Synthesis, characterization and evaluation of the photocatalytic activity of cobalt ferrite-zeolite Y nanocomposite for the degradation of *4-nitrophenol* under visible light irradiation

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ABSTRACT

This study presents A novel one-pot method for the synthesis of $CoFe_2O_4$-Zeolite Y (CFO-ZY) nanocomposite for the efficient degradation of 4-nitrophenol (4-NP) from water. The nanocomposite was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The photocatalytic activity of $CoFe_2O_4$-ZY nanocomposite was evaluated under visible light irradiation by UV-Vis analysis. The CFO-ZY nanocomposite exhibited remarkable *photocatalytic activity under visible light irradiation, achieving above 85% degradation of 4-NP in 180 minutes.*

Keywords: *Zeolite, Co ferrite, Photocatalyst, 4-nitrophenol*

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1. *INTRODUCTION*

Todays, the pollution of drinkable water sources and the destruction of aquatic habitats by organic or inorganic toxins have become the main concerns of researchers. As is clear, 4-nitrophenol has been significantly used as an intermediate for the synthesis of insecticides, synthetic dyes, and agricultural pesticides. Because of their toxicity, high solubility and chemical stability, nitro-aromatic compounds such as nitrophenols and their derivatives are among the hardest compounds in industrial wastewater. In addition, these aromatic compounds are toxic to humans and other organisms even at very low concentrations. Since nitrophenol is not biocompatible, has high stability and high toxicity, the entry of nitrophenol and its derivatives into our body causes potential problems and mutagenicity. Its carcinogenic effect has also been proven. As a result, the removal of 4-NP can be investigated as an essential issue for researchers[1].

Several conventional methods are available for nitrophenol removal such as sonolysis, solvent extraction, chemical reduction, membrane filtration, adsorption and many others. Currently, photocatalysis innovation has been described as a appropriate method to remove pollutants from wastewater [2, 3].

According to this technology, a semiconductor with reasonable bandgap energy absorbs photons of sun based energy to subsequently produce a pair of negative electrons (e-) and a positive hole (h+). After photo-excitation, these generated charge carriers are isolated from the light and exchanged to the surface of semiconductors to activate redox reactions[4].

Cobalt ferrites are a bunch of transition metal oxides that are utilized in various applications including catalysis, battery, and energy storage. These materials exhibit soft magnetic behavior at room temperature with a band gap within the extend 1.57–2.03 eV [5].

On the other hand, due to high photocatalytic activity, low solubility and chemical stability, magnetic materials are a very suitable option for use in other substrates for the ability to separate the catalyst from the reaction medium and reuse it. Using a single semiconductor, like ferrite, leads to a low efficiency of photocatalytic activity [6, 7].

As a result, various efforts have been made to optimize these catalysts by making them composite with other compounds to prevent the fast electron-hole recombination.

Zeolites are broadly used as support matrices for photocatalytic and absorbent applications due to their porous structure and high specific surface area and low cost for wide distribution of metal nanoparticles. The high activity of metal-based catalysts with the presence of metal cations or clusters can provide many active sites for reaction sites by forming inside the structure of zeolites [8].

The novel CFO-ZY nanocomposite developed in this study provides a promising solution for water pollution remediation. Its exceptional photocatalytic activity under visible light irradiation enables effective degradation of organic pollutants such as 4-nitrophenol. This development offers a more sustainable and cost-effective alternative to traditional water treatment methods. By using the magnetic properties of this nanocomposite as well as the use of visible light energy, we can help clean water sources and improve environmental quality. In addition, the use of zeolite bed has made the cost of this catalyst affordable.

Materials and method

All the chemicals used in this project were manufactured by Merck Germany. The zeolite Y was obtained from Tajran Pishgan Company and the sample of 4-nitrophenol was obtained from Alvan Thabat Company of Iran. The structure and characteristics of 4-nitrophenol are shown in Table 1. LED lamp (Nemanor Asia Company, Iran) with a power of 15 watts was used as a light source.

IUPAC Name	4-nitrophenol
Molecular Formula	$C_6H_5NO_3$
Molecular Weight	139.11 g/mol
Color / Form	Colorless to slightly yellow crystals
Boiling Point	279 °C (Decomposes)

Table1. *Chemical and physical prroperties of 4-NP[9]*

Synthesis of $CoFe_2O_4$-Zeoilte Y

Nanoparticles of spinel ferrite $CoFe_2O_4$ and zeolite were prepared using the chemical co-precipitation method. The molar ratio of ferrite to zeolite was 1:1 following a stoichiometric process. The materials were dissolved in 30 ml of deionized water and after adjusting the pH to 13, the reflux process was Carried out for 1 hour at 80 °C. After cooling to room temperature, the obtained precipitate were filtered and washed several times with distilled water. The final sample was first dried in a vacuum oven 120 °C for 12h and then calcined at 350 °C for 6 hours.

Characterization techniques

FT-IR analyzes were performed on a Shimadzu FTIR-8400S spectrophotometer using KBr pellets for sample preparation.

