



Chromium-zinc ferrite nanocomposites for the catalytic abatement of toxic environmental pollutants under ambient conditions[☆]



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HIGHLIGHTS

- Oxidizing power of zinc ferrite nanocomposites increases with chromium substitution.
- Direct correlation between surface acidity and catalytic activity of composites.
- Rate of reaction is strongly dependent on catalyst amount and its composition.
- Composite is reusable with negligible leaching, indicating heterogeneous mechanism.

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ABSTRACT

Catalytic abatement of 4-chlorophenol, 2,4-dichlorophenol and 2,4-dichlorophenoxy acetic acid in water was investigated by peroxide oxidation over chromium substituted zinc ferrite nanocomposites at ambient conditions. The structural and chemical properties of composites synthesized by sol-gel auto combustion method was studied by X-ray diffraction, Fourier Transform Infra-Red spectroscopy, Transmission Electron Microscopy, surface area, X-ray Fluorescence spectroscopy, Temperature Programmed Reduction and Desorption techniques. Complete removal of 4-CP, DCP and 2,4-D was achieved within 60, 75 and 90 min with 96.7/90.5%, 93.88/77.23% and 88.55/62.1% of COD/TOC removal respectively at 298 K and 343 K. Influence of reaction variables including reaction temperature, oxidant concentration, substrate concentration, catalyst dosage and its composition on the removal efficiency was studied. Kinetic study revealed that wet peroxide oxidation followed a first order kinetic model with rate constant and activation energy of $3.5 \times 10^{-2} \text{ min}^{-1}/10.7 \text{ kJ/mole}$, $9.5 \times 10^{-3} \text{ min}^{-1}/12.9 \text{ kJ/mole}$ and $2.29 \times 10^{-2} \text{ min}^{-1}/17.7 \text{ kJ/mole}$ respectively for 4-CP, DCP and 2,4-D. The results of five consecutive catalytic runs from X-ray diffraction, Brunauer Emmet Teller surface area and leaching studies from Atomic Absorption Spectrophotometry (AAS) revealed the excellent stability of the catalyst. Scavenging effect of *n*-butanol on hydroxyl radical indicated a heterogeneous free radical mechanism.

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1. Introduction

Chlorinated organic compounds constitute a group of priority toxic pollutants and are listed by both the US-EPA Clean Water Act and the European Union Decision 2455/2001/EC [1]. Chlorophenols (4-chlorophenol and 2,4-dichlorophenol) and 2,4-dichlorophenoxy acetic acid (2,4-D) have been recognized as important among priority toxic pollutants. 2,4-D is used as an herbicide which control

the broad-leaf weeds in agriculture and is used up worldwide in an uncontrolled manner [2]. The wide spread use of 2,4-D leads to great environmental impact because of its easy solubility in soil, leading to soil and water contamination and other related health problems. 2,4-dichlorophenol (DCP) is the prime precursor for the manufacture of 2,4-D and so is the major transformation product resulted by the solar photolysis and microbial action to 2,4-D in soil or natural water [2]. 2,4-D has been proved to cause damage to the vital organs of humans and animals, for instance developmental, behavioral, neurologic, endocrinal, reproductive and immunologic adverse health effects have also been linked to these compounds at higher doses. The inhibitory effects of phenol on microbial activity have been reported for concentrations larger than 500 ppm, and their chlorinated derivatives exhibit an even larger bio-toxicity

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at similar concentrations [1]. Because of the toxicity and related hazards of chlorinated organics and their decomposition products (2,4-dichlorophenol and 4-chlorophenol mainly), their removal in an economic way is a serious environmental concern nowadays. So the demand for a suitable and excellent procedure for the pre-treatment and detoxification of environmental pollutants is ever increasing which continues to prompt researchers to develop improved materials for this purpose.

Wet Peroxide Oxidation (WPO) processes have emerged as a suitable alternative among Advanced Oxidation Processes (AOPs) for the complete mineralization of chlorinated organic wastes in water under mild conditions [3]. Incorporating catalysts in WPO (Catalytic Wet Peroxide Oxidation, CWPO) enhance the efficiency of the treatment procedure even more to milder conditions, thus making processes economic and more attractive [3,4]. Stable and active heterogeneous catalysts find more applications in CWPO because they can easily be recovered, regenerated and reused. The catalytic activity of a broad class of simple and mixed oxides as well as supported metals has already been studied [5–7]. Spinel ferrites have been investigated up now for numerous applications because of their excellent magnetic, optic, electric and catalytic properties. Several reports are available to showcase the catalytic applications of different ferrite composites for many organic transformations [8–15]. With the rapid development of nanotechnology and its numerous applications, wide varieties of engineered nanomaterials are now being used because of their unique properties such as smaller size, larger specific area and greater reactivity. Recently we have proved stability and efficiency of cobalt, nickel and manganese doped zinc ferrite nanomaterials towards the removal of 4-CP and DCP [9,13,14]. These observations provided enough confidence to develop chromium doped zinc ferrite nanocomposites as catalysts for similar applications. Moreover, there is still enough space for improvements including the study of doping effect of different metal ions on catalytic performance, role of catalyst in reaction kinetics and mechanism, stability and recyclability for long term practical applications. In this study, we report the activity of spinel type chromium ferrite nanoparticles for the removal of 4-CP, DCP and 2,4-D from water at relatively milder conditions much more moderate than those required for non-catalyzed processes.

