Journal of Molecular Liquids 356 (2022) 119056

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Neptunium interaction with microplastics in aqueous solutions

Ioannis Ioannidis [a], Ioannis Anastopoulos [b,*], Ioannis Pashalidis [a,*]

[a] Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus
[b] Department of Agriculture, University of Ioannina, UoI Kostakii Campus, 47100 Arta, Greece

ARTICLE INFO

Article history:
Received 13 February 2022
Revised 18 March 2022
Accepted 29 March 2022
Available online 1 April 2022

Keywords:
Neptunium
PET-, PN6- microplastics
Adsorption
K_d values
Seawater

ABSTRACT

The neptunium sorption by different microplastic materials (MPs) has been studied in laboratory water and seawater samples, which had been previously traced with the Np-237 isotope. The microplastics used were polyethylene terephthalate (PET) and polyamide nylon (PN6), and the investigations included the pH effect and seawater composition on the sorption efficiency. The evaluation of the experimental data (K_d values) revealed that the sorption efficiency does not differ significantly from one microplastic to another and mainly the hydrolysis of Np(V) in alkaline conditions affects the sorption efficiency. In seawater the K_d values decline dramatically because of the increased ionic strength (salinity) and the occurrence of various cations (e.g. Ca^{2+}, Fe^{2+}), which effectively compete Np(V) sorption by the MPs.

© 2022 Elsevier B.V. All rights reserved.

1. Introduction

Microplastics when present in aqueous systems (e.g. seawater) are supposed to increase the contaminant transfer (e.g. heavy and radiotoxic substances) into the biosphere and following along the food chain into mamals including humans. The interaction of microplastics with different types of pollutants has been summarized in a recent review paper [1]. It has been demonstrated that microplastics can interact with hydrophobic organic chemicals [2], pharmaceuticals [3] and metal ions [4,5]. The sorption process seems to be complex including hydrophobic and electrostatic interactions, as well as surface complex formation [1]. Moreover, the type and size of the microplastic, pH and aqueous phase composition significantly affect the sorption efficiency [6,7].

In the present study two different types of microplastics (e.g. polyethylene terephthalate (PET) and polyamide nylon (PN6)) have been used as adsorbents. PET (polyethylene terephthalate) belongs to the polyester polymer family and is one of the most common thermoplastic materials and is used in the form of fibers for clothing and containers for liquids and food. PET consists of polymerized ethylene terephthalate ($C_{10}H_8O_4$) [6,8]. On the other hand, PN6 (polyamide nylon) belongs to the polyamide polymer family and because of its excellent physicochemical properties such as high tensile strength and elasticity, and resistance to abrasion and chemicals is used as construction material in many industries, including clothing, automotive and electronic industry and the annual demand only in Europe is about a million tones [9]. However, compared to polyesters, PN6 is only poorly biodegradable [10]. Both microplastic materials are characterized by active groups on their surface which can interact and form surface complexes with metal ions [7].

Although the interaction of microplastics with radionuclides is fundamental regarding the transport and fate of radioactive species in the environment and in living organisms, the number of relevant studies found in literature is very limited [7]. In the present study neptunium has been selected as radionuclide under investigation. Neptunium is basically man-made radioelement that is formed in kg quantities in nuclear reactors and can be extracted from the spent fuel. The longest-lived neptunium isotope is Np-237, which along with the Np-239 isotope can be found in minute amounts also in uranium ores. Depending on the solution characteristics neptunium can in different oxidation states (from Np(III) to Np(VII)). However, Np(V), which exists in the form of NpO_2^+ is the predominant oxidation state of the element under ambient conditions and is the most mobile actinide in the geosphere due to its low tendency towards sorption [11]. Np(V) behaves as a Lewis acid and starts hydrolyzing only in alkaline solutions (pH > 8) to form NpO_2OH and $NpO_2(OH)_2^-$ [12–14]. Besides hydrolysis carbonate complexation could affect the geochemical behavior of Np(V) due to formation of Np(V)-carbonato species [15]. Because of its mobility, radiotoxicity and tendency to accumulate in bones [16] studies regarding the environmental behavior of neptunium are of particular interest.

* Corresponding authors.
E-mail addresses: anastopoulos_ioannis@windowslive.com (I. Anastopoulos), pspasch@ucy.ac.cy (I. Pashalidis).

https://doi.org/10.1016/j.molliq.2022.119056
0167-7322/© 2022 Elsevier B.V. All rights reserved.

The present study deals with the interaction of Np(V) with two different microplastic materials PET (polyethylene terephthalate) and PN6 (polyamide nylon) as a function of pH and under seawater conditions.

