https://doi.org/10.36375/prepare_u.iiche.a372

# Synthesis and applications of magnetic nanoparticles in the ultrasound assisted oxidative degradation of methylene blue

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## Abstract:

In this paper, catalytic behaviours of magnetite ($Fe_3O_4$), Ni- and Zn-doped $Fe_3O_4$ in the ultrasound assisted oxidative degradation of methylene blue from water were presented. Magnetic nanoparticles were synthesized from aqueous solutions of chloride salts of Fe(III), Ni(II) and Zn(II) by co-precipitation method and characterized by X-ray crystallographic, scanning electron microscopic (SEM) and Fourier transform infrared (FTIR) spectroscopic methods. Synthesized nanoparticles were then used as heterogeneous catalysts in the $H_2O_2$ based oxidative degradation of aqueous methylene blue solution at room temperature under mild ultrasound assisted reaction conditions. Instrumental results indicate the formations of round-shaped nanostructured particles with particle size <20 nm. Results also reveal that the synthesised $Fe_3O_4$ nanoparticles can remove as much as 82.51% of total methylene blue dye present in 36 ppm solution after 30 minutes reaction time. Doping Zn and Ni enhances the catalytic activity of $Fe_3O_4$ nanoparticles and maximum amounts of dye degradation (98.04% in 30 minutes) is observed for Zn-doped nanoparticles. Pseudo first order kinetic model can efficiently explain the decomposition of methylene blue from its solutions. Decomposition rate of methylene blue is observed to be maximum for the 0.2g/L catalyst dose. Additionally, catalytic dye degradation results are also discussed considering the Fenton type reaction mechanism.

Keywords: Metal-doped magnetite, Heterogeneous catalyst, Methylene blue degradation, Sono-Fenton process, Rate constant.

## Introduction:

Dyes are essential in various types of industries such as textile, paint, ink, plastics and cosmetics[1]. However, organic dyes are normally toxic in nature and therefore several methods are used to treat dye containing wastewaters before their disposal. Methods such as advanced oxidation processes, combined anaerobic-aerobic biological treatment, catalytic degradation and adsorption using suitable adsorbents are usually applied to remove dyes from wastewaters[1]. Fenton reaction is a cost effective advanced oxidation process, which has vast applications in the treatment of different hazardous wastes and wastewaters[2]. In the process, reaction of hydrogen peroxide with $Fe^{2+}$ generates highly reactive hydroxyl radicals, which have the ability to degrade various toxic organic substances present in waste materials. However, the use of $Fe^{2+}$-$H_2O_2$ solution as homogeneous catalyst in wastewater treatment has some drawbacks such as the precipitations of $Fe(OH)_3$ due to the various reasons such as ineffective pH control, separation of catalyst at the end of the process[3]. As an alternative, heterogeneous Fenton reaction by combining $H_2O_2$ with different iron minerals is considered for the degradations of organic materials present in such wastes[4]. Magnetite ($Fe_3O_4$) is a common and low-cost iron oxide mineral, which has several important applications, one of them is catalytic[5]. The $Fe^{2+}/Fe^{3+}$ redox couple present in magnetite favours the continuous formations of reactive hydroxyl radicals and therefore enhances the efficiency of Fenton reaction. Effectiveness of the Fenton process is also dependent on the particle shape of iron particles and pH of the solution[6]. Recently, magnetite nanoparticles doped with various catalytically active metals are used in Fenton reaction to degrade various relatively stable organic contaminants present in wastewaters[5]. These modifications improve the efficiency of Fenton reaction many folds. However, catalyst deactivation as well as low catalytic activity are the major hurdles for using the magnetite as catalyst in wastewater treatment.

