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Study of different types of copper electrodes for anodic stripping voltammetric detection of trace metal ions

Domen Obrez [a,b], Mitja Kolar [b], Nikola Tasić [a], Samo B. Hočevar [a,*]

[a] Department of Analytical Chemistry, National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia
[b] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, Ljubljana, Slovenia

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ABSTRACT

Copper electrodes exhibit interesting characteristics for application in electrochemical stripping analysis and represent another alternative to their mercury counterparts. In this work, we studied different types of copper-based electrodes for anodic stripping voltammetric detection of trace metal ions. We investigated copper film (CuFE), and bulk copper electrodes, such as in-situ and ex-situ prepared CuFEs using glassy carbon and screen-printed carbon supporting electrodes, a bulk copper disk and screen-printed copper electrode, and a copper wire as the simplest, inexpensive, and readily available analog. For studying their electroanalytical performances, low concentrations (μg L^{-1}) of Cd(II) and Pb(II) were used as model ions. We examined and optimized several key parameters affecting the preparation and functioning of copper electrodes, such as the composition of the measurement solution, copper concentration for in-situ and ex-situ preparation of CuFE, deposition potential, deposition time, etc. Most of the tested copper electrodes showed favorable stripping voltammetric performances, particularly the CuFE ex-situ prepared on a glassy carbon electrode and the CuFE in-situ prepared on a screen-printed carbon substrate. Notably, a copper wire revealed an excellent electroanalytical operation with a limit of detection of 0.6 μg L^{-1} for Pb(II) and 1.8 μg L^{-1} for Cd(II). The practical applicability of a copper electrode was tested by measuring a real tap water sample.

1. Introduction

There continues to be growing interest in simple, fast, and on-site measurements of (trace) heavy metal ions originating from natural and anthropogenic sources. In particular, the emergence of new technologies and industries leads to a steady increase in environmental pollution [1,2]. In addition to conventional spectrometric, spectroscopic, and chromatographic techniques [3,4], the electrochemical methods offer attractive alternatives, especially considering the simplicity of sample preparation, the ability of direct measurement of minimally treated or even untreated samples (continuous monitoring in rivers, lakes, and oceans), low-cost and simple instrumentation, and its portability [5]. In addition, electrochemistry provides an unmatched opportunity for the miniaturization of sensing devices, making them suitable for either in-vivo measurements or their integration into more complex sensing systems [6].

In the last 60 years, various mercury electrodes, such as the dropping mercury electrode, hanging mercury drop electrode, and mercury film electrode, have dominated electrochemical (stripping) analysis [5,7]. Apart from its well-known toxicity [8], there are also problems related to the handling and storage of mercury; nowadays, the use of mercury is restricted or even banned in several countries. As a result, numerous alternative conductive materials, such as various forms of carbon (e.g., pyrolytic graphite, polycrystalline graphite, glassy carbon, carbon paste, carbon fibers, reduced graphene oxide) [9], gold [10], platinum [11], silver [12], and iridium [13] have been studied to replace mercury as electrode material; none of them, however, exhibits such outstanding electroanalytical properties. In 2000, a bismuth film electrode was introduced as an attractive replacement for its mercury counterpart [14,15], and in 2006, an antimony film electrode was investigated for its application in anodic (and cathodic) stripping voltammetry [16,17]. In parallel, there were several other studies addressing different electrode materials, such as amalgams [18], lead [19], and tin [20], as potentially promising alternatives. Recently, a copper film electrode was recognized as an interesting and nontoxic electrode material with favorable electroanalytical characteristics for anodic and cathodic stripping voltammetric measurements [21]. The copper film electrode was found to be suitable for the sensitive detection of trace mercury (LoD of 0.1 μg L^{-1},

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[*] Corresponding author.
E-mail address: samo.hocevar@ki.si (S.B. Hočevar).

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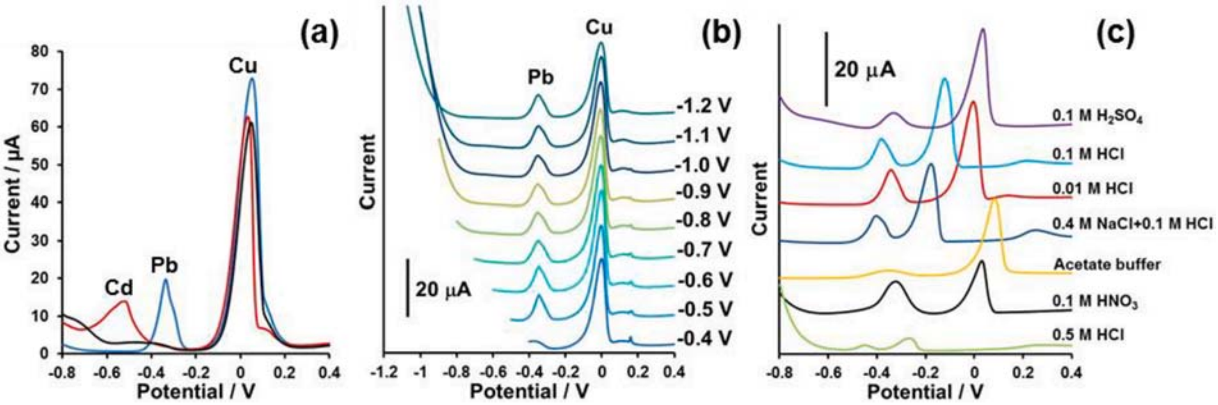

Fig. 1. Anodic stripping voltammograms (ASVs) at the in-situ prepared CuFE on the supporting GCE in 0.01 M HCl containing 500 μg L^{-1} Cu(II) of: (a) 100 μg L^{-1} Pb (II) (blue) and 200 μg L^{-1} Cd(II) (red), together with background (black) using deposition potential of −0.8 V for 100 s; (b) 70 μg L^{-1} Pb(II) using different deposition potentials in the range of −0.4 V to −1.2 V and deposition time of 60 s, and (c) 80 μg L^{-1} Pb(II) in different media containing 500 μg L^{-1} Cu(II) using deposition potential of −0.8 V for 60 s.

300 s accumulation), lead (LoD of 0.06 μg L^{-1}, 300 s accumulation), cadmium (0.01 μg L^{-1}, 210 s accumulation), and nickel (0.2 μg L^{-1}, 300 s of accumulation), as well as for the measurement of several nitroaromatic compounds [22–26]. In addition, a fully copper-based sensor for Zn(II) was fabricated with a detection limit of 9 μg L^{-1}.

With the aim of gaining more insight into the electroanalytical performance of copper-based electrodes, we studied different types of copper electrodes for trace metal detection. We investigated copper film electrodes (CuFEs) prepared on glassy carbon and screen-printed carbon substrates, and bulk copper electrodes, such as bulk copper disk electrode, screen-printed copper electrode, and copper wire. Their performances in the anodic stripping voltammetric regime are discussed, along with their advantages and limitations.

2. Experimental

2.1. Apparatus

Cyclic voltammetric and square-wave voltammetric studies were carried out using a modular electrochemical potentiostat/galvanostat PGSTAT10 (Autolab, Eco Chemie, Utrecht, The Netherlands) controlled by GPES 4.8 software (Eco Chemie). A glassy carbon disk electrode (GCE; $d = 2$ mm, Metrohm), a copper disk electrode (CuDE; RDE-Cu50, $d = 5$ mm, Metrohm), a screen-printed carbon electrode (SPCE; DRP-X-C11l, $d = 4$ mm, DropSens), a screen-printed copper electrode (SPCuE; DRP-Cu10, $d = 4$ mm, DropSens), and a commercial copper wire ($d = 1.6$ mm) from a local hardware store, were used as the supporting and working electrodes. Throughout the work, and to ensure consistent measurements, even when screen-printed electrodes were used, an Ag/AgCl/KCl(satd.) (Metrohm) and a platinum rod (Metrohm) were used as the reference and counter electrodes, respectively. Electrochemical measurements were performed at a room temperature of 23 ± 1 °C in a 20 mL one-compartment voltammetric cell in the presence of dissolved oxygen.

