Carbohydrate Polymers 92 (2013) 712–718

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Chitin-based renewable materials from marine sponges for uranium adsorption

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ARTICLE INFO

Article history:
Received 20 June 2012
Received in revised form 17 August 2012
Accepted 17 August 2012
Available online 4 September 2012

Keywords:
Chitin
Marine sponge
Uranium
Adsorption
Water treatment

ABSTRACT

Marine sponges of the order Verongida form three-dimensional networks of fibrous chitin, which can easily be extracted. In the hydrated state, these networks are flexible, mechanically stable and can be cut or pressed into any desired form. Here, we show for the first time that chitin-based networks of sponge origin are useful for effective uranium adsorption. They adsorb uranium from solution with a higher adsorption capacity than many other chitinous sorbents. Up to 288 mg/g could be achieved. Solid-state NMR, infrared, and Raman spectroscopy indicated that the uranyl is bound to the chitin by weak interactions. 90% of the uranyl could be desorbed using diluted hydrochloric acid. Uranium adsorption and desorption did not result in any destruction of the chitin-based material.

1. Introduction

Chitin (poly-β-(1,4)-*N*-acetyl-D-glucosamine) is the second most abundant natural biopolymer after cellulose and a basic structural component of fungi and yeast cell walls, as well as of numerous invertebrates (Cardenas, Cabrera, Taboada, & Miranda, 2004; Ehrlich, 2010; Muzzarelli et al., 2012; Sikorski, Hori, & Wada, 2009). Chitosan, the linear (1,4)-2-amino-2-deoxy-β-D-glucan, can be obtained from chitin by partial deacetylation (Muzzarelli et al., 2012). Both polymers are potent sorbents for various transition metals and radionuclides (Li, Hein, & Wang, 2008; Muzzarelli, 1971, 2011; Seliverstov, Trifonova, Tananaev, Ershov, & Myasoedov, 2006; Tsezos & Volesky, 1981; Varma, Deshpande, & Kennedy, 2004).

40,000–50,000 t of uranium are produced every year (OECD Nuclear Energy Agency, 2010). Mining and milling often leave behind large quantities of contaminated waste rock and soil (Brugge, deLemos, & Oldmixon, 2005), which can release radionuclides into the environment (Carvalho et al., 2005). Among the radioactive contaminants, uranium, neptunium, and plutonium are most problematic because they pose long-term environmental risks. Uranium is one of the most seriously threatening heavy metals because of its high toxic, chemical, and radiological characteristics (Dhankhar & Hooda, 2011).

Several types of biological substances have been reported as potentially useful for uranium extraction from waters, including uranium-specific binding proteins (Wegner, Boyaci, Chen, Jensen, & He, 2009), acid and phosphorylated polysaccharides (Muzzarelli, 2011; Sakamoto, Kano, & Imaizumi, 2008). Chitin-based fungal biosorption of uranium has been studied extensively because of the availability of large amounts of waste fungal biomass from fermentation industries and the amenability of microorganisms like *Aspergillus, Rhizopus* and *Penicillium* to genetic and morphological manipulation (Dhankhar & Hooda, 2011; Wang, Hu, Liu, Xie, & Bao, 2010). For instance, a maximum adsorption capacity of 180 mg uranium per gram biomass in excess of uranyl was determined for biomass of *Rhizopus arrhizus* (Tsezos & Volesky, 1981). An adsorption capacity of up to 240 mg/g at pH 5 was observed for biomass from *Mucor miehei* (Guibal, Roulph, & Le Cloirec, 1992). Up to 280 mg/g were found for the adsorption on *Talaromyces emersonii* (Bengtsson, Johansson, Hackett, McHale, & McHale, 1995). Patents have been published concerning a chitin-containing material from fungi suitable for the adsorption of uranium and other radionuclides (Gorowoi & Kosjakow, 1999).

It has often been found that chitosan has a higher adsorption capacity for metal cations than chitin (Gamage & Shahidi, 2007; Guibal et al., 1992; Humeres, Pinheiro de Souza, Debacher, & Aliev, 2002). It is assumed that amino groups rather than acetamido

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http://dx.doi.org/10.1016/j.carbpol.2012.08.090

groups coordinate to uranyl cations due to the steric hindrance of the acetamido groups (Guibal et al., 1992; Jansson-Charrier, Saucedo, Guibal, & Le Cloirec, 1995). On the other hand, chitosan is acid soluble or water soluble, depending on the degree of deacetylation and other factors (Rinaudo, 2006). It is thus often cross-linked to improve stability, making the production more elaborate and expensive.