Ultrasonic (US) methods can also generate reactive hydroxyl radicals from water and therefore effective in the degradations of some special type of organic contaminants[7]. However, US method alone is not effective in the degradation of refractory organic compounds such as non-volatile organic dyes[8]. Therefore, US method is often combined with Fenton reaction (Sono-Fenton process) to decompose a wide range of toxic organic contaminants present in wastewaters and other wastes[9]. A literature survey on the topic indicates that a very few numbers of works have been done on the use of Sono-Fenton process in presence of metal doped magnetite nanoparticles in the organic dye containing wastewater treatments. In this investigation, therefore, magnetite and Ni- and Zn-doped magnetite nanoparticles are used as catalysts in the ultrasonic oxidative removal of methylene blue from its aqueous solution.

## Materials and methods:

### *2.1 Synthesis of $Fe_3O_4$ and Ni/Zn-doped $Fe_3O_4$ by co-precipitation method*

To synthesize magnetite nanoparticles, anhydrous ferric chloride was used as the sources of $Fe^{2+}$ and $Fe^{3+}$ ions and stoichiometric amounts of potassium iodide as reductant[10]. This synthetic method consists of a few successive steps, which includes mixing of aqueous solutions of $FeCl_3$ and potassium iodide in the molar ratio of 3:1, precipitation and separation of iodine, hydrolysis of the filtrate containing $Fe^{2+}$ and $Fe^{3+}$ ions by 25% ammonia solution, separation of precipitated magnetite particles by centrifugation and filtration techniques, washing of magnetic particles by ammonium acetate solution and drying of magnetic particles in an oven at 250°C for 2 hours. Similar procedures were also adopted to synthesize 10% Ni- and Zn-doped magnetite particles by using nickel chloride hexahydrate and anhydrous zinc chloride as precursors, respectively.

### *2.2 Characterization of magnetic particles*

Fourier transform infrared (FTIR) spectra of doped and undoped $Fe_3O_4$ nanoparticles were taken by a Perkin Elmer spectrophotometer, model Spectrum 100. The spectra were recorded in the 4000 – 400 $cm^{-1}$ wave number range. For recording the good quality spectra, resolution was set to 4 $cm^{-1}$. The spectra were recorded by using standard KBr pellet method. For preparing KBr pellets, about 9 mg of spectroscopic grade KBr powder were mixed carefully with about 3 mg of oven dried magnetic nanoparticles in an agate mortar. The scanning electron micrographs of magnetic nanoparticles were recorded by a Carl Zeiss –Sigma series field emission scanning electron microscope. For preparing the samples for microscopic observations, magnetic nanoparticles were initially scattered on a carbon paper located on aluminium stubs followed by gold coating. The X-ray diffraction patterns of magnetic nanoparticles were recorded by using a X-ray diffractometer, model, D8 Focus, Bruker AXS, Germany. The patterns were recorded with Cu $K_\alpha$ radiation ($\lambda$=1.5405 Å) in the scan range of 10-70° 2θ with a scan speed of 4° per minutes.

### *2.3 Ultrasound assisted removal of methylene blue from water*

The effects of magnetite and metal doped magnetite on the sonochemical oxidative degradation of methylene blue (MB) from aqueous solution was investigated by using an ultrasonic bath (100 W, 40 kHz). Initial concentrations of MB in the solution was 36 ppm, which was prepared by dissolving accurately weighed 0.018 g of powdered MB in 500 ml distilled deionized water. The catalyst doses considered in this investigation were 0.1, 0.2, and 0.5g/L with respect to the volume of MB solution. In each of the prepared solutions, 2ml $H_2O_2$ (30%, reagent grade) was added as an oxidant. Methylene blue decomposition reaction was conducted at room temperature (i.e., at 25°C). After predefined time intervals, the concentrations of MB in the reaction mixtures were determining by measuring the absorbance at 665 nm wavelength. The experimental results reported in this investigation are the average results of three equivalent measurements. Amounts of MB removed at a particular time intervals and corresponding percentages removal of MB from different solutions were determined by using following equations:

$$\text{Amount removed (mg/L)} = C_o - C_t \qquad (1)$$

$$\text{Percentage removal (\%)} = \frac{C_o - C_t}{C_o} \times 100\ \% \qquad (2)$$

