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Research Article

REMOVAL OF THORIUM (IV) ION BY USING MODIFIED CYSTOSEIRA BARBATA

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ABSTRACT

In this work, it was tried to remove Th (IV) radioactive ions in aqueous solution by using modified Cystoseira barbata. pH, contact time, concentration effects and temperature were investigated. It was observed that the amount of the removal was not affected by pH change. Adsorption isotherm models were applied and the maximum qm value was found to be 116.95 mgg-1 at 250C.

Keywords: *Th, biosorption, Cystoseira barbata*

1. INTRODUCTION

Water pollution from industrial wastes and environmental activities is increasing (Caparkaya and Cavas., 2008; El Jamal and Ncibi, 2012). One of the sources of water pollution is heavy metals. Heavy metals are toxic and have acquired fame among environmental contaminants (Moghaddam et al., 2013). Thorium is one of the most hazardous heavy metals for industrial applications and the environment (Khani et al., 2006; Riazi et al., 2016). It is used as a nuclear fuel at power plants and its compounds are used in the field of science of technology. (Riazi et al., 2014). If Th spreads through the environment, it can reach humans through the food chain and can cause damage in various organs of the human body. Therefore, it has become important to remove Th ions in aqueous solution in recent years (Aytas et al., 2014; Keshtkar et al., 2015; Riazi et al., 2016). Many techniques are used in order to remove Th ions which include precipitation, solvent extraction and adsorption. Of these techniques, the adsorption technique is widely preferred for it is simple, easily feasible and cost-effective (Kratochvil and Volesky, 1998; Pavasant et al., 2006; Zhou et al., 2016; Huang et al., 2018). Algae have been found to be potentional biosorbents (McMullan et al., 2001; Abd-El Kareem and Taha, 2012) for their functional groups (Ariff et al., 1999; Davis at al., 2003; Lodeiro et al., 2006; Vieira and Volesky, 2010). Especially brown algaes have been great adsorption capacities among other algaes, because of alginates (Malik et al., 1999; Schiewer and Wong, 2000). In recent years, many successful separation operations have been carried out for radionuclides. There are many studies conducted on removal of Th ion from aqueous solution (Yang and Volesky, 1999; Picardo et al., 2006; Ghasemi et al., 2011; Cecal et al., 2012; Keshtkar and Hassani, 2014; Riazi et al., 2016; Kaynar and Sabikoglu, 2018). Factors such as, temperature, pH, contact time were affected the adsorption capacities (Vijayaraghavan and Yun, 2008). In addition, in some studies, it has been seen that pre-concentration with different chemicals increases the adsorption capacity (Bai et al., 2010).

In this study, it attempted to remove Th ion in the aqueous solution by using *Cystoseira barbata*, one of the brown algae, pre-concentrated with HNO_3. Studies on pH effect, time, concentration, temperature and desorption were conducted.

2. MATERIAL AND METHODS

2.1. Preparation of the adsorbent

The adsorbent was the alga *C. barbata* (Stackhouse) C. Agardh was collected from the Dardanos Campus of Canakkale Onsekiz Mart University. The biomass was washed at distilled water and dried in an oven at 60°C until constant weight was reached. The biomass was chemically modified by 0.1 M HNO_3.

Pre-treatment with HNO_3

A sample of 2.5 g of dries biomass was treated with 25 ml of 0.1 M HNO_3. The mixture was shaken for 3 hour on a shaker at 250 rpm at room temperature. The biomass was then filtered off, followed by washing with deionized and it was then dried in an oven at 60˚C for 24h. This was a modification of the pre-treatment performed by Rubin et al, 2005.

2.2. Reagent and equipment

In this study all chemicals were used analytical grade (Merck). Distilled water was used to prepare all solutions. Stock solution of Th (IV) (1000 ppm) were prepared by Th $(NO_3)_4$. The concentration of Th (IV) ion in the filtered samples was measured with Rayleigh Vis-7220G spectrophotometer at 667 nm. The pH adjustments were performed using 0.1 M HCl or 0.1 M NaOH. Samples were filtered with a Millipore Millex-HV hydrophilic PVDF 0.45 μm syringe filter. A Wise Bath WSB-30 model shaker was used for the experiments. The Fourier Transform infrared spectroscopy (FTIR) analysis was completed using a Perkin Elmer Spectrum BX-11 Model FTIR spectrophotometer.

