

The potential of electrochemistry for one-pot and sensitive analysis of patent blue V, tartrazine, acid violet 7 and ponceau 4R in foodstuffs using IL/Cu-BTC MOF modified sensor

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ABSTRACT

Since excessive use of synthetic dyes has negative effects on human health, their determination in foodstuff is necessary. A sensitive sensor was developed based on copper BTC metal–organic framework (Cu-BTC MOF) and 1-ethyl-3-methylimidazolium chloride as an ionic liquid (IL) in an attempt to modify the carbon paste electrode and to improve the active surface area and electric conductivity so that electron transfer is faster for electro analysis. For the first time, high sensitivity, excellent conductivity, and appropriate selectivity of the electrochemical sensor have been evaluated as a new study for simultaneous determination of tartrazine, patent blue V, acid violet 7 and ponceau 4R. Excellent sensing performance of the proposed electrode was confirmed for patent blue V as an outstanding sensor, according to the low limit of detection of 0.07 μM , with a wide linear concentration range of 0.08 to 900 μM and reasonable recovery. In order to characterize the electrochemical behavior of electrode, cyclic voltammetry, differential pulse voltammetry, and electrochemical impedance spectroscopy are used. Various techniques such as scanning electron microscopy (SEM) with energy dispersive X-Ray analysis (EDX), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) are employed to verify the structure of copper BTC metal–organic framework. The results revealed close packing of hierarchically porous nanoparticles and crystal structure of Cu-BTC MOF, with the edge of each particle around 20–37 nm. The analytical performance of the suggested electrochemical sensor is acceptable in foodstuffs such as jellies, condiments, soft drinks, and candies.

1. Introduction

Excessive consumption of synthetic dyes in foodstuffs like drinks, sweets and syrups is one of the most harmful threats to human health due to the presence of the azo compound (Bijad et al., 2017). This compound can cause adverse effects with the possibility of inducing cytotoxicity, toxicity, childhood hyperactivity, genotoxicity and even cancer (Zhang et al., 2015; Villasen, 1999; Akbarian et al., 2018; Bijad et al., 2017; Darabi & Shabani-nooshabadi, 2021; Ntrallou et al., 2020; Tahernejad-Javazmi et al., 2018, 2019; Villasen, 1999; Zhang et al., 2014). The determination of synthetic dyes in food and drug products has become an analytical challenge due to their excessive consumption. Patent blue V is a triarylmethane dye generally used in food (drinks, ice-creams, sweets, yogurts, beverages, etc.) and cosmetics industries

(Duman et al., 2020). The two inner salt forms (calcium and sodium), exist in the structure of patent blue V (Opinion, 2013) which can cause considerable problems and human sensitivity such as headache, asthma and allergic reactions. Up to now, many analytical methods such as gas chromatography, liquid chromatography, capillary electrophoresis, ultraviolet–visible spectroscopy, capillary electrophoresis, voltammetry and mass spectroscopy have been studied in order to analyze patent blue V in foodstuff and cosmetic products quantitatively (Beltran, 2000; Duman et al., 2020a; Özdemir & Akkan, 1999; Unsal et al., 2015; Villasen, 1999; Yoshioka & Ichihashi, 2008). Apart from that, various combinations of other dyes such as tartrazine, acid violet 7, and ponceau 4R, simultaneously used with patent blue V, are also common in food and cosmetic products. So far, various methods have been employed to determine these synthetic dyes with regard to the importance of

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measuring and monitoring their uses together (Baytak et al., 2019; Krishnakumar & Swaminathan, 2011; Ma et al., 2018; Manjunatha, 2018; Yoshioka & Ichihashi, 2008; Zhang et al., 2014; Zhang et al., 2010; Qiu et al., 2016).

Metal-organic frameworks (MOF) are a group of porous materials that possess crystalline infinite networks obtained from the bonding of metal ions, which serve as coordination centers, with poly functional organic molecules (Doménech et al., 2007). With regard to their related unique characteristics (e.g. controllability, large specific surface area, high-porosity, high thermal stability, host-guest interaction and tunable functionalities) (Tu, Gao, et al., 2020; Tu, Xie, et al., 2020), they are vastly used in different applications such as gas storage/separation (Xue et al., 2019), drug delivery (Horcajada et al., 2010), catalysis (Cui et al., 2015; Jiao et al., 2018), and sensing (Cao et al., 2019a; Li et al., 2018; Senthil Kumar et al., 2012).

One of the most cited MOFs is Copper-1,3,5-benzenetricarboxylate (Cu-BTC), and each of its atoms is connected to 4 oxygen atoms from the BTC linker with great ability and high-porosity, which meaningfully increases the effective surface area of the electrode that is widely used in electrochemical studies (Cao et al., 2019a; Chong et al., 2016; Hu et al., 2020; Shen et al., 2015; Song et al., 2018).