2.2. Reagents and solutions

Copper(II) standard solution (1001±2 mg L^{-1}), CH_3COOH (99%), CH_3COONa, and $K_3[Fe(CN)_6]$ were purchased from Sigma-Aldrich, Pb (II) and Cd(II) standard solutions (both 1000 mg L^{-1}), HNO_3 (65%), H_2SO_4 (95–95%), and $CuSO_4 \times 5H_2O$ from Merck, HCl (37%) from GRAM-MOL, NaCl was obtained from Supelco-Merck, and $K_4[Fe(CN)_6]$ from Riedel-de Haën. All other chemicals were of analytical grade purity. Water used throughout the work was purified with the Elix 10/Milli-Q Gradient unit (Millipore).

2.3. Preparation of copper (film) electrodes

Before each set of measurements, the surfaces of GCE, copper disk electrode, and the exposed tip of a copper wire ($d = 1.6$ mm, $l = 5$ mm) were hand-polished using Al_2O_3 slurry (Buehler) with a particle size of 50 nm and thoroughly rinsed with purified water. On the other hand, the screen-printed-based electrodes were only rinsed with purified water.

The CuFEs were formed either in-situ, directly during the measurement, in the presence of usually 500 or 1000 μg L^{-1} Cu(II) in 0.01 M HCl or ex-situ, in a separate modification solution usually containing 10 mg L^{-1} Cu(II) in 0.1 M HCl + 0.4 M NaCl. In the latter case, the ex-situ prepared electrode was rinsed with purified water and transferred into the measurement solution.

2.4. Electrochemical measurement procedure

The voltammetric measurements encompassed the application of a deposition potential of usually −0.8 V (unless stated otherwise) for a specified period, typically between 50 and 180 s, under stirring conditions, followed by 15 s equilibration time without stirring. Finally, a positive-going square-wave voltammetric scan was applied, usually from −0.8 V to 0.4 V (for the in-situ prepared CuFE) and from −0.8 V to −0.25 V (for the ex-situ prepared CuFE and other copper electrodes), with a frequency of 25 Hz, a potential step of 4 mV, and an amplitude of 50 mV, in a quiescent solution.

3. Results and discussion

The surprisingly good electroanalytical performance of CuFE for the detection of low concentrations of Hg(II), Pb(II), Cd(II), Ni(II), and selected nitroaromatic compounds [21–26] prompted us to further study the stripping voltammetric operation of copper as an electrode material and, in particular, to investigate different types of copper electrodes.

3.1. In-situ prepared CuFE on the supporting GCE

First, we investigated the electroanalytical properties of the in-situ prepared CuFE on the supporting glassy carbon electrode under different experimental conditions. Preliminary anodic stripping voltammetric measurements of 100 μg L^{-1} Pb(II) and 200 μg L^{-1} Cd(II) revealed relatively high and well-developed signals for both metal ions, with differences in their signal shapes, implying different deposition and/or stripping patterns of the two metal analytes. As seen in Fig. 1a, the stripping signal of Pb(II) can be detected at a potential of ca. −0.33 V, and the signal of Cd(II) at ca. −0.53 V, allowing efficient separation of

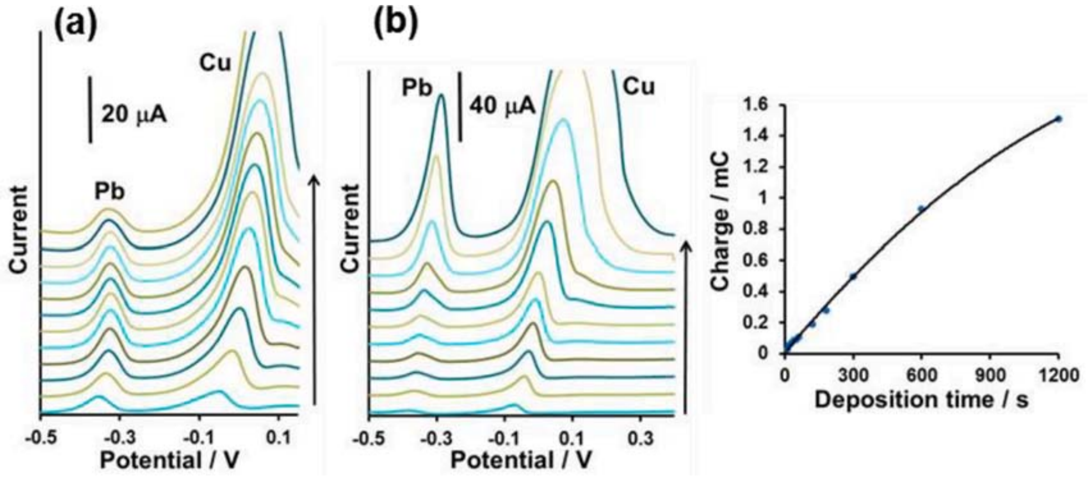

Fig. 2. ASVs at the in-situ prepared CuFE on the supporting GCE in 0.01 M HCl of: (a) 60 µg L^{-1} Pb(II) using different concentrations of Cu(II) ions (100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 2000, and 4000 µg L^{-1}) and deposition potential of −0.5 V for 100 s; (b) 50 µg L^{-1} Pb(II in 0.01 M HCl containing 500 µg L^{-1} Cu (II) using different deposition times (10, 20, 30, 40, 50, 60, 120, 180, 300, 600, and 1200s) and deposition potential of −0.5 V, together with a corresponding plot.

both analytes.

We investigated several parameters affecting the stripping voltammetric operation of CuFE; we explored the effect of the deposition potential upon the signal of 70 µg L^{-1} Pb(II) in 0.01 M HCl containing 500 µg L^{-1} Cu(II). As expected from the initial experiments and Fig. 1a, the deposition potentials less negative than −0.4 V did not provide sufficient accumulation of Pb(II), whereas more negative potentials resulted in a significant increase of the Pb(II) signal, as depicted in Fig. 1b. The deposition potentials more negative than −0.5 showed well-defined signals of Pb(II), which did not change considerably upon further decreasing the deposition potential, indicating the favorable robustness of CuFE. Moreover, the commencement of the hydrogen reduction reaction at ca. −0.8 V also did not affect the signal of Pb(II). In the case of Cd(II), a more negative deposition potential should be used, i.e., between −0.8 V and −1.0 V. Interestingly, when detecting Cd(II), we observed that the supporting GCE required somewhat more negative deposition potentials, i.e., −1.0 V, compared to other substrates studied, such as screen-printed carbon electrode, screen-printed copper electrode, copper disk electrode, and copper wire (not shown). Therefore, for measuring Cd(II) or Cd(II) and Pb(II) together at the GCE, the deposition potential of −1.0 V was chosen as optimal. In contrast, a deposition potential of −0.8 V was sufficient when using other supporting electrodes or other types of copper electrodes.

