Degradation of NO_3^- and NO_2^- pollutants in wastewater over $ZnFe_2O_4$ nanoparticles

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During the last years, environmental issues about water contamination have become one of the major concerns for society. Most domestic and industrial activities are responsible for the production of huge quantities of wastewater containing undesirable toxic contaminants. In this study, the synthesized $ZnFe_2O_4$ nanoparticles were prepared through hydrothermal method for the degradation of nitrate (NO_3^-) and nitrite (NO_2^-) in different wastewater sources. The characterization of $ZnFe_2O_4$ before and after treatment were achieved by transmission electron microscope (TEM), which indicated that the synthesized nanoparticles showed spherical morphology with a diameter between 50–100 nm. In addition, X-ray powder diffractometer (XRD), was performed, the diffraction peak of the synthesized $ZnFe_2O_4$ nanoparticles were established and catalogued at $2\theta = 35.44°$ corresponded to that of magnetite (Fe_3O_4) (311), consistent with Joint Committee on Powder Diffraction Standards (JCPDS) database. XANES spectra of Fe atom in $ZnFe_2O_4$ exhibited an absorbance feature (Fe = 7114 eV) of 1s to 3d transition. The standard Fe–O bond distance in $ZnFe_2O_4$ sample was 1.95 Å. The extended X-ray absorption fine structure EXAFS indicate that the synthesized $ZnFe_2O_4$ the first layer structure for Fe-O bond length is 1.94 ± 0.01 Å, and its coordination number is 3.81 The final results of ESCA analysis confirmed that the degradation percentage of NO_3^- and NO_2^- increases rapidly with increasing UV irradiation time in the analyzed wastewater sources.

Keywords: Zinc ferrite nanoparticles ($ZnFe_2O_4$); nitrite nitrogen (NO_2^-); nitrate nitrogen (NO_3^-), XANES/ EXAFS.

Introduction

The wastewater generated principally by the operations of industrial factories and human activities are responsible for the environmental impact making severe problems which are considered as a risk to the life of the ecosystem [1,2]. Heavy metals and hazardous compounds are presented in wastewater in huge amounts. Among them, nitrate (NO_3^-) and nitrite (NO_2^-) which are pollutants that represent a danger to ground and surface water resources worldwide. Over the last few years' nanotechnology is taking attention with the objective of intending of control and prevent the ecosystem damage [3]. Ferrites are considering iron oxide compounds that contain metallic ions. This unique nanomaterial is broadly used for pollutant removal due to its electromagnetic properties, being able to eradicate a wide range of contaminants. In this study, the synthesized $ZnFe_2O_4$ nanoparticles were prepared through hydrothermal method for the degradation of nitrate (NO_3^-) and nitrite (NO_2^-) in different wastewater sources. The physical and chemical characteristics of $ZnFe_2O_4$ was studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and field UV/Vis absorption spectroscopy (UV/Vis).

Experiments

2.1. Synthesis of Zinc ferrite nanoparticles ($ZnFe_2O_4$).
The $ZnFe_2O_4$ nanoparticles were synthesized by hydrothermal method, whereby 0.72 g of $Zn(NO_3)_26H_2O$ and 2 g of $Fe(NO_3)_39H_2O$ were dissolved 40 mL of deionized water and resulting solution was stirred for 30 min. The final precipitates were collected by centrifugation, washed with dH_2O and absolute ethanol, then dried in a hot air oven at 60 °C for 2 h. Finally, the particles were grinding and sieving to get an optimum size.

Results

This research pointed out that by the heated of ferrite nanoparticles the hydrogen activation reduction occurred. When the temperature increase above 573 K, hydrogen reacts with magnetite, and the oxygen content in the ferrite is combined with hydrogen to form H_2O, which causes the spinel structure of the magnetite to produce oxygen vacancies due to lack of oxygen, accompanied by the reduction of Fe_3^+ (tetrahedral position) to Fe_2^+ (octahedral position). The diffraction peaks for $ZnFe_2O_4$ were established and catalogued as regular spinel structure and consistent with JCPDS-ICDD. The EXAFS parameters indicate that the bond length of the first layer of Fe_3O for Fe-O is 1.95 ± 0.01 Å, and the coordination number is 3.38; in the case of the synthesized $ZnFe_2O_4$ the first layer structure for Fe-O bond length is 1.94 ± 0.01 Å, and its coordination number is 3.81. The normalized XANES for at the Fe K-edge and its first derivative spectra showed different values for the pre-edge peaks before and after hydrogenation. The peaks of $ZnFe_2O_4$ before hydrogenation showed that the Fe_2O_3 is more intense than the pre-edge peak in Fe_3O_4 and FeO. On the other hand, FeO showed a higher intense peak following by Fe_2O_3 after hydrogenation. This agreement with this compound being inverse spinel confirming the chemical structure of $ZnFe_2O_4$.

