



## Assortment of magnetic nanospinels for activation of distinct inorganic oxidants in photo-Fenton's process



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### ABSTRACT

Magnetic spinel ferrites in the nano range, having general formula  $MFe_2O_4$  ( $M = Cu, Zn, Ni$  and  $Co$ ) were prepared using facile sol–gel methodology. The physicochemical properties of prepared ferrites characterized using FTIR, powder XRD and HRTEM stipulated formation of single phase cubic spinel structure. The band gap of all the ferrites was found in the range 1.26–2.08 eV, consequently could be photo-excited by visible light. The present study evaluates the capacity of all the synthesized ferrites to activate different inorganic oxidants i.e., hydrogen peroxide ( $H_2O_2$ ), potassium peroxodisulphate ( $K_2S_2O_8$ ), potassium peroxymonosulphate ( $KHSO_5$ ) and potassium bromate ( $KBrO_3$ ) in photo-Fenton process. The results disclosed fascinating behavior of peroxymonosulphate as it could be stimulated at neutral pH while for all other oxidants, acidic medium was required. Furthermore, the concentration of peroxymonosulphate during the reactions was 4 times less than other oxidizing agents. The degradation rate was found to decrease in order  $H_2O_2 > KHSO_5 > K_2S_2O_8 > KBrO_3$ . When  $H_2O_2$  and  $KHSO_5$  were used the reactivity of ferrites followed the order  $CuFe_2O_4 > ZnFe_2O_4 > NiFe_2O_4 > CoFe_2O_4$  and  $CoFe_2O_4 > CuFe_2O_4 > NiFe_2O_4 > ZnFe_2O_4$ , respectively. The prepared materials were chemically stable and magnetically recoverable after the reaction hence, was reused without any significant loss in activity.

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### 1. Introduction

In the recent scientific progress, intensive research is being focused on development of nanomaterials that have fusion of essential aspects such as excellent reactivity, cost-effectiveness and environmentally benign mode of recovery. In this regard, magnetic nanomaterials have attracted steadily growing attention. The inherent magnetic nature and insolubility of these materials in most solvents favors easy and rapid catalyst separation from the reaction system [1]. These qualities make magnetic nanoparticles sustainable and a potential green catalyst.

Among different magnetic nanoparticles, spinel ferrites ( $MFe_2O_4$ ,  $M = Co, Ni, Cu, Zn, Mn$  etc.) are one of the most important and interesting oxides that can play a dual role of a catalyst as well as magnetically separable entity [2]. These materials have narrow band gap which makes it an effective catalyst under visible

light [3]. Besides the significant merit of easy magnetic recovery from the reaction system, these materials even offer advantage of being chemically stable and cheap; hence, can serve as an efficient photocatalyst.

In the last few decades treatment of wastewater containing recalcitrant contaminants using advanced oxidation processes (AOPs) has gained considerable attention. Among the different AOPs reported in literature, Fenton's process has been successfully applied for degradation of miscellaneous recalcitrant organics. This process involves reaction of  $Fe(II)$  with an oxidant like  $H_2O_2$  to generate hydroxyl radicals ( $HO^\bullet$ ) which are capable of attacking harmful organic contaminants present in water, thereby, mineralizing them into harmless  $CO_2$  and  $H_2O$  [4]. The role of inorganic oxidant in the Fenton's process is of utmost importance as the reactive species produced in the process depend on type of oxidizing agent used. Nowadays, the use of sulphate radical based AOPs using oxidants such as persulphate and peroxymonosulphate for chemical mineralization of different organic pollutants is being explored.

The use of ferrites as heterogeneous photofenton catalyst for the degradation of different organic pollutants using  $H_2O_2$  as oxidant has been investigated by different researchers [5–8]. Potassium

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persulphate (PDS) is an alternative oxidant in Fenton's process that has recently been examined by authors for the degradation of various pollutants. Rodrigrez et al. used persulphate activated by  $\text{Fe}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  etc., for the degradation of different pharmaceutical compounds [9]. Ahmed and Chiron also decontaminated wastewater effluent from pharmaceutical residues by using persulphate as an oxidant in photofenton process under solar light. Another oxidizing agent which is less explored in Fenton's process is potassium bromate ( $\text{KBrO}_3$ ) [10]. Despite the promising results of all the oxidizing agents in Fenton's process, major drawback is pH adjustment in acidic range prior to reaction. Therefore, use of oxidant which can work at neutral pH is a great challenge.

Potassium peroxymonosulphate (PMS) is unsymmetrical peroxide that has very strong oxidizing strength to mineralize organic pollutants in water. It can work in a wide pH range hence, is better over other oxidants. Ji et al. used porous  $\text{Fe}_2\text{O}_3$  nanoparticles for the activation of PMS to degrade RhB dye [11]. Besides this, limited literature is available on use of ferrites for degradation of organic pollutants in the presence of PMS.  $\text{CuFe}_2\text{O}_4$  magnetic nanoparticles have been used by authors to activate PMS for the degradation of different organic contaminant [12,13].

