

INVERSE SPINEL NICKEL FERRITE AS THE ANODE MATERIAL FOR ELECTROCHEMICAL OXIDATION OF PHENOL

G. SATHYA & L. JOHN BERCHMANS

Electropyro Metallurgy Division, CSIR-Central Electrochemical Research Institute, Karaikudi, India

ABSTRACT

Environmental pollution has become a major issue due to rapid industrialization and urbanization. Over the years, organic and inorganic chemical products are produced in voluminous quantities from the domestic and industrial processes. Among the organic pollutants aromatic, chlorinated hydrocarbons and pesticides are considered among most toxic compounds. They are relatively resistant to biodegradation due to strong organic bonds. The present study focuses on the possibility of using nickel ferrite as the anode, for the oxidation of phenol in alkaline medium. The electro oxidation and degradation of phenol had been investigated by cyclic voltammetry technique. Phenol can be oxidized on ferrite electrodes giving rise to benzoquinone and aliphatic organic acid. On further oxidation, the intermediate products can completely oxidized to CO₂, which is a less toxic gaseous product compared to phenol. From the study, it is concluded that the inverse spinel nickel ferrite compound is found to work as an effective anode material, which can oxidize phenol into non-toxic components like carbon dioxide and water. The treated end products are environment friendly gas and liquid which can be acceptable to the environmental consideration.

KEYWORDS: Phenol, Environmental Pollution, Nickel Ferrite Anode, Electro Oxidation

INTRODUCTION

Industrial and human activities have contributed greatly to the wide variety of organic and inorganic pollutants into the environment. Of all the polluting compounds, organic pollutants cause most of the environmental problems due to the release of toxic gases and high chemical oxygen demand (Libralato et al., 1999). The most harmful pollutants are aromatic hydrocarbons (Nicolas, 1999; Watson et al., 2004), chlorinated hydrocarbons (Chmielewski et al., 2004) and pesticides (Comminellis et al., 1995; Drever et al., 1997; Mallevalle et al., 1996; Yamaguchi et al., 2003). These organic hydrocarbons are relatively resistant to biodegradation.

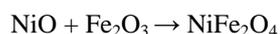
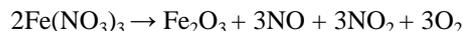
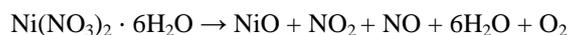
In general organic pollutants can be destroyed electrochemically by direct anodic oxidation using dimensionally stable electrodes or by an indirect oxidation route. The electrodes play an important role on the treatment of inorganic and organic compounds. Electrochemical treatment does not need any additional chemicals and is therefore environmentally compatible, versatile, safe and easy to handle (Grimm et al., 1998; Simonsson et al., 1997). Electrochemical oxidation of phenolic compounds have been tried using different electrode materials like Pt electrodes (Ureta-zanartu et al., 2001; Andreescu et al., 2003), Ta/PbO₂ anode (Tahar et al., 1998), Bi-doped PbO₂ electrodes, boron doped diamond electrode, Sb doped SnO₂ coated titanium anodes, graphite anodes (Kannan et al., 1995), carbon nanotube electrodes and Sb doped SnO₂, fluoride doped PbO₂, iridium oxide and coated electrodes (Bock et al., 2000).

Even though many electrode materials have been tried in the past, there is still a cheap, efficient and environmentally compatible anode material to be developed for this purpose. In this regard, a novel oxide electrode material, nickel ferrite has been prepared and intended for the oxidation of phenol and the results of the investigation are presented in this paper.

