

Uranium biosorption by hydroxyapatite and bone meal

Tamires Watanabe, Sabine Neusatz Guilhen, Júlio Takehiro Marumo, Leandro Goulart de Araujo*

Instituto de Pesquisas Energéticas e Nucleares, Av. Prof. Lineu Prestes 2242, São Paulo 05508-000, Brazil

Corresponding author: Dr. Leandro Goulart de Araujo

*E-mail address: lgoulart@alumni.usp.br

Abstract

Biosorption has been widely examined for the treatment of aqueous solutions containing uranium, a radiotoxic pollutant. The use of hydroxyapatite and bone meal as potential biosorbents in the removal of uranium (U) from aqueous solutions has not yet been previously addressed. In this work, the efficiency of these biosorbents in the removal of U was investigated according to their adsorption removal capacities. Surface transformations in both materials were observed after U adsorption by scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM/EDS). The biomass/U solution ratio was kept at 0.1 g/5 mL. Contact times for the batch experiments were 15, 30, 60, 120, and 180 min, and the concentration of U tested was 680 mg L⁻¹. The equilibrium was achieved in less than 15 min for both materials. The morphological characteristics of each biomass, before and after biosorption experiments were analyzed. Bone meal highlighted slightly superior adsorption results in terms of maximum capacity ($q_{max} = 33.83 \text{ mg g}^{-1}$), compared to hydroxyapatite ($q_{max} = 33.36 \text{ mg g}^{-1}$), with the removal percentages being also similar, 99.97 and 98.57 %, respectively. The results so far indicate that these materials are potential biosorbents for the treatment of uranium-contaminated solutions, especially liquid radioactive waste.

Keywords: uranium; adsorption; bone meal; hydroxyapatite.

1. Introduction

The presence of uranium (U) in aqueous streams is harmful, mainly because this radionuclide may persist in the natural environment for a long time. Sources of possible U contamination are numerous, including mineral mining, smelting, nuclear fuel manufacturing, and nuclear research. Furthermore, given the growing demands for electric energy generation in the last decades, U-containing nuclear wastes have significantly increased with the ascension of the nuclear power industry [1]. Several methods have been developed specifically for U extraction such as covalent binding [2], ion-exchange [3,4], electrostatic attraction [5], surface complexation [6–8], and Van der Waal's forces [9].

New and alternative processes are constantly being developed, aiming at removing radionuclides

from aqueous solutions, which also helps to overcome known issues of the conventional methods. To name a few, the high costs and the generation of higher volumes of liquid waste as a result of some varieties of treatment.

Biosorption can be defined as the use of biomass to uptake metal(loid) ions from aqueous environments. Examples of such biomaterials are algae, bacteria, yeast, fungi, plant leaves, and root tissues. Biosorption has many advantages, e.g. low capital and operating costs, selective removal of metals, the possibility of biosorbent regeneration and metal recovery, rapid kinetics of adsorption and desorption, and no sludge generation [10]. In this context, many biomaterials have been extensively studied for the removal of U from aqueous solutions, including biomass such as rice stem [11], *Solanum incanum* leaves [12], *Eichhornia crassipes* [13], macrophytes [14], coconut fiber [15], coffee and

rice husks [16]; microorganisms such as *Saccharomyces cerevisiae* [17,18], *Penicillium piscarium* [19], *Penicillium citrinum* [20], *Aspergillus fumigatus* [21], and biochars such as the ones derived from macauba [22], eucalyptus wood [23], *Opuntia ficus indica* [24], rice straw [25,26]; bone [27], and rice husk [28].

However, the use of bone meal for the removal of U from radioactive aqueous solutions has not yet been investigated as an alternative for the conventional adsorption processes. Therefore, as regards radioactive waste treatment, good mechanical properties are a very important feature of the biosorbent, especially if the final goal is the solidification of biomass waste. This will further impact the conditioning of the waste into a stable solid form which will allow immobilization and containment of the radioactive content for the necessary period. The application of bone meal is attractive and advantageous because it is economically feasible in comparison with commercial adsorbents. It consists of a natural, abundant substance that contains a large amount of calcium phosphate in the form of hydroxyapatite.

