

Synthesis and characterization of Co-Zeolite nanocomposite: electrocatalytic oxidation of methionine

Seyedeh-Fatemeh Mousavi¹, Mohammad Alimoradi¹, Abbas Shirmardi^{2,*}, Vahid Zare-Shahabadi³

¹Department of Chemistry, Faculty of Science, Arak Branch, Islamic Azad University, Arak, Iran

²Department of Chemistry, Masjed-Soleiman Branch, Islamic Azad University, Masjed-Soleiman, Iran

³Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

Article history:

Received: 15/ Apr /2022

Received in revised form: 02/ Jun/2021

Accepted: 05/ Dec/2022

Abstract

A cobalt-zeolite (CoY) nanocomposite was prepared and used as a modifier for construction of a carbon paste electrode (CoY/CPE) and it was applied for the determination of Methionine (Met). The surface morphology of the nanocomposite was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Energy dispersive X-ray analysis (EDX). Particle size of the prepared CoY was in the range between 31 nm and 64 nm. Electrochemical response characteristics of the modified electrode toward Met. were investigated by Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DP) in a 0.1 M phosphate buffer pH 6.2. A possible mechanism was proposed for the electrochemical response of the electrode toward Met. The electrode showed a suitable linear calibration curve in the concentration range of 3.5×10^{-7} – 5.5×10^{-6} mol L⁻¹. The detection limit of the electrode (LOD) and quantification (LOQ) were calculated 9.1×10^{-8} mol L⁻¹ and 1.3×10^{-7} mol L⁻¹. Effect of different factors on the response of the electrode such as pH, modifier, electrolyte and scan rate was also studied. It was successfully applied for the determination of Met in serum samples. also the amount of %RSD for evaluation of repeatability and reproducibility of the proposed sensor was obtained 0.13%.

Keywords: Methionine; Co-Zeolite; amino acid; Deferential pulse; Voltammetry.

1. Introduction

Early diagnosis is mandatory for many types of diseases and implemented by pursuing new biomarkers [1]. A biomarker is a countable indicator of a particular biological fluid. Biomarkers can be used potentially to figure out the changes in disease and health status, clinical diagnosis, risk assessments and many other areas such as the pharmaceutical industry [2, 3].

In literature, amino acids are reported as potential biomarkers as they are involved containing sulfur and takes many tasks in the body [6].

It is involved in regulation of metabolic processes, immune system and antioxidant capacity of organisms [7].

Therefore, its supplementation or restriction is linked with nucleic acids damage, different types of cancer, cardiovascular and neurodegenerative diseases [7].

*.Corresponding author: Assistant professor of Analytical Chemistry, Masjed-Soleiman Branch, Islamic Azad University, Masjed-Soleiman, Iran. E-mail address: ashirmardi.abbas@gmail.com

electrochemical detection [9-11], ultraviolet-visible detection and mass spectrometry [12-14] for the determination of these compounds in literature. The earliest report on the determination of methionine is back to 1960, however its electro-oxidation mechanism remained an ambiguous subject. Since that time, different mechanisms have been proposed for the electro-oxidation of methionine at the different electrodes [15-18]. Pt electrode, wax impregnated graphite electrode, rotated glassy carbon electrode and Ag/Au electrode were employed for this goal. Although these works suggest different criteria and mechanisms for electro-oxidation of methionine, they agree with participation of sulfur moiety in methionine to form either methionine sulfoxide or methionine sulfone [18]. On the other hand, literatures report that cobalt(II) ion can form a stable complex ($\text{Co}(\text{Methionine})_2$) in which methionine employs nitrogen and carboxyl groups for its complexation with cobalt ion, and sulfur moiety remained intact in these interactions [19]. Hence, complexation of methionine would be a good alternative for adsorbing methionine at the electrode surface to improve sensitivity and selectivity of its determination. Poly methionine complexes of cobalt were used as modifiers for determination of other biomolecules [20-22]. To the best of our knowledge, there is no reports on the use of cobalt ion for the determination of methionine.

Carbon paste has been widely applied in electrochemistry owing to its wide potential window ranging from -1.4 to +1.7 V versus the saturated calomel electrode (SCE) covering both oxidation and reduction of analyte of interest [23, 24, 25]. Thus, carbon paste possesses many advantages: it is inexpensive, easy to handle, easy to prepare and easy to modify. There are several reasons for modifying the carbon paste electrodes: Enhancement of electrochemical catalytic responses alteration of the physical properties of the electrode surface; preconcentration of components of the analyte, immobilization of molecules involved in electrochemical reactions; the last reason is the motivation of many researchers to use the modified carbon paste electrode for determination of analytes [26-28]. In this work we aimed

to immobilize methionine through its complexation with cobalt ion prior to its electro-oxidation. Recently we used Ag/zeolite nanocomposite for the for modification of carbon paste electrode for voltammetric determination of tryptophan [29]. The use of zeolite for incorporation of metal ions is due to its immense surface area and sustainable potential for accommodating metal ions. Meanwhile it was proved that zeolite by itself has catalytic behavior toward lots of chemical reactions [30-32]. In this work, we first synthesized and characterized a cobalt/zeolite nanocomposite and exploit its catalytic behavior for the electro-oxidation of methionine at the carbon paste electrode. The nanocomposite proved to have a stable morphology and uniform distribution of cobalt nanoparticle species (CoO and $\text{Co}(\text{OH})_2$) into the nanocomposites [19, 33-35]. The hard-hard interaction between Co^{2+} ion and nitrogen group of methionine plays a pivotal role in electrocatalytic effect of the modifier for electro-oxidation of methionine at the modified electrode [19].

