

11th ISE Satellite Student Regional Symposium on Electrochemistry

July 1st 2022

Faculty of Chemical Engineering and Technology
Zagreb, Croatia

BOOK OF ABSTRACTS



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Fakultet kemijskog
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Faculty of Chemical Engineering and Technology
Zagreb, Croatia

11th ISE Satellite Student Regional Symposium on Electrochemistry

Book of abstracts

Croatian Society of Chemical Engineers



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Preface

It was our great pleasure and honour to welcome all participants of the "11th ISE Satellite Regional Symposium on Electrochemistry" (11th ISE-SRSSE) held on July 1st, 2021. The symposium was held in a hybrid format facilitating both, on-site participation at the Faculty of Chemical Engineering and Technology, Zagreb, and online participation through the Skype platform. The meeting was held under the support of the International Society of Electrochemistry (ISE) to encourage young scientists, postgraduate and graduate students, to present their research in a friendly atmosphere.

The 11th ISE-SSRSE was successfully organized for the eleventh year, with the exception of 2020 due to the COVID-19 pandemic. This year the symposium returned to its original form, on-site participation. The symposium aimed to encourage young scientists to present their research in the form of oral presentations in the fields of electrochemistry and electrochemical engineering. The symposium was attended by 18 young scientists from Croatia and Austria, with a total of 15 oral presentations. Oral presentations covered broad aspects of electrochemical fields: electrochemistry of materials for energy storage/conversion, corrosion, environmental and analytical chemistry.

The organizing committee would like to sincerely thank all participants for their contributions and gratefully acknowledge the International Society of Electrochemistry for the given support, providing the opportunity for young researchers to exchange their working experience in various fields of electrochemistry and make connections that may result in future collaboration.

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ORAL PRESENTATIONS

Nanographite as an anode material in lithium-ion batteries

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In this paper the properties of nano graphite as anode material in Li-ion batteries and the possibility of using nano graphite as an addition to silicon to improve electrochemical properties and to create superior anode materials for lithium storage were investigated. Physical characterization of materials was carried out in order to create a correlation between structure and properties of materials. The characterization of materials by TGA analysis showed a weight loss of only 0,2 %. FTIR analysis showed the lack of water and low presence of oxygen groups, which was confirmed by TGA analysis. The particle size analysis by the DLS technique revealed a size of 420 nm with narrow distribution by volume and number of particles. B.E.T analysis showed a surface area of 61 m²/g and pore size of 19.2 Å, which belong to the micropore sizes.

Electrodes, on which electrochemical tests were conducted, were prepared by applying a paste made from nano graphite and silicon samples mixed with carbon black and polyvinylidenfluoride in various proportions, in the form of a thin film on copper foil. Electrochemical tests were conducted using methods of cyclic voltammetry, galvanostatic charge and discharge and electrochemical impedance spectroscopy. Cyclic voltammetry showed that addition of the carbon black achieves better reversibility of lithium intercalation. Nano graphite as an addition to silicon showed a loss of certain electrochemical properties due to the change in the intercalation mechanism. Voltage profiles show the stability of all materials during the charging or discharging cycles. The highest capacity of 24.01 mAh g⁻¹ was achieved for the nano graphite sample with carbon black, while for the silicon sample, 13.59 mAh g⁻¹ was achieved. Impedance measurements showed a reduction in internal resistance and resistance to charge transfer after completed charging and discharge cycles, whereby a sample of nano graphite with carbon black successfully showed the formation of the SEI layer after a few of the charging and discharging cycles.

New approach in corrosion protection based on the use of waterborne coating

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Bronze objects of art placed outside are susceptible to corrosion under the influence of aggressive compounds. Consequently they are covered with layer of corrosion products called patina. Formation of natural patina is long term process which depends on the amount of corrosion compounds in the environment. That is the reason why conservation profession is using artificial patination instead. Artificial patina is very reactive and does not provide high level of corrosion protection. That is the reason why conservation ethics is responsible for additional preservation of mentioned objects. Presently used organic solvent coatings are being replaced with waterborne coatings due to their harmful effect on environment. Even though waterborne coatings are not toxic, their level of corrosion protection is still lower than organic counterpart. One way of improving it, is through combination with self-assembled monolayers of phosphonic acid. Monolayers are modifying substrate surface and ensure better bonding between metal and coating.