The chitin isomorphs isolated so far from fungi, arthropods, and molluscs (e.g. squids) occur in the form of granules, sheets, or powders (Khor, 2001). In contrast to these materials, chitin of poriferan origin has some important advantages. The chitin-based scaffolds recently found by our groups in marine sponges (Brunner et al., 2009; Ehrlich et al., 2010a,b, 2007) are three-dimensional networks of tube-like interconnected fibers with a diameter of about 100 μm in the case of *Aplysina aerophoba* (Verongida: Demospongiae: Porifera). These networks can easily be extracted using diluted sodium hydroxide solution and acetic acid. They are mechanically stable, but flexible and can be cut or pressed into any form. Chitin is non-toxic (Rinaudo, 2006), several studies suggest that it may even be beneficial in the gastrointestinal tract of mammals (Ifuku & Saimoto, 2012; Muzzarelli, 2010).

In the present work, we have for the first time determined the performance of chitin networks from *A. aerophoba* as a renewable and reusable adsorption material for uranyl from aqueous solution. The adsorption behavior was tested in lifelike concentration ranges, i.e. in a range of some mg/l, a concentration range which can be found in tailing waters from uranium mines (Bernhard, Geipel, Brendler, & Nitsche, 1998), as well as in a concentration range of some μg/l, which is the typical range of elevated uranium concentrations for surface water in Europe (Birke, Rauch, Lorenz, & Kringel, 2010). We further attempted to desorb the uranyl in order to recover the sponge chitin and make it reusable. The kinetics of the adsorption process were examined to determine the time needed for the adsorption. The interaction mechanisms between chitin and uranyl were examined with solid-state NMR, infrared, Raman as well as time-resolved laser fluorescence spectroscopy.

2. Experimental

2.1. Materials

The marine sponge *Aplysina aerophoba* (Aplysinidae: Verongida: Demospongiae: Porifera) was collected in the Adriatic Sea (Kotor Bay, Montenegro) and dried on air. NaOH platelets were purchased from Grüssing (99%). Concentrated acetic acid was purchased from VWR (HPLC grade). α-Chitin was purchased from Carl Roth GmbH (depure). $NaClO_4 \cdot 2H_2O$, NaOH and HCl for adjusting the pH of the test solutions and the acidic desorption solution were purchased from Merck (analytical grade). Concentrated HNO_3 was purchased from Carl Roth GmbH (analytical grade) and distilled before usage. A 1000 mg/l rhodium solution was purchased from Merck (ICP-MS standard).

A stock solution of 0.102 M $UO_2(ClO_4)_2$ and an ionic strength of 0.5 M ($NaClO_4$) was prepared according to literature (Opel, Weiss, Huebener, Zaenker, & Bernhard, 2007). Perchlorate was chosen as a non-complexing counter-ion, and consequently the ionic strength was adjusted with $NaClO_4 \cdot H_2O$ to minimize the number of different ions in the solutions.

2.2. Methods

2.2.1. Extraction and preparation

The chitin was extracted according to a published procedure, by alternating incubation in 2.5 M NaOH and 20% (v/v) acetic acid at 37 °C for 24 h (Ehrlich et al., 2007, 2010a,b).

Sponge chitin stored in ultra-pure water at 4 °C was cut into pieces and squeezed on filter paper until no more humidity was left on the paper. The pieces were weighed, dried for 48 h at 105 °C in a drying oven and weighed again. The resulting correlation between the hydrated and the dry mass was used to quantify the adsorption experiments.

2.2.2. Adsorption experiments

From this stock solution, test solutions with concentration from 10 to 80 mg/l and from 10 to 50 μg/l were prepared in polypropylene vessels, the ionic strength was set to 0.1 M with $NaClO_4 \cdot H_2O$ and the pH was adjusted to values from 4 to 8 with 0.1 M NaOH or 0.1 M HCl. Solutions at pH 7 and 8 were filtered in order to remove precipitates. 2297 mg/l of hydrated, squeezed sponge chitin, corresponding to a dry mass of 210 mg/l, were added to the test solutions. Adsorption was carried out during 24 h at room temperature and constant shaking at 100 rpm on a Certomat MO II shaker (B. Braun Biotech). Reference solutions with the same uranyl concentration but without chitin were treated in the same way. Samples were taken after 24 h from test and reference solutions. For kinetic measurements, samples were taken at shorter intervals. The samples were acidified by adding 1 μl of concentrated distilled HNO_3 per 1 ml sample solution. The uranium content was determined by ICP MS. In most cases, the uranyl concentration of the reference solutions had decreased after 24 h, most probably due to adsorption of uranyl hydroxide complexes on the polypropylene vessel walls. To take this effect into account, adsorption in % and adsorption capacities in mg/g were thus always calculated from the difference of the uranium concentration in the sample solution and in the reference solution after 24 h.