It is known that the composition of the electrolyte affects both the accumulation of metal analytes and the preparation of metal film electrodes. This is particularly true for CuFE, which, for example, shows a different stripping voltammetric behavior when the chloride ion concentration is changed [21]. Moreover, it is evident from Fig. 1c that higher chloride concentrations lead to earlier stripping signals of Pb(II), i.e., at more negative potentials, due to the preferential formation of soluble species, such as $PbCl_2$, $[PbCl_3]^-$ and $[PbCl_4]^{2-}$, which is also consistent, for example, with the difference between redox potentials of $PbCl_2$ and free Pb(II) [27]:

$$PbCl_2 + 2e^- \rightarrow Pb^0 + 2Cl^- \ \left(E_r^0 = -0.268V\right)$$

$$Pb^{2+} + 2e^- \rightarrow Pb^0 \left(E_r^0 = -0.126V\right)$$

At the same time, the increasing concentrations of chloride ions also result in a negative shift of the first copper stripping signal ($Cu^0 \rightarrow Cu^+ + e^-$) and a positive shift of the second copper stripping signal ($Cu^+ \rightarrow Cu^{2+} + e^-$). This phenomenon can be beneficially exploited for the detection of trace Hg(II) [21]. It is also important to consider an accompanying effect of pH, which generally shifts the stripping signal of Pb(II) toward more negative potentials with increasing pH; however, in the case of measuring Pb(II) at the CuFE, the effect of chloride ions prevails over the effect of pH when comparing 0.5 M HCl vs. 0.1 M HCl vs. 0.01 M HCl. Compared to other electrolytes, the 0.1 M acetate buffer solution with pH 4.5 showed a relatively broad and the lowest response for 80 µg L^{-1} Pb(II), together with a poor linear response when increasing the concentration of Pb(II) in the range of 10 – 100 µg L^{-1} (not shown). A slightly improved performance was observed when using 0.1 M H_2SO_4 as an electrolyte but also accompanied by relatively poor linear behavior in the examined concentration range of 10 – 100 µg L^{-1} (not shown). On the other hand, in 0.1 M HNO_3, the CuFE showed a higher but broad signal for Pb(II) with low reproducibility, despite a favorably wide potential separation between signals for Pb(II) and copper re-oxidation, as depicted in Fig. 1c. In addition, the media, such as 0.1 M H_2SO_4, 0.1 M HNO_3, and particularly 0.5 M HCl, exhibited higher background currents due to the hydrogen evolution reaction. Overall, the highest performance of the in-situ prepared CuFE was obtained in 0.01 M HCl.

In the following study, the effect of Cu(II) concentration upon the stripping signal of Pb(II) was investigated. Fig. 2a shows the signals of 60 µg L^{-1} Pb(II) when increasing concentrations of Cu(II) in the range of 100 – 4000 µg L^{-1} Cu(II). The stripping signals of Pb(II) augmented with increasing concentration of Cu(II) up to 500 µg L^{-1}, and at higher concentrations, the signals decreased slightly and did not change significantly; a more pronounced decrease could be observed at Cu(II) concentrations higher than 1000 µg L^{-1}. However, it is important to note that higher concentrations of Cu(II) may be beneficial when measuring higher concentrations of metal analyte to avoid the effect of competition between analyte ions and copper ions in the case of the in-situ CuFE formation. Interestingly, a slight positive shift in peak potentials can be observed for both Pb(II) and Cu(II) signals, implying attractive forces between the deposited metal atoms [28].

In addition, we examined the effect of the deposition time upon the signal of 50 µg L^{-1} Pb(II) using 500 of Cu(II) µg L^{-1} in the measurement solution. As shown in Fig. 2b, the stripping voltammetric response of Pb (II) increased almost linearly with increasing deposition time in a wide range of 10 – 600 s and slightly leveled off at higher deposition times. This feature implies the combination of both the commencement of surface saturation with the analyte and the effect of the thicker copper film, as discussed in the previous paragraph. However, a relatively broad linear response enables a convenient usage of higher deposition times when measuring lower analyte concentrations and, consequently, the achievement of lower limits of detection.

The in-situ prepared CuFE on the supporting GCE exhibited good linear operation in the examined concentration range of 10 – 150 µg L^{-1} Pb(II) with R^2 of 0.995 associated with 500 µg L^{-1} Cu(II) and 50 s

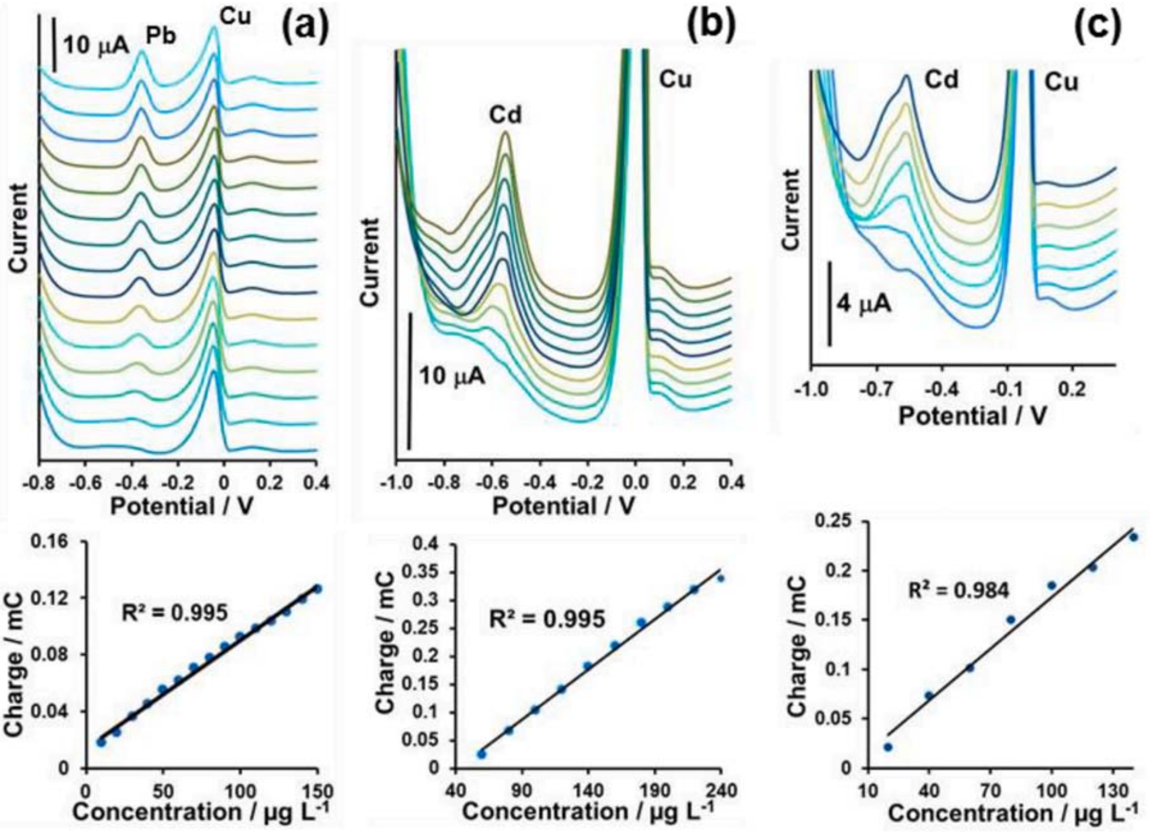

Fig. 3. ASVs at the in-situ prepared CuFE on the supporting GCE in 0.01 M HCl for increasing concentrations of: (a) Pb(II) in 10 μg L^{-1} steps, in the range of 10 – 150 μg L^{-1}, using 500 μg L^{-1} Cu(II) and deposition potential of −0.8 V for 50 s; (b) Cd(II) in 20 μg L^{-1} steps, in the range of 60 – 240 μg L^{-1}, using 1000 μg L^{-1} Cu(II), and (c) in the range of 20 – 140 μg L^{-1}, using 500 μg L^{-1} Cu(II), and deposition potential of −1.0 V for 60 s (for b and c).

