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## A new glassy carbon surface covered with 1-(2-benzothiazolyl)-3-methyl pyrazol-5-one and its characterization

Demet Uzun<sup>\*1</sup>

### Abstract

1-(2-benzothiazolyl)-3-methyl pyrazol-5-one (B3MP) was electrochemically covered on a glassy carbon (GC) electrode surface in nonaqueous medium. Properties of B3MP film were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and fourier transform infrared spectroscopy (FTIR). The number of electron transferred was calculated as 0.66 indicating that a single electron transfer process was carried out and the modification mechanism of B3MP via electrochemical oxidation on the GC electrode was suggested.

**Keywords:** Electrochemical modification, Impedance spectroscopy, Glassy carbon electrode.

### 1. INTRODUCTION

Pyrazolone derivatives have a major role in the synthesis of many drugs in the fields of pharmaceuticals [1]. In addition to their analgesics and antipyretics impacts, they possess biological properties such as antimicrobial [2], antitumor [3], anti-inflammatory [4]. They have also been utilized as analytical reagents [5] to extract and separate different metal ions [6]. Their applications have been found in other areas, such as sensors [7-8].

The synthesis of pyrazole and pyrazolone derivatives have considered by chemists because of they are reported as a new class of corrosion inhibitors [9]. It has also been reported that there are many hetarylazopyrazolone derivatives which posses different chromophoric groups [10]. It was demonstrated that some dyes such as pyrazolone derivatives can be used in protection of optical record systems and optical filters [11]. Besides their well known dying properties, these type of hetarylazo dyes have taken a great interest by their

usage in non-textile applications, especially in high technology due to their near-infrared absorbing properties [12].

Covering carbon surfaces with organic molecules via covalent grafting has been became more interesting because of their applications in the area of materials science and electrochemical analysis [13]. These grafted molecules containing different functional groups were brought stability to the surfaces, so chemical and electrochemical methods have been developed to prepare new modified carbon surfaces [14].

In this study, an organic molecule which is a pyrazolone derivative, namely B3MP, was used as a modifier for the first time to develop a modified glassy carbon electrode via electrochemical method. The properties of developed electrode was investigated by electrochemical and spectroscopic methods which are CV and EIS.

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## 2. EXPERIMENTAL

### 2.1. Apparatus and Chemicals

A CHI 660B Electrochemical Workstation was used for CV and EIS measurements. A conventional three-electrode system was used. Working electrode was a glassy carbon (GC) electrode (BAS Model), the reference electrode was an Ag/Ag<sup>+</sup> (0.01 M) used in nonaqueous medium and an Ag/AgCl/KCl (sat.) used in aqueous medium. A Pt wire was used as the counter electrode. FTIR measurements of B3MP and B3MP film on GC surface were made with a Thermo Scientific Nicolet IS5 with a grazing angle and ATR (Attenuated Total Reflectance) accessories.

As supporting electrolyte, 1.0 mM ferrocyanide/1.0 mM ferricyanide (1/1) mixture with 0.1 M KCl was prepared for EIS measurements. The frequency range from 100 kHz to 0.01 kHz was selected to perform EIS data. The ac amplitude was 5 mV and the electrode potential was 0.215 V, the formal potential of ferrocyanide/ferricyanide redox couple.

Analytical grade reagents were used in the study. Tetrabutylammonium tetrafluoroborate (TBATFB), get from Merck, was used for the supporting electrolyte in nonaqueous medium. Acetonitrile (ACN) as a solvent was provided from Sigma-Aldrich. ACN containing 0.1 M TBATFB was used to prepare ferrocene solution ( $1 \times 10^{-3}$  M).

Aqueous solutions were prepared and polished electrodes were cleaned with ultra pure quality of water (18.3 M $\Omega$ ) (Millipore Corp. Bedford, MA (USA)).

