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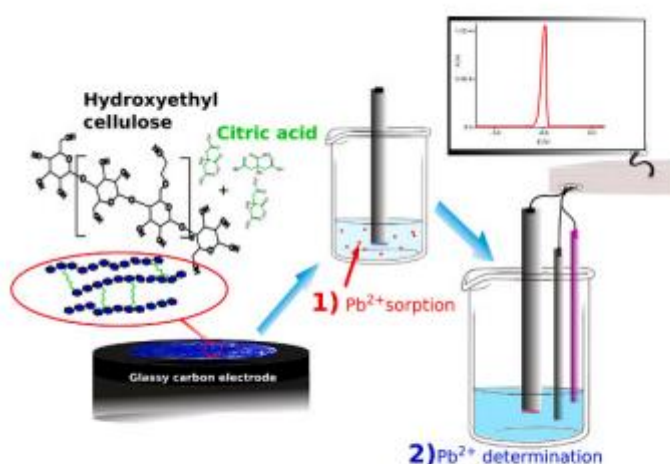
Cellulose derivatives crosslinked by citric acid on electrode surface as a heavy metal absorption/sensing matrix

Jitka Sotolářova, Štěpán Vinter, Jaroslav Filip*

Department of Environmental Protection Engineering, Faculty of Technology, Tomas Bata University in Zlín, Vavrečkova 275, Zlín 76001, Czechia

*Corresponding author. Email address: jfilip@utb.cz

GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Modification of cellulose derivatives with citric acid leads to gain in sorption capacity towards metal ions, which has been many times applied for heavy metal sequestration. This work, for the first time, investigated the in-situ coating of a carbon electrode with citric acid-crosslinked cellulose derivatives. The occurrence of crosslinking bonds was revealed using infrared spectroscopy and thermogravimetric analysis, while other features were investigated using electrochemical methods.

Experiments: Electrodes were modified by casting of aqueous solutions of cellulose derivatives (hydroxyethyl cellulose, HEC and thermally pre-treated carboxymethyl cellulose, T-CMC) mixed with citric acid (CA) on the electrode surface, followed by thermal treatment (110 °C, 1 h) to reach the requested HEC-CA and T-CMC-CA hydrogels coated on glassy carbon electrodes.

Findings: After the absorption of metal cations from solution, the electrodes coated by both HEC-CA and T-CMC-CA exhibited stripping voltammetry peaks for Pb, Cd and Cu, contrary to electrodes prepared without crosslinking. It was also observed that HEC-CA surface change its electrochemical

impedance reversibly after deposition and acid-induced removal of Pb²⁺. Assessment of Pb²⁺ sensing properties revealed the detection limit of 0.39 mg L⁻¹ and sensitivity of 9.91 pA L mg⁻¹. Therefore, the citric acid-crosslinked cellulose derivatives can be employed for the preparation of cheap and sustainable heavy metal sensors and similar surfaces.

1. Introduction

Toxic or heavy metals (lead, zinc, cadmium, mercury, ...) are severe pollutants listed in US EPA's Priority Pollutants List and regulated by national legislation due to their adverse health effects. Therefore, tools are needed for their sequestration and monitoring.

To achieve heavy metal absorption, cellulose-based materials (plant and microbial biomass) can be employed, either in pristine form or after chemical modification [1,2]. Demitri et al. have, for the first time, reported crosslinking of cellulose derivative with citric acid (CA) [3]. By dissociation of a water molecule from two adjacent carboxyls at increased temperature (for example, 80 °C overnight [3] or 8 h [4], 100 °C for 5 min [5] or 50 °C for 15 h which is temperature allowing for living bacteria incorporation [6] and so on), the polyvalent carboxylic acid can be transformed into anhydrite form which is capable to form ester bond with a hydroxyl group [7,8]. To achieve this type of crosslinking, polysaccharides should be water-soluble, and they should contain a sufficient amount of hydroxyl moieties. Therefore, hydrogels were prepared from methylcellulose [9], carboxymethylcellulose (CMC) [5,10,11], hydroxyethylcellulose (HEC) [4,12], hydroxypropylmethylcellulose [13-15], bacterial cellulose [16] and, very often, from their blends. The CA-crosslinking of cellulose-based materials has reportedly improved heavy metal sorption capacity, which has been observed by many researchers (for example, Refs. [17-21]).

Recently, Hoang et al. [22] have shown that cellulose, hemicellulose and lignin in the biomass (sugarcane bagasse) contribute equally to the esterification process with citric acid; hence the bagasse containing all three components exhibited the highest capacity for Pb²⁺ adsorption, compared to bagasse samples missing any of the aforementioned components [22]. Low price, sustainability and abundance are the main advantages of (waste)biomass-derived materials, but Daniel et al. [23] have claimed that also commercially available cellulose after the CA crosslinking may provide metal sequestration for \$10-\$50 per 1000 m³ of polluted water [23]. Wong et al. observed increased Pb and Cu absorption capacity upon modification of rice husk by tartaric acid, compared to citric acid [24], but other authors claimed that CA modification provides better results compared to other polyvalent acids [25-27]. Wierzba et al. [28] have focused on the ion exchange process and have indirectly determined the number of cations absorbed in a biomass-based matrix by measurement of the H⁺ ions released from the sorbent.

Electrochemical detection of heavy metals has a long tradition originating with polarography and, later, with stripping voltammetric methods, including differential pulse voltammetry or stripping square wave voltammetry. The current electrochemical sensors development head towards the employment of materials with an enhanced affinity towards the detected heavy metal ions. Zhao et al., in their 2017 review [29] and Wang et al. (2019) [30] pointed that conductive polymers (PANI, PPy, PVP, poly-L-lysine, and so on) are reasonable choices for such development. Cellulose has been used for the preparation of heavy metals sensors, as well, but mostly as the supporting substrate, not the analyte-binding matrix. Examples include cellulose grafted by PANI [31], nanocellulose paper-based electrode with Bi film and graphene and carbon nanotubes [32], or D-penicillamine grafted nanocellulose used for electrochemical determination of copper [33].

Furthermore, Christensen and Hoyer have reported positive effect of coating the mercury film electrodes with acetate cellulose membrane on electrochemical determination of Pb species [34]. In 2014, Almustapha et al. [35] were the first who used pristine cellulose (in powder form integrated in carbon paste electrode) for modification of electrodes employed for in-situ detection of lead ions. They achieved a sensitivity of 0.303 μA per 1 $\mu\text{g L}^{-1}$ (LOD not determined). Currently, Radotic et al. (2020) employed the same approach to compare Pb and Cu voltam-metric sensors using carbon paste electrodes filled with powder cellulose, lignin, xylene and biomass derived material. They found that cellulose is the best material for heavy metal sorbent, and their sensor could operate in sub- mg L^{-1} range [36]. Both above-mentioned devices employed particles of water-insoluble cellulose while, to the best of the author's knowledge, there are no reports on applications of water-soluble cellulose derivatives in heavy metal sensors.

