2015 International Nuclear Atlantic Conference - INAC 2015
São Paulo, SP, Brazil, October 4-9, 2015
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
***ISBN:* 978-85-99141-06-9**

XRD AND SEM/EDS CHARACTERIZATION OF COCONUT FIBERS IN RAW AND TREATED FORMS USED IN THE TRATMENT OF STRONTIUM IN AQUEOUS SOLUTION

Heverton C. O. Fonseca[1], Rafael H. L. Garcia[1], Robson J. Ferreira[1], Flávia R. O. Silva[1], Ademar J. Potiens Jr[1] and Solange K. Sakata*[1]

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
sksakata@ipen.br*

ABSTRACT

^{90}Sr, a radioactive isotope of strontium, is one of the fission products and quite often present in the radioactive waste produced by nuclear power plants. Recently, the removal efficiency of strontium by treated coconut fibers was evaluated and reached up to 95% in an aqueous solution. This work presents the characterization of raw and treated coconut fibers with different concentrations of hydrogen peroxide in basic medium using X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectroscopy (SEM / EDS). The analysis of X-ray diffraction shows a crystallinity of 37.6% for raw coconut fiber and crystallinity of 45.4% and 50.6% for coconut fibers 1 and 2, respectively. These results showed that the different degrees of degradation of organic matter can affect the crystallinity of the treated. This study of morphology and crystallinity of theses biosorbent materials with strontium will help in comprehension of the effects of alkaline hydrogen peroxide treatment and it will demonstrate the potential of strontium uptake by coconut fibers.

1. INTRODUCTION

^{90}Sr, a radioactive isotope of strontium, is one of the fission products of major radiological concern due to its relatively long half-life (28.6 years) and quite often present in the radioactive waste produced by nuclear power plants [1].

Currently, some techniques used to remove heavy metals from aqueous solution are ion exchange [2], membrane process [3], electrodeposition [4] and chemical precipitation [5]. But, these methods are costly and ineffective in low concentration of heavy metal [6]. Biosorption is a technique used to remove heavy metal with low cost and a variety of biological material can be used as biossorbent [7]. Industries by-products have been used to remove heavy metals due to the low cost and large feasibility [8] such as groundnut shells, sawdust, jute and coconut fibers.

In a previous work, the removal experiments were performed in Sr^{+2} aqueous solution ($2mg.L^{-1}$), raw coconut fiber at pH 9 for 5 minutes contact time and the presence of strontium ions in the ashes of raw coconut fiber was confirmed by thermal analyses [9].

This work presents the characterization of coconut fibers in raw and treated forms using X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectroscopy (SEM / EDS). For the chemical treatment, the coconut fibers were treated with different concentrations of hydrogen peroxide in basic medium. The presence of strontium in the fibers was also confirmed by X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectroscopy (SEM / EDS).

2. EXPERIMENTAL PROCEDURE

2.1– Materials

2.0 mg.L^{-1} solution of $Sr(NO_3)_2$ was prepared from a stock solution 200 mg.L^{-1}. The coconut (West Garden) was bought in local trade.

2.2- Pre-treatment and chemical treatment of the biomass

The raw coconuts fiber (*Cocos nucifera L.*) was washed with distilled water to remove impurities. After washing, it was dried at 80 ° C for 24 h and sterilized with UV light for 2 h. It was separated using a particle size sieves.

For the chemical treatment process 10 g of e fibers were suspended in a 200 ml solution containing 1,5g or 8.g of hydrogen peroxide of (30%) and 0,1 g of the sodium hydroxide (pH 11.5). The temperature was slowly raised to 60°C and oxidation was continued for more 2 h. The material was filtered, washed thoroughly with hot water, followed by cold water and then dried at 70°C for 24h [10].

2.3- Biosorption process

The biosorption process was performed in batch using 0,2 g of biomass and 10ml solution of $Sr(NO_3)_2$ under agitation at room temperature At the end of the experiment, the solution was filtered to separate the adsorbent and the filtrate.

2.4- SEM/EDS analyses

The morphological characteristics of the fibers, raw and treated coconut fibers, were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS). The samples were analyzed in a carbon matrix under 10 kV electron beam at magnification of 500 times.

