AN EFFECTIVE PHOTOCATALYTIC SYSTEM TO ELIMINATE CARBAMAZEPINE FROM WASTEWATER.

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Abstract

Pharmaceuticals compounds, like carbamazepine, are emerging pollutants that have been detected in wastewater and surface waters throughout the world. Their presence was demonstrated in South American rivers, particularly in the Suquía River basin, Córdoba, Argentina. There are several recent studies of applications of ferrites as photocatalyst used in the degradation of pollutants were reported. In this work cobalt, nickel and zinc ferrites synthetized by Pechini method were characterized and tested. By X-ray diffraction patterns were determine that all samples had spinel structure. A solution of 10 mg/L of carbamazepine was 98% mineralized on a photocatalytic system using Uv-germicide lamp, hydrogen peroxide as oxidant and synthetized ferrites as catalyst in 4 hours of photoreaction. The cobalt ferrite had the highest mineralization at the firstly reaction samples.

Keywords: photocatalysis, carbamazepine, spinel ferrites, degradation, wastewater.

Resumen

Los compuestos farmacéuticos como la carbamazepina, son considerados contaminantes emergentes y han sido detectados en cursos de agua superficiales y aguas residuales en diferentes lugares del mundo. Su presencia ha sido demostrada en los ríos sudamericanos, en particular en el río Suquía ubicado en la provincia de Córdoba, Argentina. Numerosos estudios recientes señalan que las ferritas presentan propiedades para ser empleadas como fotocatalizadores en la degradación de contaminantes. En este trabajo se sintetizaron, caracterizaron y testearon ferritas de cobalto, níquel y zinc. Mediante difracción de rayos X se determinó que todos los materiales presentaron estructura de espinela. Una solución de 10 mg/L de carbamazepina fue mineralizada en un 98% en 4 horas de fotoreacción. Se empleó un sistema fotocatalítico con una lámpara Uv-germicida, peróxido de hidrógeno como agente oxidante y los materiales sintetizados como catalizadores. La ferrita de cobalto fue el material que mostró una mayor mineralización en las primeras muestras de reacción.

Palabras clave: fotocatálisis, carbamazepina. ferritas espinelas, degradación, aguas residuales.

The authors would be willing to submit the present work to the special volume dedicated to CMC-2021 in high impact factor journal in case the reviewers and the scientific committee select it.

1. Introduction

Emerging pollutants (EP), among them pharmaceutical compounds, are found in surface and ground waters, suggesting their ineffective removal by conventional wastewater treatment technologies [1]. EP can cause adverse effects for the environment or human health although their presence in wastewaters is often not regulated [2][3]. EP were founded in South American rivers. Valdes et al. [4] have studied the presence of many pharmaceuticals compounds in the Suquía River basin, in Córdoba province, Argentina. Atenolol, carbamazepine, and diclofenac were the most frequently detected compounds, with concentrations ≤ of 1µg/L [4].

Carbamazepine is one of the most widely prescribed antiepileptic drugs for the treatment of epilepsy, trigeminal neuralgia and some psychiatric diseases [5]. Because of the long-term use of human beings, the concentration of CBZ in the aquatic environment has continued to rise, and it is difficult for CBZ to be effectively degraded in the conventional wastewater treatment process [6], removal was found to be extremely low (7%)[7].

Spinel ferrites (MFe_2O_4), where M represents a transition metal ion, have attracted attention by exhibiting excellent catalytic activity and structural stability [8]. Several recent studies on applications of ferrite as photocatalysts for the degradation of pollutants were reported, where ferrites resulted effective under light energy to create electron-hole (e^-/h^+) pairs on the photocatalytic surface available for oxo-reduction reactions. These processes normally include the formation of reactive oxygen species involved in the decomposition of contaminants. An oxidant agent, such as H_2O_2 is commonly added to the reaction mixture to enhance the process. On the other hand, 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].

This work is focused on the synthesis, characterization and testing of cobalt, nickel and zinc iron ferrites as photocatalyst for degradation of carbamazepine from water. The reactions were carried out using a Uv radiation and H_2O_2 as an oxidant agent.

