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Research Article

Degradation Of 4-Nitrophenol With Fe/Ni Bimetallic Nano Catalyst At Room Temperature

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Abstract

The aim of the present study is focus on the activity of semiconductor materials on the degradation of 4-Nitrophenol. Zero-valent iron (ZVI) is a valuable material for environmental remediation, because of its safeness, large availability, and inexpensiveness. Moreover, its reactivity can be improved by the addition of nanoparticles of other elements such as noble metals. The synthesized pure nano Fe and Ni were characterized using UV/Visible spectrophotometer. In the present work catalytic degradation of 4-Nitrophenol was carried out using semiconductor couple Fe/Ni under UV irradiation. The semiconductor couple of Iron (Fe) & Nickel (Ni) were used as nanocatalyst for the study. UV-Vis spectroscopic technique has been used for studying the catalytic degradation of 4-Nitrophenol. Complete degradation of 4-Nitrophenol was achieved for 90min of irradiation in presence of Fe/Ni nanocomposite.

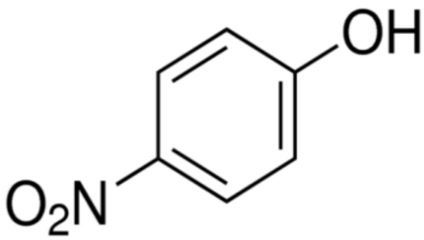
Key words: catalytic degradation, 4-Nitrophenol, Zero-valent iron (ZVI), bimetallic nanocatalyst (Fe: Ni nanocomposite).

INTRODUCTION

Recently, aromatic nitro compounds such as 4-Nitrophenol and nitrobenzene have been comprehensively employed in the industrial production of insecticides, fungicides, herbicides, dyes, and explosives.[1] However, these nitro compounds are extremely toxic contaminants that affect human health and environment, accumulating in the ecosystems and the human body.[2,3] In contrast, 4-Aminophenol, the product of 4-Nitrophenol reduction, is an industrially useful material, serving as an intermediate for the manufacture of analgesic drugs, photographic developers, corrosion inhibitors, and anticorrosion lubricants.[4,5] Therefore, the conversion of 4-Nitrophenol into the less harmful and reusable 4-Aminophenol is an essential and critical issue.[6] In order to resolve the environmental problems caused by 4-Nitrophenol, numerous approaches have been developed for its conversion into 4-Aminophenol, such as electrocoagulation,[7] electro-Fenton methods,[8] bio-degradation,[9] catalytic hydrogenation,[10] and photocatalytic degradation.[11] Bimetallic nanostructures are particularly attractive for catalytic applications, because the multiple metal components in bimetallic nanocrystals serve as active centers for the reduction reaction and enable fast and convenient access of the reactant molecules to activate the catalytic process.[12] Moreover, the two metal ions present in such nanostructures provide synergistic interaction opportunities, which lead to enhanced physical, electrical, and chemical properties, resulting in excellent performance in catalytic applications.[13] Many noble metal alloy nanoparticles are reported for the treatment of water, but application of transition metal particles (monometallic and bimetallic alloy particles) is very limited in the literature.[14-20] Over the last few years, diverse nanocatalysts have been developed for the reduction of 4-Nitrophenol to 4-Aminophenol, based on noble and transition metals such as Au, Pt, Ag, Pd, Cu, Fe, and Ni.[21-24]

4-Nitrophenol

4-Nitrophenol (also called p-nitrophenol or 4-hydroxy nitro benzene) is a phenolic compound that has a nitro group at the opposite position of the hydroxyl group on the benzene ring. The chemical formula for 4-nitrophenol is $C_6H_5NO_3$ and the molecular weight is 139.11 g/mol. It is slightly



soluble in cold water and carbon disulfide but soluble in hot water, hot benzene, alcohol, chloroform, acetone, pyrimidine, toluene, ether, fixed alkali hydroxide solutions, and carbonates. It is denser than water. 4-Nitrophenol shows two polymorphs in the crystalline state. In solution, 4-Nitrophenol has a dissociation constant (pK_a) of 7.15 at 25 °C. 4-Nitrophenol can be used as a pH indicator. A solution of 4-nitrophenol appears colourless below pH 5.4 and yellow above pH 7.5. The yellow colour of the 4-Nitrophenolate form (or 4-Nitrophenoxide) is due to a maximum of absorbance at 405 nm (ε = 18.3 to 18.4 $mM^{-1}\ cm^{-1}$ in strong alkali). In contrast, 4-Nitrophenol has a weak absorbance at 405 nm (ε = 0.2 $mM^{-1}\ cm^{-1}$). The isosbestic point for 4-Nitrophenol / 4-Nitrophenoxide is at 348 nm, with ε = 5.4 $mM^{-1}\ cm^{-1}$. 4-Nitrophenol is an intermediate in the synthesis of paracetamol. It is reduced to 4-Aminophenol, then acetylated with acetic anhydride. 4-Nitrophenol is used as the precursor for the preparation of phenetidine and acetophenetidine indicators, and raw materials for fungicides. Bioaccumulation of this compound rarely occurs. In peptide synthesis, carboxylate ester derivatives of 4-Nitrophenol may serve as activated components for construction of amide moieties. 4-Nitrophenol irritates the eyes, skin, and respiratory tract. It may also cause inflammation of those parts. It has a delayed interaction with blood and forms methaemoglobin which is responsible for methemoglobinemia, potentially causing cyanosis, confusion, and unconsciousness. When ingested, it causes abdominal pain and vomiting. Prolonged contact with skin may cause allergic response. Mechanism of degradation of 4-Nitrophenol In this reaction Ni^0 can mediate an electron transfer from Fe^{2+} to water and produce hydroxyl radicals (eq. 1-4)