Advantages of the proposed technique are the use of less toxic and cheaper materials used for the facriation of the modified electrode and hence its safe application in the measurement of methionine in biological samples, and its higher performance relative to the previously reported L-methionine electrochemical biosensors [9, 15, 17].

2. Experimental

2.1. Materials

Zeolite was prepared from Sigma Aldrich, nitrate salts of all metal ions were prepared form Merck, Germany. All required solvent and reagents were of the highest purity. Ultrapure water was prepared with a Millipore water distiller.

2.2. Preparation of Co/zeolite nanocomposite

NaY zeolite was purchased from Sigma-Aldrich, USA and was used without further purification. Preparation of Co/zeolite was implemented with the same procedure as discussed earlier. Briefly, 100 mg of NaY zeolite was dispersed in 20 ml of acetone using an ultrasonic bath and it was brought to a boil. 50 ml of aqueous 0.05 M $\text{Co}(\text{NO}_3)_2$ solution was added drop wise to the dispersed zeolite and the mixture was stirred overnight in dark [29].

The mixture was then filtered and washed with 0.05 M HNO₃. The filtered CoY was dried at room temperature and stored in a dark place for its next usage.[36,37]

2.3. Preparation of carbon paste electrode

Appropriate amount of the as prepared CoY zeolite was added to a 70 mg of spectroscopic grade graphite in a mortar and the mixture was thoroughly mixed to get homogenized and then 25 mg of paraffin oil was added to the mixture. Again, the obtained paste was mixed for at least 15 min. the homogenized carbon paste mixture was pulled into a glass tube with 6 mm internal diameter and it was pressed with a copper wire with the same size inserted from the other side of the glass tube. Finally, the outer surface of the paste was polished with a smooth paper.

2.4. Instrumental

XRD patterns of the Co-zeolite nanocomposite was obtained with a Philips, X'pert system using CuK α radiation). FESEM images were taken with FESEM, ZEISS, SIGMA VP-500). Fluorescence spectra were obtained with a Carry Eclips, Varian, Australia spectrometer.

The electrochemical measurements were carried out with an outolab-Metrohm, Switzerland. A three electrode system was applied for potentiostatic measurements. An Ag/AgCl electrode was used as the reference electrode, a graphite electrode with 3 mm was used as the counter electrode and the constructed Co-zeolite/CPE was used as the working electrode.

3. Results and Discussion

3.1. Characterization of the synthesized Co/Zeolite nanocomposite

XRD crystallography of the prepared CoY and NaY was obtained and the results were depicted in Fig. 1. As seen in Fig. 1, the prepared nanocomposite contains both Co(OH)₂ and CoO compared to the NaY XRD pattern (JCPDS card file No. 45-0031 and JCPDS card No. 78-1970) [38]. XRD pattern also revealed that crystallite size of the CoY were calculated 23 nm according to the Debye-Scherrer method [39]. FESEM images of NaY and

CoY nanocomposite were obtained. Fig. 2 show micrograph of both NaY and CoY in the same resolution. As seen from the Figure, bulky powder of the NaY zeolite was not changed with the entered Co(OH)₂ or CoO nanoparticles, indeed morphology of the nanocomposite was not changed by incorporation of the cobalt species. It is worth mentioning that particle size of nanocomposite was in the range of 31.2-62.7 nm whereas the particle size of NaY was in the range of 13.4-33.2 nm [29]. EDS of the nanocomposite was also obtained and the results were depicted in Fig. 3. As shown in Fig. 3, presence of 3.6% of cobalt justify the cobalt oxide and cobalt hydroxide compared with pristine NaY [29].

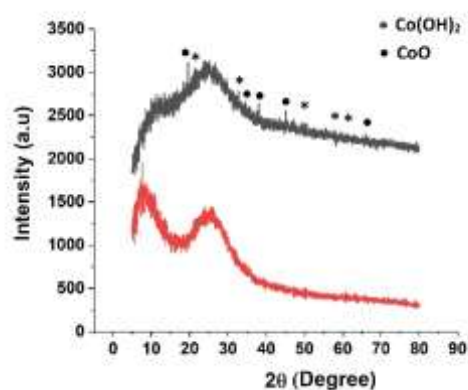


Fig. 1 XRD pattern of Co/zeolite nanocomposite (black) and NaY zeolite (blue)

3.2. Study of interaction between the nanocomposite with methionine

Interaction between modifier and analyte is key role of electrochemical behavior of the modified electrodes. In order to understand this behavior UV-visible and spectrofluorometric studies were conducted. Figs. 4 and 5 show spectrophotometric and spectrofluorometric spectra of a 10 mg of Co-zeolite dispersed in 50 mL deionized water, respectively. In these studies, 100 μ L of 1 mM methionine solution was added to the methionine solutions. As seen in Fig. 4, two isosbestic points were found in 428 nm and 589 nm regions which can be attributed to the interaction between methionine and cobalt(II) ion exist in the nanocomposite. Fig. 5 also reveals a change in the fluorescence the nanocomposite upon addition of methionine as it is evident from the isosbestic point in 436 nm. So that an interaction between methionine and the Co(II) ion in the nanocomposite was

suggested this behavior can be attributed to the complexation of methionine and Co(II) ion present in the nanocomposite.