The aim of this study is examining the level of protection of commercial waterborne coating on artificial sulphide patina on RG7 and CuSn6 bronze. Furthermore, corrosion protection is improved by pretreatment of patinated samples with self-assembled monolayers of the phosphonic acid. The influence of bronze composition is examined. Electrochemical properties are investigated using electrochemical impedance spectroscopy (EIS) in artificial acid rain (pH 5). Obtained results were compared with and without acid pretreatment. The structure of formed layers is confirmed with Fourier transform infrared spectroscopy (FTIR).

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Complexation of membrane phospholipids with cobalt in seawater

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The complexation between membrane lipids and metal ions - micronutrients, play an important role in many biological processes [1]. In this study lipid extract of the cultured green algae was used to study the interaction of metals Co(II) with the main component of the membrane-lipids. Membrane phospholipids were extracted from other biological components on TiO₂- μ SPE columns selective for the phosphate group [2]. Phospholipid extract was used for electrochemical study and determination of mixed complexes of Co(II) with phospholipid mixture. Before the study on real samples, investigations were performed on standard solutions of lipids.

Measurements were carried out by voltammetry at the static mercury drop electrode. It was found that interactions and formation of mixed complexes are possible only when 1,10-phenanthroline (Phen) is present in solution. Phen formed hydrophilic complexes with Co(II) in the subphase, followed by the mixed ligand with standard lipids or with real phospholipid extract. The reactions were carried out at a pH of 8.2, which mimics the conditions in seawater. Complex of Co(II)-Phen- PL complex reduced irreversibly at -1.65 V including adsorption of the reactant, followed by irreversible dissociation of the mixed complex, indicating a chemical reaction with two electron transfers (EC mechanism). The interactions between membrane lipids and ions, which are the subject of these studies, play an important role in many biological processes. The information on the mechanism of complex formation is an important contribution to the understanding of complex processes at natural cell membranes.

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Application of PVA hydrogel based electrolyte for electrochemical impedance spectroscopy measurements

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Electrochemical impedance spectroscopy (EIS) is a widely used technique for corrosion studies which offers a great potential for monitoring the conservation condition of metallic cultural heritage [1, 2]. However, using a traditional three-electrode cell in a liquid electrolyte represents the main issue to the application of electrochemical measurements, due to irregular surface of metal sculptures and monuments. Overcoming these difficulties is the key to a successful implementation of EIS in the field and as one of the possible solutions to this problem replacement of the conventional electrolyte solution with a gel polymer electrolyte is presented. Application of hydrogel based electrolyte for EIS measurements opens up the possibility to carry out a punctual analysis of the artefact without compromising its surface. One of the most promising candidates for this application is hydrogel electrolyte based on poly (vinyl alcohol) (PVA) due to its low cost, green preparation, stability and high water content [3]. Therefore, the aim of this work was to conduct electrochemical impedance spectroscopy measurements using hydrogel electrolytes based on PVA. The experiments were carried out on different copper and bronze substrates-bare and corroded metal and metal protected by a thin and thick layer of coating. The results were obtained by measurements in two- and three-electrode cell configuration by using PVA prepared in two different electrolytes. Finally, the results were compared with results obtained in a traditional electrochemical cell.

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Application of the electroanalytical methods for characterization of reduced sulfur species (HS^- , S^0 , S_x^{2-} , RSH , $\text{S}_4\text{O}_6^{2-}$) in natural waters

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Electroanalytical methods (EM) at the mercury (Hg) electrode are widely used for the determination of different reduced sulfur species (RSS: HS^- , S^0 , S_x^{2-} , RSH , $\text{S}_4\text{O}_6^{2-}$) in natural waters due to the strong interaction between RSS and the Hg [1, 2]. The application of EM allows the direct determination of RSS without prior processing of the natural samples, but the determination of individual RSS in mixture samples remains a challenge due to low RSS concentrations, thermodynamic unstabilities and changes in RSS speciation during sampling and sample manipulation, as well as due to different analytical windows of the used EM.

In this paper voltammetric methods: cyclic (CV), differential pulse (DPV), and sampled direct current voltammetry (SDC) were used to measure individual RSS and mixture solutions, while the euxinic water column of the marine Rogoznica Lake (RL) [1, 2] was chosen as the natural study site for application and testing of the EM.