Recently, room temperature ionic liquids (RTILs) have attracted a lot of attention in the many fields of analytical chemistry. Because of their unique properties like negligible vapor pressure, high chemical and thermal stability, good conductivity, and low toxicity, the ability of RTILs combined with carbon materials to form conductive composites makes it applicable in different electrochemical sensors electrodes. Here, as an ionic liquid, 1-ethyl-3-methylimidazolium chloride showed some advantages such as great electric conductivity and sensitivity, fast electron transfer and good antifouling capability for electroanalysis (Abo-Hamad et al., 2016; Liu et al., 2019; Ping et al., 2010; Ping, Wang, et al., 2011; Ping, Wu, et al., 2011).

For the first time, the present study shows the synthesis and utilization of the hierarchically porous Cu-BTC MOF in order to make a unique and sensitive electrode and ionic liquid for carbon paste electrode modification (CPE) (Li et al., 2018). As an effective sensor, this new electrode showed high performance for simultaneous determination of patent blue V, tartrazine, acid violet 7 and ponceau 4R, as four commonly employed dyes in foodstuffs such as drinks, jellies, candies and condiments with low detection limits, reasonable linear ranges, good reproducibility and favorable selectivity using voltammetry technique for the first time.

2. Experiments

2.1. Materials and reagents

Patent blue V, tartrazine, acid violet 7 and ponceau 4R were purchased from Sigma-Aldrich with 99% Purity. Phosphate buffer solutions (PBS) (0.1 M) using different amounts of 0.1 M sodium hydroxide aqueous solution were prepared for pH value adjusted. Doubly distilled water was applied for the preparation of all aqueous solutions. All other sample solutions and reagents were prepared of analytical grade. Chemical pure graphite powder and high viscous paraffin oil from Merck was employed for the fabrication of the working electrode.

2.2. Apparatus

All electrochemical investigations were assayed using a galvanostat/potentiostat instrument (Autolab PGSTAT 302N) run with FRA 4.9 and GPES software. The autolab along with a 3-electrode cell assembly, including an Ag/AgCl/KCl(sat) electrode, a platinum wire and a modified carbon paste electrode were applied as the reference electrode, the auxiliary electrode and the working electrode, respectively. X-ray powder diffraction studies were employed using a diffractometer with Cu-K α radiation to characterize the Cu-BTC Metal-Organic frameworks

and scanning electron microscope (SEM) images carried out on the Mira3TESCAN SEM.

2.3. Synthesis of Cu-BTC MOF

The synthesis of Cu-BTC MOF was performed by dissolved 0.25 g of Cu(NO₃)₂·6H₂O in approximately 7 mL of deionized water (A) and 0.25 g of H₃BTC in 7.1 mL of ethanol solution (B). The prepared solution A and B were mixed and take place at 423 K in the Teflon autoclave for one day. The blue powder obtained product was achieved by centrifugation and washed with water and DMF several times. Then for further use, the product was dried under vacuum at 353 K for one day (Li et al., 2018).

2.4. Fabrication of modified electrodes

The carbon paste electrode modified by 1-ethyl-3-methylimidazolium chloride and Cu-BTC MOF (IL/Cu-BTC MOF/CPE) as a proposed modified sensor was fabricated by a combination of graphite-powder (0.9 gr) and Cu-BTC MOF (0.1 gr), along with an appropriate value of paraffin-oil (~75:25 %w/w). Afterwards, the ionic liquid (0.1 gr) was added, and mixed well and then it was packed into a glass tube. A copper wire selected to electrical contact with the mixture and polished it on a paper for make a new surface of modified electrode.

2.5. Analytical method

Soft drink, jellies, candies and condiments were obtained from local shops and employed as actual-samples. Their obtained solutions were diluted in 10 mL phosphate buffer (pH 7.0). The achieved solutions were employed to analyze the patent blue V, tartrazine, acid violet 7 and ponceau 4R. The real-sample solutions were analyzed and determined by differential pulse voltammetry (DPV) under the optimum settings.

3. Results and discussion

3.1. Cu-BTC MOF characterization

The SEM analysis, XRD, EDAX, and FTIR spectroscopy was explored to assess the composition and the structure of the prepared Cu-BTC MOF. Fig. 1A and B illustrated the SEM images of Cu-BTC MOF with uniform decoration and the close packing of high-dispersive, hierarchically porous nanoparticles and crystal structure (Cao et al., 2019a; Cao et al., 2019b; Duan et al., 2019; Shen et al., 2015; Song et al., 2018). The length of each octahedral edge was found around 20–37 nm. The XRD pattern which is presented in Fig. 1C, confirmed the pure morphology of Cu-BTC MOF phase with the crystal structure along with characteristic peaks, which were referred to (200), (220), (222), (400), (331), (333), (420), and (442) of the Cu-BTC MOF structure and verified the Cu-BTC MOF has been successfully synthesized and rendered a good crystalline phase. The observed peak at 11.76° (highest intensity peak) was related to the high degree of crystallinity of the product. The attained results from EDAX Fig. 1D, shown peaks related to the elements presence of carbon, oxygen, and copper, accordingly confirming the synthesis of Cu-BTC MOF. According to FT-IR results (Fig. 1E), we could clearly detect the functional groups and the molecular structure. The band at about 484, 727 cm⁻¹, the minor peaks between 660 and 760 cm⁻¹, the bands from 800–1100, 1375, 1442 and 1645, and 3426 cm⁻¹ ascribed to the Cu–O, the bending vibration of the aromatic ring, stretching vibrations of C–O and O–C=O, the vibrations of carboxylate group of Cu-BTC, water coordinated within the Cu-MOF framework, the adsorbed-H₂O and OH group in the Cu-BTC MOF, respectively and the observed peak at 1720 cm⁻¹, it was because of the presence of benzenetricarboxylic acid in the the Cu-BTC framework (Nivetha et al., 2020).