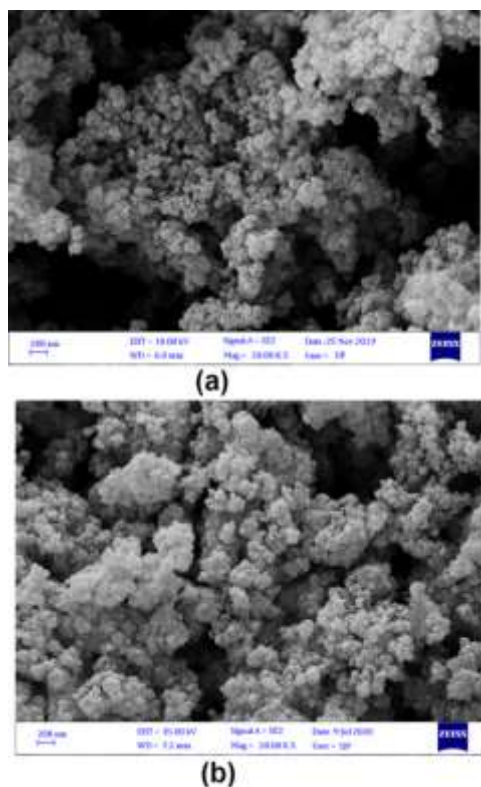


Fig. 2 FESEM images of NaY zeolite (a) and Co/zeolite nanocomposite

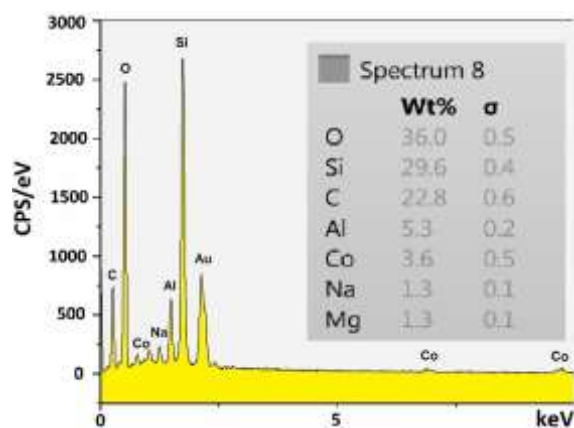


Fig. 3 EDS of the synthesized CoY

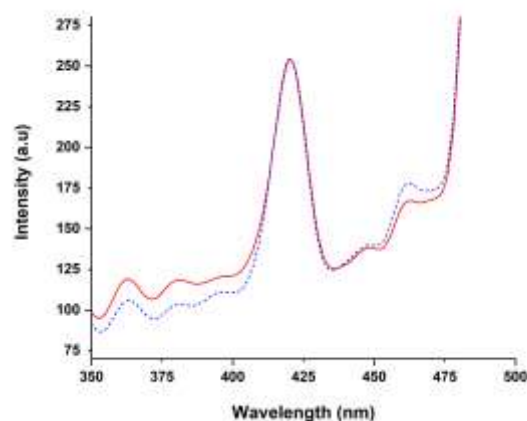


Fig. 4 UV-Vis spectra of Co/zeolite nanocomposite (dark line) and Co/zeolite and methionine (dotted line) nanocomposite

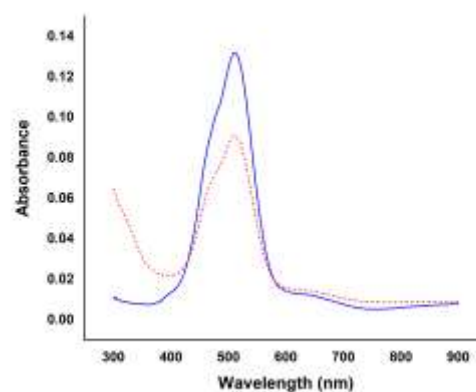


Fig. 5 Spectrofluorometric spectra of Co/zeolite in water (excitation wavelength a 250nm)

3.3. Electrochemical behavior of the modified CPE

To evaluate electrocatalytic behavior of the carbon paste electrode, cyclic voltammograms responses of the modified carbon paste electrode have been obtained for both the modified and unmodified electrodes. Fig. 6 shows CV responses of modified and unmodified electrodes. As shown in the Figure, the modified electrode shows reversible response to the ferrocyanide/ferricyanide couples while unmodified electrode did not. Meanwhile about two-fold increase in both anodic and cathodic currents have been shown compared with the responses of the unmodified electrode toward this couple, hence it can be concluded that modification of the electrode surface helps the electrode catalytic behavior. Moreover, a decrease in the potential of oxidation or reduction is seen in the case of modified

electrode. These actions can be attributed to the presence of both zeolite framework catalytic behavior and $\text{Co}(\text{OH})_2$ which can adsorb the ferrocyanide and ferricyanide couples via hydrogen bonding interaction.