CV in the solutions of HS^- , S^0 and S_x^{2-} revealed a similar HgS reduction peak around -0.68 V (vs. Ag/Ag/Cl). In the case of tetrathionate and glutathione, more positive peaks (corresponding to their Hg complexation) than HgS reduction are revealed. In mixtures of these RSS, the HgS formation and its reduction at about -0.70 V is the most pronounced, and only the HgS reduction is obtained. This peak is usually taken as a measure of the total RSS in the studied samples. DPV was used for direct determination of S_x^{2-} and recorded well-defined current minimums around -1.0 V demonstrated the presence of S_x^{2-} , which in the euxinic RL samples were measured up to 153 μM of polysulfidic S^0 . SDC measured total S^0 including soluble ($\text{S}_{8\text{-aq}}$), polysulfidic and colloidal S^0 . Obtained results indicate that each of the used EM has its own detection window which can measure different S^0 forms that produce different EM responses. DLS measurements additionally proved changes in S^0 colloidal solution visible by recording different hydrodynamic properties (radius) of S^0 upon different dilutions of the original sample. The same effect is observed in the RL euxinic samples. In such experimental conditions, it appears that RSS becomes more electrochemically active, or they are simply more easily delivered (as being faster in smaller forms) to the Hg, giving the higher current of the HgS reduction.

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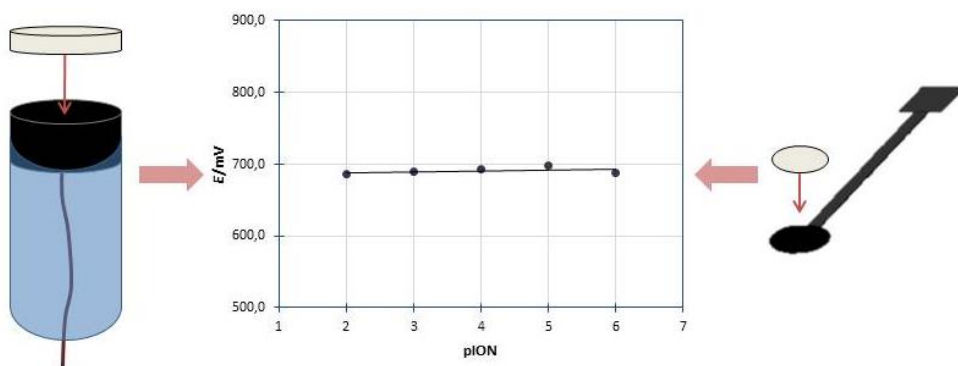
An inkjet printed all solid-state Ag/AgCl reference electrode based on polyvinyl butyral

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Miniaturized solid-state electrodes fabricated by inkjet printing provide innovative application scenarios of potentiometric sensing [1]. We present here the development of a reference paste that – when used on a printed electrical contact – gives a reference electrode. Such a paste was prepared by an innovative intense pulsed light (IPL) photoreduction of a 10% polyvinyl butyral (PVB) in a methanol solution of AgNO_3 and NaCl , yielding a silver/silver chloride reference paste (RM). Firstly, the RM was drop cast on a glassy carbon disk electrode (RM-GC) [2]. The potentiometric response of the electrode in aqueous solutions of KCl , NaNO_3 , NaCl , and CaCl_2 of different concentrations versus commercial reference electrode, as well as the response of the electrode to pH changes, was examined. A stable electrode potential was achieved by optimizing: IPL photoreduction parameters, volumes of the RM, and conditioning time. Lastly, the optimized reference membrane was transferred onto a planar inkjet printed silver electrode and characterized correspondingly.