2.3. Batch biosorption studies

Five pH values (2, 3, 5, 7 and 9) were tested in the trials. Accordingly, 100 mg biomass was put into the Falcon tubes filled with 10 ppm 10 ml. Th (IV) ion solutions at different pH values. The tubes were shaken at room temperature for 60 min at 250 rpm. After adsorption step supernatant is taken out by a syringe.

The adsorbance of value of the supernatant was measured with the spectrophotometer and the amount of adsorbed Th (IV) ion solution was calculated. The percentage of Th (IV) ion removal (R) from the aqueous solution was calculated as follows:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} * 100 \qquad \textbf{(Eq. 1)}$$

Where C_o is the initial Th (IV) concentration (mgL^{-1}) and C_e is the adsorbed Th (IV) concentration (mgL^{-1})

For determination of pH experiments, different time intervals (10, 25, 45, 60, 80, 100, 150, 200, 300 and 400 min) were applied in room temperature at 250 rpm. The amount of radioactive ion uptake, q_t (mgg^{-1}), at each interval was calculated using the following equation:

$$q_t = \frac{(C_o - C_e)}{M} * V \qquad \textbf{(Eq. 2)}$$

Where C_o is the initial Th (IV) ion concentration (mgL^{-1}), C_e is the concentration of Th (IV) ion concentration at a given time (mgL^{-1}), V is the volume of radioactive solution (L) and M is the mass of biosorbent (g) (dry weight).

The batch adsorption technique was used for sorption. 100 mg *C. barbata* was put into a falcon tubes and treated with 10 mL of Th(IV) solution at different concentration (5-10-20-50-100-150-200-300-350-400-450 and 500 mgL^{-1}). The Falcon tubes were shaken at 250 rpm at 25ºC and 45ºC. Then samples were filtered with a syringe filter and the adsorbed amount of Th(IV) ions were measured using spectrophotometer.

The equilibrium data at different temperatures were analyzed with Langmuir and Freundlich isotherms. The Langmuir model was shown below (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{q_m a_L} + \frac{C_e}{q_m} \qquad \textbf{(Eq. 3)}$$

Where q_e, (mgg^{-1}) is the amount of Th(IV) ions, C_e (mgL^{-1}) is the equilibrium concentration of the Th (IV) ions, q_m (mgg^{-1}) is the maximum adsorption capacity and a_L is the Langmuir constant related to the energy of adsorption.

A linear form of the Freundlich equation is shown below (Freundlich, 1906):

$$\log q_e = \log K_f + 1/n_f \log C_e \qquad \textbf{(Eq. 4)}$$

Where K_f (mgg^{-1}) is related to adsorption capacity and n_f is an empirical parameter that varies with degree of heterogeneity.

3. RESULTS AND DISCUSSION

3.1. Determination of optimum pH

pH is one of the most important effects that have an impact upon the biosorption. In order to examine pH that affects biosorption, pH trials at different values were undertaken. Results are given in Figure 1. It was observed that Th adsorption % values remained unaffected by pH change. When looking at overall pH values subject to the study, it was ascertained that pH does not have much effect and adsorption over 96.5% was observed.

3.2. Determination of Optimum Contact Time

During equilibrium trials, trials were conducted for different times with a view to examining the effect of the time. Results are given in Figure 2. According to results obtained, it was observed that the system reached equilibrium in the first 100 minutes.

Figure 1. Effect of pH on the biosorption of Th (IV)

