



Catalytic peroxide oxidation of persistent chlorinated organics over nickel-zinc ferrite nanocomposites



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ABSTRACT

Catalytic wet peroxide oxidation over nickel-zinc ferrite nanocomposites offers a novel way for the effective removal of Priority Toxic Pollutants (2,4-dichlorophenol and 2,4-dichlorophenoxy acetic acid) in water under mild reaction conditions. The rate of catalytic oxidation reaction was influenced by the concentration of pollutant, catalyst and oxidant, temperature and catalyst stability. The oxidation ability and acid-base properties of composites were studied by Temperature Programmed Reduction (TPR-H₂) and desorption (TPD-NH₃ and TPD-CO₂) techniques. Zinc doping increased the oxidizing power and surface acidity of nickel ferrite composites which in turn increased the catalytic efficiency. Complete removal of 2,4-dichlorophenol (DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) was achieved within 75 and 90 min with 84/73% and 83/70% of COD/TOC removal respectively at 343 K. Zinc rich compositions of Zn_xNi_{1-x}Fe₂O₄ were found to be more effective for the destructive removal of pollutants and the composite with composition x=0.75 showed the highest activity. Kinetic study revealed that peroxide oxidation reaction followed a first order kinetic model with rate constant and activation energy of $2.44 \times 10^{-2} \text{ min}^{-1}/13.26 \text{ kJ/mol}$, $3.16 \times 10^{-2} \text{ min}^{-1}/14.98 \text{ kJ/mol}$ respectively for DCP and 2,4-D. The results of five consecutive catalytic runs revealed the excellent stability and recyclability of the composite as evident from X-Ray Diffraction, Brunauer Emmet Teller and leaching studies from Atomic Absorption Spectrophotometry (AAS). Catalyst leaching increased with temperature, catalyst amount and dopant concentration. Reactive species trapping experiments with *n*-butanol indicated a heterogeneous free radical mechanism.

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1. Introduction

Chlorinated phenols and phenoxy acid herbicides have been used on large scale in agricultural sector to control the growth of weeds in vegetation. Among these, 2,4-dichlorophenoxy acetic acid (2,4-D), is used up in an uncontrolled manner because of its easy availability and simplicity in application. 2,4-D is highly mobile and persistent in aqueous media and is very difficult to decomposed due to its chemical stability and non-biodegradability [1–3]. It is considered to be carcinogenic and is one of the widely known endocrine disrupting chemical [4]. Because of its high affinity, it can be easily transferred into water and biomagnified through food chain, causing damage to the vital organs of humans and animals. These toxic compounds are therefore listed by both the US-EPA Clean Water Act and the European Union Decision 2455/2001/EC. The World Health Organization (WHO), recommended its maxi-

mum allowable concentration in drinking water as 70 µg/L [5]. 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 [6]. Therefore, the degradation of 2,4-D and other related derivatives has been a serious environmental concern.

In recent years, Advanced Oxidation Processes (AOPs) employing hydrogen peroxide as oxidizing agent has exhibited great potential as an environment friendly and sustainable treatment technology for the degradation of toxic organic compounds [7–9]. Because of the limitations of homogeneous Fenton reaction, a variety of hydrogen peroxide based heterogeneous catalytic reactions over iron based catalysts have been developed and experimented. In recent years the catalytic efficiency of iron based oxide compounds that are heterogeneous in nature have been experimented for the oxidative degradation of toxic chlorinated organics without pH adjustment [10–12]. Studies revealed that AB₂O₄ type spinel ferrites are very stable and active catalysts towards the decomposition of hydrogen peroxide and destructive removal of pollutants. Though several reports are available showing the

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catalytic applications of spinel ferrites for different organic transformation reactions, to the best of our knowledge the catalytic power of spinel ferrites are not much exploited for environmental applications. So far we have published the catalytic applications of nickel, cobalt, manganese and zinc substituted mixed ferrite nanocomposites for environmental remediation [13–15]. In spite of this, much effort is still needed to explore the doping effect of different metals on their catalytic improvements, degradation mechanism, activation energy changes, catalyst recyclability and stability against leaching to make the heterogeneous Fenton process more suitable for wide scale practical applications.

The present study aims at the catalytic application of different compositions of zinc doped nickel ferrite nanocomposites ($Zn_xNi_{1-x}Fe_2O_4$, $x=0.0, 0.25, 0.5, 0.75, 1.0$) for liquid phase oxidative destruction of 2,4-dichlorophenol (DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) under mild operating conditions. The influence of reaction parameters including reaction temperature, catalyst composition and its dosage, oxidant concentration, effect of dopant on catalyst stability and reusability were investigated. Different from our previous research outcomes [13–15], the effect of dopant on the oxidation potential and surface acidity of the catalyst was studied in detail using Temperature Programmed Desorption of ammonia (TPD-NH₃) and Temperature Programmed Reduction (TPR-H₂) using Micromeritics Chemisorb 2750 Pulse Chemisorption system. Also, the effect of temperature, catalyst dosage and dopant concentration towards catalyst deactivation was studied in detail. Based on the structural identification of transformation intermediates of DCP and 2,4-D, a plausible mechanism was also proposed.