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Phase sensitive a.c. voltammetry as a simple, fast tracking tool for studying changes in the environment

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Organic carbon (C) is an important component of many biogeochemical processes and can be a valuable indicator of environmental change [1]. The composition of organic matter (OM) in natural waters is complex, indeterminate, and variable over time. An important subset of dissolved and particulate organic C (DOC, POC) in the aquatic environment is OM with surface active properties, i.e., surface active substances (SAS) [1-3]. SAS are mainly produced autochthonously by biological activity (primary and secondary production, grazing), while part of SAS may also be introduced allochthonously (land and atmospheric input). SAS are the most reactive fraction of OM, which tend to adsorb at different phase boundaries and affect abiotic and biotic processes. Due to their strong adsorption properties, the presence of SAS in natural waters can be monitored by adsorption on the hydrophobic surface of the mercury (Hg) electrode using the electrochemical method of phase sensitive alternating current voltammetry (PSACV). PSACV can selectively measure faradic (in-phase signal) or capacitive current (out-of-phase signal) as a function of electrode potential. Out-of-phase measurements reflect the adsorption extent of all present SAS that take a part in adsorption on Hg in a competitive manner, expressed as the equivalent adsorption effect of a given amount (mg dm^{-3}) of model SAS, usually the nonionic polyoxyethylene-t-octylphenol, Triton-X-100 [1-3]. The signal depends not only on the concentration of SAS but also on its adsorption strength. Moreover, the type of OM present in the sample can be characterized by analyzes of the SAS desorption waves, which seem to be characteristic for the particular type of OM. Additional characterization is possible by normalizing SAS to the DOC content, giving normalized surfactant activity $\text{NSA} = [\text{SAS (eq. T-X-100)} / \text{DOC}]$, which can be compared to the NSA of the selected model substances that are typical or expected for the samples (systems) studied [2,3].

This study focuses on the changes in the quantity and quality of OM during the unusual phenomena in the northern Adriatic and rainfall event in central Croatia, as well as on a long-term study of OM in a eutrophic marine lake (Rogoznica lake) in the central Adriatic. Additionally, the effect of sample filtration will be presented, showing that the most reactive SAS pool belongs to the colloids, i.e. to the fraction $< 0.22 \mu\text{m}$.

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Application of the conductive paste electrolyte for the electrochemical impedance spectroscopy measurements

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The use of electrochemical impedance spectroscopy (EIS) in the diagnosis of cultural objects represents a very powerful technique that can help conservators identify which object needs intervention to evaluate the effect of a treatment. EIS is still far from being standard or routinely applied because of difficulties both in applying this technique to cultural objects-which requires in situ measurements-and in interpreting the results. A major challenge in performing EIS measurements in the field is the placement of a cell with liquid electrolyte on an irregular, uneven, and thin surface of the artefact. One approach to this problem is based on the use of a solid electrolyte instead of a liquid electrolyte.

In the present study, we investigate the concept of rapid in situ measurements on copper and bronze, as well as on patinated bronze without and with a protective layer, using a conductive paste electrolyte that provides a non-aggressive environment in a two-electrode system consisting of a substrate and a single flexible (counter/reference) electrode. Comparative measurements were performed with both a screen-printed carbon electrode and a conventional electrochemical cell.

In this way, electrochemical impedance spectroscopy measurements were performed in two- and three-electrode cell configurations using conductive paste electrolyte to better define the influence of the various parameters of the experimental setup on the recorded data.

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Application of $\text{WO}_3/\text{BiVO}_4$ electrode for the photoelectrochemical degradation of amoxicillin

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Antibiotics represent one of the main discoveries of the last century that changed the treatment of a large array of infections in a significant way. However, increased consumption has led to an exposure of bacterial communities and ecosystems to a large amount of antibiotic residues. [1] Amoxicillin is a broad-spectrum antibiotic widely used for treating both human and animal diseases, and it is excreted unchanged in the environment. Hence, it is possible to find traces of this drug or its degradation products in environmental water bodies. [2]

Therefore, the main goal of this study was to prepare $\text{WO}_3/\text{BiVO}_4$ composite electrodes that would be efficient for the photoelectrochemical degradation of amoxicillin. WO_3 was synthesized via a hydrothermal method. The electrodes were fabricated using the fluorine-doped tin oxide (FTO) glass electrode. Single layer of WO_3 was deposited on FTO glass by spin coating, afterwards single layer of BiVO_4 was deposited on WO_3 surface, forming the $\text{WO}_3/\text{BiVO}_4$ heterojunction. The photoelectrochemical characterization of the $\text{WO}_3/\text{BiVO}_4$ electrodes included measurements of open-circuit potential (OCP), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA). The measurements were carried out using a typical three-electrode system. The samples, Pt foil and $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (saturated KCl) electrode were used as working electrode, counter electrode, and reference electrode, respectively. The measurements were executed in both, 0,1 molar NaCl and 0,1 molar Na_2SO_4 solution. Based on the characterization results, the photoelectrochemical degradation of amoxicillin was carried out using CA at the potential $E = 0.8$ V vs. reference electrode. The decrease in amoxicillin concentration was monitored by high-performance liquid chromatography (HPLC).

