Sensitive Electrochemical Sensor Based On an Aminated MIL-101(Cr) MOF for the Detection of Tartrazine

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ABSTRACT: The aminated metal–organic framework H2N-MIL-101(Cr) was used as the carbon paste electrode (CPE) modifier for the determination of tartrazine (Tz) in soft drinks. The amino material was characterized by electrochemical impedance spectroscopy and showed significantly faster electron transfer with lower charge-transfer resistance (0.13 kΩ) compared to the electrode modified with the unfunctionalized MIL-101(Cr) material (1.1 kΩ). The H2N-MIL-101(Cr)-modified CPE [H2N-MIL-101(Cr)-CPE] was then characterized by cyclic voltammetry (CV) using [Fe(CN)6]3− and [Ru(NH3)6]3+ ions as the redox probes, showing good accumulation of [Fe(CN)6]3− ions on the electrode surface. A CV scan of Tz in Britton Robinson buffer solution revealed an irreversible system with an oxidation peak at +0.998 V versus Ag/AgCl/KCl. Using CV and differential pulse voltammetry, an electrochemical method for quantifying Tz in aqueous medium was then developed. Several parameters that affect the accumulation and detection steps were optimized. Optimal detection of Tz was achieved after 180 s of accumulation in Britton Robinson buffer solution (pH 2) using 2 mg of H2N-MIL-101(Cr)-CPE. Under optimal conditions, the sensor exhibited a linear response in the concentration range of 0.004–0.1 μM and good detection sensitivity (35.4 μA μM−1 cm−2), and the detection limit for Tz was found to be 1.77 nM (S/N = 3). Satisfactory repeatability, stability, and anti-interference performance were also achieved on H2N-MIL-101(Cr)-CPE. The sensor was applied to commercial juices, and the results obtained were approximately similar to those given by UV–vis spectrophotometry.

INTRODUCTION

Natural or synthetic dyes are often added to food and beverages to improve the appearance, flavor, texture, nutritional value, and shelf life of manufactured products.1 Compared to natural dyes, synthetic food dyes have seen widespread use because of their low cost as well as higher stability to light, heat, and pH variations. One of the most common synthetic azo dyes used in foodstuffs and drinks is tartrazine (Tz) (C16H9N4Na3O9S2, referred hereafter as Tz), a lemon yellow colored dye also known as E102 in the food industry.2 Unfortunately, excessive ingestion of Tz is associated with adverse effects such as allergic reactions, including asthma, chronic hives, and hyperactivity in children.3

The recommended acceptable intake of Tz is 7.5 mg/kg body weight per day, and the maximum Tz content of 150 μg/g in milk-based desserts, 200 μg/g in candied fruits and vegetables, and 100 μg/mL are permissible in soft drinks as prescribed by international organizations.4 In view of risks associated with its abusive consumption, various methods have been developed for the determination of Tz, including chromatographic methods,5,6 spectrophotometry,7,8 and capillary electrophoresis.9,10 Due to their excellent sensitivity, short analysis time, low energy consumption, and inexpensive equipment, electrochemical techniques are also increasingly being used and show promising applications in food safety analysis.11 Various types of electrochemical sensors that have already been developed include sensors based on zinc oxide nanoparticles,12 gold nanoparticles,13 graphitic carbon nitride,14 and carbon nanotubes.15 More recently, sensors based on metal–organic frameworks (MOFs) have been introduced, taking advantage of the resultant increased electrode surface area and mass transport, as well as rapid electron transfer.16,17