2.Experimental

2.1 Ferrites synthesis

The ferrites were synthesized by Pechini sol-gel method. Nitrates of Co, Ni, Zn and Fe were used as a metal sources with the molar ratio of M^{+2}:Fe 1:2 The $Fe(NO_3)_2.6H_2O$ 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. After dissolution the M^{+2} solution was added to the system. After 2 hours, ethylene glycol was added and the temperature were raised up to 120°C. Immediately the reflux system was opened. Subsequently, the obtained solutions were heated until the gel formation. The stoichiometric relationship between alcohol/acid used were 4:1. The obtained gel were calcined to form a solid foam in a muffle furnace. The thermal treatment during 2 hours at 450°C with a 4°C/min ramp. The solid foam obtained were ground in a mortar and recalcined. The second thermal treatment were for 6 hours at and 800°C with a 4°C/min ramp for each material.

2.2 Sample characterization

The structure and crystalline phases of the obtained materials were characterized by X-ray diffraction (XRD) in an X´Pert Pro-PANalytical diffractometer equipped with CuKα, λ = 1,54Å. Diffraction patterns were collected in a range 2θ from 4° to 80° degrees, step 0,026 and step time 4.45. The solid Uv-spectra in a Jasco Uv-visible V-650 spectrophotometer with diffuse reflectance. To characterize the surface morphology of the synthetized ferrites micrographs were taken by scanning electron microscopy (SEM) in an instrument model JSM-6380 LV (JEOL, Japan) equipped with a Supra 40 (Carl Zeiss, Germany). The samples were gold-coated. The temperature programed reduction (TPR) with hydrogen was performed by a Micromeritics Chemisorb 2720 machine. The experiments were carried out at a heating rate of 10 °C/min. The reactive gas composition was 5% H_2/N_2. Then, the sample was held at 150 °C under flowing nitrogen to remove the remaining adsorbed oxygen for 30 minutes. Subsequently the TPR experiments were performed up to a temperature 950 ◦C.

2.3 Catalytic performance evaluation

The carbamazepine degradation reactions were carried out at 25°C in a 500 mL tubular reactor, with recirculation by a peristaltic pump and equipped with an 8W monochromatic germicidal lamp Philips (at 254 nm). An effluent was simulated using a 10 mg/L of the aqueous solution of carbamazepine (Parapharm 99%). That solution was in contact with synthetized ferrite and H_2O_2

(Cicarelli 30%) as an oxidant under radiation. The catalyst is found in suspension during the complete process. The H_2O_2 volume is added at the beginning of the radiation expose. Samples were taken at different times to be analysed, after filtration of the catalyst.

The analysis of carbamazepine was performed by by Uv-vis spectroscopy absorbance with a Perse T7DS spectrometer. To characterize the mineralization degree of the pollutant the total organic carbon (TOC) removal efficiencies were examined. TOC was measured using a Shimadzu TOC-L CSN. The reductions in TOC were calculated by the equation: $[(TOC_{S0} - TOC_{S240}) x100]/TOC_{S0}$. The H_2O_2 consumption was evaluated by the modified iodometric titration [10]. Finally, the leaching of Fe cations into the reaction media was determined by the phenanthroline colorimetric method by spectrophotometry at 510 nm [11].

3.Results and discussion

3.1 Sample characterization

Figure 1 shows the XRD patterns of synthesized solids. 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 (■) corresponds to the synthesized ferrites (01-073-1963, 01-086-2267 and 00-002- 1045). For materials analysed the most intense peak was observed at 2θ of about 35°. This peak is characteristic of spinel structure. No impurity phase such as alpha-Fe_2O_3 or M^{+2} oxides was detected from this pattern.