2.5- X ray diffraction of fiber

The X-ray diffractograms of the fibers were obtained using the methodology as described by Park, et al. 2010 [11]. The radiation employed was Cu-Ka 1.5406 Å with nickel filter and the conditions of measurements were 40 KW and 30 mA. The scan was obtained from a range of 5-65 (Bragg angle 2θ) of 0.05 to 0.05 degrees every 15 seconds. All samples were analyzed in powdered form, previously segregated into 100 mesh sieve. However, the ashes samples used to obtain the diffraction patterns of raw coconut fibers before and after the biosorption were prepared in a muffle at a temperature of 600°C, until the formation of ashes from the fibers (about 1.5 hours).

3. RESULTS AND DISCUSSION

Coconut fiber (*Cocos Nucifera*) is composed mainly of cellulose, lignin and hemicellulose [12]. This material has the ability to remove heavy metals from aqueous solutions by biosorption process. The characterization of raw coconut fiber (RCF) and treated coconut fibers with 1.5g (TCF 1) and 8 g (TCF 2) of H_2O_2 at 60^oC were investigated by SEM/ EDS and X ray diffraction. Metal accumulation was confirmed by MEV/ESD, as well as the components of strontium formed in the ashes of raw coconut fiber after pyrolysis by X ray diffraction.

3.1. SEM analyses

Scanning electron microscope was used to evaluate the morphological characteristics of the coconut fibers, according Fig. 1.

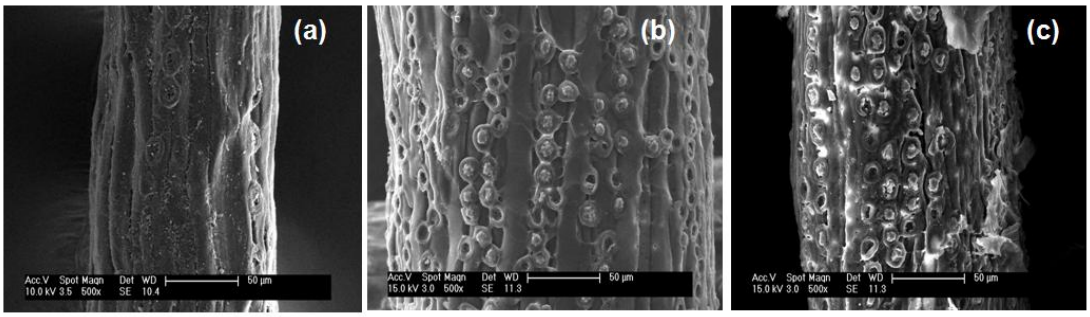


Figure 1: SEM micrographs of the RCF (a), TCF 1 (b) and TCF 2 (c)

Fig. 1(b) and 1(c) show that the treated coconut fibers (TCF 1 and TCF 2) have more pores compared to the raw coconut fiber, Fig. 1(a). The higher porosity was due to the oxidation process of the fibers components (lignin and hemicelluloses) with hydrogen peroxide in basic condition (pH 11,5).

The treatment with hydrogen peroxide is generally used in the delignification of lignocellulosic materials. The effect of degradability was more intense to the TCF 2 when compared to TCF 1 due to the amount of H_2O_2 used in the treatment of biomasses, 4% for TCF 2 and about 1% for TCF 1.

3.2. EDS analyses

The analyses of the materials before and after treatment with H_2O_2 in basic condition were analyzed by EDS qualitatively to identify the elements present in the biomass. The EDS analysis of the RCF, TCF 1 and TCF 2 are shown in Fig. 2a, 2 b and 2c respectively.

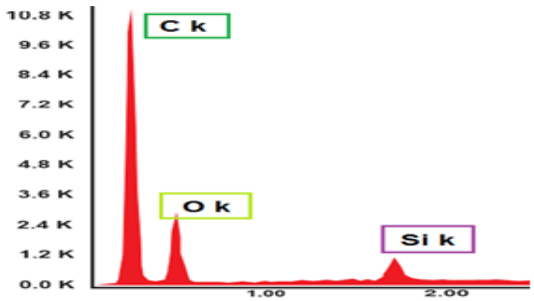
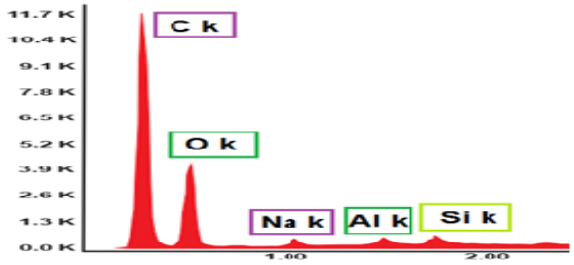


