



## Research paper

## Cobalt ferrite nanoparticles with controlled composition-peroxymonosulfate mediated degradation of 2-phenylbenzimidazole-5-sulfonic acid



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## ABSTRACT

Magnetic spinel cobalt ferrite nanoparticles with variable composition ( $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ;  $x = 0.1, 0.5, 0.7$  and  $1.0$ ) were synthesized. The nanoparticles were characterized by various surface techniques. Average sizes and surface areas of ferrites were determined in the ranges of 11–34 nm and 18.5–49.1  $\text{m}^2/\text{g}$ , respectively. Surface analysis of the nanoparticles confirmed the spinel type structures in which Co(II) incorporated into the crystal lattice. The synthesized catalysts were used to dissociate peroxymonosulphate (PMS) into reactive sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) and further into hydroxyl radicals ( $\text{HO}^{\cdot}$ ) to degrade a target pollutant, 2-phenylbenzimidazole-5-sulfonic acid (PBSA) in absence of heat and light. As the molar ratio of cobalt (i.e.,  $x$ ) in the ferrite catalyst increased from 0.1 to 1.0, PBSA degradation enhanced from 24 to 75% in 240 min. The removal of PBSA increased significantly with the increase in PMS concentration up to 0.1 mM, followed by a decrease at PMS levels of  $> 0.1$  mM. Nitrogen content in PBSA was mineralized by the cobalt ferrite-PMS system mostly into  $\text{NO}_3^-$  and  $\text{NH}_4^+$  ions with minor formation of  $\text{NO}_2^-$ . Only 32% TOC removal was observed over a 240 min reaction time, indicating carbon content in PBSA was not completely mineralized. A chemical probe method, based on free radical scavenging, revealed the contribution of both  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$  species in PBSA degradation. Fifteen reaction intermediates were identified using LC/Q-TOF-ESI-MS analysis. Hydroxylation, elimination of sulfonate moiety, and ring cleavage processes were involved in the major degradation pathways. Catalyst reuse experiments demonstrated PBSA degradation efficiency either retained or increased with each subsequent reuse. The magnetic spinel Co-ferrite nanoparticles can be applied effectively to activate PMS without energy aiding for degrading harmful emerging organic contaminants in water.

## 1. Introduction

Homogeneous metal catalysts have been widely used in the treatment of different emerging contaminants in water due to their advantage of solubility in the reaction medium [1,2]. However, the applications of these catalysts in the field of water treatment have drawbacks such as separating the used catalyst from the reaction mixture after use and handling of air-sensitive catalysts in the environment of their applications [3,4]. Among numerous homogeneous materials, first-row transition metals are being investigated for their promising applications, including energy storage,

biomedical applications, and treatment of air and water [5–9]. For example, iron-based spinel metal oxides (or ferrites) have been studied to disinfect and to degrade organics in polluted air and water [10–12]. More recently, interest in cobalt ferrite nanoparticles has been increasing due to their high magnetic anisotropy ( $1.8\text{--}3.0 \times 10^5 \text{ J m}^{-3}$  at 300 K), which is important in magnetic recording applications [13]. Cobalt nanoparticles also play an important role in oxygen reduction electrocatalysis and production of highly reactive species to degrade organic contaminants in water [14–16]. The present paper demonstrates the efficient use of cobalt ferrite for the effective degradation of 2-phenylbenzimidazole-5-sulfonic acid (PBSA) in water.

