$CoFe_2O_4$ spinel used as a catalyst for the degradation of organic dyes

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Abstract

Spinel ferrites have been widely studied owing to their structural, optical, dielectric, and magnetic properties leading to numerous applications. $CoFe_2O_4$ nanoparticles have been synthesized directly *via* the sol-gel method with glycine as a fuel. The Rietveld refinement of the X-ray diffraction patterns revealed the formation of a single cubic structure with a space group, no secondary phase was observed. The lattice parameter and the average crystallite size of powders produced from the standard and alkaline solutions were 8.36/8.38 Å, and 511/1060 Å, respectively. The characteristic vibrations modes of the spinel structure have been revealed by Fourier Transform Infrared spectroscopy. $CoFe_2O_4$ powders were tested for Fenton catalysis, and their performance was investigated for dye degradation.

Experimental

The cobalt ferrite powders were prepared by the sol-gel method by mixing iron nitrates [$Fe(NO_3)_3.9H_2O$], cobalt nitrates [$Co(NO_3)_2.6H_2O$], and glycine [$C_2H_5NO_2$] at the considered proportions. Nitrates were used as the oxidizers and the glycine as the fuel. The mixture were dissolved in 100 mL of dionized water. The first preparation of this mixture (standard, S) was heated at 100°C and the second one (alkaline, A) was regulated at pH = 11 by adding droplets of ammonia solution [NH_4OH].

The two products were characterized by means of X-ray diffraction (PANalytical Empyrean diffractometer) and Fourier Transform Infrared Spectroscopy, FT-IR, (Spectrum two model FTIR spectrometer).

Results

1- XRD analysis

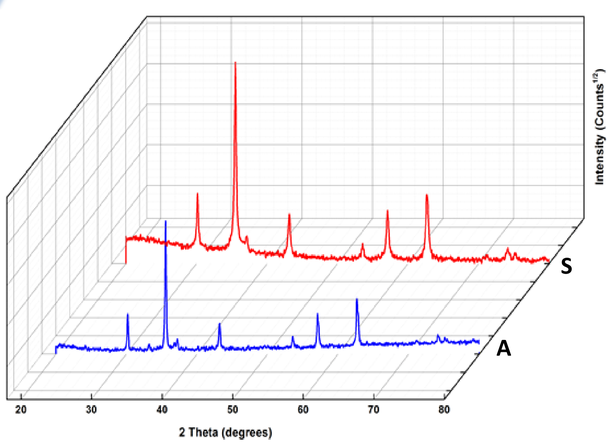

***Fig.1**: Evolution of the XRD diffractograms of the standard (S) and alkaline (A) samples.*

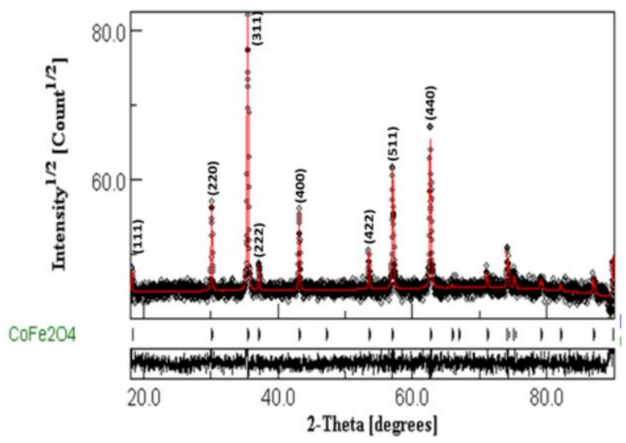

***Fig.2**: Rietveld refinement of the XRD pattern of the standard sample.*

Table 1: crystal structure, lattice parameter (a), and crystallite size (< L >) of the standard (S) and alkaline (A) samples.

Sample	Space group	a (Å)	< L > (Å)
S	Fd-3m:1	8.36	511
A	Fd-3m:1	8.38	1060

The XRD patterns show well resolved and intensive diffraction peaks indicating a good crystallinity. The formation of $CoFe_2O_4$ type structure is confirmed by the presence of the most important diffraction peaks. The indexed (111), (220), (311), (222), (400), (422), (511), and (440) planes are in good agreement with those of the cobalt ferrite structures.