2.3. Desorption experiments

Uranium was adsorbed on chitin during 24 h in a solution containing 10 mg/l uranyl at pH 6 as described before. Then, the chitin pieces were removed from the uranium solution, washed for 1 min in 10 ml ultra-pure water and squeezed on filter paper. They were desorbed in 5 ml ultra-pure water or 0.1 M HCl for 24 h at room temperature at 100 rpm on a Certomat MO II shaker (B. Braun Biotech). The uranium content of both the adsorption and the desorption solutions were determined by ICP MS.

2.4. Instrumental analyses

Nitrogen physisorption was measured at 77.3 K using a Quantachrome Instruments Nova 4000e. Prior to analysis, the sample was activated first by freeze-drying and then under vacuum at room temperature for 12 h. The Brunauer–Emmett–Teller (BET) surface was determined at 0.3 p/p_0.

ICP-MS measurements were carried out on an ELAN 9000 spectrometer (Perkin Elmer) with a quadrupole mass analyzer (radio frequency 1200 W) in the positive detection mode. A 1000 mg/l rhodium solution was used as internal reference.

Solid-state nuclear magnetic resonance measurements were performed on an Avance 300 spectrometer (Bruker) with a resonance frequency of 74.47 MHz for ^{13}C and 30.43 MHz for ^{15}N. Cross polarization magic angle spinning (CP MAS) spectra were recorded in a double-resonance 2.5 mm MAS NMR probe at a sample spinning rate of 16 kHz, if not noted differently in the figures. ^{1}H–^{13}C CP with a contact time of 4 ms and SPINAL ^{1}H decoupling was used. The high-power decoupling (HPDEC) experiment for determining the degree of acetylation was performed in a 4 mm double resonance MAS probe at a spinning rate of 14 kHz and a delay time of 200 s. As reference substances, adamantane for ^{13}C and ammonium nitrate for ^{15}N measurements were used. The ^{15}N signal of $NH_4{}^{15}NO_3$ was set to −5 ppm.

Energy dispersive X-ray spectroscopy (EDX) measurements were performed on an AXS QUANTAX 200 spectrometer (Bruker) with a light element X flash detector 4010 and an energy resolution of 127 eV.

ATR FTIR spectra were recorded on a Nicolet 210 spectrometer with a Golden Gate device. The spectra were averaged over 250 scans from 650 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The data were normalized, submitted to an ATR and a two-point baseline correction.

Raman spectra were recorded on a RFS 100 spectrometer (Bruker) with an Nd-YAG laser at an excitation wavelength of 1024 nm and a power of 1000 W. The spectra were averaged over 500 scans from 50 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The data were submitted to a multi-point baseline correction.

For TRLFS measurements, the uranyl was excited by a Minilite laser (Continuum) at an excitation wavelength of 266 nm and an average pulse energy of 250 μJ. Spectra were recorded from 271.4 to 647.3 nm by accumulating 50 pulses with a gate-time of 2 μs. The luminescence was detected by a spectrograph iHR 550 with an ICCD camera and analyzed with Labspec (all HORIBA Jobin Ivon).

Prior to measurement, the chitin pieces adsorbed with uranyl were removed from the uranium solution, washed for 1 min in 10 ml ultra-pure water and squeezed on filter paper. They were adjusted in the laser beam and the luminescence was detected in a 90° angle. The corresponding solutions (50 mg/l, pH 4–8) were adjusted in the laser beam in cuvettes.

For light microscopy, an upright light microscope by an Axioscope 2 FS mot (Zeiss) was used equipped with an objective Epiplan 5 ν/0.13 (Zeiss) and a filter set No. 1 (Zeiss). The fluorescence was excited by a mercury arc lamp HBO50.