The important areas of our investigation are (i) preparation of different compositions of chromium-zinc ferrite nanocomposites (ii) investigation of the heterogeneous catalytic behaviour of synthesised materials towards the oxidative removal of 4-CP, DCP and 2,4-D at ambient conditions (iii) evaluation of the influence of reaction parameters such as reaction temperature, oxidant concentration, substrate concentration, catalyst dose and its composition on the catalytic efficiency and (vi) to attempt to get a better understanding on the reaction mechanism, kinetics and activation energy changes during reaction, stability and recyclability of the catalyst. Catalysts containing different compositions of $\text{Cr}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles ($x = 0, 0.25, 0.5, 0.75, 1$) were prepared by sol-gel auto combustion method. Among different synthetic procedures adopted for the synthesis of substituted zinc ferrites, sol-gel method offers many advantages such as low processing temperature, ability to control homogeneity, composition, high surface area and porosity of the materials produced. Moreover, phase purity and product yield are also high in this method [16,17]. These were characterized by X-ray diffraction (XRD), Transmission Electron Spectroscopy (TEM), BET surface area, X-ray fluorescence spectroscopy (XRF), Fourier Transform Infra-Red spectroscopy (FT-IR), Temperature Programmed Reduction (TPR- H_2) and desorption (TPD- NH_3 and TPD- CO_2) techniques. Electronic characteristics, AC conductivity and dielectric property were also investigated using impedance analyzer.

2. Experimental

2.1. Preparation and characterization of $\text{Cr}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$) nanocomposites

Pure (99.9%) ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ethylene glycol (Merck Chemicals, Mumbai, India) were used for preparation of ferrite nanocomposites. Different compositions of $\text{Cr}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$) were prepared by the sol-gel auto combustion method. The metal nitrates were taken in the requisite stoichiometric ratio and dissolved in minimum amount of ethylene glycol at room temperature and heated at 60°C to obtain a wet gel. This gel then dried at 120°C self-ignites to form a fluffy product which was sintered at 300°C for 4 h to achieve transformation into cubic spinel phase. The ferrite powder so obtained was then sieved in 90 mesh and used for catalytic reactions.

Phase identification of the prepared nanocomposites were carried out using Bruker AXS D8 Advance X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) as the radiation source. The average crystallite size (D), lattice parameter (a), X-ray density (d_x), bulk density (d_b) and porosity (P) were calculated from X-ray diffraction data. The size, distribution and surface morphology of nanoparticles were confirmed using pH ILIPS Model CM 200 Transmission Electron Microscope with a resolution of 2.4 \AA with the help of Image J software. Stoichiometry of the prepared composites was verified using Bruker PIONEER model X-ray Fluorescence spectrometer. The Fourier Transform Infra-Red spectral studies were carried out in KBr medium using Thermo Nicolet, Avatar 370 model spectrometer in the range of $400\text{--}4000 \text{ cm}^{-1}$ with resolution of 4 cm^{-1} . The specific surface area of the nanocomposites were performed by N_2 adsorption measurements on a Micromeritics Gemini VII instrument after degassing the sample at 300°C under vacuum. Temperature Programmed Reduction (TPR- H_2) and Temperature Programmed Desorption of ammonia (TPD- NH_3 and CO_2) using Micromeritics ChemiSorb 2750 Pulse Chemisorption System. The TPR analysis was carried out in a stream of hydrogen and argon with a flowing rate of 50 ml/min . The amount of hydrogen consumption during reduction was estimated with a thermal conductivity detector. For TPD- NH_3 and CO_2 analysis, sample was pre-treated under He flow of 10 ml/min at 400°C . NH_3/CO_2 adsorption was carried out under standard condition by flowing $10\% \text{ NH}_3/\text{He}$ and $10\% \text{ CO}_2/\text{He}$ over the ferrite composite till saturation and then desorption of NH_3/CO_2 by temperature-programmed analysis under constant He flow from 30 to 800°C with a heating rate of 10°C/min . Dielectric properties were checked using Agilent 16451B Impedance analyzer in parallel mode at frequency ranging from 40 to 1 MHz .

2.2. Catalytic wet peroxide oxidation studies

4-Chlorophenol and 2,4-dichlorophenol (LobaChemie), 2,4-dichlorophenoxy acetic acid (Himedia Laboratories Ltd), hydrogen peroxide and *n*-butanol from Merck, India, were used for catalytic reactions. AgSO_4 , HgSO_4 , H_2SO_4 , ferrous ammonium sulphate and $\text{K}_2\text{Cr}_2\text{O}_7$ from Merck India were used for COD measurements. KMnO_4 (Merck India) was used for the estimation of residual hydrogen peroxide. The stock solutions of 4-CP, DCP and 2,4-D were prepared by dissolving suitable amount in deionized water and all the chemicals were used as such without any further purification.

Catalytic activity of different compositions of chromium doped zinc ferrite nanocomposites towards the oxidation of 4-CP, DCP and 2,4-D in liquid phase using hydrogen peroxide were studied under ambient conditions. Each pollutant was treated separately for the evaluation of catalytic performances. CWPO reactions were carried out in a 250 ml two necked RB with continuous stirring on a magnetic stirrer under controlled temperature and stirring

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