In this study, carbon electrodes coated by the sustainable citric acid-crosslinked cellulose derivatives were for the first time employed for electrochemical detection of Pb^{2+} . The water-soluble cellulose derivatives (thermally treated CMC or HEC) were crosslinked directly on the electrode surface with citric acid under an elevated temperature, avoiding organic solvents. This fast, facile and inexpensive procedure leads to the formation of water-insoluble film on the electrode surface, which is rich with moieties for binding metal ions. Their positive influence on Pb^{2+} detection was observed, and the prepared sensor could also operate under "uncontrolled" conditions of real environmental samples.

2. Materials and methods

2.1. Materials

Hydroxyethyl cellulose of middle viscosity (HEC; "Cellosize® WP-40", viscosity of 2 % solution in water 75-125 mPa s) was purchased from Fluka AG, citric acid monohydrate was purchased from Lachema, Czechia, nitric acid and potassium chloride were purchased from Penta chemicals (Czechia). Heat-treated carboxymethylcellulose (T-CMC) in the form of a film was prepared at the Institute of Chemistry of the Slovak Academy of Sciences in Bratislava.

2.2. Methods

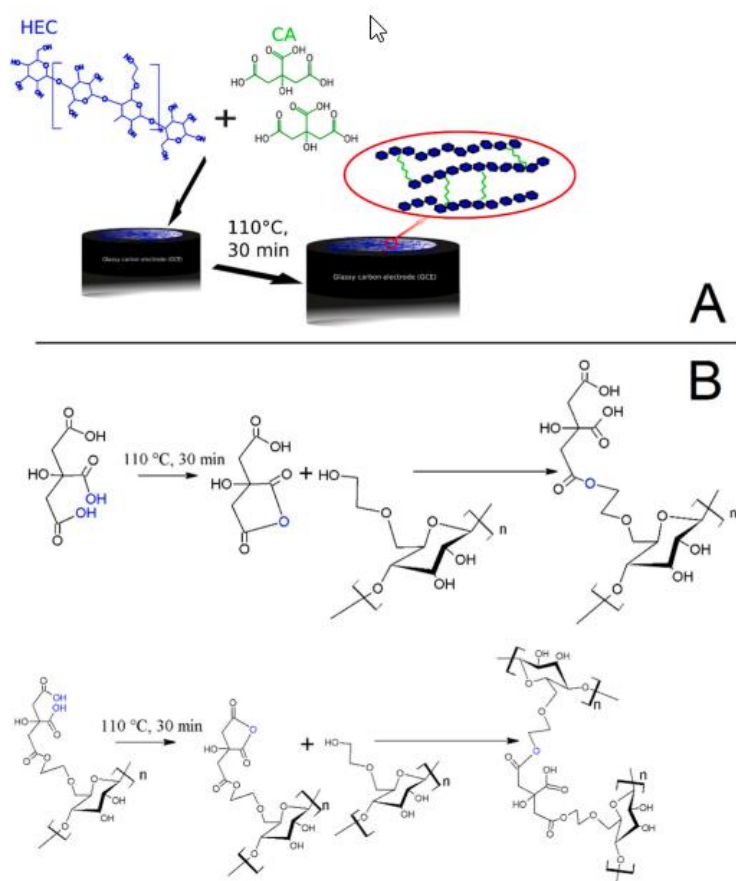
T-CMC was prepared from a commercially available medium molecular weight CMC as follows: 1.0674 g of CMC powder was mixed with 180 mL of H_2O and, after stirring at RT (2 h/500 RPM), the solution was poured onto a Teflon pan, which was warmed to 200 °C. After pouring onto the pan, the heater was immediately turned off and the sample was allowed to dry in a refrigerator for 24 h. Subsequently, the resulting suspension was poured onto a petri dish and dried to constant weight at RT.

T-CMC and HEC solid film and powder, respectively, were dissolved in deionized water (DW) using magnetic stirrers. These solutions were further mixed with the aqueous solution of CA, and drop-coated on the surface of precleaned glassy carbon (GCE) electrodes. Their employment provides some advantages, including easy cleaning, sufficient stability and, above all, they are great substrate for the deposition of stable polymer films. Such coated GCEs were placed into the laboratory drying oven preheated to apply the desired temperature for different times. The synthesis parameters (CA, T-CMC and HEC concentrations, volumes applied to electrodes, crosslinking temperature and time) were subjects of assessment and their values are indicated further in the text. The

prepared electrodes are denoted as GCE=T-CMC-CA and GCE=HEC-CA, respectively. Schematic illustration of the electrodes preparation can be found in the **Scheme 1**.

For FTIR measurements, 50 μ L of CMC and HEC mixed with CA and the same volume of the pristine T-CMC and HEC were applied on aluminum foil, followed by drying at room temperature (for non-crosslinked polysaccharides) or in an oven at 110 °C for 1 h. After drying and cooling, the layers were measured using NICOLET iS 10 (Thermo Fisher Scientific, USA).

Thermogravimetric analysis (TGA) was performed with samples prepared by casting 50 mL of 10 mg mL⁻¹ aqueous solution of HEC or its mixture with 0.1 M citric acid on a glass petri dish and treating at 110 °C for 1 h. The prepared film was removed from the substrate and the resulted solid was loaded to the TGA analyzer (TGA Q500, TA Instruments, USA) without further treatment. To investigate the possible influence of Pb²⁺ ions absorbed in the HEC-CA structure, the prepared, thermally treated HEC-CA film was soaked with 20 mg L Pb²⁺ solution for 5 min, rinsed with water and dried at 60 °C. These films were treated and analyzed in the same way as the HEC-CA. The analyses were performed under N₂ atmosphere, with the temperature set from 25° to 800 °C with the increase rate of 10 °C min⁻¹.



Scheme 1. A - Schematic illustration of GCE=HEC-CA preparation by in-situ crosslinking. B - proposed reaction scheme for HEC crosslinking with citric acid.