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Scan Rate on The Oxidation Peak Current of B3MP

The scan rate's effect on the oxidation peak current of B3MP at the GC surface (Figure 1) was studied by CV in ACN containing 0.1 M TBATFB in the range of 25–150 mV s<sup>-1</sup>. A plot of logarithm of the

oxidation peak current vs. logarithm of scan rate (inset of Figure 1) gave a straight line with a slope of 0.8229 (R<sup>2</sup>=0.991) showing that the electrooxidation of B3MP at the GC surface is adsorption-controlled electrode reaction. Cathodic peak was not observed in the reverse scan, displaying that the charge transfer is electrochemically irreversible in the electrode process.

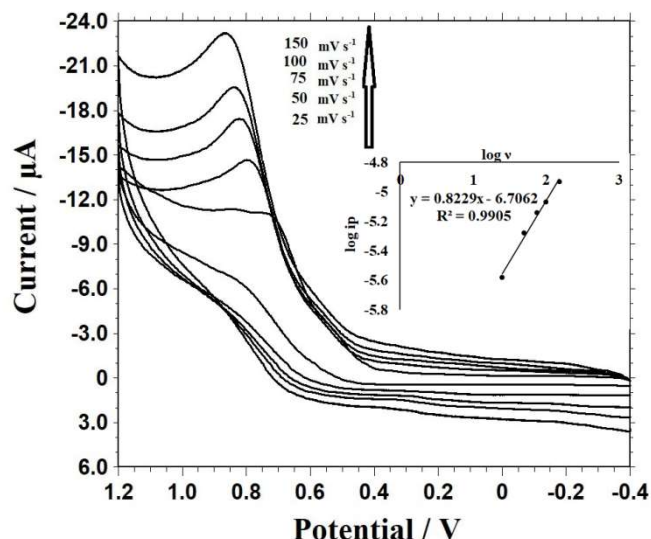


Figure 1. CVs of 1 mM B3MP at GC electrode in ACN containing 0.1 M TBATFB with different scan rates (25, 50, 75, 100, and 150 mV s<sup>-1</sup>) vs. Ag/Ag<sup>+</sup> (0.01 M) Inset: The plot of logarithm of peak current vs. logarithm of scan rate.

It was noticed that while the scan rate was increased, the anodic peak potential (E<sub>p</sub>) at about 0.7 V was shifted to positive direction (Figure 2) [15]. As for an adsorption-controlled and totally irreversible electrode process, E<sub>p</sub> is defined by the following equation [16],

$$E_p = E^{o'} + \frac{2.303 RT}{\alpha n F} \log \frac{RTk^o}{\alpha n F} + \frac{2.303 RT}{\alpha n F} \log v \quad (1)$$

E<sub>p</sub> vs. logarithm of scan rate was linear according to the equation:

$$E_p (\text{V}) = 0.1799 \log v + 0.4777 \quad (R^2 = 0.9879) \quad (2)$$

The  $\alpha n$  value was calculated as 0.33 from the slope of the E<sub>p</sub> vs. log v plot ( $2.303 RT / \alpha n F$ ) using the Laviron's equation [16]. In irreversible electrode process,  $\alpha$  is assumed as 0.5 [17]. Hence, the number of electrons in the reaction was calculated to be  $0.66 \approx 1$  indicating that a single electron transfer process was carried out between B3MP and GC electrode in the redox reaction.

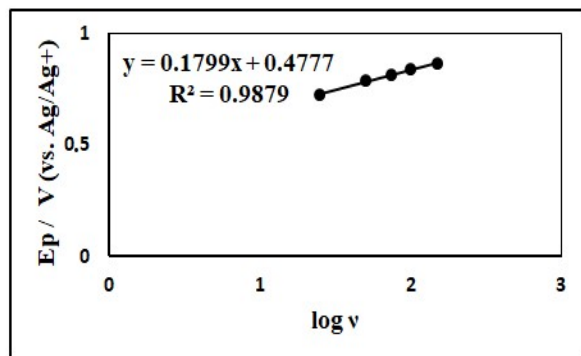


Figure 2. The plot of peak potential vs. logarithm of scan rate.