EXPERIMENTAL

Preparation of Nano Nickel Ferrite Powders

Analard grade chemicals such as nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (All chemicals of analytical grade were purchased from Merck Specialties private limited, Bangalore, India) were used as starting materials without any further purification. An aqueous solution of metal nitrates containing Ni^{2+} , Fe^{3+} , and hexamine was prepared according to the stoichiometric ratio. The mixed solution was taken in a quartz bowl and stirred for 1 hour to obtain a homogeneous solution. Then the bowl was placed over a hot plate (Science tech – SE 299) and heated at 300 °C. On thermal treatment, the solution boils, foams, ignites, and burns with an incandescent flame temperature, producing fine ash composed of the oxide product. The combustion reaction is completed at 2 hours. Evolution of gases like carbon dioxide, water, nitric oxide and nitrogen dioxide results in the formation of fine particles of nickel ferrite as reported in the literature (Patil et al., 1993). Then the synthesized powders were sintered at 700 °C for 5 h in air by keeping the product in an electrical resistance furnace (Morgan – Model Number 3953). Thermal decomposition of starting materials can be expected to follow the sequence:



From the above reactions, it has been noted that the decomposition of hexamine is highly exothermic due to the evolution of large amount of gases. As synthesized powders were characterized using a Philips analytical X-ray diffractometer with Cu-K_α (1.54 Å) radiation and also studied by Laser Raman Spectroscopy (Reneishaw-Invia Laser Microscope, 200-800 cm^{-1}). The morphology of the fine powders was exemplified from scanning electron microscopy using a JEOL-JSM-3.5 CF instrument.

Electrode Preparation

The electrodes were prepared by coating (brush painting), on the glassy carbon support (dia 3 mm), with a suspension of nickel ferrite powder along with a suitable binder such as tetrafluoroethane and Triton X-100. After each application, the solvent was removed by drying for 10 min in a pre-heated oven at 400 °C in air. This operation was repeated until the desired oxide loading (5 mg cm^{-2}) was attained (Godinho et al., 2002; Singh et al., 2000). The electrodes were finally annealed in air at the same temperature for 1 h. Before coating, the glassy carbon support was mechanically polished with emery paper, rinsed with plenty of water and finally washed with Millipore water (Merck India Private limited, Bangalore, India) in an ultrasonic bath (Labman Scientific Instruments Private Limited, Chennai, India).

Electrochemical Apparatus and Electrodes

A conventional three-electrode electrochemical cell was used. The cell was consisting of a glassy carbon working electrode (GC), a platinum auxiliary electrode and mercury and mercurous chloride in 1 M KCl is used as the reference electrode. All the potential values mentioned in this study are against the reference electrode. All chemicals were of analytical grade and triple distilled water was used for the preparation of solutions. Various concentrations of phenol were prepared and used for the studies. Cyclic voltammetric studies were performed in 0.5 M NaOH solution with different concentrations of phenol. The oxidation behavior was studied at different scan rates on a NiFe₂O₄ coated glassy carbon electrode. The current potential transient curve was recorded between (-0.4 to 1.0 V) using Wenking potentiostat (POS 73) and X-Y recorder (Rikadenki, model RW-201T). For each trial freshly coated electrode was used for the studies. Cyclic voltammograms were recorded at room temperature with different concentrations of phenol at various scan rates.

RESULTS AND DISCUSSIONS

X-Ray Diffractometer (XRD)

The XRD pattern of the synthesized NiFe₂O₄ compound is shown in Figure 1.

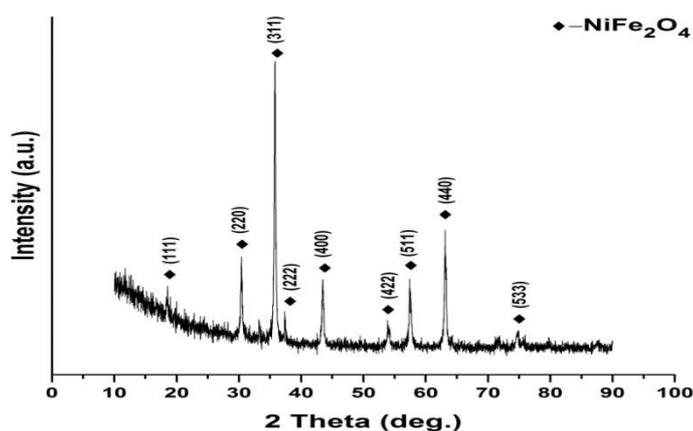


Figure 1: XRD Pattern of Nano Crystalline NiFe₂O₄ Compound

From the XRD spectrum, it follows that the x-ray spectrum is well matched with the standard data, thus confirming the single phase cubic NiFe₂O₄ compound as reported in the literature (JCPDS PDF 10-0325) (Kamala Bharathi et al., 2008). The well defined inverse spinel structure with fcc – (Fd – 3m space group-227) phase was identified without any impurity phases. The average particle size of NiFe₂O₄ samples has been calculated from the XRD line broadening of (311) high intensity peak using Debye-Scherrer's formula (Gul et al., 2007; Balaji et al., 2005).

$$D = K \lambda / \beta \cos \theta$$

From the above data, it was inferred that the average crystallite size of the powders is within the range 22–34 nm.

