Journal of Hazardous Materials 297 (2015) 183–190

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Translocation of uranium from water to foodstuff while cooking

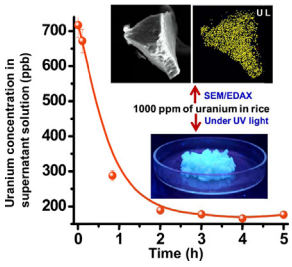
K.C. Krishnapriya [1], Ananya Baksi [1], Swathi Chaudhari [1], Soujit Sen Gupta, T. Pradeep *

DST Unit of Nanoscience (DST UNS), and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

HIGHLIGHTS

- Rice can efficiently uptake uranium from water contaminated with uranyl nitrate hexahydrate ($UO_2(NO_3)$ 2.6 H_2O), while cooking.
- Unusual uranium uptake to the extent of about 1000 ppm is observed when rice is cooked in highly concentrated uranium contaminated water (1240 ppm).
- Nature of interaction of uranium with carbohydrates is probed using small monosaccharides like glucose and mannose.
- Electrospray ionization mass spectrometry showed UO_2^{2+} to be the most stable species in water in such solutions which can form complexes with sugars.
- The species (UO_2^{2+}) is also observed in the case of water exposed to the common mineral, uranium oxide (UO_2) and similar type of complexation is observed with sugars.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 November 2014
Received in revised form 31 March 2015
Accepted 13 April 2015
Available online 27 April 2015

Keywords:
Uranium contamination
Uranium–rice interaction
Uranyl–carbohydrate adducts
ICP-MS
ESI-MS

ABSTRACT

The present work report the unusual uranium uptake by foodstuff, especially those rich in carbohydrates like rice when they are cooked in water, contaminated with uranium. The major staple diet in South Asia, rice, was chosen to study its interaction with UO_2^{2+}, the active uranium species in water, using inductively coupled plasma mass spectrometry. Highest uptake limit was checked by cooking rice at very high uranium concentration and it was found to be good scavenger of uranium. To gain insight into the mechanism of uptake, direct interaction of UO_2^{2+} with monosaccharides was also studied, using electrospray ionization mass spectrometry taking mannose as a model. The studies have been done with dissolved uranium salt, uranyl nitrate hexahydrate ($UO_2(NO_3)_2{\cdot}6H_2O$), as well as the leachate of a stable oxide of uranium, UO_2(s), both of which exist as UO_2^{2+} in water. Among the eight different rice varieties investigated, Karnataka Ponni showed the maximum uranium uptake whereas unpolished Basmati rice showed the minimum. Interaction with other foodstuffs (potato, carrot, peas, kidney beans and lentils) with and without NaCl affected the extent of chemical interaction but was not consistent with the carbohydrate content. Uranium interaction with D-mannose monitored through ESI–MS, under optimized instrumental parameters, identified the peaks corresponding to uranyl adduct with mannose

* Corresponding author. Tel.: +91 44 2257 4208; fax: 91 44 2257 0545/ 0509.
[1] Contributed equally.

http://dx.doi.org/10.1016/j.jhazmat.2015.04.041
0304-3894/

monomer, dimer and trimer and the species were confirmed by MS/MS studies. The product ion mass spectra showed peaks illustrating water loss from the parent ion as the collision energy was increased, an evidence for the strong interaction of uranium with mannose. This study would constitute the essential background for understanding interaction of uranium with various foods. Extension of this work would involve identification of foodstuff as green heavy metal scavengers.