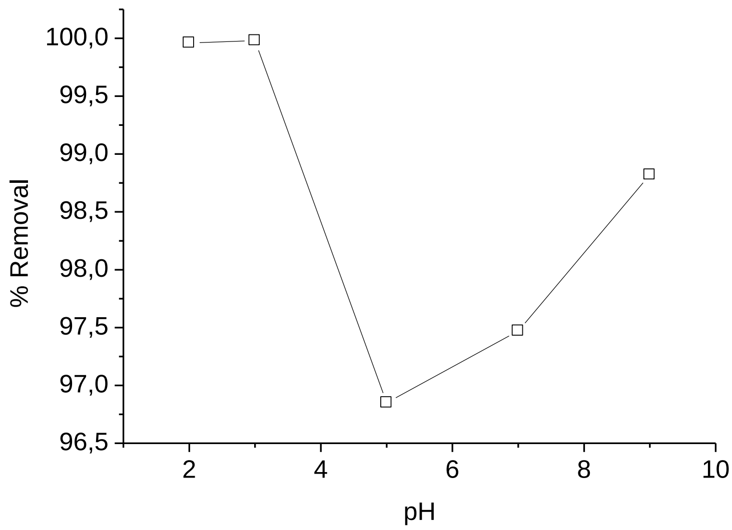
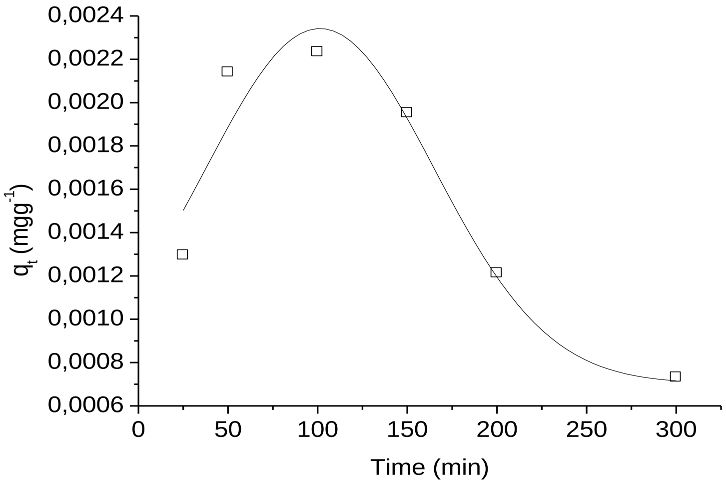


Figure 2. Effect of contact time on the biosorption of Th (IV)



3.3. Adsorption isotherms

Isotherm studies were conducted on Th (IV) ions at different temperatures. Table 1 shows Langmuir and Freundlich isotherm parameters. It was observed that, at 25^{0}C, Langmuir isotherm model adapted better. At 25^{0}C, de q_m value was 116.96 mgg^{-1} and 92.94 mgg^{-1} at 45^{0}C. According to results, it was observed that q_m value decreased as the temperature increased.

Table 1. Langmuir and Freundlich isotherm models of *C. barbata* for Th (IV) ion at different temperatures

		Langmuir isotherm models			Freundlich isotherm models		
	Temperature (°C)	q_m(mgg^{-1})	a_L	R_L^2	n_f	K_f(mgg^{-1})	R_F^2
0.1 M HNO_3 *C. barbata*	25	116.96	21.08	0.9537	1.13	1.893	0.9009
0.1 M HNO_3 *C. barbata*	45	92.94	27.20	0.9108	0.49	106.836	0.9182

Table 2 shows maximum Th (IV) ion adsorption capacities of different adsorbents. According to results, it was established that modification of *C. barbata* caused an increase in adsorption capacity (q_{max}). It was observed that the modified *C. barbata* has a high q_m value.

Table 2. Maximum Th (IV) ion adsorption capacities of different adsorbents

Biyomas	q_{max}(mg/g)	Referance
Rhizopus arrhizus	238.1	Abbasizadeh et al.,(2013)
Cystoseiraindica	169.49	Keshar and Hassani (2014)
Aspergillus niger	22	Tsezos and Volesky (1981)
Cystoseira indica (pretreated $CaCl_2$)	195.7	Riazi et al., 2014
Cystoseira barbata	39.45	Ozudogru (2019)
Cystoseira barbata (with modified)	116.96 (25ºC) 92.94 (45ºC)	This study

3.4. Desorption study

For desorption studies of Th (IV) ion, trials were conducted with different times and different eluents. Results obtained are given in Table 3. 1 M HNO_3 was found to be the best chemical for 30 minutes (99.60%). It was found to be 93.34% at 10 minutes for 0.5 M HNO_3.

Table 3. Desorption of Th (IV) ion by different eluents

Biomass 0.1 M HNO_3 *C. barbata*	Eluent	Time (min.)	% Removal of Th (IV) ions
	0.5 M HNO_3	30	62.20
	1 M HNO_3	30	99.60
	0.5 M HNO_3	20	74.56
	1 M HNO_3	20	96.96
	0.5 M HNO_3	10	93.34
	1 M HNO_3	10	94.82

4. CONCLUSION

In the present study, it was attempted to remove Th (IV) ion in the aqueous solution by using modified *Cystoseira barbata*. At each pH studied, it was observed that the biosorption capacity was over 96%. Concentration trials were conducted at 2 different temperatures and the highest adsorption capacity was found to be 116.96 mgg^{-1} at $25^{0}C$. For recovery of the Th (IV) ion charged, it was ascertained that the most effective chemical was 1 M HNO_3 (99.60%) at 30 minutes. Desorption studies showed that Th (IV) ion charged can be recovered. To conclude, modified *C. barbata*, a natural and environmentally friendly adsorbent, can be used for removal of Th (IV) ion in aqueous solution.