### 3.2. Preparation of B3MP-GC Electrode

In the first step of the electrode modification, a bare GC electrode was polished with 0.05  $\mu\text{m}$  alumina slurry. Polished electrode were sonicated in ultra-pure water and then with ACN for 5 min, respectively. Then, GC electrode was rinsed with ACN.

The multi cyclic voltammograms (CVs) for 1 mM B3MP at GC surface in nonaqueous solution (in ACN containing 0.1 M TBATFB) vs.  $\text{Ag}/\text{Ag}^+$  (0.01 M) are shown in Figure 3. An irreversible oxidation peak (at 0.7 V) was decreased until the 20th cycle in the potential range of -0.4 V and 1.2 V with a scan rate of  $100 \text{ mV s}^{-1}$ . The GC surface was passivated [18] and became stable state in this cycle due to inhibition of electrode surface by covalent modification resulting of the reaction between -OH and the  $\text{sp}^2$  carbon atoms on the GC surface [13]. After modification, the passivation of the surfaces is significant to protect the materials against corrosive impacts. Also, passivation of the surface due to film is advantage for using B3MP-GC in the positive potential region processes [19].

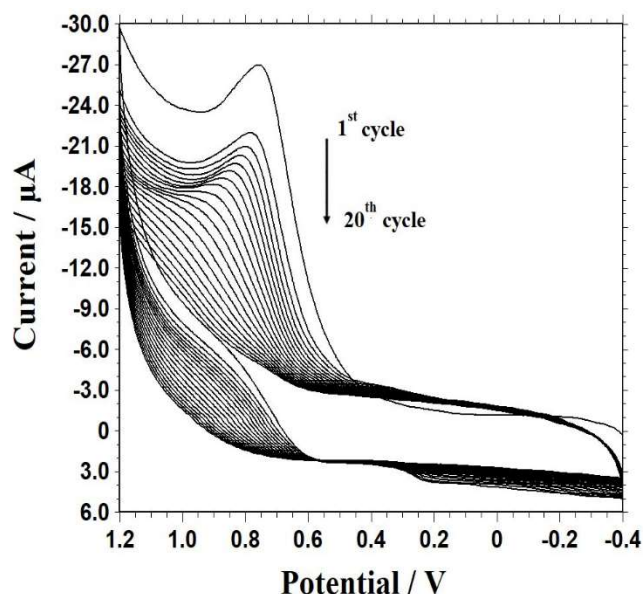


Figure 3. The cyclic voltammetric sweeps of 1 mM B3MP solution prepared in ACN containing 0.1 M TBATFB at GC electrode vs.  $\text{Ag}/\text{Ag}^+$  (0.01 M), scan rate is  $100 \text{ mV s}^{-1}$ .

### 3.3. Electrochemical Characterization of the B3MP-GC Surface Using Redox Probes

B3MP-GC surface was firstly characterized by electrochemical method using redox probes that are ferricyanide and ferrocene. For this purpose the CVs of redox probes were taken at the bare GC and B3MP-GC covered with different scan cycles shown in Figure 4(a) and Figure 4(b), respectively. Figure 4 showed that redox peaks' currents were decreased and disappeared in ferricyanide. The completely blocking was occurred at 20 cycle that is why it was chosen as optimum condition for the prepare of the modified electrode. The completely blockage of oxidation and reduction of mentioned ferricyanide redox probe is a reliable indication of B3MP layer formation on the surface of GC electrode. Whereas, the results showed that there was no completely blocking effect for ferrocene. This distinguished difference in electrochemical behaviors between ferricyanide and ferrocene at the B3MP-GC electrode should be due to the electrostatic effects of the carrying charges of the electrochemical probes and the surface charges of the B3MP layers at the GC surface [20].

