Uranium fixation by *Cladophora spec*.

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Abstract. Shaking and throughput flow column experiments were carried out using different species of filamentous green algae. Only *Cladophora aegagropila* allowed operating a column with live algae for app. 36 hours without blockage. Column experiments resulted in much higher retention of uranium than shaking experiments.

Introduction

Downstream of uranium mining residues (tailings and dumps) very high uranium and radium concentration may occur. In the waters of some of these contaminated sites neutral-alkaline pH-values are measured, on the one hand caused by carbonates added during the conditioning process (Wismut 1999) and on the other hand by the paragenesis of the ore: uranitite in combination with different carbonates (Dahlkamp 1993).

Algae are generally able to accumulate heavy metals inclusive radionuclides compared to the surrounding water (Kalin and Smith 1986; Kalin et al. 2002b; Kalin et al. 2005; Vymazal 1995). This ability is important for the application of algae for waste water treatment, e.g. in Constructed Wetlands or throughput flow reactors. Technical use of filamentous algae for eliminating uranium, however, is almost impossible because of the development of mats, which affect diffusion and may clog the reactor.

At the former Wismut mining site Pöhla Characeae are successfully used (Kalin et al. 2002a; Kiessig et al. 2004), which have been tried efficiently in Canadian wetlands where they grow naturally for waste water treatment, however, they are not endemic in the Saxon ore mountains.

Downstream of the aforementioned former uranium mining sites (Lengenfeld, Helmsdorf, Neuensalz; see Fig. 1), green algae were found, some forming dense mats. Obviously, these algae are well adapted to the chemical conditions of dump and tailing waters (e.g. neutral-alkaline milieu, uranium contents several $\mu g*L^{-1}$ to several $mg*L^{-1}$). Uranium concentrations in algae from these waters vary between

20 and 400 µg*g^{-1} (DM) (Dienemann et al. 2002, Kalin et al. 2005, Vogel et al. 2004).

Cladophora spec. was found main species besides *Ulothrix spec*. (Dienemann et al. 2002). Many Cladophora-species are known to form dense algal mats (Pokorný et al. 2002, Paalme et al. 2002), but some may also appear as bowl-like aggregations, which have been subject to investigation for several decades (Potonié 1912). Nowadays, these bowls are e.g. used to treat the water in aquariums.

Unlike *Cladophora fracta* and *Cladophora glomerata Cladophora aegagropila* does form balls instead of mats, so the working hypothesis was that Cladophora aegagropila may be successfully used in a throughput flow reactors eliminating more uranium from the water than filamentous Cladophora-species without clogging the reactor.

Fig.1. Locations: italics: coal mining residues, other: uranium mining residues

Materials and Methods

Material

Three different species of Cladophora were used: *Cladophora fracta*, *Cladophora glomerata* and *Cladophora aegagropila*. *Cladophora aegagropila* was ordered via aquarium-specialized trade and adapted to laboratory conditions for 3 months.

Cladophora fracta was gathered from water from the cooling towers of Boxberg power station. Before adapting and keeping it in the laboratory it was carefully cleared of all debris.

Cladophora glomerata forms stronger filaments than *Cladophora fracta*. It was collected in the downstream areas of the former uranium mining site Neuensalz and kept for more than 6 months under laboratory conditions.

In all algae uranium contents - measured shortly before the experiments - were less than 1 mg/kg TM.

Methods

Uranium solutions (Uraniumacetate, Fa.Chemapol, p.A.) were adjusted by Na_2CO_3 to pH 7.5 in order to induce the formation of uranium-carbonate-complexes. *Cladophora glomerata* and *Cladophora fracta* were used for batch-experiments (m=6gFM, V=100ml, t=20 min, n=4). Algal material and uranium solution were (slowly) shaken via overhead-shaker (Fa. Heidolph; 5 rpm).

Cladophora aegagropila was used for column experiments. A plexiglass column (Makrolan, Fa. PCH) was filled with *Cladophora aegagropila* and water containing LiCl (Tracer; Fa Merck, p.A.). Uranium concentration of the uranium

Fig.2. *Cladophora aegagropila*

solution was app. 1700 µg*L^{-1}. Pore volume (250 mL) and exposure time were measured by an extra tracer (KBr (Fa Merck, p.A.)) Flow rate was adjusted to 2ml*min^{-1} (Minipuls, Fa. Gilson)..

Uranium concentration in the uranium solution was measured every 90 minutes, uranium solutions had to be changed after 6 hrs. and after 25 hrs., column outflow was sampled every 30 minutes, all samples were filtrated (0,45µm celluloseacetate, Fa. Sartorius) and concentrations were measured by ICP-MS (Pq2+, Fison/TJA) on isotopes U-238; U-235, Li-7, Br-79 and Br-81.

