



Heterogeneous catalytic oxidation of persistent chlorinated organics over cobalt substituted zinc ferrite nanoparticles at mild conditions: Reaction kinetics and catalyst reusability studies



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ABSTRACT

This study explores the destructive removal of Persistent Organic Pollutants (POPs) like 2,4-dichlorophenol (DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) from water by wet peroxide oxidation method at ambient conditions using cobalt substituted zinc ferrite nanocomposites catalysts. The structural properties of catalysts were characterised by Fourier Transform Infra-Red spectroscopy (FTIR), Temperature Programmed Reduction (TPR- H₂) and desorption (TPD- NH₃ and TPD- CO₂) techniques. TPR study revealed that the oxidation property of zinc ferrite composite increase with cobalt substitution. Complete removal of DCP and 2,4-D occurred within 90 min over Co_xZn_{1-x}Fe₂O₄ catalysts with 94.84%/75.60% and 83.5%/49.2% of removal of Chemical Oxygen Demand (COD)/Total Organic Carbon (TOC) respectively. The effect of reaction variables like reaction time, pollutant concentration, catalyst composition and its dosage, temperature and oxidant concentration on the removal efficiency was optimized. Co_xZn_{1-x}Fe₂O₄ was found to be effective catalysts for destructive removal of pollutants and the composite with composition x=1.0 showed the highest activity. Atomic Absorption Spectrophotometry (AAS) proved the catalysts to be stable against leaching. The catalysts were reusable without any significant structural change as indicated by X-ray diffraction (XRD) and BET surface area studies. The active hydroxyl radical trapping experiments using *n*-butanol indicated a heterogeneous free radical mechanism.

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1. Introduction

Phenolic compounds are toxic environmental pollutants introduced into the environment as a result of different chemical and pharmaceutical activities like plastic, pesticide and other organo-chemical industries and research centres [1,2]. Phenols and its chlorinated derivatives are toxic even at very low concentrations and have long persistence in the environment and they are biomagnified through food chain, causing serious health problems. They 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 [3]. 2,4-dichlorophenol (DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) have both been recognised as priority pollutants by US-EPA. 2,4-D is widely used to control broad-leaf weeds in agriculture [4]. DCP is the major transformation product

of 2,4-D resulted by the solar photolysis and microbial action in soil or natural water [4]. 2,4-D has been proved to cause damage to the vital organs of human and animals, for instance, kidneys and liver at high doses. Because of the toxicity of 2,4-D and its decomposition products, their removal in an economic way is a serious environmental concern. Various abatement techniques including biological, thermal and chemical treatments have been developed in the last few years for the detoxification of Persistent Organic Pollutants (POPs) [5–7]. However, the costs of chemical oxidation alone can often be a limitation for waste water treatment. A comparison of cost effectiveness of different types of Advanced Oxidation Processes (AOPs) has already been studied and reported [8]. Among different AOPs, Catalytic Wet Oxidation using hydrogen peroxide (CWPO) stand out, for the complete mineralization of organic wastes at moderate conditions due to its simplicity and efficiency in action [9–11]. Hydrogen peroxide is used as the liquid oxidant, which avoids gas-liquid mass transfer limitations. Hydroxyl radicals are produced from H₂O₂ using homogeneous methods such as Fenton reaction or heterogeneous catalysts like metal oxides, clays, supported metal catalysts, etc. Heterogeneous

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catalytic wet peroxide oxidation has many advantages over the classical Fenton like homogeneous catalysis, such as enhancement of catalytic activity, lack of secondary pollution because of leaching and widening of pH range and the possibility of reusing the catalyst in successive cycles in a cost effective way [12,13].

Development of active, stable and efficient catalysts would play a significant role in the destruction of POPs in catalytic wet peroxide oxidation. Attention has been focused on different kinds of catalysts based on transition metal oxide compounds, metal exchanged zeolites, metal-exchanged clays and hydrotalcite like compounds [14–18]. Spinel type ferrites with the general formula $M^{2+}Fe_2^{3+}O_4$, have received considerable attention nowadays for a wide variety of applications as a catalyst because of their unique structural properties in addition to its thermal and chemical stability [19,20]. A spinel is formed by the distribution of divalent and trivalent metal ions among tetrahedral and octahedral coordination sites resulted by the cubic close packing of oxide ions. The catalytic activity of spinel ferrites exclusively depends on the redox properties of metal ions present in octahedral sites. Since the surface of spinel structure mostly contains octahedral sites and consequently its catalytic activity is directly related to the octahedral cations [21,22]. Also the catalytic effectiveness of these compounds is due to the ability of metallic ions to migrate between the sub-lattices without altering the crystal structure. These properties make this material an efficient catalyst for many organic transformation reactions [23–29]. Ramankutty et al. reported the rate of decomposition of hydrogen peroxide has been compared with controlled nano-sized magnetite powders as catalyst and in this case the catalytic activity related with the surface area [30]. Though spinel type ferrite compounds have been studied, their application as a candidate for environmental remediation is very limited. With this view, we had investigated the catalytic activity of different compositions of spinel type cobalt-zinc; manganese-zinc and nickel-zinc ferrite nanoparticles for the destructive removal of 4-chlorophenol (4-CP) from water under mild conditions [31–33].

