Global NEST Journal, Vol 25, No X, pp 1-4

The effect of temperature on the U-232 and Am-241 adsorption by PN6 microplastics in aqueous solutions

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Received: 15/09/2023, Accepted: 03/10/2023, Available online: 20/11/2023
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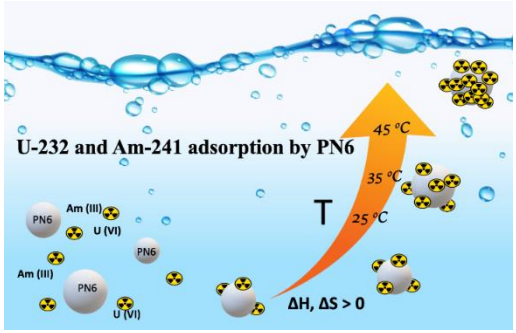
https://doi.org/10.30955/gnj.005392

Graphical abstract



Abstract

The effect of temperature on the adsorption of U-232 and Am-241 by PN6 has been investigated in laboratory and environmental water samples (e.g. seawater and wastewater) in the picomolar concentration range. Generally, increasing temperature favors radionuclide adsorption, indicating that radionuclide binding by PN6 is an endothermic and entropy-driven process. In environmental waters, K_d values are significantly lower than the corresponding values in de-ionized water solutions, because of the presence of various cations (e.g., Ca^{2+}, Fe^{2+}) that compete the radionuclide adsorption by PN6 and the presence of complexing anions (e.g. CO_3^{2-}), which complex and stabilize the actinide cations in solution.

Keywords: uranium, americium, PN6 microplastics, adsorption, temperature effect, thermodynamics

1. Introduction

Aquatic ecosystems (e.g. oceans, lakes) are exposed to pollution from human activities. In recent years, many emerging and persistent pollutants have accumulated in oceans, because for many years the oceans have been used as dumping grounds for industrial waste, chemicals, sewage, garbage and many other waste types, including plastic waste (Rose *et al.* 2023; Tang *et al.* 2021). Plastic materials in the environment are slowly broken down into smaller pieces called microplastics (MPs) (Wang *et al.* 2023). Microplastics are persistent pollutants and their accumulation in marine environments has become an emerg issue of environmental concern and attracted the interest of the research community (Luo *et al.* 2022). MPs are a present and rising environmental issue on a global scale due to large amounts released, their enormous specific surface area (Kurniawan *et al.* 2023; Brennecke *et al.* 2016) and ability to absorb and transport pertinent contaminants like organic compounds (Hartmann *et al.* 2017), heavy metals (Luo *et al.* 2022; Kurniawan *et al.* 2023; Brennecke *et al.* 2016) and radionuclides (Ioannidis 2021, 2022a, 2022b, 2022c, 2022d, 2022e). Following, contaminant-loaded MPs could be ingested by aquatic organisms and enter the food chain (Tang *et al.* 2021; Kurniawan *et al.* 2023; Brennecke *et al.* 2016).

A recent review focuses on the interaction of MPs with heavy metals (Kinigopoulou *et al.* 2022), because heavy metals (including radionuclides) are very toxic, persistent and can be bioaccumulated in living organisms causing severe health problems and even death (Ali *et al.* 2019.) The interaction of radionuclides with different microplastic types and possible interaction mechanisms between the MPs' surface and radionuclides is discussed in another study (Ioannidis *et al.* 2023).

The interaction of radioactive metals such as U (Ioannidis *et al.* 2022a, 2022b) and Am (Ioannidis *et al.* 2022b) has been extensively studied indicating remarkable adsorption of the radionuclides by MPs (Ioannidis *et al.* 2021, 2022a, 2022b, 2022d, 2022e), which strongly depends on the type and particle size of the MPs, pH, and metal's aqueous chemistry (Ioannidis *et al.* 2021, 2022a, 2022b, 2022c 2022d, 2022e).

Uranium is a naturally existing radioactive element, belongs to the actinide series and has three naturally occurring isotopes: U-238, U-235, and U-234, all of which are radioactive (Smedley and Kinniburgh 2023). In terms of its aquatic behavior, uranium can exist in various oxidation states, including IV, V, and VI. However, the most prevalent forms of uranium in nature are IV and VI, under anoxic and oxic conditions, respectively (Seaborg *et al.* 1968). On the contrary, americium, is a man-made radioactive metal and its primary stable oxidation state in water-based solutions

is III. Its chemical properties closely resemble those of trivalent lanthanides. Typically, Am^{3+} prevails in acidic aqueous solutions, and under neutral conditions the Am(III)-hydroxo ($AmOH^{2+}$, $Am(OH)_2^+$) and carbonate species ($AmCO_3^+$, $Am(CO_3)_2^-$) govern its aqueous chemistry (Ioannidis *et al.* 2022b).

