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Synthesis and Caracterisation of Spinel $CoFe_2O_4$: Application for Methylene Blue Photocatalytic Degradation.

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Highlights

- The $CoFe_2O_4$ nanoparticles with a high photocatalytic performance is obtained by hydrothermal synthesis.
- XRD characterization revealed the presence of spinel as the major phase.
- The photocatalytic activity is favored at low mass ratio and basic pH.

1. Introduction

Spinel ferrites nanomaterials of type MFe_2O_4 (M=Co, Ni, Mn, Zn, Cd… etc.) have received much attention in degradation of contaminants in waste water because of their optic, magnetic and catalytic properties. Among them, the spinel $CoFe_2O_4$ is a good photocatalyst with band gap inferior to 1.5 eV, making them capable to absorb visible light irradiation [1, 2]. The physical and chemical properties of spinel nanoparticles are strongly affected by the synthesis route. However, the hydrothermal method is known to be suitable for the synthesis of spinel particles with small size crystallite and high specific surface area compared with coprecipitation and sol- gel methods [3].
The aim of the present work is (i) to synthesis cobalt ferrite $CoFe_2O_4$ nanoparticles by hydrothermal route, (ii) to investigate their photocatalytic degradation activity toward a common dye, methylene blue (MB).

2. Methods

$CoFe_2O_4$ particles were prepared via hydrothermal reaction in a stainless-steel autoclave with a Teflon liner under autogenously pressure. In a typical synthesis process, 0.05 mol of $Co(NO_3)_2$ and 0.07 mol of $Fe(NO_3)_3$ were dissolved in deionized water. Then, 1 mol/L of NaOH solution was added dropwise to the above solution under stirring until the pH reached 10. The resulting suspension was transferred into the autoclave and maintained at 160 °C for 20 hours. After the reaction completed, the resulting solid products were collected by centrifugation, washed with deionised water to remove impurities, and then dried at 80°C for 12 hours.
The structural and textural properties of the materials were carried out by powder X-ray diffraction (PXRD) and nitrogen adsorption-desorption isotherm measurement. The band gap energy was determined using diffuse reflectance spectroscopy (DRS). The electrochemistry study by Mott-Schottky allowed us to estimate the semiconducting behavior of the nanoparticles.
The photocatalytic activity of the as prepared nanoparticles was evaluated by the degradation of MB under visible light using a 40 Watt tungsten halogen lamp at room temperature (20°C). The initial dye concentration was 10 mg/L and different amount of $CoFe_2O_4$ (0.1, 0.2 and 0.4 g) were used to obtain the ratio of 1/2, 1 and 2, respectively. The pH of the solution was varied between 6 and 12. Before illumination, the suspension was stirred in the dark for 30 min to reach the adsorption equilibrium of MB on the catalyst. At given irradiation time intervals, the residual concentration of MB was determined by measuring the absorbance of the solution at 665 nm using a UV-Vis spectrophotometer.

3. Results and discussion

The diffraction pattern of the sample obtained at 160°C for 20 h (Fig.1) showed a reflection peaks characteristic of $CoFe_2O_4$ with cubic structure. Diffraction lines of the figure 1 present the spinel $CoFe_2O_4$ as the major phase (95.4%). The estimated lattice parameter is a = 8.34 Å, close enough to the theoretical value

(JCPDS Card No. 22-1086, a=8.392 Å). Based on a Gaussian distribution, the mean crystallite size is C_S = 5.56 ± 1.37 nm, calculated from the FWHM of all the diffractogram peaks.

The adsorption-desorption isotherm (Fig.2) showed a large hysteresis confirming that the as prepared nanoparticles by hydrothermal method are typically mesoporous. The specific surface area was calculated based on Brunauer-Emmet-Teller (BET) equation. The BET surface area was 99.07m^2/g. This value is of the same order of magnitude as those obtained by Y. HAMMICHE and al (2016), at different operating conditions. The band gap calculation based on the intersection of the linear part of $(\alpha h\nu)^2$ with the axe of the hν abscissa, gived a band gap of 1.5 eV (Fig.3). Thereby, the (C^{-2}-V) Mott-Schottky plot of the $CoFe_2O_4$ reveals an evolution of the photocurrent in the anodic direction which confirms the *n* type of the semiconductor (Fig.4).