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Modification of electroanalytical method for analysis of metal amounts from marine plastic surfaces

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For the past seven decades plastic waste has been accumulating in environment, which is especially significant and alarming for marine systems. Marine plastic litter under influence of UV-radiation and different physico-chemical factors can degrade and defragment into smaller particles. Plastic fragments can adsorb different pollutants, including potentially ecotoxic trace metals, and become vector for their transport, which is especially significant for coastal areas.

To determine the amount of metals adsorbed on plastic particles (sampled in the Croatian coastal area), metals were extracted by mixture of acids from plastic surfaces. Consequently, acid solution was additionally prepared for analysis. Concentrations of metals were measured by differential pulse anodic (Zn, Cd, Pb and Cu) and cathodic (Ni and Co) stripping voltammetry by Metrohm Autolab modular potentiostat/galvanostat Autolab PGSTAT204, connected with a three-electrode system Metrohm 663 VA STAND (Utrecht, The Netherlands). Working electrode used was static mercury drop electrode. Voltammetry is low-cost, reliable and relatively simple method with low detection limits, including well established methods for measuring metals in environmental samples. Method modification, as well as some challenges that were usually encountered during analysis of this kind of samples will be discussed.

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Investigation of the effects of temperature and exposure time on the corrosion behavior of a ferritic steel in CO₂ environment using the optimized linear polarization resistance method

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The oil and gas industry faces several problems in transportation and production due to corrosion of carbon steel that consequently leads to ecological accidents, large losses of products, and expenses [1]. Electrochemical techniques are powerful tools for fast and reliable determination of corrosion rates in such environments. However, there is scarce information about the effect of different input values of the electrochemical technique with regard to different parameters (e.g. time, temperature) of CO₂ corrosion.

In this work, linear polarization resistance (LPR) was used to instantly evaluate corrosion behavior of a ferritic steel under conditions representative in oilfields (1.5 wt% NaCl solution purged with 1 bar CO₂). Input values of LPR method, scan rate and time of measurement, respectively, were optimized and the results were compared with separately conducted Tafel polarization experiments. In addition, LPR measurements were utilized to study the influence of exposure time and temperature (30, 60 and 90°C) on formation of protective layers on the surface of carbon steel. SEM/EDS analyses were performed to characterize formed layers.

The results of the Tafel polarization experiment were used to validate the optimization of the LPR method successfully. With increasing temperature, the oxygen content increased while the content of carbon in the layer of corrosion products decreased and iron carbonate (FeCO₃) was detected as the main component of the layer. Therefore, higher temperature resulted in a thicker protective layer and a lower corrosion rate.

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Electrochemically determined metallothioneins as indicators of wastewater-borne metal exposure in the Krka River

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Among various pollutants in the aquatic ecosystems, metals pose a serious threat due to their toxicity and potential for bioaccumulation. To assess the overall impact of metal exposure in aquatic environments, bioindicator organisms are commonly used. An early warning biological sign of metal exposure is the induction of metallothioneins (MTs), cytosolic proteins responsible for metal homeostasis and detoxification [1].

In this study, MT levels were used to evaluate metal exposure in fish intestinal parasite *Dentitruncus truttae* Sinzar, 1955 and its host brown trout (*Salmo trutta* Linnaeus, 1758) from the karst Krka River. Although the lower part of the Krka River course was proclaimed a national park, its upper course is impacted by inadequately treated wastewaters, which are the main anthropogenic source of metals in the river. MT concentrations were compared among fish liver, as a site of metal detoxification, fish intestine, as a site of metal uptake, and *D. truttae*, which absorb nutrients from the intestinal tract of fish but also efficiently accumulate metals. Fish were caught at the Krka River source (KRS), the reference site, downstream of the wastewater outlets (KRK) and at hydropower plant Miljacka, situated in the national park (KNP). MTs were quantified by differential pulse voltammetry (DPV) using modified Brdička procedure, a commonly used electrochemical method for the determination of proteins containing thiol groups.

