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Peptide-based recovery of gallium

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High-tech metals such as gallium, are almost ubiquitous in our everyday lives. Due to their great importance for the electronics industry, the demand is continuously growing.

Gallium is an important component of many semiconductor products and part of light-emitting diodes (LED) and photovoltaic elements as well. The supply is currently mainly covered from primary raw material sources. Efficient strategies for the recovery of gallium from secondary raw materials are missing [1].

A possible starting point to overcome this gap is the processing of industrial wastes to recover gallium. This approach offers the additional appeal of being able to establish a circular economy that enables companies to act in a more resource-efficient manner. This qualifies to more economical and sustainable company operations.

Biotechnological approaches can make a valuable contribution to the development of sustainable recycling systems. These include various methods for mobilising, complexing, concentrating and selectively separating certain metals [2]. Biosorption, i.e. the passive interaction of biomass with certain ligands in aqueous solution, is particularly promising with regard to metal recovery from wastewater containing heavy metals [3]. In particular, the targeted use of peptides as biosorbents has many advantages, since these biomolecules can exhibit high stability, metal specificity and affinity for individual ions.

In so-called biopanning experiments, different phage that express individual peptide sequences are selected against a specific target material. The phage display technology is used for this purpose. It enables the representation of certain or random amino acid sequences on the particle surface of bacteriophage. This is achieved by fusing the peptide sequence with a viral capsid protein using recombinant DNA technology. All resulting variants of a bacteriophage population form a phage display library, which can be used for selection against a specific target [4].

Here, the phage display technology was used to identify specific gallium binding peptides.

A total of 5 putative gallium binding bacteriophage clones from a commercial phage display library, that presents random peptides at the PIII protein, could be selected (Ph.D.™-C7C Phage Display Peptide Library, NEB, US). These were further characterized in single clone experiments. The binding affinity of the best gallium binding phage clones for a gallium-loaded sepharose material (Cube Biotech, Germany) was determined and compared with the binding properties of a clone without an additional expressed peptide sequence (wild type, Wt). All 5 tested clones showed a higher affinity for the target material than the wild type (see Figure 1). The clones that showed the highest binding affinity for gallium were C10.20 (HGGQTVA) with 32-fold better binding and C12.16 (SIKHAST) with 47-fold better binding.

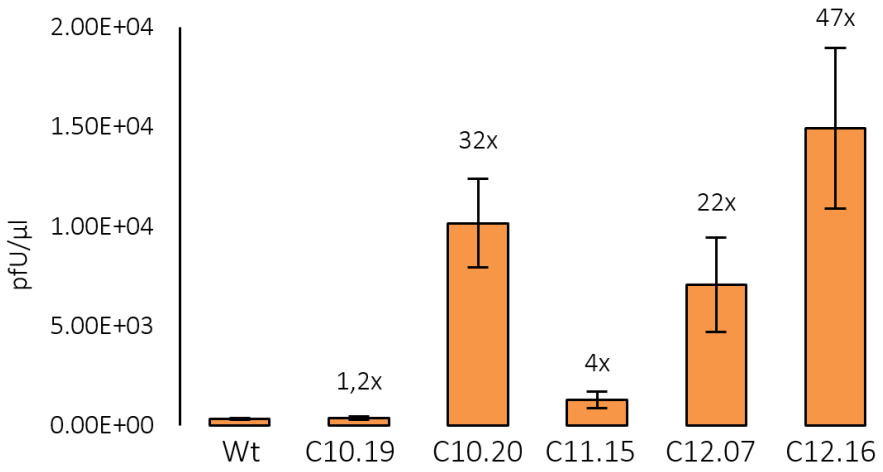
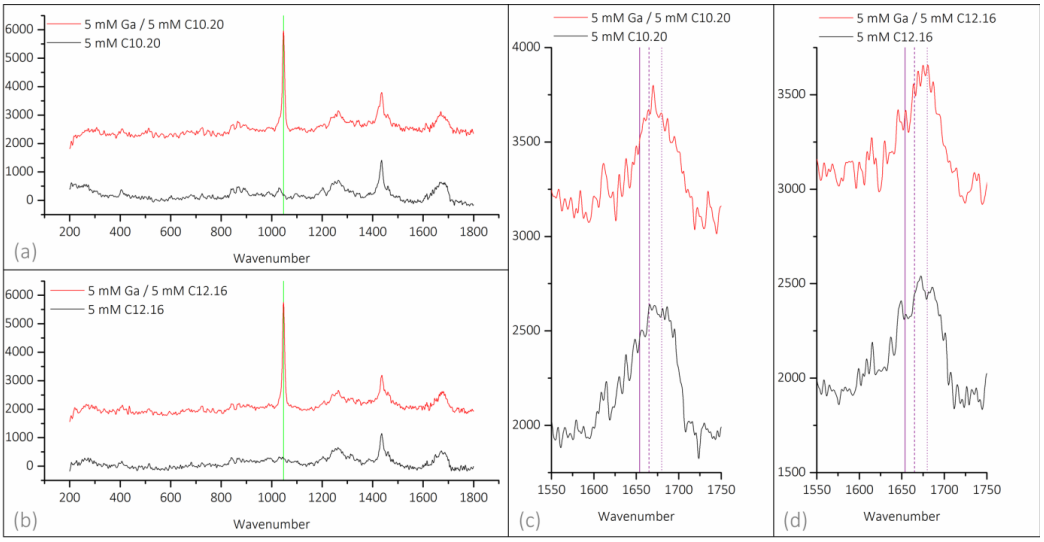


Figure 1: Single clone binding studies. In titer assay detected bacteriophage concentration bound to Ga-loaded NTA sepharose.

In further experiments, two peptides were characterized independently of the bacteriophage. Both peptides were purchased by Fmoc-based solid phase synthesis (GL Biochem, China).

In a first experiment the binding of gallium ions in aqueous solution was investigated using Raman spectroscopy (Malvern, UK). In Figure 2 Raman spectra of the putative gallium binding peptides C10.20 and C12.16 in the presence and in the absence of equimolar concentrations of gallium nitrate are shown. With the aid of Raman spectroscopy, among other things, conclusions can be obtained about non-elastic light scattering of abiotic and biotic samples in aqueous solution. The peak at 1047 cm^{-1} signals the presence of the gallium nitrate compound [5]. The amide I region between 1600 cm^{-1} and 1700 cm^{-1} states about the secondary structure of peptide samples. The Raman shift that could be observed for the investigated peptides in the presence of gallium nitrate indicates conformational changes due to the formation of a peptide complex with gallium ions.



Marker bands: (—) 1047 cm^{-1}, (—) 1654 cm^{-1}, (---) 1665 cm-1, (····) 1680 cm^{-1}

Figure 2: Raman spectra of putative gallium binding peptides in the presence and absence of equimolar concentrations of gallium nitrate. Raman spectroscopy was performed in ultrapure water for (a) 5 mM peptide C10.20 (ACHGGQTVACGGGS) and (b) 5 mM peptide C12.16 (ACSIKHASTCGGGS). A close-up those spectra is shown for the amide I region (O=C-N-H stretch) of (c) peptide C10.20 and (d) peptide C12.16. The Raman shift in this region indicates conformational changes due to the formation of a peptide complex with gallium ions.

In future experiments, an additional cysteine at the C-terminus will allow the immobilization of peptides *via* a thiol group on different surfaces such as silanized glass, gold chips or gold nanoparticles [6]. By this, peptide-based materials can be generated for the selective extraction of gallium from industrial wastewaters.

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