Removal of heavy metals, arsenic and uranium from model solutions and mine drainage waters

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Abstract. The aim of this work was to study the suitability of a new ceramic-based biomass, called Biocer. Different carrier materials were developed to investigate and improve the mechanical and hydrolytical stability of the Biocer material. In this work, the different materials should be compared. The biosorption of the materials was realised in batch equilibrium and first column experiments. First preliminary experiments with the Biocer I material in columns with real mine drainage waters resulted in a good removal of uranium and other heavy metals.

Introduction

Pit waters and seepage from mine tailings or dumps contain a huge potential of harmful substances like arsenic and heavy metals. In the former uranium mining areas in Germany, especially uranium and arsenic are contaminants of enhanced environmental attention. The wastewaters from the flooded pits there as well as seepage waters from the large spoiled piles contain a high future contamination potential.

Many approaches were developed and tested to solve this problem; one of them is the use of biosorption for the treatment of mine drainage waters (Volesky 1990, Allen and Brown 1995, Gadd and White 1993, Tzezos and Volesky 1981, Edgington et al. 1970). In the last years, several sorption experiments with different biomaterials were successfully implemented (Hakajama et al. 1982, Macaskie et al. 1988, 1992, Tsezos and Mac Cready 1989, Naja et al. 1999, Volesky and Tsezos 1983, 2001, Guibal et al. 1992, 1998, Hu et al. 1996, Horikashi et al. 1979, Byerley et al. 1987, Kuyucak and Volesky 1990 Chen and Yiakoumi 1997, Baes et al.

1997, Min and Hering 1998, Rorrer et al. 1993, Dambies et al. 1999, 2000, 2002, Fournel et al. 2001, Vincent and Guibal 2001, Hatzikioseyan et al. 2001, Sasaki et al. 2001, Loukidou et al. 2003, Kratochvil and Volesky 1998, Kefala et al. 2000, Groudev et al. 1999). *Bacillus sphaericus*, the Bacillus strain used here, is known for its excellent sorption capacity of uranium and other heavy metals (Selenska-Pobell et al. 1999, Panak et al. 2000). In this context, a new biosorption material, called Biocer, was developed combining the good sorption properties of the bacteria with mechanical stability by means of the sol-gel technology (Soltmann et al. 2003). The name Biocer means here the combination of a biological component with ceramic material. The vegetative cells are firmly bound in this ceramic material, whereas harmful metal ions can diffuse through the pores of the ceramics and then they become sorbed on the cell walls.

With an optimised grain size, the Biocer material will later be used in column reactors for the treatment of contaminated waters. Such reactors may be applied as small decentral constructions for especially low concentrations of harmful metal ions and arsenic. The Biocer material can also be used for the postprocessing of discharges of conventional treatment units in order to keep the limits of environmental contaminants in the surface water.

The aim of this work was to study the suitability of the new ceramic-based biomass. In first column experiments with the Biocer material and real waste water it was observed that the sorption-active surface and the carrier material were degraded by fouling processes. For this reason different carrier materials were developed to investigate and improve the stability of the Biocer material. In this work, the different materials should be compared in batch equilibrium and kinetic experiments.

Materials and methods

Material

The Biocer materials were supplied by "Kallies Feinchemie AG" Sebnitz (Germany). The Biocer A was a modification of the original Biocer material. It was produced with an ethanolic sol instead of an aqueous sol in the biomass coating. The carrier material used for the Biocer A was the same like for the original Biocer, a SiO_2- based nanosol (Horak et al. 2003).

The Al_2O_3-Biocer contained a composit of Al_2O_3 mixed with nanosol and the biomass. The Al_2O_3 carrier was used to improve the mechanical and hydrolytic stability of the Biocer material against fouling processes.

The Geopolymer material was supplied by the WISUTEC (carrier material) (Kunze et al. 2002) and the Biocer coating by "Kallies Feinchemie AG" Sebnitz (Germany). A problem in working with this material was the coating of the Geopolymer carrier with the biomass nanosol.