Phosphate-derived materials have been studied extensively to efficiently extract uranium from the aqueous phase owing to their adsorption capability, which has been ascribed to the surface complexation and mineralization of phosphate with U [29]. It can also be used to remove radionuclides from liquid aqueous solutions, such as liquid radioactive waste generated in many industrial or research activities. This biomaterial may be able to remove significantly hazardous radionuclides, heavy metals, and organic substances from radioactive liquid waste. Previous research has indicated that hydroxyapatite alone is capable to efficiently remove thorium from aqueous solutions [30]. Furthermore, studies indicate that radionuclides such as $^{90}\text{Sr}^{2+}$ [31], $^{208}\text{Tl}^+$, $^{226}\text{Ra}^{2+}$, $^{212}\text{Bi}^{3+}$ and $^{228}\text{Ac}^{3+}$ [32] were also adsorbed by hydroxyapatite.

The objective of this work was to evaluate the adsorption capacity of hydroxyapatite and bone meal for uranium removal from aqueous solutions. Moreover, the morphological characteristics of both materials were evaluated by Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS).

2. Materials and methods

2.1. Biosorbents

Bone meal (Super Verde, Fênix Indústria e Comércio de Fertilizantes LDA-ME) and hydroxyapatite (produced in CCTM/IPEN) were ground and sieved to obtain particle sizes between 0.297 mm and 0.125 mm. Subsequently, they were stored in sealed polyethylene flasks in the laboratory for later use.

2.2. Synthetic solution

A synthetic solution of U was prepared by adding 0.165 g of uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 100 mL distilled water (2.91 mmol L^{-1}). pH was adjusted to 4 by adding nitric acid (Merck, Brazil) or sodium hydroxide (Merck, Brazil). Initial pH was adjusted at 4 because it is the measured pH of the radioactive liquid waste stored at the Radioactive Waste Management Laboratory of the Nuclear and Energy Research Institute (IPEN-CNEN/SP). Our concern is to investigate how bone meal and hydroxyapatite behave under real radwaste conditions. Moreover, according to [33] and software projection, pH 4 favors the biosorption of a great number of species because of its speciation. At this pH, most of the U ions in solution is in the form of non-complexed free uranyl ions (UO_2^{2+} or U(VI)). pH behavior was evaluated during the experiments.

2.3. Biosorption experiments

2.3.1 Adsorption study

Batch biosorption experiments were performed to determine the metal uptake capacity under different contact times. The vials containing the solution and the biosorbent were stirred (130 rpm) at controlled temperature ($25 \text{ }^\circ\text{C}$). The mass of 0.1 g of the bone meal was suspended in 5 mL of U aqueous solutions and kept in contact during different time intervals: 0, 15, 30, 60, 120, and 180 min. The bone meal was removed by filtration in a vacuum system. The experiments were carried out in duplicate. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the concentration of U. The uptake amount of U onto the biomaterial was calculated using equation Eq. (1) [34].

$$q = \frac{(C_0 - C)V}{m} \quad (1)$$

where q is the uptake of uranium (mmol g^{-1}), C_0 is the initial uranium concentration in solution (mmol L^{-1}), C is the equilibrium concentration in solution (mmol L^{-1}), V is the volume of solution (L), and m is the mass of the biosorbent (g).

2.4. Equipment and analytical methods

Scanning electron microscopy (SEM) images of the biosorbents were collected by a Hitachi TM3000 (Tokyo, Japan) tabletop microscope. EDS data were collected by this microscope coupled with a tungsten source and acceleration voltages of 5 and 15 kV with an electron beam resolution of 30 nm. Images were obtained with magnification from 500 to 1500 times. The determination of U in the adsorbate solutions was made by ICP-OES from Perkin Elmer (EUA), model Optima 7000 DV.

3. Results and discussion

3.1. Morphological analysis

Morphological analysis by SEM was conducted to investigate surface transformations during U adsorption. Fig. 1 shows the micrographs and X-ray spectrometry (EDS) for hydroxyapatite and bone meal before biosorption and Fig. 2 after the treatment.