2. Experimental

2.1. Materials and analytical methods

The experiments were carried out using 30 mL polyethylene bottles under ambient atmospheric conditions and temperature (23 ± 2 °C). The test and reference solutions were prepared using Np-237 standard solution (National Physical Laboratory, UK) and the total activity of the solutions was 0.5 mBq/mL. The microplastics used in this study were polyethylene terephthalate (PET, Sigma-Aldrich) and polyamid nylon (PN6, GoodFellow) in the form of granules (2.5 mm × 2 mm × 2 mm). The experiments were carried out in laboratory solutions made of de-ionized water and the pH was adjusted at different values (pH 2, 4, 7 and 9) using diluted aqueous NaOH and HCl solutions. The seawater samples were collected from a coastal area in Cyprus and their composition is given elsewhere [17]. The of Np-237 analysis was performed by means of an alpha-spectrometer (Canberra) using stainless steel planchets on which the neptunium isotope was previously electrodeposited, as depicted elsewhere [18].

2.2. Sorption experiments

The sorption experiments were carried out similar to previous studies on the sorption of U-232 on MPs [7]. 0.5 g of the MP material were added to 20 mL of the Np-237 solution. The solution volume was 20 mL and the Np-237 activity concentration equal to 25 Bq/L, which corresponds to a molar concentration, [Np-237] = 4 nmol/L. The mixture in the PE screw capped bottles was agitated (45 min^{-1}) on an linear shaker (SK-R1807, DLAB) at room temperature (23 ± 2 °C). After 10 days contact time, an aliquot of 100 μL was drawn from the solution and the Np-237 concentration was analyzed by alpha spectroscopy. The alpha spectrometer was prior sample analysis calibrated using a standard reference source. In addition, the effect of the salinity was investigated by adding defined amounts of NaCl in the test solutions to prepare solutions of different ionic strength (0.1 M, 0.5 M and 1 M). Because the neptunium isotope concentration is in the nanomole range and the binding sites (B) of the MP surface are in great excess compared to the initial radionuclide concentration, the partition coefficient, K_d describes adequately the equilibrium related to neptunium sorption:

$$K_d = C_{ads}/\, C_{aq}(l/kg) \quad (1)$$

where C_{ads} (Bq/g) is the Np-237 amount adsorbed by the MP, C_{aq} (Bq/L) is the equilibrium concentration of Np-237 in solution. The amount of neptunium, which is adsorbed by the MPs is calculated by subtracting the amount of neptunium adsorbed on the walls of the PE bottle from the total amount of neptunium adsorbed. This correction is needed because the amount of neptunium adsorbed on the bottle is significant and has to be considered, when sorption experiments at nano concentration levels are performed. In the present study the relative sorption on the bottle walls was evaluated performing the sorption experiments under similar conditions without microplastic addition. The value of the relative sorption on the bottle walls was calculated to be ∼ 70% of the initial Np concentration.

3. Results and discussion

3.1. Effect of pH on the Np-237 sorption by MP's

The sorption efficiency for the Np-237 upatake by the two MP types at different pH values is evaluated by means of the associated the K_d values, which are summarized in Fig. 1. It obvious that the maximum K_d values are observed in the acidic and near neutral pH region and decline in the alkaline pH region. The decline at the alkaline pH region is ascribed to the hydrolysis of Np(V), which is favored in alkaline solution. The hydrolysis of Np(V) starts at pH > 7 resulting in the formation of the neutral NpO_2OH species, which predominates at pH ∼ 9 [14]. The neutral species is less attracted by the negatively polarized surface moieties (e.g. carbonyl groups) resulting in the decline of the Np(V) sorption efficiency and highlighting the role of the electrostatic interactions in the sorption of Np(V), which is expected occur via formation of outer-sphere complexes.

Np(V) has a weak tendency to form complexes and the complex formation constants even with chelating carboxylate ligands have relatively low values ($\log K_1$ ∼ 2) [19]. Moreover, it has been observed that even sodium and calcium cations did effectively prevent complexation of the neptunyl ion with fulvic acid [20], indicating that the interactions between the ligand molecule and the Np(V) cation are not specific and occur rather through coulombic attraction. Similarly, it is expected that the NpO_2^+ cations are attracted by the negatively polarized carbonyl groups of the PN6 and PET microplastics to form outer-sphere surface complexes as schematically illustrated in Fig. 2.