Polyamide nylon 6 (PN6) is a microplastic (MP) of particular interest because PN6 is widely used in the textile industry, plastic nylon, electronic industries and food industries (Vagholkar *et al.* 2016; Sewidan *et al.* 2020). PN6 is a semicrystalline polyamide polymer and consists of repeating carbonyl - amide bonds (–CO-NH–) in a six-carbon chain (Vagholkar *et al.* 2016; Didovets *et al.* 2022). PN6 has been reported to be able to adsorb various radionuclides such as U-232 (Ioannidis *et al.* 2022a, 2022b; 2022e) and Am-241 (Ioannidis *et al.* 2022b), possibly due to hydrogen bonding and cation dipole interactions that amino and carboxyl groups can develop on the MP's surface (Ioannidis *et al.* 2022a, 2022b, 2022e).

Several studies have been carried out dealing with the radionuclide adsorption by PN6 particularly on the parameters affecting its adsorption capacity such as MP's size and mass, contact time, solution pH and the nature of the aquatic system (Ioannidis *et al.* 2021, 2022a, 2022b, 2022c, 2022d, 2022e). However, to the best of our knowledge there are no studies regarding the temperature effect on the heavy metal/radionuclide adsorption. Hence, the present study focuses on the effect of temperature and the evaluation of thermodynamic parameters (standard enthalpy, ΔH^o and standard entropy, ΔS^o) associated with the adsorption of radionuclides (U-232 and Am-241) in different aqueous solutions (e.g. laboratory, seawater and waste water solutions).

2. Experimental

2.1. Materials and methods

All the experiments were performed at the Radioanalytical Chemistry Laboratory at the Chemistry Department of the University of Cyprus. The experiments took place in 30 mL polyethylene screw cap flasks under ambient atmospheric conditions. The standard tracer solutions used were U-232 (4.923 kBq/g) and Am-241 (12.05 kBq/g) from the National Physical Laboratory and North America Scientific Inc., respectively. The reference and test solutions, with an initial activity concentration of 0.5 mBq/mL for each radionuclide, were prepared using these standard tracer solutions.

The total volume of each test solution used in the present experiments was 20 mL. The aqueous solutions used were deionized water (DI) at different pH (pH= 4, 7 and 9), seawater (SW) and wastewater (WW). The seawater samples correspond to surface waters and were obtained from a coastal area in the southern part of the island of Cyprus (Larnaca district) and the wastewater, which corresponds to secondary treatment effluent, was supplied by a local water treatment facility. The composition of the environmental water solutions (e.g. sea- and wastewater) is given elsewhere (Georgiou *et al.* 2022). An alpha spectrometer (Canberra) was used to analyze the radionuclides U-232 and Am-241 after a small amount of the sample was electrodeposited onto stainless steel discs as previously described (Kiliari and Pashalidis 2010).

2.2. 2.2 Adsorption experiments

The experiments related to the temperature effect on the radionuclide adsorption by PN6 were performed similarly to previous batch-type adsorption experiments using U-232 (Ioannidis *et al.* 2021, 2022a, 2022b, 2022d), Np-237 (Ioannidis *et al.* 2022c), and Am-241 (Ioannidis *et al.* 2022b). The total volume of the test solutions was 20 mL and the mass of PN6 (5–50 μm, average 15–20 μm, in diameter, granular form, GoodFellow) was 0.5 g. The activity concentration of each isotope was equal to 25 Bq/L, corresponding to a molar concentration of about 0.1 pmol/L and about 1 pmol/L for U-232 and Am-241, respectively. All the experiments were carried out in screw cap polyethylene bottles at three different temperatures (25, 35 and 45 ^oC) and under ambient conditions. The pH of laboratory solutions was adjusted to three different pH values (pH 4, 7 and 9), whereas the temperature effect in the environmental water samples was investigated at their initial pH. After 10 days of contact time to assure equilibrium conditions, 100 μL of the test solution were obtained and the radionuclides electrodeposited on a stainless steel planchet. The radionuclide concentration was determined by alpha spectroscopy, using an alpha spectrometer that had been previously calibrated with a 6.6 Bq mixed standard calibration source (U-238/234, Pu-239, Am-241, Eckert & Ziegler) and a standard reference solution (1.02 Bq/mL standard reference solution U- 232).

