalysis by Zinc substituted Cobalt zinc ferrite ($\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_{1.8-x}\text{O}_4$ = 0.2, 0.4, 0.6 and 0.8) annealed at 1000 °C

Photo catalytic activity of Zn substituted Co-Cu-Zn ferrite compositions ($\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_{1.8-x}\text{O}_4$ = 0.2, 0.4, 0.6 and 0.8) annealed at 1000 °C was also evaluated and change in absorption spectra with time after one hour is exemplified in Fig 5.8. Zinc ion has both tetrahedral and octahedral site preference [83,84]. The increase in the catalytic activity with increasing concentration of substituent ion may be attributed to the substitution of trivalent iron ions with divalent zinc ions, which might have led to the
development of oxygen vacancies on the surface of catalyst, thereby, increasing their degradation capacity [85].

Fig. 5.8: Change in absorption with time of methyl orange solution in the presence of Co_{0.6}Zn_{0.4}Cu_{0.2}Zn_xFe_{1.8-x}O_4 annealed at 1000 °C

(v) Catalysis by Nickel substituted Cobalt zinc ferrite (Co_{0.6}Zn_{0.4}Cu_{0.2}Ni_xFe_{1.8-x}O_4 with x=0.2, 0.4, 0.6 and 0.8) annealed at 1000 °C

The effect of nickel metal ion substituted Co-Cu-Zn nano ferrites on the dye degradation was shown in Fig. 5.9. It is clear from Fig. 5.8 the photo-catalytic activity was best for the Co_{0.6}Zn_{0.4}Cu_{0.2}Ni_{0.2}Fe_{1.6}O_4 composition where Fe:Ni ratio is maximum and thereafter it decreases with further decreased in this ratio. Similar results were reported by Pawar et al. [86] in the Sr_xCa_{1-x}Fe_2O_4 (0.0 ≤ x ≤ 1.0) composition.
Fig. 5.9: Change in absorption with time of methyl orange solution in the presence of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Ni}_{x}\text{Fe}_{1.8-x}\text{O}_4$ annealed at 1000 °C

5.5.4. Mechanism of degradation of dye using ferrites

On the basis of the experimental results and literature [87] the photo-catalytic degradation mechanism of dyes by the $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{M}_{x}\text{Fe}_{1.8-x}\text{O}_4$ under visible light irradiation was proposed, as show in scheme 2 and equations (10-14).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^- \quad (10)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^- + H^+ \quad (11)$$

Step-1: Photo-excitation of semiconductor valence band electron creating hole ($h^+$) and free electron ($e^-$)

$$\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{M}_{x}\text{Fe}_{1.8-x}\text{O}_4 + h\nu \rightarrow \text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{M}_{x}\text{Fe}_{2-x}\text{O}_4(e^-_{cb} + h^+_{vb}) \quad (12)$$
Step-2: Formation of HO• radicals by the reaction of valence band hole (h^+VB) with adsorbed H_2O or HO^– ions:

\[ Co_{0.6}Zn_{0.4}Cu_{0.2}Mn_xFe_{1.8-x}O_4(h^+_{vb}) + H_2O \rightarrow H^+ + OH^– \] (13)

\[ Co_{0.6}Zn_{0.4}Cu_{0.2}Mn_xFe_{1.8-x}O_4(h^+_{vb}) + OH^- \rightarrow OH^• \] (14)

Step-3: Degradation of substrate (MO dye) of valence band hole (h^+) or by HO• radical h^+

\[ OH^–, HO_2, O_2^-, h^+_{vb} + MO \rightarrow \text{degradation product} \]

Scheme 2: Schematic representation of mechanism of nano ferrite as photo catalyst

5.5.5. Chemical Kinetics

Fig.5.10 shows that the linear relationship between ln(C_0/C_t) and irradiation time, suggesting a pseudo first order reaction for typical Co_{0.6}Zn_{0.4}Cu_{0.2}Mn_{0.8}Fe_{1.0}O_4
composition. Similar behavior was observed for all other compositions of frites. The rate constant for dye degradation can be calculated using Langmuir-Hinshelwood model [78].

\[
\ln \left( \frac{C_0}{C_t} \right) = kt
\]  

(15)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5_10.png}
\caption{Typical Plot of $\ln \frac{C_0}{C_t}$ vs. irradiation time for photo catalytic degradation of MO.}
\end{figure}

The calculated rate constant values of all the compositions of ferrites are given in Table 5.1. The collective effect of all the metal ions substitutes was shown in Fig. 5.11. It is clear from Table 5.1 and Fig.5.11 that the rate constant values enhanced with increase in all metal ion concentration except nickel. Among all the metals the best catalytic results were obtained in case of Mn. However in the case of nickel substituted Co-Cu-Zn nano ferrite the catalytic activity was maximum at $x = 0.2$ concentration. Thereafter a decrease in rate constant was observed as discussed earlier also.
Table 5.1: First order rate constant, $k$ (min$^{-1}$) for the degradation of MO dye by substituted Cobalt Zinc ferrites, $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{M}_x\text{Fe}_{1.8-x}\text{O}_4$ annealed at 1000 °C