Before starting the experiments, the material was conditioned with physiological sodium chloride solution. Therefore, 0.1 g of the material was washed four times for 15 min with 3 ml of the salt solution. After conditioning, the Biocer material was suspended in the metal containing solutions to perform the biosorption experiments.

Biosorption experiments

The measurement of the sorption isotherms was carried out in batch experiments in closed test tubings. 1% of the Biocer material (w/v) was added to the metal(loid) solutions, and all was mixed in an overhead shaker for 2 hours. The concentration of the metal(loid) solutions used ranged from 0.1–250 mg/l and they were prepared by dilution of stock solutions in deionised water. The pH of the experimental solutions was adjusted to the appropriate value by adding HNO_3 and NaOH as required. Finally, the metal content of the sample supernatants was analysed by atomic absorption spectroscopy (AAS, Perkin Elmer 4100).

Desorption experiments

The desorption experiments were carried out directly after the end of the sorption experiments. Therefore, the Biocer material was separated from the metal solution, and suspended in a 0.005 M citric acid adjusted to pH 3.2. The desorption experiments were carried out by mixing in an overhead shaker over a time of 20 h.

For a new sorption cycle, the Biocer materials were conditioned again 3-4 times with a physiological sodium chloride solution, as described in point 2.1., and further used as described above.

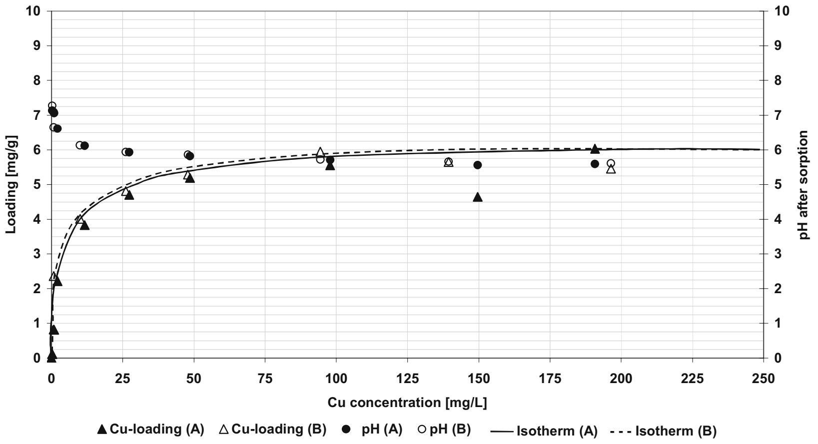

Fig. 1. Isotherms of the loading of the Biocer material with Cu^{2+} in tap water (unbuffered, initial pH 4.5).

Sorption experiments in columns

Sorption experiments were carried out in columns of a length of 25 cm and a diameter of 1.5 cm with real mine drainage waters. The uranium inflow concentration was 2 mg/l, the pumping rate was 30 ml per day.

Results and discussion

Biosorption of Cu, Zn and As on the original Biocer material

Biosorption of Cu^{2+}

The first biosorption results for Cu^{2+} on the Biocer material were already reported by Horak et al. (2003). In that research work, a specific sorption capacity up to 6 mg Cu^{2+}/g Biocer was determined at an initial pH of 5 of the solution. In these experiments, a Cu^{2+} sorption was performed again to compare the data for this material charge with the former ones.

The sorption experiments were carried out with tap water as solvent. The influence of additional ions, e.g. in drinking water, should be investigated. In Fig. 1 the sorption isotherms for Cu^{2+} in tap water are shown. A maximum specific sorption capacity of 5.71 mg Cu^{2+}/g Biocer in average was achieved in the experiment.