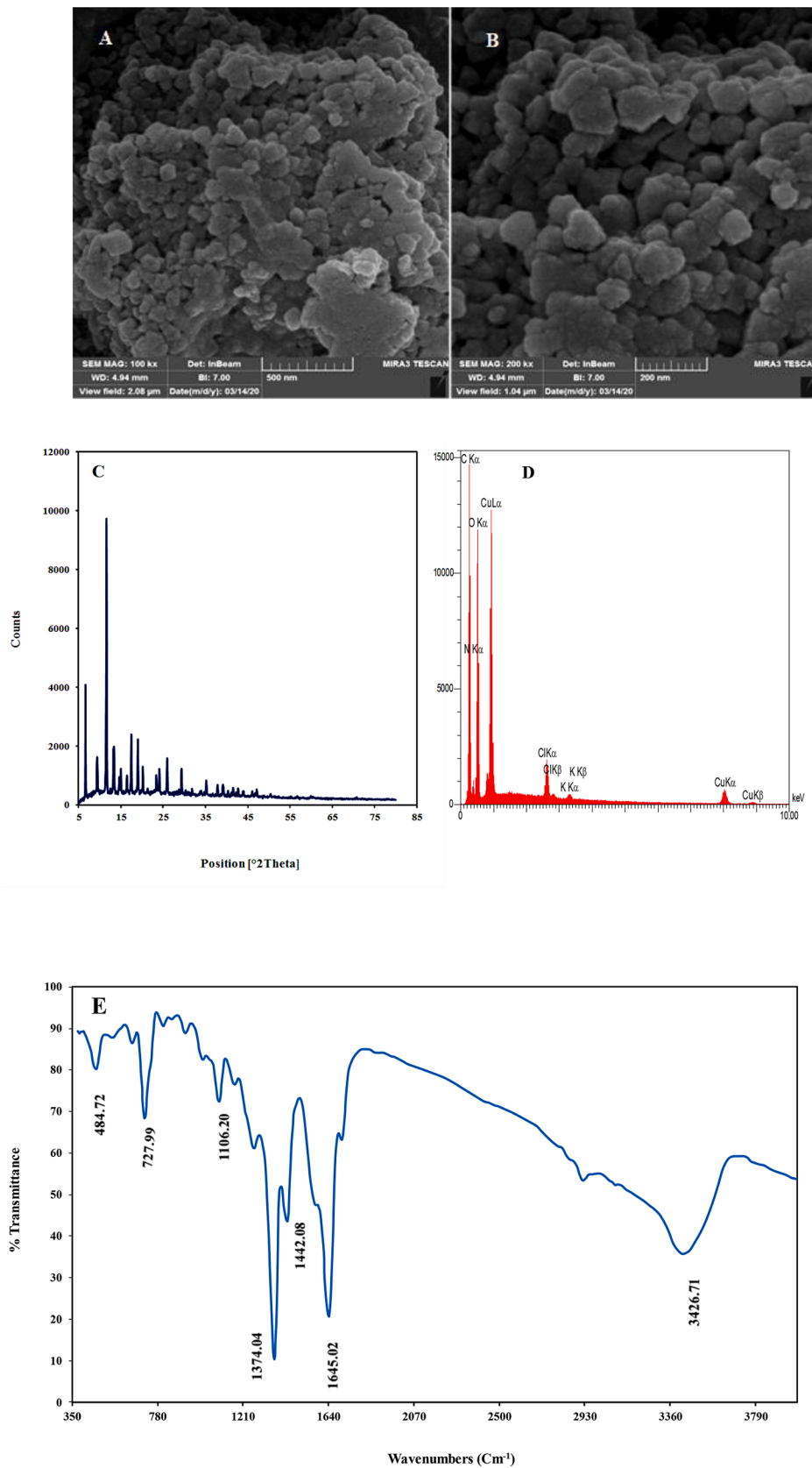


Fig. 1. A, B) SEM image of Cu-BTC MOF, C) XRD, D) EDX patterns, and E) FT-IR spectra patterns of Cu-BTC MOF synthesized in this work.