In eqns. (1) and (2), $C_o$ and $C_t$ represent the concentrations of MB in solution at the initial and at any time, t respectively. The rate constants (k) of the degradation processes were then evaluated by equation (3):

$$\ln (C_o/C_t) = k.t \qquad (3)$$

Here, k is first order rate constant in $min^{-1}$. Thus a plot of ln $(C_o/C_t)$ vs. t (time in minutes) will give a straight line, which will pass through the origin of the graph. The k value of a catalytic decomposition process can therefore be determined from the gradient of the linear plot.

## Results and Discussions:

### *3.1 Characterization of catalysts by FTIR analysis*

Fig. 1 depicts the FTIR spectra of various magnetic nanoparticles. Assignments of various spectral bands are also presented in Table 1.

The vibrational bands observed at 634(s), 565 (s), 447 (m) $cm^{-1}$ in the FTIR spectra of magnetic particles are the characteristic bands of spinel structured magnetite[10, 11]. The intense band appears at 564 $cm^{-1}$ could be assigned to the $T_{1u}$ symmetric vibration mode of the $Fe^{2+}–O^{2-}$ functional group. The doublet bands appear around 634 $cm^{-1}$ are due to symmetry degeneration on octahedral B sites of spinel structured $Fe_3O_4$ crystals[11]. The octahedral iron sites of synthesised spinel structured doped and undoped $Fe_3O_4$ particles also exhibit a band near 447 $cm^{-1}$ due to the Fe-O stretching vibration. The bands appear in the range of 1000-1200 $cm^{-1}$ can be assigned as the symmetric and asymmetric stretching vibrations of O-C=O fragment, respectively[12]. The two moderately strong bands observed at 2924 and 2853 $cm^{-1}$ wavenumbers can be assigned as the asymmetric band of methylene group. These bands also indicate that some amounts of organic species are deposited on the surface of magnetite particles during washing.

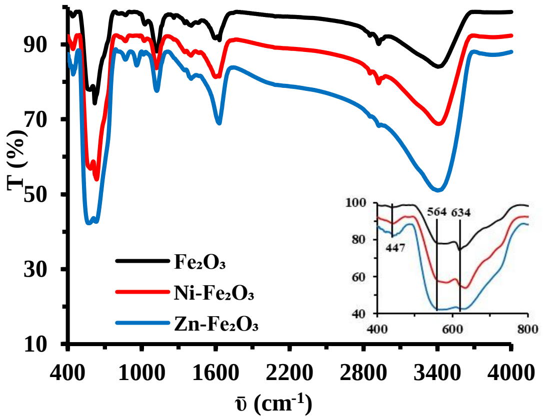


Fig. 1. FTIR patterns of magnetic particles.

The absorption bands appear in the 877 - 1020 $cm^{-1}$ wavenumber range can be assigned as the bending vibrations associated to OH group. For strong hydrogen bridges, its maximum lies at observed range of wave number. The peak appears at 1621 $cm^{-1}$ can be assigned as Fe-O vibration of iron minerals and/or the bending vibrations of surface adsorbed water molecules. Similarly, the broad band with absorption maximum at about 3388 $cm^{-1}$ is the characteristic band of OH stretching vibration, which may indicates the presence of small amounts of ferric hydroxides and goethite (FeOOH) with the magnetic nanoparticles and/or the surface adsorbed water molecules of the magnetic nanoparticles. Thus, the results reveals that some amounts of iron hydroxides are precipitated on the surfaces of $Fe_3O_4$ particles due to the reaction between the $Fe^{3+}$ and $OH^-$ ions during hydrolysis. For example, the formation of FeOOH from $Fe^{3+}$ and $OH^-$ ions in oxidizing condition can be represented by the following chemical reaction scheme:

$$Fe^{3+} + OH^- + 1/2O_2 \rightarrow FeOOH \qquad (RS1)$$

The doping of Ni and Zn into $Fe_3O_4$ slightly shifts the band observed at 564 $cm^{-1}$ to higher frequency, which indicates that added divalent zinc and nickel cations occupy the tetrahedral sites of $Fe_3O_4$ crystals. Consequently, the band appears at 447 $cm^{-1}$ shifted to higher frequency (around 465 $cm^{-1}$) and become intense and broad in Ni- and Zn-doped magnetite molecules.