Scanning Electron Microscopy (SEM)

The SEM micrograph is shown in Figure 2.

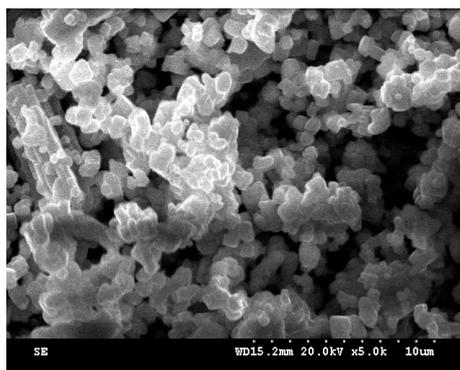


Figure 2: SEM Image of Nanocrystalline NiFe₂O₄ Compound

The SEM picture has shown the agglomerated crystals of nano-structured NiFe₂O₄ particles which are suitable for the fabrication of electrodes.

Energy Dispersive Spectroscopy (EDS)

The elemental composition of the ferrite powders was determined by EDS analysis is shown in Table 1. The spectrum exhibits the presence of Fe, Ni, and O in appropriate concentrations in the compound. The spectral information confirms that the synthesized material is a pure phase of nickel ferrite.

Cyclic Voltammetry (CV)

Initially the cyclic voltammetric curve was recorded for the background electrolyte, followed by recording the voltammograms in the presence of phenol solution. It was observed that the oxidation reaction of phenol was found to occur at 0.3 V with respect to Hg/Hg₂Cl₂. On further addition, the oxidation peak was gradually increased with increase in concentrations. From the graphs, the dependence of the oxidation potential (E_p) and the oxidation current (I_p) were determined at various scan rates. On increasing the scan rate, the I_p values are found to increase for different concentrations of phenol. The cyclic voltammogram of 3.8 ppm of phenol in 0.5 M NaOH on nickel ferrite coated GC electrode at different scan rates is shown in Figure 3.

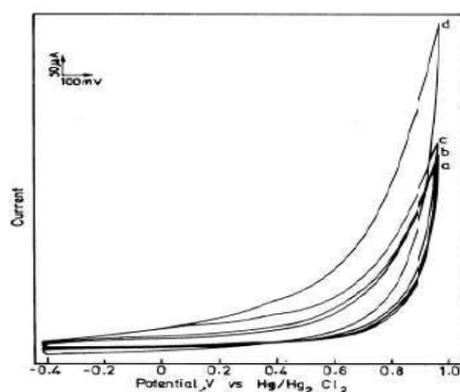


Figure 3: Cyclic Voltammogram of 3.8 PPM of phenol in 0.5 M NaOH GC Electrode with Different scan rates. (a) Blank, (b) 20 mV/s, (c) 50 mV/s, (d) 100 mV/s Modified Electrodes.

The CV curves recorded at different concentrations of phenol on glassy carbon electrode are also shown in Figure 4.

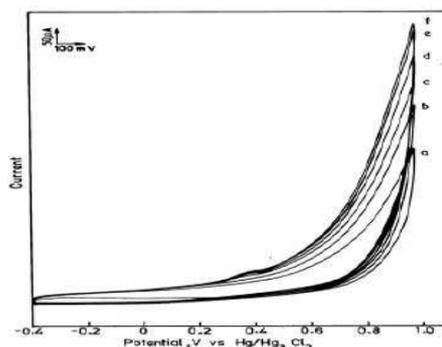


Figure 4: Cyclic Voltammogram of Different Concentrations Phenol in 0.5 M NaOH GC Electrode, (a) 3.8 ppm, (b) 7.4 ppm, (c) 10.7 ppm, (d) 13.7 ppm, (e) 16.6 ppm.