Electrochemical measurements were performed using glass electrochemical cell equipped with Ag/AgCl reference electrode, Pt-foil counter electrode (both Metrohm, Switzerland) and modified GCE electrodes (BVT technologies, Czechia) and connected to PGSTAT 101N potentiostat/galvanostat (Metrohm, Netherlands). In the first step of determination, the modified GCE electrodes were immersed in a solution containing the metal ion. Then they were rinsed with DW, transported to an electrochemical cell filled with electrolyte (100 mM KCl), and anodic square wave stripping voltammetry (ASWSV) measurement followed. To achieve desorption of the metal ions from the modified GCE surfaces, the electrodes were immersed in nitric acid solution for a certain time and rinsed with DW. Electrochemical impedance spectroscopy (EIS) measurements were performed in electrochemical cells filled with 10 mL of supporting electrolyte (100 mM KCl) containing 5 mM ferri-cyanide/ferrocyanide. The applied potential was 200 mV, the amplitude of 10 mV and frequency range from 100 mHz to 100 kHz were chosen. The same electrodes were employed as for the ASSWV measurements, connected to ZIVE SP1 workstation (WonATech, Korea). All potentials are given against silver-silver chloride reference electrode filled with 3 M KCl.

The real samples were prepared by leaching detonation chamber dust (DCD; Slavice, Czechia) and galvanic sludge from plating industry obtained from galvanic wastewaters after precipitation and filter press (GS; Uherske Hradiste, Czechia). The dry powders were assessed using X-ray fluorescence spectroscopy using ElvaX device (Elvatech, Ukraine). For the sample preparation, the EPA protocol [37] was followed: 15 g of solid waste was leached in 300 mL of 0.1 M acetic acid for 20 h and consequently filtrated using 0.45 μ m glass fiber filter papers. The metal content in the obtained leachates was measured using atomic absorption spectrometry (AAS) performed using ContrAA 800D device (Analytik Jena AG, Germany).

3. Results

3.1. FTIR characterization

Prior to the electrochemical measurements, crosslinked HEC and T-CMC were characterized using FTIR spectroscopy with results displayed in Fig. 1. Before crosslinking, all samples exhibited peaks typical for saccharide ring in cellulose ($900\text{-}1200\text{ cm}^{-1}$). Since these structures are supposed to be present in all samples, a specific wavenumber (1052 cm^{-1}) from this region can be chosen as a reference one and used for the normalization.

This process allows for a more precise evaluation of the acquired spectra. After the CA crosslinking significant increase at $1180\text{-}1188\text{ cm}^{-1}$ was observed, which may be attributed to C-O-C stretching [5,22] while the absorption band at about 1020 cm^{-1} , attributed to C-O-H deformation [5], could be detected only at untreated polysaccharides. Furthermore, significant absorption band at $1708\text{-}1712\text{ cm}^{-1}$ appeared at CA-crosslinked polymers, which is the region ascribed by some authors to ester bonds formed by CA crosslinking [15,23]. This is in accordance with the proposed chemistry of CA crosslinking, that is, by the formation of ester bonds from carboxyl (anhydride) of CA and hydroxyls of cellulose derivatives. The same increase of absorbance at about 1724 cm^{-1} was described by other authors who assigned this band to carbonyls [22,38]. In addition, FTIR spectra were acquired from the samples washed by distilled water and dried in air stream to check whether some absorption bands are not a result of CA present but unbound in the crosslinked polymer matrix. From **Fig. 1** it is obvious that FTIR pattern remained the same, although the intensity of some absorption bands decreased. It confirmed the stability of crosslinking bonds in the prepared films.

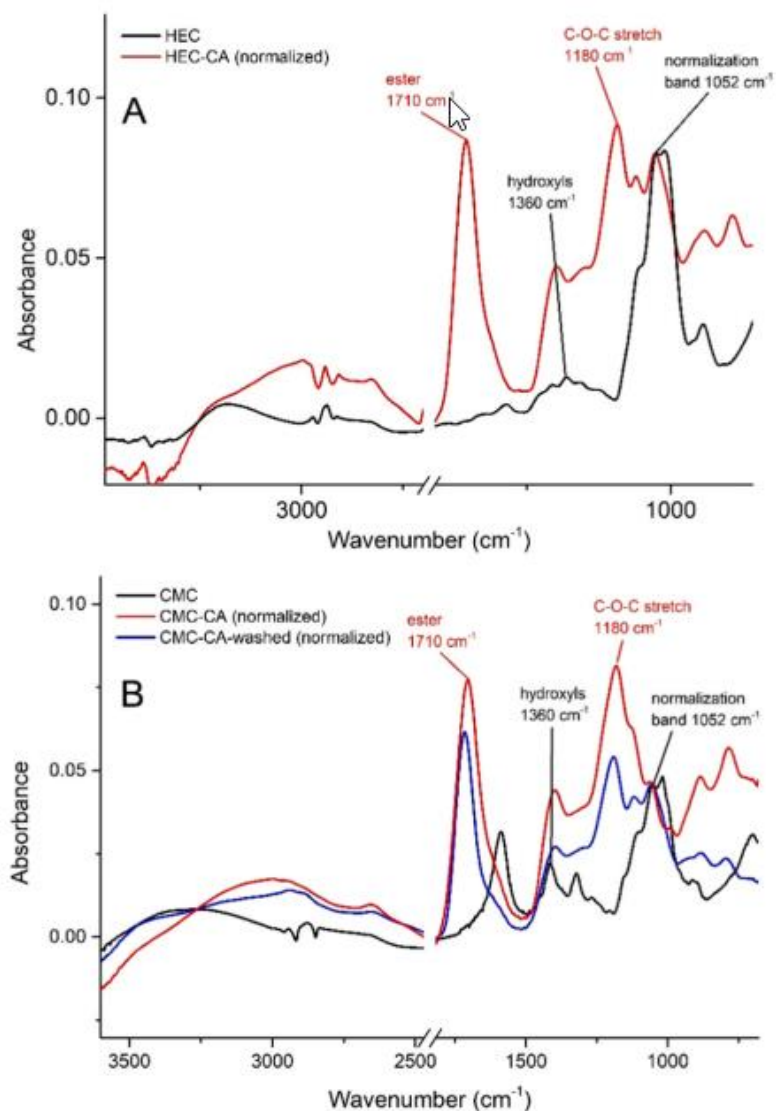


Fig. 1. FTIR spectra of HEC (A) and T-CMC (B) before (black curves) and after (red curves) 1 h crosslinking with 0.1 M CA at 110 °C. For T-CMC-CA, FTIR spectra obtained after washing with DW are shown, as well (blue curves). All data are normalized according to the absorbance at 1052 cm⁻¹ (“normalization band” in the figures) and absorption bands of the newly formed C-O-C stretching and ester bonds are noted, as well as absorption band for hydroxyls.