Results

Fig. 3 shows the results of the batch-experiment with *Cladophora fracta* combined with results from Dienemann et al. 2005 of batch-experiments with the same species and identical experimental design with uranium concentrations of 100 and 250 µg*L^{-1}.

At the end of the experiment, *Cladophora fracta* contained 360 µgU*g^{-1} (DM) (at a water concentration of app. 2700 µgU*l^{-1}).The batch-experiments resulted in no significant difference between *Cladophora fracta* and *Cladophora glomerata* with an average uranium concentration of app. 300 µg*L^{-1}.

Fig. 4 shows the initial concentration (blank values) in the columns for the experiment with *Cladophora aegagropila*. Unfortunately, the necessary re-supply of uranium solution (originally planned to last for 6 hrs.) after 6 and 25 hrs. is clearly marked (arrows).

The application of tracers (Li, KBr) allowed estimating the length of stay in the column (Fig. 5), which is 2 hrs.

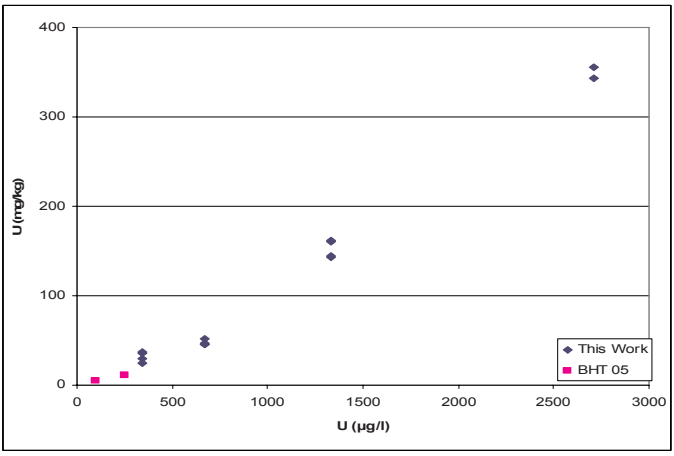

Fig.3. Uranium contents (µg*g^{-1} TM) of *Cladophora fracta* (batch-experiment n=4) of this work combined with results from Dienemann et al. 2005 (r^2 = 0,98)

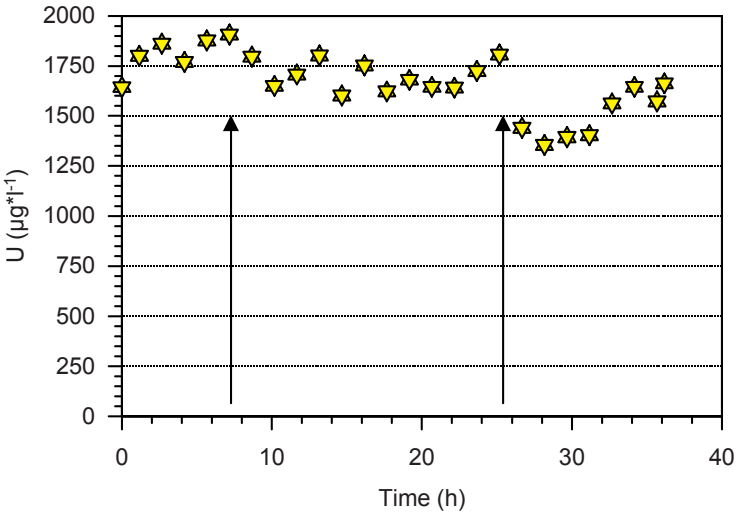

Fig.4. Initial uranium concentrations, experiment with *Cladophora aegagropila*, arrows indicate re-supply of solution

