

Supporting Information

An Iron Metal-Organic Framework-based Electrochemical Sensor for Identification of Bisphenol-A in Groundwater Samples

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Reagents and Materials

A typical aqueous solution including 0.5 mM Bisphenol-A ((BPA, 97%) purchased from Alfa Aesar) was prepared and kept at 4 °C. Mono and disodium phosphate was shipped by Merck; FeCl₃.6H₂O, 98%; ferric (III) chloride, H3BTC, 98%; Benzene-1,3,5-tricarboxylic acid, Fluka, 5 Wt%; Nafion, K₃[Fe(CN)₆], 99%; potassium ferricyanide, supplied by Sigma-Aldrich. Chemicals of analytical quality have been implemented, although no additional refining processing has been carried out. All of the remedies were made utilizing deionized water with a resistance of not lower than 18.2 MΩ.cm being the medium.

Instrumentation Details

Implementing the KBr pellet technique, Fourier transform infrared (FT-IR) spectra in the 500–4000 cm⁻¹ range were gathered employing Thermo Scientific Nicolet iS5. Employing a Shimadzu (RF5301PC) spectrofluorometer, the manufactured samples' photoluminescence spectra were recorded. The material's optical characteristics were explored by incorporating a UV-vis spectrophotometer with BaSO₄ acting as a reference material (T90+ double beam, PG Instruments, UK). Fe-MOF sample's phase identification and crystalline structure were looked at using the wide-angle Rigaku D/max-2500 X-ray diffractometer. Cu-Kα radiation (~ 1.54 Å) was the source of radiation, and the voltage generated was 40 kV. The spectra were obtained in the 2-theta degree spectrum, which spans 10 degrees to 90 degrees, at an approximate rate of 2 degrees per minute. The elements were determined by utilizing an energy-dispersive analyzed X-ray spectrometer (EDAX, Oxford Inc.) coupled with an FE-SEM and bright elemental image mappings. Employing field emission scanning electron microscopy (FESEM model JEOL, JSM-6700F), high-resolution transmission electron microscopy (HR-TEM model FEI Tecnai G² F20 instrument guided at 300 kV), and chosen selected area electron diffraction (SAED), we examined the sample's surface form and the microscopic structure.

The electrochemical detection of BPA was performed using the CHI 650C electrochemical workstation (Austin, TX, USA), which is equipped with three electrodes: a platinum wire serving as the auxiliary electrode, an Ag/AgCl electrode saturated with KCl

acting as the reference electrode, and a glassy carbon electrode serving as the working electrode. These electrodes directly interacted with the analyte mixture within the electrochemical cell. The experiments were conducted under controlled conditions at $27 \pm 3^\circ\text{C}$.

Generation of Fe-MOF fabricated GC electrode

The electrochemical studies were conducted at the ambient temperature using a solution of PBS (0.1M; pH 7). The surface of our glassy carbon electrode (GCE) was meticulously polished by applying alumina ($\alpha\text{-Al}_2\text{O}_3$) slurries having pore dimensions of 1, 0.3, and 0.05 μm prior to testing. subsequently, Millipore water was utilized to disinfect the electrode. A 10 μL aliquot of generated Fe-MOF suspension (1 mg of Fe-MOF in 1 ml of D.I. water) was dropped onto the surface of pre-treated bare GC electrodes afterward it had been dried in the air at ambient temperature. Ultimately, before electrochemical assessments were made, every generated GCE was dried at room temperature, covered by a binder, and 2 μL of a Nafion mixture was added. For BPA oxidation, a bare GCE was also made as a benchmark.

Electrochemical detection conditions

The electrochemical impedance spectroscopy (EIS) investigation and the cyclic voltammetry (CV) technique were performed in a 10.0 mL mixture comprising 5 mmol/L of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 mol/L of KCl as electrochemical probes. CV was measured at a scanning rate of 50 mV/s in the potential region of -0.2 to 0.6 V. EIS was performed with an amplitude of 5 mV and a potential of 0.3 V, covering a frequency that ranges from 1 Hz to 100 kHz. Furthermore, in 5.0 mL of PBS (0.1 M, pH 7.0) with 1 mL of 60 μM /L BPA, CV observations were carried out in the range of +0.2 V to +1.0 V at a scan rate of 50 mV/s. Differential pulse voltammetry (DPV) was performed to assess various concentrations of BPA in a 5.0 mL PBS (0.1 M, pH 7.0) mixture. The measured values for the pulse width, quiescent duration, and period were 0.05 s, 2 s, and 0.5 s, respectively. With a scan speed of 10 mV/s, the scanning stretch was +0.2 V to +1.0 V. In a 5.0 mL PBS (0.1 M, pH 7.0) mixture comprising 60 μM /L BPA, square wave voltammetry (SWV) observations were performed at a scan rate of 25 mV/s, a frequency of 15 Hz, and a quiet time of 2 s, accordingly, in the range of +0.2 V to +1.0 V. Prior to the testing, nitrogen gas must be introduced to completely cleanse the electrolyte PBS buffer. At least three measurements have been made to determine the BPA concentration.

Real sample collection and analysis

For the collection of the actual water specimen from the interior of Trichy, Tamil Nadu, India, a random sampling technique was chosen. A 1 mL genuine sample was treated with the BPA standard, and the mixture was subsequently diluted in 5 mL of PBS buffer (0.1 molL^{-1}) at the ideal pH for the evaluation. Next, BPA amounts in the extracted specimens of water are found.