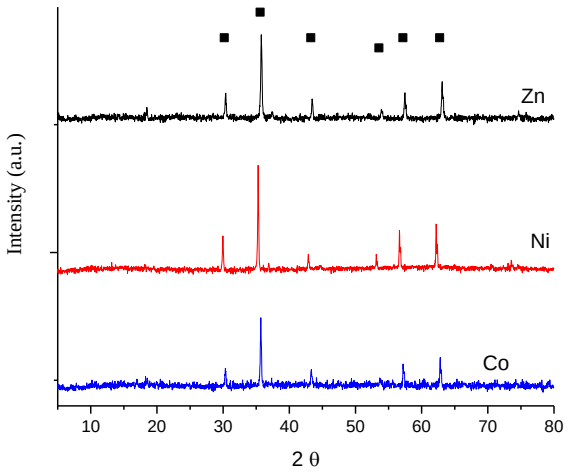


Figure 1. XRD patterns of ferrites. (■)AB_2O_4 pattern

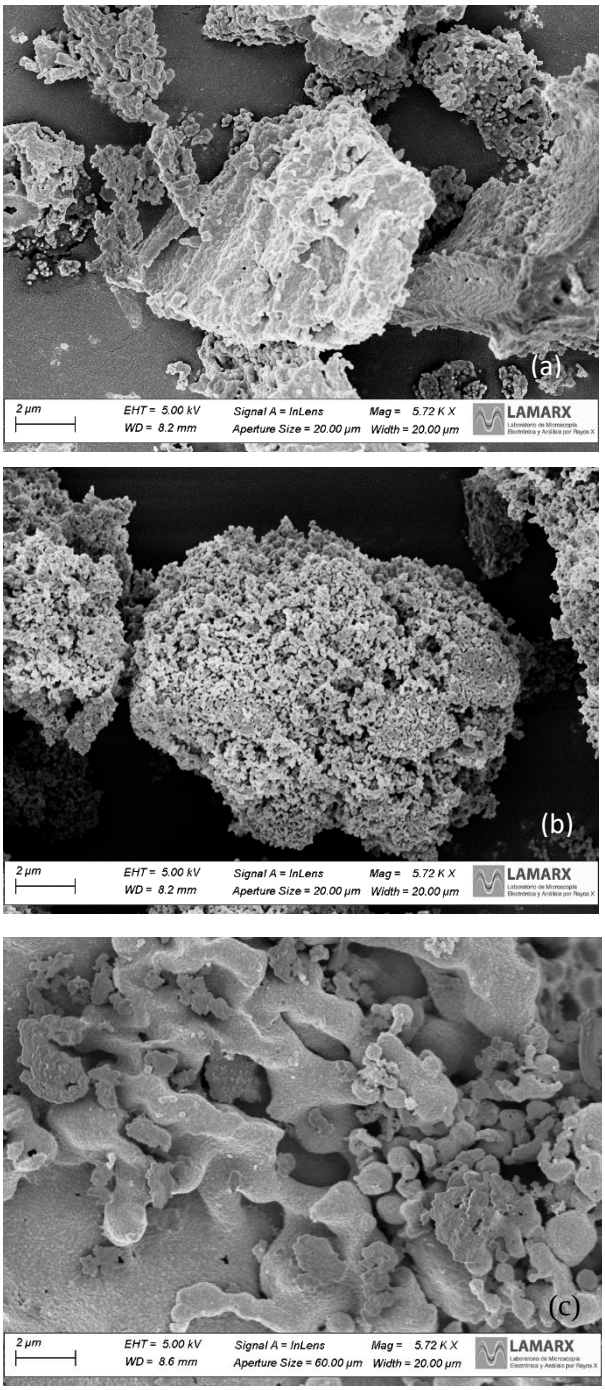


Figure 2. SEM images of (a) $ZnFe_2O_4$, (b) $NiFe_2O_4$ and (c) $CoFe_2O_4$

Figure 2 shows the surface morphology for the prepared samples. The ferrites revealed a morphology composed of irregular particle agglomerates interconnected and resembling to a solid foam.

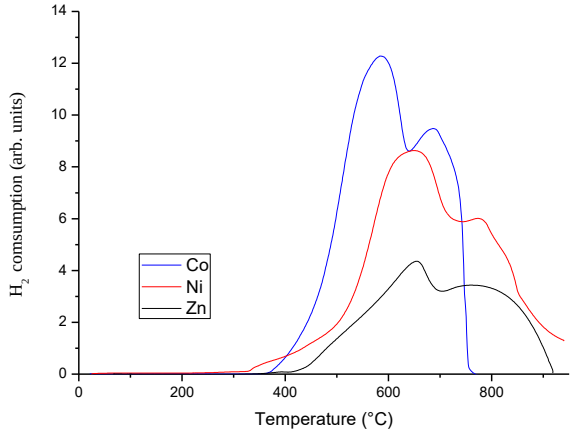


Figure 3. TPR profiles for synthetized ferrites

TPR profiles showed two bands (Figure 3) for the synthesized samples. The first band observed could be assigned to the reduction of M^{+2} to M^0, in conjunction with the reduction of Fe^{+3} to Fe^{+2}, metals present in the 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. Tonge et al. [12] have found that, on TPR profiles, the maximum of the reduction peak is shifted at higher temperatures when the particle size is increased. This could indicate that Co ferrite particle size is smaller than Zn or Ni ferrites according to which were observed in SEM images.