Figure 2a: EDS diffractgram of the RCF



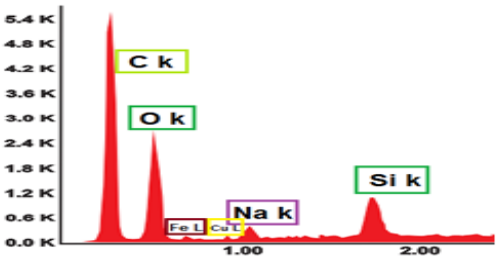


Figure: EDS diffractgram of TCF 1 (2b) EDS diffractgram of TCF2 (2c)

EDS analysis of treated coconut fibers shows sodium (Na) in their structures. The presence of this metal ion was to sodium hydroxide (NaOH) in the oxidative treatment of the biomasses. The deprotonated of the functional groups of carboxylic acids can explain the introduction of sodium [13].

3.3 X ray diffraction of the fibers

X-ray diffraction analyses were performed in the RCF, TCF 1 and TCF 2 in order to characterize the crystalline structure of each fiber, as shown in figure 3.

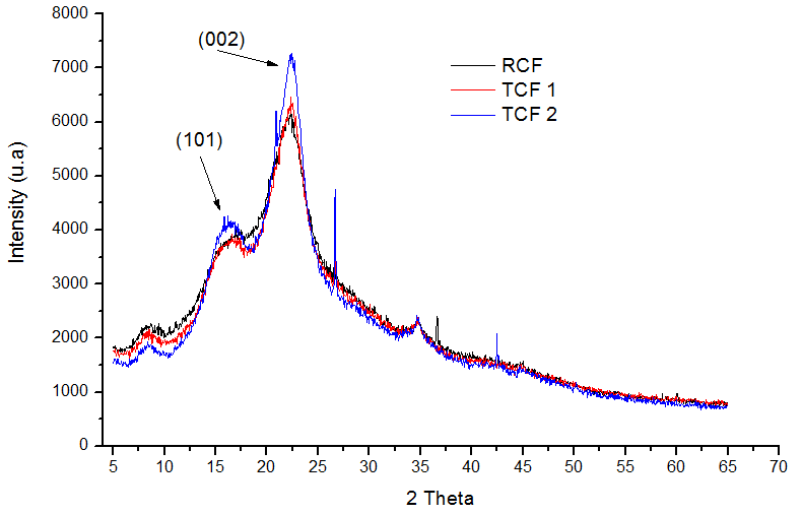


Figure 3: X ray diffraction patterns of the raw coconut fiber (RCF) and treated coconut fibers (TCF 1 and TCF 2).

In diffraction pattern the narrower peaks indicating crystalline part of the material, while the amorphous part of fibers involve wider peaks [14]. Then, it is found that the diffraction patterns of the fibers have low crystallinity (amorphous).

The amorphous characteristic of raw coconut fiber is due to the high lignin content (amorphous compound) in its structure [15]. Generally admits that the more lignin and hemicellulose content (amorphous compounds) present in the lignocellulosic materials lower crystallinity to the material.

The Bragg angles of 16^o, 22^o and 35^o are characteristic of cellulose [16] and the peak corresponding to crystalline region is located in a Bragg angle 2θ of 22^o [17]. The crystallinity ratios (Cr.R.) of the fibers were calculated using the Equation 1 [18].

$$Cr.R. = 1 - (I_1 / I_2) \quad (1)$$

Where, I_1 is the intensity at the minimum (2θ = 18-19^o for cellulose I) and I_2 is the intensity of the crystalline peak at the maximum (2θ = 22-23^o for cellulose I).

The crystallinity ratio (TCR.) of the fibers was presented in Tab. 1. The crystallinity values is presented with the intuited to check the degree of crystallinity in the fibers before and after treatment.

Table 1: Cristallinity ratio (Cr.R.) of the fibers

Biomass	Cristallinity (Cr.R.)
RCF	39 %
TCF 1	46 %
TCF 2	51 %

Softwasre: Bruker, DIFRRAC.EVA – 3.1 version

According to literature, the crystallinity index of raw coconut fiber is about 40%, [19] and the result obtained for the studied raw coconut fiber (RCF) was in accordance with the literature.