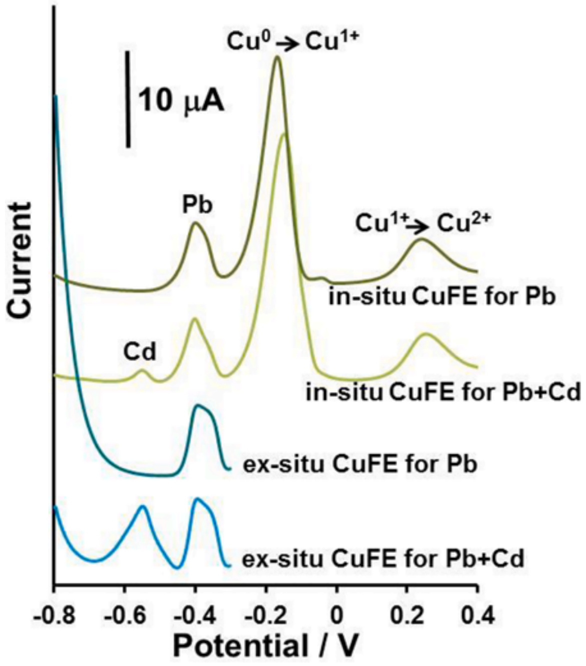

Fig. 4. ASVs for 50 μg L^{-1} Pb(II) and 50 μg L^{-1} Pb(II) + 50 μg L^{-1} Cd(II) at the in-situ and ex-situ prepared CuFE on the supporting GCE in 0.01 M HCl (and 500 μg L^{-1} Cu(II) for the in-situ prepared CuFE) using deposition potential of −0.8 V for 100 s.

deposition at −0.8 V, and the limit of detection (3σ criterion) of 0.4 μg L^{-1} in combination with an accumulation time of 180 s. With increasing concentration of Pb(II), we observed the shift of the hydrogen reduction reaction toward more negative values, as expected due to the deposition of lead at the CuFE electrode (Fig. 3a). Moreover, the observed decrease of the Cu(II) stripping signal with higher concentrations of Pb(II) is a consequence of the intermetallic compound formation among Cu(II) and Pb(II). In the case of Cd(II), the electrode revealed better-developed stripping signals when using 1000 μg L^{-1} Cu(II) in the measurement solution, together with slightly lower sensitivity in comparison to 500 μg L^{-1} Cu(II). Namely, the CuFE exhibited a satisfactory linear operation for Cd(II) in the examined concentration range of 60 – 240 μg L^{-1} with the R^2 of 0.995 when using 1000 μg L^{-1} Cu(II) (Fig. 3b) and in the range of 20 – 140 μg L^{-1} with the R^2 of 0.984 when using 500 μg L^{-1} Cu(II) (Fig. 3c), both in combination with 60 s deposition time at −1.0 V. In comparison to Pb(II), the CuFE revealed higher limit of detection (3σ criterion) for Cd(II), i.e., 3.9 μg L^{-1}, accompanied with 180 s accumulation.

3.2. *Ex-situ prepared CuFE on the supporting GCE*

The preliminary experiments involving the comparison of the in-situ and ex-situ prepared CuFE were carried out in 0.01 M HCl. The stripping voltammograms revealed an advantage of the ex-situ prepared analog, particularly for the simultaneous detection of Cd(II) and Pb(II). As seen in Fig. 4, the in-situ prepared CuFE exhibited well-defined stripping signals for 50 μg L^{-1} Pb(II) in the presence and absence of 50 μg L^{-1} Cd (II), whereas the signal of Cd(II) was very low under the in-situ regime. On the contrary, the ex-situ prepared CuFE revealed a similarly high signal for 50 μg L^{-1} Pb(II) as in the case of the in-situ prepared CuFE, and after the addition of 50 μg L^{-1} Cd(II), the ex-situ prepared CuFE

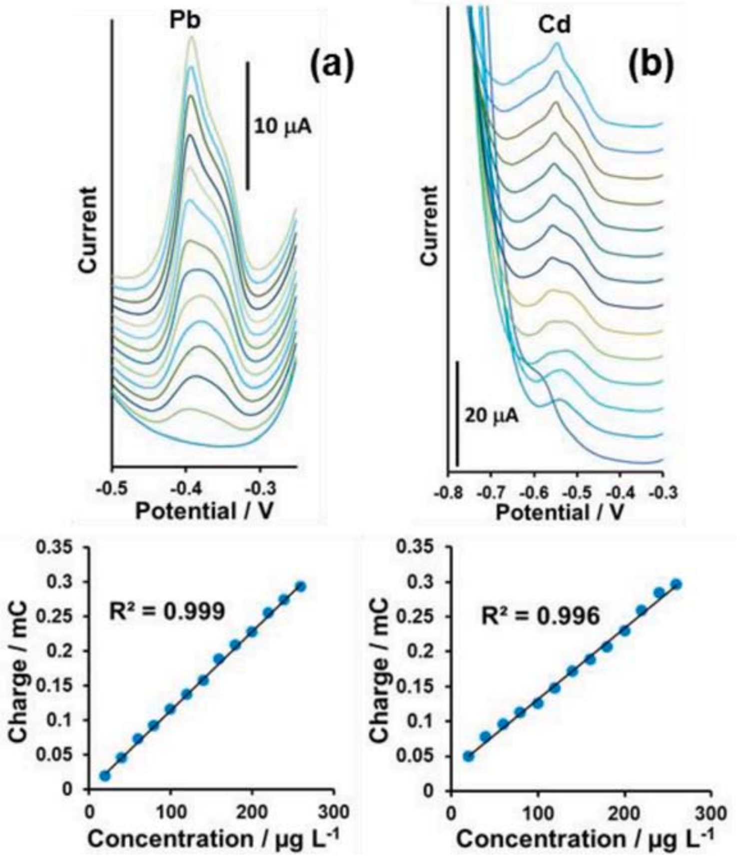

Fig. 5. ASVs at the ex-situ prepared CuFE on the supporting GCE in 0.1 M HCl + 0.4 M NaCl for increasing concentrations of: (a) Pb(II) and (b) Cd(II) in 20 µg L^{-1} steps in the range of 20 – 260 µg L^{-1} using deposition potential of −0.8 V for 60 s. Ex-situ deposition of CuFE at −0.8 V for 300 s, c(Cu) = 10 mg L^{-1}.

exhibited well-developed signals for both metal ions; moreover, the addition of Cd(II) did not significantly affect the signal of Pb(II).

In continuation, the effect of the supporting electrolyte was also examined; among 0.01 M HCl, 0.1 M HCl, 0.1 M HCl + 0.4 M NaCl, 0.01 M H_2SO_4, and 0.1 M H_2SO_4, the solution containing 0.1 M HCl + 0.4 M NaCl unveiled the most favorable electroanalytical performance of the ex-situ prepared CuFE, particularly considering the electrode reproducibility. Further optimization studies suggested that the most suitable concentrations of Cu(II) in the modification solution for the preparation of the ex-situ CuFE should be in the range of 5 – 30 mg L^{-1} Cu(II) (examined in the range of 500 µg L^{-1} to 100 mg L^{-1}, not shown), whereas the optimal deposition times for copper film were in the range of 240 – 600 s (examined in the range of 0 to 2400s, not shown). Importantly, when using higher concentrations of Cu(II) in the modification solution and/or prolonged deposition times, which results in thicker copper films, the stripping signal of Pb(II) started to split, implying a different stripping pattern of Pb(II) from thicker copper-lead intermetallic deposits. In contrast, when using lower concentrations of Cu(II) (or considerably shorter deposition times), a second signal at more negative potentials appeared, indicating and coinciding with the re-oxidation of Pb(II) directly from the bare supporting glassy carbon electrode. Indeed, this signal gradually decreased, and the one for Pb(II) re-oxidation/stripping from the CuFE concurrently increased with increasing concentrations of Cu(II) (and/or with longer deposition times of copper films).