MOFs are crystalline porous hybrid materials, consisting of metal cluster nodes which are bridged by polytopic organic ligands. Owing to the tunability of their structure as well as their pore surface chemistry via a linker or metal-cluster functionalization, MOFs show promising applications in many fields. These applications include gas storage, capture and separation; catalysis; heat transformation; and electroanaly-
In particular, the chromium(III) terephthalate MOF denoted as MIL-101(Cr) has previously been reported as an excellent electrode material for the detection of analytes like ascorbic acid (AA) and sulfites. In addition to its huge surface area (up to 4000 m$^2$ g$^{-1}$), presence of coordinatively unsaturated Cr sites (CUS), and hydrothermal and chemical stability, MIL-101(Cr) features a mesoporous structure to accommodate large-sized/bulky analytes like Tz. Moreover, functionalization of its framework with an organic group like the amino group could further improve the sensitivity and/or selectivity of the electrode. Amino functionalization of MOFs demonstrated to improve adsorptive properties toward the uptake of target molecules such as methyl orange, p-nitrophenol, and CO$_2$. Herein, we report the electrochemical detection of Tz using a carbon paste electrode (CPE) modified with the amino-functionalized MOF H$_2$N-MIL-101(Cr). The electrode response was compared with the signals recorded on the bare CPE and H$_2$N-MIL-101(Cr)-CPE in order to highlight the specific input of amino functional groups in the detection of Tz. The obtained H$_2$N-MIL-101(Cr)-CPE electrode was optimized and then successfully applied for the determination of Tz in commercial soft drink samples.

## RESULTS AND DISCUSSION

**Synthesis and Characterizations.** Upon synthesis, the aminated MOF was structurally characterized by X-ray diffraction (XRD), IR spectroscopy, and N$_2$ sorption experiments [Brunauer–Emmett–Teller (BET) method]. As shown by Figure S1 (Supporting Information), its powdered pattern matched well with the simulated MIL-101(Cr) curve, characterized by a well-established crystallinity, which is usual for this mesoporous material. The diffraction peaks and the XRD pattern of NH$_2$-MIL-101(Cr) were in good agreement with those reported previously, indicating the successful synthesis of NH$_2$-MIL-101(Cr).

As shown by Figure 1a, the Fourier transform infrared (FT-IR) spectra of H$_2$N-MIL-101(Cr) and MIL-101(Cr) materials exhibited similar absorption bands in the range 1500–400 cm$^{-1}$; while additional bands appeared between 3200 and 3500 cm$^{-1}$, at 1621 and 1340 cm$^{-1}$ for H$_2$N-MIL-101(Cr). The double bands at 3490 and 3383 cm$^{-1}$ were assigned to the asymmetric and symmetric stretching vibrations of −NH$_2$, while the bands at 1621 and 1340 cm$^{-1}$ were attributed to the N–H bending vibration and C$_{atom}$−N stretching, respectively. This is consistent with the amino functionalization of H$_2$N-MIL-101(Cr) with respect to unmodified MIL-101(Cr) as also reported in other works.

Nitrogen sorption experiments conducted on MIL-101(Cr) and H$_2$N-MIL-101(Cr) at 77 K yielded type Ib isotherms for MIL-101(Cr) and pore volume of 0.65 cm$^3$ g$^{-1}$ for H$_2$N-MIL-101(Cr). The decrease in the specific surface area and pore volume in H$_2$N-MIL-101(Cr) material was attributed to the steric occupation of the pores by −NH$_2$ groups. All data obtained for the comparative characterization of MIL-101(Cr) and H$_2$N-MIL-101(Cr) indicated the successful modification by grafting of the pristine MOF.

**Electrochemical and Morphologic Characterization of Modified Electrodes.** Multisweep cyclic voltammetry was applied to investigate the charge selectivity properties of the MIL-101(Cr) MOFs before and after its modification. Thus, unmodified CPE, MIL-101(Cr)-CPE, and H$_2$N-MIL-101(Cr)-CPE were prepared and tested in 0.1 M KCl (at pH 2) toward the accumulation of [Fe(CN)$_6$]$^{3-}$ and [Ru(NH$_3$)$_6$]$^{3+}$ electroactive probes, as shown in Figure 2.