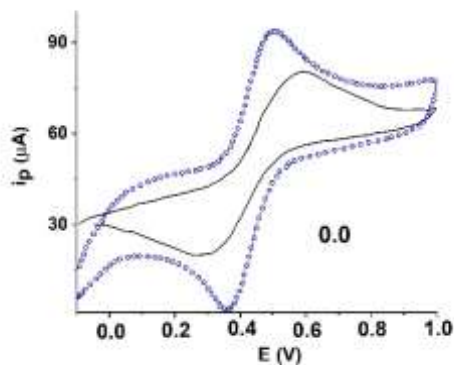


Fig. 6 Cyclic voltammograms of 1 mmol L^{-1} solution of $\text{K}_4\text{Fe}(\text{CN})_6$ by using the modified CPE (dotted line) and unmodified CPE (solid line)

3.4. Response of the electrode toward methionine

Cyclic voltammetry is a good technique for tracing electrodynamic of a system. In order to obtain information about mechanism of the electrode reaction, response of the modified electrode toward a 1 mmol L^{-1} solution of methionine was obtained. The response of an unmodified electrode toward the 1 mmol L^{-1} solution was also obtained and the results were depicted in Fig. 7. As seen, oxidation of methionine occurs at 0.64 V , while its reduction occurs at 0.4 V , hence a 240 mV difference between the anodic and cathodic peaks proposes a quasi-reversible response of the electrode toward methionine, while unmodified electrode does not respond toward methionine. Meanwhile it is worth mentioning that electro-oxidation of methionine has been occurred at lower potential compared to that reported in literatures [15, 17, 41, 42, 43, 45-47]. So that electrocatalytic behavior of the electrode toward methionine was confirmed. This effect can be attributed to the role of cobalt species dispersed into the zeolite.

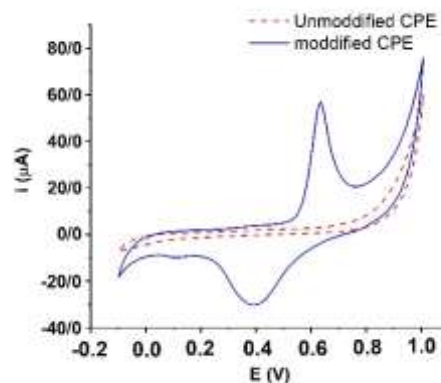


Fig. 7 Cyclic voltammograms of a $10 \mu\text{mol L}^{-1}$ of methionine solution using a modified CPE (blue) and a bare CPE (dash line)

3.5. Effect of the amount of modifier on the response of the electrode

Different amounts of CoY zeolite in the range of $1\text{-}12 \text{ mg}$ were applied for preparation of different carbon paste electrodes. Response of the electrodes toward a $10 \mu\text{mol L}^{-1}$ solution of methionine have been studied and the results were depicted in Fig. 8. As seen from Fig. 8, a shape of cyclic voltammogram with a large increase in both anodic and cathodic currents have been occurred in the case was obtained for incorporation of 6 mg of modifier to the electrode paste, while the other electrodes did not show considerable response toward the methionine solution. This can be due to the increase of electrode resistance due to the higher amounts of the CoY zeolite. The reason for the weak responses of the lower amount of the modifier can be due to the lower amounts of cobalt ion which needed for complexation and hence adsorption of methionine at the electrode surface, hence lower sensitivities have been achieved in these cases.

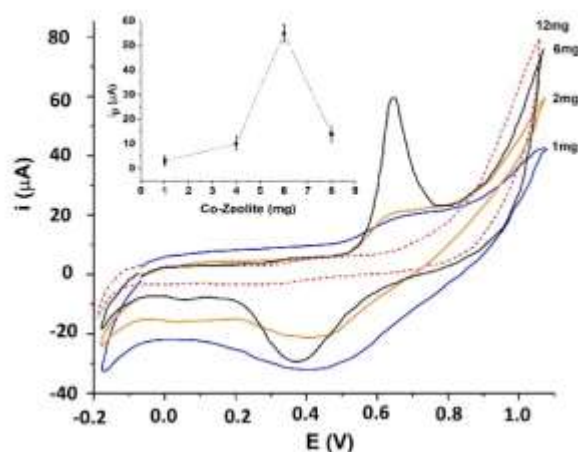


Fig. 8 Effect of the different amounts of Co/zeolite (1-12 mg) on the electrode response toward a $10 \mu\text{mol L}^{-1}$ of methionine solution. Inset shows anodic peak current versus amount of modifier.