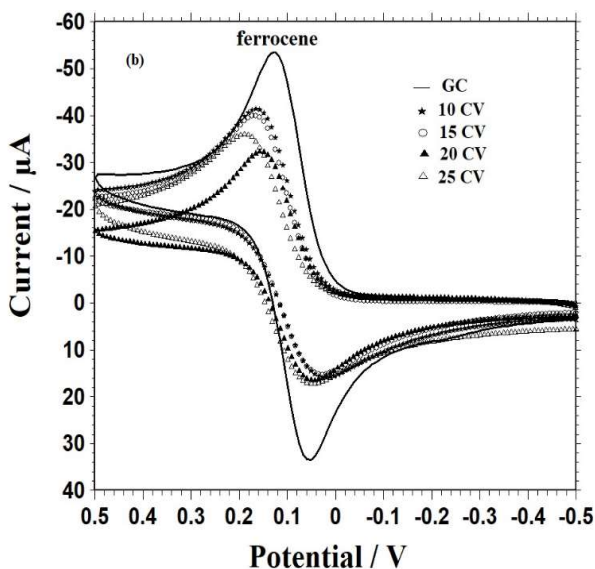
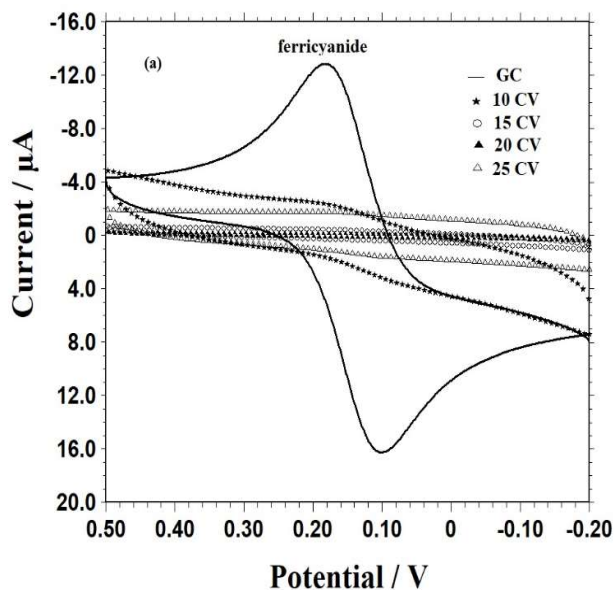
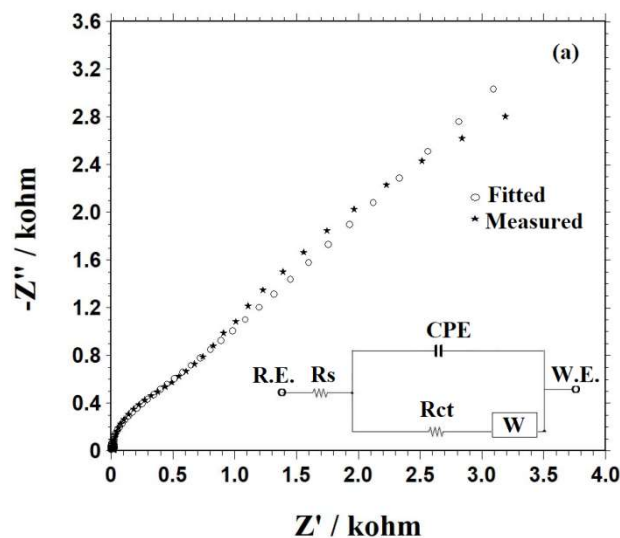


Figure 4. CVs of 1 mM (a) ferricyanide (in 0.1 M KCl) vs. Ag/AgCl/KCl (sat.) and (b) ferrocene (in ACN containing 0.1 M TBATFB) vs. Ag/Ag<sup>+</sup> at the bare GC and B3MP-GC electrodes, scan rate is 100 mV s<sup>-1</sup>.