3.2. Electrochemical analyses

The cyclic voltammetry of patent blue V (500 μM) at the surfaces of different electrodes was performed in pH 7 (PBS 0.1 M) with a scan rate of 50 mV s^{-1} . Fig. 2 describes the cyclic voltammograms of the CPE (Curve a), Cu-BTC MOF/CPE (Curve b), IL/CPE (Curve c) and IL/ Cu-BTC MOF /CPE (Curve d) as an irreversible signal. After modifying the electrode with Cu-BTC MOF, the peak current increased because of excellent conductivity and high-porosity of nanoparticles, increase in the effective surface area of the electrode and ionic liquid due to great electric conductivity and ability to transfer electron fast. However, in the case of IL/ Cu-BTC MOF /CPE (Curve d), the peak current was larger than that for the bare carbon paste electrode. According to the results, the presence of both Cu-BTC MOF and ionic liquid cause a significant increase in the oxidation peak current of modified electrode IL/ Cu-BTC MOF /CPE around 0.88 mV with a peak current of 140 μA . The oxidation currents of IL/CPE, Cu-BTC MOF/CPE, and CPE are about 116, 85, 51 μA , respectively, in the same condition. The results demonstrated that the attendance of Cu-BTC MOF along with IL had a significant improvement in the current response because of the outstanding characteristics used to modify the electrode compared to CPE.

In order to investigate the pH influence, the phosphate buffer solutions were used in different pH values (3.0–9.0). Fig. S1 indicates the pH

value of the supporting electrolyte with a considerable effect on the peak potential of the oxidation of patent blue V. With an increase in the pH, the peak potential (E_p) was shifted to more negative potentials. By considering the results, pH 7.0 was chosen for all the experiments. As a result, there was a linear relationship between the oxidation peak potential and the pH of the solution with a slope of -26.1 mV and $R^2 = 0.991$; therefore, it can be concluded that the mechanism of oxidation was performed by two electrons and one proton.

The impact of the scan rate on the peak potential (E_p) and peak current (i_p) of 500 μM of patent blue V was investigated in the range of 10–150 mVs^{-1} at the IL/ Cu-BTC MOF /CPE electrode surface (Fig. S2). The results confirmed that there was a linear relationship between the peak current electro-oxidation of patent blue V and the square root of scan rate ($v^{1/2}$) ($R^2 = 0.9927$) (Fig. S2-A). Therefore, oxidation of patent blue V was accrued under a diffusion-controlled process. As can be seen, there was a negative peak potential shift with an increase in the scan rate, which confirmed the irreversibility of the electrochemical reaction (Fig. S2-B). Furthermore, by considering the Tafel plot (Fig. S2-C) with the slope equal to $2.3RT/n(1-\alpha)F$, the electron transfer coefficient (α) was calculated approximately 0.86.

Chronoamperometric signals (Fig. S3) were performed using IL/ Cu-BTC MOF /CPE by setting the working electrode potential at about 0.8 V vs. Ag/AgCl/KCl_{sat} for various concentrations of patent blue V in the buffer solutions, pH 7.0. According to the Cottrell equation ($I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$), the value of diffusion coefficient (D) was found to be $0.56 \times 10^{-8} \text{ (A} = 0.40 \text{ cm}^2, n = 2, \text{ and } F = 96485 \text{ C mol}^{-1}\text{)}$. The electrooxidation was under diffusion control with a linear relation between current response of 100, 200, 300, and 400 μM of patent blue V and $t^{-1/2}$ in pH 7.0.

For electrochemical impedance spectroscopy (EIS), investigation of Nyquist-diagrams (the imaginary impedance (Z_{im}) vs. real impedance (Z_{re})) was shown in Fig. 3A. They were obtained at different electrodes of CPE (a); Cu-BTC MOF /CPE (b); IL/CPE (curve c), and IL/ Cu-BTC MOF /CPE (d) in the presence of 0.5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl, pH 7.0, respectively. By comparing different electrodes, the values of the charge transfer resistance (R_c) were calculated to be 617, 471, 261, 116 ohm for CPE, Cu-BTC MOF /CPE, IL/CPE and IL/ Cu-BTC MOF /CPE, respectively (Fig. 3B). All these results confirmed that the synergistic effect of Cu-BTC MOF and the employed ionic liquid in the modified electrode were important due to their properties such as increase in the conductivity of the electrode and the improved electron transfer.

The differential pulse voltammetry (DPV) was employed to explore the sensitivity of IL/ Cu-BTC MOF /CPE for analysis of patent blue V (Fig. 4). The obtained plot of peak current vs. different concentrations included two distinct linear ranges with different slopes of 1.19 and 0.016 μM in the concentration ranges of 0.08–10 and 10–900 μM , respectively. The limit of detection (LOD) was calculated to be 0.07 μM by using equation $3\sigma/m$, where σ was the standard deviation of the blank and m illustrated the slope of the calibration curve. According to the results, the linear range, RSD and limit of detection for patent blue V obtained in this work are comparable to those of previous works (Table S2) (Beltran, 2000; Desimoni et al., 2006; Duman et al., 2020b; Unsal et al., 2015; Yoshioka & Ichihashi, 2008).

As the main object of this work, in order to investigate the ability of IL/ Cu-BTC MOF /CPE as a newly proposed sensor, simultaneous determination of some other dyes including tartrazine, acid violet 7 and ponceau 4R was performed by altering the concentration of these food dyes on-pot (Fig. 5). The obtained results indicated well-defined current peaks at potentials of 0.53, 0.62, 0.80 and 0.96, referring to the oxidation of tartrazine, acid violet 7, patent blue V and ponceau 4R, respectively, and demonstrating the possibility of one-pot oxidation processes. According to the obtained results, it can be claimed that the proposed sensor for simultaneous determination of these four food dyes was conceivable.