One can observe in Figure 2a that, by continuously cycling, [Fe(CN)$_6$]$^{3-}$ ions were progressively accumulated on H$_2$N-MIL-101(Cr)-CPE as the anodic ($I_a$) and cathodic ($I_c$) currents increased between cycles. Upon saturation, the anodic and cathodic peak currents recorded on H$_2$N-MIL-101(Cr)-CPE were 260.1 and 259.5 µA, respectively. These values were greater than those measured on MIL-101(Cr)-CPE ($I_a = 132.9$ µA and $I_c = 115.9$ µA) and on bare CPE ($I_a = 89.7$ µA and $I_c = 89.6$ µA) (Figure 2b). This difference was explained by the electrostatic attraction between the protonated NH$_4^+$ groups on H$_2$N-MIL-101(Cr) and the negatively charged [Fe(CN)$_6$]$^{3-}$ ions. By replacing [Fe(CN)$_6$]$^{3-}$ by [Ru(NH$_3$)$_6$]$^{3+}$ ions, performing the same experiment (Figure S2a, Supporting Information) yielded stable voltammograms with peak current values of 34.5 µA ($I_a$) and 46.2 µA ($I_c$), suggesting no uptake of the cationic probe. Even on MIL-101(Cr)-CPE, similar results were obtained (Figure S2b, Supporting Information). This behavior (non-accumulation) was ascribed to the repulsion between [Ru(NH$_3$)$_6$]$^{3+}$ ions and protonated amine groups on H$_2$N-MIL-101(Cr), as described by previous works performed using aminated clay minerals. These results clearly show that H$_2$N-MIL-101(Cr) materials could be applied as an electrode material for the electrochemical detection of anionic compounds. It was further used to build a sensor for analysis of Tz.

The morphology of the CPE before and after its modification in turn by MIL-101(Cr) and H$_2$N-MIL-101(Cr) was studied by scanning and transmission electron microscopy (STEM) combined with energy-dispersive X-ray
spectroscopy (EDX). As shown by Figure S3 (Supporting Information) and EDX data, the STEM image for the unmodified CPE was very bright due to the high amount of carbon (96.77 %At by EDX). The STEM−EDX of MIL-101(Cr)-CPE showed mainly the presence of carbon (particles with less contrast) and chrome, while H2N-MIL-101(Cr)-CPE showed agglomerated nanoparticles, probably Cr-NPs as compared with powder X-ray diffraction results.

The active surface areas of all the prepared working electrodes were evaluated by analyzing the cyclvolttammograms of these electrodes, recorded in 0.1 M KCl + 1 mM \([\text{Fe(CN)}_6]^{3-}\) using H2N-MIL-101(Cr)-CPE (a) and MIL-101(Cr)-CPE (b). The dot red line in b corresponds to the bare CPE.

Figure 2. Multisweep cyclic voltammograms recorded at 50 mV s\(^{-1}\) in 0.1 M KCl solution containing 1 mM \([\text{Fe(CN)}_6]^{3-}\) using H2N-MIL-101(Cr)-CPE (a) and MIL-101(Cr)-CPE (b). The dot red line in b corresponds to the bare CPE.

Figure 3. Nyquist diagrams recorded in 0.1 M KCl containing 1 mM \([\text{Fe(CN)}_6]^{3-/4-}\) on CPE (a), MIL-101(Cr)-CPE (b), and H2N-MIL-101(Cr)-CPE (c).

Electrochemical Behavior of Tz and Effect of Detection Medium. The redox behavior of Tz, investigated by CV on all prepared electrodes is shown on Figure 4. On these electrodes, Tz exhibited an irreversible anodic peak around +0.998 V. The peak intensity (12.40 μA) obtained on the H2N-MIL-101(Cr)-CPE (Figure 4a) was 1.19 and 1.40-fold greater than those obtained on MIL-101(Cr)-CPE (\(I_{pa} = 10.46\) μA, Figure 4b) and CPE (\(I_{pa} = 9.19\) μA, Figure 4c). As explained in the previous section, this result was assigned to favorable electrostatic attractions between Tz and \(\text{H}_2\text{N-MIL-101(Cr)}\) materials. The obtained result indicated that H2N-MIL-101(Cr) has improved the electro-oxidation of Tz. Because the detection medium usually plays an important role in the sensitivity of each electrochemical method, the effect of the nature of detection solution was investigated.

Thus, three media at the same concentration were tested: phosphate buffer, Britton Robinson buffer, and acetate buffer solutions, in the presence of 0.4 mM Tz. Figure S5 (Supporting Information) shows a CV of 0.4 mM Tz on H2N-MIL-101(Cr)-CPE in these three media at pH 4. The
results show a better anodic peak current with Britton Robinson buffer solution, which was chosen as the detection medium for subsequent experiments.