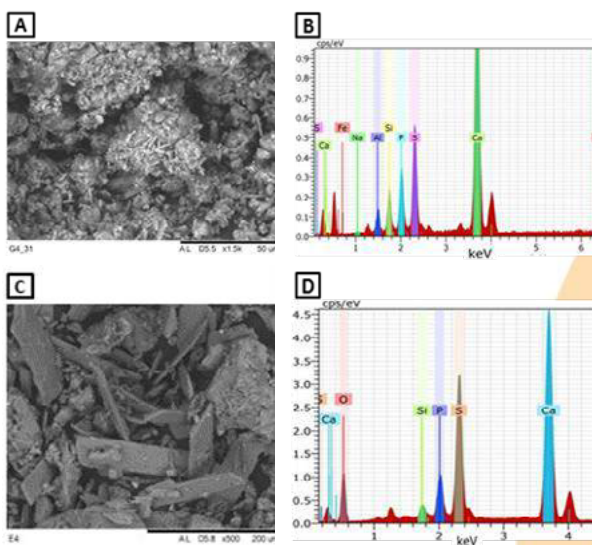


Fig. 1. Morphological analysis of raw material: (A) Micrograph of the bone meal; (B) X-ray spectrometry (EDS) of bone meal; (C) Micrograph

of hydroxyapatite; (D) X-ray spectrometry (EDS) of hydroxyapatite.

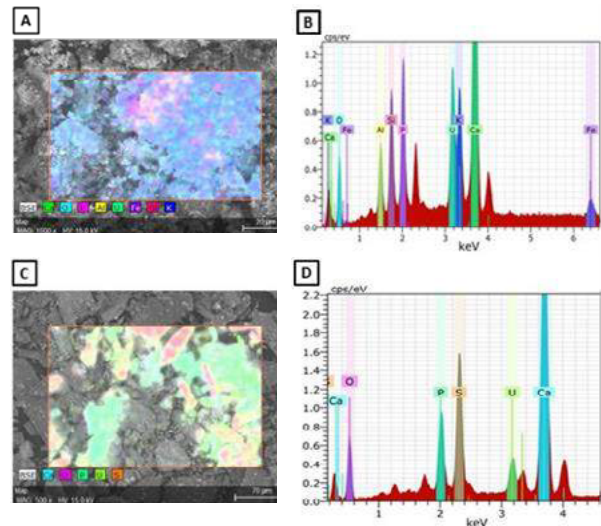


Fig. 2. Morphological analysis after 30 min in contact with the solution: (A) Micrograph of the bone meal; (B) X-ray spectrometry (EDS) of bone meal; (C) Micrograph of hydroxyapatite; (D) X-ray spectrometry (EDS) of hydroxyapatite.

The predominance of Ca and P was observed in the EDS, which is consistent with the composition of both hydroxyapatite and bone meal. After treatment, it was possible to observe a peak of U in both materials, evidencing its adsorption.

3.2. Experimental data obtained through the biosorption technique

The efficiency and the equilibrium adsorption capacity of each adsorbent were evaluated by adsorption over 180 min. The effect of the contact time on the removal of uranium by bone meal and hydroxyapatite is shown in Fig. 3. Although most of the uranyl ions had been removed after approximately 15 min, a minimum of 30 min was necessary to reach pH and adsorption equilibrium, at which the adsorption capacities were of 34 mg g^{-1} for both biosorbents ($> 98\%$ removal efficiency).