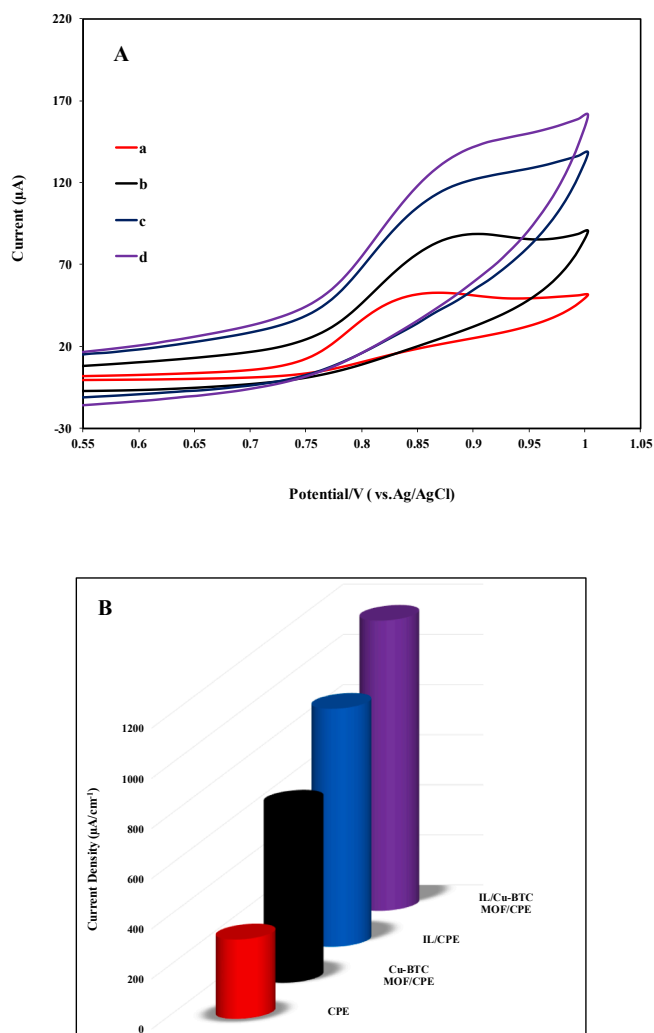


Fig. 2. A) Cyclic voltammograms of a) CPE, b) Cu-BTC MOF, c) IL/CPE, and d) IL/Cu-BTC MOF/CPE in the presence of 500 μM patent blue V at pH 7.0, respectively. B) The current density derived from cyclic voltammogram responses of 500 μM patent blue V at pH 7.0 at the surface of different electrodes.

