INORGANIC ION EXCHANGER BASED ON TIN/TITANIUM MIXED OXIDE DOPED WITH EUROPIUM TO BE USED IN RADIOACTIVE WASTE.

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ABSTRACT

This work presents the results of synthesis and characterization of an inorganic ion exchanger based on tin/titanium mixed oxides doped with europium ($SnO_2/TiO_2:Eu^{3+}$) to be used in environmental field. The adsorption study of nickel was realized in this exchanger to recover the nickel metal which is in thorium-nickel alloys used as electrode of discharge lamps. The studied exchanger was synthesized by neutralization of tin chloride (IV) and titanium chloride (III) mixed solution and characterized by thermogravimetric measurement (TG), Differential Scanning Calorimetry (DSC), X-Ray Powder Diffraction (XRD), Infrared Spectroscopy (IR) and Scanning Electron Microscopy (SEM). The adsorption study showed that these inorganic ion exchangers are good materials to recovery nickel with high weight distribution ratios (Dw_{Ni}^{2+}) and percent adsorption.

1. INTRODUCTION

The inorganic ions exchangers are adsorptions with high capacity and fast speed ionic exchange, they have thermal, chemical and radioactive stability [1]. A class of synthetic inorganic exchangers is the mixed exchangers that improve the separation process and also present high selectivity for different ions [2-6].

The interest in using inorganic exchangers with rare earths ions is due to the ability of these ions, for example, increasing the acid sites in the structure of catalysts, [7] improve the adsorption.

In the past decade, nanometer solid materials have become more and more important due to their special properties [8]. Nanomaterials possess a series of unique physical and chemical properties. One of their important properties is that most of the atoms which have highly chemical activity and adsorption capacities to many metal ions are on the surface of the nanoparticles [9]. The surface atoms are unsaturated, and therefore, are subject to

combination with other ions by static electricity [10]. Consequently, nanometer sized materials can absorb metal ions with great adsorption speed. Recently nanomaterials have been used as sorbent due to their improved intrinsic properties such as chemical activity and fine grain size in compared with the classical substances such as normal scale titanium dioxide, alumina, etc [11–13]. Nanomaterials have high surface areas and therefore, they can strongly adsorb many substances such as trace metals [14] and polar organic substances [15]. Nanomaterials can be prepared by various techniques such as chemical vapor deposition [16] and sol–gel method [17,18]. From the literature survey, it can be seen that a lot of different nanomaterials have been synthesized and used as a sorbent for trace metal preconcentration [19–22]. Investigations of the surface chemistry of highly dispersed oxides, e.g., TiO_2 and ZrO_2, indicate that these materials have very high adsorption capacities and give promising results when used for trace metal analyses of different types of solution samples [8,12]. Nano-sized materials were chemically modified by a reagent to obtain a new and selective solid phase extractant for the preconcentration of metal ions [11,12].

Nickel has a many applications such as stainless steel production, batteries, catalysts and alloys with different metals. One of these alloys is the thorium-nickel that is used in discharge lamps electrode [23].

The purpose of this research is to fabricate nano TiO_2/SnO_2 as a new solid phase extractor and to investigate the feasibility of it for using metal enrichment. To the best of our knowledge this is the new solid phase extractor used for this purpose. In this study, the synthesized material was first characterized by using scanning electron microscope (SEM), thermal analyses (TA) infrared spectroscopy (IR) and X-ray diffractometer methods (XRD) and then used as solid phase extractor for the separation and/or preconcentration of nickel(II).

2. EXPERIMENTAL SECTION

2.1. Synthesis of Inorganic Ion Exchangers

The mixed oxide SnO_2/TiO_2:Eu^{3+} was prepared by neutralization of a mixing solution of tin (IV) chloride, titanium (III) chloride and europium chloride with ammonia solution in a reactor type batch. To this solution it was added ammonium hydroxide until neutralization, pH 7. The molar composition of the metals solution was 0.25mols of Sn, 0.03mols of Ti and 1.05×10^{-3}mols of Eu. The particles were aged in the solution mother liquor for 48h. The precipitated was very thin particles therefore it was opted to do the migration of chloride ions by using cellophane membranes, and the power for the separation process was the gradient concentration of chloride ions between the solutions. For analytical control of chloride ions in the particle fluid it was used $AgNO_3$ test. After removal of chloride ions, the material was dried at 110ºC in a heater.