3.6. Effect of supporting electrolyte

Supporting electrolyte plays a pivotal role on voltammetry due to their effect on charge transfer, and intra-molecular interactions. 0.1 mol L^{-1} solutions of potassium nitrate, ammonium nitrate, sodium acetate and phosphate buffer solution (PBS) (pH=6.2) were used as the supporting electrolytes. All of the solutions were spiked with $10 \mu\text{mol L}^{-1}$ of methionine. CV of the modified electrodes toward the aforementioned solutions were obtained and the results were depicted in Fig. 9. As seen from Fig. 9, response of the modified electrode toward methionine was improved in the case of PBS compared with the other supporting electrolytes. This behavior can be attributed to the hydrogen bonding between hydrogen phosphate and hydroxyl group or oxygen groups of cobalt hydroxide or cobalt oxide nanoparticles in the modified electrode and methionine molecule as Zwitterion compound in this pH, that it can help adsorption of these molecules at the electrode surface and hence better electrode response has been achieved.

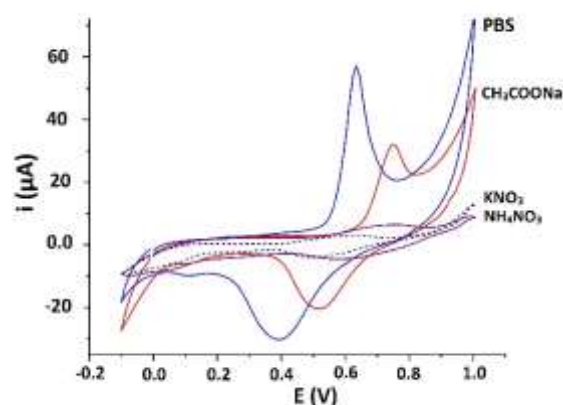


Fig. 9 Effect of the different supporting electrolyte on CV of a $10 \mu\text{mol L}^{-1}$ of methionine solution

3.7. Effect of pH

CV of the different $10 \mu\text{M}$ solutions of methionine buffered with 0.1 M PBS in different pHs ranging from 2.2 to 10.2, were obtained and the results were depicted in Figs. 10 and 11. As seen, potential of electro-oxidation of methionine is pH dependent and it was shifted toward lower potential with increasing pH, slope of $E_{p/2}$ vs pH is -0.063 which suggests the equal number of protons and electrons associated with the electro-oxidation of methionine which it can be 4 according to the literature [15, 18, 40], hence based on this finding and the previous spectroscopic studies, Scheme 1 can be proposed for the electro-oxidation process. So that it can be concluded that the electrode process involved with deprotonation of methionine. Inset of the Figure shows peak current versus pH. As seen, the maximum peak current and sensitivity was obtained in pH 6.2, hence in the rest of the study, the methionine solutions were buffered with 0.1 mol L^{-1} PBS at pH 6.2.

3.8. Differential pulse voltammetry (DPV)

Differential pulse voltammetry is a favorite technique due to its higher sensitivity compared to the linear sweep voltammetry owing to the elimination of charging current associated with electrode reaction. Hence DPV of the different solutions were taken by scanning potential from positive values from 0.2 V to 1.0 V . The results were depicted in Fig. 12. As seen in the Figure, well-shaped peaks were obtained in 0.64 V correspond to oxidation of methionine, the peak

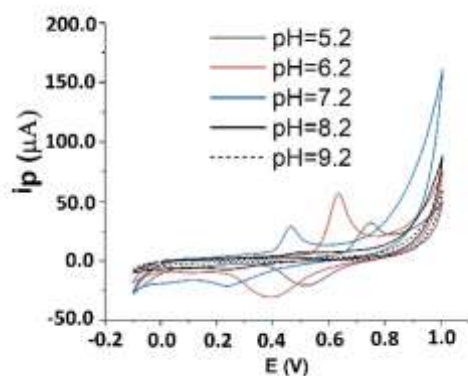
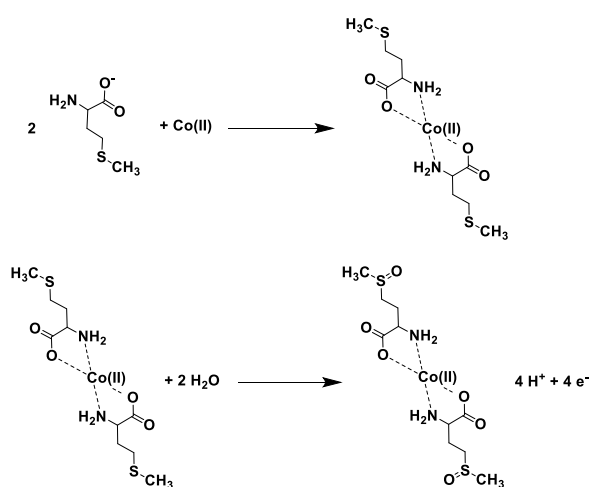


Fig. 10 Effect of pH on CV of a 10 µmol L⁻¹ of methionine solution buffered with 0.1 mol L⁻¹ phosphate buffer solutions of the different pHs at scan rate of 50 mV s⁻¹



