

**STUDY OF PHOTOCATALYTIC ACTIVITY OF COBALT FERRITE IN THE
DICLOFENAC SODIUM DEGRADATION.**

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Abstract

Pharmaceuticals compounds, like sodium diclofenac, are emerging pollutants that have been detected in wastewater and surface waters throughout the world. Their presence was demonstrated in South American rivers, in particular in the Suquía River basin, Córdoba, Argentina. There are several recent studies on applications of ferrite as photocatalyst used in the degradation of pollutants were reported. In this work cobalt ferrites synthesized by Pechini method were calcined at 600°C and 800°C. By XRD patterns were determined that both samples had spinel structure. By XPS and Mössbauer spectroscopy it was found that the material calcined at 600°C is an inverse spinel with a 74% of inversion. The ferrite calcined at 800°C presented a higher percentage (83%) of inversion in its structure. Both materials showed good magnetic properties, which is promising to facilitate their recovery from wastewater effluents. A solution of 40 ppm of sodium diclofenac were 100% degraded in 15 minutes of the photoreaction using Uv-germicide lamp, H₂O₂ as an oxidant and a cobalt ferrite as catalyst. The cobalt ferrite calcined at 800°C reached 86% of mineralization in 4 hours of photoreaction.

Keywords: cobalt ferrite, sodium diclofenac, degradation, photocatalysis.

Estamos dispuestos a someter este trabajo al volumen especial dedicado al CICAT 2020 en alguna de las revistas internacionales: Catalysis Today o Topics in Catalysis en caso de que los revisores y el comité científico lo seleccionen.

1. Introduction

In recent years, have started to talk about emerging pollutants (EP). EP are synthetic or natural organic chemical substances whose presence in wastewaters is commonly not regulated, but they can cause adverse effects for the environment or the human health [1]. Pharmaceuticals compounds are subclasses of EP that have been detected in wastewater and surface waters throughout the world [2]. Emerging organic contaminants are found in the environment and South American rivers are not an exemption as it was demonstrated by the presence of many pharmaceuticals in the Suquía River basin, in Córdoba province, Argentina. Atenolol, carbamazepine and diclofenac were the most frequently detected compounds in both dry and wet seasons, with concentrations $\leq 1 \mu\text{g L}^{-1}$. The possible effects of these compounds on the native biota should be addressed in future research [3]. Although their concentrations in aquatic environments are very low, they have unpredictable impacts on ecological system and human health [4]. Among the various pharmaceutical compounds, diclofenac is the widely used. Diclofenac is a non-steroidal anti-inflammatory drug used to reduce inflammation and can act as an anodyne for rheumatoid arthritis and osteoarthritis. On the other hand, diclofenac has shown adverse effects on aquatic and terrestrial vertebrates [5].

Wastewater treatment plants are commonly not designed to eliminate micro pollutants like pharmaceuticals [3]. Advanced oxidation processes (AOPs) have been widely investigated for their potential application in treatment of sewage, particularly where the water sources contain high concentration of ambiguous, refractory and recalcitrant chemical compounds such as aromatics, pesticides, pharmaceuticals, personal care products, drugs and endocrine disruptors among others [6]. Heterogeneous photocatalysis involves a group of oxidative-reductive reactions which can be incited by the formation of highly reactive chemical species in the presence of semiconductor oxides under light irradiation. This process does not create sludgers and therefore not produce the secondary pollution. Furthermore, the catalyst is not consumed during the photocatalytic process and it can be reused by successive catalytic runs [5].

With respect to the catalysis, spinel ferrites (AFe_2O_4), where A represents a transition metal ion, have been attracted attention exhibiting

excellent catalytic activity and structural stability. Ferrites are described being reduced to a cation excess composite and reoxidized to their initial state, while conserving the spinel structure [7]. Several recent studies on applications of ferrite as photocatalysts for the degradation of pollutants were reported where ferrites alone have been shown to be effective photocatalysts by utilizing light energy to create e^-/h^+ pairs on the photocatalytic surface. The e^-/h^+ pairs are then available for oxidation and reduction processes, which usually involve the formation of reactive oxygen species, such as $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, which then further aid in the decomposition of contaminants. In order to enhance the production of reactive oxygen species, oxidants such as H_2O_2 are added to the reaction mixture. With the addition of this substance, a Fenton-type system is created in which iron cations react with H_2O_2 [8]. For its part, the inherent magnetic characteristics of the synthesized materials probably allow simple and efficient separation of them from the reaction mixture thereby minimizing the subsequent procedure costs [9].