2.2. Characterization

The exchanger was characterized by thermogravimetric measurement (TG), Differential Scanning Calorimetry (DSC), X-Ray Powder Diffraction (XRD), Infrared Spectroscopy (IR)

and Scanning Electron Microscopy (SEM). The study of adsorption of the metal nickel was made by spectrophotometric method with dimetilglioxime in a strongly alkaline medium in the presence of the potassium persulphate oxidant agent [24].

3. RESULTS AND DISCUSSION

3.1 Thermal Analysis

Fig. 1 shows TG and DTG measurement to $SnO_2/TiO_2:Eu^{3+}$ exchange. The exchanger presented good thermal stability and it is possible observe two events of mass losses which were attributed to the dehydration and the crystallization water loss together with losses of hydroxyl groups respectively. These losses occur in the interval at $33 - 133\ ^oC$ (8,82 %) and $131 - 551\ ^oC$ (5,96 %) [25,26].
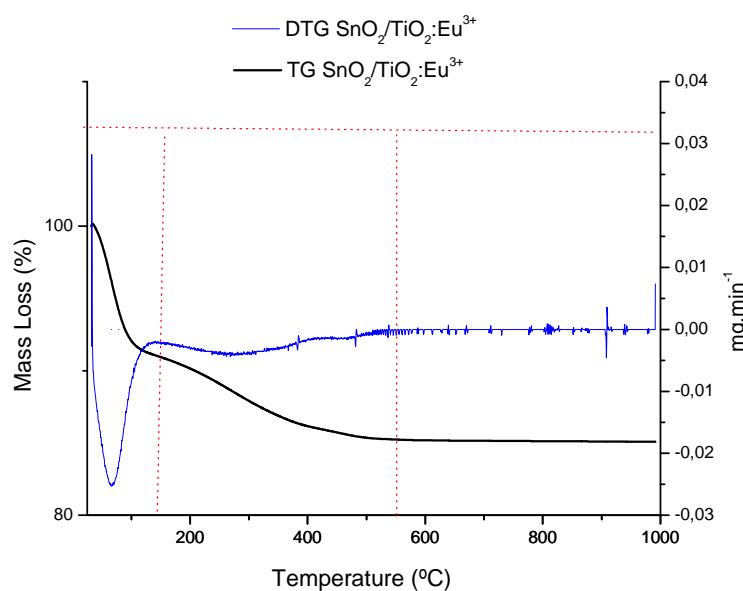

Figure 1. TG/DTG curves to $SnO_2/TiO_2:Eu^{3+}$

In Fig. 2 it is showed DSC curve where it can be see two events, the first one in $126\ ^oC$ (-3422,04 mJ) and the second in $294\ ^oC$ (-82,48 mJ). It is evident the endothermic character of the process of H_2O loss and crystalline rearrangement of the studied system.
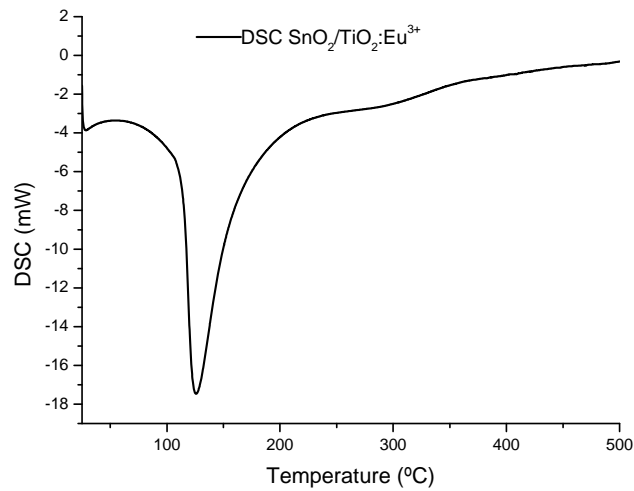
Figure 2. DSC curve to SnO$_2$/TiO$_2$:Eu^{3+}

