2021 International Nuclear Atlantic Conference – INAC 2021
Virtual meeting,Brazil,November 29 – December 2, 2021

ISBN: 978-65-594-1256-3

Adsorption of amoxicillin by irradiated gadolinium-doped nickel ferrite nanoparticles

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1.Introduction

In recent years, scientific advances and industrialization have brought great benefits to the populations. Despite this, several environmental problems emerged, such as contamination of the soil, air and water. The main problems related to drinking water are groundwater depletion, contamination of water resources and high demand for fresh water, due to accelerated population growth and urbanization [1]. Among the different forms of contamination, antibiotics have become a potential source of pollution [2] because they are widely used in the prevention and treatment of bacterial infections [3].

According to the report published in 2018 by the World Health Organization, β-lactam class antibiotics, such as amoxicillin, are currently the most consumed drugs due to their effect against a range of bacterial infections [4]. As a result, the presence of amoxicillin in water has become a global concern, as long-term ingestion can induce chronic allergic reactions, toxic effects and potential development of resistant bacteria [5]. The permanence of amoxicillin in the environment results from the low efficiency of the conventional wastewater treatment processes [2].

Thus, several processes involving nanomaterials have attracted the attention of the scientific community [1,3]. Among them, spinel ferrites, iron oxides of the MFe_2O_4 type (M=divalent metals), have been the focus of many studies due to their magnetism and several applications as catalysts [6] and adsorbents [1].

In addition, the incorporation of a small amount of rare earth (TR) cations in the ferrite network causes changes in the superexchange interaction and in the Fe^{3+} - TR^{3+} and TR^{3+}-TR^{3+} bonds, with modifications in their magnetic properties [7,8]. Another way to change the structural and magnetic properties of ferrites is by using gamma irradiation [9]. There are few studies on the effect of gamma irradiation on NPs of TR-doped ferrites. The articles found showed that irradiation increases crystallographic defects, such as porosity and lattice parameter and causes a reduction in crystallite size [9]. These defects can favor the performance of ferrites in the removal of antibiotics present in water resources. In this context, this work aims to investigate the structural and magnetic properties of nickel ferrite NPs doped with rare earth elements and irradiated with doses of 50 kGy and dose rate 3.855 $kGy.h^{-1}$.

2.Methodology

Synthesis of gadolinium doped nickel ferrites nanoparticles with different molar composition

Gadolinium-doped nickel ferrite nanoparticles with compositional formula $NiGd_xFe_{2-x}O_4$ (x = 0.00, 0.02 and 0.06) were synthesized by sol-gel method. Nanoparticles were prepared using nickel nitrate hexahydrate and ferric nitrate nonahydrate as precursors and gadolinium nitrate hexahydrate was used as the dopant. The formed gel was annealed at 300°C for 1 h to get the final products.

3. Results and Discussion

The diffractograms of the samples of $NiGd_xFe_{2-x}O_4$ (x= 0, 0.02 and 0.06) are shown in Fig. 1.

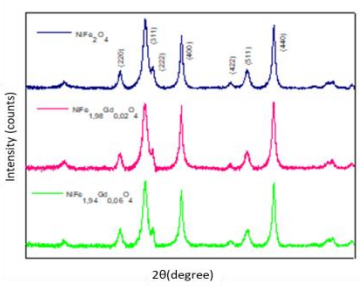

Figure 1: X-ray diffractograms of $NiGd_xFe_{2-x}O_4$.

The diffraction patterns of the samples synthesized using gadolinium nitrate showed the reflections of the characteristic nickel ferrite diffraction planes (111), (220), (311), (222), (400), (422), (511), (440), as described in the crystallographic record (ISCD-084677). It is possible to observe the presence of traces of impurities, such as nickel oxide, NiO, in all samples. The presence of NiO may be associated with the homogeneity of the gel formed, due to iron deficiency.