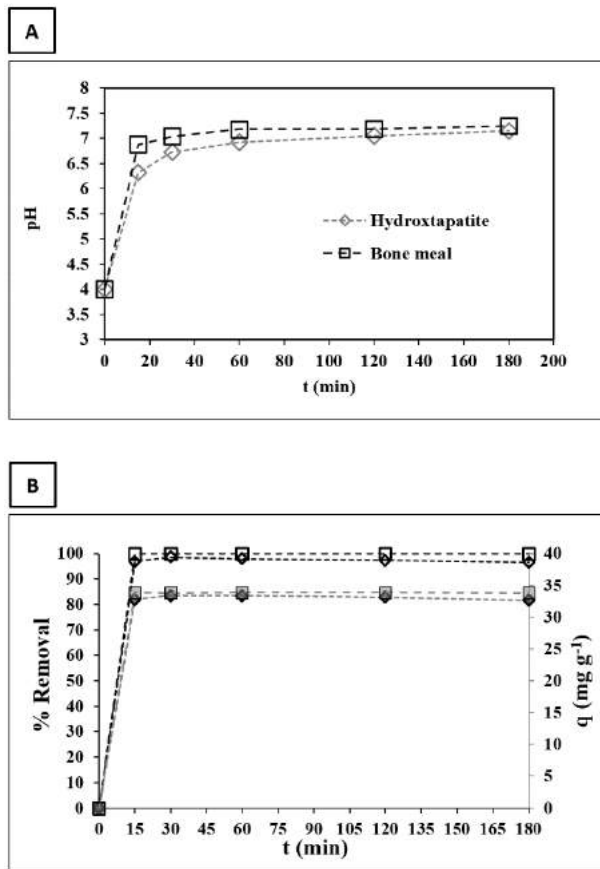


Fig. 3. Effects of experimental condition on uranium adsorption ability: (A) pH value, (B) contact time. In (B), q (mg g^{-1}) values are given by (filled square) – hydroxyapatite and (filled diamond) – bone meal; % Removal is given by (empty square) – hydroxyapatite and (empty diamond) – bone meal.

4. Conclusions

The adsorption capacity to remove U from aqueous solution by bone meal and hydroxyapatite was evaluated in this work. The application of these biomaterials for this purpose is attractive and advantageous because of their efficiency in removing this hazardous radionuclide and for being low cost materials. The uptake of U was fast and achieved in approximately 15 min. The biosorption assays were carried out in a batch system and indicated a viable treatment procedure for extracting U. Further investigations might be necessary to ascertain the biosorption performance by these materials by analyzing changes in variables such as concentration and pH.

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References

- [1] S. Kahouli, Re-examining uranium supply and demand: New insights, *Energy Policy*. 39 (2011) 358–376. <https://doi.org/10.1016/j.enpol.2010.10.007>.
- [2] S. Chen, J. Hong, H. Yang, J. Yang, Adsorption of uranium (VI) from aqueous solution using a novel graphene oxide-activated carbon felt composite, *J. Environ. Radioact.* 126 (2013) 253–258. <https://doi.org/10.1016/j.jenvrad.2013.09.002>.
- [3] A.C.Q. Ladeira, C.A. Morais, Uranium recovery from industrial effluent by ion exchange-column experiments, *Miner. Eng.* 18 (2005) 1337–1340. <https://doi.org/10.1016/j.mineng.2005.06.012>.
- [4] E. Rosenberg, G. Pinson, R. Tsosie, H. Tutu, E. Cukrowska, Uranium remediation by ion exchange and sorption methods: A critical review, *Johnson Matthey Technol. Rev.* 60 (2016) 59–77. <https://doi.org/10.1595/205651316X690178>.
- [5] C. Zhao, J. Liu, G. Yuan, J. Liu, H. Zhang, J. Yang, Y. Yang, N. Liu, Q. Sun, J. Liao, A novel activated sludge-graphene oxide composites for the removal of uranium(VI) from aqueous solutions, *Elsevier B.V.*, 2018. <https://doi.org/10.1016/j.molliq.2018.09.069>.
- [6] A. Waychunas, Uranium (VI) adsorption to ferrihydrite: application of a surface complexation model, *Int. J. Rock Mech. Min. Sci. Geomech. Abstr.* 32 (1995) A261. [https://doi.org/10.1016/0148-9062\(95\)99083-a](https://doi.org/10.1016/0148-9062(95)99083-a).
- [7] J.A. Davis, D.E. Meece, M. Kohler, G.P. Curtis, Approaches to surface complexation modeling of Uranium(VI) adsorption on aquifer sediments, *Geochim. Cosmochim. Acta.* 68 (2004) 3621–3641. <https://doi.org/10.1016/j.gca.2004.03.003>.
- [8] F.M. Coutelot, J.C. Seaman, M. Baker, Uranium(VI) adsorption and surface complexation modeling onto vadose sediments from the Savannah River Site, *Environ. Earth Sci.* 77 (2018). <https://doi.org/10.1007/s12665-018-7316-7>.
- [9] M. Sprynskyy, T. Kowalkowski, H. Tutu, E.M. Cukrowska, B. Buszewski, Adsorption performance of talc for uranium removal from aqueous solution, *Chem. Eng. J.* 171 (2011) 1185–1193. <https://doi.org/10.1016/j.cej.2011.05.022>.
- [10] I. Ismail, T. Moustafa, Biosorption of heavy metals, *Heavy Met. Sources, Toxic. Remediat. Tech.* (2016) 131–174.
- [11] Z. Xiao-Teng, J. Dong-Mei, X. Yi-Qun, C. Jun-Chang, H. Shuai, X. Liang-Shu, Adsorption of Uranium(VI) from Aqueous Solution by Modified Rice Stem, *J. Chem.* 2019 (2019). <https://doi.org/10.1155/2019/6409504>.
- [12] O.Y. Bakather, N. Zouli, A. Abutaleb, M.A. Mahmoud, A. Daher, M. Hassan, M.A. Eldoma, S.O. Alasweda, A.A. Fowad, Uranium (VI) ions uptake from liquid wastes by *Solanum incanum* leaves: Biosorption, desorption and recovery, *Alexandria*