Discussion

EXAFS patterns reported different values due to the fact that the position of the Fe in the Fe_3O_4 structure and its position are complicated, causing a difference in the coordination number, bond length and layer structure. The bond length of the first layer structure Fe-O is within the error range, so it can be judged that zinc oxyporite and Fe_3O_4 have the same reverse spinel structure. Besides, the XANES regions and pre-edge of the absorption spectrum are crucial due to both enclose on the immediate environment electronic information of the absorbing atom. The pre-edge intensity is also valence-dependent since the electronic configuration has to be factored in when associating the target atom intensities with different valences. These peaks are valuable because their intensities and sites are sensitive to the immediate symmetry of the metal. When the $ZnFe_2O_4$ is reduced by the H_2 its edge position is shifted lower energy, this phenomenon occurred due to the oxidation valence changed significantly because of the hydrogen reduction. In addition, the synthesized nanoparticles showed that the peaks have the same valence and atomic symmetry as the iron element of Fe_3O_4 demonstrating the presence of the crystal lattice.
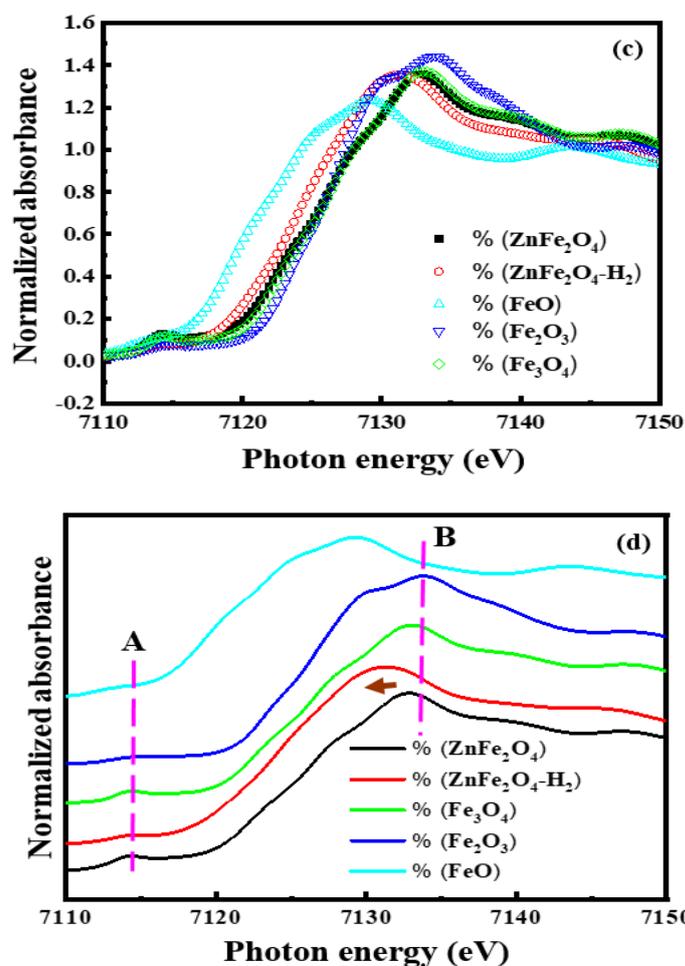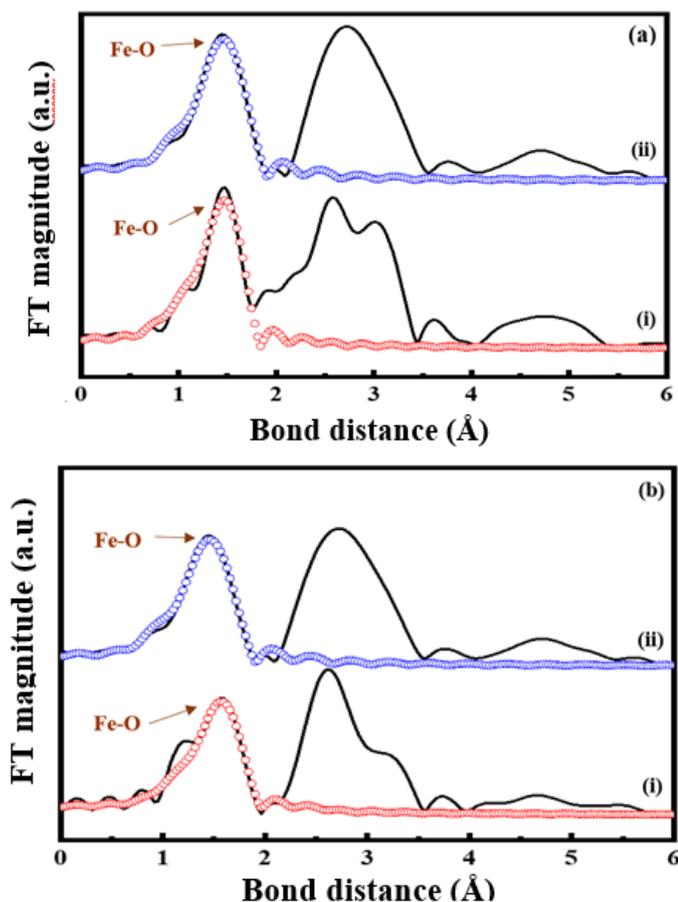

Fig. 1. EXAFS pattern of $ZnFe_2O_4$ (a) before and (b) after hydrogenation and iron standard. (c-d) Fe K–edge derivative XANES spectra of $ZnFe_2O_4$ and iron standards.

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