3. Results and discussion

3.1. Structural specifics of sponge chitin

The structure and composition of the three-dimensional chitin networks found in *A. aerophoba* have been analyzed in detail previously (Ehrlich et al., 2010a,b). A ^{13}C HPDEC NMR spectrum of the dry chitin was recorded to determine the degree of acetylation. The intensity of the signal due to the methyl group was divided by 1/6 of the summed intensities of the signals caused by the carbon atoms C1 to C6. HPDEC excitation is better suited for this purpose than cross-polarization experiments, as cross-polarization may distort peak intensities due to the proton polarization transfer. The HPDEC spectrum showed a relative intensity of the methyl group of 103%, which means the sponge chitin is completely acetylated within the limits of experimental error.

It is important to note that the extracted fibers consist of concentrically arranged and loosely packed tubular structures with hollow spaces in between. The special structure of sponge chitin is sensitive to drying. Chitin networks dried at air at room temperature collapsed and lost their three-dimensional structure and their porosity. They were thus not useful for adsorption experiments any more. Freeze-dried chitin maintained its three-dimensional shape. The specific surface of the sponge chitin was determined on freeze-dried samples with nitrogen adsorption using the Brunauer–Emmett–Teller method. A value of 4 m^2/g was found. The adsorption isotherm shows typical behavior of a macroporous material (Sing et al., 1985). However, uranyl adsorption did not yield reproducible results for freeze-dried sponge chitin. It must be assumed that the porous structure closed at least partly during freeze-drying and that the surface area value might be higher in hydrated chitin.

Therefore, the sponge chitin was stored at 4 °C in ultra-pure water and used after squeezing it on filter paper. The hydrated

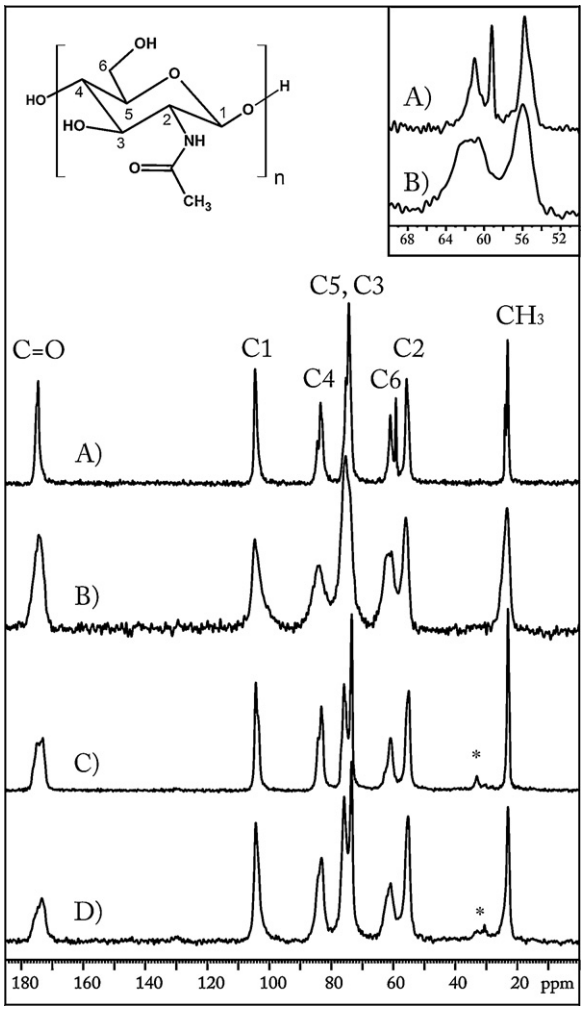

Fig. 1. ^{13}C CP solid-state NMR spectra of (A) hydrated sponge chitin from *A. aerophoba* (49,000 scans), (B) dry sponge chitin from *A. aerophoba* (47,000 scans, 14 kHz), (C) α-chitin hydrated in water for 24 h (40,000 scans) and (D) dry α-chitin (35,000 scans, 14 kHz). *denotes an impurity. The C6 signal from *A. aerophoba* is magnified for clearity.

sponge chitin from *A. aerophoba* still contained approx. 90 wt% water as could be determined from the mass difference before and after drying the chitin at 105 °C (chitin pieces collapsed when dried at 105 °C). It is likely that a significant part of the water is stored in the spaces within the fibers.

