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Electrochemical Investigation of Chlorophenols at Different Carbonaceous Composite Electrodes for Their Voltammetric Detection in Brewing Water and Beers

Running title: Detection of Chlorophenols in Brewing Water and Beer

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SUMMARY

Research background. Nowadays, any portable electroanalytical device applicable to the monitoring of chlorophenols concentration levels in technologically used water does still not exist, especially in the brewing industry. This problem could be solved by developing a screening electroanalytical method based on their anodic oxidation.

Experimental approach. The electrochemical behaviour of the target chlorophenols had to be investigated to find the optimum working conditions for their selective electrochemical detection in beers.

Results and conclusions. Electrochemical oxidation pathways of each investigated chlorophenol were proposed. The sum of all chlorophenols present in brewing water, expressed as the concentration equivalent of 2,6-dichlorophenol, can be determined electrochemically for possibilities of future real-time monitoring of chlorophenols in individual stages of the beer production

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process. Moreover, the cathodic reduction of their oxidation products proved to be a suitable electroanalytical tool for the selective detection of their presence in beers.

Novelty and scientific contribution. The research demonstrates that electroanalytical approach could be useful in the control of the beer biotechnology to prevent its sensory changes caused by the chlorophenols formed.

Keywords: beers; brewing water; chlorophenols; electrochemical detection; liquid chromatography; food quality

INTRODUCTION

Beers always contain naturally occurring phenolic compounds, especially polyphenols. They are derived directly from hops and malt (*1*). Chlorophenols are formed by the presence of chlorine and chloramine in the brewing water that bond to metabolites of polyphenols that yeast produce during fermentation (*2*). Contamination by wild yeasts and insufficient removal of chlorine-based cleaning agents can be considered as other sources of chlorophenols in beer (*3,4*). The yeast binds these phenols to the chlorine compounds as a way to protect themselves, but it results in beers with a pretty undesirable taste. This is the main reason why chlorophenols are responsible for specific off-tastes in beers, described as clove, medicinal, smoky or "band-aid" (*5*). For example, 2,6-dichlorophenol (2,6-DCP) is considered a defect in any beer when it is possible to smell the typical flavour of mouthwash. The cause of this defect is usually poorly washed packaging or tanks after sanitation. Additionally, it was experimentally proven, that 2,6-DCP can be formed by the gradual chlorination of 2-chlorophenol (2-CP) even to 2,4,6-trichlorophenol (2,4,6-TCP) during common water chlorination with chloramine (*6*). Since these chlorophenols can be expected in brewing water and mainly top-fermented wheat beers (*7,8*), they became the subject of the present electrochemical study. Fundamental technological guidelines, how to minimize the formation of sensory active chlorophenols in beer, are listed below.

Prevention of chlorophenols occurrence in beer

Chlorophenols could be minimised by the following: (*i*) using yeast cultures that produce fewer phenols. (*ii*) Pure yeast cultures must be used to avoid contamination by wild yeasts. (*iii*) Tap water should be filtered, boiled, or at least minimally allowed to stand to remove free chlorine, which occurs in concentrations of 0.05 to 0.25 mg/L. (*iv*) If chlorine-based cleaning products are used, all equipment must be thoroughly washed, or such products should be avoided. (*v*) Malt should not be ground to a very fine coarseness to prevent increased release of phenolic substances. (*vi*) The sweetening water must be kept at pH 6 and below 76 °C. (*vii*) Fads below φ~0.82 % EtOH content should not be collected.

The concentration of chlorophenols in beer, at which they become noticeable, can be very low. These compounds have intense aroma and flavour even at small quantities. Unfortunately, the specific threshold concentration is not explicitly stated, but their presence is monitored in brewing. The threshold concentration of chlorophenols in drinking water varies according to different standards and recommendations. For example, the US Environmental Protection Agency (EPA) requires 0.2 mg/L with a maximum of 4.0 mg/L, while the World Health Organization (WHO) allows up to 5 mg/L (*9*). In the Czech Republic, Decree No. 252/2004 Coll. sets hygiene requirements for drinking water, namely 0.1 µg/L 2-CP (*10*).

Due to their low concentration, numerous voltammetric methods based on anodic oxidation at predominantly modified sensors have already been developed. Table 1 offers only some examples (*11-21*), in which it is demonstrated that any selective voltammetric method has not yet been developed for the single or simultaneous determination of chlorophenols. The main reason for the impossibility of their selective determination could be their similar electrochemical properties, which lead to obtain relatively broad anodic peaks. Therefore, it seems that only the sum of all chlorophenols present in brewing water and beer could be determined voltammetrically.