#### 3.4. EIS Characterization of the B3MP-GC Surface

EIS is a powerful and sensitive method to learn about the features of electrode's surfaces [21]. Figure 5 shows the Nyquist plots for the bare GC and the B3MP-GC surfaces. Bare GC shows almost a straight line impedance plot at the low frequency region with a small semicircle at the high frequency region. But a high semicircle is observed for the B3MP-GC at the high frequency region, showing that the electron transfer is

blocked between redox couple and the B3MP-GC. The equivalent circuits for bare GC and B3MP-GC are shown inset of Figure 5(a) and (b), respectively. An electrolyte solution resistance ( $R_s$ ), a constant phase element (CPE), charge-transfer resistance ( $R_{ct}$ ) and the Warburg resistance ( $w$ ) resulting from the diffusion of ions from the bulk of the electrolyte to the interface are presented in this equivalent circuit [22]. CPE and  $R_{ct}$  values were found by fitting the impedance spectra using this equivalent circuit.  $R_{ct}$  values were calculated for redox couple at bare GC and the B3MP-GC as 0.38 k $\Omega$  and 21 k $\Omega$ , respectively. The charge transfer resistance' value at the B3MP-GC is higher than at the bare GC, hence it can be said that the passivation of the film is possible on B3MP-GC. The values of CPE for GC and B3MP-GC are found to be 0.2  $\mu$ F and 0.07  $\mu$ F, respectively. The Warburg resistance of the bare GC and B3MP-GC surfaces is 26.9 and 4.7, respectively. The surface coverage ( $\theta$ ) of the B3MP film can be calculated from equation  $\theta=1-R_{ct}^0/R_{ct}$  [23]. The obtained surface coverage is 98.2%. This value is accepted for a dense film.





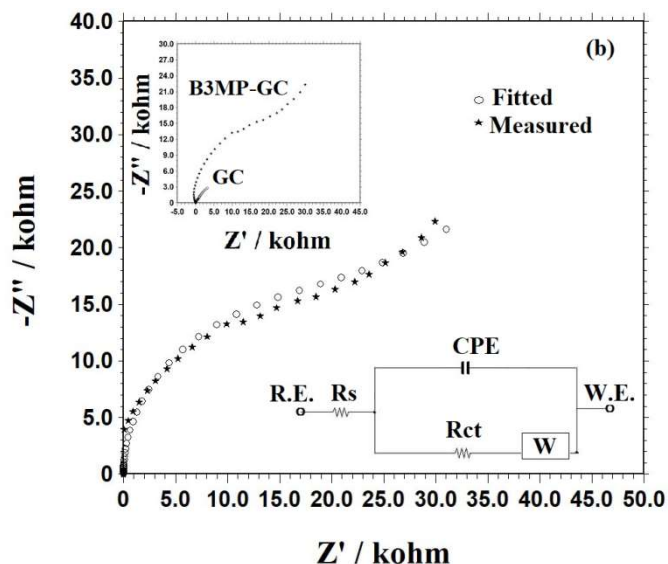


Figure 5. Nyquist plots for (a) bare GC and (b) B3MP-GC in 1 mM ferrocyanide/ferricyanide containing 0.1 M KCl. The Randle's equivalent circuit models for each electrode are at the bottom on the right hand side. Frequency range is 100 kHz-0.01 kHz with 5 mV wave amplitude at a formal potential of 0.215 V.

### 3.5. FTIR spectrum of the B3MP-GC surface

The IR data were used to characterize B3MP-GC surface and investigate the coupling sites. IR spectra of solid B3MP and B3MP film on the GC surface were recorded and compared with each other to see the differences between them. The IR of solid B3MP (curve a) and RAIRS spectra of B3MP film (curve b) were presented in Figure 6.

The heteroaromatic compound with N-H group, stretching vibration was appeared at  $3136\text{ cm}^{-1}$  while it was disappeared at GC surface. This significant change in the N-H band of B3MP film on the GC surface recommends that the N-H group plays a role in the modification process of the GC surface.

