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Metal-Organic Framework (MOF)-based Materials for Electrochemical Sensing

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Summary:
Metal-Organic Frameworks (MOFs) are widely explored in electrochemical sensing due to their high surface area, tunable porosity, and structural versatility. In this work, MOF-derived hybrid materials were investigated for their potential in electrochemical applications. These materials preserve the hierarchical framework of the precursor MOFs while exhibiting enhanced electrical conductivity, making them promising candidates for the development of highly sensitive electrochemical sensors. Their performance in detecting target analytes in aqueous media, including heavy metal ions, was assessed using differential pulse anodic stripping voltammetry (DPASV), demonstrating their potential for environmental monitoring.

Keywords: Electrochemical sensors, MOFs, MOF-derived hybrid materials, Heavy metals.

Background, Motivation and Objective

Metal-Organic Frameworks (MOFs) are a class of hybrid organic-inorganic crystalline materials characterized by a periodic arrangement of metal clusters interconnected by organic linkers [1]. This highly tunable structure results in materials with exceptionally high surface area, well-defined porosity, and diverse chemical functionalities, making them ideal candidates for applications ranging from gas storage and catalysis to drug delivery and chemical sensing [2]. The ability to control their composition at the molecular level enables the design of MOFs with tailored adsorption properties and specific interactions with target analytes. However, their low conductivity limits direct electrochemical applications. A possible strategy to overcome this limitation is the pyrolysis of MOFs to obtain carbon-derived materials, which preserve the porous structure of the original MOFs while enhancing electrical conductivity and stability in aqueous environments [3]. These features make them ideal for electrochemical sensing. For example, carbon-based ZIF-8 modified with bismuth has been successfully employed for the detection of Cd(II) and Pb(II), owing to their hierarchical porosity and high surface area [4]. Electrochemical techniques are widely employed for the sensitive and selective detection of metal ions in solutions [5]. In this study, differential pulse anodic striping voltammetry (DPASV), known for its low detection limits and high sensitivity [6], is used to evaluate the sensing performance of MOF-derived hybrid materials, with a particular focus on detecting cadmium and lead in aqueous solutions. The conductive properties of these materials enhance charge transfer, while their porous structure facilitates analyte diffusion, resulting in improved detection limits. ZIF-8 was selected as the MOF precursor due to its high surface area and porosity, which contribute to its effectiveness in sensing applications. This approach, however, can be extended to other MOFs, which will be explored in future work.

Method

ZIF-8 was synthesized using a hydrothermal approach, with Zn^{2+} as the metal and 2-methylimidazole as the ligand, using water as the solvent. ZIF-8 was subjected to a pyrolysis process in a nitrogen atmosphere for one hour to obtain the corresponding carbon-based hybrid material. This material was characterized using X-ray diffraction, and electrochemical techniques including cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS). For sensor fabrication, a suspension of the corresponding MOF-derived hybrid material in Nafion solution was drop-casted onto the working electrode surface of a screen-printed electrode (SPE) producing a uniform coating of the sensitive material. To evaluate the sensing performance, DPASV was performed in a buffer solution containing 20 mM H_2SO_4 and 30 mM KCl.

Results

The electrochemical analysis of ZIF-8-derived carbon-based material performed by DPASV technique aimed to the quantitative determination of cadmium and lead ions in model solutions. From Figure 1 can be seen that as the concentration increases, the intensity of the oxidation peak current signal continuously increases. The corresponding calibration curve was constructed to assess the sensor response across a concentration range of 2 to 10 µM, as shown in Figure 2. The sensor demonstrated a reliable linear relationship between analyte concentration and its corresponding signal, enabling accurate detection within this range.