Scheme 1. Probable sequence of methionine interaction with the modified electrode

currents were increased with the increase of methionine concentration. Fig. 13 depicts the linear calibration curve of the different solutions of methionine at pH 6.2, 0.1 mol L⁻¹ PBS buffer obtained by DPV. It reveals that DPV response is linear in the range, $3.5 \times 10^{-7} - 5.5 \times 10^{-6}$ mol L⁻¹ with a slope of 98.37 ± 1.10 and $R^2 = 0.9993$. Limit of detection was found to be 9.1×10^{-8} mol L⁻¹ based on 3σ , Limit of quantitation was found based on $LOQ = 3LOD$, so that this value was calculated to be 2.7×10^{-7} mol L⁻¹. The performance of the proposed technique was compared to that of previously reported L-methionine electrochemical biosensors and the results were summarized in Table 1. As seen in the Table the proposed technique has shown better performance compared with the reported techniques, because of the lower detection

limit and working in a nearly neutral condition. Moreover, it employs less toxic chemicals so it is safer to apply in biological environment.

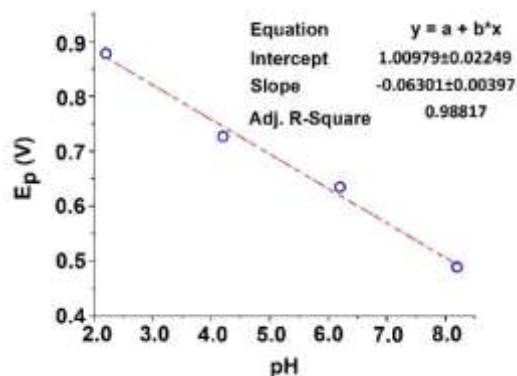


Fig. 11 Effect of pH on $E_{p/2}$ related to the oxidation peak of methionine in a 10 µmol L⁻¹ of methionine solution in phosphate buffer solutions of the different pHs at scan rate of 50 mV s⁻¹

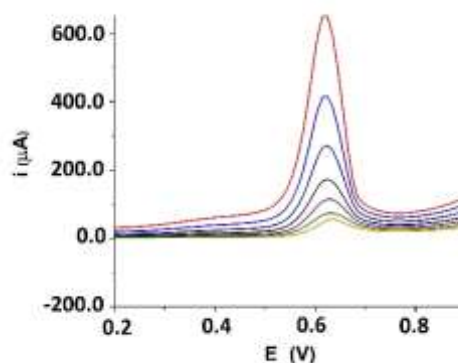


Fig. 12 DPV response of the modified CPE toward the different concentration of methionine in the range between 0.25 µmol L⁻¹ to 0.55 µmol L⁻¹

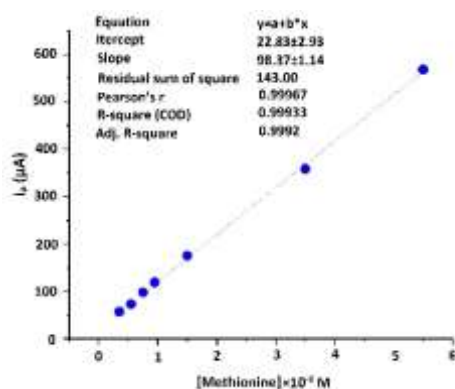


Fig. 13 Calibration curve for the determination of methionine using the modified CPE based on the DPV technique

Table 1 comparison of performance of the proposed technique with the previously reported voltammetric sensor for the determination of methionine

Electrode	Linear range (mol L ⁻¹)	Detection limit (mol L ⁻¹)	pH	E _p (V)	Reference
Screen printed macroelectrode	(0.05-5)×10 ⁻⁶	95×10 ⁻⁶	7 (PBS)	1.1	[41]
p-4α-Cu-TAPC	(50-500)×10 ⁻⁶	2.7×10 ⁻⁶	4.0	1.3	[17]
ZnO nanorode/3, 4', AAZCPE	3×10 ⁻⁷ -1×10 ⁻⁷	5.6×10 ⁻⁸	7.0	-	[9]
Ag/Au core-shell /GCE	(50-500)×10 ⁻⁶	30×10 ⁻⁶	7.0	0.75	[15]
Colloidal gold-cysteamine/CPE	(1-100)×10 ⁻⁶	5.9×10 ⁻⁷	7.0	0.90	[42]
AgO/graphite pencil electrode	(60-500)×10 ⁻⁶	0.42×10 ⁻⁶	13.7 (0.1 M NaOH)	0.65	[43]
MWCNTNFMP/DGLPE	(0.08-10) ×10 ⁻⁶	0.02×10 ⁻⁶	2.0 PBS	0.14	[44]
Graphite-3d-printed electrodes	(5.0–3000) ×10 ⁻⁶	1.39×10 ⁻⁶	7.4 PBS	1.1	[45]
Ru(II)terpyridine/carbon composite electrode	(1.0-10) ×10 ⁻⁶	0.6×10 ⁻⁶	7.0	1.1	[46]
MWNT/GCE	(3.3-6.9)×10 ⁻⁶	0.27×10 ⁻³	0.96 (0.1 M H ₂ SO ₄)	0.80	[47]
CoY/CPE	3.5×10 ⁻⁷ –5.5×10 ⁻⁶	9.1×10 ⁻⁸	6.2 (0.1M PBS)	0.64	This work