<table>
<thead>
<tr>
<th>Ferrite composition</th>
<th>$x$</th>
<th>$k$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}<em>{0.6}\text{Zn}</em>{0.4}\text{Cu}_{0.2}\text{Cr}<em>x\text{Fe}</em>{1.8-x}\text{O}_4$</td>
<td>0.2</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.021</td>
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<td>0.8</td>
<td>0.045</td>
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<td>$\text{Co}<em>{0.6}\text{Zn}</em>{0.4}\text{Cu}_{0.2}\text{Mn}<em>x\text{Fe}</em>{1.8-x}\text{O}_4$</td>
<td>0.2</td>
<td>0.037</td>
</tr>
<tr>
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<td>0.100</td>
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<tr>
<td></td>
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<td>0.123</td>
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<tr>
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<td>0.213</td>
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<tr>
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<tr>
<td>$\text{Co}<em>{0.6}\text{Zn}</em>{0.4}\text{Cu}_{0.2}\text{Zn}<em>x\text{Fe}</em>{1.8-x}\text{O}_4$</td>
<td>0.2</td>
<td>0.027</td>
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<tr>
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<td>0.4</td>
<td>0.037</td>
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<tr>
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<td>0.056</td>
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<tr>
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<td>0.8</td>
<td>0.061</td>
</tr>
<tr>
<td>$\text{Co}<em>{0.6}\text{Zn}</em>{0.4}\text{Cu}_{0.2}\text{Ni}<em>x\text{Fe}</em>{1.8-x}\text{O}_4$</td>
<td>0.2</td>
<td>0.107</td>
</tr>
<tr>
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<tr>
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<td>0.006</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.004</td>
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Fig. 5.11: Plots of rate constant with metal ion concentration in cobalt zinc ferrites
for photo catalytic degradation of MO.

5.6. RECYCLABILITY AND MAGNETICALLY SEPARABLITY

One of the commendable advantages of using ferrites as heterogeneous catalysts is the easy magnetic separation, which establishes the stability of the catalyst over various catalytic runs. For executing the recyclability experiment the catalyst was separated using a magnet after the completion of the photo catalytic reaction. In order to test the stability and long-term use of ferrites as heterogeneous photo-Fenton catalysts, the same sample was reused four times after separation as shown in Fig.5.12. All the ferrites presented stable catalytic behavior without any significant loss in degradation efficiency even after four cycles. Thus the results illustrated ferrites to be stable magnetically separable heterogeneous photo-Fenton catalysts with potential application in the long-term process of waste water treatment. The magnetic separation of all the catalyst was after the reaction is shown in Fig.5.13.
Fig. 5.12: Recyclability of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{Cr}_{0.8}\text{Fe}_{1.0}\text{O}_4$ photo catalyst for the degradation of MO for 4 cycles.
5.7 CONCLUSIONS

In the present investigation, the photo catalytic activity of \((\text{Co}_{0.6}\text{Zn}_{0.4}\text{Cu}_{0.2}\text{M}_x\text{Fe}_{1.8-x}\text{O}_4=0.2, 0.4, 0.6 \text{ and } 0.8)\) annealed at 1000 °C was also evaluated. The organic pollutant chosen for the photo catalytic activity is methyl orange. The following conclusions were drawn from the experimental investigations:

- The generation of hydroxyl radicals was confirmed by the Terephthalic acid Photoluminescence probing technique.
- The catalytic efficiency was increase with increasing \(\text{Cr}^{3+}, \text{Mn}^{3+}, \text{Co}^{3+} \text{and } \text{Zn}^{2+}\) concentration of substituent ions. This was attributed to the increase in the concentration of catalytically active ions in the octahedral sites of the ferrite lattice, redox potential and the presence of defects on the surface of catalyst.
- However, in the case of nickel substituted cobalt zinc ferrites shown exceptional behavior. The catalytic activity was found to be maximum at \(x =0.2\) and thereafter it decreases with increase in nickel substitution. The maximum photo catalytic activity is observed where the Ni:Fe ratio is maximum.
- Among all the metal substituted cobalt zinc ferrites \(\text{Mn}\) substituted nano ferrites show highest catalytic activity with the rate constant of as high as 0.213 min\(^{-1}\) as compared that of other metal substituted cobalt zinc nano ferrite.
The catalytic was recovered using magnet and reused four times without any significant loss in their catalytic activity.

All the ferrites are magnetically separable and reused many times. By virtue of these properties of all the ferrites compositions, especially manganese substituted Co-Cu-Zn ferrites can be used for the degradation of textile dyes and other organic pollutants.