The stripping voltammetric operation of the ex-situ prepared CuFE was examined in a wide concentration range of 20 – 260 µg L^{-1} for both metal ions in a solution of 0.1 M HCl+0.4 M NaCl. The electrode unveiled an excellent linear response with the R2 of 0.999 for Pb(II) and 0.996 for Cd(II) in combination with only 60 s accumulation time at −0.8 V, as shown in Fig. 5. The limits of detection (3σ criterion) were 0.5 µg L^{-1} for Pb(II) and 0.3 µg L^{-1} for Cd(II), using accumulation times of 120 s and 180 s, respectively. Despite the somewhat asymmetric signals, it appears that the relatively high sensitivity toward Cd(II) at the ex-situ prepared CuFE (ca. 10-times higher compared to the in-situ prepared

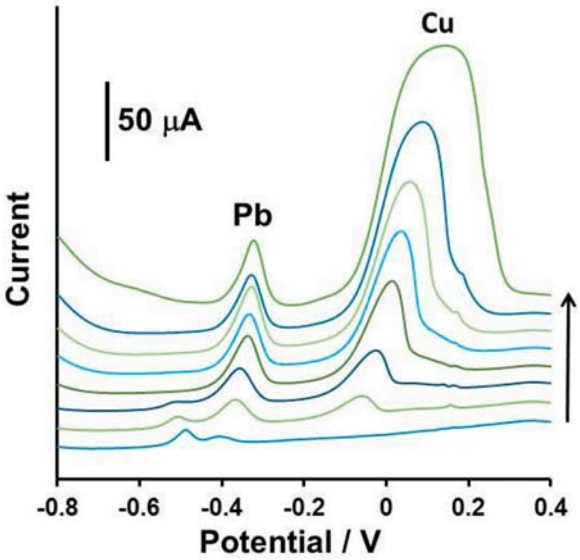

Fig. 6. ASVs of 100 µg L^{-1} Pb(II) at the in-situ prepared CuFE on the supporting SPCE in 0.01 M HCl containing different concentrations of Cu(II) ions: 0, 100, 200, 500, 750, 1000, 2000, 5000 µg L^{-1}. Deposition potential of −0.8 V for 120 s.

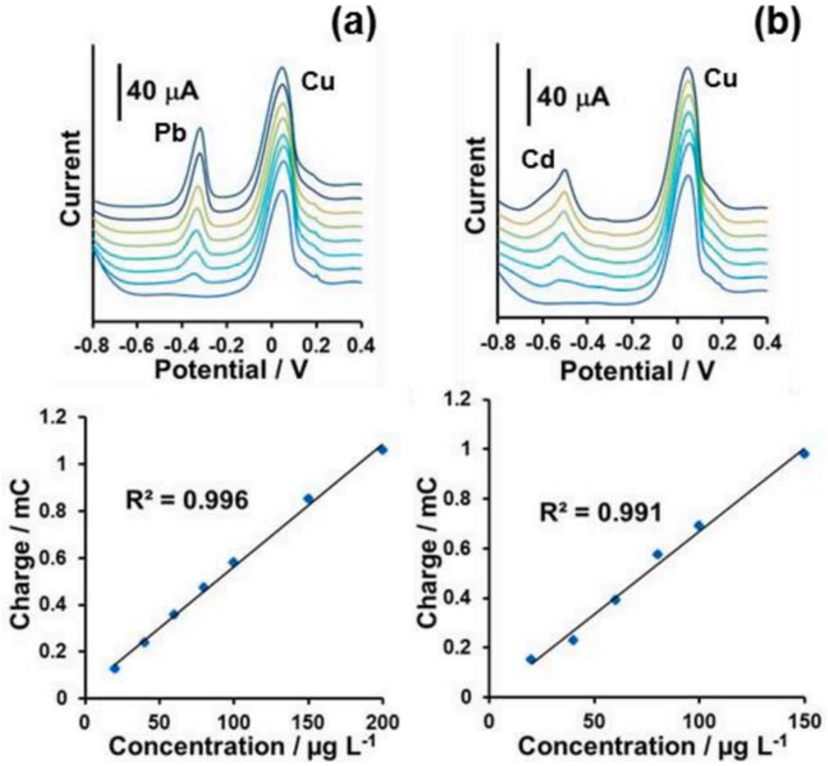

Fig. 7. ASVs at the in-situ prepared CuFE on the supporting SPCE in 0.01 M HCl containing 1000 μg L^{-1} Cu(II) for increasing concentrations of: (a) Pb(II) in the range of 20 – 200 μg L^{-1} and (b) Cd(II) in the range of 20 – 150 μg L^{-1} using deposition potential of −0.8 V for 60 s.

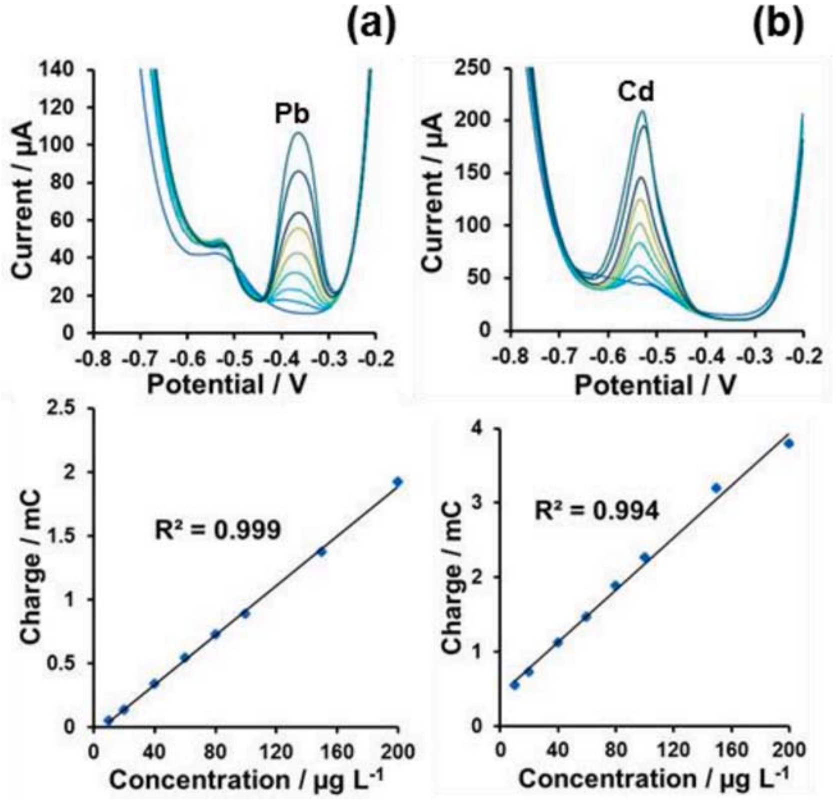

Fig. 8. ASVs at the CuDE in 0.1 M HCl + 0.4 NaCl for increasing concentrations of: (a) Pb(II) and (b) Cd(II) in the range of 10 – 200 μg L^{-1}, using deposition potential of −0.8 V for 120 s.