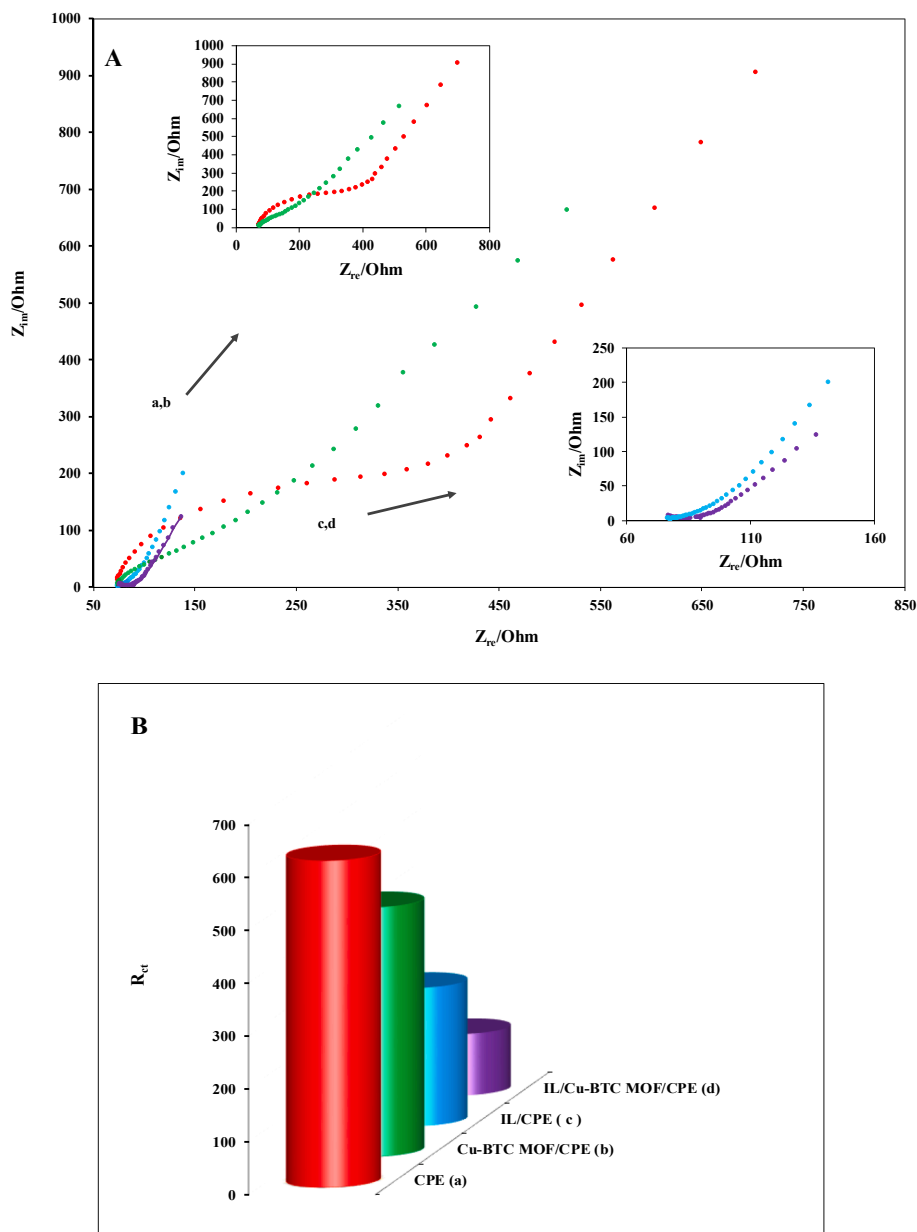


Fig. 3. Nyquist plots of a) CPE, b) Cu-BTC MOF/CPE, c) IL/CPE, and d) IL/Cu-BTC MOF/CPE. Conditions: 0.5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl, pH 7.0.

3.3. Interference study

The effect of different foreign species was investigated under optimum condition along with 50 μM of patent blue V at pH 7.0. For this purpose, the common substances found with patent blue V, tartrazine, acid violet 7 and ponceau 4R in foodstuff such as Na^+ , K^+ , Zn^{2+} , Cu^{2+} , Ca^{2+} , NO_2^- , Cl^- , SO_4^{2-} , CO_3^{2-} and glucose were investigated. According to the obtained results (Table S1), the concentration of at least 500 times of these interfering compounds has no critical influence on determination of these dyes. The results confirming the selectivity of the proposed sensor in the current work.

3.4. Stability and reproducibility

In order to investigate the stability and reproducibility of IL/Cu-BTC MOF/CPE, cyclic voltammetry was applied for the determination of patent blue V. The relative standard deviation (RSD%) for ten successive assays was 0.97%, and the value of RSD% was calculated 1.13 by using

seven different electrodes. The results confirm that IL/Cu-BTC MOF/CPE has high stability and good reproducibility for determining of patent blue V.

3.5. Real sample analysis

The proposed method was used to analytical applicability of IL/Cu-BTC MOF/CPE in real samples such as soft drinks, condiments, jellies and candies. The real samples containing mentioned food dyes, were prepared separately. The attained results were compared to the actual values described by manufacturer and expressed good agreement with the actual values of the four colorants. After spike the specific amount of dyes according to Table 1, the results repeated four times and then the standard-addition method was applied for determination of these dyes in foodstuff ($\hat{A}\bar{x} \pm \frac{ts}{\sqrt{N}}$) which, \bar{x} is the average concentration of analytes, t , is confidence level, s , is standard deviation and N , is the number of results replication). The analysis of the oxidation peak current for four dyes has been shown the recovery was between 85% and 98% for soft