- Eng. J. (2020). <https://doi.org/10.1016/j.cej.2020.03.013>.
- [13] Z. J. Yi, J. Yao, H. L. Chen, F. Wang, Z. M. Yuan, X. Liu, Uranium biosorption from aqueous solution onto *Eichhornia crassipes*, *J. Environ. Radioact.* 154 (2016) 43–51. <https://doi.org/10.1016/j.jenvrad.2016.01.012>.
- [14] L.C. Vieira, L.G. de Araujo, R.V. de Padua Ferreira, E.A. da Silva, R.L.S. Canevesi, J.T. Marumo, Uranium biosorption by *Lemna* sp. and *Pistia stratiotes*, *J. Environ. Radioact.* 203 (2019) 179–186. <https://doi.org/10.1016/j.jenvrad.2019.03.019>.
- [15] R.V.P. Ferreira, E.A. Silva, R.L.S. Canevesi, E.G.A. Ferreira, M.H.T. Taddei, M.C. Palmieri, F.R.O. Silva, J.T. Marumo, Application of the coconut fiber in radioactive liquid waste treatment, *Int. J. Environ. Sci. Technol.* 15 (2018) 1629–1640. <https://doi.org/10.1007/s13762-017-1541-6>.
- [16] R.V. de P. Ferreira, L.G. de Araujo, R.L.S. Canevesi, E.A. da Silva, E.G.A. Ferreira, M.C. Palmieri, J.T. Marumo, The use of rice and coffee husks for biosorption of U (total), ^{241}Am , and ^{137}Cs in radioactive liquid organic waste, *Environ. Sci. Pollut. Res. Int.* (2020). <https://doi.org/10.1007/s11356-020-09727-8>.
- [17] M. Liu, F. Dong, X. Yan, W. Zeng, L. Hou, X. Pang, Biosorption of uranium by *Saccharomyces cerevisiae* and surface interactions under culture conditions, *Bioresour. Technol.* 101 (2010) 8573–8580. <https://doi.org/10.1016/j.biortech.2010.06.063>.
- [18] J. Zhang, X. Chen, J. Zhou, X. Luo, Uranium biosorption mechanism model of protonated *Saccharomyces cerevisiae*, *J. Hazard. Mater.* 385 (2020) 121588. <https://doi.org/10.1016/j.jhazmat.2019.121588>.
- [19] E. Coelho, T.A. Reis, M. Cotrim, M. Rizzutto, B. Corrêa, Bioremediation of water contaminated with uranium using *Penicillium piscarium*, *Biotechnol. Prog.* (2020). <https://doi.org/10.1002/btpr.3032>.
- [20] C. Pang, Y.H. Liu, X.H. Cao, M. Li, G.L. Huang, R. Hua, C.X. Wang, Y.T. Liu, X.F. An, Biosorption of uranium(VI) from aqueous solution by dead fungal biomass of *Penicillium citrinum*, *Chem. Eng. J.* 170 (2011) 1–6. <https://doi.org/10.1016/j.cej.2010.10.068>.
- [21] J.S. Wang, X.J. Hu, Y.G. Liu, S.B. Xie, Z.L. Bao, Biosorption of uranium (VI) by immobilized *Aspergillus fumigatus* beads, *J. Environ. Radioact.* 101 (2010) 504–508. <https://doi.org/10.1016/j.jenvrad.2010.03.002>.
- [22] S.N. Guillhen, O. Mašek, N. Ortiz, J.C. Izidoro, D.A. Fungaro, Pyrolytic temperature evaluation of macauba biochar for uranium adsorption from aqueous solutions, *Biomass and Bioenergy.* 122 (2019) 381–390. <https://doi.org/10.1016/j.biombioe.2019.01.008>.
