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Sensing Penicillin V in aqueous media with MIP nanoparticle coatings on QCM

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Summary:

Molecularly imprinted polymers (MIP) based on an acrylic system have proven useful for sensing Penicillin V in aqueous solvents by the means of quartz crystal microbalances (QCM). Herein we carry that concept further by synthesizing molecularly imprinted polymer (MIP) nanoparticles (NPs) as sensitive matrices due to some considerable properties including high surface-to-volume ratio, low cost and straightforward preparation and handling. Herein, we report the sensitivity and selectivity results of MIP NPs with rapid screening method based on QCM. The approach indicates selective response of sensors to Pen V toward similar molecular structures and clearly reveals concentration-dependent reversible signals in terms of different concentration of target.

Keywords: Penicillin V, Molecularly Imprinted Polymer, Quartz Crystal Microbalance, Polymer Nanoparticles

Introduction

Most pharmaceuticals are deposited in the environment through human consumption and excretion, and are often filtered ineffectively by municipal sewage treatment. Persistence of pharmaceuticals and active drugs in wastewater are detrimental, because they are not only potential environmental pollutants, but are also pharmaceutically active. They also have the potential to accumulate in soil and plants that have been irrigated with wastewater and reclaimed water. Especially antibiotics are considered harmful for promoting the development of antibiotic-resistant bacteria in nature. Various analytical techniques can be utilized for measuring concentrations of antibiotics in wastewater effluent. Molecular imprinting is a comparably recent method for generating artificial recognition matrices toward both biological and synthetic species. Combined with suitable transducers, e.g. QCM, they allow for rapid and reproducible sensing [1]. The project underlying this presentation aims at sensing the antibiotic Penicillin V (Pen V) with both MIP nanoparticles and bulk MIP via QCM measurements. During the first stage, we studied corresponding MIP thin films based on radical polymerization of acrylic monomers. QCM sensor characteristics revealed a limit of detection at 0.02 mg/ml. Selectivity was investigated against Penicillin G and Amoxicillin, which have similar chemical structures [2].

The second step involves preparation of polymer Nanoparticles (NPs). The advantages of MIP NPs compared to bulk polymer is to enhance sensing efficiency due to their increased surface-to-volume ratio: it provides larger number of accessible binding sites for molecular recognition. This study reports on synthesis methods for improving the recognition properties of MIP NPs.

Preparing Penicillin V MIP NPs

Herein, MIP NPs were synthesized by precipitation polymerization of methacrylic acid (MAA) as the functional monomer, and trimethylolpropane trimethacrylate (TRIM) as the cross-linker and Pen V as the template in the acetonitrile. After thermal polymerization at 60°C, particles in the size range of 200 nm were prepared and spin-coated onto QCM electrodes. The corresponding non-imprinted (NIP) sensor was prepared in the same manner without template.

Results

Fig. 1 shows the outcome of MIP particle synthesis: one can clearly see that the process leads to large numbers of uniform particles in the size range of 200nm. In a first step towards generating the sensor it is necessary to extract the template from the polymer to reveal cavities. For that purpose, we stirred the particles in a mixed solution of Methanol and Acetic acid for 24 hours.

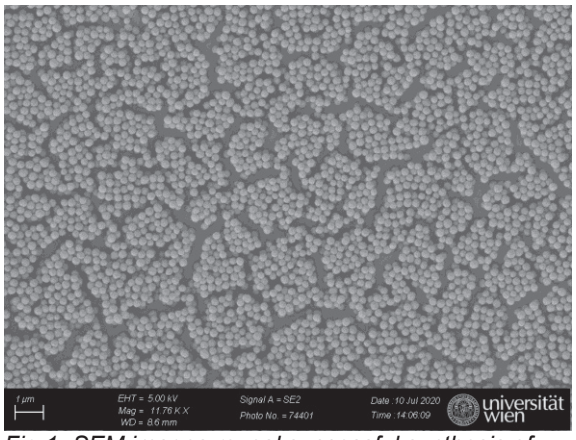


Fig.1. SEM images reveal successful synthesis of NPs in the size range of 200 nm

Then, QCM measurements served to assess sensitivity and selectivity of the sensors. Figure 2 shows the outcome of a sensitivity test: the sensor signals depend on the concentration of Pen V: they are roughly twice as large at 50mM, than at 25mM. After each injection we removed the analyte by washing with distilled water. To ensure reproducibility of the QCM response, every measurement repeated three times for each concentration. This led to a standard deviation of 1.2.

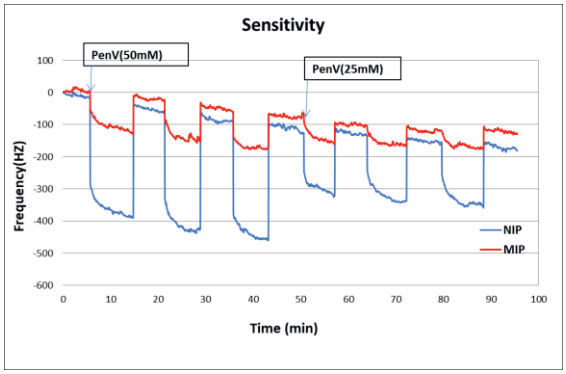
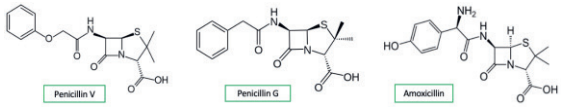


Fig.3. MIP and NIPQCM results at concentrations of 50 mM and 25 mM Pen V, respectively

For every signal, the frequency shifts recorded for MIP NPs are higher than those of NIP NPs: it exceeds the latter by a factor of three.

Fig. 2 summarizes the QCM selectivity pattern of the MIP NPs. To investigate selectivity, we utilized Penicillin G and Amoxicillin as competitive analytes against Pen V, because their structures are very similar to each other, as can be seen in Figure 2.



The results shown the highest response obtained when the sensors exposed to Pen V at a concentration of 50mM with selectivity factors around 1.3 each.

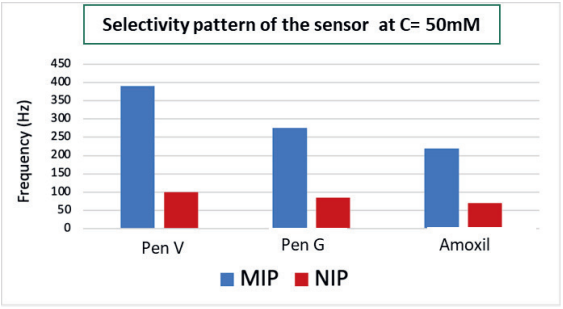


Fig.2. Selectivity of sensors at a concentration of 50 mM towards competing analytes.

In summary, we successfully developed MIP NPs that selectively bind Pen V and thus are potentially useful for establishing sensor systems for detecting wastewater effluents.

Acknowledgement

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References

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