3.9. Interference study

Response of the modified electrode towards the several potential interfering species was tested under the optimal conditions. These species were commonly present together with methionine in real samples. The amino acids including, arginine, glycine, phenylalanine, tryptophan, histidine, cysteine, glucose, lactose, benzoic acid, uric acid, urea, and ionic species such as NH₄⁺, Al³⁺, Mg²⁺, F⁻, Cl⁻, S²⁻ and SO₄²⁻ were evaluated. The tolerance limit of each species was defined as the highest concentration which can lead to an anodic current not more than ± 5%, at E_p of 0.64 V corresponding to the electro-oxidation of methionine. The results showed none of the coexisting species led to considerable interferences above their tolerance level, under the experimental conditions.

3.10. Validation of the modified electrode

The validity of the Co/zeolite-modified electrode was evaluated by measuring the concentration of methionine in human blood serum samples. The human blood serum samples were collected from domestic clinical laboratory. The standard addition technique was used to examine the recovery of L-Met in serum samples. 2 mL of the serum sample was diluted to 25 mL of 0.1 mol L⁻¹ PBS pH 6.2. then 100 μmol L⁻¹ of methionine was spiked with the blood serum sample.

The recovery results were obtained and the results are summarized in Table 2. The proposed technique showed a good recovery for methionine spiked in the serum samples, indicating the applicability of the modified Co/zeolite in the determination of methionine in real samples.

Table 2 summary of results of methionine recovery in the different serum samples

Sample	Spiked (μmol L ⁻¹)	Found (μmol L ⁻¹)	Recovery (%)	RSD (%)
Serum 1	2.1	2.2	104.7	1.3
Serum 2	3.6	3.5	97.2	1.6
Serum 3	4.5	4.4	97.8	2.1

4. Conclusion

Incorporation of cobalt nanoparticles in the zeolite caused dispersion and homogeneity of the prepared nanocomposite. The nanocomposite was found as a convenient material for modifying carbon paste electrode for the determination of methionine in the real samples. Complexation of cobalt ion in the nanocomposite nanostructure was discussed by using spectrophotometric and spectrofluorimetric studies. Cyclic voltammetric studies confirmed electrocatalytic effect of the prepared nanocomposite on the modified electrode. The modified electrode revealed limit of detection of 9.1×10⁻⁸ mol L⁻¹ for the determination of methionine in pH close to neutral (pH 6.2) which is

compatible with real samples. Whereas some other reported biosensors suffer from the drawback of their application in the harsh acidic or basic condition. In addition, the electrode has other advantages such as the combination of safe, non-toxic and inexpensive materials, which enable the electrode to be used in biological and analytical applications.

Conflicts of interest

The authors declare no conflicts of interest for the present study.

Acknowledgements

The authors acknowledge Mahshahr Branch, Islamic Azad University for supporting us during the electrochemical measurements.

References

- [1] C.E. Ventetuolo, M.M. Levy, *Clin. chest med.*, **29**(4) (2008) 591.
- [2] A.J. Bayer, *Age and ageing* **47**(5) (2018) 641.
- [3] W. Han, S. Waikar, A. Johnson, R. Betensky, C. Dent, P. Devarajan, J. Bonventre, *Kidney Int.*, **73**(7) (2008) 863.
- [4] A. Tom, K.S. Nair, *J. Nutr.*, **136**(1) (2006).324S.
- [5] T. Sakata, G. Ferdous, T. Tsuruta, T. Satoh, S. Baba, T. Muto, A. Ueno, Y. Kanai, H. Endou, I. Okayasu, *Pathol. Int.*, **59**(1) (2009) 7.
- [6] M. Bouyeh, *Ann.. Biol. Res.*, **3**(7) (2012) 3218.
- [7] Y. Martínez, X. Li, G. Liu, P. Bin, W. Yan, D. Más, M. Valdiviá, C.-A.A. Hu, W. Ren, Y. Yin, *Amino acids*, **49**(12) (2017) 2091.
- [8] W. Wang, P.M. Kramer, S. Yang, M.A. Pereira, L. Tao, *J. Chromatogr., B* **762**(1) (2001) 59.
- [9] E. Molaakbari, A. Mostafavi, H. Beitollahi, *Sens. Actuators B*, **208** (2015) 195.
- [10] A.J. Jeevagan, S.A. John, *Bioelectrochem.*, **85** (2012) 50.
- [11] W.e.T. Tan, J.e.K. Goh, *Electroanalysis*, **20**(22) (2008) 2447.
- [12] A. Zinellu, S. Sotgia, M.F. Usai, E. Zinellu, A.M. Posadino, L. Gaspa, R. Chessa, A. Pinna, F. Carta, L. Deiana, *Anal. Biochem.*, **363**(1) (2007) 91.
- [13] R. Mashima, T. Nakanishi-Ueda, Y. Yamamoto, *Anal. Biochem.*, **313**(1) (2003) 28.
- [14] S. McSheehy, L. Yang, R. Sturgeon, Z. Mester, *Anal. Chem.*, **77**(1) (2005) 344.
- [15] M. Murugavelu, B. Karthikeyan, *Mater. Sci. Eng.*, **70** (2017) 656.
- [16] V.C. Diculescu, T.A. Enache, *J. Electroanal. Chem.*, **834** (2019) 124.
- [17] A.J. Jeevagan, S.A. John, *Bioelectrochem.*, **85** (2012) 50.
- [18] L. Agüi, J. Manso, P. Yáñez-Sedeño, J. Pingarrón, *Talanta*, **64**(4) (2004) 1041.
- [19] C. McAuliffe, J.V. Quagliano, L. Vallarino, *Inorg. Chem.*, **5**(11) (1966) 1996.
- [20] E.S. Gomes, F.R.F. Leite, B.R.L. Ferraz, H.A.J.L. Mourão, A.R. Malagutti, *J. Pharm. Anal.*, **9**(5) (2019) 347.
- [21] H.R.A. Hasanjani, K. Zarei, *J. Iranian Chem. Soc.*, **1** (2021).
- [22] H. Chen, W. Ma, D. Sun, *Chin. J. Appl. Chem.*, **29** (2012) 576.
- [23] J. Lindquist, *Anal. Chem.*, **45**(6) (1973) 1006.
- [24] R.N. Adams, *Anal. Chem.*, **30**(9) (1958) 1576.
- [25] M.Rahimnejad, R.Zokhtare, A.Moghadamnia, M.Asghary.*Applied chemistry*, 47 (1397) 91-104. In Persian.