- [23] V. Mishra, M.K. Sureshkumar, N. Gupta, C.P. Kaushik, Study on sorption characteristics of uranium onto biochar derived from Eucalyptus Wood, *Water. Air. Soil Pollut.* 228 (2017). <https://doi.org/10.1007/s11270-017-3480-8>.
- [24] L. Hadjittofi, I. Pashalidis, Uranium sorption from aqueous solutions by activated biochar fibres investigated by FTIR spectroscopy and batch experiments, *J. Radioanal. Nucl. Chem.* 304 (2014) 897–904. <https://doi.org/10.1007/s10967-014-3868-5>.
- [25] L. Dong, J. Yang, Y. Mou, G. Sheng, L. Wang, W. Linghu, A.M. Asiri, K.A. Alamry, Effect of various environmental factors on the adsorption of U(VI) onto biochar derived from rice straw, *J. Radioanal. Nucl. Chem.* 314 (2017) 377–386. <https://doi.org/10.1007/s10967-017-5414-8>.
- [26] S.M.E. Yakout, A.A. Abdeltawab, K. Elhindi, A. Askalany, Uranium dynamic adsorption breakthrough curve onto rice straw based activated carbon using bed depth service time model, *BioResources.* 13 (2018) 9143–9157. <https://doi.org/10.15376/biores.13.4.9143-9157>.
- [27] A. Ashry, E.H. Bailey, S.R.N. Chenery, S.D. Young, Kinetic study of time-dependent fixation of UVI on biochar, *J. Hazard. Mater.* 320 (2016) 55–66. <https://doi.org/10.1016/j.jhazmat.2016.08.002>.
- [28] S. Wang, W. Guo, F. Gao, Y. Wang, Y. Gao, Lead and uranium sorptive removal from aqueous solution using magnetic and nonmagnetic fast pyrolysis rice husk biochars, *RSC Adv.* 8 (2018) 13205–13217. <https://doi.org/10.1039/c7ra13540h>.
- [29] L. Kong, Y. Ruan, Q. Zheng, M. Su, Z. Diao, D. Chen, L. Hou, X. Chang, K. Shih, Uranium extraction using hydroxyapatite recovered from phosphorus containing wastewater, *J. Hazard. Mater.* 382 (2020) 120784. <https://doi.org/10.1016/j.jhazmat.2019.120784>.
- [30] E.G.A. Ferreira, E. Alves, R.V.P. Ferreira, V.L.K. Isiki, E.A. Silva, R.L. Canevesi, J.T. Marumo, Biosorption of Thorium by Bone Meal. WM2015 Conference, March 15–19, 2015, Phoenix, Arizona, USA
- [31] J. Kim, N.S. Sambudi, K. Cho, Removal of Sr^{2+} using high-surface-area hydroxyapatite synthesized by non-additive in-situ precipitation, *J. Environ. Manage.* 231 (2019) 788–794. <https://doi.org/10.1016/j.jenvman.2018.10.100>.
- [32] R. Akkaya, Thermodynamic parameters of Ti^{+} , Ra^{2+} , Bi^{3+} and Ac^{3+} adsorption onto polyhydroxyethylmethacrylate-hydroxyapatite composite, *J. Radioanal. Nucl. Chem.* 292 (2012) 771–775. <https://doi.org/10.1007/s10967-011-1513-0>.
- [33] J. Yang, B. Volesky, Biosorption of uranium on *Sargassum* biomass, *Water Res.* 33 (1999) 3357–3363.
- [34] H.N. Tran, S.J. You, A. Hosseini-Bandegharai, H.P. Chao, Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review, *Water Res.* 120 (2017) 88–116. <https://doi.org/10.1016/j.watres.2017.04.014>.