3.2 X-Ray Powder Diffraction

The X-ray powder diffraction to mixed oxide, SnO$_2$/TiO$_2$:Eu^{3+} are presented in (Fig. 3), and shows broad peaks suggests although it is crystalline exchange it shows nanometric crystalline size. The mixed oxide, SnO$_2$/TiO$_2$:Eu^{3+} presented anatase structure [1] with lines of diffraction in 2θ: 27.25 (TiO$_2$) (JCPDS 34-0180), 52.35 (Ti$_2$O$_3$) (JCPDS 12-0754) and 34.4(SnO$_2$), 38.2(SnO$_2$) (JCPDS 41–1445) [27-30]. The X-ray diffraction was refined by least squares fit method and the average diameter was calculated using the showing 5nm size.
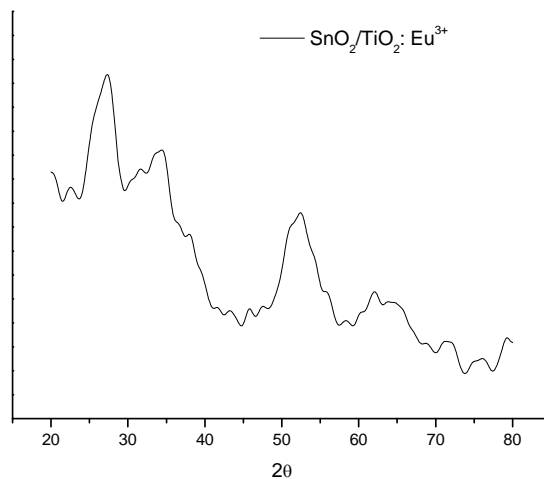

Figure 3. X-ray powder diffraction SnO$_2$/TiO$_2$:Eu^{3+}.

3.3 Infrared Spectroscopy

The infrared spectra, Fig. 4, shows a broad band in the region of 3413-3190 cm^{-1} attributed to the OH stretching, νOH, of the water and hydroxyl group linked to the metal with different metals oxygen distances and a band in the region of ~1636 cm^{-1} was attributed to the angular deformation δ_{HOH} of the hydration water. The band in the region of 1026 cm^{-1} was attributed to the stretching νSn-O and in the region 662-564 cm^{-1} was related to the deformation δSn-O-Sn and the stretching νTi-O respectively [31].

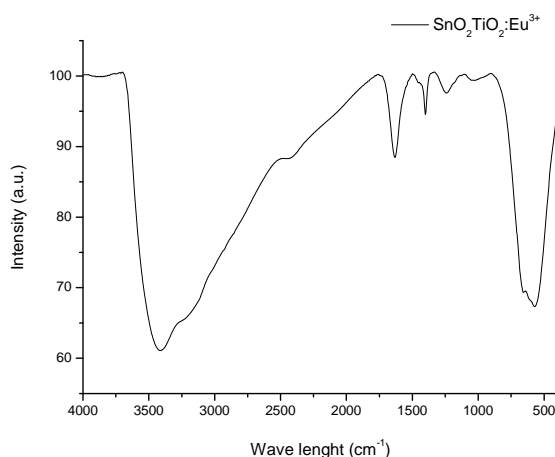**Figure 4. Infrared spectra of the SnO$_2$/TiO$_2$:Eu^{3+} exchanger.**

3.4 Scanning Electron Microscopy (SEM)

The micrograph of SnO$_2$/TiO$_2$:Eu^{3+} (Fig. 5) indicated that the exchange is in agglomeration form with homogeneous surfaces. The crystalline agglomerations are distributed by heterogeneous size and mostly with diameter <20 μm [32,33]. These results corroborate with X-ray data and it can be concluded that nano-scale material, which is one of the purpose of the study, could be obtained by the method described above.
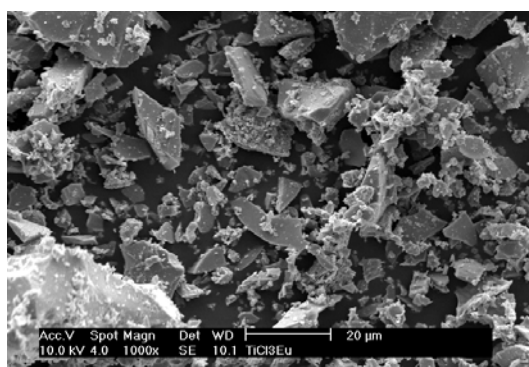

Figure 5. SEM of exchange SnO$_2$/TiO$_2$:Eu^{3+}.