**Effect of Potential Scan Rate.** In order to identify the transport process of the analyte at the surface of H$_2$N-MIL-101(Cr)-CPE, the influence of the potential scan rate on the electrochemical response of Tz was studied by CV. As can be seen in Figure 5, the anodic peak current ($I_{pa}$) increased with the scan rates ($v$) in the studied range (10−100 mV s$^{-1}$) (Figure 5a), while a linear dependence was observed between $v^{1/2}$ and $I_{pa}$ (Figure 5b), expressed by eq 1

$$I_{pa} = 2.349 \times v^{1/2} - 2.461 (R^2 = 0.996) \quad (1)$$

This indicated a diffusion-controlled process that was also confirmed by plotting the double logarithm of $I_{pa}$ versus $v$ (see Figure S6a, Supporting Information) characterized by a slope of 0.59 greater than the expected 0.5, the indicative and significant value for a diffusion-controlled electron-transfer mechanism. One can conclude that the electro-oxidation of Tz is a mixture of absorption and diffusion-controlled processes with diffusion predominating. Also, the presence of a non-zero intercept point (~2.461) on the $y$-axis ($I_{pa}$ vs $v^{1/2}$) indicated and confirmed the presence of some adsorption process associated with the diffusion-controlled electron-transfer mechanism. With the increase of scan rate, the oxidation peak potentials ($E_p$) moved to the positive direction. The peak potential ($E_p$) was linearly proportional to $\log v$ (Figure S6b, Supporting Information), according to eq 2

$$E_p = 1.08 + 0.026 \log v (R = 0.983) \quad (2)$$

Confronting eq 2 with the Laviron’s eq 3 for an irreversible electrode process$^{33}$ allowed to obtain some kinetics parameters such as $\alpha$ (transfer coefficient) and the standard rate constant of the reaction $k^0$ (cm s$^{-1}$).

$$E_p = E^0 + \frac{2.303 \Delta F}{n} \log \left( \frac{RTF}{a_nF} \right) + \frac{2.303 \Delta F}{a_nF} \log v$$

$n$ is the number of electrons transferred, $v$ is the scan rate, and $E^0$ is the formal redox potential. From the slope of $E_p$ vs $\log v$, $an$ was calculated to be 2.31.

Bard and Faulkner equation: $\alpha = 47.7/(E_p - E_{p/2})$ was used for the calculation of $\alpha$. From the above-mentioned equation, $\alpha = 1.4$, while the number of electrons transferred was $1.65 \approx 2$.

**Effect of the Amount of H$_2$N-MIL-101(Cr) in the CPE.** The optimal mass of H$_2$N-MIL-101(Cr) within the CPE is a key data for the best response of the sensor. Hence, several H$_2$N-MIL-101(Cr)-CPEs were prepared, containing 0, 1, 2, 3, 4, and 5 mg of MIL-101(Cr)—NH$_2$, corresponding to 0, 2, 4, 6, 8, and 10% wt MIL-101(Cr)—NH$_2$. Afterward, they were tested for the determination of Tz. As shown in Figure 6, there was a significant increase in peak current up to 2 mg of H$_2$N-MIL-101(Cr), followed by a slight decrease in the electrode response as the amount of H$_2$N-MIL-101(Cr) increased. The increase in peak current was probably due to the augmentation of binding sites on the electrode surface, available to bind more Tz molecules. The decrease in peak current observed above 2 mg was obviously due to the decrease in the conductivity of the electrode. For further experiments, the percentage of H$_2$N-MIL-101(Cr) in the CPE was kept at 4% wt.