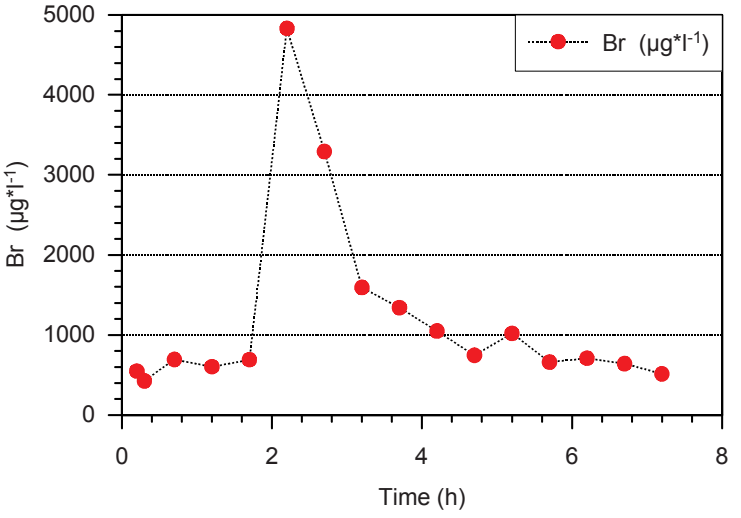

Fig.5. Concentration of tracer for estimation of length of stay in the column (added immediately at the beginning of the experiment) – peak after 2 hrs.

Flow rates were relatively constant (± 10%). Fig. 6 displays differences in uranium concentrations at the column input and output under consideration of the exposure time.

Uranium retention in the column was much higher than expected. Saturation concentration of *Cladophora aegagropila* appears to be app. 800 mg*kg^{-1} DM.

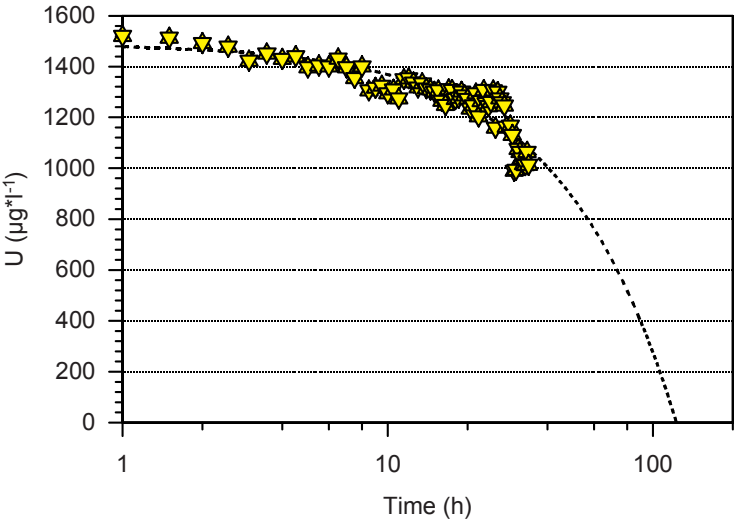

Fig.6. Differences in uranium concentrations at the column input and output under consideration of the exposure time of 2h

Discussion

Batch-experiments show – as expected – relative low uranium retention (see Kalin et al. 2005). Equations comparing the uranium contents in algae of the experiment to those from an artificial flow-path (bypass) in the area of Neuensalz (Vogel and Dudel 2004) correlate.

Differences between filamentous and bowl-like Cladophora species could be explained by differing experiment design, e.g. much longer exposure time in the column experiment. If this were the only reason, it should be possible to find green algae with uranium contents of 700 mg*kg^{-1} DM in the field, which has so far not been the case, although many samples were taken from several former uranium mining sites.

Another difference in the experimental design is the continuous pumping of uranium solution over algae along a column row. It is assumed that at the beginning of the exposition an exchange resp. retention of calcium-ions takes place. Since columns consisted of transparent plexiglass, supposedly live activities of the algae caused CO_2 to be removed from the solution, which would result in a shift of the calcium carbonate-carbonic acid-equilibrium causing carbonate- and calcium concentration to decrease. As these ions are crucial for the uranium speciation, this may result in a change of the uranium species, which increases the sorptive fixation onto the algal material (Dienemann et al. 2005)as well as the probability of reductive fixation (Brooks et al. 2003).

This explanation is also supported by considering the surface of *Cladophora aegagropila*, which appears like a bowl consisting of numerous filaments. So the actual surface is significantly bigger and allows additionally biofilms to grow. Bacteria and fungi may accumulate uranium (Suzuki et al. 2002; Suzuki et al. 2003; Suzuki et al. 2005). Development of biofilms is depending on time.

Algae sampled from the respective ponds usually contained more uranium than found in the water (Dienemann et al. 2002).

Conclusions

Application of *Cladophora aegagropila* allows using conventional throughput flow column reactors for water treatment. Typical problems - like blockage - occuring while using filamentous green algae did not occur. On a larger scale enough light must be provided as well as possibly developing gases considered.

Acknowledgements

Thanks for financial support to BMBF and TU Dresden.
Many thanks for support in keeping all algae and throughout the experiments to K. Hesse, K. Klinzmann and M. Förster. Special thanks to A. Weiske for quick ICP-MS-measurements, even during early morning and late evening hours.

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