2- FT-IR analysis

FT-IR spectra of the synthesized ferrite powders reveal the characteristic peaks associated with the vibrations corresponding to cobalt and iron ions. In the wavenumber range of 385−450 cm^{-1} , the metal–oxygen bands are divided into two types: the first type, which is observed in the range of 500 – 600 cm^{-1} is due to intrinsic stretching vibrations of $Fe^{3+} - O^{2-}$ ions in tetrahedral sites, while the second type in the range of 385–450 cm^{-1} which is attributed to the stretching vibrations of $Co^{2+} - O^{-2}$ at octahedral sites.

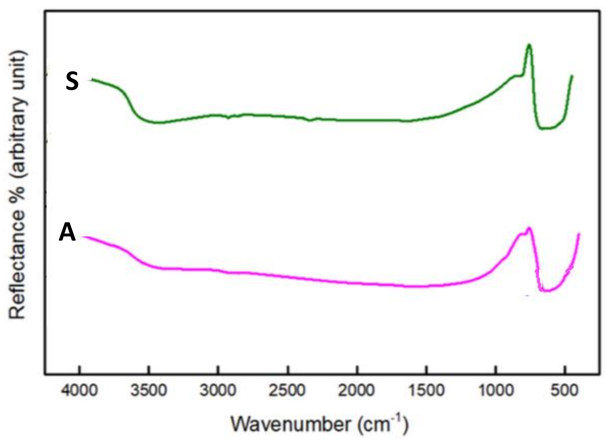

***Fig.3**: FT-IR spectra of the standard (S) and alkaline (A) samples.*

3- Activity of spinel ferrites in the discoloration of methyle orange (MO)

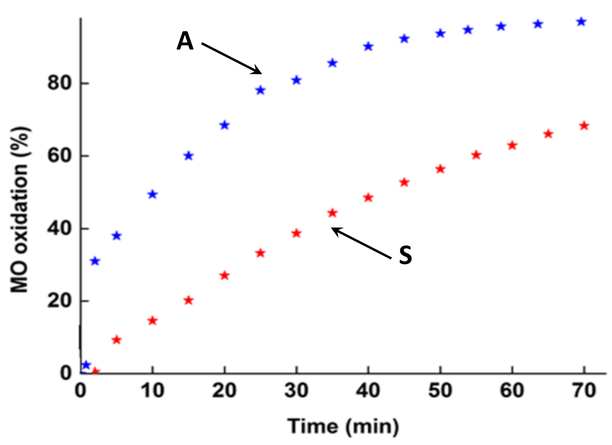

***Fig.4**: Methyle orange oxidation by spinel ferrites.*

In oxic conditions, systems formed by metals/O2 may produce H_2O_2 in situ via the reduction of the dissolved oxygen in water by these metals. In this case, the oxidation of the metal and the reduction of oxygen occurred simultaneously:

$M \leftrightarrow M^{n+} + ne^-$ and $O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2$

The formed M^{n+} and H_2O_2 allows the implementation of Fenton process (an advanced oxidation process) thereby hydroxyl radicals are generated:

$M^{n+} + H_2O_2 \leftrightarrow M^{n+1} + OH^- + \bullet OH$

Hydroxyl radicals (•OH) with redox potential of 2.8 V are non-selective oxidants that aggressively attack all organic pollutants.

Increasing the pH of the solution improved the discoloration efficiency of MO. In fact, it increased from 64 to 91 % when the pH increased from 7 to 11 attained after 70 min of reaction.

Conclusions

- Ferrite powders were elaborated using the sol- gel process, the precursors are iron nitrate and cobalt nitrate. glycine was used as complexation and polymerization agent. The characterization techniques are X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR).
- The Rietveld refinement of the XRD patterns reveals the formation of the spinel ferrite cubic structure. Increasing the pH of the solution causes a slight change in the lattice parameter and crystallite size values.
- FT-IR spectroscopy results confirm the formation of the spinel ferrite structure. Two types of metal oxygen bands are observed. The first type that appears for $CoFe_2O_4$ spectrum, in the range of 385 – 450 cm^{-1} , is attributed to the stretching vibrations of $Co^{2+} - O^{-2}$ ions. While the second type that appears in the range of 500 – 600 cm^{-1} is linked to intrinsic stretching vibrations of $Fe^{3+} - O^{2-}$ ions.

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