From the graph, the E_p and I_p values are calculated and presented in Table 2.

It is observed that E_p values are found to shift with increase in concentration of phenol. It is also noticed that the oxidation current I_p is found to increase with increase in concentrations of phenol.

Table 3, shows the E_p and I_p values at different scan rates with increase in concentration of phenol using NiFe_2O_4 coated GC electrode. The oxidation potential of phenol is found to vary from 290 to 360 mV vs $\text{Hg}/\text{Hg}_2\text{Cl}_2$ electrode. It is also inferred that an increase in concentration of phenol shows a small shift in the anodic potential and also a linear increase in the I_p values. The cyclic voltammograms obtained with different concentrations of phenol are shown in Figure 5.

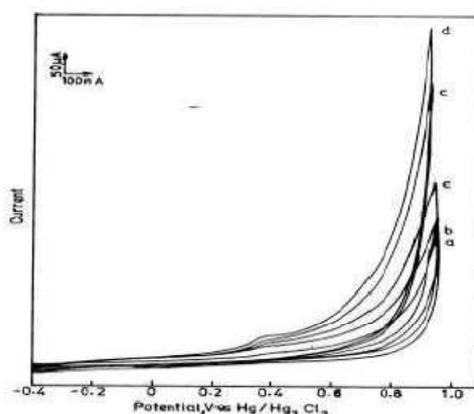
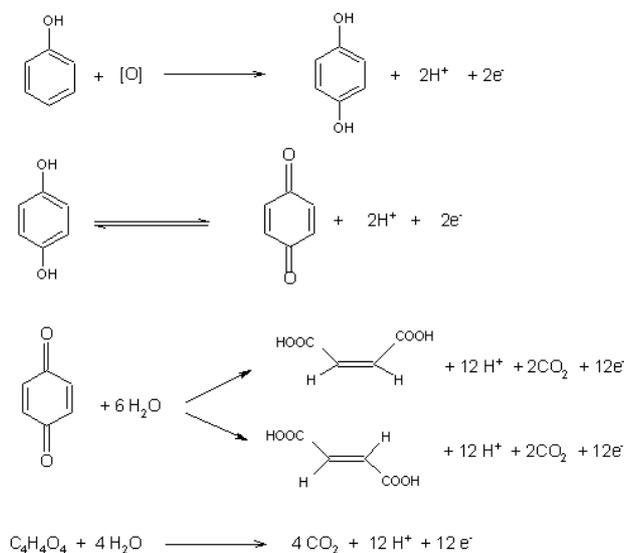


Figure 5: Cyclic Voltammogram of Phenol in 0.5 M NaOH at NiFe_2O_4 Coated GC Electrode with Different Concentrations of Phenol. (a) 3.8 ppm, (b) 7.4 ppm, (c) 10.7 ppm, (d) 13.7 ppm.

From the CV studies, the mechanism of oxidation of phenol can be predicted by following the oxidation pathway. The overall mechanism for the electrochemical oxidation of phenol involves the following three consecutive steps (Tahar et al., 1998)

- Oxidation of phenolic compound to a quinoid compound.
- Ring opening reaction with formation of aliphatic acids.
- Mineralization to CO_2 .

The oxidation pathway of phenol is as follows,



Several researchers have proposed the above mechanism (Hu et al., 2005; Iniesta et al., 2001), which is acceptable for the oxidation of phenol. The oxidation of phenol starts with one electron transfer leading to a phenoxy radical leading to benzoquinone formation. It is believed that benzoquinone is an important intermediate, which is produced on the oxidation of phenol and in the second stage benzoquinone is further oxidized in to various carboxylic acid, under various electrode/electrolyte conditions. During the electro oxidation process, it is observed that initially the electrolyte turned to yellow-brown color and then become darker and finally paled and become colorless. It can be concluded that the color change represents the process of the oxidation of phenol to benzoquinone and subsequently to carboxylic acids. Benzoquinone is an important intermediate and in the second stage which is further oxidized to various carboxylic acids as reported in the literature (Chopra et al., 1983).