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The sunscreen ingredient PBSA is the most frequently used chemical in personal care products (PCPs) due to its ability to absorb ultraviolet (UV) rays [17–19]. It is a water soluble UV absorber and is frequently detected in the environment [19]. Since PBSA and many other organic UV absorbers are endocrine disrupting chemicals in the environment [19], there is a critical need to eliminate such contaminants from water. Degradation of PBSA has been studied using  $\text{TiO}_2$  photocatalysis [20] and homogenous photochemical- $\text{H}_2\text{O}_2$  [19] processes. In these processes, hydroxyl radical ( $\text{HO}^\bullet$ ) are predominantly generated, causing the degradation of target contaminants. Previous studies demonstrated the essential role of light to irradiate  $\text{H}_2\text{O}_2$  and activate  $\text{TiO}_2$  catalyst systems to decompose PBSA [19–21]. Lately, emphasis on the use of highly reactive sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) to degrade different organic water contaminants was put forth due to its high oxidation potential (i.e., 2.4 V) and attack to certain chemical bonds in organic compounds [16,22–25]. Typically,  $\text{SO}_4^{\bullet-}$  can be generated by various techniques such as photolysis, pyrolysis or chemical activation of peroxymonosulfate (PMS) [22,26,27]. Of the various transition metallic ions, a combination of  $\text{Co}^{2+}$  and PMS has shown superior performance, however, retaining  $\text{Co}^{2+}$  after use in water is not an easy task. Studies on cobalt-based materials such as magnetic cobalt ferrite nanoparticles are forthcoming [10,28]. Yet, a limited research has been conducted on using these nanoparticles to degrade PBSA in water such as the recent study by Zhang et al. who utilized composite nanomaterial (i.e., nitrogen- and sulfur-co-doped carbon nanotubes-COOH loaded copper ferrite ( $\text{CuFe}_2\text{O}_4$ )) for PBSA degradation [29]. The current study presents, for the first time, the development of simple cobalt ferrite nanomaterial with controlled composition to effectively degrade PBSA in water without additional use of heat or energy. Moreover, the magnetic property of synthesized cobalt ferrite nanoparticles allows the separation of the catalyst using a magnet.

In this study, recyclable magnetic  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  nanoparticles of variable compositions were synthesized, followed by their detailed characterization using BET surface area analysis and scanning electron microscopy (SEM), selected area electron diffraction (SAED), high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy techniques. The catalytic activity of synthesized nanoparticles for degrading PBSA was evaluated in the presence of PMS. The study included identification of organic products of PBSA oxidation by liquid chromatography-mass spectrometry (LC-MS) technique in addition to determination of total organic carbon (TOC) and inorganic nitrogen-containing products ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$ ) to learn the mineralization of PBSA by  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  nanoparticles-PMS system. Finally, proposed reaction pathways, based on identified reaction products and reactivity of involved oxidizing species ( $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$ ) are presented.

## 2. Experimental

### 2.1. Synthesis of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ magnetic nanoparticles

A modified combustion method was used to synthesize cobalt ferrite nanoparticles [30–32]. In this method, a mixture of cobalt(II) acetylacetonate (97%, Sigma Aldrich) and iron(III) chloride (anhydrous, 97%, Fisher Scientific) was initially prepared at a 1:2 molar ratio of cobalt(II) to iron(III). This molar ratio was then varied to produce 4 different stoichiometries where the adequate number of grams of each chemical was determined by multiplying its corresponding ratio by its molecular weight (i.e.,  $\text{Co}_{0.1}\text{Fe}_{2.9}$ ,  $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ,  $\text{Co}_{0.7}\text{Fe}_{2.3}\text{O}_4$ , and  $\text{Co}_{1.0}\text{Fe}_{2.0}\text{O}_4$ ). Polyvinyl alcohol (PVA, 88% hydrolyzed, average molecular weight of 22000) was added to the reaction mixture in a 1:1 ratio by mass. The mixture was grinded and mixed very well with 15 mL Milli-Q water. This mixture was placed in a muffle furnace and then calcined at 500 °C for 30 min causing self-ignition of PVA that ultimately generate magnetic nanoparticles of cobalt ferrite.

To prepare the magnetic cobalt ferrite nanoparticles, a series of different polymers were used. Out of the tested polymers, PVA proved to be the most efficient in synthesizing catalysts with better magnetic properties by hand magnet separation. The alcoholic groups of the PVA

helps to drive the reaction and the gases released stabilize the crystal phase of the cobalt ferrite polymer [33]. Compared to traditional magnetic ferrite synthesis methods, the current procedure is less complicated as it did not require any pretreatment or certain vessels as in hydrothermal methods. The developed method for the nanoparticles synthesis is environmentally friendly due to the use of water and non-toxic, biodegradable polymers. Moreover, no organic solvents or non-biodegradable chemicals (i.e., surfactants) were required for cobalt ferrite preparation which are commonly used in sol-gel techniques [34,35].