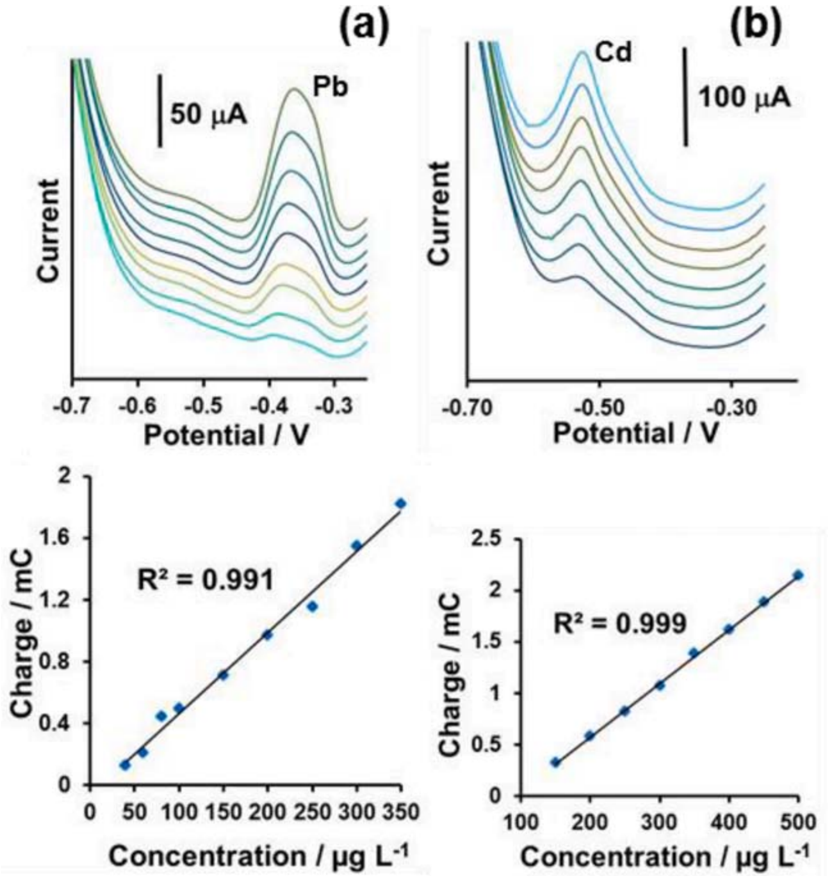

Fig. 9. ASVs at the SPCuE in 0.1 M HCl + 0.4 NaCl for increasing concentrations of: (a) Pb(II) in the range of 40 – 350 µg L^{-1} using deposition potential of −0.8 V for 120 s and (b) Cd(II) in the range of 150 – 500 µg L^{-1} using deposition potential of −0.8 V for 60 s.

CuFE) can be attributed to a different deposition pattern of Cd(II), i.e., at the ex-situ prepared CuFE, there is no competition between Cd(II) and Cu(II) for active electrode sites.

3.3. *In-situ and ex-situ prepared CuFE on the supporting SPCE*

We investigated the in-situ preparation of the CuFE on the supporting screen-printed carbon electrode. The effect of Cu(II) concentration upon the signal of 100 µg L^{-1} Pb(II) accumulated for 120 s at −0.8 V is depicted in Fig. 6. For the measurement solution, we choose 0.01 M HCl as in the case of the in-situ prepared CuFE on the supporting GCE. The stripping signal of Pb(II) increased significantly with increasing the Cu (II) concentration in the range of 100 – 1000 µg L^{-1} and then started to level off, similar to the case of the glassy carbon substrate shown in Fig. 2a.

At concentrations of Cu(II) lower than 200 µg L^{-1}, another signal of Pb(II) was observed at more negative potentials, i.e., at ca. −0.49 V, which can be attributed to the re-oxidation of deposited lead from the bare screen-printed carbon substrate due to the insufficient deposition of the copper film. In this case, the optimal concentration of Cu(II) for the in-situ preparation of CuFE was 1000 µg L^{-1}.

The in-situ prepared CuFE on SPCE exhibited good linear operation in the examined concentration range of 20 – 200 µg L^{-1} for Pb(II) with the R2 of 0.996 and in the range of 20 – 150 µg L^{-1} for Cd(II) with the R2 of 0.991 combined with 1000 µg L^{-1} Cu(II) and the accumulation time of 60 s at −0.8 V (Fig. 7). The limits of detection were favorably low, i.e., 0.6 µg L^{-1} and 1.2 µg $L-1$ for Pb(II) and Cd(II), respectively, both in combination with 180 s accumulation.

However, when using the ex-situ CuFE preparation protocol, which was similar to the case of the supporting GCE (in 0.1 M HCl + 0.4 M NaCl), the CuFE exhibited a double signal for Pb(II) at its concentrations higher than 50 µg L^{-1} along with lower sensitivity. The second signal was obtained at lower potentials corresponding to the stripping of Pb(II) at the unmodified SPCE, implying an insufficient deposition of copper film onto the supporting screen-printed carbon substrate under these conditions. This behavior is similar to the case of the ex-situ prepared CuFE on GCE when using lower Cu(II) concentrations or lower Cu(II) deposition times and to the case of lower Cu(II) concentrations at the in-situ prepared CuFE on SPCE. Such a phenomenon indicates that with higher concentrations of Pb(II), the probability of its deposition on the unmodified sites of the carbon substrate increases. Although the so-prepared CuFE (ex-situ) showed a linear response with an increasing concentration of Pb(II) in the examined range of 25 – 250 µg L^{-1} with R^2 of 0.994, we did not further study this type of CuFE. Moreover, a combination of the SPCE and the ex-situ preparation protocol of CuFE proved to be even more challenging in the case of detecting Cd(II). We can expect that the introduction of an additional chemical or electrochemical surface pretreatment protocol might improve the performance of these commercially available SPCEs, as already shown in another recent study [29].

3.4. *Copper disk electrode (CuDE)*

The initial experiments confirmed that the most appropriate electrolyte solution for the bulk CuDE is the same as when CuFE was prepared ex-situ on the supporting glassy carbon substrate, i.e., 0.1 M HCl + 0.4 M NaCl. We also examined the effect of different types of copper surfaces, i.e., a bare solid copper disk and the in-situ and ex-situ copper films deposited on the existing supporting bulk CuDE. The latter two types were investigated to follow a possible effect of the copper substrate