3.5 Adsorption study of nickel

The parameters of Ni^{2+} adsorption were expressed in terms of distribution coefficients and efficiency of the adsorption. It was studied the influence of pH and concentration of nickel in the adsorption. Weight distribution ratios, Dw $(ml.g^{-1})$, were calculated according to the following equation [34]:

$$D_w=[(C_0-C_s)/w]/(C_s/V) \tag{1}$$

where C_0 and C_s are the aqueous phase concentration before and after equilibration, w the weight of resin (g) and V the volume of the aqueous phase (ml). Quintuplicate experiments showed that the reproducibility of the Dw measurements was generally within 10.
The capacity of the inorganic ion exchanger $SnO_2/TiO_2:Eu^{3+}$ for nickel sorption was measured in batch experiments in which a weighed amount of resin (ca. 100 mg) was kept in contact for ten minutes with 0.4 ml of a $0,3g.L^{-1}$ solution of nickel nitrate. After centrifugation and filtration, samples of the supernatant solution were analyzed for nickel by spectrophotometric method with dimetilglioxime in a strongly alkaline medium in the presence of the potassium persulphate oxidant agent [24]. The amount of metal sorbed by the Inorganic ion exchanger was calculated by mass balance.

3.5.1 Influence of pH to Ni^{2+}

The pH value plays an important role to the adsorption of ions on sorbents pH also strongly influences the speciation and the sorption availability of the heavy metals. Therefore, the retention of metal ions on the exchanger containing nano-scale $SnO_2/TiO_2:Eu^{3+}$ synthesized was studied as a function of pH. For that purpose, the pH values of standard sample solutions were adjusted to a range of 2–8 with buffer of acetic acid /ammonium acetate solutions keeping the other parameters constant and the general preconcentration procedure was applied. As shown in Fig. 6, the optimum pH of the sample solution was 7 for effective adsorption of nickel(II). At this pH value, the recovery of the nickel(II) is calculated to be 99,96%. The decrease in the recoveries of the nickel(II) at the lower pH values could be due to the competition between protons and the nickel(II) for the adsorption sites of the inorganic ion exchanger material. Therefore, a pH of 7 was selected in further experiments.
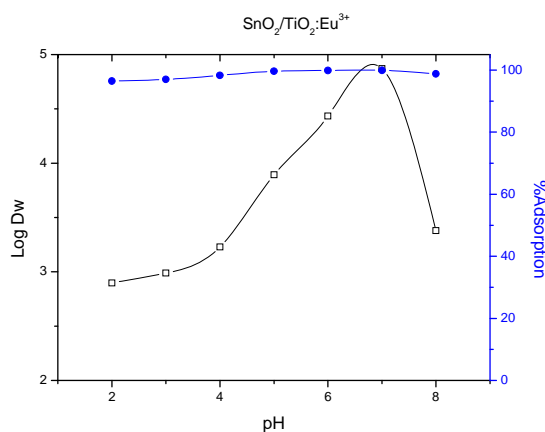

Figure 6. Influence of pH according in log Dw and % Adsorption versus pH.

3.5.2 Influence of Ni^{2+} concentration

The influence of Ni^{2+} concentration in the recovery parameters is presented in Fig. 7. For that purpose, the nickel concentration values of standard sample solutions were adjusted to a range of from 0.1 to 0.7 $g.L^{-1}$ Ni^{2+}. The contact time and pH in the process were pre-established be 10min and 7 respectively. The exchanger presented high values of D_w, but the saturation is reached at the lowest concentration studied.
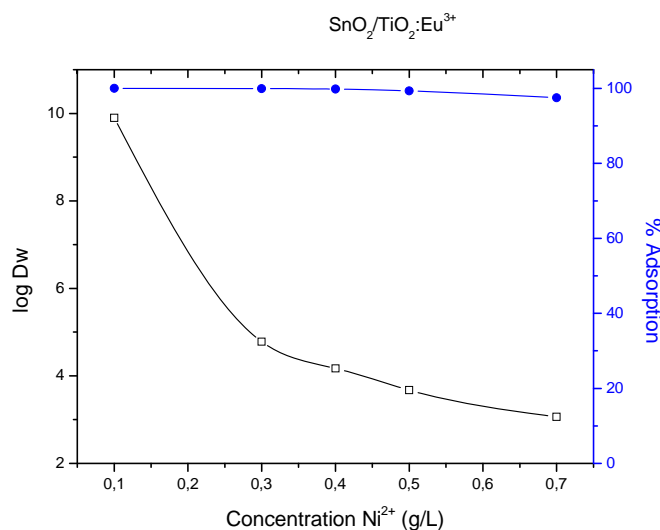

Figure 7. Influence of Ni^{2+}concentration in log Dw and % Adsorption versus Ni^{2+} at pH 7

4. CONCLUSIONS

The synthesis of $SnO_2/TiO_2:Eu^{3+}$ exchange was effective. The exchange presented in the form of agglomerations with homogeneous surfaces and nanometric crystalline size. It showed good thermal stability, endothermic character and anatase structure. In adsorption study the exchange showed to be effective with best distribution coefficient at pH 7 and high adsorption percentage (~100%). Nano $SnO_2/TiO_2:Eu^{3+}$ composite material as a new inorganic ion exchanger provides a simple, selective, accurate, economical, rapid and precise method for the preconcentration and determination of nickel.

