Application of alginate protective layers for screen printed carbon electrodes (SPCE)

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Bioelectrodes play a critical role in electrochemical sensing, with applications in areas such as environmental monitoring (Tsai *et al* (2021)), glucose detection (Mross *et al* (2015)), and more. Enzyme-based bioelectrodes are key components of biosensors, leveraging the specificity of enzymes (biorecognition elements) to detect and quantify target substances in complex fluids, such as wastewater and biological fluids (George *et al* (2022)). However, enzymes are highly sensitive and prone to inactivation after prolonged exposure to high temperatures (Wang *et al* (2016)) and their performance is often hampered by interferences (Campuzano *et al* (2019)).

Various coatings, including Nafion (Trouillon *et al* (2009)), alginate (Zhang *et al.* (2019)), chitosan (Hlavatá *et al* (2014)) and polyurethane (Yu *et al* (2006)) layers, have been utilized to protect biosensors from (bio)fouling. These coatings offer antifouling protection by preventing non-specific adsorption and the presence of low and high molecular weight substances that impede the active surface of the bioelectrode (Ambrózy *et al* (2013)). Despite their protective properties, they often reduce detection capability by interfering with the sensing process. To address this issue, we propose the development of transient protective coatings designed to completely detach from the bioelectrode during use. These coatings will protect biosensors during storage (increased self-time) and prior to detection, preventing (bio)fouling without compromising sensing performance.

Among other substances, alginate is a naturally occurring polysaccharide that has been employed as the primary polymer chain in the synthesis of biodegradable thickeners (Vasile, 2011). Alginates are the salts of alginic acid, a linear polysaccharide derived from brown algae composed of two uronic acids as repeating units: mannuronic acid (M) and guluronic acid (G). These units are arranged in both homopolymeric sequences (MM- or GG-blocks) and heteropolymeric sequences (MG- or GM-blocks), as illustrated in Figure 1.

The significance of alginate primarily resides in its hydrocolloid characteristics, such as its capacity to absorb water in both hot and frigid environments, resulting in the formation of viscous solutions, dispersions, or gels. Alginate is considered an exceptional polysaccharide for gel systems due to its distinctive properties, including biocompatibility, biodegradability, low immunogenicity, and non-toxicity (Kim et al., 2008). Alginates are, consequently, distinctive due to their properties as emulsifiers, thickeners, stabilizers, gelling agents, and film formers, which enable a wide range of applications within the food and pharmaceutical industries (Soledad Lencina *et al.* (2014)).

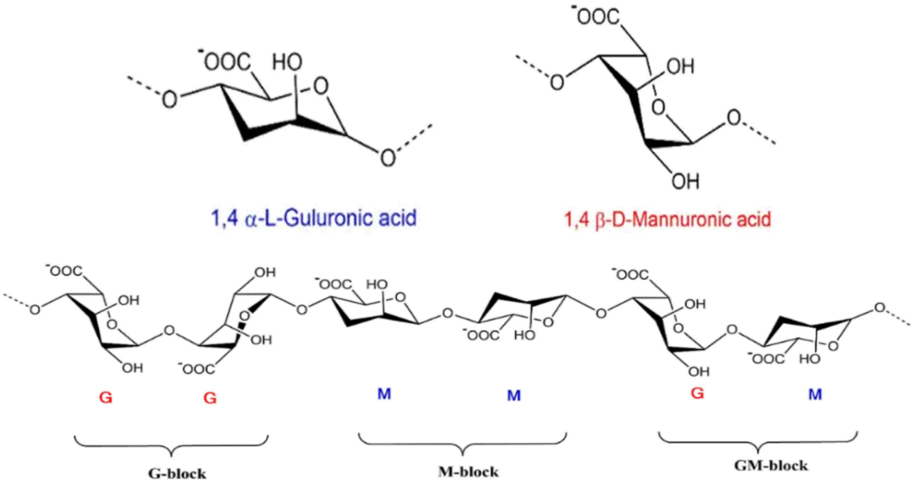

Figure 1. Alginate monomers and blocks distribution in alginate salt (Abasalizadeh (2020))

