

Removal of Oxoanions From Water: Comparison of a Novel Schwertmannite Adsorbent and an Iron Hydroxide Adsorbent

Elisabeth Simon¹, Diana Burghardt¹, Johannes Richter¹, Susan Reichel², Eberhardt Janneck²

¹*Technische Universität Dresden, 01062 Dresden, Germany, Elisabeth.Simon@tu-dresden.de*

²*G.E.O.S. Freiberg Ingenieurgesellschaft mbH, 09633 Halsbrücke, Gewerbepark ‚Schwarze Kiefern‘, Germany, e.janneck@geosfreiberg.de*

Abstract

An agglomerated, filter stable adsorbent was developed based on biotechnologically synthesized schwertmannite (SHM) from lignite mine water containing iron and sulfate. The adsorbent ‘SHM-sorpP’ was obtained by compacting SHM in a briquette press. As investigated by Fukushi et al. (2003) and Peiffer et al. (2012), SHM and SHM-based adsorbents offer excellent adsorption properties towards arsenic.

SHM-sorpP was tested in comparison to the commercially available iron hydroxide adsorbent Ferrosorp®Plus (HeGoBiotec GmbH) with regard to its suitability for the removal of the oxoanions antimonate, molybdate, vanadate, chromate or phosphate from synthetic water. For this purpose, laboratory batch tests with $c(\text{oxoanion}) = 20 \text{ mg/L}$ and $c(\text{phosphate}) = 100 \text{ mg/L}$ respectively and $c(\text{adsorbent}) = 0.5 \text{ g/L}$ were performed for 21 days to estimate adsorption kinetics and capacities for the adsorbents mentioned above. The oxoanions were added as salts to tap water, the starting pH was adjusted to pH 7.5 with 1 M NaOH. During the test time, no pH-buffering was done.

Phosphate was adsorbed more efficiently by Ferrosorp®Plus than by the schwertmannite adsorbent (36.6 mg/g Ferrosorp®Plus vs. 24.7 mg/g SHM-sorpP within 24 hours). In contrast, antimonate, molybdate and vanadate were adsorbed significantly more efficiently to the schwertmannite adsorbent: within 24 hours, between 11.2 and 17.9 mg oxoanion/g adsorbent could be removed from the solutions in the batch tests with SHM-adsorbent, whereas only between 1.1 and 10.7 mg oxoanion/g Ferrosorp®Plus were analysed. The removal of chromate was markedly lower, about 5 mg chromate/g schwertmannite adsorbent and no chromate adsorption to Ferrosorp®Plus were determined.

Key words: schwertmannite, oxoanions, water treatment

Introduction

Within the recently finished BMBF funded research projects SURFTRAP and SURFTRAP II two different methods were investigated to develop filter stable adsorbents based on biotechnologically synthesized schwertmannite (Janneck et al. (2015)). This schwertmannite is generated in a worldwide unique pilot plant (Janneck et al. (2010)) which is located as a bypass at the water treatment plant of the open pit lignite mine Nochten (Lusatia/ Germany) and is operated by Vattenfall Europe Mining AG and G.E.O.S. company. These adsorbents showed maximum adsorption capacities to arsenite and arsenate in former laboratory tests (Janneck et al. (2015)). With this study we investigated the adsorption behaviour of further oxoanions as antimonate, molybdate, vanadate, chromate, and phosphate to the schwertmannite based adsorbent SHM-sorpP versus Ferrosorp®Plus to demonstrate further applications in industrial waste water purifying.

Materials and Methods

Adsorbents

SHM-sorpP (fig. 1) was fabricated by high pressure compaction of the schwertmannite from the pilot plant. Details of the high pressure compaction are given in EU patent application EP2664376A1. The adsorption properties relating to the different oxoanions of the new SHM-based adsorbent should be compared to a commercially available iron hydroxide adsorbent like Ferrosorp®Pus (HeGo Biotec GmbH).



Figure 1 SHM sorpP

Test solution

All laboratory tests were done with tap water which was stocked with 20mg/L of the oxoanion, respectively with the exception of phosphate where a concentration of 100mg/L was used. Table 1 summarizes the used chemicals.