On the other hand, the particle structure was analyzed by powder X-ray diffractometer (XRD, Bruker AXS D8 advance).

Photocatalytic experiments

The photocatalytic activity of CFO-ZY nanocomposite on the degradation of 4-NP solution was investigated. In a typical process, the catalytic reaction was carried out in a 100 mL photoreactor, which contained 30 mL of pollutant solution (10 mg/L) and 0.03 g of catalyst. Before irradiation, the solution was stirred in a dark *condition (180 min) to access the initial physical adsorption of 4-nitrophenol on the catalyst surface. Irradiation process was performed using a 15 W LED lamp (with an emission wavelength range of about 550 nm cool white). All photocatalytic experiments were completed under the same conditions. To determine the photocatalytic effect, 3 ml of each sample was collected. Photocatalytic activity was investigated by relating light absorption to degradation rate using a UV-Vis* at the range *of 350-500 nm.*

Results and discussion

Photocatalysis mechanism

Irradiation of light on a nano metal oxide in aqueous medium excites electrons and subsequently produces holes. Then, it leads to the formation of hydroxyl radicals (•OH), which are strong oxidizing agents capable of degrading pollutants. Nevertheless, the lifetime of radical species is very short and they react quickly in the vicinity of the catalyst surface. In addition, the agglomeration process is inevitable for magnetic metal oxides. Using a porous substrate, such as zeolite, will be a suitable solution to avoid these two problems. The porous structure and high surface area of zeolite prevents agglomeration of the catalyst and improves its dispersion and stability. increasing the surface-to-volume ratio leads to an enhancement in the number of active reaction sites and a decrease in the recombination e/h. As a result, the use of zeolite in the structure prevents the electron-hole recombination through the electrons produced inside the zeolite structure [10, 11].

This study has confirmed the use of this nanocomposite as an agent for the destruction of the toxic pollutant nitrophenol.

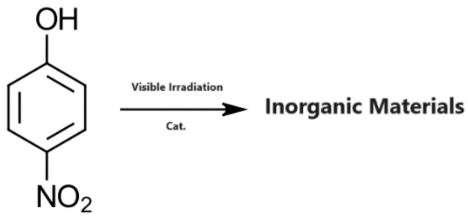

***Fig1**. photodegradation of 4-Nitrophenol*

CFO-ZY composite characterization

FTIR spectra of the prepared zeolite Y and Co-ferrite zeolite are shown in Fig 1. *The bands located at 459 and 578 cm^{-1} belong to internal bonds (Al or Si elements) tetrahedral units and bending vibrations of two six-ring external bonds of zeolite Y, while the absorption bands identified at 719 cm^{-1} and 788 cm^{-1} can be assigned to external bonds and vibrations, respectively. As a result, the peak of bonds in the region of 700 to 1500 cm^{-1} indicates the stretching and bending vibrations of Si-O and Al-O in Y Zeolite.*
The bands in the range of 1700 to 3410 cm^{-1} can be attributed to the vibrations of hydroxyl groups and absorbed H_2O molecules, bonds including O-H bond and H-O-H successive bending in the structure of Zeolite Y. Furthermore, the bands of the FTIR spectrum of pure $CoFe_2O_4$ is given the observed bands at around 3450 cm^{-1} and 1581 cm^{-1} are due to H_2O molecules adsorbed on the $CoFe_2O_4$ surface. The absorption bands regions between 400 and 600 cm^{-1} also are related to stretching vibrations of Co-O and Fe-O bonds[12, 13].