Thermogravimetric analysis (TGA) has already revealed that the decomposition temperature of hydroxyethyl cellulose increases as a result of the CA crosslinking [38]. We have achieved the same results (**Fig. 2**) - the highest rate of the weight loss indicated by a peak on derivative of TGA curve was observed at 279 and 300.5 °C, respectively, for hydroxyethyl cellulose before and after the crosslinking. Analysis of the crosslinked hydroxyethyl cellulose treated with Pb solution revealed that this step had no influence on the thermal stability of the formed hydrogel matrix. Such a result indicated that Pb²⁺ ions bind to those moieties of HEC-CA matrix, which are not involved in the crosslinking.

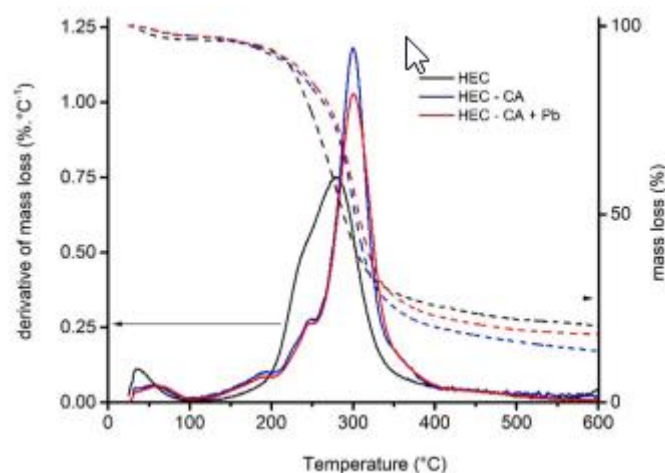


Fig. 2. TGA (dotted curves, right Y axis) curves and their derivatives (solid curves, left Y axis) of HEC (black), HEC crosslinked with CA (HEC-CA, blue) and HEC crosslinked with CA and incubated with Pb solution (HEC-CA + Pb, red).

3.2. Electrotechnical characterization

The first step was to find conditions of T-CMC and HEC crosslinking appropriate for absorption and consequent electrochemical detection of lead ions. To achieve this, electrodes modified under different conditions were dipped into $96.5 \mu\text{M PbNO}_3$ ($20 \text{ mg L}^{-1} \text{ Pb}^{2+}$) solution for 1 min to achieve absorption of Pb^{2+} into modified cellulose films. Consequently, the electrodes were gently washed by DW to remove loosely bound particles or molecules and transferred into the electrochemical cell where anodic square wave stripping voltammetry (ASWSV) was performed in 100 mM KCl using deposition time 30 s, deposition potential -1200 mV , frequency 25 Hz and amplitude 50 mV. Unless stated otherwise, these parameters were used for all the measurements. The height of the voltammetric peaks attributed to oxidation of deposited and reduced lead retained by the crosslinked polymer film was considered as the analytical output.

First, the influence of the crosslinking temperature was investigated. GCEs modified by $10 \mu\text{L}$ of 1:1 mixture of HEC (10 mg mL^{-1}) and CA (0.1 M) were treated at laboratory temperature, 55 and $110 \text{ }^\circ\text{C}$ for 30 min. The following electrochemical characterization revealed that only the $110 \text{ }^\circ\text{C}$ was sufficient for crosslinking, as deduced from the electrochemical response of $111 \pm 9 \mu\text{A}$ (see **Fig. 3**). Electrodes treated at laboratory temperature and $55 \text{ }^\circ\text{C}$ provided no electrochemical response. To prove that CA is indeed the crosslinking agent, GCE=HEC electrode without CA was thermally treated (1 h, $110 \text{ }^\circ\text{C}$), and it provided only the peak height of $2.8 \mu\text{A}$. Furthermore, this response dropped to $0.6 \mu\text{A}$ after the third consecutive measurement repeated with the same electrode. Such behavior is obviously the result of washing out the coating films from electrode surfaces (note that both T-CMC and HEC are water-soluble). For comparison, the response of unmodified electrodes was investigated, with the result confirming that no measurable amount of lead ions were adsorbed on GCE (data not shown).

Application of different amounts of the reaction mixture (10 mg mL^{-1} HEC or T-CMC and 0.1 M CA, 1:1) on individual electrodes revealed that the previously chosen 10 iL provided the highest responses (111 ± 5 and $70 \pm 3 \mu\text{A}$, respectively, for GCE=HEC-CA and GCE=T-CMC-CA; see **Fig. 4**). Low responses observed with 2 and $5 \mu\text{L}$ of the applied mixture are probably the result of a fewer number

of available bonding sites for Pb^{2+} , while with higher amounts (15 μL per electrode) the electron insulation effect may prevail.

10 μL of the reaction mixtures (5 μL of polymer solution + 5 μL of CA) was applied on electrodes in the next series of experiments where different concentrations of polysaccharides were tested. It was found (**Fig. 4**) that for HEC the highest response ($102 \pm 5 \mu\text{A}$) was achieved with the highest (10 mg mL^{-1}) concentration tested while, for T-CMC, 1 mg mL^{-1} provided the highest response ($100 \pm 6 \mu\text{A}$ achieved). Application of 10 mg mL^{-1} T-CMC resulted at the lower response ($63 \pm 4 \mu\text{A}$) compared to 1 mg mL^{-1} suggesting that the insulation effect may be more significant at T-CMC than at HEC. 0.01 mg mL^{-1} HEC and T-CMC provided a significantly lower response (6 ± 1 and $4.4 \pm 0.7 \mu\text{A}$, respectively) which is in accordance with the decrease of number of available binding sites.