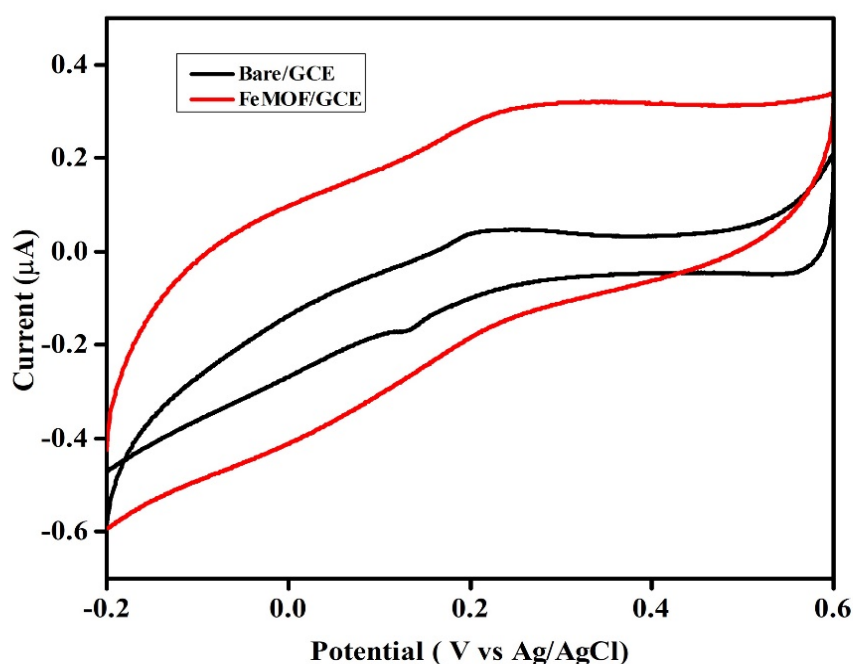


Figure S1: Assessment of all the bare and Fe-MOF-modified GC electrodes performing CV experiments in $5.0 \text{ mmol/L } [\text{Fe}(\text{CN})_6]^{3-/4-}$ including 0.1 mol/L KCl at a scanning speed of 50 mV/s .

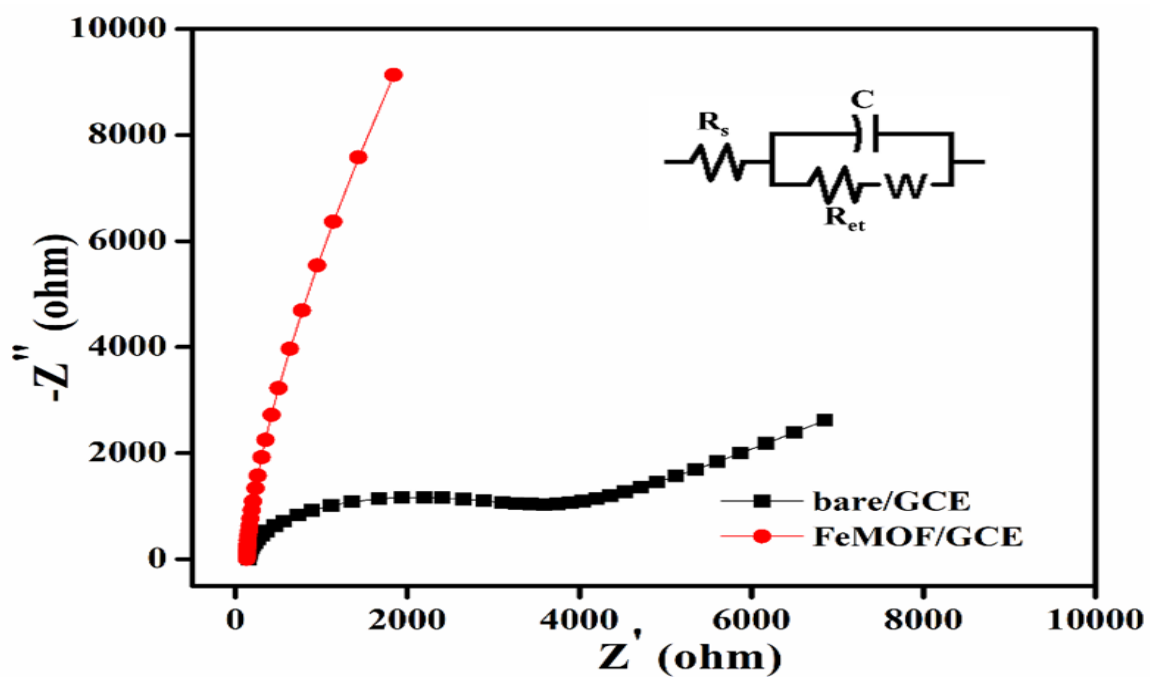


Figure S2: Complex impedance plots of bare and Fe-MOF modified GC electrodes in 5.0 mmol/L $[\text{Fe}(\text{CN})_6]^{3-/4-}$ comprising 0.1 mol/L KCl and (inset equivalent electrical circuit applied to fit the spectra).

Table ST1: Identification of BPA traces in real water samples by Fe-MOF modified GC electrode.

Samples	Added ($\mu\text{mol/L}$)	Original ($\mu\text{mol/L}$)	Found ($\mu\text{mol/L}$)	Recovery (%)
Real water sample	-	10	9.5 \pm 0.3	98.1
	10	20	19.8 \pm 0.1	99.3
	10	30	30 \pm 0.6	102.0
	10	40	40 \pm 0.5	101.2
	10	50	50 \pm 0.2	100.4