By the crystallinity values of the treated coconut fibers (Tab. 1), it was possible to verify that the processing conditions of the oxidative treatment can affect the crystallinity of the material. According Abraham et al. (2013) the treatment with hydrogen peroxide in basic medium allows the removal of constituents with amorphous structures such as lignin and hemicellulose increasing consequently the crystallinity of these lignocellulosic materials [20]. As shown in the results, the crystallinity of the FCA 2 was higher compared to FCA 1 due to the greater amount of organic matter with amorphous characteristics dissolved during the oxidation treatment.

The conformation of cellulose structure changes after chemical treatment, Sangian et al. (2015) verified that the decrease of the peaks related to the planes 002 and 101 (Fig. 6), located close to Brag angles (2θ) of 16 and 22, respectively, showed the conformation transition of cellulose I to cellulose II, which is more amorphous [11].

3.4 SEM/EDS analyses of RCF and TCF 1 after strontium uptake

Scanning electron microscope and energy dispersive spectroscopy of RCF and TCF 1 after metal uptake are shown in Fig. 4 and 5, respectively. The regions analyzed by EDS on the fibers are also shown in the SEM micrographs.

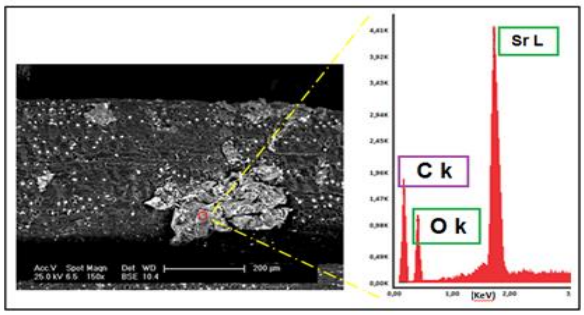


Figure 4: SEM/EDS analyses of the RCF

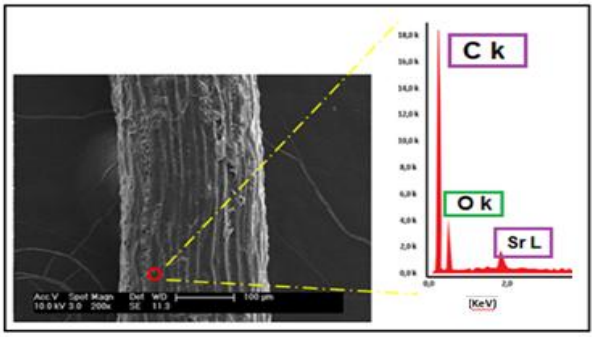


Figure 5: SEM/EDS analyses of the TCF 1

The presence of strontium ion in the surface regions of the coconut fibers was confirmed by the EDS spectra shown in Fig. 4 and 5.

3.5 X ray diffraction of the ashes

In Fig. 6 shows the analysis of X-ray diffraction of the ashes of raw coconut fibers before and after the biosorption of Sr^{2+}. The ashes were obtained by the pyrolysis process at 600^{o}C.

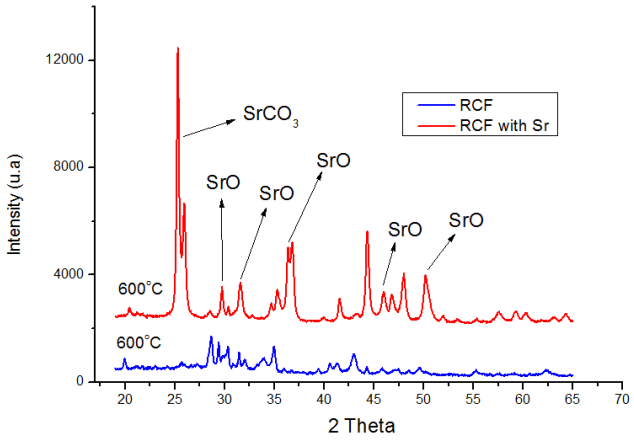


Figure 6: X ray diffratogram of ashes of raw coconut fiber before and after biosorption of strontium ion

The samples of raw coconut fibers used in this analysis were obtained under the following conditions, in a solution of strontium (40 $mg.L^{-1}$) at pH 9, and with a contact time of 90 minutes. The calculation of wavelengths corresponding to the peaks of the XRD patterns and the angles 2θ were obtained through Equation 2 (Bragg's Law).