Interestingly, the ^{13}C CP MAS NMR spectrum of hydrated chitin exhibits much narrower signals than that of dry sponge chitin. Furthermore, several line splittings are visible, especially at the C6 signal (Fig. 1A and B). Both effects have already been described for hydrated squid pen β-chitin (Tanner, Chanzy, Vincendon, Roux, & Gaill, 1990). A partial shift of the C6 signal has also been observed by us in silicified β-chitin from diatom spines, which is due to hydrogen bonds with Si—OH groups (Spinde et al., 2011). It is thus probable that the C6—OH group also develops hydrogen bonds with adsorbed water molecules in hydrated sponge chitin. For comparison, crab chitin was wetted in water for 24 h. The material only took up 25 wt% water. A much less pronounced narrowing of the lines and no splitting were observed (Fig. 1C and D). It can be concluded that sponge chitin does not only store water in the hollow spaces, but also has the ability to hydrate, similar to the highly amorphous squid pen β-chitin (Tanner et al., 1990). This results in an increased mobility of the polymer chains and thus narrower NMR signals. It is probable that in hydrated sponge chitin,

Table 1
Adsorption and adsorption capacity q at a uranium concentration of 10 mg/l at different pH values.

pH	Adsorption in %	q in mg/g
4	6.1 ± 0.5	3.0 ± 0.2
5	45.7 ± 3.9	21.6 ± 1.8
6	77.0 ± 2.6	34.6 ± 0.7
7	80.7 ± 0.7	31.8 ± 0.5
8	74.5 ± 3.4	32.1 ± 2.0

intercalated water molecules are part of the chitin structure, which leads to a structure loss when the chitin is dried.

3.2. Uranium speciation

The uranium speciations in solution were calculated with the program EQ3/6 by Wolery (Wolery, 1992) using the Nuclear Energy Agency Thermochemical Database (NEA TDB) (Guillaumont et al., 2003) for pH values from 4 to 8 and at a uranium concentration of 10 mg/l. In aqueous solution, uranium(VI) is always present as the uranyl cation UO_2^{2+} either in its free form or bound into different complexes. 92% of the uranium occurred as free UO_2^{2+} at pH 4 and 22 % at pH 5. The remaining uranyl was bound in different hydroxide complexes. At pH 6 and 7, a mixture of hydroxide and carbonate complexes occurred. At pH 8, only different carbonate complexes were present.

3.3. pH dependence of the adsorption

The adsorption of uranyl species on sponge chitin from aqueous solutions was tested in the pH range from 4 to 8. Uranyl was only weakly removed from the solution at pH 4. However, the uranyl removal strongly increased with increasing pH, resulting in a maximum removal of 81 ± 1 % at pH 7 (Table 1). By simply exchanging the water stored in the hydrated sponge with uranyl containing solution, less than one percent of the uranyl would be removed from the solution. The observed effect must thus be due to interactions between the chitin and the uranyl, inducing real uranyl adsorption.

Uranyl adsorption on the chitin was confirmed qualitatively by EDX measurements of the fibers before and after the adsorption. The spectrum of the pure chitin only shows signals corresponding to carbon, nitrogen and oxygen from the chitin, gold due to preliminary sputtering of the samples and small amounts of sodium as a residue of the NaOH extraction procedure. Chitin loaded with uranyl shows distinct signals at 3.6 and 3.8 keV corresponding to uranium. The signals of sodium and chlorine are due to the sodium perchlorate present in the adsorption solutions.

3.4. Adsorption isotherms and desorption

The adsorption capacity q in mg/g as a function of the uranium concentration in solution was determined at pH 6, 7 and 8, because these pH values were favorable for uranyl adsorption and cover the range of interest for water decontamination. Solutions at pH 7 and 8 were filtered before the adsorption in order to remove insoluble precipitates, such as UO_2CO_3 or $UO_2(OH)_2$, which form at higher pH values. Thus, precipitation during the adsorption experiments – which could falsify the results – was excluded. At pH 6, up to 288 ± 11 mg/g uranium could be adsorbed on the chitin at a uranium concentration of 76 mg/l (Fig. 2). The increasing loading with uranyl became visible by an increasingly intense yellow color of the chitin due to uranyl hydroxides (Fig. 3).