The objectives of the present research were characterization and testing two CoFe_2O_4 spinel ferrites in a photo-catalytic degradation of sodium diclofenac using Uv germicide lamp and H_2O_2 .

2. Experimental

Ferrites synthesis

The Co-Fe ferrites were synthesized by Pechini sol-gel method. Co and Fe ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as a metal sources with the molar ratio of Co:Fe 1:2. The $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in distilled water and stirred to be the uniform solutions with citric acid as a chelating agent at 60°C in a reflux system. Then the Co solution was added to the system. After 2 hours, ethylene glycol was added and the temperature was raised up to 120°C . Immediately the reflux system was opened. Subsequently, the obtained solutions were heated until the gel formation. The stoichiometric relationship alcohol/acid used was 4:1. The obtained gel was calcined to form solid foam during 2 hours at 450°C with a $4^\circ\text{C}/\text{min}$ ramp. The obtained solid foam was ground in a mortar and recalcined. A second temperature treatment was performed for 6 hours at 600 or 800°C with a $4^\circ\text{C}/\text{min}$ ramp obtaining the two samples synthesized in this work.

Solids characterization

The structure and crystalline phases of the obtained materials were characterized by X-ray diffraction (XRD) in a X'Pert Pro-PANalytical diffractometer equipped with $\text{CuK}\alpha$, $\lambda = 1.54\text{\AA}$. Diffraction patterns were collected in a range of 2θ from 4 to 80° . Uv-Visible diffuse reflectance spectroscopy (DRUv-Vis) was used to determine band gap energy (semiconductor character) of the calcined samples. The band gap values were obtained by plotting $(h\nu * KM)^2$ vs $(h\nu)$ [10]. The samples spectra were recorded using a spectrometer Jasco V-650, in the wavelength range 200-800 nm. The reducibility of the materials was measured by temperature-programmed reduction (TPR) experiments in a Micromeritics Chemisorb 2720. In these experiments, the samples were held at 150°C under flowing nitrogen to remove the remaining adsorbed oxygen for 30 minutes. Then, samples were heated at a rate of $10^\circ\text{C}/\text{min}$ in the presence of H_2 (5% H_2/N_2 flow, 20 mL/min STP), and the reduction reaction was monitored by H_2 consumption. The TPR experiments were performed up to 950°C . The magnetic properties: hysteresis loop and magnetic saturation, were measured by vibrating sample magnetometer (VSM) LakeShore 7300. The magnetization (M_s) was measured at room temperature and 1,3 T is the maximum applied field. The present species and spinel structure were determined by X-ray photoelectron and Mössbauer spectroscopy. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Scientific K-alpha spectrometer operated using Al $\text{K}\alpha$ (1486.6 eV) monochromatic X-ray source. The Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer. A source of ^{57}Co in a Rhmatrix of nominally 50 mCi was used. Velocity calibration was performed against a 12 μm thick $\alpha\text{-Fe}$ foil.

Catalytic performance evaluation

The sodium diclofenac degradation reactions were carried out at 25°C in a 500 mL tubular reactor, with recirculation and equipped with an 8W monochromatic germicidal lamp Philips at 254 nm). An effluent was simulated using a 40 mg L^{-1} of aqueous solution of sodium diclofenac (Parapharm 99%). Two cobalt ferrite concentrations were tested (0.2 and 1 mg L^{-1}). As an oxidant, a certain amount of H_2O_2 (Cicarelli 30%) was also added to reach a H_2O_2 :pollutants millimolar ratio of 42. Then the lamp was turned on for start the reaction. Samples were taken at different times to be analysed, after filtration of the catalyst.

The analysis of sodium diclofenac was performed by high performance liquid chromatography (HPLC) on a Perkin Elmer Serie2020 with Agilent Zorbax Eclipse Plus C18 4.6x250mm column and Uv-Vis detector and by Uv-vis spectroscopy with a Perse T7DS spectrometer. To characterize the mineralization degree of the pollutant the total organic carbon (TOC) removal efficiencies were examined. TOC was measure using a Shimadzu TOC-L CSN. The reduction in TOC was calculated by the equation: $[(\text{TOC}_{\text{M0}} - \text{TOC}_{\text{M240}}) \times 100] / \text{TOC}_{\text{M0}}$.