$$\Lambda = 2d.sen\theta \quad (2)$$

The presence of strontium ion in the ashes of raw coconut fiber can confirmed by the presence of new peaks compared to the spectrum of the ashes of raw coconut fiber. The characteristic peaks of strontium compounds on Bragg angles 2θ of 29,67º; 31,13º; 36,66º, 46,98º and 50,85º were related to the strontium oxide (SrO), while in 25,13º corresponds to the strontium carbonate ($SrCO_3$), [21]. According to Barros et al. 2009 [22] when the biomass is heated to high temperatures the dissolution of organic matter occours with the formation of highly reactive radicals such as hydroxyl and carboxylate ($R\text{-}OH^-$ and $R\text{-}COO^-$). Consequently, the metals ions in the biomass can react with these radicals and strontium hydroxide under high temperatures can form oxides [23].

Another possible explanation of $SrCO_3$ into the coconut fiber structure is by physical adsorption, a portion of strontium solution can form strontium carbonate ($SrCO_3$) at pH 9 [24].

3. CONCLUSIONS

The characterization of RCF, TCF 1 and TCF 2 using X ray diffraction indicated crystallinity values at 39, 46 and 51, respectively. These results showed that the removal of amorphous compounds (lignin and hemiceluloses) in the oxidation treatment arise the cristallinity of the materials (TCF 1 and TCF 2). The presence of strontium was confirmed by MEV/EDS analyses on the surface of RCF and TCF 1, and by X ray diffraction analyzes. The chemical composition of strontium in the ashes of raw coconut fiber were SrO and $SrCO_3$. Thus raw and treated coconut fibers have adsorptive characteristics for strontium ions and this work can help in the choosing of a biosorbent for ^{90}Sr treatment present in liquid radioactive wastes.

4. ACKNOWLEDGMENTS

The authors would like to thank: Coordenação de Aperfeiçoamento do Pessoal de Nível Superior (CAPES) for the student fellowship.

5. REFERENCES

1. Abdel Rahman RO, Ibrahium HA, Hung Y-T. "Liquid radioactive wastes treatment: a review", *Water,* v. **3**:551-65, 2011.
2. AMANO, H.; YANASE, N. "Measurement of ^{90}Sr in environmental samples by cation-exchange and liquid scintillation counting", *Talanta,* **v. 37**:6, p. 585-590, 1990.

