RETICULAR COVALENT ORGANIC FRAMEWORK MODIFIED PRINTED ELECTROCHEMICAL STRIPS FOR DECENTRALISED BIOMONITORING OF PARAQUAT AND CARBENDAZIM IN URINE

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Occupational exposure to pesticides remains a persistent health concern for rural workers. However, routine biomonitoring is still constrained by laboratory-centred workflows, logistics, and sample processing. We report a flexible, screen-printed electrochemical strip platform modified with a reticular covalent organic framework (COF), RIO17. The device is designed for decentralised, non-invasive testing of two widely used agrochemicals, paraquat and carbendazim, in untreated urine. RIO17 is employed as an interface-engineering nanomaterial that combines permanent porosity with tunable surface chemistry. The COF coating is designed to facilitate analyte adsorption at the interface and to improve interfacial electron transfer. This is attributed to complementary non-covalent interactions, including hydrogen bonding, p–p interactions, hydrophobic interactions, and electrostatic attractions. The intrinsic porosity of the COF is also expected to facilitate ion access to the electrode surface, thereby accelerating reaction kinetics and improving measurement repeatability. Collectively, these features are intended to improve signal definition and measurement repeatability in complex matrices. The strip architecture is fabricated on polyethylene terephthalate using scalable screen

printing of carbon and silver electrodes. The working electrode is conditioned electrochemically, followed by deposition of an aqueous RIO17 dispersion. Materials and device characterisation support the formation of a porous COF coating on the printed electrode. The coating increases the effective interfacial area and facilitates charge transfer at the sensing interface. Square-wave voltammetry enables the simultaneous readout of both pesticides within a single scan. The assay operates with a small sample volume of 100 µL. It does not require urine pre-treatment or dilution. Analytical performance in synthetic urine spans 0.05 to 10 µM for each analyte. The limits of detection are 0.01 µM for paraquat and 0.05 µM for carbendazim. Selectivity was evaluated against glucose and uric acid, as well as lactate, nitrate, nitrite, amoxicillin, fipronil sulfone, 2,4-D, and glyphosate. The responses showed only minor changes in the paraquat and carbendazim signals, supporting discrimination under urine-relevant conditions. Clinical-context validation is demonstrated using urine samples from nine rural workers. At least one of the target pesticides is detected in every individual. This finding reinforces the need for practical on-site exposure assessment tools. Overall, the study shows that incorporating the reticular COF RIO17 into printed electrodes improves charge-transfer characteristics and enables robust, simultaneous voltammetric readout of paraquat and carbendazim in urine. This provides a concrete basis for using COF coatings to engineer matrix-tolerant, deployable electrochemical strips for pesticide biomonitoring.

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Palavras-chave: covalent organic frameworks (cofs); printed electrochemical sensors; square-wave voltammetry; pesticide biomonitoring; urine analysis.