The lattice parameter and the crystallite size are presented in Table 1. As Gd ions are added, it is possible to verify a slight increase in the lattice parameter of the doped NPs in relation to the non-doped ones. These results suggest the introduction of Gd^{3+} ions (0.938 Å) with high ionic radius when compared to the ionic radius of Fe^{3+} ions (0.645 Å) which caused an expansion of the spinel ferrite crystal lattice [7,10].

Table 1: Lattice parameter, crystallite size and adsorbent capacity (q) in removing amoxicillin from gadolinium-doped ferrite nanoparticles

Samples	Lattice parameter (Å)	Crystallite size (nm)	$q(mg_{Amox}.g^{-1}_{adsorbent})$
$NiFe_2O_4$	8.41	10	34
$NiGd_{0,02}Fe_{1,98}O_4$	8.43	8.6	38
$NiGd_{0,06}Fe_{1,94}O_4$	8.42	9.4	33

Preliminary adsorption tests were carried out in order to quantify the adsorption capacity of $NiGd_xFe_{2-x}O_4$ NPs (x= 0, 0.02 and 0.06) and determine which of these samples has the best performance for the adsorption of amoxicillin. For this study the samples were submitted to triplicate adsorption tests. The adsorption capacity of $NiGd_xFe_{2-x}O_4$ is shown in Table 1.

From Table 1, it was possible to verify that the sample of $NiGd_{0.02}Fe_{1.98}O_4$ exhibited better performance in the adsorption of amoxicillin. In order to evaluate the effect of irradiation on the structural and magnetic properties, and on the adsorption capacity, NPs of $NiGd_{0.02}Fe_{1.98}O_4$ was selected.

The XRD diffractograms obtained from non-irradiated and ^{60}Co source irradiated $NiGd_{0.02}Fe_{1.98}O_4$ samples are shown in Fig. 2 a. XRD measurements did not indicate the formation of secondary peaks for the irradiated sample, in addition to the NiO phase that was already present in non-irradiated $NiGd_{0.02}Fe_{1.98}O_4$.

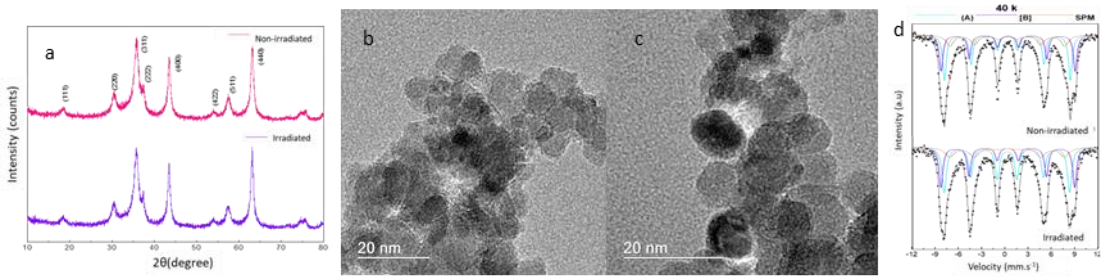

Figure 2: (a) X-ray diffractograms, (b) TEM image for non-irradiated and (c) irradiated and (d) Mössbauer spectroscopy of samples of $NiGd_{0.02}Fe_{1.98}O_4$.

After irradiation, it is possible to verify a slight increase in the lattice parameter, which can be attributed to the interaction process of the γ rays with the outermost electrons of the lattice, in which some Fe^{3+} ions (0.64 Å) are converted into Fe^{2+} (0.76 Å), Table 2 [7,9].

Table 2: Lattice parameter and crystallite size.

Samples	Lattice parameter (Å)	Crystallite size (nm)
Non-irradiated	8.315	8.90
Irradiated	8.322	9.15

Fig. 2 b and Fig. 2c show transmission electron microscopy images of non-irradiated and irradiated samples. The nanoparticles from both samples are monocrystalline. Samples show significant agglomeration of the samples, which can be attributed to the reduction of surface energy and the dipole interaction between magnetic NPs [7].

