FATE OF ^{14}C-LABELLED CALCIUM POLYSTYRENE SULPHONATE (CaPSS) MICROPLASTIC IN WASTE WATER TREATMENT AT ENVIRONMENTALLY RELEVANT CONCENTRATIONS

Michael Hüben[1], Dieter Hennecke[1], Boris Meisterjahn[1], Markus Simon[1], Mike Kruse[1], Alexandra Kroll[2], Andreas Häusler[2], Erik Wischerhoff[3]

[1] Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Schmallenberg, Germany; [2] GAB Consulting GmbH, Stade, Germany; [3] Fraunhofer IAP, Potsdam-Golm, Germany;

Contact: michael.hueben@ime.fraunhofer.de

Introduction & objectives

Wastewater is assessed to be one of the most relevant pathways for microplastic particles (MP) used in specific personal care products and in medical applications into the environment.
Due to lack of a sensitive detection system enabling an easy analysis of MP at low concentrations in a complex matrix such as sludge, there is not much information about behavior of MP in wastewater treatment plants (WWTPs). The aim of the present work was to determine the fate and mass balance of a model polymer, cross-linked polystyrene sulfonate (PSS), in a simulated WWTP using ^{14}C-radiolabeled polymer.

Synthesis of ^{14}C-labelled CaPSS

^{14}C-CaPSS was synthesized in a suspension polymerization procedure downscaled from an industrial size to a 6 g scale. During the downscaling process a series of experiments was necessary to produce the desired polymerization product. The final product with a specific radioactivity (radioactivity per mass) of 9.8 kBq/mg enables a matrix independent detection of CaPSS and possible degradation product at low µg range corresponding to approx. 100 CaPSS particles with a diameter of 50 µm. Analysis of particle size distribution determined by laser diffraction and by IR showed no significant difference between ^{14}C-CaPSS and the commercial reference product (CaPSS-Purolite, Figure 1).

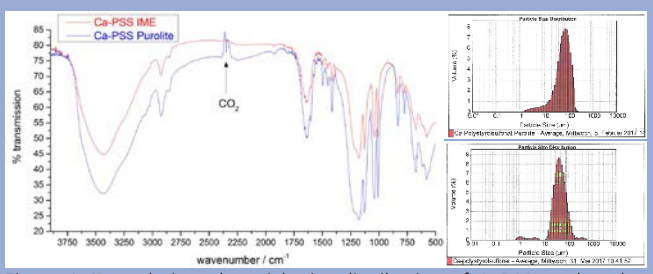
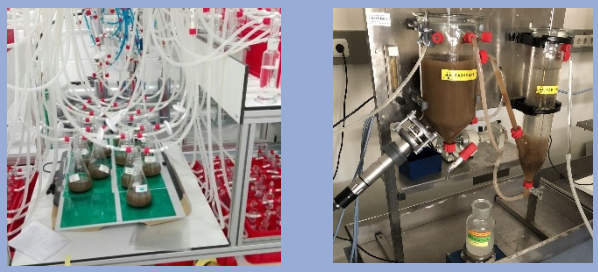


Figure 1: IR-analysis and particle size distribution of CaPSS produced (CaPSS-Purolite = reference polymer)

Activated sludge and WWTP simulation study

The ^{14}C-CaPSS was applied in an activated sludge and a WWTP simulation study (OECD 314B and 303A, Picture 1).



Picture 1: Incubation of activated sludge samples applied with ^{14}C-CaPSS; left: OECD 314B, right: OECD303A

Study Outline:	**OECD 314B**	**OECD 303A**
Inoculum conc.	4 g dry mass/L	2.5 g dry mass/L
Sample volume	250 mL	3 L
^{14}C-CaPSS conc.	39.2 kBq/L ≅ 4 mg/L ≅ 40000 MP/L	150 kBq/d ≅ 15 mg/d
Incubation time	28 d	21 d

Mineralization ($^{14}CO_2$) was monitored by traps containing 2N NaOH (OECD 314B only). At sampling time points the radioactivity was determined separately in the aqueous layer and the bio-solids. Results are summarized in Figure 2.

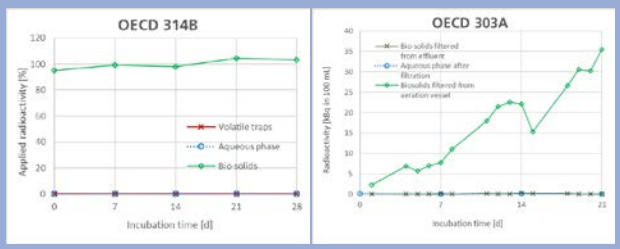


Figure 2: Distribution of radioactivity

Conclusion

The complete amount of ^{14}C-CaPSS was found to be bound to the bio-solids. Neither soluble breakdown products nor mineralization (OECD 314B) was detected.

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Fate of ^{14}C-labelled Calcium Poly(styrene sulphonate) (CaPSS) Microplastic in waste water treatment at environmentally relevant concentrations

M. Hüben[1], D. Hennecke[1], M. Simon[1], M. Kruse[1], A. Kroll[2], A. Häusler[2] and E. Wischerhoff[3]

[1]Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Auf dem Aberg 1, 57392 Schmallenberg, Germany
[2]GAB Consulting GmbH, Germany
[3]Fraunhofer Institute for Applied Polymer Research IAP, Germany

Wastewater is one of the exposure pathways of microplastic into the environment. Microplastic enters the wastewater e.g. as an ingredient of cosmetics or from specific pharmaceutical applications. Wastewater treatment plants (WWTPs) are generally considered to remove microplastic from the wastewater stream and to protect the receiving river. However, there is not much information to prove this assumption experimentally at environmental relevant concentrations. This is due to the fact that so far no sensitive detection systems are available to analyse organic polymers in a complex sludge matrix at such low concentrations.

In view of these limitations, the aim of this work was to determine the fate of a model polymer, crosslinked polystyrene sulfonate (PSS), in a simulated WWTP using radiolabeled material. PSS is a polymer which is widely used as an ion exchange resin in various applications. The polymer is insoluble in water and is not degraded in the human body. Calcium loaded PSS (CaPSS) was synthesized in a procedure downscaled from an industrial method with ^{14}C-radiolabelled styrene monomer. This is a key step in the entire project as the radioactivity of the monomer interferes with the polymerization reaction.

The resulting ^{14}C-polymer was characterized by comparison with commercial non-labelled CaPSS to prove success. The ^{14}C-radiolabelling enables detection in sludge matrix as well as the determination of potential water soluble degradation products and $^{14}CO_2$ from mineralization. A mass balance was established to identify the most relevant processes for the fate of CaPSS in WWTPs. Due to the high sensitivity of ^{14}C-detection, the test can be performed at realistic/environmentally relevant concentrations. As the detection limit of ^{14}C-microplastic in environmental matrices is currently orders of magnitudes below that of non-radiolabelled polymer particles, this study can serve as an example how future studies on the general topic “microplastics in the environment” can be supported.