ACKNOWLEDGMENTS

REFERENCES

1. G. V.Tagliaferro; M. L. C. P. Silva and G. L. J. P. Silva. "Influência do agente precipitante na preparação do óxido de nióbio (v) hidratado pelo método da precipitação em solução homogênea." *Química Nova*, **v.28**, pp.250–254 (2005).
2. D. C. Schnitzler,; M. S. Meruvia; I. A. Hu¨Mmelgen and A. J. G. Zarbin, "Preparation and Characterization of Novel Hybrid Materials Formed from (Ti,Sn)O2 Nanoparticles and Polyaniline." *Chem. Mater.* **v.15**, pp.4658–4665 (2003).
3. L. Cao; H. Wan; L. Huo and S. Xi. "A novel method for preparing ordered SnO_2/TiO_2 alternate nanoparticulates films." *Journal of Colloid and Interface Science*, **v.244**, pp.97–101 (2001).
4. R. Subasri and T. Shinohara. "Investigations on SnO_2-TiO_2 composite photoelectrodes for corrosion protection." *Electrochemistry Communications*, **v. 5**, pp.897–902 (2003).
5. F. Edelman; H. Hahn. et al. "Structural evolution of SnO_2-TiO_2 nanocrystalline films for gas sensors." *Materials Science and Engineering*, **v.B69-70**, p.386–391, (2000).
6. F. R Sensato,.; R. Custodio; E. Longo; A. Beltran and J. Andres. "Electronic and structural properties of $Sn_xTi_{1-x}O_2$ solid solutions: a periodic DFT study." *Catalysis Today*, **v.85**, pp.145–152 (2003).
7. "Effects of Rare Earth Oxides in FCC Catalysts." http://www.refiningonline.com/engelhardkb/crep/TCR4_23.htm (2007).
8. Y. Zhai, X. Chang, Y. Cui, N. Lian, S. Lai, H. Zhen and Q. He, "Selective determination of trace mercury(II) after preconcentration with 4-(2-pyridylazo)-resorcinolmodified nanometer-sized SiO2 particles from sample solutions." *Microchim. Acta,* **v.154,** pp.253–259 (2006).
9. Y. Liu, P. Liang and L. Guo, "Nanometer titanium dioxide immobilized on silica gel as sorbent for preconcentration of metal ions prior to their determination by inductively coupled plasma atomic emission spectrometry", *Talanta,* **v.68,** pp.25–30 (2005).
10. Y. Hang, Y. Quin, Z. Jiang, and B. Hu, "Direct analysis of trace rare earth elements by fluorination assisted ETV-ICP-AES with slurry sampling through nano-sized TiO2 separation/preconcentration." *Anal. Sci.,* **v.18**, pp.843–846 (2002).
11. A. R. Türker, "New sorbents for solid-phase extraction for metal enrichment." *Clean,* **v.35**, pp.548–557 (2007).
12. V.A. Lemos, L.S.G. Teixeira, M.A. Bezerra, A.C.S. Costa, J.T. Castro, L.A.M. Cardoso, D.S. Jesus, E.S. Santos, P.X. Baliza and L.N. Santos, "New materials for solid-phase extraction of trace elements." *Appl. Spectrosc. Rev.,* **v.43**, pp. 303–334 (2008).
13. L. Zhang, T. Huang, M. Zhang, X. Guo and Z. Yuan, "Studies on the capability and behavior of adsorption of thallium on nano-Al2O3." *J. Hazard. Mater.*, **v.157,** pp.352–357. (2008)
14. Y. Cui, X. Chang, Y. Zhai, X. Zhu, H. Zheng and N. Lian, "ICP-AES determination of trace elements after preconcentratedwith p-dimethylaminobenzaldehyde-modified nanometer SiO2 from sample solution." *Microchem. J.*, **v.83,** pp.35–41 (2006).
15. Z.L.Wang, *Characterization on Nanophase Materials*, Wiley-VCH, Verlag,Weinheim, (2000).
16. B.H. Kim, J.Y. Lee, Y.H. Choe, M. Higuchi and N. Mizutani, "Preparation of TiO2 thin film by liquid sprayed mistCVDmethod." *Mater. Sci. Eng.*, **v.B.107**, pp.289–294 (2004).
17. X.-M. Wu, L. Wang, Z.-C. Tan, G.-H. Li andS.-S. Qu, "Preparation, characterization, and low-temperature heat capacities of nanocrystalline TiO2 ultrafine powder." *J. Solid State Chem.,* **v.156**, pp.220–224 (2001).