### 2.2. Characterization of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticles

The resulting  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  nanoparticles were characterized using several materials characterization methods including SEM, HR-TEM, XRD, XPS and Raman spectroscopy. A JEM-2010F (JEOL) HR-TEM with a field emission gun at 200 kV was used after the samples were prepared in isopropyl alcohol (99.8%, Pharmco), followed by 30 min of ultrasonication (2501R-DH, Branson). Each sample was fixed on a lacey/carbon 300 mesh copper grid (LC325-Cu, EMS). The selected area electron diffraction (SAED) was obtained with low resolution TEM technique and analyzed using the open-source program, Diffraction Ring Profiler. Electron diffraction simulations were performed using the commercial software, Desktop Microscopist, with the input of the well-known space group information.

A Cu-K $\alpha$  wavelength Bruker AXS D8 Discover XRD was used to confirm crystal structure of synthesized samples with a receiving slit of 0.3 and 0.2 scan step size from 10 to 70°. Raman spectroscopy measurements were performed with a Renishaw In-Via Reflex dispersive micro-Raman spectrometer with  $< 2 \text{ cm}^{-1}$  resolution. The laser beam (excitation in the NIR at 785 nm with total laser power below  $0.001 \text{ mW}/\mu\text{m}^2$ ) was focused on a spot of about 6.8  $\mu\text{m}$  in diameter with a x20 magnification lens. Rayleigh scattering was rejected with a  $110 \text{ cm}^{-1}$  cut-off dielectric edge filter, and analysis of the scattered beam was performed on a 250 mm focal length spectrometer along with suitable diffraction gratings (1200 lines/mm for NIR) and a high-sensitivity charge-coupled device (CCD). All room temperature (RT) Raman spectroscopy measurements were performed in air and at different laser powers to assure that the intensities used did not induce changes in the spectra. The surface analysis studies were performed in a UHV chamber ( $P < 10^{-9}$  mbar), equipped with a SPECS LHS-10 hemispherical electron analyzer.

The XPS measurements were carried out at room temperature using unmonochromatized MgK $\alpha$  radiation under conditions optimized for maximum signal (constant  $\Delta E$  mode with pass energy of 97 eV giving a full width at half maximum (FWHM) of 1.6 eV for the Ag 3d $_{5/2}$  peak of a reference foil). The analyzed area was an ellipsoid with dimensions  $2.5 \times 4.5 \text{ mm}^2$ . The XPS core level spectra were analyzed using a fitting routine, which allows the division of each spectrum into individual mixed Gaussian-Lorentzian components after a Shirley background subtraction. The samples were pressed in indium foil circular substrate with diameter  $\sim 1 \text{ cm}^2$ . Wide Scans were recorded for all samples, while the core level peaks that were recorded in detail were: O1s, Fe2p, Co2p and C1s. Errors in our quantitative data are found in the range of  $\sim 10\%$  (peak areas) while the accuracy for BEs assignments is  $\pm 0.1 \text{ eV}$ .

### 2.3. Catalytic activity of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticles

To evaluate the catalytic activity of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  ( $\text{Co}_{0.1}\text{Fe}_{2.9}\text{O}_4$ ,  $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ,  $\text{Co}_{0.7}\text{Fe}_{2.3}\text{O}_4$  and  $\text{Co}_{1.0}\text{Fe}_{2.0}\text{O}_4$ ), 5.0 mg of catalyst was added to 29 mL Milli-Q water in separate 40 mL glass vials. Sonication for 15 min at 40 kHz (input energy 19 W) was applied to further disperse the catalyst in water. Then, 0.1 mL of 0.2 mM PBSA was added to water containing the catalyst (i.e., final concentration of PBSA = 4.0  $\mu\text{M}$ ). To start the reaction, appropriate volumes of a stock solution of PMS (30.0 mM) were added to the solutions based on the final desired concentrations to evaluate the effect

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