Table 1 Chemicals for stocking the test solution

| oxoanion | chemical |
|------------|---------------------------------------|
| chromate | K_2CrO_4 |
| molybdate | $Na_2MoO_4 \cdot 2H_2O$ |
| antimonate | $NaSbO_3 \cdot 3H_2O$ |
| vanadate | NaO_3V |
| phosphate | $NaH_2PO_4 \cdot H_2O$ and KH_2PO_4 |

Methods

Several batch tests were performed to investigate the adsorption kinetic of the oxoanions. A water volume of 250 mL and an adsorbent concentration of 0.5 g/L were used. Within the 21 d test period 12 samples were taken, filtrated (0.2µm) and analyzed by ICP-OES (Optimal 3200XL, Perkin Elmer) for Sb, Mo, V and Cr and UV-vis (UV-vis spectrometer Lambda 10, Perkin Elmer, wave length 80 nm) for PO_4 . The start pH value was adjusted to 7.5 with 1M NaOH but no pH buffering was done during the test.

Results

In the following graphs (figures 2 a-d) the adsorption behaviour of the determined oxoanions is shown. Chromate, molybdate, antimonate and vanadate were removed significantly more efficiently by the new schwertmannite based adsorbent SHM-sorpP.

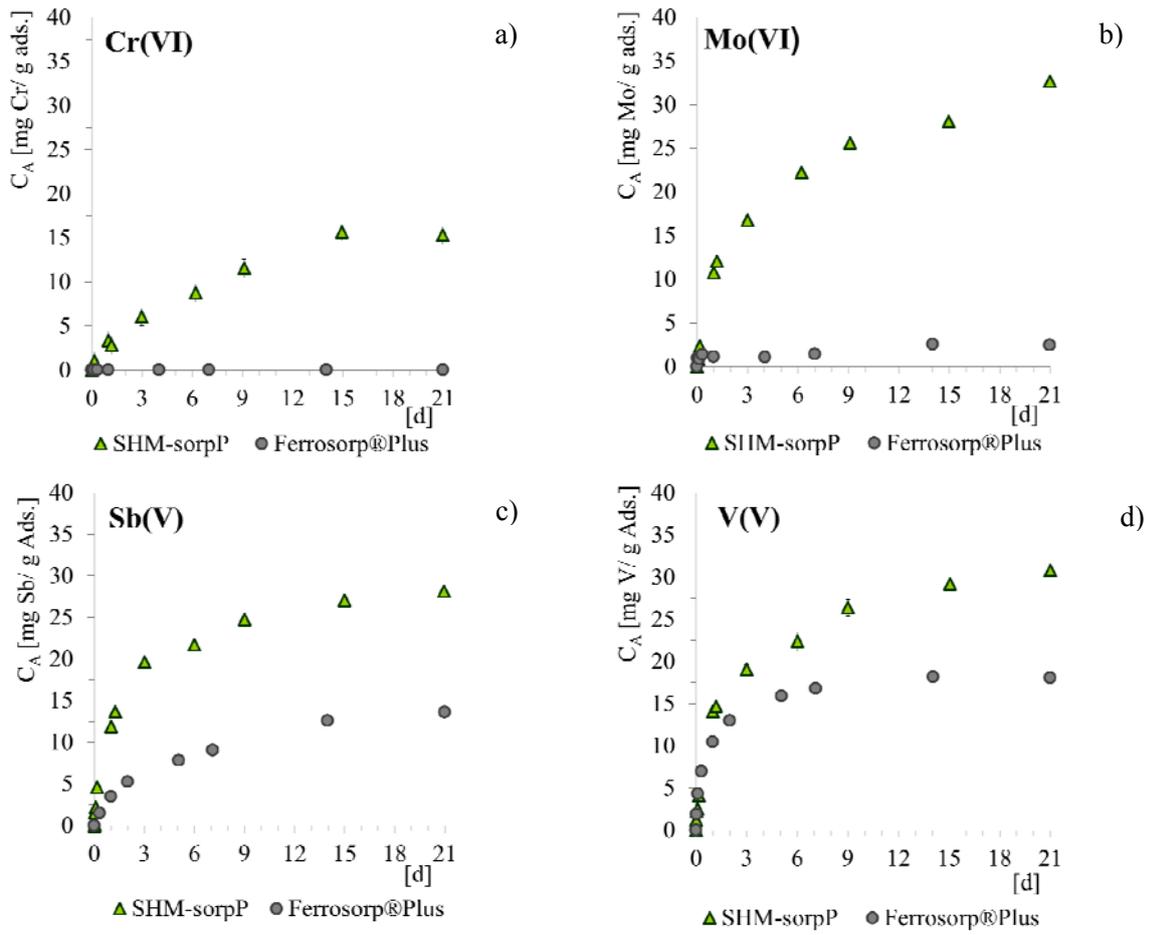


Figure 2 a-d Adsorption behaviour of the oxoanions chromate, molybdate, antimonite and vanadate

In contrast, phosphate was removed slightly more efficiently by Ferrosorp®Plus within the first days of the batch experiment. At the end of the test period no significant difference between the load of SHM-sorpP and Ferrosorp®Plus was measured (figure 3).

