Biomembranes for the combined separation and enzymatic treatment of microplastic samples

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Highlights

- Biomembranes were prepared to improve the treatment of MP samples.
- Enzymes were successfully immobilised on commercial membranes.
- Microparticles were identifiable on the exterior of the biomembrane.

1. Introduction

In recent years, microplastics (MPs) have emerged as a critical environmental concern due to their ubiquitous presence in the world's oceans, freshwater systems, soil, and even the air we breathe. Accurately detecting and analysing MPs remains a significant challenge for scientists worldwide. MPs samples for analysis are typically prepared through multiple cycles of filtration, oxidation and/or enzymatic treatment to remove co-contaminants. This multi-step process is time-consuming and costly, and therefore requires simplification and standardisation. The purpose of the presented research was to improve the utilisation of enzymatic catalysis in preparing MPs samples.

2. Methods

Several methods were applied to characterise membranes before and after the process, as well as examine their catalytic properties including membrane surface charge (SurPASS 3 Anton Parr, Austria), water contact angle (Drop Shape Analysis System DSA100E, Krüss GmbH, Germany), SEM ijmages (Phenom ProX G6 Thermo Scientific), and AFM images (Park NX10, Park Systems Corp., Suwon, Korea). The produced membranes' flux properties, including water flux and water flux recovery, were measured using the dead-end Amicon 8010 filtration cell and the synthetic air was used as a driving force in the experiments at four distinct pressure levels of 100, 200, 300 and 400 mbar. Based on the experimental data, the pure water flux and flux recovery after fouling, along with the total enzyme elution during backwashing and water uptake capacity (WUC) were calculated. The enzymes were immobilised on the membranes using an Amicon 8010 cell. Based on the spectrophotometric measurements, activity of the free and immobilised enzymes and activity recovery of the immobilised enzymes were determined, as well as the immobilisation yield (%). The possibility for multiple use of the immobilised enzymes was determined over 5 repeated catalytic cycles of a model enzymatic reaction. Further, during the storage stability and reusability study, the enzyme elution in the biocatalytic membranes was determined. Finally, experiments were conducted to evaluate the usability of the created biocatalytic systems in microplastic sample preparation with the LDIR 8700 (Agilent, USA). For this purpose, model solutions of lipids, proteins and cellulose were tested, and the results were compared for immobilised and free enzymes.

3. Results and discussion

Both morphological (Fig. 1A and 1B)and spectrophotometric analysis (Fig. 1D) of the membranes after immobilisation confirmed successful immobilisation of the enzymes on the membrane surface. Moreover, the membrane flux remained stable after immobilisation (Fig. 1C). A higher total amount of immobilised enzymes was deposited onto the Au-based membrane and reached 166.5 mg, whereas for the Al-based membrane total enzyme amount was 164 mg. In turn, among the enzymes analysed, regardless of the membrane used, lipase and laccase were the most immobilised. However, it is worth noting that for both membranes, the amount of immobilised enzyme and immobilisation efficiency followed the same trend, indicating chemical similarity between the two analysed materials. The slightly larger amount of enzyme deposited on the gold membrane may result from its slightly less hydrophilic

nature, which creates more hydrophilic-hydrophobic interactions between the enzyme and the membrane surface.

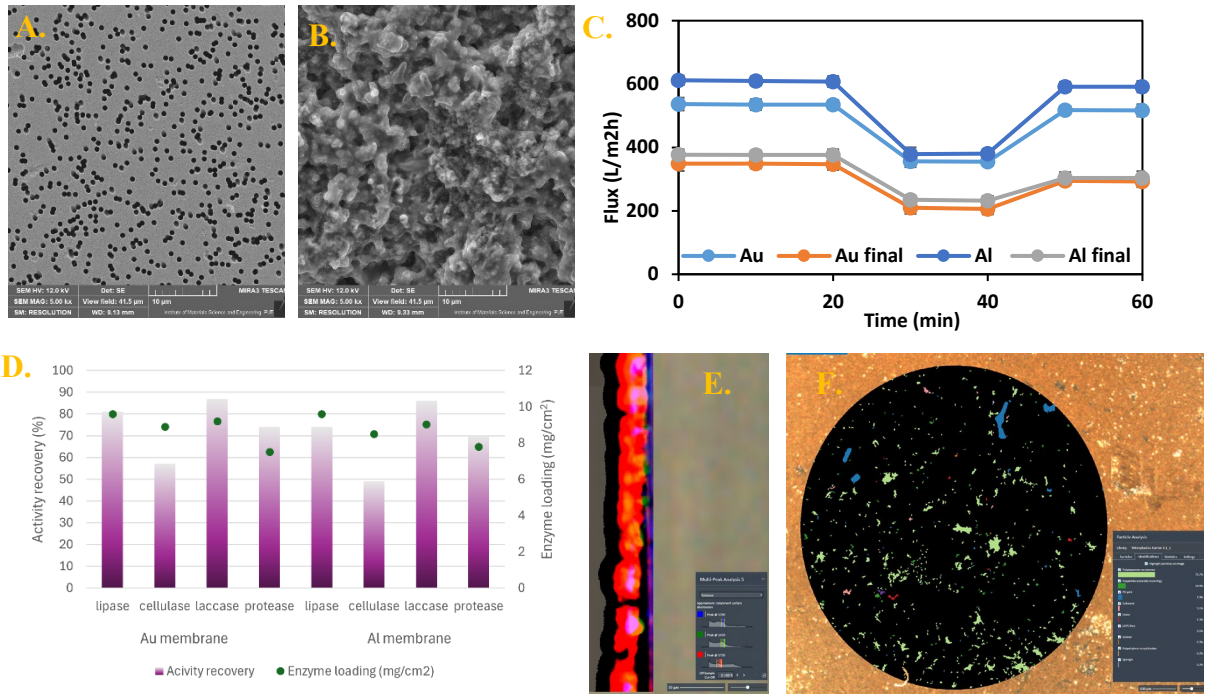

Figure 1. SEM images of pristine (A) and modified (B) AU membranes; membrane flux for pristine samples and biomembranes (C), enzyme load and activity after immobilisation (D), LDIR images of the biomembrane cross-section (E) and biomembrane surface with the tested polymers solution (F).

Furthermore, cross-section images confirmed enzyme deposition on the membrane surface (Fig. 1E), whereas further analysis succeeded in the identification of polymer fragments on the surface of membranes covered with immobilised enzymes and polydopamine (Fig. 1F).

4. Conclusions

The experiments showed that the biocatalytic membranes could be a valuable tool in preparing MPs samples for analysis and identification. However, further work is being conducted to ensure the most efficient removal of co-contaminants, particularly from more complex samples.

Keywords
Enzyme immobilisation, biomembrane, microplastic analysis.

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