$$Fe^0 \longrightarrow Fe^{2+} + 2e^- \quad (1)$$

$$Fe^{2+} + Ni^0 \longrightarrow Fe^0 + Ni^{2+} \quad (2)$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad (3)$$

$$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + OH + H^+ \quad (4)$$

Alternatively, zero valent iron (Fe^0) can react with dissolved oxygen and produce Fe^{2+} and O_2^{2-}; the latter reacts with hydrogen to form H_2O_2 and produces hydroxyl radicals through Fenton's reaction.[25,26] Hydroxyl radicals, which are strong oxidants (redox potential +2.8 V), can initiate the formation of radical centers. Thus, metallic iron can initiate the reductive degradation of 4-Nitrophenol.

2. Experimental Procedure

Materials

Powder form of synthesized pure Fe:Ni nanocomposite, 4-Nitrophenol (M.Wt: 139.11 g/mol), Double distilled water was used for preparation of various solutions.

4-Nitrophenol dye solution preparation

The catalytic degradation efficiency of as-synthesized Fe/Ni catalyst was evaluated by performing the 4-Nitrophenol degradation reaction at room temperature. In catalytic dye degradation experiment prepared 100 ml of 20 ppm dye solution in 250 ml beaker and 20 mg of catalyst semiconductor was added and mixture was stirred to obtain uniform suspension. 5 ml of dye solution was taken and centrifuged and the absorbance was measured by using UV spectrophotometer and it is noted as initial concentration. Stirring process is continued and the absorbance value was measured for 5 ml reaction mixture every 5 minutes until the colour degraded. A gradual decrease in the absorbance values was observed.

3. Characterization

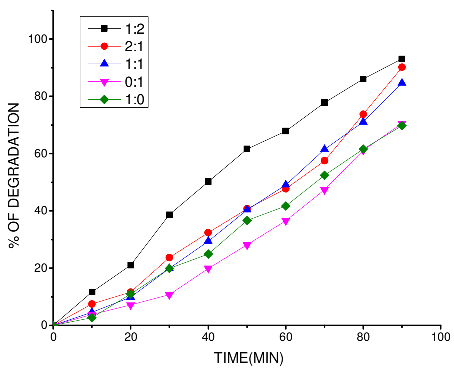
UV-Vis spectral changes

Ultraviolet/visible spectroscopy can also be used to study reaction rates. If a reagent or a product of the reaction absorbs radiation at a particular frequency the spectrometer can be set to measure the absorption at that frequency as a function of time. The absorption peaks corresponding to 4-Nitrophenol, diminished and finally disappeared under reaction which indicated that the 4-Nitrophenol had been degraded. The spectrum of 4- Nitrophenol in the visible region exhibits a main band with a maximum at 333 nm. The decrease of absorption peaks of 4np at λmax = 333 nm in the figure indicated a rapid degradation of 4-Nitrophenol. Complete degradation of 4-Nitrophenol was observed in 90 min in the optimized conditions.

4. Results and discussions

UV- visible spectral changes

Among these compositions 1:2, 2:1, 1:1, 0:1, 1:0, 1:2(Fe : Ni) has the highest rate constant and highest activity. It is highly efficient, nontoxic and chemically stable catalyst. The larger surface area of this catalyst causes greater adsorption of the 4-Nitrophenol.



Comparative graph of Fe/Ni nanocomposite for 4-Nitrophenol degradation

5. Conclusion

The Present paper indicated that pure nano Fe/Ni couple could be efficiently used to degrade the 4-Nitrophenol. The degradation kinetics of 4-Nitrophenol was found to be fast with maximum efficiency within 90 min using Fe:Ni (1:2) catalyst. The synthesized material was characterized using UV–visible spectroscopic techniques.

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