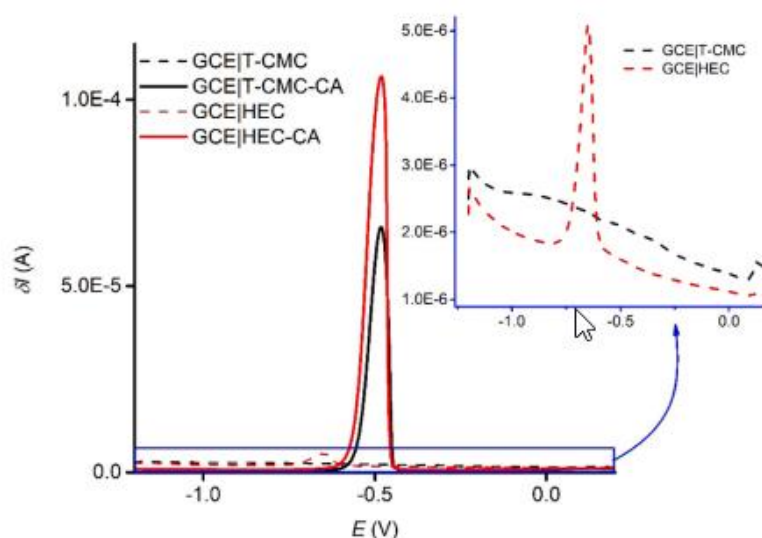


Fig. 3. ASSWV of GCE electrodes modified with non-crosslinked (black dashed) and CA-crosslinked T-CMC (black solid) and non-crosslinked (red dashed) and CA-crosslinked HEC (red solid). Inset - magnification of GCE=T-CMC and GCE=HEC voltammograms.

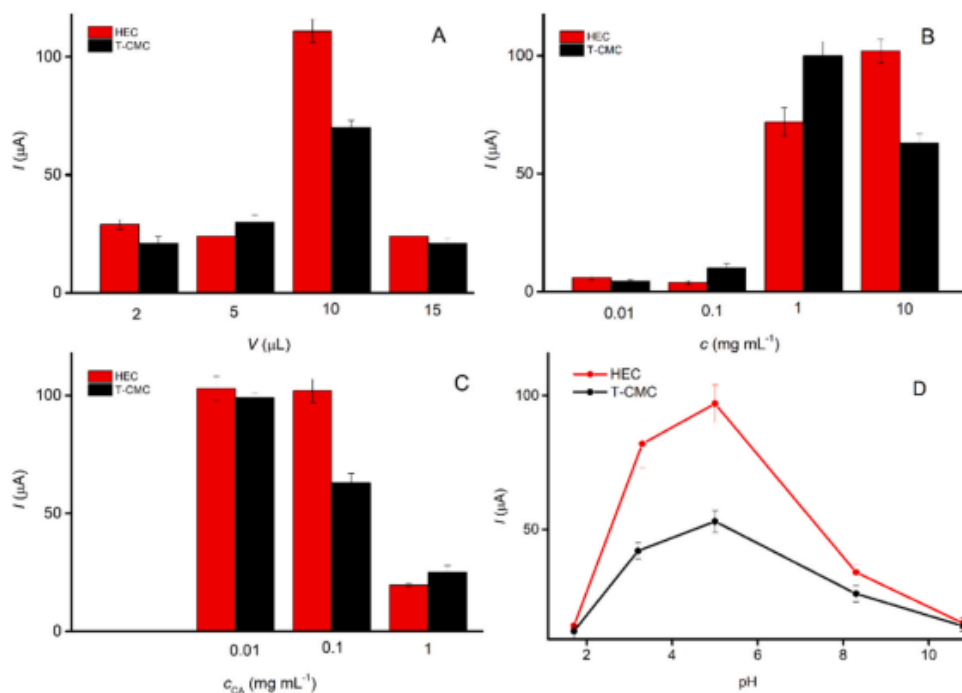


Fig. 4. Mean peak heights obtained for GCE=HEC-CA (red) and GCE=T-CMC-CA (black) with changed volume of the applied reaction mixture (A), polysaccharide concentration (B), citric acid concentration (C) and pH of the analyzed solution (D).

In addition, different CA concentrations were employed to the 1:1 mixture of 10 mg mL⁻¹ polysaccharides (10 μL applied to electrodes, crosslinked 1 h at 110 °C). Both polysaccharides provided a very high response (**Fig. 4**) even when the lowest CA concentration (0.01 M) was applied. For T-CMC-based electrodes, this was the maximum, and the response drop was observed with 0.1 M CA (63 ± 4 μA compared to 99 ± 2 achieved with 0.01 CA). On the other side GCE=HEC-CAs response remained practically unchanged when CA concentration increased ten-fold (103 ± 5 and 102 ± 5 pA for 0.01 and 0.1 M CA, respectively), and a further significant drop was observed for both polysaccharides when 1 M CA was used. It can be speculated that too high CA concentration results in the formation of particles or features disturbing the crosslinked polymer matrix, but this assumption should be experimentally assessed in further work. It is also obvious that HEC is more resistant to such negative effect of higher CA concentration

3.3. Properties of the optimized electrodes

The next series of experiments was aimed to characterize properties of GCE=T-CMC-CA and GCE=HEC-CA electrodes modified by 1:1 vol/ vol mixture of 10 mg mL⁻¹ T-CMC or HEC (5 pL) with 0.1 mM CA (5 pL) treated for 60 min at 110 °C. The separate incubation step and the consequent ASWSV measurement remained the same as described in the previous section.

3.3.1. Absorption pH and lead desorption

Acidity plays an important role in the ion sorption process, therefore the voltammetric response was recorded with different pH of the sorption solution. Results shown in **Fig. 4** indicated that for both GCE=HEC-CA and GCE=T-CMC-CA the highest voltammetric response was achieved with the sorption at pH 5, which corresponds to literature data [36]. In the more acidic environment, excess H^+ is a competitive cation lowering Pb^{2+} sorption [39] while at $pH > 5$ Pb^{2+} ions become less available in the soluble form.

To reuse the electrodes, the adsorbed metal ions can be removed by washing with mineral acids [39]. It was found that GCE=HEC-CA and GCE=T-CMC-CA could be reverted to the state where no Pb response could be observed by 1.5 min submerge into 0.5% HNO_3 . When 0.1% acid was used, the lead desorption was less efficient, and the rinse had to be repeated twice to achieve zero ASWSV peak of Pb. At an even lower acid concentration (0.01%), approximately 75% of the original Pb response was observed after 4 desorption steps. Therefore, to secure the fasted renewal of electrode, 0.5% HNO_3 was chosen as the desorption solution for other experiments.

3.3.2. Electrochemical impedance

EIS study (**Fig. 5**) revealed substantial difference between the sensors prepared from the crosslinked HEC and T-CMC. The latter exhibited the charge transfer resistance (R_{ct}) shifts seemingly with no correlation to the absence or presence of Pb in the T-CMC-CA matrix. Notably, the observed R_{ct} were always significantly higher for T-CMC-CA coated electrodes compared to ones modified by HEC-CA (data not shown). It may point to a higher negative charge in the former coating matrix, hindering the transport of negatively charged ferricyanide probe. The electrodes modified by HEC-CA exhibited R_{ct} increase after each incubation with the Pb^{2+} ions. It may be attempting to correlate this shift directly to the absorption of Pb^{2+} , but the most probable cause is protonation of hydroxyls during acidic removing of the previously adsorbed Pb^{2+} . The protonated hydroxyls bear a positive charge which strongly facilitates diffusion of negatively charged ferri/ferro-cyanide probe used for acquisition of the EIS signal.