Table 1: Assignments of FTIR bands.

| Frequency ($cm^{-1}$) | Type of vibrations | Functional groups or components |
|---|---|---|
| 3390 | O-H stretching | Surface water or Surface OH groups of iron hydroxides such as $Fe(OH)_3$, goethite (FeOOH). |
| 2924, 2853 | -$CH_2$ stretching | Acetic anhydride and its derivatives |
| 1626 | H-O-H, bending<br>Fe-O | Surface adsorbed water;<br>Magnetite |
| 1402 | Fe-O stretching | Magnetite |
| 1121 | -CO stretching | Acetic anhydride and its derivatives |
| 877- 1020 | O-H bending | FeOOH and $Fe(OH)_3$ |
| 635 | Fe-O stretching | Magnetite |
| 564 | Fe-O stretching | Magnetite |
| 447 | Fe-O vibrations | Magnetite, $Fe_2O_3$ |

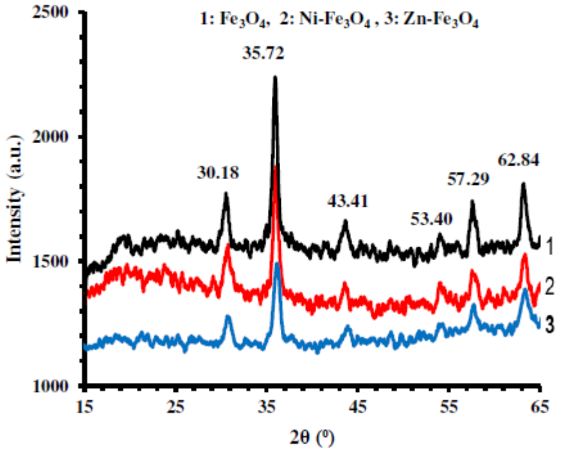


Fig. 2. XRD patterns of magnetic particles.

Fig. 2 shows the XRD patterns of various magnetic particles. X-ray diffraction patterns of all the samples exhibit strong peaks at 2θ = 30.18°, 35.72°, 43.41°, 53.40°, 57.29° and 62.84°, which correspond to the (220), (311), (400), (422), (511) and (440) reflection planes of highly crystalline cubic spinel structured magnetite ($Fe_3O_4$) particles (JCPDS No.: 880315). The relatively broad and weak intensity peaks appeared in the XRD pattern of magnetite indicate that the sizes of $Fe_3O_4$ particles are in the nanometre range. The XRD patterns of Ni- and Zn-doped magnetite show the shifting of the band positions of two major peaks appeared at 2θ = 30.18° and 35.72° to higher frequencies, which indicates that the crystal sites of $Fe_3O_4$ are occupied by Ni(II) and Zn(II) ions.

Scherrer’s equation was also used to estimate the crystal sizes of magnetic particles. The equation is based on the principle that the small crystallites exhibit wide diffraction peaks. Scherrer’s equation can be expressed as:

$$D_N = \frac{k \times \lambda}{\beta \times Cos\theta} \qquad (4)$$

Here, $D_N$ is mean size of crystals, k is known as shape function, $\lambda$ is wavelength of incident radiation in angstrom, $\beta$ is full width at half maximum (FWHM) in radian and $\theta$ is Bragg’s angle in radian. The FWHM values of magnetic particles are determined from the peak appear at $2\theta = \sim 35.72°$. The FWHM is determined by using Origin software and the peak is non-linearly fitted using Gaussian function. The $\lambda$ value for this investigation is 1.5405 Å since Cu $K_\alpha$ radiation was used to record the XRD patterns. It is assumed that the particles of $Fe_3O_4$ are spherical in nature and therefore k value is taken as 0.94. The mean crystal sizes of $Fe_3O_4$, Ni-$Fe_3O_4$, and Zn-$Fe_3O_4$ are calculated as 14.56, 14.32 and 11.64 nm respectively and well within the range reported for $Fe_3O_4$ synthesized by various methods$^{13}$.