The above discussion clearly illustrates the importance of oxidizing agents in AOPs. To date, there are very few reports available on the comparative use of different oxidants in Fenton's process. Considering all the facts, present work explores the effect of different inorganic oxidants such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), potassium peroxodisulphate ( $\text{K}_2\text{S}_2\text{O}_8$ ), potassium peroxymonosulphate ( $\text{KHSO}_5$ ) and potassium bromate ( $\text{KBrO}_3$ ) activated by spinel ferrites  $\text{MFe}_2\text{O}_4$  ( $\text{M}=\text{Cu}$ ,  $\text{Ni}$ ,  $\text{Co}$  and  $\text{Zn}$ ) on the degradation of Remazol Black 5 (RB5) which was used as a model textile dye contaminant. The assessment of different operating variables such as catalyst loading, pH, oxidant dosage and light on photo-oxidative remediation of textile dye in the presence of all the ferrites was explored in detail. The main focus of this study was to scrutinize a single catalyst out of all the chosen ferrites for the stimulation of different oxidants. The most crucial feature of a sustainable and green catalyst is its feasible recovery and recyclability. In order to illustrate this, reusability of catalyst was also studied.

## 2. Experimental

### 2.1. Chemicals

All the chemicals used during the experiments were available commercially and used without further purification. Ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98%), cupric nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 99.5%), nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 96%), cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99%) citric acid (99.57%) and hydrogen peroxide (30% w/v) were obtained from Fisher Scientific. Ethylene glycol (99%), potassium bromate (99%), and potassium persulphate (>99%) were supplied by Merck. Oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ), which is a source of potassium peroxymonosulphate ( $\text{KHSO}_5$ ) was procured from Avra Synthesis. All the aqueous solutions were prepared in distilled water.

### 2.2. Synthesis of ferrite

Magnetic spinel ferrites having general formula  $\text{MFe}_2\text{O}_4$  ( $\text{M}=\text{Cu}$ ,  $\text{Zn}$ ,  $\text{Ni}$  and  $\text{Co}$ ) were synthesized using sol-gel method as reported previously [14]. In a typical synthesis procedure ferric nitrate and metal nitrate based on stoichiometric ratio were mixed in minimum amount of distilled water and heated at 80–90 °C. Citric acid and ethylene glycol were added to the resulting mixture and the solution was heated with magnetic stirring until gel formation. The

gels were dried and crushed to obtain powder which was annealed at 400 °C for further characterization and application.

### 2.3. Photocatalytic activity

The catalytic photodegradation of RB5 dye was carried out under visible light in ambient conditions. In each experiment, appropriate amount of catalyst was added to 100 mL of RB5 (50 mg/L) solution. In order to ensure adsorption desorption equilibrium between dye and catalyst, mixture was stirred in dark for 30 min. Known amount of oxidizing agent was added to mixture prior to irradiation under Xe-lamp. At fixed interval of time sample was withdrawn, centrifuged and analyzed using UV-vis spectrophotometer.

### 2.4. Physical characterization

Thermal decomposition mechanism of all the raw spinel nanoferrites was studied using thermogravimetric analyzer, SDT Q600 in the temperature range of 20–700 °C at heating rate of 10 °C/min. The fourier transform infrared spectroscopy (FTIR) was recorded on PerkinElmer spectrophotometer in the range 400–800  $\text{cm}^{-1}$ . For high resolution transmission electron microscopy (HRTEM) images and scanning transmission electron microscopy (STEM) analysis FEI Tecnai (G2 F20) operating at 200 keV was used. Energy dispersive X-ray spectroscopy (EDAX) was performed using an adjacent EDAX Inc. system. Structure and crystallinity of all the ferrite samples was determined using powder X-ray diffraction patterns recorded using XRD, model Bruker, D8 Advance with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) in the range  $2\theta = 20\text{--}80^\circ$ . The optical properties of powder samples were recorded using Ana-lytikjena specord-205 spectrophotometer. The magnetic properties of prepared samples were measured at room temperature by a vibrating sample magnetometer (VSM) (155, PAR) up to a magnetic field of  $\pm 20 \text{ kOe}$ . The surface area was determined by Brunauer-Emmett-Teller (BET) surface area analyzer ((11-2370) Gemini, Micromeritics, USA). All the photocatalytic experiments were carried out under 150 W Xe lamp having 96,000 Lux. The change in concentration of dye solution was analyzed using UV-visible spectrophotometer (JASCO, V-530) by following the absorbance at 597 nm.

## 3. Results and discussion

### 3.1. Characterization of catalyst

#### 3.1.1. Thermogravimetric analysis (TGA)

Thermogravimetric curves were used to study the thermal stability of as synthesized ferrite samples which is based on weight loss as a function of temperature. The TGA curves for all the ferrites as shown in Fig. A1 (Supporting information) suggested that the thermal degradation of all the samples occurred in two steps. The first step in the temperature range of 50–100 °C was attributed to loss of water from the sample while the second degradation step in the range 300–400 °C was owed to decomposition of ethylene glycol and nitrates into  $\text{CO}_2$  and  $\text{NO}_x$ , respectively [15]. Heating the sample beyond 400 °C did not show any characteristic weight loss indicating formation of pure ferrite. Fig. A1 clearly indicated TGA curves of all the samples were similar. Because of this factor, all the raw samples were subjected to heat treatment at 400 °C before characterization and performing catalytic experiments.

#### 3.1.2. Fourier transform infrared spectroscopy (FTIR)

Absorption bands of FTIR in solids are due to vibration of ions in crystal lattice. In case of ferrites, metal ions are distributed in tetrahedral (A) site and octahedral (B) site. According to Raut et. al [16] vibration mode between tetrahedral metal ion and oxygen complex

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