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REFERENCES

ABBASIZADEH, S., KESTHAR, A.R. and MOUSAVIAN, M.A., 2013, Preparation of a novel electrospun polyvinyl alcohol/titanium oxide nanofiber adsorbent modified with mercapto groups for uranium(VI) and thorium(IV) removal from aqueous solution, *Chemical Engineering Journal*, 220, 161-171.

ABD-EL-KAREEM, M. S., and TAHA, H. M., 2012, Decolorization of malachite green and methylene blue by two microalgal species, *International Journal of Chemical and Environmental Engineering*, 3(5): 297-302.

ARIFF, A.B., MEL, M., HASAN, M.A. and KARIM, M.I.A., 1999, The kinetics and mechanism of lead (II) biosorption by powderized *Rhizopus oligosporus*. World Journal of Microbiology and Biotechnology, 15(2) : 291-298.

AYTAS, S., GUNDUZ, E. and GOK, C., 2014, Biosorption of uranium ions by marine macroalga *Padina pavonia,Clean Soil Air Water* , 42 (4), 498-506.

BAI, J., YAO, H., FAN, F., LIN, M., ZHANG, L., DING, H., LEI,F., WU, X., LI, X., GUO, J. and QIN, Z., 2010, Biosorption of uranium by chemically modified *Rhodotorula glutinis*, *Journal of Environmental Radioactivity*, 101(11), 969–73.

CAPARKAYA, D. and CAVAS, L., 2008, Biosorption of methylene blue by a brown alga *Cystoseira barbatula* Kützing, *Acta Chimica Slovenica*, 55(3): 547-553.

CECAL, A., HUMELNICU, D., RUDIC, V., CEPOI, L., GANJU, D. and COJOCARI, A., 2012, Uptake of uranyl ions from uranium ores and sludges by means of *Spirulina platensis*, *Porphyridium cruentum* and *Nostoklinckia* alga, *Bioresource Technology*, 118, 19–23.

DAVIS, T.A., VOLESKY, B. and MUCCI, A., 2003, A review of the biochemistry of heavy metal biosorption by brown algae, *Water Resource*, 37: 4311–4330EL JAMAL, M. M. and NCIBI, M. C., 2012, Biosorption of methylene blue by *Chaetophora elegans* Algae: Kinetics, Equilibrium and Thermodynamic Studies, *Acta Chimica Slovenica*, 59(1): 24-31.

FREUNDLICH, H., 1906, Over The Adsorption in Solution, *The Journal of Physical Chemistry*, 57:385.

GHASEMI, M., KESHTKAR, A. R., DABBAGH, R. and JABER SAFDARI, S., 2011, Biosorption of uranium (VI) from aqueous solutions by Ca-pretreated *Cystoseira indica* alga: breakthrough curves studies and modeling, *Journal of Hazardous Materials*, 189(1-2), 141–9.

KESHTKAR, A.R. and HASSANI, M.A., 2014, Biosorption of thorium from aqueous solution by Ca-pretreated brown algae *Cystoseira indica*, *Korean Journal of Chemical Engineering*, 31 (2): 289-295.

KESHTKAR, A.R., MOHAMMADI, M. and MOOSAVIAN, M.A., 2015, Equilibrium biosorption studies of wastewater U(VI), Cu(II) and Ni(II) by the brown alga *Cystoseira indica* in single, binary and ternary metal systems, *Journal of Radio analytical and Nuclear Chemistry*, 303, 363-376.

KHANI, M. H., KESHTKAR, A. R., MEYSAMI, B., ZAREA, M.F. and JALALI, R,.2006, Biosorption of uranium from aqueous solutions by nonliving biomass of marine algae *Cystoseria indica*, *Journal of Biotechnology*, 9 (2),100-106.

HUANG, Y., HU, Y., CHEN, L., YANG, T., HUANG, H., SHI, R., LU, P. and ZHONG, C., 2018, Selective biosorption of thorium (IV) from aqueous solutions by ginkgo leaf, PlosOne, 13(3):1-25.