Ultra Violet Spectroscopy (UV)

The Figure 6 shows the absorption spectrum of NiFe₂O₄ powder.

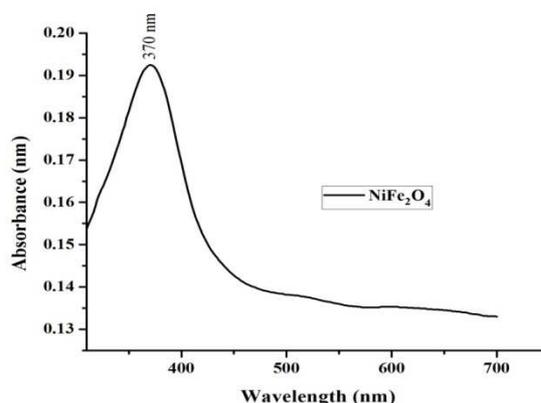


Figure 6: UV Absorption Spectrum of NiFe₂O₄ Compound

It exhibits a strong absorption band at about 370 nm. The band gap calculated from UV cut off is found to be 3.35 eV and by using the equation $E=h\nu$.

UV spectral analysis of the treated solution revealed the presence of benzoquinone in the treated solution. It indicates the absorbance peak around at 370 nm. The absorbance value is found to vary on continuous electrolysis of the solution as reported in the literature (Feng et al., 2003). On the oxidation of benzoquinone, a decrease in pH is noticed indicating the oxidation product might be the carboxylic acid. The carboxylic acid oxidation is more complicated than benzoquinone. Several mechanisms are proposed for the oxidation of benzoquinone. If benzoquinone is absorbed onto the electrode surface and gives up an electron, an adsorbed -OH radical attacks the benzoquinone molecule. When this process repeats itself at the para position, the ring could be opened to form maleic acid and another small organic compound, which is believed to be ethylene or oxalic acid. The formation of the intermediate maleic acid has been proven by the UV spectral analysis. It is suggested that maleic acid is reduced to succinic acid at the cathode followed by the oxidation to malonic and acetic acid and then finally to carbon dioxide by anodic oxidation. In our studies also, similar observations have been noticed using nickel ferrite as the anode material.

The proposed mechanism for oxidation of phenol is well supported (Cominellis et al., 1988; Lund et al., 1991). From the above investigation, it is clear that the phenol could be electrochemically oxidized on inverse spinel nickel ferrite electrode surface in to quinones, oxalic acid, acetic acid and finally carbon dioxide and water. These oxidized products are considered as less toxic, environmentally friendly and amenable for discharge into the common sewage for further treatment.

CONCLUSIONS

Phenol can be electrochemically oxidized using a inverse spinel NiFe_2O_4 as the anode material. The electrochemical oxidation of phenol follows the oxidation path which initially gets oxidized to benzoquinone, acetic acid, oxalic acid and finally to carbon di oxide and water. The oxidation potential for phenol is found to be lower on nickel ferrite electrode material which is considered to be less energy and the degradation. From the above investigation, it has been concluded that the toxic phenol can be electrochemically oxidized on the surface of nickel ferrite electrode.

Table 1: The Elemental Composition Data for NiFe_2O_4

Element	Wt %	Atomic %
Ni	17.97	11.07
Fe	59.78	38.68
O	22.25	50.26

Table 2: The Cyclic Voltammetry Data of GC Electrode at Different Concentrations of Phenols

γ (mV/s)	Concentration of phenol in 100 ppm (ml)	E_p (mV)	I_p (μA)	$I_p/\gamma^{1/2}$
50	1	350	10	1.414
50	2	360	15	2.1211
50	3	360	20	2.828
50	4	370	25	3.535
50	5	380	30	4.242

Table 3: Cyclic Voltammetry Studies on NiFe₂O₄ Coated GC Electrodes at Different Scan Rate