Given that the concentration of the radionuclide is extremely low and the binding sites (B) of the MP surface are in large excess compared to the initial concentration radionuclides, the distribution coefficient, K_d, accurately describes the equilibrium associated with the sorption of U-232 and Am-241.

$$K_d = \frac{C_{ads}}{C_{aq}} \quad (1)$$

where Cads (Bq/g) is the amount of radionuclide adsorbed by the MPs, C_{aq} (Bq/L) is the radionuclide concentration in solution at equilibrium. Experiments were performed in duplicate and mean values have been used for data evaluation and graphical presentations.

The calculation of the associated standard enthalpy (ΔH^o) and standard entropy (ΔS^o) was performed using the following formula:

$$\ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (2)$$

where K_d (in L/kg) is the linear distribution coefficient, R (in J/mol.K) is the gas constants and T is the temperature (in K).

3. Results and discussion

3.1. Adsorption of U(VI) and Am(III) from laboratory solutions

The adsorption efficiency ($\log_{10}K_d$) of U(VI) and Am (III) by polyamide microplastics (PN6) in the acidic, neutral and alkaline pH region (pH 4, 7 and 9) and as a function of

temperature is shown in Figure 1(a) and 1(b) for U(VI) and Am(III), respectively. Generally, the K_d values increase with temperature assuming an endothermic adsorption mechanism for both radionuclides.

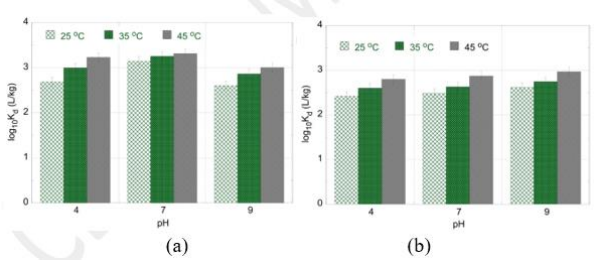


Figure 1. $\log_{10}K_d$ values determined for (a) U(VI)- and (b) Am(III)-adsorption by PN6 as a function of temperature and at three different pH regions. Experimental conditions: 0.5 mBq/mL for each (a) U(VI) and (b) Am(III), at pH = 4, 7, 9 and T =25, 35, 45 °C

Moreover, regardless of pH and temperature U(VI) is adsorbed more efficiently by PN6 compared to Am(III) and this is attributed to the multisite binding of U(VI) by the PN6 surface moieties (Ioannidis *et al.* 2022b) as schematically illustrated in Figure 2. In contrast to U(VI), the adsorption of which is favored in the neutral pH area, the adsorption efficiency of Am(III) increases with increasing pH. The latter is attributed to the competitive interaction of hydrogen cations with the surface moieties, whereas the decline of the U(VI) adsorption efficiency in the alkaline pH region is attributed to the formation of U(VI)-tricarbonato complexes (e.g. $UO_2(CO_3)_3^{4-}$), which stabilize U(VI) in solution resulting in lower adsorption efficiency (Ioannidis *et al.* 2022a, 2022b).

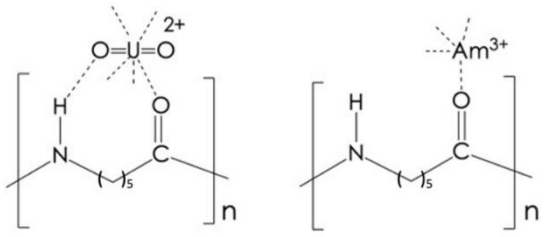


Figure 2. Schematic illustration of the interaction of U(VI) and Am(III) cations with the PN6 surface moieties

3.2. Thermodynamics of the U(VI) and Am(III) adsorption by PN6 in laboratory solutions

In order to evaluate the standard enthalpy (ΔH^o) and standard entropy (ΔS^o) values, the K_d values obtained at different temperatures have been evaluated using the Van't Hoff plot (eq. 2).

The evaluated ΔH^o and ΔS^o values, which are graphically summarized in Figures 3(a) and 3(b), indicate that the adsorption of both U(VI) and Am(III) is an endothermic and entropy-driven process. The ΔH^o values, which generally have values below 50 kJ mol^{-1}, indicate non-covalent bonds between the surface moieties and the actinide species. On the other hand, the positive ΔS^o values indicate increase of disorder at the solid/solution interphase upon adsorption, which can be most probably attributed to deliberation of complex- or surface-bound water molecules upon adsorption.