2. Materials and methods

2.1. Chemicals used for catalytic evaluation

2,4-Dichlorophenol (Loba Chemie), 2,4-dichlorophenoxy acetic acid (Himedia Laboratories Ltd), hydrogen peroxide and *n*-butanol from Merck, India, were used for catalytic reaction studies. AgSO₄, HgSO₄, H₂SO₄, ferrous ammonium sulphate and K₂Cr₂O₇ from Merck India were used for COD measurements. KMnO₄ (Merck India) was used for the estimation of residual hydrogen peroxide. The stock solutions of 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.

2.2. Catalyst preparation and characterization

Different compositions of $Zn_xNi_{1-x}Fe_2O_4$ ($x=0.0, 0.25, 0.50, 0.75, 1.0$) nanocomposites were prepared by sol-gel auto combustion method [13] and characterized by different physicochemical tools such as X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), X-ray Fluorescence (XRF) and Fourier Transform Infra-Red spectral (FTIR) studies. Phase identification and purity of the prepared composites were performed using Bruker AXS D8 Advance X-ray diffractometer with CuK_{α} ($\lambda = 1.5406 \text{ \AA}$) as the radiation source. The particle size, distribution of nanoparticles and surface morphology were confirmed using pH ILIPS Model CM 200 Transmission Electron Microscope with a resolution of 2.4 Å with the help of Image J software. Stoichiometry of prepared catalysts 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 FTIR spectrometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . The synthesis and characterization of the nanoferrite composites were reported in our previous publication [13]. The TPR analysis was carried out to study the redox nature of the cata-

lyst, 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-NH₃ and CO₂ analyses were conducted to study the acid-base properties. For that samples were pre-treated under He flow of 10 ml/min at 400 °C. NH₃/CO₂ adsorption was carried out under standard condition by flowing 10% NH₃/He and 10% CO₂/He over the ferrite composite till saturation and then desorption of NH₃/CO₂ by temperature-programmed analysis under constant He flow from 30 to 800 °C with a heating rate of 10 °C/min. The specific surface area of nanocomposites was performed by N₂ adsorption measurements on a Micromeritics Gemini VII instrument after degassing the sample at 300 °C under vacuum. X-ray diffractograms of the reused catalysts were analysed and phase identification was carried out by comparison with JCPDS data cards and the average crystallite size was calculated by Debye-Scherrer equation.

2.3. Experimental procedure for catalytic wet peroxide oxidation (CWPO) of 2,4-dichlorophenol (DCP) and 2,4-dichlorophenoxyacetic acid (2,4-D)

Prior to oxidation experiments, the possibility of adsorption of pollutants on catalyst surface was checked and chance of removal via adsorptive way was completely ruled out. All experiments were carried out in a 250 ml two necked RB with 25 ml of pollutant stock solution (1 g/L DCP and 0.3 g/L 2,4-D). Afterwards, this was placed on a magnetic stirrer at a fixed temperature for two hours with a stirring speed of 230 rpm. To initiate the reaction, definite amount of catalyst and hydrogen peroxide according to the stoichiometry of reactants were added. At every 15 min regular interval of time, samples were withdrawn from the reaction mixture, filtered and analysed. The effect of each reaction variables on the degradation rate was studied by changing that variable while keeping all other parameters as constant. The initial pH of reaction mixture at the initial stage was respectively 6.2 and 4.3 for DCP and 2,4-D. The active species trapping experiments were carried out using 200 mM/L *n*-butanol (*OH scavenger) during the WPO reaction under the same conditions. All experiments were conducted in triplicate to observe the reproducibility.

The progress of removal of DCP and 2,4-D from aqueous medium was analysed periodically using PerkinElmer Clarus 580 Model GC equipped with an Elite-5 capillary column and Flame Ionization Detector (FID). The pH of the reaction system was checked during the course of reaction using a EUTECH digital pH meter. COD measurements were carried out by standard dichromate method and the reduction in COD was calculated as $\{[COD]_0 - [COD]_t\} / [COD]_0 \times 100$ where $[COD]_0$ and $[COD]_t$ are at initial and at a time *t* respectively. The residual amount of peroxide was studied at its higher concentrations using permanganometry, since hydrogen peroxide can interfere with the COD value by consuming oxidizing agent. The COD contribution due to the presence of residual peroxide results in overestimation of COD by 0.47 mg/L and its amount is removed from the actual COD value [16]. To substantiate GC and COD results, reaction progress was analysed via the reduction in Total Organic Carbon (TOC) using Shimadzu TOC-L pH 200 analyser. The oxidation intermediates of DCP and 2,4-D were identified by GC-MS analysis on a Varian 1200I Single Quadrupole spectrometer using Helium as the carrier gas. The error percentage between the results of analyses is less than 5%.

2.4. Recycling and leaching studies

To evaluate the reusability of zinc doped nickel ferrite composites in catalytic applications, the used catalyst was collected immediately by filtration at the end of each catalytic run, washed with deionized water and then with acetone to remove organ-

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