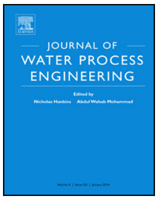
Journal of Water Process Engineering 8 (2015) e37–e49

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe



Heterogeneous Fenton behavior of nano nickel zinc ferrite catalysts in the degradation of 4-chlorophenol from water under neutral conditions

Manju Kurian*, Divya S. Nair

Department of Chemistry, Mar Athanasius College, Kothamangalam 686666, India

ARTICLE INFO

Article history:
Received 26 May 2014
Received in revised form
14 September 2014
Accepted 25 October 2014
Available online 8 December 2014

Keywords:
Nanoferrites
Advanced Oxidation Processes
Wet Peroxide Oxidation
Heterogeneous Fenton's catalysis
Catalyst stability

ABSTRACT

An evaluation of heterogeneous Fenton behavior of nano nickel-zinc ferrite catalysts in the Wet Peroxide Oxidation for the degradation of 4-chlorophenol is presented. A series of spinel type $Ni_xZn_{1-x}Fe_2O_4$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0$) catalysts were prepared by sol-gel auto combustion method and characterized by X-ray diffraction, Transmission Electron Microscopy, X-ray fluorescence and Fourier Transform Infra-Red spectroscopy. Fenton's reaction was performed over different compositions of nickel zinc ferrite catalysts under neutral conditions and the catalytic activities were studied. The yield of the reaction, based on Gas Chromatographic and Chemical Oxygen Demand (COD) parameters were very high and the experimental results indicated complete degradation of target pollutant with significant reduction of COD with all catalysts within 75 min. Zinc substitution enhanced the catalytic activity of nickel ferrite and the un-substituted $ZnFe_2O_4$ degraded the target compound completely within 45 min. Catalysts were found to be reusable and the extent of iron leaching, quantified by Atomic Absorption Spectroscopic studies was negligible after five consecutive cycles indicating the mechanism to be heterogeneous. Phase analysis of catalyst using XRD after the completion of each catalytic cycle confirmed the stability of the catalyst toward the Wet Peroxide Oxidation of 4-chlorophenol.

1. Introduction

The growing pollution of the hydrosphere has stimulated the need for developing new technologies for water and waste water treatment. Phenol and its chlorinated derivatives are among the most persistently existing organic pollutants found in industrial waste waters because of their extensive use in petrochemical units, oil refineries, polymer and pharmaceutical industries [1,2]. Chlorophenols represent an important class of Persistent Organic Pollutants (POPs) released into the environment mainly from the plastic and pesticide industries and is listed by the US EPA in the clean water act and by the European Union Decision, due to their high toxicity and low biodegradability. Inhibitory effects of phenol on microbial activity have been reported for concentrations larger than 500 ppm, and chlorinated phenols exhibit an even larger biotoxicity at similar concentrations [3,4]. In people, developmental, behavioral, neurologic, endocrinal, reproductive and immunologic adverse health effects have been linked to these compounds.

Environmental concerns have led to extensive research on the safe and effective removal of hazardous organic compounds from aqueous streams. An ideal waste treatment process must completely mineralize the toxic species present in the waste streams without leaving behind any hazardous residues in a cost-effective manner. Numerous classes of abatement techniques including biological, thermal and physico-chemical treatments have been developed in the last few years for the detoxification of organic pollutants present in water [5]. Biological treatments usually require a long residence time for the micro organisms to degrade the pollutant, because they are affected by chlorophenol toxicity; thermal treatments present considerable emission of other hazardous compounds and physico-chemical techniques, which include processes such as flocculation, precipitation etc. require a post treatment to remove the pollutant from the newly contaminated environment [4,5]. Advanced Oxidation Processes (AOP's) is an efficient alternative for the complete removal of organic pollutants and have been defined as aqueous phase oxidation based on the use of highly reactive hydroxyl radical as oxidizing agent [6]. Wet Air Oxidation (WAO) and Wet Peroxide Oxidation (WPO) are of special interest under this category [7–9], as they enable complete abatement of organic pollutants to carbon dioxide and water [10,11]. Unlike

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* Corresponding author. Tel.: +91 485 2822512; fax: +91 485 2822512.
E-mail address: mk@macollege.in (M. Kurian).

http://dx.doi.org/10.1016/j.jwpe.2014.10.011
2214-7144/

WAO, WPO takes advantage of employing hydrogen peroxide as the liquid oxidant, avoiding gas-liquid mass transfer limitations. Also the severe operating conditions of temperature in the range 200–300 °C and pressure in the range 20–80 bar make WAO more capital intensive, whereas WPO demands a lower capital [8]. Catalysis is an integral component in green processing technology, serving as an important tool to support sustainable development. Incorporating catalysts in WAO and WPO (becoming CWAO and CWPO) can enhance treatment performance at even milder operating conditions, thus making processes economic and more attractive [12,13]. Heterogeneous catalysts in CWPO consist most commonly of transition metal oxides or noble metals which can be easily recovered, regenerated and reused [14]. For these reasons, several studies have been addressed on the incorporation of active iron or copper based species such as amorphous silica, zeolites and pillared clays in WPO [15]. The oxidation of organic compounds by Fenton's reagent has gained an increasingly important role in the development of alternative technologies for water and wastewater remediation. The process uses ferrous ion as catalyst to generate hydroxyl radicals ($^{\bullet}OH$) from hydrogen peroxide along with other side reactions [16–18],