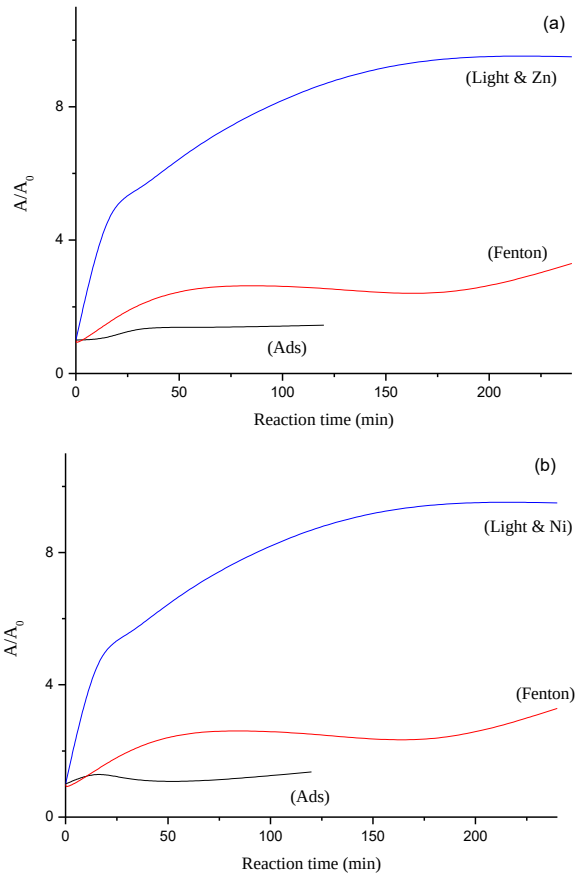
Table 1. Band Gap values of each material

Material	Band Gap (eV)
$ZnFe_2O_4$	1.95
$CoFe_2O_4$	1.08
$NiFe_2O_4$	1.45

The band-gap energy (Eg) is the energy required for the formation of electron-hole (e−/h+) pairs on the semiconductor solid surface. Table 1 shows the Eg values obtained. These results can be explained because the band gap of the semiconductors had been found to be particle size dependent. All materials would be able to be used as photocatalysts because they have band gaps less than 3eV. Moreover, the obtained low Eg values evidence the ability of the synthesized materials to absorb radiation in the Uv-vis region, which indicates that the samples are potential catalysts for the photo-Fenton reaction and can be useful in wastewater treatment [13].

3.2 Catalytic evaluation

Before degradation tests, the study of different blank assays was performed. In Figure 4 are shown the ratios between the areas under the curve of Uv-vis absorbance of each sample concerning the area of starter sample, this is A/A_0. In no cases, carbamazepine degradation was obtained: Adsorption test with each catalyst, like Fenton test process (Cat & H_2O_2), Photolysis, the simulated effluent in contact with only H_2O_2 (H_2O_2 test) and the Photolysis test combined with the presence of ferrite (Light & Cat). Tusnelda et al.[7] founded that carbamazepine absorbed most of the incoming radiation in relation to the other tested pharmaceuticals, but has the lowest degradation rate constants. This can be explained by the lower transmission of the samples at concentrations higher than 0.1 mg/L of carbamazepine[7]. Finally, radiation and H_2O_2 test (Light & H_2O_2) showed a carbamazepine degradation because of the decrease to the area curve and a mineralization of 7.35%.