γ (mV/s)	Concentration of phenol in 100 ppm (ml)	E _p (mV)	I _p (μ A)	I _p / $\gamma^{1/2}$
50	1	360	5	0.7071
100	2	360	10	1.000
150	3	290	70	5.715

REFERENCES

1. G. Libralato, A.V. Ghirardini and F. Avezzù, *J.Hazard. Mater.*, **153**, 928 (2008).
2. J.M. Nicolas, *Aquat. Toxicol.* **45**, 77 (1999).
3. G.M. Watson, O-K. Andersen, T.S. Galloway and H. Michael, *Aquat. Toxicol.* **67**, 127 (2004).
4. A.G. Chmielewski, Y.X. Sun, S. Bulka and Z. Zimek, *Radiat. Phys. Chem.*, **71**, 437 (2004).
5. Ch. Comninellis and A. Nerini, *J. Appl. Electrochem.* **25**, 23 (1995).
6. J.I. Drever and R.A. Mcconnin, Upper saddle River, N.J. Prentice-Hall, 3rd ed., 119 (1997).
7. J. Mallevialle, P.E. Odendaal and M.R. Wiesner, McGraw-Hill, New York, (1996).
8. N. Yamaguchi, D. Gazzard, G. Scholey and D.W. Macdonald, *Chemosphere*, **50**, 265 (2003).
9. X. Fan and X. Zhang, *Mater.Lett.*, **62**, 1704 (2008).
10. Ch. Comninellis and E. Plattner, *Chimia*, **42**, 250 (1988).
11. J. Grimm, D. Bessarabov and R. Sanderson, *Desalination*, **115**, 285 (1998).
12. D. Simonsson, *Chem. Soc. Rev.* **26**, 181 (1997).
13. M.S. Ureta-zanartu, P. Bustos, M.C. Diez, M.L. Mora and C. Gutierrez, *Electrochim. Acta*, **46**, 2545 (2001).
14. S. Andreescu, D. Andreescu and O.A. Sadik, *Electrochem. Commun.*, **5**, 681 (2003).
15. W.B. Tahar and A. Savall, *J. Electrochem. Soc.*, **145**, 3427 (1998).
16. N.Kannan, S.N. Sivadurai, L. John Berchmans and R. Vijayavalli, *J. Environ. Sci. Health A*, **30**, 2185 (1995).
17. C. Bock and B. MacDougall, *J. Electroanal. Chem.*, **491**, 48 (2000).
18. K.C. Patil, *Bull. Mater. Sci.*, **16**, 533 (1993).
19. M.I. Godinho, M.A. Catarino, M.I. Da Silva Pereira, M.H. Mendonça and F.M. Costa, *Electrochimica Acta*, **47**, 4307 (2002).
20. R.N. Singh, S.K. Tiwari, S.P. Singh, N.K. Singh, G. Poillierat and J.F. Koenig, *Electrochim. Acta*, **45**, 1911 (2000).
21. K. Kamala Bharathi, K. Balamurugan, P.N. Santhosh, M. Pattabiraman and G. Markandeyulu, *Phys.Rev.B*, **77**, 172401 (2008).
22. I.H. Gul, A.Z. Abbasi, F. Amin, M. Anis-ur-Rehman and A. Maqsood, *J. Magn. Magn. Mater.*, **311**, 494–499,

- (2007).
23. S. Balaji, R. Kalaiselvan, L. John Berchmans, S. Angappan, K. Subramanian and C. O. Augustin, *Mater. Sci. Eng. B*, **119**, 119 (2005).
 24. C.G. Hu, W.L. Wang and B. Feng, *J. Metastable and Nanocrystalline Materials*, **23**, 289 (2005).
 25. J. Iniesta, P.A. Michaud, M. Panizza, G. Cerisla, A. Aldaz and Ch. Comninellish, *Electrochimica Acta*, **46**, 3573 (2001).
 26. K.L. Chopra, S. Major and D.K. Pandya, *Thin Solid Film*, **102**, 1 (1983).
 27. Y.J. Feng and X.Y. Li, *Water Res.*, **37**, 2399 (2003).
 28. H. Lund and M.M. Baizer, *Organic Chemistry*. New York: Marcel Dekker, **616** (1991).