- [26] M. Mouhandess, F. Chassagneux, B. Durand, Z. Sharara, O. Vittori, *J. Mater. Sci.*, **20**(9) (1985) 3289.
- [27] M.K. Halbert, R.P. Baldwin, *Analytical Chemistry* **57**(3) (1985) 591.
- [28] M. Akhoundian, T. Alizadeh, M.R. Ganjali, F. Rafiei, *Biosens. Bioelectronics.*, **111** (2018) 27.
- [29] S.-F. Mousavi, M. Alimoradi, A. Shirmardi, V. Zare-Shahabadi, *J. Porous Mater.*, **27**(5) (2020) 1505.
- [30] A.Z. Abidin, N.A. Bakar, E. Ng, W. Tan, *J. Taibah Uni.Sci.*, **11**(6) (2017) 1070.
- [31] M.R. Guascito, D. Chirizzi, R.A. Picca, E. Mazzotta, C. Malitesta, *Mater. Sci. Engin. C*, **31**(3) (2011) 606.
- [32] T.C. Brown, *Carbon*, **39**(5) (2001) 725.
- [33] E. Cooper, F. Krebs, M. Smith, R. Raval, *J. electron spectrosc. Relat. Phenom.*, **64** (1993) 469.
- [34] R.N.V. Krishna Deepak, B. Chandrakar, R. Sankararamkrishnan, *Biophys. Chem.*, **224** (2017) 32.
- [35] F. Sang, X. Zhang, F. Shen, *Microchim. Acta*, **186**(6) (2019) 1.
- [36] H. Ghaedi, F.Karimi, H.Karimi-Maleh, *Applied chemistry*, **52** (1398) 217-228. In Persian.
- [37] M.Abbasghorbani, *Applied chemistry*, **52**(1398) 77-86. In Persian
- [38] R. Shokrani-Havigh, Y. Azizian-Kalandaragh, *J.Optoelectron. Adv. Mater.*, **19** (2017) 283.
- [39] A. Taylor, H. Sinclair, *Proc. Phys. Soc.*, **57**(2) (1945) 126.
- [40] H. Lund, O. Hammerich, *Org. Electrochem.*, M. Dekker New York (2001).
- [41] M. Gómez-Mingot, J. Iniesta, V. Montiel, R.O. Kadara, C.E. Banks, *Sens. Actuators B*, **155**(2) (2011) 831.
- [42] L. Agüí, J. Manso, P. Yáñez-Sedeño, J.M. Pingarrón, *Talanta*, **64**(4) (2004) 1041.
- [43] N.A. Odewunmi, A.-N. Kawde, M. Ibrahim, *Sens. Actuators B*, **281** (2019) 765.
- [44] B.B. Prasad, I. Pandey, A. Srivastava, D. Kumar, M.P. Tiwari, *Sens. Actuators B*, **176** (2013) 863.
- [45] C. Kalinke, N.V. Neumsteir, P. Roberto de Oliveira, B.C. Janegitz, J.A. Bonacin, *Anal. Chim. Acta*, **1142** (2021) 135.
- [46] S.D. Holmstrom, J.A. Cox, *Anal. Chem.*, **72**(14) (2000) 3191.
- [47] G. Ziyatdinova, L. Grigor'eva, M. Morozov, A. Gilmutdinov, H. Budnikov, *Microchim. Acta*, **165**(3) (2009) 353.