3.3.3. Kinetic studies

To elucidate the kinetics of the absorption process, ASWSV was recorded after different absorption lengths. It should be noted that such kinetic study differs from the ones published in studies aimed to the metal removal from contaminated water in two substantial parameters: (1) the applied amount of the sorbent is 50 μg (deposited on one electrode), compared to tens of milligram employed in "standard" kinetic studies [40-43]. It can be assumed that the absorption of ions into the polymer matrix on the electrode surface will not change the properties of the sorption solution. This, in principle, makes the determination of thermodynamic properties undeterminable by the conventional methods. (2)

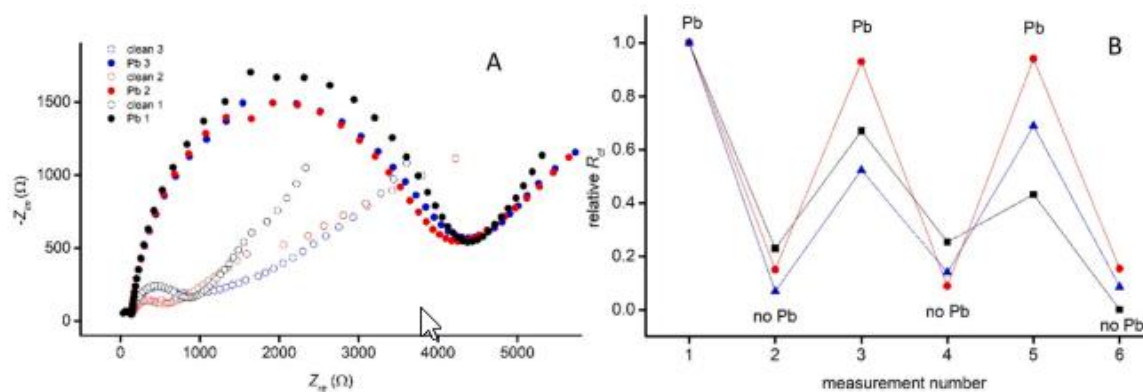


Fig. 5. A - Illustrative Nyquist plots obtained after the GCE=HEC-CA electrode was incubated in $5 \text{ mg L}^{-1} \text{ Pb}^{2+}$ solution for 5 min (filled dots) and after removing remained Pb^{2+} on the surface by washing with $0.5\% \text{ HNO}_3$ (empty circles). Black dots - first sequence of sorption and desorption of Pb^{2+} ; red and blue dots - second and third cycles of sorption and desorption of Pb^{2+} , respectively. B - relative R_{ct} values for three independent GCE=HEC-CA electrodes after three cycles of sorption (measurement numbers 1, 3 and 5) and desorption of Pb^{2+} (measurement numbers 2, 4, 6).

The total amount of Pb^{2+} absorbed on the electrode surface should be derived from the electrochemical signal instead of other analytical methods. Although there are mathematic descriptions of the measured anodic stripping square wave voltammograms, with an initial concentration of the reduced Pb being one of the model parameters [44, 45], they are applicable for cases when electrodes are submerged in the solution containing species to be oxidized/reduced. In this work, a different experimental setup has been used (that is, stripping voltammetry performed in the solution with zero level of Pb), therefore integrated area of the ASWSV voltammogram peaks were chosen as the approximation of not the total mass of the absorbed metal ions, but of the electrochemically active species. This parameter is obviously more relevant for electrochemical detection than the total amount of absorbed metal ions.

Fig. 6A shows the results achieved with GCE=HEC-CA electrodes and with sorption from the $5 \text{ mg L}^{-1} \text{ Cd}^{2+}$, $5 \text{ mg L}^{-1} \text{ Cu}^{2+}$, $5 \text{ mg L}^{-1} \text{ Cu}^{2+}$, and, additionally, from $1 \text{ mg L}^{-1} \text{ Pb}^{2+}$ solutions. For Cd, the maximum peak area was recorded as soon as after 15s incubation and for Cu, the highest peak area appeared after 2 min incubation. For Pb absorption from 1 mg L^{-1} solution, the highest peak area was observed after 45 s incubation, but it was lower compared to the response of Cu and Cd. After the increase of lead ion concentration to 5 mg L^{-1} , the highest peak area appeared after 15 s incubation, faster than for absorption from the lower concentration. It is also worthy to mention that observed peak areas decreased with longer incubation times of Cd and Cu, while for Pb, the peak area grew with the longer incubation time. These results suggested that the prolonged incubation would lead to preferable sorption of lead over the other ions. It is in agreement with the improvement of the sensing properties after prolonging the absorption step from 1 to 5 min discussed in **Section 3.3.4**.

To ensure that the composition of the measurement solution is not a limiting factor in the kinetics experiments, the above results were compared with the ones where ASWSVs were recorded in acidified KCl (100 mM KCl acidified to $\text{pH } 1.9$ with $5\% \text{ HNO}_3$). This decision was based on a report by Radotic et al. [36], who used acidic solution for stripping analysis of heavy metal cations absorbed in the carbon paste containing cellulose particles. The results are shown in **Fig. 6 B** and illustrate the general pattern, that is, the highest peak area reached after relatively short incubation (30 s for Cu and Pb, 15 s for Cd), following by decreased electrochemical peak area with the prolonged incubation

time. It can be assumed that the acidic solution cause quite significant removal of the Cu and Cd ions that have initially been absorbed into the polymer matrix, making them inaccessible for reduction and consequent oxidation during ASWSV measurements. This is a significant difference compared to previously described carbon paste electrodes containing cellulose or similar materials [35,36]. The influence of acidic measurement electrolyte on the absorption of Cd, Cu and Pb is illustrated more comprehensively in **Figs. S1A, S2A and S3A in the Supplementary Information**.