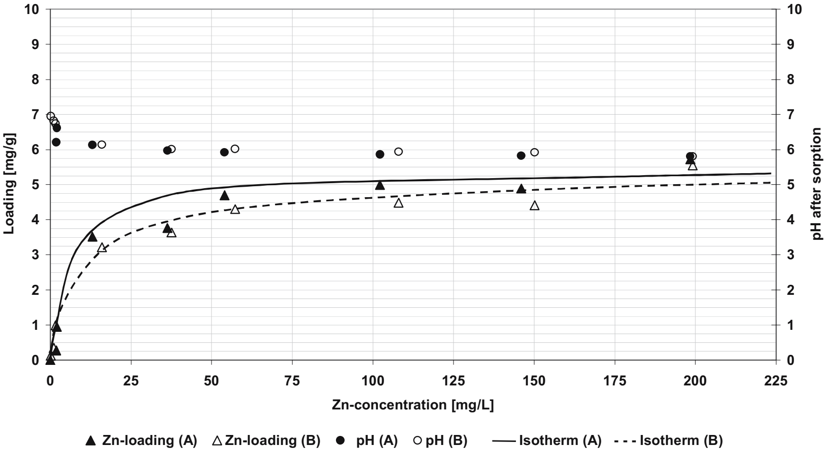

Fig. 2. Isotherms of the loading of the Biocer material with Zn^{2+} in deionised water (unbuffered, initial pH 5.5).

This maximum specific sorption capacity probably includes the precipitation of copper species on the surface of the material, e.g. Antlerite [$Cu_3SO_4(OH)_4$] and Brochanite [$Cu_4SO_4(OH)_6$] (Volesky et al. 1999).

The measurement data correspond extremely well with the sorption data of the former experiments (Horak et al. 2003). According to these experimental results, the Biocer material used here showed a good reproducibility of its sorption characteristics in different production charges.

Biosorption of Zn^{2+}

Zn^{2+} shows a more advantageous speciation characteristic in aqueous solutions compared to Cu^{2+}. It exists up to a pH of 8 as a free cation Zn^{2+} (O'Neill et al. 1998). Thus, no side reactions are expected by precipitation of Zn^{2+} species on the surface of the biosorbens in these sorption experiments. For this reason Zn^{2+} was used in the following biosorption experiments.

A maximum specific sorption capacity of 5,7 mg Zn^{2+}/g Biocer was achieved in the first biosorption cycle (see Fig. 2). The loading of the Biocer with Zn^{2+} is in a compareable range with the Cu^{2+} loading.

In further loading cycles after the desorption of the Zn^{2+} and a regeneration of the material, only up to 3 mg Zn^{2+}/ g Biocer were obtained. The specific sorption capacity demonstrated a strong dependence from the pH of the bulk solution.

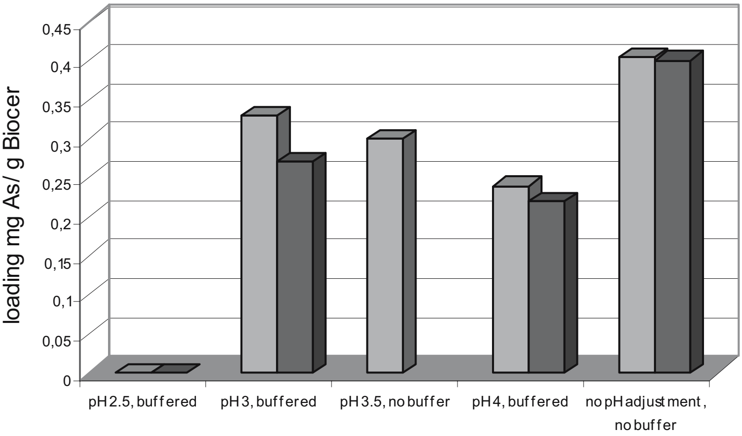

Fig. 3. Comparison of the loading of the Biocer material with As(V) at different pH in deionised water.