The value of 288 mg/g at pH 6 is higher than many other biomass adsorption capacities reported in the literature (Guibal et al., 1992; Tsezos & Volesky, 1981). It should be emphasized that the

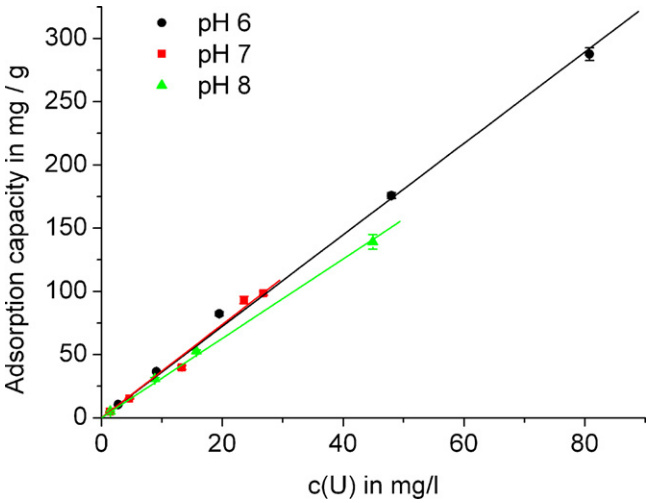

Fig. 2. Adsorption isotherms of uranium on *A. aerophoba* chitin at pH 6, 7 and 8. The error bars partly lie within the symbols.

adsorption capacity of the sponge chitin grew linearly with the uranyl concentration in solution at pH 6, 7 and 8 (Fig. 2). This is in contrast to other materials (e.g. biomass from *R. arrhizus* (Tsezos & Volesky, 1981) and *M. miehei* (Guibal et al., 1992)), which exhibited a saturation adsorption capacity with adsorption curves ending in a plateau. It can be concluded that sponge chitin has not achieved its maximal loading yet and could still adsorb more uranyl if more was available. It seems that the fibrous structure with hollow spaces and the unusual permeability to water strongly increase the available surface and the adsorption capacity of the hydrated sponge chitin.

The average uranyl adsorption of the adsorption isotherms (averaged over the single data points) was 81 ± 5% at pH 6, 73 ± 9 % at pH 7 and 69 ± 3% at pH 8. This incomplete adsorption – while the chitin could theoretically be loaded with more uranyl – indicates that the adsorption is an equilibrium process.

A range of uranium concentrations from 10 to 50 μg/l at pH 6 was designed to mimic uranium concentrations found in slightly contaminated surface or drinking water. This range also comprises the current maximum guideline value of 15 μg/l established by the World Health Organization (Birke et al., 2010). Adsorption values up to 98% were achieved in this concentration range (Table 2).

From chitin pieces loaded with 39 mg/g uranium, an amount of 70 ± 15% could be desorbed by shaking the chitin in ultrapure water for 24 h. This again indicates that the adsorption is a reversible process. For recovering the chitin, the pieces loaded with uranyl were shaken in 0.1 M HCl at room temperature for 24 h. 90 ± 1% of the uranyl which had been adsorbed on the chitin before

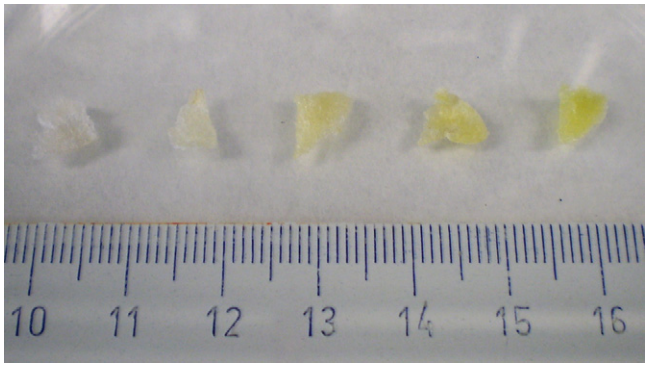

Fig. 3. From left to right: *A. aerophoba* chitin pieces after 24 h of adsorption loaded with 10, 37, 82, 176, 288 mg/g uranium. Scale in cm.

Table 2
Adsorption and adsorption capacity q for small concentrations in a range of some μg/l uranium at pH 6. The measured uranium concentration refers to the reference solution concentration after 24 h.

c(U) prepared in μg/l	c(U) measured in μg/l	Adsorption in %	q in μg/g
10	6.5	94.6 ± 4.8	29.1 ± 1.4
20	8.5	97.8 ± 2.2	39.6 ± 1.3
50	27.2	77.7 ± 14.6	100.8 ± 19.1

were detected in the solution afterwards. After this desorption procedure, the chitin did not show any macroscopic structural changes. Furthermore, the ^{13}C CP MAS NMR spectrum (Fig. 4C) did not differ from that of untreated chitin. That means, the chitin was not chemically altered by uranyl adsorption and incubation in 0.1 M HCl and it can thus be re-used. By application of several successive washing steps or by using a column arrangement with a constant acid flow, it might be possible to fully desorb the uranium and use the chitin in multiple cycles of adsorption and desorption.