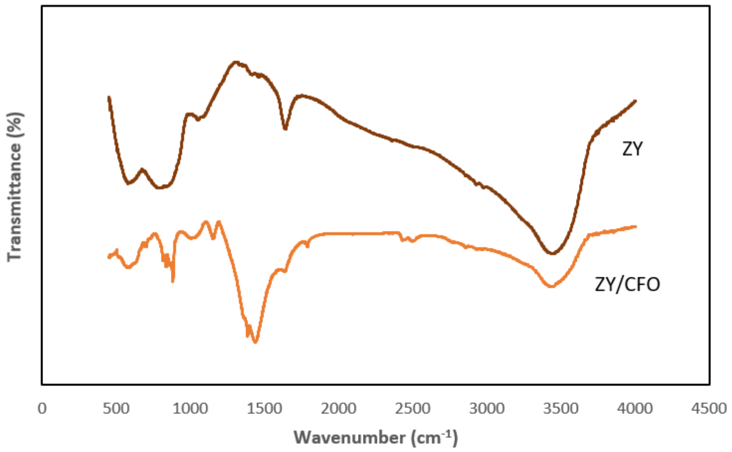

Fig2. *FTIR spectra of ZY and ZY/CFO*

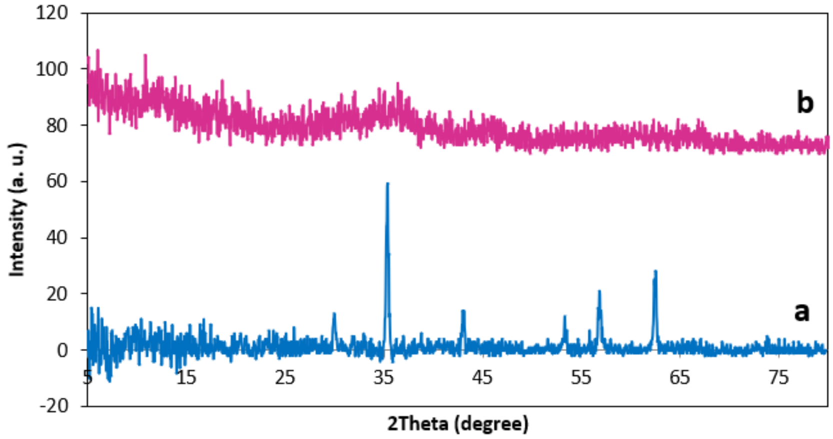

Fig3. *XRD patterns of the prepared a. CFO and b. CFO-ZY.*

Figure illustrates the XRD pattern of Zeolite Y and COFe$_2$O$_4$/ Zeolite Y. It can be seen that all the intense peaks of zeolite Y were specified at 2q angles of approximately 6.28, 10.17, 11.95, 15.73, 18.73, 20.43, 23.71, 27.13 and 32.54 at the attachment angles. (111), (220), (311), (331), (511), (440), (533), (620), and (733) crystallized in structure with JCPDS card (41-0118))[14]. Besides, in the XRD pattern of CoFe$_2$O$_4$, the position of all diffraction peaks corresponds well with the final composite (with JCPDS standard card no 01-1121*) at 35.67, 30.34˚, 57.20˚, 62.82˚[15]. In the XRD patterns of CFO-ZY (b), it can be seen that all added peaks are in good agreement with Co-ferrite.*

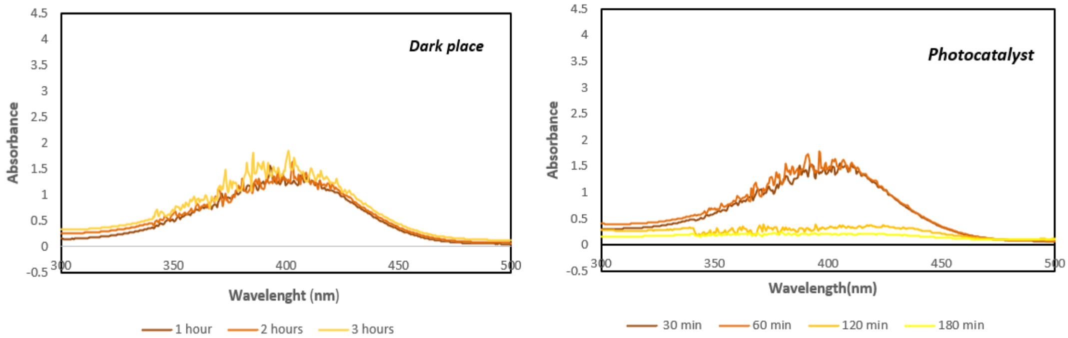

Fig4. *Adsorption and Photocatalytic performance for 4-NP.*

The ferrite part in the CFO-ZY nanocomposite absorbs visible light and leads to electron excitation from the ground state to a higher energy level. The excited electron from the ferrite is transferred to the conduction band of the zeolite component and creates an electron-hole pair. The zeolite part can be used as a support and enhancer to improve charge separation, by suppressing the recombination of electron-hole pairs, increasing the lifetime of charge carriers. The generated electron can react with oxygen molecules and reactive oxygen species (ROS) such as hydroxyl radicals (• OH) to produce. The holes can react with water molecules to produce additional OH radicals. Highly reactive •OH radicals attack the 4-NP molecule, which leads to its oxidation. The nitro group (NO_2) is converted to nitrate ions (NO_3^-) and the aromatic ring is finally decomposed into simpler organic compounds or carbon dioxide and water.

In summary, the removal of 4-NP by CFO-ZY nanocomposite involves a synergistic combination of adsorption and photocatalytic degradation. The adsorption process first adsorbs 4-NP molecules on the surface of the nanocomposite, while the photocatalytic process involves the generation of reactive species that decompose the adsorbed 4-NP molecules[16-18].

conclusion

This nanocomposite specifically removes harmful pollutants from the environment. The 85% degradation of 4-NP achieved in 180 minutes using CFO-ZY nanocomposite under visible light irradiation shows its high efficiency. Over time, after 120 minutes, a significant improvement of the process can be seen . The magnetic properties of $CoFe_2O_4$ allow easy recovery and reuse of the nanocomposite, making it more stable and cost-effective.

This level of degradation is significant because 4-NP is a common and persistent organic pollutant in wastewater. The ability of the nanocomposite to effectively remove such contaminants highlights its potential as a promising solution to water treatment challenges.

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