Biosorption of As

Besides the sorption experiments with metal cations, also sorption experiments with As(V) were carried out. The sorption of As ions is of high interest for the treatment of contaminated ground-, waste- and seepage waters. The experiments were carried out at different pH values to find out the optimum conditions, because of the speciation characteristics of the As ions and the equilibrium characteristics of the binding-active groups on the surface of the Biocer material (O'Neill et al. 1998, Niu and Volesky 2001). Initial pH values of 4.0, 3.5, 3.0 and 2.5 were adjusted in the sorption solutions. Two experiments were carried out in unbuffered solutions to prove the effect of buffering onto the sorption behaviour (Fig. 3).

The biosorption capacity of As onto the Biocer material is only low compared to the results with the metal cations (Zn^{2+}, Cu^{2+}, see Fig. 1-3). In real groundwaters or seepage waters, As will be sorbed on the Biocer only in low amounts besides the other metal ions, therefore an additional As sorbens will be necessary at enhanced As concentrations. As a result, the Biocer material demonstrated the best sorption characteristics in solutions of dissolved cationic metals compared to the As solutions, in which As exists as an anionic species.

The best sorption results for As(V) were achieved with 0.405 mg As/g Biocer in an unbuffered solution with no pH adjustment (see Fig. 3). In such solutions no competing effects of other anions seem to occur with the As ions for the binding places on the surface of the Biocer material.

In dependency of the initial pH of the sorption solutions, the best results were obtained at an initial pH of 3 with 0.33 mg As/g Biocer (see Fig. 3). The number of binding-active protonated groups on the surface of the Biocer is declining with increasing initial pH of the bulk solution, so that less of the As anions can be sorbed (see Fig. 3). The results of the experiments are corresponding with literature data (Dambies et al. 1999, Niu and Volesky 2001).

Comparison of different Biocer materials

Different carrier materials were coated with the biomass nanosol (see chapter 2.1.) to improve the long-term mechanical and hydrolytic stability of the biosorbens. Sorption experiments for comparison of the different biosorbents were carried out in aqueous Zn^{2+} solutions because the Zn^{2+} sorption showed the least side reactions in the sorption process (see chapter 3.1), so that it was good suited for model investigations. The results of the sorption experiments illustrates Fig. 4. With exception of Biocer A, all desorption data correlated well with the Langmuir model; the correlation coefficients were in average between 98 and 100%.

A modification of the sorption-active surface by processing of the biomass-nanosol coating with ethanol (Biocer A) results in no improvement of the binding capacity (2.48 mg Zn^{2+}/g Biocer) in comparison to the original Biocer material (see Fig. 4).

The use of Al_2O_3 as carrier material improved the mechanical stability of the material, but not its sorption characteristics (3.22 mg Zn^{2+}/g Biocer, see Fig. 4).

The sorption characteristics after the regeneration of the Al_2O_3 Biocer especially were not satisfactory. The material showed a loss of activity after only a few regeneration cycles. Another problem was the lower pH of the sorption solutions after regeneration which arose lower sorption results compared to the first loading. An explanation for this behaviour might be a lower binding of the biomass-nanosol composite to the Al_2O_3 carrier and thereby a loss of the sorption-active coating after regeneration.

With the Geopolymer Biocer, a high increase of pH was observed in the experiments and for this reason the best elimination results of up to 12.39 mg Zn^{2+}/g Biocer (see Fig. 4). A partial precipitation of Zn^{2+} on the surface additionally to the sorption process is possible at the high solution pH after the sorption experiments (final pH of the bulk solution up to 7.2). The Geopolymer had a good mechanical and chemical stability in addition to the good sorption results; therefore it was chosen for further sorption experiments with the real seepage waters.

Finally, after testing the different biosorption materials, the original Biocer material and the Geopolymer Biocer were chosen for further experiments with the real contaminated waters. The modification of the carrier material resulted in an improved stability of the Biocer, but not necessarily in better sorption results.