1. Introduction

Heavy metal contamination of the environment and livestock has been a growing concern of multidisciplinary interest, the impact of which has socio-political to scientific implications. The legacy of metal contamination so far comprises mostly of arsenic [1,2] followed by lead, [3–7] cadmium [4,6–10] and mercury [7,11] with more elements being identified as industrial exploitation increases. Extensive studies have been carried out on arsenic contamination of water resources, soil, vegetation and various environmentally relevant systems. Studies on the adverse effects of Cd, Pb and Hg have also been carried out and effective treatment methods have evolved [3,6,7,11–19]. Many documented cases of contamination due to other transition and rare earth elements also exist [1,20,21]. Other heavy metals including radioactive ones are also drawing attention lately [20,22–29]. Uranium has received significant attention over the last few decades owing to its promising applicability as a prospective energy power. These studies are important in India where it is estimated that uranium production will increase, as a result of the use of pressurized heavy water reactor technology utilizing enriched uranium. The principal ores of uranium are urania (mostly UO_2) and coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$). Solubility products of these oxides (in terms of $\log K_{SP}$) are in the range of −8.5. In natural waters it exists as uranyl hydroxide and carbonate species. Recently efforts have been made to find the basis of uranium mobility and its effects on the environment have been reported. Pompe et al. [30] have investigated the interaction of UO_2^{2+} with humic acids (HAs) with and without modification and found that phenolic OH groups decide the complexationbehavior of HAs. Uranium complexes formed after the uptake by plants were studied by Nitsche et al. [28]. In another work, the authors have reported different uranium speciation in water near to uranium mines by experimental determination as well as by modelling for the different U(VI) species, at specific pH range [29]. Compounds of relevance include $Ca_2UO_2(CO_3)_3$ (aq) in carbonate- and calcium-containing mine waters from Schlema, Germany at pH 7.1. Uranium speciation changes depending on the pH and the ions and concentrations present in water. They have found that in carbonate-containing and calcium-poor tailing water from Helmsdorf at pH 9.8, $UO_2(CO_3)_3^{4-}$ is the most abundant uranium species, while UO_2SO_4 (aq) was the most abundant uranium species from sulfate-rich mine water in Königstein, Germany at pH 2.6 [29].

Even though respiratory intake and epidermal contact of uranium can cause health issues, it is through drinking water and food consumption the major propagation and biomagnification of uranium takes place in animals [31]. Recent studies on other mammals like rats and rabbits suggest that even the non-radioactive isotopes can cause hazardous effects in biosphere[23]. Studies based on the intake of uranium by animals showed that solubility of uranium is a crucial factor that determines its metabolism in the body. It appears that the amount of soluble uranium accumulated internally is proportional to the intake from ingestion or inhalation [22,32]. Igarashi et al. [26] has reported that the maximum allowed limit of uranium in humans is 40 μg/kg with approximate 40% present in the muscles, 20% in the skeleton and 10%, 4%, 1% and 0.3% in the blood, lungs, liver and kidneys, respectively. Health hazards caused by exposure to uranium in rats and rabbits were evaluated by several research groups and changes in organs including kidney and liver were monitored [23,24]. Effect on humans consuming uranium contaminated drinking water in countries all over the world especially in Canada, Finland, Sweden, Ireland and USA suggested renal tissues are affected primarily [25].

The uranium poisoned environment and ecosystem demand effective remediation which should start with research on the basics of uranium interaction with biomolecules. From previous studies, it was found that many heavy metals bind with various carbohydrate moieties and contribute to the spread of contamination in environment and health hazards in vegetation [33,34]. Our investigation substantiates the need to list uranium in the category of heavy metals capable of strongly interacting with foodstuff.Since rice is the staple food in many countries (mainly Asian countries), even small uptake of uranium by the same deserves an extensive study as the permissible World Health Organization (WHO) limit for drinking water is 15 microgram/L. To study the mechanism of uranium-rice interaction, we chose D-mannose as a model monosaccharide and investigated the product using electrospray ionization mass spectrometry (ESI–MS).

2. Experimental section

2.1. Materials

Uranyl nitrate hexahydrate ($UO_2(NO_3)_2{\cdot}6H_2O$) was purchased from Thomas Bakers. Glucose and mannose were purchased from Sigma–Aldrich and Sisco Research Laboratories Pvt. Ltd., respectively. All the rice varieties and other foodstuff used in the study were obtained from the local market. All the chemicals were used without further purification and deionized water was also used throughout the experiment. Urania (UO_2) was gifted by IGCAR, India.

2.2. Instruments

Inductively coupled plasma-mass spectrometry (ICP–MS) measurements of the samples were done with a PerkinElmer NexION 300X instrument. Prior to ICP–MS analysis, the non liquid samples were digested using an Anton Paar microwave digester at 800 W for 20 min. Scanning electron microscopy (SEM) and energy dispersive analysis of the X-ray (EDAX) images were collected using an FEI QUANTA-200. X-ray photoelectron spectroscopy (XPS) studies were conducted with an Omicron ESCA probe spectrometer with polychromatic Mg Kα X-rays ($h\upsilon$ = 1253.6 eV). Electrospray ionization mass spectrometry (ESI–MS) analysis was carried out using Applied Biosystems 3200 QTRAP LC/MS/MS system in the mass range of m/z 80 to 1700. The optimized conditions used are as follows: declustering potential (DP) = 60 V, entrance potential (EP) = 10 V, ion spray voltage (IS) = 3 kV, collision energy (CE) = 10–60 V, collision cell exit potential (CXP) = −1 V.