Results and discussion

Figure 1 shows the XRD patterns of synthesized ferrites. The peaks positions were matched with the International Centre of Diffraction Data (ICDD). The pattern corresponding to the spinel generic structure like AB_2O_4 (■) correspond to the synthesized cobalt ferrite CoFe_2O_4 (00-002-1045). For the analyzed materials calcined at both, 600 and 800°C , the most intense peak was observed at 2θ of about 35° . This peak is characteristic for spinel structure. Comparing the intensity of the mentioned peak, it could be inferred that on these materials, the thermal treatments at higher temperatures improve the cristanillity.

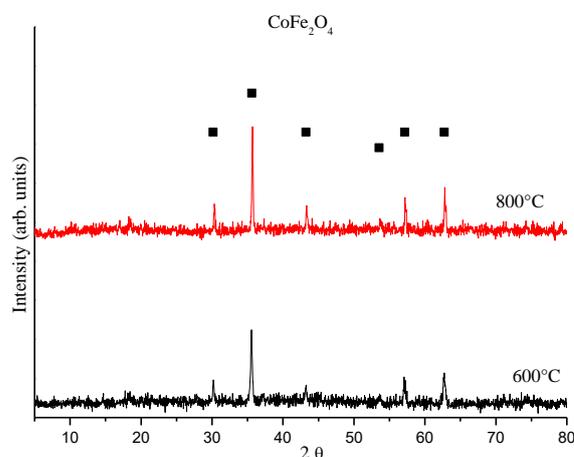


Figure 1. XRD patterns of CoFe_2O_4 calcined at 600 and 800°C .

The band-gap energy (E_g) is the energy required for the formation of electron-hole (e^-/h^+) pairs on the semiconductor solid surface. The E_g values obtained were 1.89 and 1.08 for CoFe_2O_4 at 600 and 800°C , respectively. Both materials would be able to be used as photocatalysts because they have a band gap less than 3eV . Moreover, the obtained low E_g values evidence the ability of the synthesized materials to absorb radiation in the Uv-Vis region [12].

Figure 2 shows the TPR profiles of both synthesized samples. The first band observed in Figure 2 could be assigned to the reduction of Co^{+2} to Co^0 , in conjunction with the reduction of Fe^{+3} to Fe^{+2} , both metals present in ferrite phase. The second band would correspond to the reduction of Fe^{+2} to Fe^0 . The wide range of this reduction band could be attributed to the particle size effects. In both samples, the presence of Co^{+3} were discarded because the reduction bands at temperatures lower than 260°C were not observed [11].

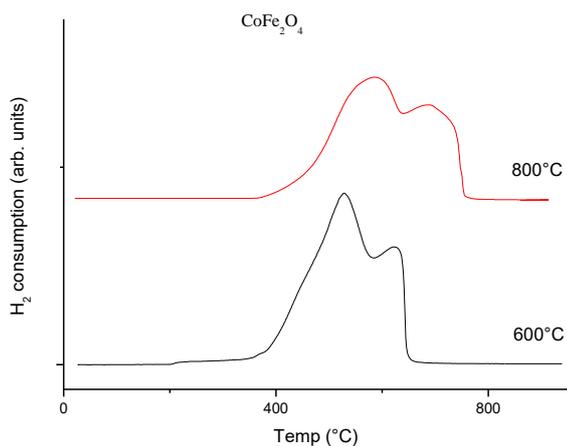


Figure 2. TPR profile for CoFe_2O_4 calcined at 600 and 800°C .

The XPS analysis was performed to obtain information about the surface composition of the spinel phase.

The $\text{Co } 2p_{3/2}$ transition is characterized by a main peak (780.58 eV and 779.81 eV for the ferrite calcined at 600°C and 800°C , respectively) with a satellite at higher binding energy indicating cobalt in bivalent chemical state. In this sense the $\text{Co } 2p_{1/2}$ - $\text{Co } 2p_{3/2}$ energy separation peaks near 15 eV also indicates the presence of Co^{2+} (15.3 eV and 15.8 eV for each material) [12]. The presence of this characteristic satellite is believed to be a direct consequence of the band structure associated with octahedral Co^{+2} in the spinel lattice [13].

For the XPS spectra in the region of Fe (Figure 4), the $2p_{3/2}$ and $2p_{1/2}$ characteristic peaks around 711 eV and 724 eV were decomposed in two contributions, (Table 2). The presence of these two peaks indicates that the Fe^{+3} species exist in different coordination environments of Fe, such as octahedral and tetrahedral sites respectively [13].