The photocatalytic activity was evaluated in term of the degradation efficiency (%) of MB. The results showed the highest photocatalytic activity obtained for the small ratio 1/2 (Fig.5) where the degradation efficiency of MB reached ~80 %. In addition, an enhance in the photocatalytic activity when the pH solution becomes basic (Fig.6) was observed, which is probably due to the cationic character of methylene blue dye.

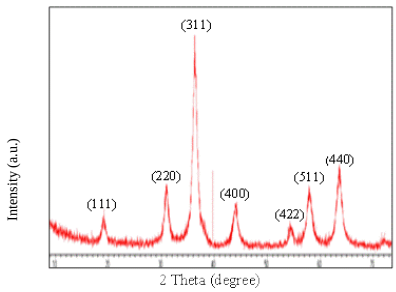

Figure 1: XRD pattern of the $CoFe_2O_4$

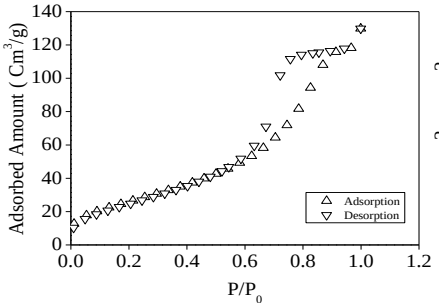

Figure 2. Adsorption-desorption isotherms

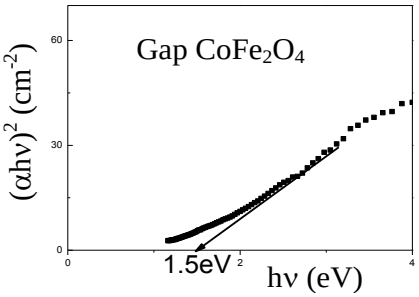

Figure 3. UV-Vis diffuse reflectance spectra of $CoFe_2O_4$

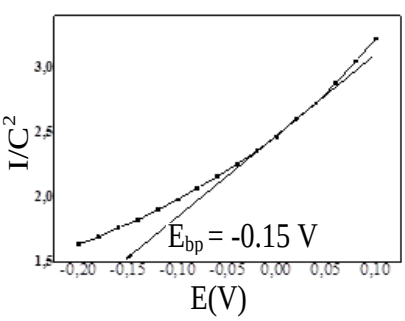

Figure 4. Mott- Schottky plot of $CoFe_2O_4$

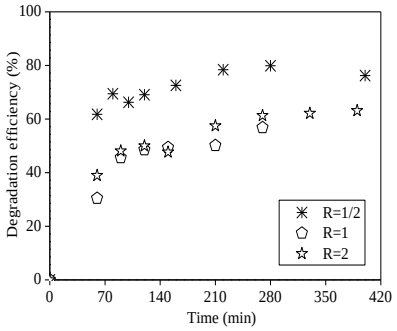

Figure 5. Effect of mass ratio solution on MB degradation

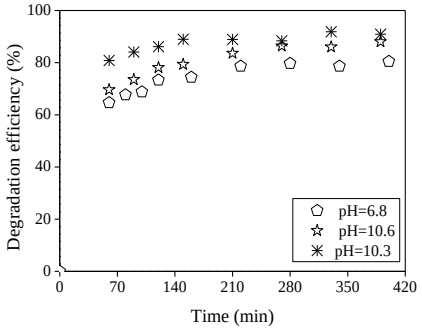

Figure 6. Effect of pH solution on the MB degradation

Conclusions

A cobalt ferrite nanoparticles with spinel structure was successfully prepared by the hydrothermal method. Their photocatalytic activity toward MB was investigated. The results showed that the efficiency of the degradation of the methylene blue is strongly affected by the operating conditions. The highest photocatalytic activity was obtained for the small ratio 1/2 and in a strongly basic medium.

References

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Keywords: $CoFe_2O_4$ spinel, hydrothermal method, photocatalytic degradation, methylene blue dye.