DPV was confirmed as a reliable and sensitive method for measuring MTs in biological samples. MT concentrations were significantly higher in *D. truttae* than in fish gut and liver, and represent the first data for these parasites [2]. *D. truttae* also showed differences among locations, with the highest MT levels in KRK (2,2 mg g⁻¹ wet tissue), indicating metal-induced stress near the wastewater outlets.

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Development of a system for measuring the concentration of ethyl alcohol

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A system for measuring the concentration of ethyl alcohol in liquid solution using interdigital capacitive sensor and arduino is developed. The system consists of an interdigital capacitive sensor, capacitance to digital converter and an Arduino microcontroller. The sensor is used to measure the capacitance of the solution, and the converter is used to convert the capacitance into a digital signal. The microcontroller is used to read the digital signal and to calculate the concentration of ethyl alcohol in the liquid. The system is calibrated using a standard solution of known concentration. The resulting sensor was used to construct a calibration curve in the concentration range of 0 to 80 vol% ethanol. For the linear regression analysis, only a set of measurement data from ethanol was taken because the standard deviation is the same for all points in the range.

From the above, it can be concluded that with the given technology (with certain modifications) it is possible to make very precise sensors that could be used in the chemical, biotechnological, and food industries.

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Procedure optimization for the formation of polymer nanocoatings from elaidic acid

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In this research, the optimal procedure for the formation of polymer nanocoatings (PNCs) on copper and the longevity of their protection in a simulated urban atmosphere was investigated. Elaidic acid (EA), $C_{18}H_{34}O_2$, an unsaturated fatty acid with one double bond in trans position was used for self-assembling on copper. After the immersion, EA spontaneously self-assembles on copper into layers of nanometer thickness. Once the molecules are arranged on the surface of copper, they are crosslinked using ionizing irradiation into a 3D structure via a double bond, forming coatings with improved properties. The protective properties of the coatings were investigated using electrochemical methods with direct and alternating currents. Tafel extrapolation method, linear polarization resistance method (LPR), and electrochemical impedance spectroscopy (EIS) were used. Contact angle goniometry was used to characterize the formed coatings.

The obtained results showed that the optimal procedure for the formation of SAM EA on the copper is with oxidation and adsorption of 24 h and without drying, with a 10 mM concentration of an ethanolic EA solution. The crosslinked PNCs showed longer and better protective properties in simulated rain solution compared to non-crosslinked coatings. Whether the molecules are crosslinked or not, the presence of EA on the copper makes the surface hydrophobic.

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Influence of surface-active organic molecules on electrochemical determination of copper complexing capacity in seawater

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More than 99% of copper ions in seawater are present in organic complexes which determine their bioavailability and toxicity. To characterise organic ligands, we group them based on similar affinities of the copper ion binding functional groups and copper complexing capacity parameters are determined (ligand group concentration L_i , apparent stability constants $\log K_i$). In this study, we explored the effects of interferences such as the surface-activity of (1) specific organic molecules in model solutions and (2) natural organic matter in seawater samples, on the Cu peak detection in complexometric titration. We used differential pulse anodic stripping voltammetry on hanging mercury drop electrode. Fulvic acid, BSA protein and carbohydrates dextran, Na-alginate, chitosan and ι -carrageenan were model organic substances, while seawater samples were collected from the bottom and surface during the spring and summer seasons at the North Adriatic station 101. We investigated the possibility of reducing the interference of each adsorbed molecule on the electrode by applying the desorption potential E_d [1] and adding T-X-100, the non-ionic [2], SDS, the anionic and TMAB, the cationic surfactant. The optimal conditions for natural samples were selected by analysing the results obtained for model solutions: the addition of 1 mg dm^{-3} T-X-100 together with $E_d = -1.4 \text{ V}$ for 1 s competitively inhibits the adsorption of surface-active natural organic matter on the electrode, greatly improving the shape and height of the Cu reoxidation peak. Two classes of ligands were determined in all samples at concentrations ranging from 12.0 to 45.3 nmol dm^{-3} for L_1 and 22 to 71.5 nmol dm^{-3} for L_2 with $\log K_1$ 10.01 – 11.17 and $\log K_2$ 8.42 – 9.8, respectively. Ligand concentrations were highest in the surface layer in May and June, probably due to the spring activities of phytoplankton, which include exudation of surface-active organic compounds.

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