As can be deduced from Table 1, variously modified electrodes, mainly glassy carbon electrode (GCE), have been employed in the development of voltammetric methods for determination of chlorophenols in tap water. Two recently published scientific papers suggest that even composite carbon materials could find their application in chlorophenols electrosensing. These reports from 2023 include graphitic carbon nitride nanosheets decorated with Fe_3O_4 nanospheres composite-modified screen-printed carbon electrodes for real-time detection of 2,4,6-trichlorophenol in environmental samples (*22*) and carbon paste electrode (CPE) modified with cellulose nanofibers containing Fe_3O_4 for monitoring of 4-chlorophenol as a water pollutant (*23*). Both of these electroanalytical methods were also based on direct anodic oxidation using pulse voltammetric techniques and were not sufficiently selective to distinguish individual chlorophenols. A fundamental lack of knowledge of the electrochemical behaviour of chlorophenols represents the key reason why their subsequent electrode reactions were not favoured.

In this study, the electrochemical behaviours of different chlorophenols at composite carbonaceous electrodes were therefore investigated. A conventional CPE (*24*), CPE prepared from highly conductive spectroscopic graphite powder (GPE), CPE modified with w=5 % multi-walled carbon nanotubes (CPE/MWCNTs), and glassy carbon paste electrode (GCPE) were employed. Phenol (PhOH) and three chlorophenols with various number and position of chlorine atoms in the benzene rings, namely 2-chlorophenol (2-CP), 2,6-dichlorophenol (2,6-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP), were studied in different aqueous media by using cyclic voltammetry at different scan rates over the potential range of −0.6 V to +1.6 V *vs.* silver/silver chloride reference electrode. A square wave anodic voltammetric method was proposed to find out whether it will be possible to adjust the working conditions so that each of the investigated chlorophenols gives comparable current yields of the electrode reactions.

MATERIALS AND METHODS

Chemicals and reagents

Phenol, 2-chlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol were obtained from Merck KGaA (Darmstadt, Germany). Their stock solutions with a concentration of 0.01 mol/L were prepared in 10 mL volumetric flasks. Due to the low solubility of 2,6-dichlorophenol, and 2,4,6-trichlorophenol in pure water, all standards had to be dissolved in an absolute ethanol (EtOH) of ≥99.5 % purity. Glacial acetic acid, sodium acetate, disodium hydrogen phosphate, sodium dihydrogen phosphate dihydrate, ammonium chloride, and w=24 % ammonia solution were purchased from Lach-Ner, s.r.o. (Neratovice, Czech Republic) and used for the preparation of 0.1 mol/L acetate (AcB) of pH 4.5, sodium phosphate (SPB) of pH 7.0, and ammonia buffers (AmB) of pH 10. An ultrapure water with resistivity lower than 18.3 MΩ cm was prepared by a Milli-Q® deionization unit from Merck Millipore (Burlington, USA).

Instrumentation

Each voltammetric measurement was carried out in a standard voltammetric cell containing 10 mL of 0.1 mol/L aqueous buffer as working solution with immersed GCPE, followed by silver/silver chloride reference electrode with 3 mol/L KCl salt bridge from Metrohm (Herisau, Switzerland), and a platinum sheet from Elektrochemické detektory (Turnov, Czech Republic), acting as auxiliary electrode. All mentioned electrodes were connected to a potentiostat/galvanostat (Autolab/PGSTAT101) operated with Nova 1.11 software from already mentioned Metrohm company (*25*).

Preparation of different carbon paste electrodes

Four types of carbon pastes were prepared by hand mixing of 0.5 g chemically purified natural graphite powder (particle size of less than 5 µm) from Graphite Týn, (Týn nad Vltavou, Czech Republic), spectroscopic graphite powder (particle size of 10–25 µm) from Ringsdorff-Werke (Bonn, Germany), or glassy carbon powder Sigradur-G (distribution of particle size 5–20 µm) from HTW Hochtemperatur-Werkstoffe GmbH (Maintingen, Germany) and 0.085 g mineral oil from Merck KGaA (Darmstadt, Germany) in ceramic mortal for minimally 20 min. In addition, the carbon paste prepared from natural graphite powder was modified with w=5 % multi-walled carbon nanotubes (MWCNTs) from Shenzhen Nanotech Port Co. (Shenzhen, China), characterised with a diameter of 10–30 nm, length of 5–15 µm, and specific surface area of 40–300 m^2/g. Furthermore, glassy carbon paste was enriched by w=5 % reduced graphene oxide (RGO), from ACS Material, LLC (Medford, USA), characterised by resistivity ≤0.30 Ω cm and specific surface area 400–1000 m^2/g.