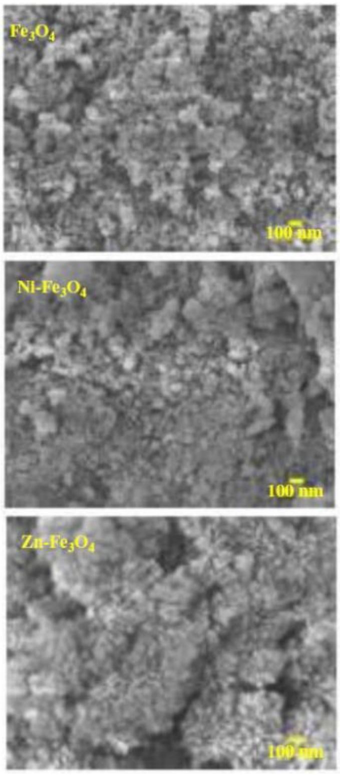
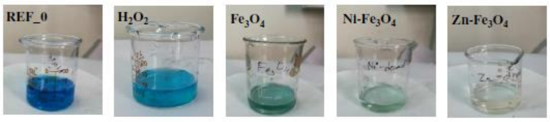


Fig. 3. Scanning electron micrographs of magnetic particles.

Fig. 3 shows the scanning electron micrographs of $Fe_3O_4$, Ni-$Fe_3O_4$, and Zn-$Fe_3O_4$. All the micrographs show that the magnetic particles are spheroid shaped with the evidence of agglomeration taking place in some places. The observed agglomeration is a characteristic feature of magnetic nanoparticles due to the interactions of individual magnetic particles. A rough measurement indicates that the size of the particles is below 20 nm, which is in accordance with the crystal sizes measured by X-ray crystallography.

### *3.2. Removal of dye*

In order to assess the catalytic activities of magnetic nanoparticles, removal of methylene blue (MB) dye from its aqueous solution during ultrasonic treatment were investigated. The solutions collected after 30 minutes of ultrasonic treatment time along with the original (Ref_0) are presented in Fig. 4. Results indicate that the colour of the solutions declines after 30 minutes reaction time due to the degradations of MB in applied reaction conditions. From the Fig., it is observed that the decomposition of MB by $H_2O_2$ under applied treatment condition is insignificant. Colours of the MB solution obtained after $Fe_3O_4$ treatment indicate significant degradation of MB under applied reaction condition. Results also reveal that the catalytic performance of magnetite is significantly enhanced when $Fe_3O_4$ is doped with Ni (II) and Zn (II) ions. It is observed that the solution collected after 30 minutes of reaction time becomes almost colourless when Zn-doped magnetite is used as a catalyst in applied experimental conditions.



Ref_0 $H_2O_2$ $Fe_3O_4$ Ni-$Fe_3O_4$ Zn-$Fe_3O_4$

Fig. 4. Colour of the MB solutions (Ref_0) and after 30 minutes of ultrasonic treatment (magnetic particle amount: 0.2 g/L).

Decomposition of methylene blue (MB) is highly dependent on several reaction parameters. Catalyst dose, shape of magnetite particles, dye concentrations, amount of $H_2O_2$ added, ultrasonic radiation frequency, temperature and pH are some major parameters that affect the dye removal performance. It was reported earlier that the maximum degradation of MB was observed when the pH of the dye solution was kept around 3. However, rate of degradation of MB decreases quickly with increasing pH$^6$. Similarly, at higher catalyst dose, the catalytic activity of magnetite decreases due to agglomeration$^6$.