The C-H stretching vibrations on aromatic ring were exhibited in B3MP at the regions  $3070\text{--}3052\text{ cm}^{-1}$  but these vibrations weren't observed in surface spectrum suggesting that there were  $\pi\text{-}\pi$  interactions between the aromatic ring and the graphitic rings systems of the GC [24]. Aliphatic C-H bands were also recorded at  $2872\text{--}2991\text{ cm}^{-1}$  for solid B3MP and  $2843\text{--}2960\text{ cm}^{-1}$  for surface film [6].

The infrared bands from B3MP in the solid state observed at  $1650$  and  $1622\text{ cm}^{-1}$  were assigned to C=O stretching and C=C stretching, respectively [6]. Surface spectrum has a broad and weak band with a frequency shift in this region at about  $1619\text{ cm}^{-1}$  in the surface spectrum assigned to C=C group but it was not correctly detected because of overlapping. C=O band wasn't observed in the surface spectrum.

C=N stretching vibration [6] was observed at  $1596$  and  $1521\text{ cm}^{-1}$  in solid B3MP spectrum and only one band at  $1517\text{ cm}^{-1}$  in the surface spectrum. The strong band observed at  $1229\text{ cm}^{-1}$  in solid B3MP spectrum was assigned to C-N stretching vibration. It was weakly observed at  $1222\text{ cm}^{-1}$  in surface spectrum.

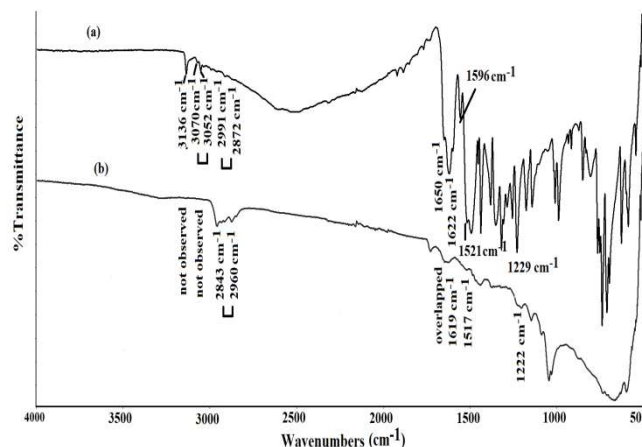


Figure 6. IR spectrum of (a) solid B3MP and (b) B3MP film on the GC surface

All mentioned above showed that the B3MP was covered to surface. The modification mechanism was proposed from the scan rate, CV and FTIR results, shown in Figure 7. According to that the -NH group in B3MP molecule was oxidized first with one-electron generating radical cation [25]; then the radical cation delocalized in the heteroaromatic ring and -OH radical cation was occurred and the radical cation reacted with the GC surface forming C-O-C linkages with giving one  $\text{H}^+$  [26-28].

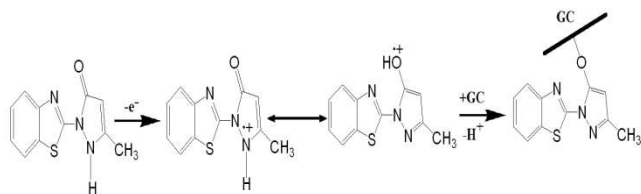


Figure 7. The proposed modification mechanism of GC with B3MP.

#### 4. CONCLUSIONS

In this paper, B3MP was firstly covered to GC electrode via electrochemical method in nonaqueous medium to develop a new electrode. The properties of new surface were evaluated by CV, EIS and FTIR. From the EIS results, B3MP-GC showed a high surface coverage value (98.2%) as a result of increasing charge transfer resistance for redox couple. The electrochemical coverage mechanism of B3MP to the GC surface has been also investigated. It was supposed that the B3MP was covered to GC surface from its  $-OH$  group with releasing one electron. This modified electrode can be used in the corrosion studies because of its high electro-inactive property and also in diverse applications such as energy storage, sensing, etc.