Mössbauer spectroscopy analyzes for $NiGd_{0.02}Fe_{1.98}O_4$ non-irradiated and irradiated samples were performed at 40 K. The spectra are shown in Fig. 2 d. The adjustments performed indicated that the non-irradiated and irradiated NPs presented superparamagnetic behavior even at low temperature. The hyperfine parameters did not show considerable changes in the irradiated sample. This fact indicates that the dose used in the irradiation was not enough to cause a change in the sample structure.

The nitrogen adsorption/desorption isotherms of non-irradiated and irradiated $NiGd_{0.02}Fe_{1.98}O_4$ NPs are shown in Fig. 3.

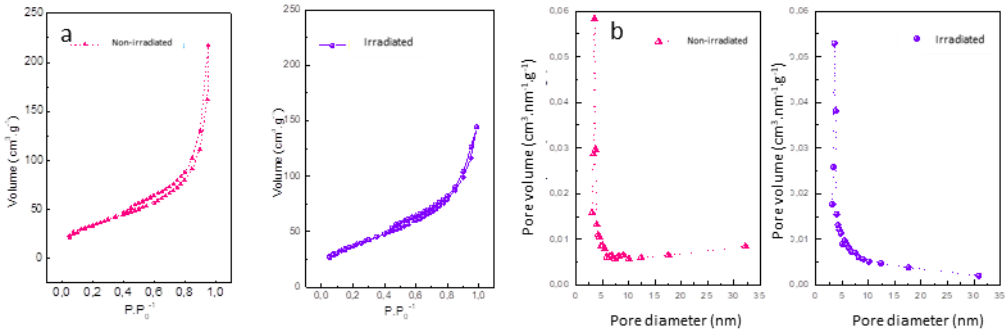

Figure 3: (a) N_2 adsorption and desorption isotherms and (b) pore diameter of the samples.

It was noticed that irradiation did not change the shape of the adsorption isotherm, the samples exhibited very similar isotherm profiles typical of mesoporous materials, isotherm IV, as slit-shaped pores [11]. However, it is possible to observe a reduction in the pore volume of the irradiated sample (Table 3), which may be related to the reorganization of atoms on the surface. The pore diameter profiles showed a narrow range of size distribution (Fig. 3b), in which most pores exhibited a diameter in the range of 3 to 18 nm.

Table 3: Surface area, volume, diameter pore and adsorbent capacity of non-irradiated and irradiated samples.

Samples	Specific surface area ($m^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Pore diameter (nm)	q($mg_{Amox}.g^{-1}$ adsorbent)
Non-irradiated	114	0.333	3.509	38
Irradiated	132	0.166	3.507	37

The adsorption capacity of the non-irradiated and irradiated sample did not show significant changes

(Table 3). This fact may be related to adsorption being a surface phenomenon and the irradiation used was not enough to considerably increase the specific surface area.

4. Conclusions

Sol-gel synthesis of $NiGd_xFe_{2-x}O_4$ with low gadolinium contents can be successfully performed. The presence of gadolinium resulted in an increase in the adsorption capacity of AMX at pH close to neutral, indicating its potential application to remove this antibiotic. Considering the application at an industrial level, this is a good result, since it does not need to adjust the pH of the medium. The analysis of the effect of gamma irradiation revealed that the exposure dose of 50 kGy was not enough to cause changes in the structural and magnetic properties of the NPs. However, Mössbauer spectroscopy indicated a small change in the iron population, such as its increase in the tetrahedral site and reduction in the octahedral one. Furthermore, it was possible to observe a slight reduction in the pore volume of the irradiated sample, which may be associated with the reorganization of atoms on the surface. However, new tests with doses of 100, 200 and 300 kGy will be performed.

Acknowledgements

The authors would like to acknowledge the Brazilian agencies CNPq, CAPES, FAPEMIG and CNEN for financial support.

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