Experiments with real mine drainage waters

First preliminary experiments with the Biocer I material resulted in a good removal of uranium and other heavy metals. Fig. 5 presents the breakthrough curve of U in column experiments when the Biocer I material was applied. Due to the degrading stability of the Biocer material after some time of the experiment, a re-

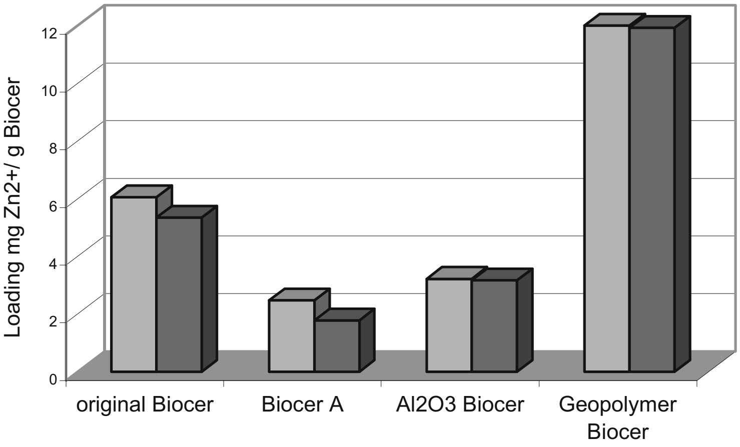

Fig. 4. Specific loading of Zn^{2+} on the different Biocer materials (deionised water, unbuffered; initial pH adjusted).

markably enhanced outflow concentration of U was observed after 800 – 1100 exchanged bed volumes of the column.

An improvement of the sorption behaviour of the material should be achieved by modification of the material and of the biosorption reaction conditions to enhance the stability of the Biocer.

Conclusions

In the biosorption experiments with Cu^{2+} and Zn^{2+} on the Biocer material good results were obtained. The material seems to be well suited for the removal of such metal ions from contaminated waters. The sorption capacity of the Biocer for As was low; further investigations have to be performed to improve the sorption characteristics or to use an additional sorbens for the complete removal of As from contaminated waters.

The sorption of Zn^{2+} on the Biocer occurs in a fast process, and the desorption is nearly quantitative. These results are good characteristics for a fast regeneration of the Biocer material and the subsequent processing of the metal solutions.

The Biocer material was compared with 3 other modified biosorbents for its sorption characteristics. As a result, the Biocer and a Geopolymer coated with the biomass-nanosol were chosen for further experiments with the real contaminated

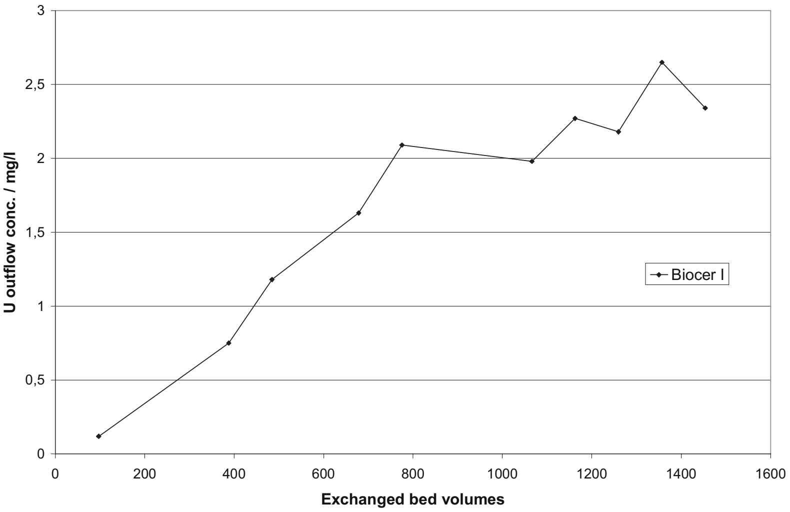

Fig. 5. Breakthrough curve of U in real mine drainage.

waters due to their good sorption characteristics.

First preliminary experiments with the Biocer I material resulted in a good removal of uranium and other heavy metals. With an improved stability of the Biocer material, better sorption results and particularly an enhanced sorption- and life time of the biosorbens are expected, which shall be reported in a future article.

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