#### REFERENCES

- [1] K. Brune, "The early history of non-opioid analgesics," *Acute Pain*, vol. 1, pp. 33–40, 1997.
- [2] S. M. Sondhi, S. Kumar, N. Kumar, P. Roy, "Synthesis anti-inflammatory and anticancer activity evaluation of some pyrazole and oxadiazole derivatives," *Medicinal Chemistry Research*, vol. 21, no. 10, pp. 3043–3052, 2012.
- [3] A. Zaoui, L. Hammal, N. Bennamane, S. Merabtene, B. Nedjar-Kolli, "A catalytic method for the synthesis of pyrazolone derivatives using heteropolyacids and study of the antibacterial activity," *International Journal of Pharmaceutical, Chemical and Biological Sciences*, vol. 3, no. 3, pp. 732–737, 2013.
- [4] E. Bagdatli, E. Altuntas, U. Sayin, "Synthesis and structural characterization of new oxovanadium(IV) complexes derived from azo-5-pyrazolone with prospective medical importance," *Journal of Molecular Structure*, vol. 1127, pp. 653–661, 2017.
- [5] N.V. Trofimov, N.N. Nekhaer, N.A. Kanaev, A.I. Busev, "Pyrazolone derivatives as analytical redox-reagents. Determination of cerium and hydrogen peroxide with bis-(1-phenyl-3-methylpyrazolone-5)," *Zhurnal Analiticheskoy Khimii*, vol. 37, pp.1445–1451, 1982.
- [6] E. Aktan, B. Çatıkkaş, "Infrared and Raman spectra, DFT investigation of the tautomerism, conformational equilibrium, structure and vibrational assignment of 1-(2-benzothiazolyl)-3-methyl pyrazol-5-one," *Vibrational Spectroscopy*, vol. 67, pp. 92–100, 2013.
- [7] T. Ito, C. Goto, K. Noguchi, "Lanthanoid ion-selective solvent polymeric membrane electrode based on 1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone," *Analytica Chimica Acta*, vol. 443, pp. 41–51, 2001.
- [8] V. Kumar Gupta, S. Jain, S. Chandra, "Chemical sensor for lanthanum(III) determination using aza-crown as ionophore in poly(vinyl chloride) matrix," *Analytica Chimica Acta*, vol. 486, pp. 199–207, 2003.
- [9] A. S. Fouda, A. A. Al-Sarawy, E. E. El-Katori "Pyrazolone derivatives as corrosion inhibitors for C-steel in hydrochloric acid solution," *Desalination*, vol. 201, pp. 1–13, 2006.
- [10] M.S. Yen, I. J. Wang, "A facile syntheses and absorption characteristics of some monoazo dyes in bis-heterocyclic aromatic systems part I: syntheses of polysubstituted-5-(2-pyrido-5-yl and 5-pyrazolo-4-yl)azo-thiophene derivatives," *Dyes and Pigments*, vol. 62, pp. 173–180, 2004.
- [11] H. Bach, K. Anderle, Th. Fuhrmann, J. H. Wendorff, "Biphoton-induced refractive index change in 4-Amino-4'-nitroazobenzene/polycarbonate," *The Journal of Physical Chemistry*, vol. 100, pp. 4135–4140, 1996.
- [12] E. Aktan, N. Ertan, T. Uyar, "Synthesis, characterization and theoretical study of new hetarylazopyrazolone dyes and investigation of their absorption spectra," *Journal of Molecular Structure*, vol. 1060, pp. 215–222, 2014.