18. M. Thiruchitrambalam, V.R. Palkar and V. Gopinathan, "Hydrolysis of aluminum metal and sol-gel processing of nano alumina." *Mater. Lett.,* **v.58**, pp.3063–3066 (2004).

19. S.K. Jeong, S.B. Kim, S.S. Kim, X. Chen and P. Biswas, "Simultaneous removal of Cd and Pb from flue gases using in-situ generated nano-sized sorbents." *J. Ind. Eng. Chem.,* **v.13**, pp.1154–1161 (2007).

20. S.-H. Huang and D.-H. Chen, "Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent." *J. Hazard. Mater.*, **v.163**, pp.174-179 (2009).

21. M.A. Abu-Daabes and N.G. Pinto, "Synthesis and characterization of a nanostructured sorbent for the direct removal of mercury vapor from flue gases by chelation." *Chem. Eng. Sci.,* **v.60**, pp.1901–1910 (2005).

22. O.R. Zhang, B.C. Pan, B.J. Pan,W.M. Zhang, K. Jia and Q.X. Zhang, "Selective sorption of lead, cadmium and zinc ions by a polymeric cation exchanger containing nano-Zr(HPO3S)(2)." *Environ. Sci. Technol.*, **v.42**, pp.4140–4145 (2008).

23. P. Atkins; L. Jones. *Princípios de Química - Questionando a Vida moderna e o meio Ambiente.* Bookman 3.ed. Porto Alegre, Brasil (2006).

24. Z. Marczenko *Separation and spectrophotometric determination of elements.* Ellis Horwood, New York, USA (1986).

25. D. C. Schnitzler; M. S. Meruvia; I. A. Hu Mmelgen; A. J. G. Zarbin. "Preparation and Characterization of Novel Hybrid Materials Formed from (Ti,Sn)O_2 Nanoparticles and Polyaniline." *Chemistry Material.* **v.15**, pp.4658-4665 (2003).

26. J. Read; D. Foster; Wolfenstine; W. Behl. "SnO_2-carbon composites for lithium-ion battery anodes." *Journal of Power Souces*, **v.96**, pp.277–287 (2001).

27. D. Cai; Y. Sut; Y. Chen; J. Jiang; Z. He; L. Chen; "Synthesis and photoluminescence properties of novel SnO_2 asterisk-like nanostructures." *Materials Letters*, **v.59**, pp.1984 – 1988 (2005).

28. P. M. Kumar; S. Badrinarayanan; M. Sasatry. "Nanocrystalline TiO_2 studied by optical, FTIR and X-ray photoelectron spectroscopy: correlation to presence of surface states." *Thin Solid Films*, **v.358**, pp.122-130 (2000).

29. L. Zhao; J. Yu; B. Cheng. "Preparation and characterization os SiO_2/TiO_2 composite microspheres with microporous SiO_2 core/mesoporous TiO_2 shell." *Journal of Solid State Chemistry*, **v.178**, pp.1818-1824 (2005).

30. D. Cai; Y. Su; Y. Chen; J. Jiang; Z. He; L. Chen. "Synthesis and photoluminescence properties of novel SnO_2 asterisk-like nanostructures." *Materials Letters*, **v.59**, pp.1984-1988, (2005).

31. A. C. F. M. Costa; M. A. Vilar; H. L. Lira; R. H. G. A. Kiminami; L. Gama. "Síntese e caracterização de nanopartículas de TiO_2." *Cerâmica*, **v.52**, pp.255-259 (2006).

32. P. R. Barbaroto. "Microscópio Eletrônico de Varredura: Medidas para caracterização e análise de materiais." http://www.dsif.fee.unicamp.br/~furio/IE607A/SEM.pdf (2006).

33. J. Goldstein. *Scanning Electron Microscopy and X-Ray Microanalysis.* Plenum Press, New York, USA (1984).

34. M. L. Dietz, E. P. Horwitz, L. R. Sajdak and R. Chiarizia, "An improved extraction chromatographic resin for the separation of uranium from acidic nitrate media." *Talanta*, **v.54**, pp.1173–1184 (2001).