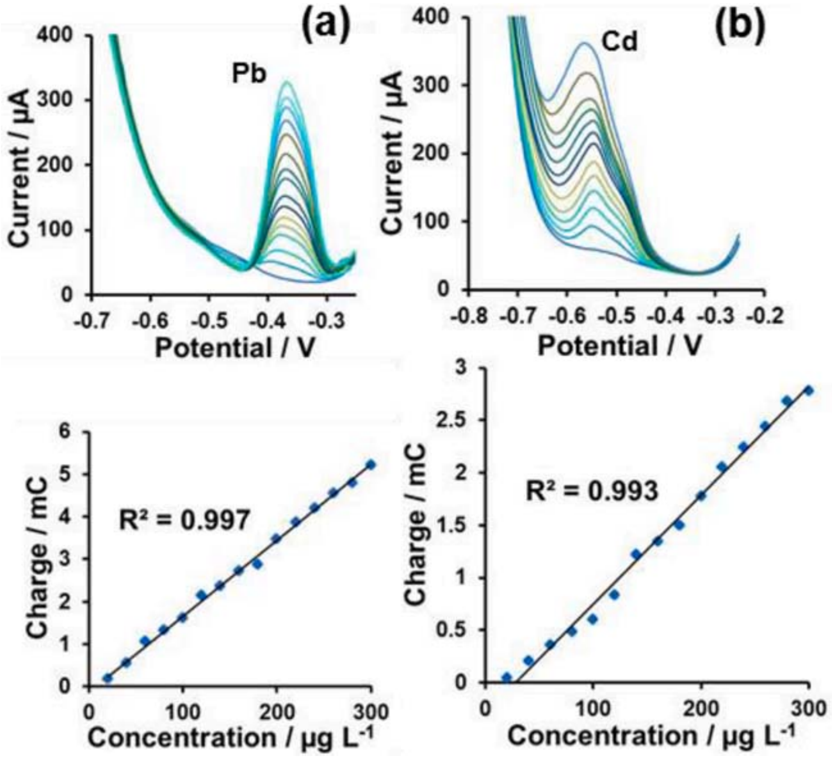

Fig. 10. ASVs at the copper wire in 0.1 M HCl + 0.4 NaCl for increasing concentrations of: (a) Pd(II) and (b) Cd(II) in the range of 20 – 300 μg L^{-1} using deposition potential of −0.8 V for 60 s.

upon further deposited copper films. The measurements of Cd(II) and Pb (II) revealed the highest stripping voltammetric performance for both analytes at pristine CuDE, whereas the additional deposition of copper films did not show any significant improvements. With increasing concentrations of Pb(II) and Cd(II), the anodic stripping voltammetric responses linearly increased in the examined range of 10 – 200 μg L^{-1} with excellent R^2 of 0.999 for Pb(II) and R^2 of 0.994 for Cd(II), using 120 s accumulation for both metal ions, as depicted in Fig. 8. The limits of detection (3σ criterion) after 180 s accumulation at −0.8 V were 0.6 for Pb(II) and 5.0 for Cd(II). A lower limit of detection for Cd(II) at the CuDE, despite even somewhat higher sensitivity, was also due to lower reproducibility (RSD of 8.3%).

3.5. Screen-printed Cu-electrode (SPCuE)

Among copper-based electrodes, the SPCuE showed the lowest electroanalytical performance for measuring both Pb(II) and Cd(II) as test metal ions. Nevertheless, the response of this electrode in 0.1 M HCl+0.4 M NaCl for increasing concentrations of the metal analytes revealed a linear operation in the range of 40 – 350 μg L^{-1} for Pb(II) with R2 of 0.991 associated with 120 s accumulation and in the range of 150 – 500 μg L^{-1} for Cd(II) with R2 of 0.999 accompanied with 60 s accumulation (Fig. 9). Under these conditions, the concentrations of Pb(II) below 40 μg L^{-1} and of Cd(II) below 150 μg L^{-1} could not be quantified. The application of longer deposition times could increase the sensitivity; however, the problems of relatively low sensitivity and reproducibility, particularly for Pb(II) (RSD of 9.1%), remained. Since the preliminary experiments implied lower reproducibility and overall sensitivity, we did not continue with further studies on this type of copper electrode.

3.6. Copper wire

Finally, we tested copper wire as an inexpensive and readily available electrode material. Surprisingly, this type of electrode showed very favorable electroanalytical performance; the anodic stripping voltammetric signals for both Pb(II) and Cd(II) increased linearly over a broad examined concentration range of 20 – 300 μg L^{-1} with an R2 of 0.997 for Pb(II) and 0.993 for Cd(II) using accumulation time of only 60 s at −0.8 V in 0.1 M HCl+0.4 M NaCl, as shown in Fig. 10. The reproducibility was even better than, for example, that of the CuDE, i.e., 1.6% and 6.3% vs. 5.3% and 8.3% for Pb(II) and Cd(II), respectively, and, in the case of Pb(II), the reproducibility approached that of the CuFE in-situ prepared on the glassy carbon substrate. Moreover, when using a 180 s accumulation time, the obtained limits of detection were 0.6 μg L^{-1} for Pb(II), i.e., the same as at the CuDE, and 1.8 μg L^{-1} for Cd(II). These results indicate an unexpectedly good electroanalytical performance of copper wire; apart from the affordability of such an electrode together with its ease of use, it certainly deserves further attention in modern electroanalysis.

3.7. Interference study

We investigated the influence of various interferants upon the electroanalytical performance of selected Cu-based electrodes, such as the in-situ and ex-situ prepared CuFEs on the supporting glassy carbon and screen-printed carbon electrodes, and copper wire electrode. We examined the effect of 50 and 200 μg L^{-1} Na(I), K(I), Ca(II), Mg(II), and Zn(II) and the effect of 300, 600, and 900 μg L^{-1} Triton X-100 and humic acid upon the signal of 50 μg L^{-1} Pb(II) as the model metal analyte. The study revealed that the examined metal ions did not show any significant change in the signal of 50 μg L^{-1}, i.e., the signals were generally in the frame of the reported RSDs, except at the ex-situ prepared CuFE on the SPCE that showed poor performance, as already mentioned in the previous discussion, and was not investigated further. In addition, the signal at the ex-situ prepared CuFE on the glassy carbon electrode decreased for ca. 10% after the addition of 200 μg L^{-1} K(I), and at copper wire also for ca. 10% after introducing 200 μg L^{-1} Zn(II). Interestingly, the additions of surfactants showed different effects upon the signal of 50 μg L^{-1} Pb(II); at the in-situ prepared CuFE on the glassy carbon electrode, the first addition of Triton X-100 induced 15% decrease of the

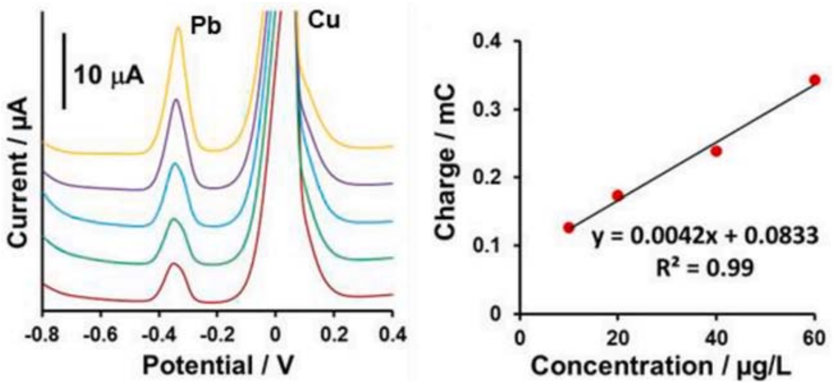

Fig. 11. ASVs obtained in a real sample and after four standard additions of 10 and three times 20 μg L^{-1} Pb(II), together with the corresponding standard addition plot.

Table 1
Electroanalytical performances of copper-based electrodes.