Amount of MB decomposes during ultrasonic treatment at three different catalyst concentrations are presented in Fig. 5. Sonochemical decompositions of methylene blue in presence of $H_2O_2$ was a slow process and about 54.7 % MB are removed from the solution after 30 minutes reaction time. It is observed that the addition of magnetic particles as catalysts significantly increases the MB degradation amounts with increasing reaction time.

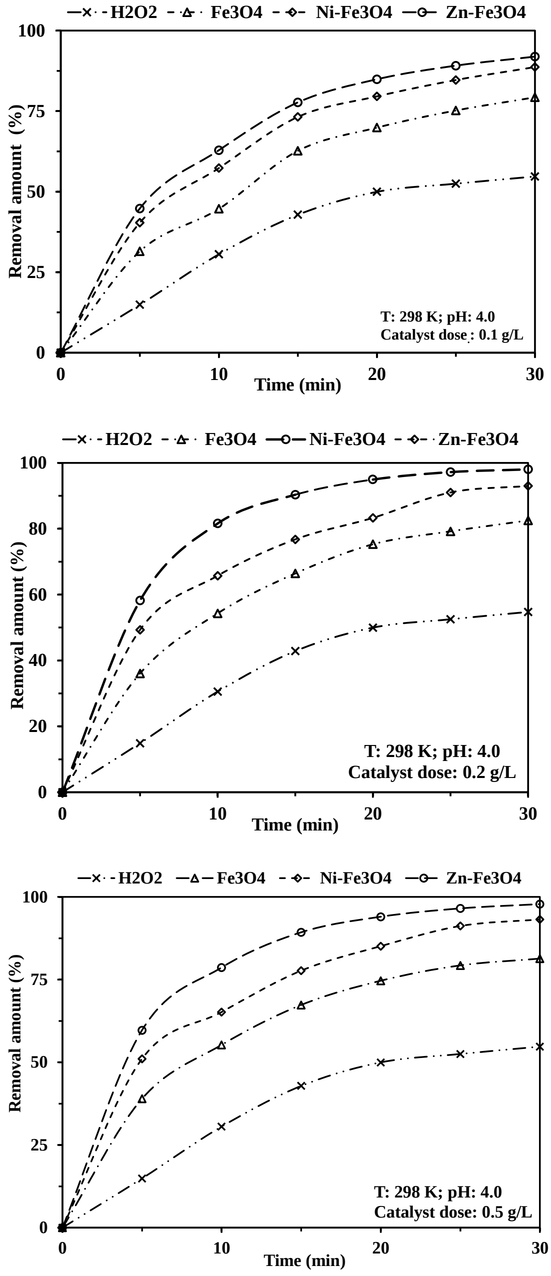


Fig. 5. Methylene blue removal amounts (%) at different sonication time.

Irrespective of catalyst types, maximum amounts of MB decomposition was observed when 0.2 g/L catalyst was added into the dye solution. At this catalyst dose, the amounts of MB removed from the solutions for magnetite, Ni- doped magnetite and Zn-doped magnetite after 30 minutes degradation time are 82.51, 92.97 and 98.04%, respectively. On the other hand, amounts of MB removed from the solutions for 0.5% catalyst dose are 81.35, 93.20 and 97.81% for magnetite, Ni- doped magnetite and Zn-doped magnetite, respectively. Therefore, our results clearly indicate that the 0.2% catalyst dose is optimum catalyst amounts for the sonochemical removal of MB from solution in applied experimental conditions.