3.5. Adsorption kinetics

The adsorption kinetics was determined at a uranium concentration of 10 mg/l and pH 6. A reversible reaction of pseudo-first order was chosen as model, given that a maximum of 80% of the uranyl was adsorbed in preliminary experiments and that the chitin concentration was much higher than the uranyl concentration, such that changes in the number of available adsorption sites could be neglected. A corresponding exponential function was fitted to the data points. The process is rather slow. More than 24 h are needed to reach the equilibrium at room temperature.

3.6. Interactions between uranyl and chitin

Previous work investigating the adsorption of uranyl on chitosan has shown changes in IR spectra. While amino bands at about 1590–1630 cm^{-1} were observed in the unloaded chitosan, bands ressembling amide I and II vibrations developed upon

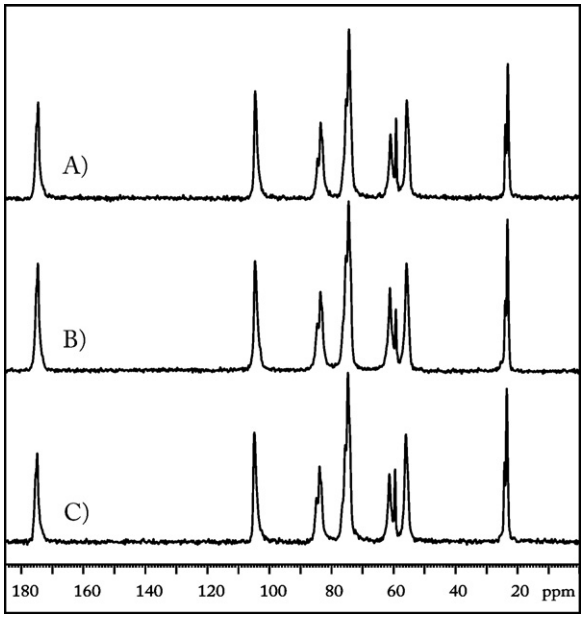

Fig. 4. ^{13}C CP solid state NMR spectra of (A) hydrated sponge chitin from *A. aerophoba* (39,000 scans), (B) hydrated sponge chitin loaded with 188 mg/g uranium at pH 6 (118,000 scans) and (C) sponge chitin after uranyl desorption in 0.1 M HCl (33,000 scans).

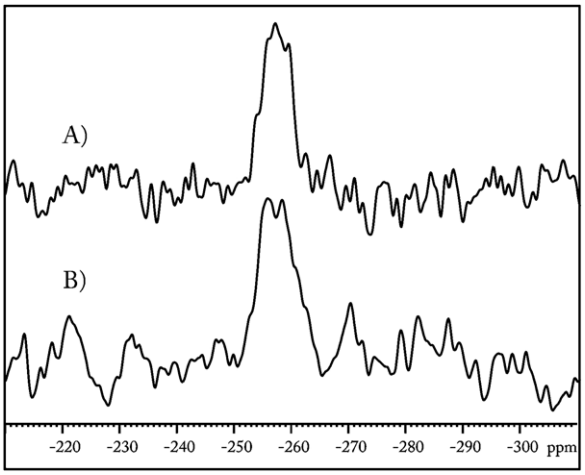

Fig. 5. ^{15}N CP solid state NMR spectra of (A) dry sponge chitin (34,000 scans) and (B) dry sponge chitin loaded with 188 mg/g uranium (89,000 scans).

loading with uranyl, indicating coordination of uranyl to the amino groups (Guibal, Roulph, & Le Cloirec, 1995; Jansson-Charrier et al., 1995).