**Effect of pH on the Peak Current and Potential.** To select the suitable pH value for Tz electrochemical determination, the pH of Britton Robinson buffer solution employed as a detection medium was varied between 2 and 9 (Figure 7). It was observed that the signal of Tz oxidation is highly dependent on the acidity of the supporting electrolyte (Figure 7a). The best electrode signal was obtained at pH 2, while the electro-oxidation of Tz became less significant with an increase in pH as protons are directly involved in the redox reaction at a H$_2$N-MIL-101(Cr) sensor. Moreover, the peak potential of Tz shifted toward more negative values with the increase in pH [curve (ii), Figure 7b] in accordance with the following equation: $E_p = 1.454 - 0.03$ pH ($R^2 = 0.997$). The value of the
slope (−0.03 V/pH) not close to the theoretical Nernstian value of (−0.059 V/pH) suggested that the number of electrons involved in the oxidation of Tz is different from the number of protons. Clearly, it appeared that two electrons and one proton are involved in the oxidation of Tz, as proposed in Scheme 1. As the pH of the supporting electrolyte increased, the anodic peak current of Tz decreased [Figure 7b see curve (i)]. Interestingly, the peak current rose to the maximum value (19.63 μA) at pH 2. It is known that Tz presents two strong sulfonic acid groups (pK_a = 2), one acetate weak acid group (pK_a = 5), and one azo group (pK_a = 10.86).35 From pH 2 to 5, the azo group is protonated and the two strong sulfonic acid groups are deprotonated, a charge of Tz is 1−. After pH 5 (and up to 9), the charge is 2− with deprotonation of acetate acid group and the molecule is highly hydrophilic.

In acidic media, the oxidation process is facilitated due to easy protonation of the azo group resulting in the decreased electron density and thus in the increased voltammetric signal. On the other hand, the highly improved voltammetric signal over aminated MIL-101(Cr) could be explained similarly, together with a possible ion–dipole interaction between the −SO_3^− anionic group of Tz and the −NH_2^+ protonated function of H_2N-MIL-101(Cr).

Scheme 1. Proposed Electrochemical Reaction of Tz at H_2N-MIL-101(Cr)-CPE

At higher pH values, the net charge is increased (1− to 2−) and Tz is not adsorbed on the electrode surface, due to the electrostatic repulsion between the deprotonated two sulfonic acid (−SO_3^−), one acetate acid (−COO^−) group present on Tz, and electron pairs of oxygen in the hydroxy of terephthalic acid.

Because 0.1 M BRBS (pH 2) was the optimum pH, this medium was used in all further experiments. Effect of the Accumulation Time. Accumulation time is another useful parameter in electrochemical analysis. It was investigated and Figure 8 shows a rapid response of the electrode with a peak current of 19.6 μA after 10 s of accumulation. Afterward, the peak intensity was stabilized due to saturation of the fixation sites on the electrode surface. 180 s was therefore chosen as the optimal time for further investigation.

Calibration Curve. Keeping the optimized experimental conditions, differential pulse voltammetry (DPV) was performed to establish the relationship between the peak current and the concentration of Tz at H_2N-MIL-101(Cr)-CPE. Figure 9 shows the corresponding i-E curves: the oxidation peak current increased with increasing concentration of Tz in the range of 0.004 to 0.1 μM. The plot of anodic peak current as a function of Tz concentration was linear, as shown by the inset in Figure 9. The calibration curve followed the equation I_p (μA) = 0.908 + 35.4[Tz] (μM), with a correlation coefficient of 0.999. A sensitivity of 35.4 μA μM⁻¹ obtained
Experiments were performed in triplicate. The lowest values reported for Tz detection (Table 1), which reveals that a H2N-MIL-101(Cr)-CPE electrochemical sensor is sensitive for the determination of Tz. The limit of detection (LOD) corresponds to the lowest concentration of an analyte that can be detected. Based on a signal-to-noise ratio of 3, a LOD of 0.004 μM was obtained using the equation LOD = 3 S/m, where S is the standard deviation of blank and m is the slope of the regression line. The obtained LOD is one of the lowest values reported for Tz detection (Table 1), which reveals that a H2N-MIL-101(Cr)-CPE electrochemical sensor is sensitive for the determination of Tz.

Figure 9. DPV responses recorded on H2N-MIL-101(Cr)-CPE in 0.1 M BRBS (pH 2) containing Tz at different concentrations: (a=1): 0.004–0.1 μM. Inset shows the corresponding calibration graph. Experiments were performed in triplicate.