Electrode	Medium	Pb			Cd		
		LOD, t_d	LOQ, t_d	RSD, t_d	LOD, t_d	LOQ, t_d	RSD, t_d
In-situ GCE	0.01 M HCl	0.4 μg L^{-1}, 180 s	1.1 μg L^{-1}, 180 s	1.2%, 100 s	2.9 μg L^{-1}, 80 s	9 μg L^{-1}, 80 s	3.2%, 80 s
Ex-situ GCE	0.1 M HCl + 0.4 M NaCl	0.5 μg L^{-1}, 120 s	1.6 μg L^{-1}, 120 s	3.3%, 100 s	0.3 μg L^{-1}, 180 s	0.8 μg L^{-1}, 180 s	6.4%, 100 s
In-situ SPCE	0.01 M HCl	0.6 μg L^{-1}, 180 s	1.8 μg L^{-1}, 180 s	3.5%, 60 s	1.2 μg L^{-1}, 180 s	3.5 μg L^{-1}, 180 s	4.1%, 60 s
Ex-situ SPCE	0.1 M HCl + 0.4 M NaCl	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
SPE Cu-10	0.1 M HCl + 0.4 M NaCl	9 μg L^{-1}, 180 s	27 μg L^{-1}, 180 s	9.1%, 60 s	4 μg L^{-1}, 180 s	12 μg L^{-1}, 180 s	4.7%, 60 s
Cu disk electrode	0.1 M HCl + 0.4 M NaCl	0.6 μg L^{-1}, 180 s	1.9 μg L^{-1}, 180 s	5.3%, 100 s	5 μg L^{-1}, 180 s	15 μg L^{-1}, 180 s	8.3%, 100 s
Cu wire electrode	0.1 M HCl + 0.4 M NaCl	0.6 μg L^{-1}, 180 s	1.7 μg L^{-1}, 180 s	1.6%, 60 s	1.8 μg L^{-1}, 180 s	5.6 μg L^{-1}, 180 s	6.3%, 60 s

signal, whereas further additions had no significant impact. Also the additions of humic acid did not affect the signal of Pb(II). On the contrary, in the case of the in-situ prepared CuFE on the screen-printed electrode, all three additions of Triton X-100 did not show any significant effect upon the electrode performance, whereas the last two additions (i.e., 600 and 900 μg L^{-1}) of humic acid caused the signal to decrease for 15% and additional 19%, respectively. Such electroanalytical behavior can be attributed to the differences of the surface properties of supporting electrodes. Moreover, when testing the ex-situ prepared CuFE on the glassy carbon electrode, there were no changes after all three additions of Triton X-100 and the first two additions of humic acid; however, when increasing the concentration of humic acid

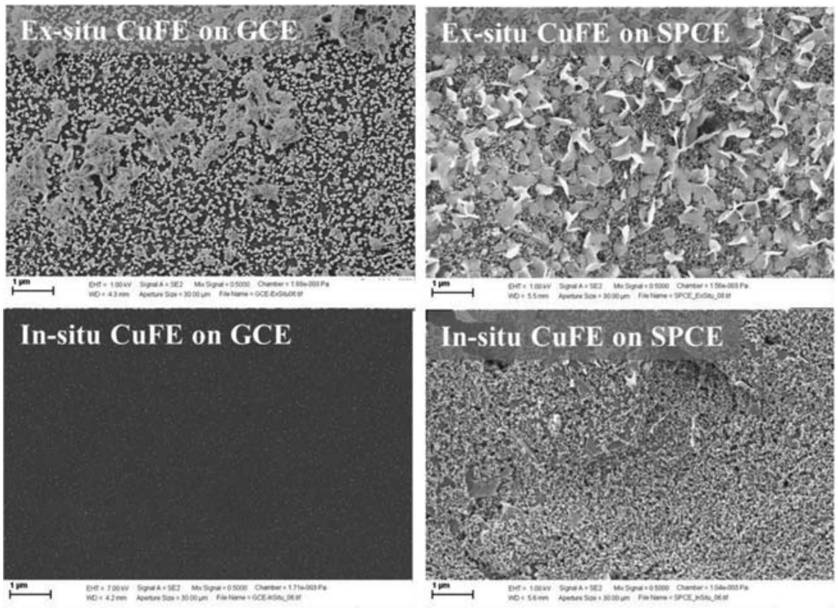

Fig. 12. The SEM images of the in-situ and ex-situ prepared CuFEs at the glassy carbon and screen-printed carbon electrodes.

to 900 μg L^{-1}, the signal of Pb(II) decreased for 13%. In the case of copper wire, considerable changes were observable only after the addition of 900 μg L^{-1} humic acid that caused the decrease of the stripping signal for ca. 25%.

3.8. Real sample measurement

The practical application of the copper electrode was tested for measuring Pb(II) and Cd(II) in a real tap water sample obtained from the city of Ljubljana. The sample was acidified to provide 0.01 M HCl, and 500 μg L^{-1} Cu(II) was added for in-situ preparation of CuFE on a supporting GCE. Fig. 11 shows a clearly visible signal for Pb(II) and no readable signal that can be assigned to Cd(II). After applying the standard addition method involving four additions, i.e., one of 10 and three of 20 μg L^{-1} Pb(II), the calculated value gave the concentration of 5.5 μg L^{-1} Pb(II).

Some of the characteristics of copper-based electrodes investigated in this study are summarized in Table 1.

3.9. Morphology study

The scanning electron microscopy showed interesting differences of the coper film structure when comparing the in-situ and ex-situ prepared CuFEs at the surface of the glassy carbon electrodes and SPCEs, as shown in Fig. 12. As expected, the surfaces of the ex-situ prepared CuFEs revealed significantly denser copper deposits, whereas the in-situ prepared electrodes exhibited sparsely dispersed nuclei. Interestingly, the ex-situ prepared CuFE at the surface of the SPCE exhibited relatively uniform and flake-like copper deposits of ca. 0.5 μm, although its stripping performance was relatively poor. The deposits of the ex-situ prepared CuFE at the surface of the glassy carbon electrode, which shows significantly better electroanalytical performance, are asymmetrical flower-like copper structures, exhibiting also higher size-heterogeneity, i.e., being surrounded by a smaller particle fraction of ca. 100 nm. At the first glance, it can be concluded that the smaller copper deposits assure improved electroanalytical performance; however, a direct relation between the electrode surface structures and their electrochemical performances is not straightforward.

The present work provides additional insight into the promising characteristics of various copper and copper film based electrodes, along with their preparations for application in electrochemical stripping analysis of trace metal ions. In particular, the copper wire electrode deserves further attention due to its favorable electroanalytical stripping performance.

4. Conclusions

In this work, we investigated several types of copper electrodes, such as the in-situ and ex-situ prepared copper film electrodes, screen-printed copper electrode, bulk copper disk electrode, and copper wire, the latter as the simplest and the most affordable electrode. Almost all types of copper electrodes showed promising electroanalytical characteristics for the sensitive anodic stripping voltammetric detection of trace Pb(II) and Cd(II), except the ex-situ prepared CuFE on the screen-printed carbon electrode for the detection of Cd(II), whereas the screen-printed copper electrode showed the lowest sensitivity for both Pb(II) and Cd(II). Interestingly, a copper wire revealed an excellent anodic stripping voltammetric operation, exhibiting a limit of detection of 0.6 μg L^{-1} for Pb (II) and 1.8 μg L^{-1} for Cd(II), in combination with an accumulation time of 180 s. This study demonstrates that copper-based electrodes, apart from other metal-based analogs, such as bismuth, antimony, tin, lead, amalgam, and others, represent another promising alternative to mercury electrodes for environmentally friendly electrochemical stripping analysis. Considering their overall performance, they definitely deserve further investigation towards detecting other metal ions and organic species.

Author contributions

DO: Methodology, Investigation, Data curation, Data evaluation, Formal analysis, Visualization. **MK:** Data evaluation, Formal analysis, Writing – review & editing. **NT:** Data evaluation, Formal analysis, Writing – Original draft. **SBH:** Conceptualization, Methodology, Data evaluation, Formal analysis, Funding acquisition, Supervision, Writing – Original draft, review & editing.

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.

Data availability

Data will be made available on request.

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