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \quad (2)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HOO^{\bullet}/O_2{}^{\bullet} \quad (3)$$

$$Fe^{2+} + HOO^{\bullet}/O_2{}^{\bullet} \rightarrow Fe^{3+} + H_2O_2 \quad (4)$$

$$HOO^{\bullet}/O_2{}^{\bullet} + HOO^{\bullet}/O_2{}^{\bullet} \rightarrow H_2O_2 \quad (5)$$

$$HO^{\bullet} + HOO^{\bullet}/O_2{}^{\bullet} \rightarrow H_2O + O_2 \quad (6)$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (7)$$

The main disadvantage of this process is the continuous loss of the catalyst through the effluent which causes further pollution. Besides, this process requires acidification of the solution since the optimum operating pH is around 3, corresponding to the maximum concentration of the active ferrous ion species. To overcome these drawbacks, heterogeneous Fenton like systems using MFe_2O_4 (Fe, Ni, Zn) and Fe^0/Fe_3O_4 were employed. Among these MFe_2O_4 type materials received extensive applications as a catalyst because of its structural composition and thermal and chemical stability toward various reaction conditions.

Ferrites with spinel structure have the general chemical formula $M^{2+}Fe_2{}^{3+}O_4$, where M^{2+} is a divalent metallic ion such as Mn, Co, Ni, Zn, Cr, Cu or a mixture of these. The spinel configuration is based on cubic close packing of oxide ions, forming tetrahedral and octahedral coordination sites that can be occupied either by divalent or trivalent metal ions. The catalytic activity of spinel type ferrites containing transition metal ions depends mainly on the redox properties of ions and on their distribution among octahedral and tetrahedral coordination sites. The surface of spinel structure mostly contains octahedral sites and consequently its catalytic activity is related to the octahedral cations [19,20]. In addition to the chemical modifications, physical modifications of spinel ferrites such as particle size also can be tuned by selecting a particular route of synthesis since the experimental conditions used in the preparation of these materials play an important role in the cation distribution and hence the catalytic activity of the ferrite nanoparticles produced. Nanoferrites with controlled chemical structure, crystallite size and crystallite distribution can be obtained through sol–gel auto combustion method using ethylene glycol as the gelating agent described in our previous publications [21,22]. Recent literature studies have reported that spinel ferrites containing Ni, Co, Zn and Cu have technological significance as catalysts due to their special electronic and magnetic properties. The presence of these metals in ferrite spinel lattices strongly modifies their stability and redox properties toward catalytic reactions. Many reactions including decomposition of hydrogen peroxide [23], oxidation of carbon monoxide [24], oxidation of propane [25] oxidation of phenol and its derivative compounds [26], decomposition of cyclic organic peroxides [27], etc. show the activity of the ferrite as a catalyst. We have reported the catalytic efficiency of cobalt-zinc ferrite nanoparticles toward the complete degradation of 4-chlorophenol from water under mild conditions [26].

The present study evaluates the effectiveness of mixed ferrite nanoparticles for the degradation of 4-chlorophenol using peroxide oxidation in aqueous phase. $Ni_xZn_{1-x}Fe_2O_4$ nanoparticles ($x = 0$, 0.25, 0.5, 0.75 and 1) were prepared by sol–gel auto combustion method. The catalysts were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), X-ray Fluorescence (XRF) and Fourier Transform Infra-Red Spectroscopy (FTIR). Liquid phase catalytic peroxide oxidation of 4-chlorophenol (4-CP) over the prepared ferrite nanoparticles under mild conditions was studied by Gas Chromatography (GC) and Chemical Oxygen Demand measurements (COD). The reaction products were analyzed by Gas Chromatography–Mass Spectroscopic (GCMS) technique. The catalytic decomposition of H_2O_2 and its residual amount were studied using permanganometric method [28]. The contribution of residual peroxide toward COD analysis was theoretically calculated on the basis of the equation,

$$K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2$$

The theoretical COD value for 1 g of H_2O_2 based on above equation is 470.6 mg, which makes the COD overestimation ratio 0.47 mg/L [29]. The influence of different reaction variables like reaction time, temperature, 4-CP concentration, peroxide concentration and catalyst concentration were also studied in detail. The reusability of the catalysts was investigated for five consecutive cycles and the possibility of iron leaching was checked using Atomic Absorption Spectroscopy (AAS). Based on the products obtained, a plausible reaction mechanism is also suggested.

2. Experimental

2.1. Preparation and characterization of catalysts

The mixed spinels of $Ni_xZn_{1-x}Fe_2O_4$ ($x = 0.0$, 0.25, 0.5, 0.75, 1.0) were prepared by the sol–gel auto combustion method, using ethylene glycol as the gelating agent. Pure (99.9%) $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and ethylene glycol from Merck, India were used as starting materials. Required stoichiometric ratio of $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were 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-ignited to form a fluffy product which was calcined at 800 °C for 4 h to achieve transformation into spinel phase. The ferrite powder was then sieved through a 90 mm mesh. The prepared ferrite compositions were $ZnFe_2O_4$, $Ni_{0.25}Zn_{0.75}Fe_2O_4$, $Ni_{0.5}Zn_{0.5}Fe_2O_4$, $Ni_{0.75}Zn_{0.25}Fe_2O_4$ and $NiFe_2O_4$, hereafter designated as Z 1, Z 2, Z 3, Z 4 and N 1 respectively.

Phase identification of the prepared particles was performed using Bruker AXS D8 Advance X-ray diffractometer with CuK_{α} ($\lambda = 1.5406$ Å) 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 diffractograms [21]. The particle size, distribution of nanoparticles and surface morphology were confirmed using PHILIPS 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