Table 1. Comparison of the Performance of Some Tz Sensors Based on Modified Electrodes

| electrode configuration          | method   | detection medium (pH) | detection limit (μM) | ref |
|----------------------------------|----------|-----------------------|----------------------|-----|
| gold nanoparticles/CPE           | DPV      | PBS (4.0)             | 0.002                | 13  |
| g-C3N4/graphite                  | DPV      | PBS (2.1)             | 0.21                 | 14  |
| MWCNTs/GCE                       | DPV      | PBS (7.0)             | 0.22                 | 35  |
| Gr/PLPA/PGE                      | DPV      | PBS (7.0)             | 0.154                | 38  |
| hemin/GCE                        | SWV      | PBS (7.4)             | 0.36                 | 39  |
| MIP/GCE                          | SWV      | PBS (7.0)             | 0.001                | 40  |
| H2N-MIL-101(Cr)-CPE              | DPV      | PRBS (2.0)            | 0.00177              | this work |

*a-g-C3N4: graphic carbon nitride. b-MWCNTs: multiwalled carbon nanotubes. Gr/PLPA/PGE: graphene/poly(1-phenylalanine)/pencil graphite electrode. SWV: square wave voltammetry. MIP: molecularly imprinted polymer.

The stability and reproducibility of the proposed aminated MOF-modified electrode were also checked by measuring within days and for 5 successive days the signal (5 replicates) of 0.02 mM Tz in 0.1 M BRBS (pH 2.0). The voltammograms obtained (Figure S7, Supporting Information) evaluated the relative standard deviation at 3.5%, indicating an acceptable level of sensor reproducibility.

Interference Study and Analytical Application. The influence of potential interfering compounds such as AA, citric acid (CA), sodium benzoate, sodium sulphite, tartaric acid (TA), lactose, gallic acid (GA), curcumin (CUR), and butylated hydroxyanisole (BHA) at known concentrations (0.2, 2, 10, and 20 μM) on an oxidation peak current of 2 μM Tz in 0.1 M BRBS (pH 2) at H2N-MIL-101(Cr)-CPE was examined. The results obtained are presented in Table 2. The tolerance limit was considered to be the concentration ratio of the additive to Tz causing a relative error of less than 5.0%. The results in Table 2 show that the tolerance limits of Tz in the presence of 1-fold of BHA, 5-fold of lactose, and 10-fold of sodium sulfithe, Ca2+, and Cl− were less than 5%, implying that the proposed modified electrode possessed excellent anti-interference ability and good selectivity.

Meanwhile, the oxidation peak of Tz was strongly affected by the presence of AA, CA, sodium benzoate, and GA. Thus, a sensor described herein is not advisable for media containing such compounds.

Finally, a H2N-MIL-101(Cr)-CPE sensor was applied to the quality control of soft drinks from two different companies. The results obtained are presented in Table 3. For comparison purposes and to validate the developed electroanalytical method, Tz content of these samples was also determined by UV−vis spectrophotometry. In this experiment, the concentration of Tz was calculated using the standard addition method.

From the results obtained (Table 3), it can be noticed that the data from UV−vis spectrophotometry and voltammetric determinations are of the same order of magnitude, as the difference between the mean values is not significant.

According to European standards, the maximum amount of Tz present in soft drinks should be 100 mg L−1. The results of these analyses, therefore, show the compliance with the standards by both companies. These results confirm the usefulness of the method and the sensor proposed herein.

## CONCLUSIONS

In this work, a sensitive amperometric sensor based on the aminated H2N-MIL-101(Cr)-modified CPE was proposed for the detection of Tz. The proposed sensor displayed great affinity toward the quantification of Tz, allowing its detection at the lowest concentration of 1.77 nM. Nevertheless, the H2N-MIL-101(Cr)-CPE sensor showed interesting analytical performance, good stability, and reproducibility and may constitute an analytical tool of choice for the determination of Tz. Finally, MOF-modified electrodes could be used to create
smart devices for the sensing of biomolecules and other compounds, with a high level of reliability.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01106.

Chemicals, materials, and procedures; synthesis of MIL-101(Cr) and H$_2$N-MIL-101(Cr); physico-chemical characterization; preparation of modified CPEs; electrochemical equipment and procedures; powder XRD analysis; STEM analyses; electrochemical characterization of modified electrodes using [Ru(NH$_3$)$_6$]$^{3+}$ ions; electroactive surface area determination; effect of detection medium; effect of potential scan rate; and reproducibility of H$_2$N-MIL-101(Cr)-CPE (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors, who have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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