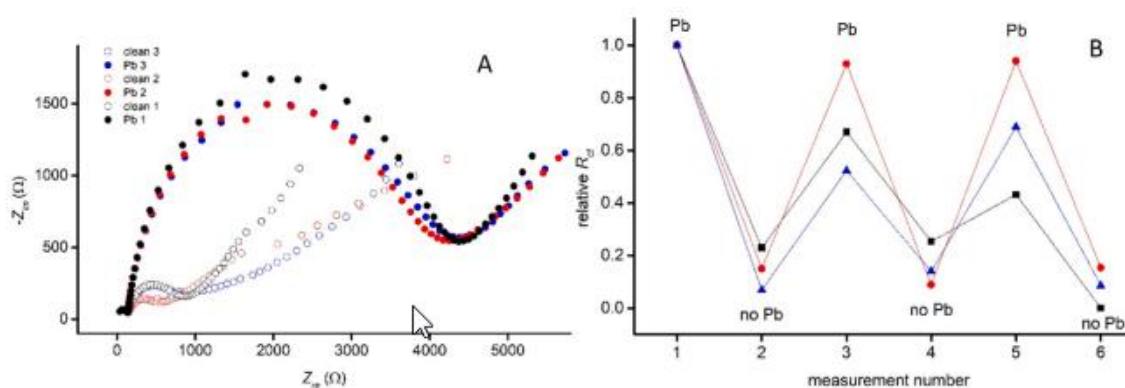


Fig. 6. ASWSV peak areas dependence on incubation time from 1 mg L⁻¹ Pb²⁺ (blue), 5 mg L⁻¹ Pb²⁺ (cyan), 5 mg L⁻¹ Cu²⁺ (red) and 5 mg L⁻¹ Cd²⁺ (black) solutions. SWVs obtained in 100 mM KCl (A) and in 100 mM KCl with pH adjusted to a value of 1.9 by 5 % HNO₃ (B). Electrodes: GCE=HEC-CA, all experiments performed at least triplicate.

The Pb, Cu and Cd absorption from 5 mg L⁻¹ solutions was also recorded with GCE=T-CMC-CA electrodes (**Figs. S1, 2 and 3B**). The results indicated that while metal ions could be easily washed out by acidic electrolytes from HEC-CA matrix (**Figs. S1-3A**), they are obviously retained inside the T-CMC-CA (**Figs. S1-3B**). This behavior can be attributed to a higher negative charge in the T-CMC-CA matrix compared to the HEC-CA (see Section 3.3.2 Electrochemical impedance), which helps to retain metal cations in the hydrogel matrix. On the contrary, poor results in terms of ASWSV peak areas were obtained with GCE=T-CMC-CA when measured in neutral KCl solution. These results strongly favor the application of the HEC-CA-based sensors for measurements in neutral solutions.

For better comprehension, **Fig. S4** shows plots of ASWSV peak areas obtained in acidic solution against the time of absorption of Cd, Cu and Pb into T-CMC-CA and HEC-CA. The graphs therein clearly illustrate the above-mentioned higher retention (and therefore the higher voltametric response) of Cu and Pb by T-CMC-CA in acidic solution, compared to HEC-CA. On the contrary, the absorption (from “default” pH 5 solution) and retention of Cd in the acidic measurement solution are not changed very much regardless of the type of electrode coating.

3.3.4. Sensing properties

To evaluate the operational features of the sensors, the calibration curve was established by ASWSV measurements of both sensors dipped for 1 min in pH 5 aqueous solution of Pb(NO₃)₂ containing 0.02-20 mg L⁻¹ Pb²⁺. They exhibited linear response only up to 10 mg L⁻¹ with the sensitivity of 5.16 and 8.84 μA L mg⁻¹ (see **Fig. 7**) for GCE=T-CMC-CA and GCE=HEC-CA, respectively and the respective limits of detection 0.39 and 0.65 mg L⁻¹. The achieved properties were improved by increasing the

length of the incubation step from 1 to 5 min. In this case, LOD values of 0.54 and 0.24 mg L⁻¹ were achieved for GCE=T-CMC-CA and GCE=HEC-CA, respectively, and the respective sensitivities of 8.67 and 9.91 $\mu\text{A L mg}^{-1}$. It is worth note that the higher sensitivity of HEC-based sensor was not accompanied by an expected lower LOD compared to GCE=T-CMC-CA. Presumably, Pb sorption to T-CMC-CA was faster than to HEC-CA, but the latter material provided higher sorption capacity. The achieved results were compared with other electrochemical sensors and summarized in **Table 1**. The electrochemical sensors of Pb²⁺ employing cellulose-based materials published so far have reported detection limits of 2 $\mu\text{g L}^{-1}$ [36] or the information was not available [35], and linear range much narrower in one case (0.02-0.06 [35] mg L⁻¹ compared to 0.02-10 mg L⁻¹) while Radotic et al. reported 0.02-0.1 and 1-20.7 mg L⁻¹ linear ranges with different sensitivities using carbon paste electrode with embedded cellulose particles [36]. LOD in sub- $\mu\text{g L}^{-1}$ range was achieved by electrodes modified by sophisticated (nano)materials (modified carbon nanotubes, nanoparticles coated by self-assembled monolayers...) or when preconcentration step is employed [46]. It can be concluded that the prepared sensors do not offer ultratrace analysis performance, but they operate well in mg L⁻¹ range, suitable, for example, for the determination of heavy metals in different types of waste. Furthermore, the devices introduced in this work exhibited a wider linear range compared to most of the mg L⁻¹ range sensors (bolded in the **Table 1**), and acceptable LOD with a very simple modification protocol was employing environmentally friendly materials.

Fig. 7. Calibration curves for GCE=HEC-CA (A) and GCE=T-CMC-CA (B). For each sensor, absorption steps of 1 min (black dots) and 5 min (red dots) were employed. Data acquired by ASWSV using following parameters: electrolyte - 0.1 M KCl, quiescent, deposition time 30 s, deposition voltage — 1200 mV, frequency 25 Hz, amplitude 50 mV.

Table 1

Operational parameters of and specification of real samples measured with the selected voltammetric Pb sensors. Bolded lines denote the devices working in the mg L⁻¹ range.

TCA-MWCNT - thiocalixarene-modified multiwalled carbon nanotubes; TCA-SPE - thiolated calixarene-modified screen printed electrode; Ac-Phos SAMMS - car-bamoylphosphonic acid self-assembled monolayer on mesoporous silica; SPGEs - screen-printed gold electrodes; DEP-On-Go - pocked potentiostat equipped with unmodified carbon electrode; SAMMS - thiol-ended self-assembled monolayer on mesoporous silica; CPE - carbon paste electrode; SWCNT-PANI-EDTA - single-walled carbon nanotubes modified by polyaniline and ethylenediaminetetraacetic acid. a After preconcentration with thiol-modified magnetic nanoparticles.

Calibration ranges with different sensitivity. c Non linear, hyperbolic calibration curve.