In our study, commercial screen-printed carbon electrodes were modified with alginate using two distinct deposition techniques: drop-casting and electrodeposition In drop-casting method, alginate solution was deposited on the surface of the working electrode. This was followed by the addition of a $CaCO_3$ solution at half the volume of the alginate added. Electrodeposition was carried out by applying 150mA for 60 seconds while the electrode was dipped into an alginate/$CaCO_3$ solution. To evaluate the efficiency of the two deposition methods, Infrared Reflection-Absorption Spectroscopy (IRRAS) cyclic voltammetry (CV) were performed. The cyclic voltammogram of a $[Fe(CN)_6]^{3-/4-}$ solution shows a slight decrease in the oxidative current for the drop-cast electrode compared to the bare screen-printed gold electrode, whereas an even smaller decrease in oxidative current is observed for the electrodeposited film. However, the general shape of the CV remains largely unchanged in both cases. The CV of alginate coated gold electrode in a blank solution confirms that alginate is electrochemically inactive, indicating that alginate is a suitable candidate for electrode protection. The IRRAS measurements confirm the presence of alginate on the electrodes for both deposition methods when compared to an alginate-coated gold plate used as a reference. However, the alginate fingerprint signals are significantly lower in intensity for the electrodeposited films compared to those prepared by drop-casting. After washing the alginate coated electrodes, with a Phosphate-buffered saline (PBS) the IRRAS measurement was carried out It can be seen that the main alginate-related signals disappear, indicating that the coating can be removed and the electrode surface recovered. This was further confirmed by measuring the CV of a $[Fe(CN)_6]^{3-/4-}$ solution using the recovered electrode, where both redox peaks corresponding to the $Fe^{2+/3+}$ and $Fe^{3+/2+}$ couples were fully restored.

Overall, these results indicate that alginate can be considered a suitable, biocompatible protective layer for electrodes. To further improve the electrodeposition process, parameters such as higher alginate concentrations, longer deposition times, and increased deposition currents should be explored.

This research aims to address the challenges of biosensor storage and biofouling through sustainable, cost-effective coating techniques that preserve and potentially enhance the sensing capabilities of bioelectrodes.

References

Ambrózy, A.; Hlavatá, L.; Labuda, J. *Acta Chimica Slovaca* **2013**, *6 (1), 35–41.*

Abasalizadeh, F. et al. *Journal of biological engineering* **2020**, 14(1), 8.

Campuzano, S.; Pedrero, M.; Yáñez-Sedeño, P.; Pingarrón, J. *International Journal of Molecular Sciences* **2019**, *20 (2), 423.*

George, J.; Anand, S. S.; Kumar, et al. *Environmental Chemistry Letters* **2022**, *20 (3), 1897–1927.*

Hlavatá, L.; Vyskočil, V.; Beníková, K.; et al. *Open Chemistry* **2014**, *12 (5), 604–611.*

Kim, W.; Chung, H.; Shin, I.; et al., Characterization of calcium alginate and chitosan-treated calcium alginate gel beads entrapping allyl isothiocyanate, Carbohydr Polym, **2008**, 71, 566-573

Mross,S.; Fürst,P.; Pierrat, S.; et al. *IEEE Sensors J*ournal **2015**, 15*, 7096–7104.*

Soledad Lencina, M.M. et al. European Polymer Journal **2014**, 61, 33–44

Trouillon, R.; Combs, Z.; Patel, B.A.; O'Hare, D. *Electrochemistry Communications* **2009**, *11 (7), 1409–1413.*

Tsai, S.-T.; Cheng, W.-J.; Zhang, Q.-X.; Yeh, Y.-C. *ACS Synthetic Biology* **2021**, *10 (12), 3576–3582.*

Vasile, C.; Nita, L.E., Carbohydr Polym, **2011**, 86 (1), 77-84

Wang, C.; Sirimuvva Tadepalli; Luan, J.; et al. *Advanced Materials* **2016**, *29 (7).*

Yu, B.; Long, N.; Moussy, Y.; Moussy, F. *Biosensors and Bioelectron* **2006**, *21(12), 2275–228*

Zhang, S., et al. J. Wuhan Univ. Technol.-Mater. Sci. Ed. 34, 744–751.