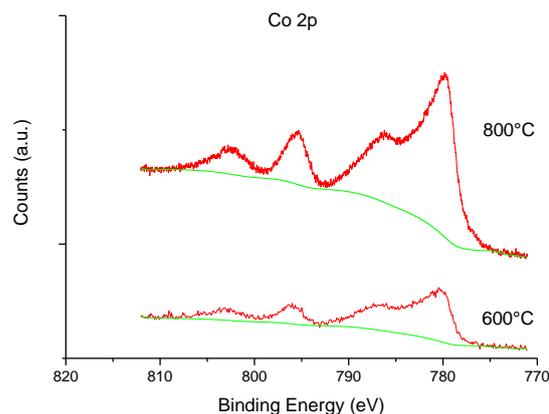


Figure 3. XPS of CoFe_2O_4 at 600 and 800°C : $\text{Co } 2p$ spectra.

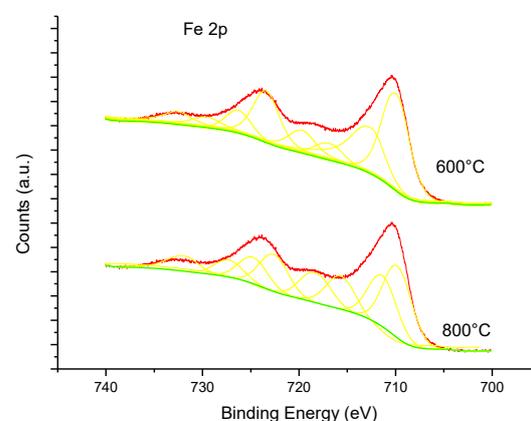


Figure 4. $\text{Fe } 2p$ XPS spectra of CoFe_2O_4 calcined at 800 and 600°C :

Table 1. XPS of CoFe_2O_4 values of $\text{Fe } 2p$ spectra

CoFe_2O_4	Site	$2p_{3/2}$ (eV)	$2p_{1/2}$ (eV)	% Occupy
600°C	T	712.52	726.28	37
	O	709.9	723.42	63
800°C	T	711.38	724.77	42
	O	709.8	722.63	58

Spinel structure has the follow molecular formula: $(\text{Fe}_{(2-2x)}\text{Co}_{(1-2x)})_{\text{T}}(\text{Fe}_{(2x)}\text{Co}_{(2-2x)})_{\text{O}}\text{O}_4$ were T and O are tetrahedral and octahedral sites and x is the % of Fe^{+3} in octahedral site. Through this analysis, it was found that the ferrite calcined at 600°C has a 75% of inversion on its structure. By the other hand, the ferrite calcined at 800°C has also an inverse spinel structure, with an 83% of inversion.

The $\text{O } 1s$ spectra (not showed) has a binding energy at 530.08 eV and 529.05 eV for the ferrite calcined at 600° and 800°C , respectively. This peak is usually associated with lattice O^{2-} in a

number of rocksalt and spinel 3d metal oxides [13].

By Mössbauer spectroscopy (that is not presented on this work) it was confirmed that cobalt ferrite calcined at 600°C is an inverse spinel with a 74% of inversion with the following chemical formula $(Co_{0.26} Fe_{0.74})[Co_{0.74} Fe_{1.26}]O_4$. According to that the ferrite calcined at 800°C presents the follow chemical formula $(Co_{0.17} Fe_{0.83})[Co_{0.83} Fe_{1.17}]O_4$.

In ferrimagnetic materials, the magnetic moments of tetrahedral sites and octahedral sites are aligned in anti-parallel, showing ferrimagnetism with a net magnetization or magnetic moment expressed in Bohr magnetons for collinear spin arrangement at any temperature T ($T \leq T_c$) [14].

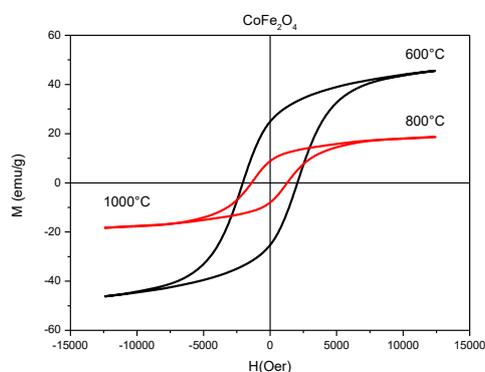


Figure 3. VSM profile of ferrite calcined at 600 and 800 °C.