Sponge chitin from *A. aerophoba*, is completely acetylated. That means, it does not exhibit a significant fraction of glucosamine units. We compared the ^{13}C and ^{15}N CP MAS NMR spectra (Figs. 4 and 5, resp.) of hydrated sponge chitin loaded with 188 mg/g uranium to those of unloaded, hydrated chitin. Adsorption of uranyl did not result in significant changes of the spectra. This indicates that the uranyl ion UO_2^{2+} is neither covalently nor coordinatively bound to chitin, since the formation of strong bonds should be visible in the NMR spectra, e.g., as measurable chemical shift changes. ATR FTIR and Raman spectra both showed the presence of UO_2^{2+} with peaks at 931 cm^{-1} in IR and at 935 cm^{-1} in the Raman spectrum corresponding to the asymmetric and the symmetric stretching vibration, respectively. However, these methods did not show changes of the chitin bands either, in contrast to chitosan (Guibal et al., 1995; Jansson-Charrier et al., 1995). The lack of any visible changes in the measured spectra strongly indicates that there are no strong interactions between sponge chitin and uranyl. A possible interaction mechanism which may explain these observations is the formation of hydrogen bonds between the hydroxyl groups of the different uranyl complexes and the polymer. Such weak interactions would favor the reversible reaction and the easy desorption of the metal. The evaluation of the pH dependence of the adsorption showed that the adsorption capacity improved with increasing pH. Increasing pH also induced a growing percentage of uranyl hydroxides from pH 4 to 6 and a growing percentage of uranyl carbonates from pH 7 to 8. Thus, it seems to be likely that hydroxide and carbonate complexes are preferentially adsorbed on the chitin because the numerous OH^- and CO_3^{2-} ligands facilitate the formation of hydrogen bonds.

To further analyze the uranyl specimen bound to the chitin, time-resolved laser induced fluorescence spectra (TRLFS) were measured on chitin pieces adsorbed with uranyl and on the corresponding adsorption solutions. The free UO_2^{2+} shows six distinct luminescence bands which increasingly overlap due to peak broadening with increasing concentration of uranyl hydroxides, i.e. with increasing pH (Moulin, Decambox, Moulin, & Decaillon, 1995). Fig. 6A shows such a spectrum of the solution at pH 6. Uranyl adsorbed on the chitin also emits luminescence light. Due to the lower intensity of the signals, the bands are not discernible any more. However, it can be seen that the emission maximum is shifted to higher wavelengths (Fig. 6B), showing that the environment of the uranyl in the chitin is different from the solution state. Further conclusions

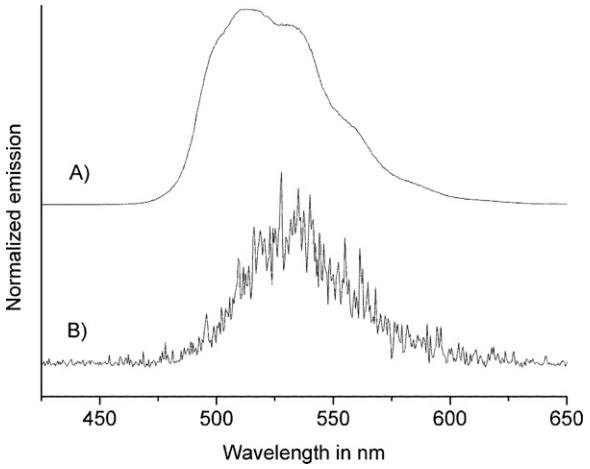

Fig. 6. TRLF spectra of (A) solution with 50 mg/l uranium at pH 6 and (B) piece of chitin with adsorbed uranium prepared in this solution.

about the nature of the uranyl specimen bound to the chitin cannot be made yet due to a lack of comparable data.

4. Conclusion

Chitin networks from marine sponges were shown to be promising materials for the purification of water from uranium contamination. They can be extracted using few, non-toxic chemicals. Their natural network structure makes them well-suited as a filter material and the internal structure of the fibers offers a high surface area for uranyl adsorption. Sponge chitin effectively sorbs uranyl. At relatively high concentrations up to 80 mg/l, adsorption capacities up to 280 mg/g could be achieved. At low concentrations of some μg/l – which may be found in drinking water – uranyl was efficiently adsorbed as well. A large part of the uranyl could be desorbed using diluted hydrochloric acid. Other non-toxic acids like acetic or citric acid might also be used. In summary, *A. aerophoba* sponge chitin is a material with favorable properties for water purification by both industry and consumers. Marine sponges provide a renewable material and could possibly be cultivated using marine ranching technology in order to ensure a sustainable use of this resource.

Acknowledgement

The authors would like to thank Gudrun Mueller for EDX measurements, Ursula Schaefer and Aline Ritter for ICP MS analysis. Thanks are further due to Prof. Dr. Stefan Kaskel and Florian Wisser for BET measurements. Dr. Hermann Ehrlich thanks the Deutsche Forschungsgesellschaft for financial support of the project EH 394/1–1.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.08.090.

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