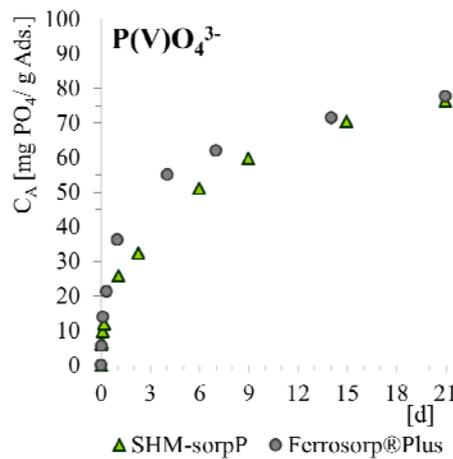


Figure 3 Adsorption behaviour of phosphate

Table 2 compares the adsorbent loadings of SHM sorpP and Ferrosorp®Plus related to the oxoanions chromate, molybdate, antimonate, vanadate, and phosphate.

Table 2 Adsorbent loadings of SHM-sorpP and Ferrosorp®Plus after 21 days

| adsorbent | chromate | molybdate | antimonate | vanadate | phosphate |
|----------------|---------------------------|-----------|------------|----------|-----------|
| | (mg oxoanion/g adsorbent) | | | | |
| SHM-sorpP | 15.80 | 32.66 | 28.15 | 30.77 | 76.41 |
| Ferrosorp®Plus | 0.00 | 2.47 | 13.61 | 18.08 | 77.59 |

Conclusions

The new schwertmannite based adsorbent ‘SHM sorpP’ for the use in passive water treatment systems showed a very effective removal of the oxoanions chromate, molybdate, antimonate, vanadate, and phosphate from synthetic water. In comparison to the commercially available Ferrosorp®Plus SHM-sorpP significantly better loadings were reached for chromate, molybdate, antimonate, and vanadate respectively and nearly similar loadings for phosphate. These results are very promising for further application of SHM-sorpP in passive water treatment plants to purify different industrial waste waters.

Acknowledgements

This study was financed by the research programme ‘KMU-innovativ’ (FKZ 02WQ1309), which is funded by the German Federal Ministry of Education and Research (BMBF). We thank Christian Marx for performing the batch experiments in our laboratory as well as for the phosphate analytics. Furthermore we thank Jutta Eckert (Department of Hydrology, University Bayreuth) for the numerous ICP analytics.

References

- EP 2664376A1 An adsorbent comprising schwertmannite, a method of preparing the adsorbent and the use of the adsorbent for purifying water or gas; 14.05.2012
- Fukushi, K., Sato, T., Yanase, N. (2003): Solid-solution reactions in As(V) sorption by schwertmannite, *Environmental Science and Technology* 36, 3511-3516, 2003
- Janneck, E., Arnold, I., Koch, Th., Meyer, J., Burghardt, D., Ehinger, S. (2010): Microbial synthesis of schwertmannite from lignite mine water and its utilization for removal of arsenic from mine waters and for production of iron pigments. *Proceedings IMWA Conference, Sydney, NS, Canada*
- Janneck, E., Burghardt, D., Simon, E., Peiffer, S., Paul, M., Koch, Th. (2015): Development of an adsorbent comprising schwertmannite and its utilization in mine water treatment. *Proceedings IMWA 2015 Conference, Santiago, Chile*
- Peiffer, S., Burghardt, D., Simon, E., Rostan, M., Janneck, E., Fischer, H., Patzig, A., Lambrecht, J., Schlömann, M., Wiacek, C., Kipry, J., Mosler, S. (2012): Fertigstellung von Verfahren zur biotechnologischen Schwertmannit-Synthese und zur passiven Wasseraufbereitung durch Herstellung eines Schwertmannit-Agglomerates. BMBF-Abschlussbericht, FKZ 03G0821, TIB Hannover, 2012