Among the two different types of MPs, it is clear that PN6 shows slightly higher sorption affinity for Np(V). The K_d values for PN6 range between 113 L/kg < K_d < 2177 L/kg, whereas the corresponding values for PET range between 200 L/kg < K_d < 1440 L. The K_d values differ from one material to another because of the different surface active groups, which are the amide moieties for PN6 and the phthalate moieties for PET. The formation of actinyl-complexes with carbonyl- and amide-containing ligands in solution is described in the literature [21].

3.2. Np-237 sorption by MP's in seawater solution

To study the Np(V) sorption in seawater solutions, the MPs have been added in seawater samples, which had been traced with Np-237 (25 Bq/L). From Fig. 3, which graphically summarizes the K_d values evaluated from the experimental data obtained from the

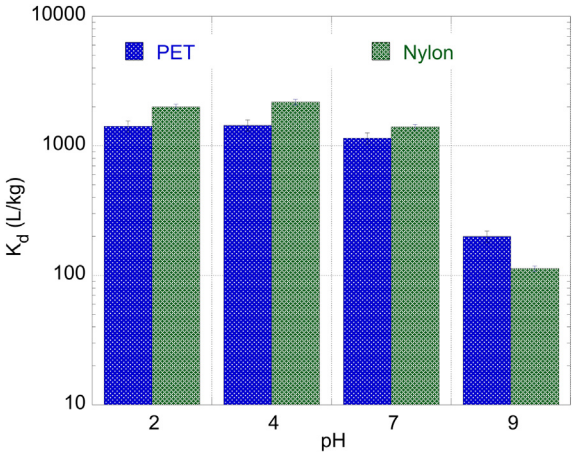

Fig. 1. K_d values for the Np(V) sorption by PET and PN6 microplastics as a function of pH.

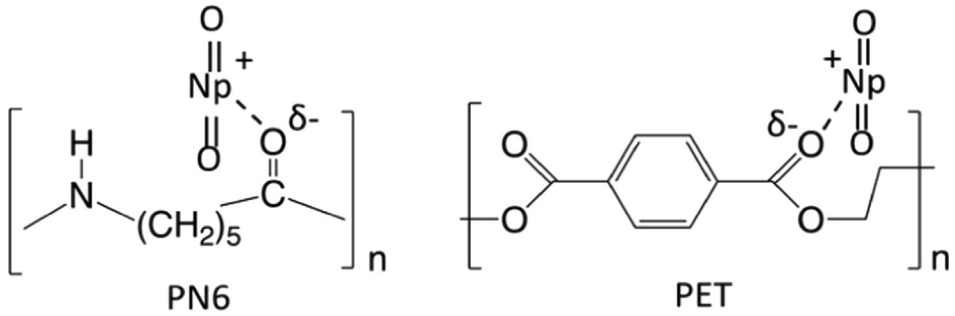

Fig. 2. Schematic illustration of the interaction between Np(V) and the carbonyl moiety of the PN6 and PET MPs .

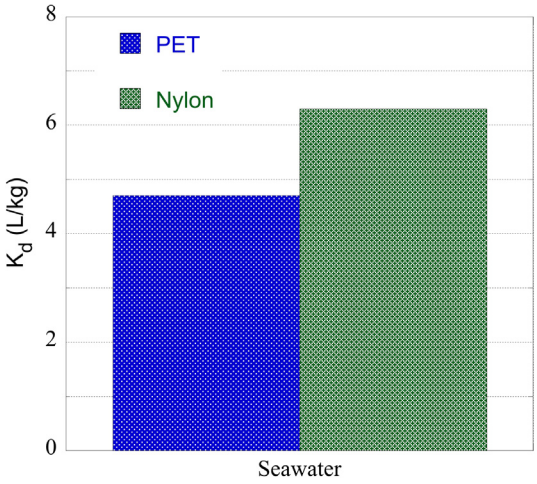

Fig. 3. K_d values corresponding to the Np(V) sorption by the two studied MPs in seawater.

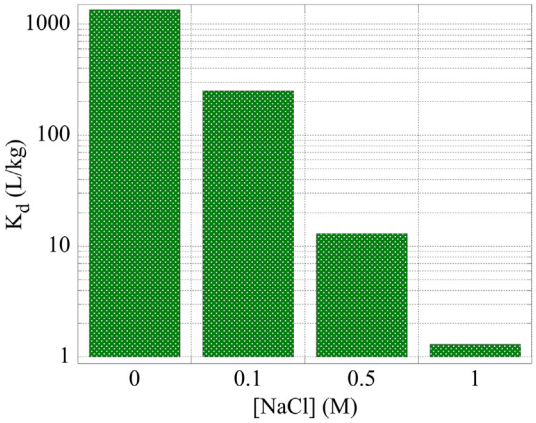

Fig. 4. Salinity effect on the Np(V) sorption by PN6.