In the present work, we investigate the catalytic applications of different compositions of cobalt substituted zinc ferrite [$Co_xZn_{1-x}Fe_2O_4$ ($x=0.0, 0.25, 0.50, 0.75, 1.0$)] nanocomposites for the wet oxidative destruction of 2,4-dichlorophenol (DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) at mild conditions along with an exhaustive structural analysis of catalysts. DCP and 2,4-D were selected as the target compounds for the present study because of its toxicity and lack of consistent research on the catalytic applications of ferrite nanoparticles. The acid-base properties and the redox nature of the catalysts were studied by Temperature Programmed Desorption of ammonia (TPD-NH₃) and Temperature Programmed Reduction (TPR-H₂) using Micromeritics ChemiSorb 2750 Pulse Chemisorption system. The influence of cobalt substitution on the catalytic activity of zinc ferrite was investigated by a detailed study on the influence of other reaction variables like reaction time, temperature, pollutant concentration, peroxide concentration, catalyst composition and its dosage etc. with the help of Gas Chromatography (GC), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) measurements. The reusability of the catalyst was checked for five consecutive cycles and catalyst deactivation via leaching was checked using Atomic Absorption Spectroscopy (AAS). The structural and textural studies of the catalyst during reusability stages were done by XRD and BET tools.

2. Materials and methods

2.1. Chemicals

DCP from LOBA Chemie, 2,4-D from Hi-Media laboratories India Ltd, hydrogen peroxide and *n*-butanol from Merck, India were used

for the catalytic runs. The stock solutions of DCP and 2,4-D were prepared in deionized water and all the chemicals were used as such without any further purification. AgSO₄, HgSO₄, H₂SO₄, ferrous ammonium sulphate and K₂Cr₂O₇ from Merck India were used for COD measurements.

2.2. Catalyst preparation and characterization

Different compositions of $Co_xZn_{1-x}Fe_2O_4$ ($x=0.0, 0.25, 0.50, 0.75, 1.0$) were prepared by sol-gel auto combustion method. The mixed spinels of $Co_xZn_{1-x}Fe_2O_4$ ($x=0, 0.25, 0.5, 0.75, 1.0$) were prepared by the sol-gel auto combustion method. Required stoichiometric ratio of Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O were dissolved in minimum amount of ethylene glycol at room temperature and heated at 60 °C to obtain a wet gel. This gel dried at 120 °C self-ignited to form a fluffy product which was calcined at 700 °C for 4 h to achieve transformation into spinel phase. The ferrite powder was then sieved through a 90 mm mesh. The synthesis and characterization of the catalysts was detailed in our previous publications [31–33]. 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 TPR analysis was carried out in a stream of hydrogen and argon (50 ml/min). The amount of hydrogen consumption during reduction was estimated with a thermal conductivity detector. For TPD-NH₃ and CO₂ analysis, sample was 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 the nanocomposites were performed by N₂ adsorption measurements on a Micromeritics Gemini VII instrument after degassing the sample at 300 °C under vacuum. Phase purity of the reused catalysts were analysed by XRD by its comparison with JCPDS data cards and the 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)

The catalytic activity of different compositions of cobalt doped zinc ferrite nanoparticles towards the oxidation of DCP and 2,4-D in liquid phase using hydrogen peroxide was studied under ambient reaction conditions. For a typical catalytic oxidation reaction, 25 ml of 1 g/L DCP solution was taken in a 250 ml two necked RB, 0.5 g/L catalyst in powder form was added into it and DCP to oxidant ratio was maintained as 1:14. Once the selected temperature (343 K) was reached the system reacted for 120 min with a constant and continuous stirring on a magnetic stirrer. The reaction system was first analysed to check if any adsorption of DCP and 2,4-D over the catalyst surface. Then hydrogen peroxide (30% v/v) was added to this mixture with continuous stirring. During the reaction, 1–2 ml of reaction mixture was withdrawn from the reaction system at 15 min regular intervals up to two hours. The experimental set-up was same for 2,4-D also except the concentration of 2,4-D was 0.5 g/L, with a catalyst dose of 0.7 g/L, 2,4-D: H₂O₂ ratio was 1:17. A detailed study was carried out on the influence of reaction time, temperature, pollutant: H₂O₂ ratio, effect of catalyst dosage and its composition towards efficient oxidative removal was studied in detail for designing an effective experimental procedure for CWPO for the complete mineralization of chlorinated pollutants by minimizing the operation cost due to the over usage of chemicals. Before

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