Table 2. Magnetic properties of $CoFe_2O_4$

$CoFe_2O_4$	M_s (emu/g)	H_c (Oer)
600°C	45.5	4156.7
800°C	18.3	2608.14

The decrease of the M_s between cobalt ferrite calcined at 600°C and the cobalt ferrite calcined at 800°C could be due to the last material is an inverse spinel with a higher percent of inversion. The greatest presence of high spin Co^{+2} is found in octahedral sites.

Catalytic activity evaluation

Before the degradation tests, the study of the adsorption equilibrium in the dark was performed for 60 minutes, where the sodium diclofenac solution and catalyst were in contact. The adsorption values after reaching the adsorption/desorption equilibrium were less than 1.0%. Then, an initial sample was taken (M_0). After that, the oxidant was added and the light turn on. During the reaction, samples were taken at different times.

By the Uv-Vis spectroscopy profile (not showed) of the reaction samples taken throughout the reaction, the sodium diclofenac degradation under different experimental conditions was studied in order to elucidate the activity of the synthesized materials. In the absence of radiation, sodium diclofenac has not been degraded, in both cases: with and without H_2O_2 in presence of catalyst. Only under light (without catalyst neither H_2O_2), we obtained a 100 % degradation of the pollutant molecule resulting in the presence of sub products. For test only with light and H_2O_2 , the degradation of sub products was not obtained. Finally, for the test using light and catalyst (in the absence of H_2O_2) is observed a further degradation of the generated sub products but not the mineralization of them.

With respect to the catalytic test, it was found that the sodium diclofenac was completely degraded after 15 minutes of the reaction with both materials as catalysts. Important differences related to the catalyst mass were not found at any of the catalysts. Therefore, 0.2 gm/L concentration results enough to degraded the contaminant.

By the Uv-Vis profiles of the reaction samples, (Figure 5) it can be determined different reaction velocities. It can be observed the catalyst calcined at 800 °C is faster in the generation of degradation sub product between the M_{180} and M_{240} spectra.

The catalyst calcined at high temperature reached the maximum mineralization of the organic carbon (the TOC removal of 86%).

The transfer of charge in ferrites is described by an electron hopping mechanism between the ions located in the octahedral sites (B) of the network. It is an indirect exchange type with predominant BB interaction. The oxidation of Co^{+2} to Co^{+3} is possible if it is compensated by an iron reduction from Fe^{+3} to Fe^{+2} or the migration of Co^{+2} to a tetrahedral site [13]. The higher percent of mineralization reached with the ferrite calcined at 800°C could be attributable to a more presence of high spin ions Co^{+2} in octahedral sites than that of the ferrite calcined at 600°C.

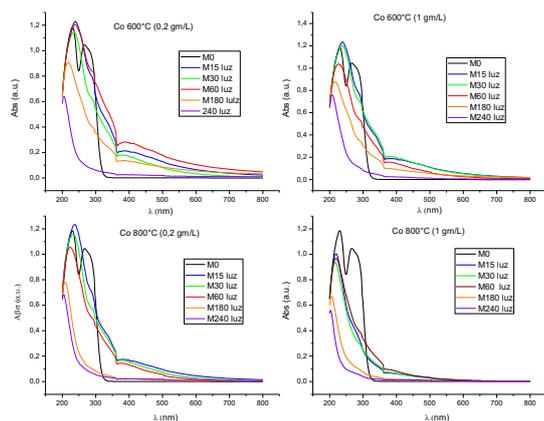


Figure 5. Uv-Vis spectra of the pollutant solution with the increase of irradiation time using both catalysts and two different concentrations.

Table 3. TOC reduction of CoFe_2O_4 .

	0.2 g/L	1 g/L
600°C	59.61%	50.02%
800°C	85.92%	86.61%

3. Conclusiones

Cobalt ferrites were synthesized by Pechini method with modifications. From XRD patterns was determined that all samples have spinel structure. By XPS and Mössbauer spectroscopy it was found that the material calcined at 600°C is an inverse spinel with a 74% of inversion. The ferrite calcined at 800°C has an 83% of inversion in its structure. Both materials showed good magnetic properties adequate to be used as a catalyst of easier recovery from aqueous solutions. Finally, a solution of 40 ppm of sodium diclofenac were 100% degraded in 15 minutes of the photoreaction using Uv-germicide lamp, H_2O_2 as an oxidant and a cobalt ferrite as a catalyst. The major percent of mineralization obtained with in the ferrite calcined at 800°C (86%) could be attributable to a more presence of high spin Co^{2+} ions in octahedral sites than the ferrite calcined at 600°C.

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5. References

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