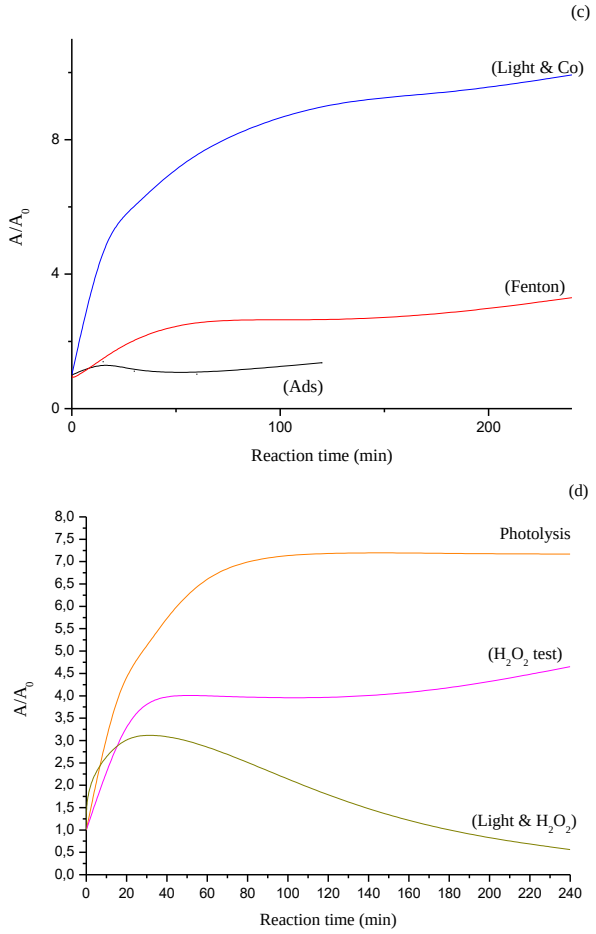


Figure 4. Reaction blanks (carbamazepine concentration 10 mg/L, H_2O_2 concentration: 0.2mL/L, catalyst amount 0.2 g/L). (a) $ZnFe_2O_4$, (b) $NiFe_2O_4$, (c) $CoFe_2O_4$, and (d) with no catalyst

In order to evaluate the catalytic activities of the synthesized materials, the reactions were taken place with an effluent solution simulated using a 10 mg/L of carbamazepine, 0.2 g/L ferrite as catalyst, 0.2 mL/L H_2O_2, and Uv radiation. The three materials were tested (Figure 5) and the TOC of M_{240} were > 0.1 mg/L, which is the TOC analyzer detection limit. These TOC values indicate a 98% of the TOC mineralization. The H_2O_2 consumption was a 90% with each catalyst. The concentration of leached iron for all materials tested was lower than 0.1 mg/L, which indicates that the catalyst was stable during the reaction.

With the propose of select the best material for this process, we evaluated the TOC values at the first 15 minutes (Table 2).

Based on the collected data, cobalt and nickel ferrites were the best catalyst for this degradation tests. Cobalt ferrite had the faster mineralization ratio at the beginning of the reaction (Table 2) and had the minor absorption at the end of the reaction (Figure 5). Because of that, cobalt ferrite is the materials with the best activity for this process.

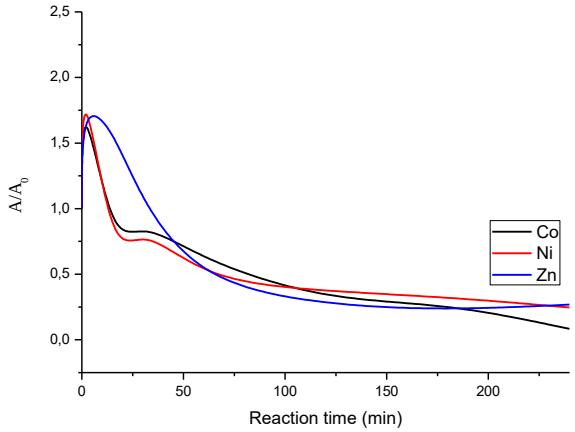


Figure 5. Catalytic tests (carbamazepine concentration 10 mg/L, H_2O_2 concentration: 0.2mL/L, catalyst amount 0.2 g/L)

Table 2. Percent of TOC removal at the 15 minutes of the reaction with each material

Material	% TOC removal
$ZnFe_2O_4$	19.4
$CoFe_2O_4$	38.1
$NiFe_2O_4$	26.4

4.Conclusions

Cobalt, nickel and zinc ferrites were synthesized by the Pechini method. From XRD patterns was determined that all samples have spinel structure. All materials would be able to be used as photocatalysts because they have band gaps less than 3eV. Finally, a solution of 10 mg/L of carbamazepine was 98% mineralized in 4 photoreaction hours using a Uv-germicide lamp, H_2O_2 as an oxidant and a synthetized ferrite as a catalyst. The cobalt ferrite showed the highest mineralization values at initial time and the minors Uv-vis absorptions at the end of the reaction.

5.References

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