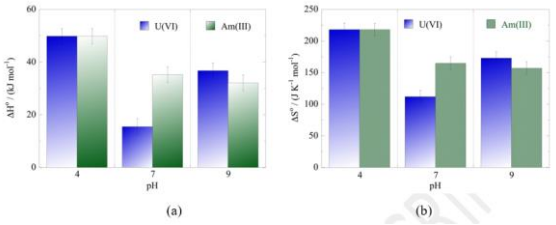


Figure 3. (a) Standard enthalpy (ΔH^o) and (b) standard entropy (ΔS^o) values the adsorption of U(VI) and Am(III) by PN6 microplastics in de-ionized water solutions at different pH values

3.3. Adsorption of U(VI) and Am(III) from environmental waters

The radionuclide adsorption (e.g. U(VI) and Am(III)) in environmental waters (e.g. seawater and wastewater samples) is also an endothermic process, which is favored with increasing temperature. The decline of the K_d values, particularly in the case of Am(III), can be attributed to the presence of competing cations (e.g. Ca^{2+}, Fe^{3+}), which are present in environmental waters at concentrations of several orders of magnitude higher than the radionuclide concentrations used in the present study. The competing cations occupy surface active sites resulting in lower K_d values associated with the radionuclides (Figure 4).

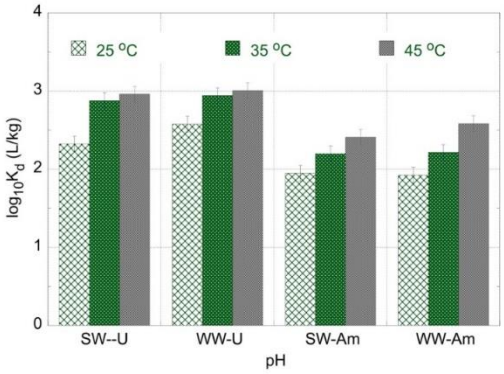


Figure 4. $\log_{10}K_d$ values determined for U(VI)- and Am(III)-adsorption by PN6 as a function of temperature in seawater (SW) and wastewater (WW) samples. Experimental conditions: 0.5 mBq/mL for each (a) U(VI) and (b) Am(III), at different media solutions and T =25, 35, 45 °C

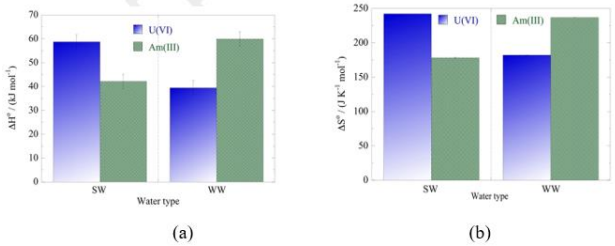


Figure 5. (a) Standard enthalpy (ΔH^o) and (b) standard entropy (ΔS^o) values the adsorption of U(VI) and Am(III) by PN6 microplastics in environmental water solutions

Regarding the standard enthalpy (ΔH^o) and standard entropy (ΔS^o) values, these have been evaluated also for the radionuclide adsorption by PN6 in environmental samples. In contrast to seawater samples, the radionuclide adsorption in wastewater samples is closer to the adsorption behavior in laboratory solutions (de-ionized water), assuming that the increased salinity of the

seawater samples significantly affects the thermodynamics of the radionuclide adsorption by PN6 (Figures 5).

4. Conclusions

The effect of temperature on the adsorption of the U-232 and Am-241 radionuclides by PN6 has been investigated in laboratory and environmental water samples (e.g. seawater and waste water) and in the acidic, neutral and alkaline pH region. The results reveal that there is a significant effect of the temperature on the sorption efficiency (K_d) of radionuclides by PN6 under the given conditions. Generally, increasing temperature favors radionuclide adsorption, indicating that binding of the radionuclides by PN6 is an endothermic and entropy-driven process. Evaluation of adsorption data reveals that partition coefficient values (K_d) differ significantly between laboratory and environmental waters. In environmental waters, K_d values are significantly lower because of the presence of various cations (e.g., Ca^{2+}, Fe^{2+}) that compete with U-232 and Am-241 adsorption and occupy adsorption sites on the PN6 surface and the presence of complexing anions (e.g. CO_3^{2-}), which may complex and stabilize the radionuclides in solution.

Competing Interests

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work.

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