

Electrochemical Sensor for the Controlled-Release of Curcumin from a Novel Polyacrylamide Hydrogel

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Abstract:

In this study, we applied an electrochemical detection approach to study the release of curcumin from a polyacrylamide-based hydrogel. Cross-linked polyacrylamide hydrogels have often been utilized for their controlled-release properties. Differential pulse voltammetry (DPV) of curcumin enabled a rapid and cost-effective method to determine the release kinetics from the hydrogel matrix with a detection limit of 100 nM.

Keywords: electrochemical detection, polyacrylamide, high-swelling hydrogel, controlled-release, curcumin

Introduction

Acrylamide monomers, when polymerized with a cross-linker, such as N,N'-Methylenebisacrylamide (MBA), form high-swelling hydrogels. The structure and size of pores within the polymer can be easily controlled through varying the concentration of cross-linker [1]. Furthermore, due to the three-dimensional network, small molecules can be introduced and trapped inside the matrix. The polymer matrix protects the small molecules from degradation and allows their controlled-release under desired conditions [2].

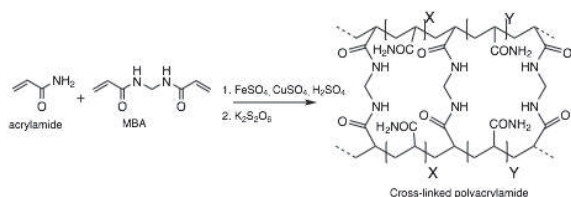


Fig. 1A. Chemical structure of acrylamide, MBA, and cross-linked polyacrylamide (MBA-PAA)

Conventional methods to analyze the controlled-release processes often involve spectroscopic and chromatographic set up that require sample pretreatment prior to data acquisition [3]. With electrochemistry, however, direct in-situ detection of the compounds released by the hydrogel can be performed in an easy-to-use and cost-effective set-up. We have applied differential pulse voltammetry (DPV), which is a highly sensitive and reproducible technique.

In this study, curcumin was chosen as the model compound due to its well-described electrochemical properties [4].

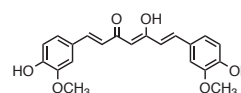


Fig. 1B. Chemical structure of curcumin

Curcumin is a natural colorant compound found in turmeric. Previous studies showed curcumin has positive effects on human health, but due to the chemical structure, curcumin can undergo hydrolysis, protein-induced degradation, and oxidation in the biological systems [5,6]. This not only significantly reduces the bioavailability of curcumin, but also, causes individuals to have to consume a large dose of curcumin in order to have a significant impact. Thus, we hypothesized that, if curcumin can be trapped into the hydrogel matrix, and in turn, released into the aqueous environment in a controlled manner.

Methods

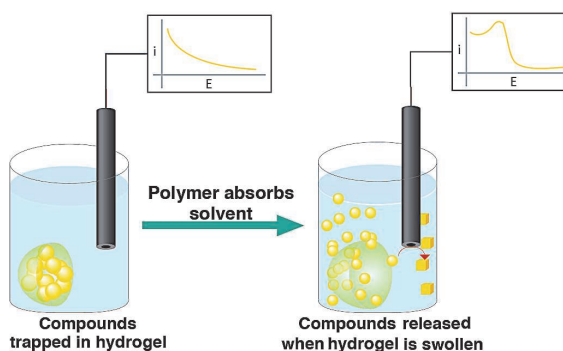


Fig. 3. Experimental set-up of electrochemical detection of curcumin trapped in MBA-PAA polymer.

PAA-MBA hydrogel was synthesized by dissolving acrylamide, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in

distilled water respectively, under stirring to 50°C to achieve a homogenous solution. Then, H₂SO₄ was added to acidify the solution. The solution was cooled to room temperature and curcumin was added at a desired concentration. *N,N'*-Methylenebisacrylamide (MBA) was introduced as the cross-linking agent and finally, a saturated K₂S₂O₈ catalytic solution was added to induce polymerization of the hydrogel. The polymer was dried overnight in a 60°C oven to remove all the water. Glassy carbon electrodes (GCEs) were polished to a mirror-like finish using 0.3, and 0.05-micron alumina powder respectively. GCEs were then washed with distilled water and anhydrous ethanol. Three-electrode system was utilized with GCE as the working electrode and a Pt wire as a counter electrode with a Ag/AgCl reference electrode. Before measurement, the hydrogel was combined with 1xPBS (pH 7.4) and 100 mM KCl. In the defined time increments, clean blank GCEs were exposed to the hydrogels in buffer to perform DPV at a pulse amplitude of 50 mV, a pulse width of 0.2 s, and a pulse period of 0.5 s.

Results and Discussion

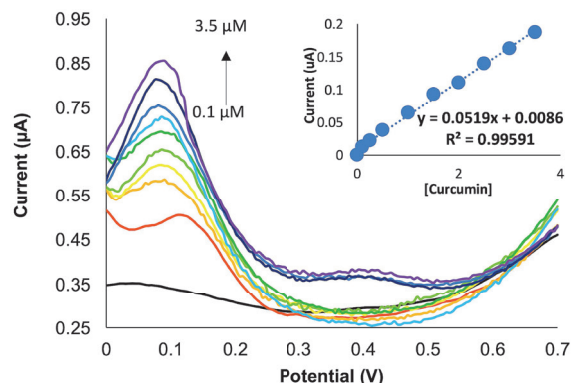


Fig. 4A. Differential pulse voltammograms of curcumin at different concentrations using GCE in 1xPBS (pH 7.4) with 100 mM KCl (blank signal in black). The inset shows the calibration curve.

As shown in Fig. 4A, I_{pa} peak correlates to the electrochemical oxidation of curcumin at 0.9 V (vs. Ag/AgCl), which showed linear relationship with concentration. The limit of detection was determined as 100 nM.

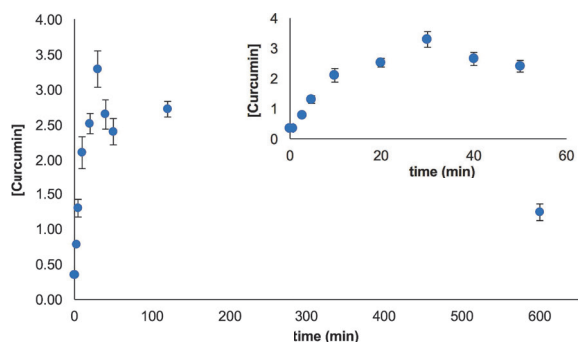


Fig. 4B. Release of 10 μ M curcumin from PAA-MBA polymer in acetonitrile 1 x PBS (pH 7.4) solution from 0 to 10 h (inset shows the time range from 0 min to 60 min, $n=3$)

As summarized in Fig. 4B, a sharp increase of curcumin release was observed from 0 to 30 min. After 40 min, electrochemical signals slowly decreased. This was attributed to the hydrolysis of curcumin within the aqueous environment. However, the signals remained constant after 24 h. Since the peak potential did not significantly shift, we hypothesized that PAA-MBA hydrogel was able to suppress the degradation of curcumin and sustained the releasing process.

Conclusions

In this work, a novel PAA-MBA hydrogel was shown to maintain a sustained release of curcumin into the buffer solution. Results indicated PAA-MBA was able to prevent hydrolysis of curcumin prior to release. Our electrochemical approach enabled a rapid and cost-effective chemical sensor to detect and monitor curcumin release process from a novel high-swelling hydrogel.

References

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