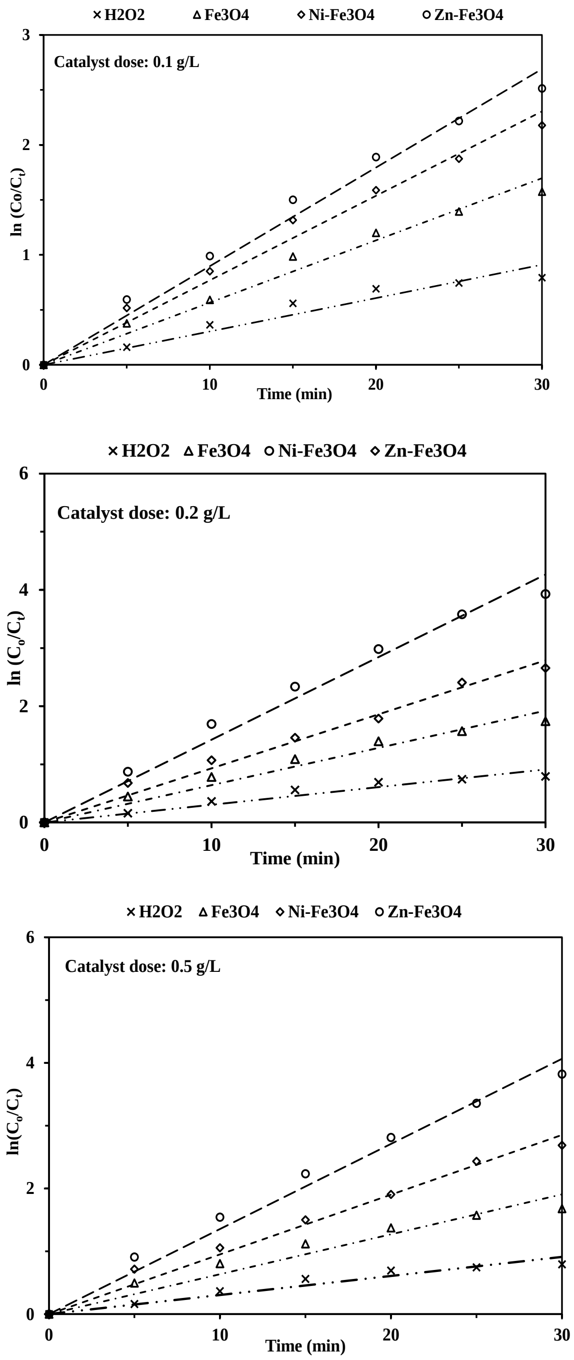


Fig. 6. Linear variation of ln (Co/Ct) versus sonication time for sonocatalytic degradation of methylene blue (MB) dye present in aqueous solution by $H_2O_2$ and ($H_2O_2$+magnetic nanoparticles).

First order linear plots of ln ($C_t/C_o$) as a function of ultrasonic treatment time for non-catalytic and magnetic particles catalysed decomposition processes are presented in Fig. 6. The correlation coefficient ($R^2$ values) of all the linear plots are in the range of 0.93-0.98. The large $R^2$-values obtained in this investigation allow us to determine the rate constants of the catalytic and non-catalytic MB decomposition processes.

Rate constants as determined by eqn. 3 are presented in Fig. 7. The first order rate constants for reference oxidative treatment process ($H_2O_2$ as oxidant) is 0.0304 $min^{-1}$. Rate constants for the $Fe_3O_4$ catalysed processes are 0.0566, 0.0642 and 0.0635 $min^{-1}$ at the 0.1, 0.2 and 0.5 g/L catalyst doses, respectively. Similar values for Zn-$Fe_3O_4$ catalysed oxidative processes are respectively 0.897, 0.1422 and 0.1355 $min^{-1}$ and for Ni-$Fe_3O_4$ catalysed samples, these values are 0.0768, 0.0930 and 0.0950 $min^{-1}$ respectively. These values indicate that Zn-doped $Fe_3O_4$ has the highest catalytic activity, which is maximum at 0.2 g/L catalyst dose. At this dose, the process is more than fourfold efficient than the hydrogen peroxide based ultrasonic oxidative treatment process.