3. DING, S.; YANG, Y.; HUANG, H.; LIU, H.; HOU, L. “Effects of feed solution chemistry on low pressure reverse osmosis filtration of cesium and strontium”. *Journal of Hazerdous Materials*, **v. 294**, p. 27-34, 2015.
4. KIM, J. S.; JUNG, C. H.; OH, W. Z.; RYU, S. K. “Electrosorption and separation of Co^{2+} and Sr^{2+} ions from decontaminated liquid wastes”. *Carbon Science*, **v. 3**, p. 6-12, 2002.
5. KADIRVELU, K.; GOEL, J. “Eco-friendly technologies for removal of hazardous heavy metal from water and industrial wastewater”. *Hazardous Materials and Wastewater: Treatment, Removal and Analysis*. Nova York: Nova Science Publishers, p. 126-148, 2007.
6. KHANI, M. H.; KESHTKAR, A. R.; MEYSAMI, B.; ZAREA, M. F. JALALI, R. “Bisorption of uranium from aqueous solution bynonliving biomass of marinealgae cystoseira indica”, *Eletronic Jornal of biotechnology*, **v. 9**, p. 100-106, 2006.
7. GOK, C.; AYTAS, S. “Biosorption of Uranium(IV) from Aqueous Solution Using Calcium Alginate Beads”. *Journal of Hazardous Materials*, **v. 168**, p. 369-375, 2009.
8. AMANO, H.; YANASE, N. “Measurement of ^{90}Sr in environmental samples by cation-exchange and liquid scintillation counting”, *Talanta*, **v. 37**:6, p. 585-590, 1990.
9. FONSECA, H. C. O.; CASTRO, B.; BROCARDO, L. D. M.; HIROMOTO, G.; POTIENS Jr, A.; FERREIRA, R. J.; SILVA, F. R. O.; SAKATA, S. K. “*Thermal decompositon of treated coconut fiber used to remove Sr^{2+} from aqueous solutions*”, IX Congresso Brasileiro de Análise Térmica e Calorimetria, Serra Negra (SP), 2014.
10. SHUKLA, S. R.; GAIKAR, V.G.; ROSHAN, S. P. “Batch and column adsorption of Cu(II) on unmodified and oxidized coir”. *Sepraration Science and Technology*, **v. 40**, p. 40-62, 2009.
11. PARK, S.; BAKER, J. O.; HIMMEL, M. E.; PARILLA, P. A.; JOHNSON, D. “Cellulose crystallinity indes: measurement techniques and their impact on interpreting cellulose performance”, *Biotechnology for Biofuels*. **v. 3**:10, p. 1-10, 2010.
12. KODAMA, Y. “Avaliação dos efeitos da radiação ionizante em compósitos de PCL/PLLA com fibra de coco”, Tese (doutorado) – Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, 2011.
13. HUBBE, M. A.; HASAN, S. H.; DUCOSTE, J. J. “Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. metals”. *Bioresources*, **v. 6**:2, p. 2161-2287, 2011.
14. RAMIREZ, M. G. L. “Desenvolvimento de biocompósitos de amido termoplástico reforçados por fibra de coco verde”. Tese (doutorado) – Universidade Federal do Paraná, Curitiba, 2011.
15. ROSA, M. F.; MEDEIROS, E. S.; MALMONGE, J. A.; GREGORSKI, K. S.; WOOD, D. F.; MATTOSO, L. H. C.; GLENN, G. “Cellulose nanowhiskers from coconut husk fibers: effect of preparation conditions on their thermal and morphological behavior”, *Carbohydrate Polymers*, **v. 81**, p. 83-92, 2010.
16. TOMCZAK, F.; SYDENSTRICKER, T. H. D.; SATYANARAYANA, K. G. “Studies on lignocellulosic fibers of Brazil. Part II: Morphology and properties of Brazilian coconut fibers”, *Composites: Part A*, **v. 38**, p. 1710-1721, 2007.
17. BUSCHILE-DILLER, G.; ZERONIAN, S. H. “Enhancing the reactivity and strength of cotton fibers”, *J. Appl. Polym. Sci.*, **v. 6**, p. 967-979, California, 1992.
18. HE, Y.; PANG, Y.; LIU, Y.; LI, X.; WANG, K. “Physicochemical characterization of rice straw pretreated with sodium hydroxide in the solid state for enhancing biogas production”, *Energy & Fuels*, **v. 22**, p. 2775-2781, 2008.

19. ABRAHAM, E.; DEEPA, B.; POTHEN, L. A.; CINTIL, J.; THOMAS, S.; JOHN, M. J.; ANANDJIWALA, R.; NARINE, S. S. “Environmental friendly method for the extraction of coir fibre and isolation of nanofibre”, *Carbohydrate Polymers*, **v. 92**, p. 1477-1483, 2013.
20. SANGIAN, H. F.; KRISTIAN, J.; RAHMA, S.; DEWI, H. K.; PUSPASARI, D. A.; AGNESTY, S. Y.; GUNAWAN, S.; WIDJAJA, A. “Preparation of reducing sugar hydrolyzed from high-lignin coconut coir dust pretreated by the recycled ionic liquid [mmim][dmp] and combination with alkaline”. *Bulletin of Chemical Reaction Engineering & Catalysis (BCREC)*, 2015.
21. Barros, A. J. M.; Santos, J. C. O.; Prasad, S.; Leite, V. D.; Souza, A. G.; Soledade, L. E. B.; Duarte, M. S. B.; Santos, V. D. “Thermal decomposition study of sewage sludge and of organic waste used in the sorption of metals”, *J Therm Anal Calorim*, **v. 83**:2, p. 291-295, 2007.
22. ROPP, R. C. “Encyclopedia of the alkaline earth compounds”. *Elsevier*, 2012
23. ROMANCHUK, A. Y.; SLESAREV, A. S.; KALMYKOV, S. N.; KOSYNKIN, D. V.; TOUR, J. M. “Graphene oxide for effective radionuclide removal”, *Phys. Chem. Chem. Phys.*, **v. 15**, p. 2321-2327, 2013.
24. ROMANCHUK, A. Y.; SLESAREV, A. S.; KALMYKOV, S. N.; KOSYNKIN, D. V.; TOUR, J. M. “Graphene oxide for effective radionuclide removal”, *Phys. Chem. Chem. Phys.*, **v. 15**, p. 2321-2327, 2013.