Fig. 8. ASWSV of GCE=HEC-CA recorded after incubation in solution containing Pb²⁺ (black solid), Pb²⁺ and Cu²⁺ (black dashed), Pb²⁺ and Cu²⁺ and Cd²⁺ (black dotted), Cu²⁺ (red) and Cu²⁺ and Cd²⁺ (red dashed), Cd²⁺ (blue) and Pb²⁺ and Cd²⁺ (blue dashed). Concentration of each metal is 20 mg L⁻¹. Inset - enlarged curves obtained under the same conditions to highlight the smaller peaks for Cd²⁺ and Cu²⁺.

3.4. Interferences

Voltammetric responses towards other metals and their combinations were acquired using the same electrode modification and sequence of adsorption (1 min) and voltammetry steps as for the calibration.

Besides Pb, both GCE=HEC-CA and GCE=T-CMC-CA could provide distinguish stripping peaks also for 20 mg L⁻¹ Cd and Cu at - 741 and - 109 mV, respectively (Fig. 8). Their heights, acquired from the solutions without any interfering metals, reached only 43.2% (Cd) and 3.4% (Cu) of Pb peak height, even though the molar concentration of both Cd (178 μ M) and Cu (315 μ M) was higher than that of Pb (96 μ M). This fact most probably reflects the different absorption rate of metal cations to the polysaccharide matrix, in accordance with previously reported results [28]. The presence of either Cd, Cu and Cd + Cu (all 20 mg L⁻¹) decreased the Pb stripping peak height, namely by 36.2%, 56.5% and 52.9%, respectively. It can be explained in terms of competing occupation of polysaccharide matrix bonding sites by the metal cations [28]. Radotic et al. have also reported a decrease in stripping square wave voltammetric peak for Cu when they performed separate absorption and measurement steps with cellulose-containing carbon paste electrodes, therefore they have preferred the single step procedure (absorption and measurement in the one solution) [36]. Our results suggested that Cu, as the cation with the highest molar concentration, causes the highest decrease of Pb response, i.e. could occupy the highest number of available bonding sites. Such effect was even stronger for cadmium - its original ("Cd-only") response was decreased by 17%, 78.7% and 96.1% by Pb, Cu and Pb+Cu presence, respectively. Interestingly, Cu behaved in the opposite manner, and its original response gained 4.8-, 5.7- and 7.3-fold in the presence of Pb, Cd and Pb+Cd. Such results are opposite to ones observed on cellulose-containing carbon paste electrode [36] and suggested that larger Pb²⁺ and Cd²⁺ cations support either diffusion or enhanced absorption of smaller Cu²⁺ ions and, importantly, their effect is cumulative. What is also worthy to mention is the appearance of other peaks at - 377 and - 494 mV when more metals is present in the solution. Presumably, metal cations interact with each other forming structures with oxidation potential diverse from the one of "pure" metal cations [55]. It can be concluded that the HEC-CA exhibit favorable properties in terms of enhanced absorption of Cu²⁺ cations in the presence of other ions, which can be employed in further heavy metal sensors.

3.5. Real samples

The prepared GCE=HEC-CA sensors were also employed for assessment of real environmental samples, namely leachates from detonation chamber dust (DCD) and galvanic sludge from the plating industry (GS). The obtained liquid phases were measured by the optimized GCE=HEC-CA sensor employing the same sorption (5 min) and consequent ASWSV in KCl as described in the previous

section. In GK samples, voltammetric peaks ascribed to Pb were detected, but they were too low (37 ± 1 nA) to calculate Pb concentration. These samples also exhibited significantly larger and a broad peak at about -740 mV suggesting that the Pb response may be suppressed by the presence of other metals (especially Cd) in the sample. In contrast with that, DCD samples exhibited a very high voltammetric response of Pb. A mean peak height of 19.5 ± 3.0 μ A was achieved in the filtrated leachate diluted 300-fold by DW. The calculated Pb concentration in the leachate (530 ± 93 mg L⁻¹) was compared with the values obtained by AAS, which revealed 684 ± 22 mg L⁻¹, that is, 22.4% higher than the value acquired by the HEC-CA-based sensor. The observed mismatch with the control analytical method results very probably from interference of other metal ions leached to the measured sample. Their presence in the solid was confirmed by XRF, revealing signals for Cu, Cd, Al, Fe, Zn, Ni... For the precise real sample measurement, some tool for elimination of other metal interferences should be developed, for example, mathematical correction of the analytical signal based on sample conductivity or on some other easily obtained parameter. Reproducibility would also be addressed in future work because the calculated RSD for the sample measurements was 15.3% ($n = 5$).

4. Conclusions

In this work simple protocol was introduced for the first time for modification of glassy carbon electrodes by water-soluble cellulose derivatives carboxymethyl cellulose (T-CMC) and hydroxyethyl cellulose (HEC) relying on coating electrode surface with polysaccharide solution and consequent in-situ crosslinking using citric acid (CA) at 110 °C. The method allows to omit employment of harmful chemicals (for example, divinyl sulfone as a crosslinking agent). The prepared HEC-CA hydrogel exhibits pH-switchable electrochemical impedance properties potentially applicable for the fabrication of impedance sensors. Furthermore, T-CMC-CA provided improved electrochemical properties in acidic solution while the HEC-CA hydrogel could perform much better under neutral pH, which can be applied to prepare surfaces with demanded features. The hydrogel-modified electrodes were applied for the determination of lead in solution and in real samples using the absorption of lead ions, followed by stripping voltammetry performed in a separate electrochemical cell. Detection limits of the sensors prepared from T-CMC-CA and HEC-CA were 1.13 and 0.4 mg L⁻¹, respectively, but it was improved to 0.75 and 0.15 mg L⁻¹ when the absorption step was prolonged from 1 to 5 min. Furthermore, interference caused by other metal ions was measured, and it was found that the stripping voltammetric peak of Pb can be decreased by slightly more than 50% in the presence of 3-fold molar excess of Cu²⁺, but the peak for the latter cation increased significantly in the presence of either Pb²⁺ or Cd²⁺. It can be concluded that the herein introduced in-situ crosslinked cellulose derivatives represent versatile, adjustable and cheap modification materials with intriguing properties applicable in electrochemical sensors of heavy metals.

CRedit authorship contribution statement

Jitka Sotolarova: Investigation, Data curation, Writing - review & editing. Stepan Vinter: Investigation, Writing - review & editing. Jar-oslav Filip: Conceptualization, Funding acquisition, Writing - original draft.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2021.127242.

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