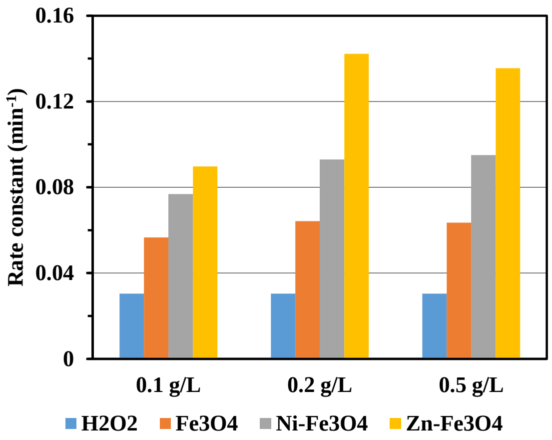


Fig. 7. First order rate constants of the catalytic methylene blue decomposition processes.

It was reported earlier that the use of only $H_2O_2$ as catalyst did not have any significant effect on the sonochemical degradation of MB solution[14]. However, the uses of $Fe^{2+}$ ions with $H_2O_2$ can enhance catalytic performance due to the generation of hydroxyl radicals (•OH). Presence of $Fe^{3+}$ ions in the solution further enhances the degradation of MB by forming more amounts of hydroxyl radicals and $Fe^{2+}$ ions:

$$Fe^{3+} + H_2O_2 + h\nu \rightarrow Fe^{2+} + 2(\bullet OH) \qquad \text{(RS2)}$$

Additionally, de-agglomeration of magnetic nanoparticles due to ultrasound induced acoustic cavitation exposes more catalytically active surfaces, which also enhances the productions of more amounts of hydroxyl radicals[9]. Doping of $Ni^{2+}$ and $Zn^{2+}$ into magnetite crystal generates more amounts of hydroxyl radicals by creating facile electron transport processes, which ultimately enhances MB degradation rate. Crystal size is another factor that can be considered to explain the observed trend of rate constants. The smaller crystal sizes of Ni- and Zn-doped magnetites as compared to magnetite can also be related with the higher catalytic activities of doped magnetic particles as compared to magnetite nanoparticles[15]. These results also corroborate the results reported for various other similar types of magnetic nanoparticles[16, 17].

## 4. Conclusions:

Magnetite ($Fe_3O_4$) nanoparticles with and without the presence of Ni and Zn in its structure were successfully synthesized by using a co-precipitation method. FTIR spectroscopic and X-ray crystallographic characterizations indicate the formations of high purity spinel structured $Fe_3O_4$. The change in the positions of some bands in the FTIR spectra and peaks in the XRD patterns of Ni and Zn doped $Fe_3O_4$ indicate the presence of these elements in the crystal sites of $Fe_3O_4$. X-ray crystallographic results indicate the formations of magnetic nanoparticles with average crystal sizes < 15 nm. Scanning electron microscopic investigation also supports the results obtained from XRD analysis. Additionally, scanning electron microscopic investigation indicates the formations of spherical shaped agglomerated particles, which is one of the important characteristics of magnetic nanoparticles. Sonochemical treatment of MB solution in presence of $H_2O_2$ can remove about 54% MB from the solution after 30 minutes treatment time. The $Fe_3O_4$ addition into the reacting mixture enhances the MB removal amounts which indicates that the add magnetite acts as a catalyst in the MB degradation process. The removal amount of MB is further enhanced when MB solutions are treated with Ni- and Zn-doped magnetic nanoparticles. At the catalyst dose of 0.2g/L, amounts of MB removed from solution by $Fe_3O_4$, Ni-$Fe_3O_4$ and Zn-$Fe_3O_4$ after 30 minutes degradation time are 82.51, 92.97 and 98.04%, respectively. The highest degradation rate is observed when 0.2g/L catalyst dose is applied for the treatment of MB-solution and high reactivity is observed for Zn-doped $Fe_3O_4$.

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