Chitosan coated magnetite nanoparticles applied in effluent treatment for uranium removal

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1. Introduction

Uranium is a natural chemical element found in rocks in the earth's crust, discovered in 1789 by German scientist Martin Klaproth. It is radioactive and one of the natural elements with the highest atomic number, being surpassed only by netunium and plutonium [1]. Traces of uranium are found in various places in the earth's crust. The most easily found uranium ore is pitchblende, which is a composition of UO_2 with U_3O_8 [7]. Every process that involves the handling of uranium in its production chain results in radioactive waste. These can be solids or liquids that become environmental liabilities [5]. The management of tailings and its destination is based on the concentration levels of radionuclides present and their physicochemical characteristics [4].

Due to the risk that radioactive liquid effluents can bring to humans, it is necessary to remove uranium before this effluent reaches the sewage collection. There are several techniques for removing this element, the main ones being: ion exchange, adsorption, chemical precipitation, membrane separation, solvent extraction and electrodialysis [13]. The main objective of this work is to separate uranium in concentrations of around $100 \ \mu g. \ mL^{-1}$ present in aqueous solutions and evaluate the suitability of nanostructured materials in the treatment of effluents for uranium recovery in compliance with environmental legislation and regulatory actions.

2. Methodology

To carry out the adsorption experiments with chitosan magnetic nanoparticles, effluent samples provided by the Institute for Energy and Nuclear Research (IPEN) were used. These effluents were obtained in the nuclear fuel production cycle after the fluoridation step to obtain UF_4 (uranium tetrachloride) and UF_6 (uranium hexafluoride). NMQs were prepared in four steps: simultaneous precipitation of ferric and ferrous ions; preparation of acetic chitosan solution; coating the particles and solidifying the chitosan [11].

3. Results and Discussion

From the TEM images (Figure 1) it is possible to verify that the magnetite particles coated with chitosan have a compact shape, faceted and rounded corners. These characteristics may indicate that at some point the particles had a spherical shape and with aging or under the action of the magnetic field of the TEM lenses they acquired this faceted characteristic. Visually, the particle size is on the order of 20 nm with both downward and upward variations.
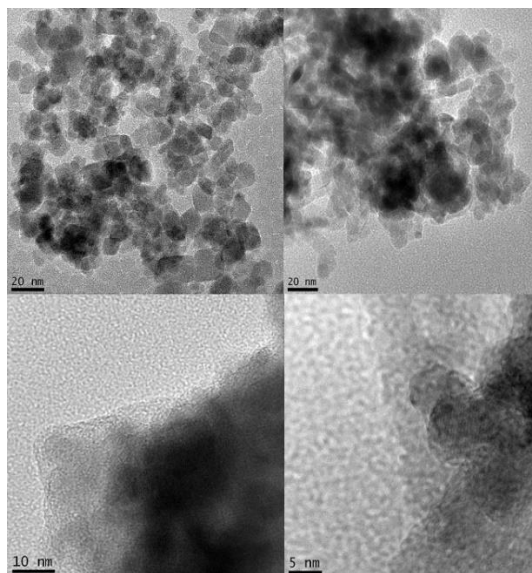
Figure 1: Transmission electron microscopy of the chitosan-coated magnetite sample

Figure 2 presents a standard diffractogram of magnetite nanoparticles that indicates the structure of Fe_3O_4. It is possible to verify that the peaks are similar, at $2\Theta \approx 30°$ and $35.6°$ and $43.2°$. This indicates that the sample obtained in this work is composed of Fe_3O_4 in its entirety (Figure 2).
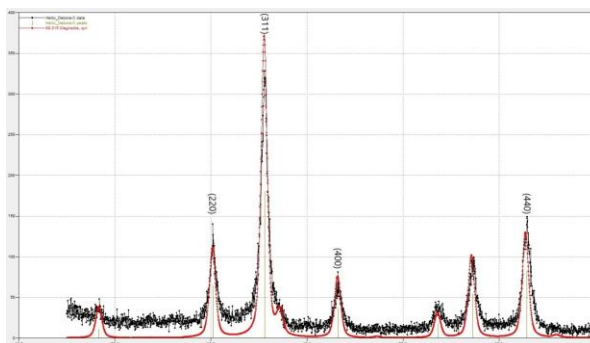

Figure 2: X-ray diffractograms of chitosan-coated magnetite samples.

The uranyl ion has a wide range of species according to the pH in the solution. Considering the characteristic of the element, a pH range varying between 2 and 10 was used. 15 mL of effluent with 163 $\mu g.mL^{-1}$ of uranium was also used and 50 mg of magnetic nanoparticles was added, with a fixed stirring time of 40 minutes , in medium gradient of agitation speed at 360 rpm.

The removal percentage values for each point are shown in Table I. All samples were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the concentration of uranium remaining in the solutions.