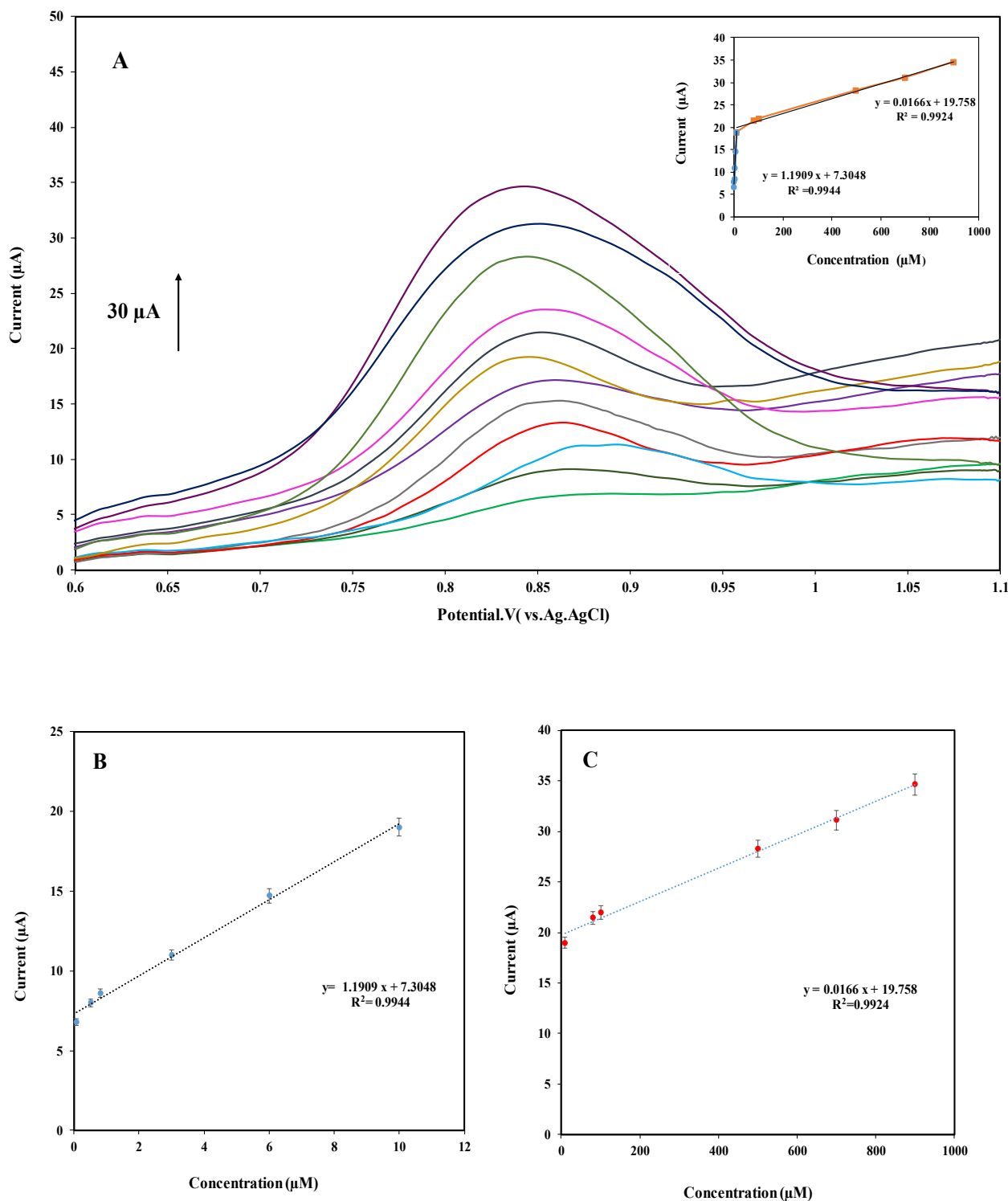


Fig. 4. A) DPVs for various concentrations of patent blue V, C) 900, 700, 500, 100, 80, 10 and B) 10, 6, 3, 0.8, 0.5, 0.08 μM (from top to down) in buffer solutions of pH 7.0.

drinks, 82% to 108% for condiments, 94% to 110% for jellies and 94% to 110% for candies. The outstanding recovery values and sensitivity of the selected samples affirmed that the IL/ Cu-BTC MOF /CPE sensor can be effectively employed in the analysis of these dyes in foodstuff (Table 1).

4. Conclusion

In this work, a novel and high sensitive electrochemical sensor based

on Cu-BTC MOF and 1-ethyl-3-methylimidazolium chloride as an ionic liquid (IL) in an attempt to modify the carbon paste electrode have been investigated for simultaneous determination of four common food dyes, patent blue V, acid violet 7, tartrazine and ponceau 4R for the first time. The modified electrode exhibits high selectivity and sensitivity with a low detection limit for simultaneous determination of these dyes. Under the optimized conditions, a low detection limit of 0.07 μM, with a wide linear concentration range 0.08 to 900 μM was obtained compared to