corresponding investigations, it is clear that PN6 presents slightly higher sorption affinity (K_d = 6.3 L/kg) than PET (K_d = 4.7 L/kg) also under seawater conditions. However, there is a dramatic decline (orders of magnitude) in the sorption efficiency compared to the de-ionized water solutions indicating the impact of competing cations and supporting the assumption of the outer-sphere complex formation [22]. In contrast to U(VI) [7], not only complex forming cations (e.g. Ca^{2+} and Fe^{3+}) but also conservative cations such as Na^+ and K^+ are expected to affect the sorption efficiency of MPs for Np(V). In addition the presence of carbonate anions that may form stable complexes with Np(V) in aqueous solutions in the form of Np(V)-carbonato species (e.g. $NpO_2(CO_3)^-$) [23]. The determined K_d values in seawater are relatively low reflecting the very low sorption tendency of Np(V). The K_d values obtained for the Np(V) by the studied MPs are in the range and even higher than the K_d values (-0.2 L/kg < logK_d < 4.78 L/kg) obtained for the Np (V) sorption by soils and sediments [24] highlighting the significant role of MPs as Np(V) carriers in the geosphere. However, it has to be noted that in soil systems competing cations (Na^+, K^+, Ca^{2+}, etc.) are present, which affect the NpO_2^+ sorption resulting in a significant decrease of the Np(V) sorption efficiency. On the other hand, some minerals may also contain redox-active components which can reduce NpO_2^+ to Np^{4+} and change completely the sorption behavior of the element [24] .

In order to prove the effect of salinity certain amounts of NaCl salt were added to the test solutions in order to adjust different ionic strength values (0.1 M, 0.5 M and 1.0 M). The experiments were performed using PN6 microplastic samples and the results obtained are summarized in Fig. 4 clearly indicating the negative effect of salinity on the Np(V) sorption [22]. The dramatic decrease of the sorption efficiency with increasing salinity supports the assumption that Np(V) forms outer-sphere complexes with the surface active moieties of the microplastic and is agreement with fact that Np(V) forms relatively weak complexes even with chelating ligands [15,23].

4. Conclusions and future work

PN6 and PET microplastic can sorb Np(V) even in the nano concentration range. The degree of sorption depends on the solution pH and the formation of the NpO_2OH species, as well as the composition of the aqueous solution. In de-ionized water the K_d values obtained range between 113 and 2177 L/kg. However, in the presence of competing cations, including conservative cations such as Na^+ results in a dramatic decline of the sorption efficiency assuming Np(V) sorption by the MPs via pure coulombic interactions and outer-sphere complex formation. Nevertheless, even under seawater conditions the studied MPs have similar sorption affinities for Np(V) as soils and sediments assuming that MPs can be effective carriers for neptunium in environmentally relevant systems. Future studies in more complex systems including complexing species (e.g. humic acids) and reducing conditions could be performed to investigate their impact on the sorption of Np(V) by MPs. In addition, investigations based on sophisticated spectroscopic methods (e.g. XPS, EXAFS) could be carried out to characterize surface-bound species and evaluate the sorption mechanism.

CRediT authorship contribution statement

Ioannis Ioannidis: Investigation, Data curation. **Ioannis Anastopoulos:** Conceptualization, Writing – review & editing. **Ioannis**