Table I: Removal percentage of uranyl ions using magnetite nanoparticles as adsorbent.

pH	% Removal
2	83,0
5	98,3
7	86,5
8	89,1
10	90,5

In this step, the mass of adsorbent was varied between 20 and 60 mg of NMQ in 15 mL of solution containing uranium. Agitation time was 40 minutes for all vials with an average speed of 360 rpm. Table II shows the results, in percentage, of the removal of UO_2^{2+} ions according to the NMQ doses.

Table II: Uranium removal as a function of NMQ dose

NMQ (mg)	Dose (g.L^{-1})	% Remoção
20	1,3	65,0
30	2	80,0
40	2,6	85,0
50	3,3	92,0
60	4	98,0

The aim of this study was to verify the influence of the samples' agitation time on the adsorption of uranium by the NMQ. Five 15 mL samples containing 163 µg.mL^{-1} and 50 mg of chitosan magnetic nanoparticles were used. The stirring time varied between 20, 30, 40, 50 and 60 minutes, the stirring speed was set at 360 rpm. In Table III, it was possible to verify the percentage of uranium removal in the experiments.

Tabela III: Porcentagem de remoção de UO_2^{2+} em função do tempo de agitação das amostras

Agitation time	% Removal
20	82,0
30	84,1
40	90,5
50	97,0
60	99,0

4. Conclusions

The results obtained indicate that the chitosan-coated magnetite nanoparticles presented satisfactory morphology and particle size when prepared by the precipitation method.

The characterization of the samples by the analytical techniques of TEM and XRD allowed to confirm the production of magnetite, particles in nanometric scale and morphology close to the spherical and the "visualization" of the chitosan layer around the magnetite.

The influence test of the main variables, such as: pH, uranium concentration, stirring time and amount of magnetite nanoparticles, found that it was possible to verify that magnetite nanoparticles are efficient in the process of removing uranium from aqueous solutions.

The results obtained indicate that it was not possible to reach the necessary values to reach the detection limit of CONAMA Resolution 357/2005. However, the results showed that the percentage of removal of uranium ions was 99%.

Acknowledgements

References

[1] ANM. Cadastro Nacional de Produtores de Brita. Agência Nacional da Mineração, Brasília, 2017. Disponivel em: <http://www.anm.gov.br/dnpm/publicacoes/serie-estatisticas-e-economia-mineral/outras-publicacoes-1/2-3-uranio>. Acesso em: 2020.

[2] BELGACEM, A. et al. The removal of uranium (VI) from aqueous solutions onto activated carbon developed from grinded used tire. Environ Sci Pollut Res, p. 684–694, 2014.

[3] CONAMA. Resolução nº 357, de 17 de março de 2005. Ministério do Meio Ambiente, 2005. Disponivel em: <http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=459>. Acesso em: 25 Novembro 2020.

[4] DOMINGOS, É. N. Simulação de incêndio em depósito de rejeitos radioativos e o risco radiológico associado a esse cenário. Dissertação de Mestrado em Ciência e Tecnologia Nuclear, Rio de Janeiro, 2018.

[5] DULAMA, M.; IORDACHE, M.; DENEANU, N. *Treatment of uranium contaminated wastewater.* Institute for Nuclear Research Pitesti, Romania, p. 80-86, 2013.

[6] IAEA. Inernational Atomic Energy Agency. Inernational Atomic Energy Agency, 2020. Disponivel em: <https://www.iaea.org/>. Acesso em: 1 Julho 2020.

[7] INB. Indústriais Nucleares do Brasil, Rio de Janeiro, 2020. Disponivel em: <www.inb.gov.br>. Acesso em: 23 Junho 2020.

[8] KRAJňÁK, A. et al. Sorption of uranium anionic species from aqueous solutions on HDTMA-bentonite Jelšový potok. CHÉMIA, Bratislava, 2014.

[9] SILVEIRA, E. D. Pesquisa FAPESP. Revista de pesquisa FAPESP, 2014. Disponivel em: <https://revistapesquisa.fapesp.br/instrumento-de-radiacao/>. Acesso em: 1 Julho 2020.

[10] SOUZA, A. T. D. Síntese e caracterização de nanopartículas magnéticas de óxido de ferro para aplicações biomédicas – um estudo citotóxico em linhagem celular de carcinoma cervical humano (células HeLa). Dissertação de Mestrado em Biofísica Molecular, São José do Rio Preto, 2011.

[11] STOPA, L. C. B. Quitosana magnética para remoção de urânio (VI). Dissertação (Mestrado em Ciências na área de Tecnologia Nuclear), São Paulo, 2007.

[12] TOALDO, L. T. Microesferas magnéticas de quitosana para remoção do corante violeta de metila 2B em meio aquoso. Dissertação (Mestre em Engenharia e Ciência dos Materiais), Caxias do Sul, 2015.

[13] WANG, J.; MENG, G.; TAO, K.; FENG, M.; ZHAO, X.; LI, Z.; XU, H.; XIA, D.; LU, JIAN R. *Immobilization of Lipases on Alkyl Silane Modified Magnetic Nanoparticles: Effect of Alkyl Chain Length on Enzyme Activity.* Plos One, v. 7, n. 8, 2012.