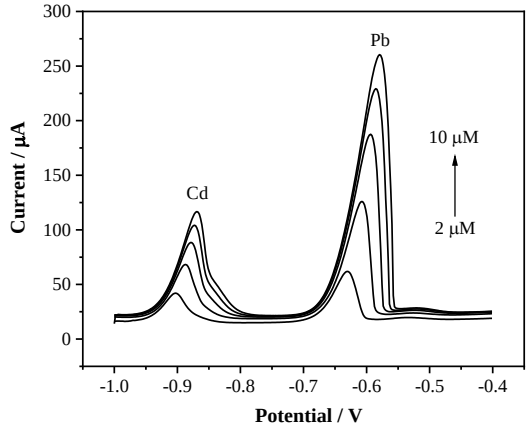

Fig. 1. DPASV response of ZIF-8-derived carbon-based material for detection of Cd(II) and Pb(II).

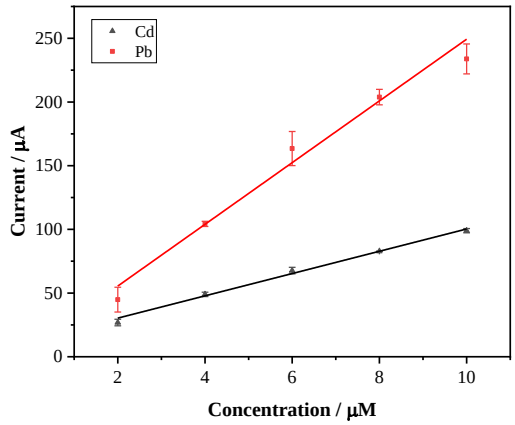

Fig. 2. The corresponding linear plots of Cd(II) and Pb(II).

The formula for the calculation of the limit of detection (LOD) from a calibration curve is as follows:

$$LOD = \frac{3.3\sigma_{blank}}{m} \quad (1)$$

Where σ_{blank} is the standard deviation of the blank, representing the variability in measurements of a sample with no analyte, indicating the background noise. The slope of the calibration curve is the rate of change in the current (I) with respect to the analyte concentration (C), obtained from the linear regression of the calibration data. The detection limits (LOD) for Cd(II) and Pb(II) obtained from the electrochemical analysis DPASV using the ZIF-8-derived carbon-based material were below 0.05 µM and 0.007 µM, respectively. These values are comparable and, in some cases, lower than those estimated implementing classical carbon-based materials. These preliminary results demonstrate the suitability of the MOF-derived hybrid materials in the development of sensors for the determination of heavy metals in aqueous solutions, with potential applications in environmental monitoring.

References

[1] L. Jiao, J. Y. R. Seow, W. S. Skinner, Z. U. Wang, H.-L. Jiang, Metal–organic frameworks: Structures and functional applications, *Materials Today* 27, 43-68 (2019); doi: 10.1016/j.mattod.2018.10.038

[2] B. Li, H.-M. Wen, Y. Cui, W. Zhou, G. Qian, B. Chen, Emerging Multifunctional Metal–Organic Framework Materials*, Adv. Mater.* 28, 8819-8860 (2016); doi: 10.1002/adma.201601133

[3] J. M. Gonçalves, P. R. Martins, D. P. Rocha, T. A. Matias, M. S. S. Julião, R. A. A. Munoz, L. Angnes, Recent trends and perspectives in electrochemical sensors based on MOF-derived materials, *J. Mater. Chem. C* 9, 8718–8745 (2021); doi: 10.1039/d1tc02025k

[4] L. Xiao, H. Xu, S. Zhou, et al., Simultaneous detection of Cd(II) and Pb(II) by DPASV at a nitrogen-doped microporous carbon/Nafion/bismuth-film electrode *Electrochim. Acta*, 143, 143-151 (2014); doi: 10.1016/j.electacta.2014.08.021

[5] D. Shi, W. Wu, X. Li, Multiplexed detection of aqueous Cd2+, Pb2+ and Cu2+ ions at mercury-on-graphene film modified electrode by DPASV, *Sens Biosensing Res* 34 100464 (2021); doi: 10.1016/j.sbsr.2021.100464

[6] F.R. Simões, M.G. Xavier, Electrochemical Sensors*, Nanoscience Appl., Micro Nano Technol*. 6 155–178 (2017); doi: 10.1016/B978-0-323-49780-0.00006-5.

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