- [13] D. Morales-Martínez, F. J. González, "Reversible reorganization of alkyl ester groups grafted on glassy carbon electrode: Induction by a redox probe," *Electrochemistry Communications*, vol. 62, pp. 21–23, 2016.
- [14] V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, "Functionalization of graphene: Covalent and non-covalent approaches, derivatives and applications," *Chemical Reviews*, vol. 112, pp. 6156–6214, 2012.
- [15] L. Arrue, T. Barra, M. B. Camarada, X. Zarate, E. Schott, "Electrochemical and theoretical characterization of the electro-oxidation of dimethoxycurcumin," *Chemical Physics Letters*, vol. 677, pp. 35–40, 2017.
- [16] E. Laviron, "Adsorption, autoinhibition and autocatalysis in polarography and in linear potential sweep voltammetry," *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, vol. 52, no. 3, pp. 355–393, 1974.
- [17] Y. Li, Y. Gao, Y. Cao, H. Li, "Electrochemical sensor for bisphenol A determination based on MWCNT/melamine complex modified GCE," *Sensors and Actuators B*, vol. 171–172, pp. 726–733, 2012.
- [18] S. Bouden, G. Trippé-Allard, J. Ghilane, H. Randriamahazaka, "Electrochemical immobilization of redox active molecule based ionic liquid," *Electrochemistry Communications*, vol. 58, pp. 65–68, 2015.
- [19] D. Uzun, H. Arslan, A. Balaban Gündüzalp, E. Hasdemir, "Preparation of modified glassy carbon surface with N-(1-H-indole-3yl) methylene thiazole-2-amine and its characterization," *Surface & Coatings Technology*, vol. 239, pp. 108–115, 2014.
- [20] Y. Chen, L.-R. Guo, W. Chen, X.-J. Yang, B. Jin, L.-M. Zheng, X.-H. Xia, "3-mercaptopropylphosphonic acid modified gold electrode for electrochemical detection of dopamine," *Bioelectrochemistry*, vol. 75, pp. 26–31, 2009.
- [21] H. Chen, J.-H. Jiang, Y. Huang, T. Deng, J.-S. Li, G.-L. Shen, R.-Q. Yu, "An electrochemical impedance immunosensor with signal amplification based on Au-colloid labeled antibody complex," *Sensors and Actuators B*, vol. 117, pp. 211–218, 2006.
- [22] M. Khoshroo, A. A. Rostami, "Characterization of the organic molecules deposited at gold surface by the electrochemical reaction of diazonium salts," *Journal of Electroanalytical Chemistry*, vol. 647, pp. 117–122, 2010.
- [23] R. Zhang, G.-D. Jin, D. Chen, X.-Y. Hu, "Simultaneous electrochemical determination of dopamine, ascorbic acid and uric acid using poly(acid chrome blue K) modified glassy carbon electrode," *Sensors and Actuators B*, vol. 138, pp. 174–181, 2009.
- [24] D. Deletioğlu, E. Hasdemir, A.O. Solak, Z. Üstündağ, R. Güzel, Preparation and characterization of poly(indole-3-carboxaldehyde) film at the glassy carbon surface, *Thin Solid Films*. 519 (2010) 784–789.
- [25] R. N. Goyal, N. Kumar, N. K. Singhal, "Oxidation chemistry and biochemistry of indole and effect of its oxidation product in albino mice," *Bioelectrochemistry and Bioenergetics*, vol. 45, pp. 47–53, 1998.
- [26] R. S. Deinhammer, M. Ho, J. W. Anderegg, M. D. Porter, "Electrochemical oxidation of amine-containing compounds: A route to the surface modification of glassy carbon electrodes," *Langmuir*, vol. 10, pp. 1306–1313, 1994.
- [27] Y. Li, X. Lin, "Simultaneous electroanalysis of dopamine, ascorbic acid and uric acid by poly (vinyl alcohol) covalently modified glassy carbon electrode," *Sensors and Actuators B*, vol. 115, pp. 134–139, 2006.
- [28] V. K. Gupta, M. L. Yolac, N. Atar, A. Osman Solak, L. Uzun, Z. Üstündağ, "Electrochemically modified sulfisoxazole nanofilm on glassy carbon for determination of cadmium(II) in water samples," *Electrochimica Acta*, vol. 105, pp. 149–156, 2013.