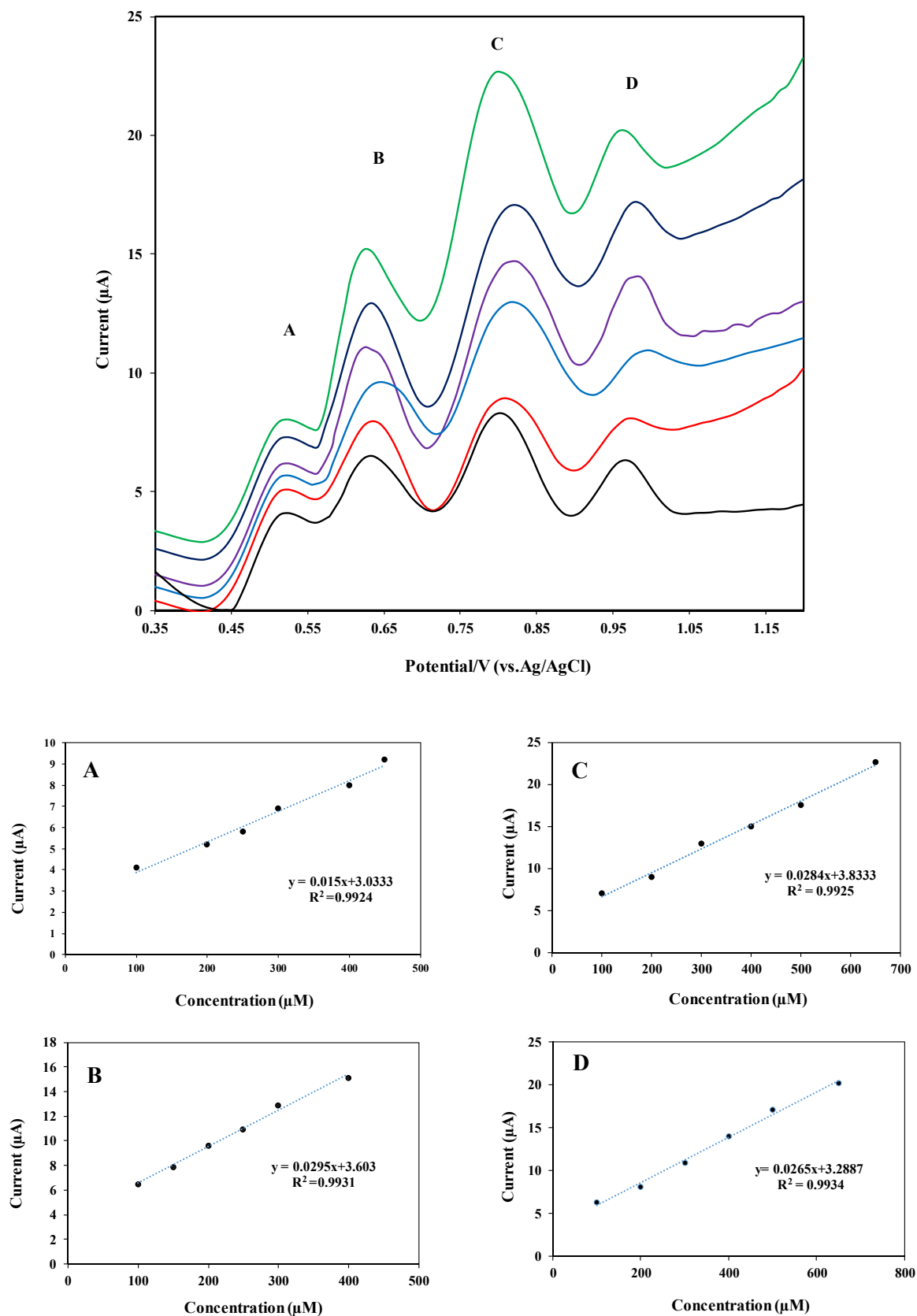


Fig. 5. The DPVs of IL/Cu-BTC MOF//CPE at pH 7.0 phosphate buffer containing different concentrations of A) Acid Violet 7, B) Ponceau 4R, C) Patent Blue V and D) Tartrazin, with (A): 100.0 + 200.0 + 250.0 + 300.0 + 400; (B): 100.0 + 150.0 + 200.0 + 250.0 + 300.0, 400.0; (C): 100.0 + 200.0 + 300.0 + 400.0 + 500.0 + 600.0; (D): 100.0 + 200.0 + 300.0 + 400.0 + 500.0 + 650.0 μM, respectively.

Table 1

Determination of Patent Blue V (A), Tartrazine (B), Acid Violet 7 (C) and Ponceau 4R (D) in foodstuff.

Analyte	Added (μM)				Found (μM)				Recovery (%)			
	A	B	C	D	A	B	C	D	A	B	C	D
Soft drinks	-	-	-	-	4.2 ± 0.047	4.8 ± 0.034	6.5 ± 0.04	5.7 ± 0.035	-	-	-	-
	10	10	10	10	13.8 ± 0.5	14.6 ± 0.52	15 ± 0.54	14.5 ± 0.48	96	98	85	88
Condiments	-	-	-	-	9.6 ± 0.028	7.8 ± 0.025	8.5 ± 0.2	9 ± 0.2	-	-	-	-
	15	30	20	30	22 ± 0.28	35.7 ± 0.03	30.2 ± 0.24	41 ± 0.24	82	93	108	106
Jellies	-	-	-	-	6 ± 0.039	4.7 ± 0.028	5.7 ± 0.03	6.3 ± 0.025	-	-	-	-
	10	15	15	20	17 ± 0.6	21.0 ± 0.035	19.8 ± 0.1	27.8 ± 0.05	110	108	94	107
Candies	-	-	-	-	7 ± 0.07	8.5 ± 0.08	4.8 ± 0.2	6.3 ± 0.08	-	-	-	-
	20	15	10	15	28 ± 0.1	25.6 ± 0.12	14.2 ± 0.23	22.4 ± 0.1	105	110	94	107

other electrochemical methods. On the other hand, some kinetic and thermodynamic parameters were investigated by electrochemical methods ($\alpha = 0.86$ and $D = 0.56 \times 10^{-8}$). This work reveals that IL/Cu-BTC MOF/CPE could be a favorable and promising sensor, which may have wide potential applications in some selected food products with satisfactory recovery. The reproducibility and stability of the electrode was investigated, affirming the successfully proposed sensor. According to our knowledge, it was the first time simultaneous determination of four food dyes that using Cu-BTC MOF and ionic liquid to fabricate the electrode with high ability in the developed method.

CRediT authorship contribution statement

Rozhin Darabi: Investigation, Writing - original draft. **Mehdi Shabani-Nooshabadi:** Supervision, Validation. **Hassan Karimi-Maleh:** Project administration, Validation. **Ali Gholami:** Resources, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2021.130811>.

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