KAYNAR, U., H., ŞABİKOĞLU, İ., 2008, Adsorption of thorium by amorphous silica; response surface modeling and optimization, Journal of Radio analytical and Nuclear Chemistry, 318 (2): 823-834.

KRATOCHVIL, D. and VOLESKY, B., 1998, Biosorption of Cu from ferruginous wastewater by algal biomass, *Water Research*, 32(9): 2760-2768.

LANGMUIR, I., 1918, The adsorption of gases on plane surfaces of glass, mica and platinum, *Journal of American Chemical Society*, 40: 1361–1403.

LODEIRO, P., BARRIADA, J.L., HERRERO, R. and SASTRE DE VINCENTE, M.E., 2006, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium (II) and lead (II) removal: kinetic and equilibrium studies, *Environmental Pollution*, 142: 264–273.

MALIK, D. J., STREAT, M. and GREIG, J., 1999, Characterization and Evaluation of Seaweed-Based Sorbents for Treating Toxic Metal-Bearing Solutions, *Process Safety and Environmental Protection*, 77 (4): 227-233.

MC MULLAN, G., MEEHAN, C., CONNEELY, A., KIRBY, N., ROBINSON, T., NIGAM, P., BANAT, I. M., MARCHANT, R. and SMYTHET, W. F., 2001, Microbial decolourisation and degradation of textile dyes, *Applied Microbiology and Biotechnology*, 56: 81-87.

MOGHADDAM, M. R., FATEMI, S. and KESHTKAR, A., 2013, Adsorption of lead (Pb^{2+}) and uranium cations by brown algae; experimental and thermodynamic modeling, *Chemical Engineering Journal*, 231, 294–303.

OZUDOGRU, Y., 2019, *Cystoseira barbata* ile toryum biyosorpsiyonu, *Dokuz Eylül Üniversitesi Fen ve Mühendislik Dergisi*, 21: 461-468.

PAVASANT, P., APIRATIKUL, R., SUNGKHUM, V., SUTHIPARINYANONT, P., WATTANACHIRA, S. and MARHABA, T. F., 2006, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*, *Bioresource Technology*, 97(18): 2321-2329.

PICARDO, M.C., DE MELO FERREİRA, A.C. and AUGUSTO DA COSTA, A.C., 2006, Biosorption of radioactive thorium by *Sargassum filipendula*, *Applied Biochemistry and Biotechnology*, 134: 193-206.

RIAZI, M., KESHTKAR, A.R. and MOOSAVIAN, M.A., 2014, Batch and continuous fixed-bed column biosorption of thorium (IV) from aqueous solutions: equilibrium and dynamic modeling, *Journal of Radio analytical and Nuclear Chemistry*, 301 (2) : 493-503.

RIAZI, M., KESHTAR , A.R. and MOOSAVAIAN, M.A. 2016. Biosorption of Th(IV) in a fixed-bed column by Ca-pretreated *Cystoseira indica*. Journal of Environmental Chemical Engineering, 4: 1890-1898.

RUBIN, E., RODRIGUEZ, P., HERRERO, R., CREMADES, J., BARBARA, I. and E SASTRE DE VICENTE, M., 2005, Removal of Methylene Blue from aqueous solutions using as biyosorbent *Sargassum muticum*: an invasive macroalga in Europe, *Journal of Chemical Technology and Biotechnology*, 80 (3): 291-298.

SCHIEWER, S. and WONG, M. H., 2000, Ionic strength effects in biosorption of metals by marine algae, *Chemosphere*, 41 (1–2): 271-282.

TSEZOS, M. and VOLESKY, B., 1981, Biosorption of uranium and thorium, *Biotechnology and Bioengineering*, 23, 583-604.

VIEIRA, R. H. S. F. and VOLESKY, B., 2010, Biosorption: a solution to pollution?, *International Microbiology*, 3: 17–24.

VIJAYARAGHAVAN, K. and YUN, Y. S., 2008, Bacterial biosorbents and biosorption, *Biotechnology Advances*, 26: 266-291.

YANG, J. and VOLESKY, B., 1999, Biosorption of uranium on *Sargassum* biomass, *Water Research*, 33 : 3357-3363.

ZHOU, L., WANG, Y., ZOU, H., LIANG, X., ZENG, K., LIU, Z. and ADESINA, A.A., 2016, Biosorption characteristics of uranium (VI) and thorium (IV) ions from aqueous solution using $CaCl_2$- modified *Giant Kelp* biomass, *Journal of Radio analytical Nuclear Chemistry*, 307: 635-644.