Pashalidis: Conceptualization, Supervision, Data curation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] V. Kinigopoulou, I. Pashalidis, D. Kalderis, I. Anastopoulos, Microplastics as carriers of inorganic and organic contaminants in the environment: a review of recent progress, J. Mol. Liq. (2022).
[2] N.B. Hartmann, S. Rist, J. Bodin, L.HS. Jensen, S.N. Schmidt, P. Mayer, A. Meibom, A. Baun, Microplastics as vectors for environmental contaminants: exploring sorption, desorption, and transfer to biota, Integr. Environ. Assess. Manage. 13 (3) (2017) 488–493.
[3] J. Li, K. Zhang, H. Zhang, Adsorption of antibiotics on microplastics, Environ. Pollut. 237 (2018) 460–467.
[4] N. Öz, G. Kadizade, M. Yurtsever, Investigation of heavy metal adsorption on microplastics, Appl. Ecol. Environ. Res. 17 (2019) 7301–7310.
[5] V. Godoy, G. Blázquez, M. Calero, L. Quesada, M. Martín-Lara, The potential of microplastics as carriers of metals, Environ. Pollut. 255 (2019) 113363.
[6] I. Anastopoulos, I. Pashalidis, B. Kayan, D. Kalderis, Microplastics as carriers of hydrophilic pollutants in an aqueous environment, J. Mol. Liq. 350 (2022).
[7] I. Ioannidis, I. Anastopoulos, I. Pashalidis, Microplastics as radionuclide (U-232) carriers, J. Mol. Liq. 351 (2022) 118641.
[8] S.K. Das, S.K. Eshkalak, A. Chinnappan, R. Ghosh, W. Jayathilaka, C. Baskar, S. Ramakrishna, Plastic recycling of polyethylene terephthalate (PET) and polyhydroxybutyrate (PHB)—A comprehensive review, Materials Circular Economy 3 (2021) 1–22.
[9] I. Spyridakis, V.A. Tzanakakis, I. Pashalidis, D. Kalderis, I. Anastopoulos, Polyamide nylon 6 as a potential carrier of nitrate anions in aqueous environments, J. Mol. Liq. 352 (2022).
[10] Y. Tokiwa, B.P. Calabia, C.U. Ugwu, S. Aiba, Biodegradability of plastics, Int. J. Mol. Sci. 10 (2009) 3722–3742.
[11] T. Wu, S. Amayri, J. Drebert, L.R.V. Loon, T. Reich, Neptunium (V) sorption and diffusion in Opalinus Clay, Environ. Sci. Technol. 43 (2009) 6567–6571.
[12] V. Neck, J. Kim, B. Kanellakopulos, Solubility and hydrolysis behaviour of neptunium, V, Radiochim. Acta 56 (1992) 25–30.
[13] J.P. Kaszuba, W.H. Runde, The aqueous geochemistry of neptunium: Dynamic control of soluble concentrations with applications to nuclear waste disposal, Environ. Sci. Technol. 33 (1999) 4427–4433.
[14] V.G. Petrov, D. Fellhauer, X. Gaona, K. Dardenne, J. Rothe, S.N. Kalmykov, M. Altmaier, Solubility and hydrolysis of Np (V) in dilute to concentrated alkaline NaCl solutions: formation of Na–Np (V)–OH solid phases at 22° C, Radiochim. Acta 105 (2017) 1–20.
[15] W. Runde, M. Neu, D. Clark, Neptunium (V) hydrolysis and carbonate complexation: Experimental and predicted neptunyl solubility in concentrated NaCl using the Pitzer approach, Geochim. Cosmochim. Acta 60 (1996) 2065–2073.
[16] R.C. Thompson, Neptunium: the neglected actinide: a review of the biological and environmental literature, Radiat. Res. 90 (1982) 1–32.
[17] E. Georgiou, G. Raptopoulos, M. Papastergiou, P. Paraskevopoulou, I. Pashalidis, Extremely Efficient Uranium Removal from Aqueous Environments with Polyurea-Cross-Linked Alginate Aerogel Beads, ACS Applied Polymer Materials, DOI 10.1021/acsapm.1c01400(2022).
[18] T. Kiliari, I. Pashalidis, Simplified alpha-spectroscopic analysis of uranium in natural waters after its separation by cation-exchange, Radiat. Meas. 45 (2010) 966–968.
[19] K. Takao, S. Takao, A.C. Scheinost, G. Bernhard, C. Hennig, Complex formation and molecular structure of neptunyl (VI) and-(V) acetates, Inorg. Chem. 48 (2009) 8803–8810.
[20] K. Müller, T. Sasaki, Complex formation of Np (V) with fulvic acid at tracer metal concentration, Radiochim. Acta 101 (2013) 1–6.
[21] F. Ortu, S. Randall, D.J. Moulding, A.W. Woodward, A. Kerridge, K. Meyer, H.S. La Pierre, L.S. Natrajan, Photoluminescence of Pentavalent Uranyl Amide Complexes, J. Am. Chem. Soc. 143 (2021) 13184–13194.
[22] M. Konstantinou, G. Kasseta, I. Pashalidis, Boron adsorption on alumina (Al2O3) and magnesia (MgO) in aqueous solutions: a comparative study, Int. J. Environ. Technol. Manage. 6 (2006) 466–479.
[23] J.E. Banaszak, D.T. Reed, B.E. Rittmann, Speciation-dependent toxicity of neptunium (V) toward Chelatobacter heintzii, Environ. Sci. Technol. 32 (1998) 1085–1091.
[24] D.R. Fröhlich, Sorption of neptunium on clays and clay minerals–a review, Clays Clay Miner. 63 (2015) 262–276.