Then, each resulting homogenous paste was pressed into the cavity (diameter of 3 mm) of Teflon® piston-like electrode holder. Herein, it is necessary to note that the height of paste column must not exceed 2 cm due to difficult extrusion of compact glassy carbon paste. Furthermore, it is recommended not to measure with freshly made paste electrodes due to their rather unstable electrochemical behaviour caused by an incomplete homogenization, but to leave at the laboratory conditions for one day. After this self-homogenization process, all resulting paste electrodes were ready for following voltametric measurements.

Voltammetric measurements

Repetitive cyclic voltammetric measurements (three cycles) of each 0.5 mmol/L chlorophenol at glassy carbon paste electrode (GCPE) (*26*) in 0.1 mol/L acetate (AcB) of pH 4.5, sodium phosphate buffer (SPB) of pH 7.0, and ammonium buffer (AmB) of pH 10, all with φ=5 % EtOH content, performed in the potential range from −0.4 to +1.4 V at potential step E_{step}=2.5 mV and scan rate of v=50 mV/s were used for investigation of electrochemical behaviour of the variously substituted chlorophenols.

Anodic square wave voltammetric measurements of 0.01–10 µmol/L PhOH, 2-CP, 2,6-DCP, and 2,4,6-TCP at conventional CPE, GPE, CPE/MWCNTs, GCPE/RGO and GCPE in the environment of tap water, imitating the brewing water, performed in the potential range from 0 to +1.0 V at E_{step}=2.5 mV, potential amplitude E_{ampl}=25 mV, and frequency f=4 Hz were used to decide whether the partial contributions of the anodic oxidation of individual chlorophenols can be added to their total content. On the other hand, cathodic square wave voltammetric measurements of wheat beers were performed at GCPE in the potential range from +1.4 to −0.4 V at deposition potential E_{dep}=+1.4 V for deposition time t_{dep}=120 s, equilibrium time t_{eq}=5 s, E_{step}=−2.5 mV, E_{ampl}=−25 mV, and f = 4 Hz.

Samples

Four different wheat beers were chosen for voltammetric analysis, namely Blue Moon (Belgian white beer of alcohol: 5.4 %) and Hoegaarden® (alcohol: 4.9 %) both from Pivovary Staropramen s.r.o., (Prague, Czech Republic), Weizen (alcohol: 4.8 %) from Primátor a.s., (Náchod, Czech Republic), and Paulaner Weißbier (alcohol: 5.5 %) from Paulaner Brauerei GmbH & Co. KG. (München, Germany). A common tap water was used as a sample of brewing water. Prior to any voltammetric investigation, the beer samples of 50 mL were sonicated at laboratory conditions for 30 min. If the presence of chlorophenols was not detected electrochemically in these samples, they were subsequently spiked to have no more than 100 µmol/L content of 2,6-DCP.

Statistical data processing

Each point of the calibration curve was measured at least five times (N=5). The final peak area values were calculated and presented as confidence intervals $\bar{x} \pm st_{1\text{-}\alpha}/\sqrt{n}$ where $\bar{x}$ is the arithmetic mean, s the standard deviation, and $t_{1\text{-}\alpha}$ the critical value of Student's t-distribution for ten (4 degrees of freedom) determinations (2.776) at a significance level α of 0.05 (95 % probability). Finally, y-intercept significance of the corresponding calibration curve, plotting the linear dependence of peak area (A_{p}), presented as averages of five replicate measurements (N=5), on actual concentration (c) was tested using a statistical software QC-Expert v. 3.3.0.4 from TriloByte Statistical Software (Pardubice, Czech Republic) (*27*).

RESULTS AND DISCUSSION

Electrochemical behaviour of phenol and variously substituted chlorophenols

First, phenol together with selected chlorophenols had to be electrochemically investigated using repetitive cyclic voltammetry at glassy carbon paste electrode (GCPE) in several aqueous working media to propose their anodic oxidation pathways and determine the optimum working conditions for electrosensing of chlorophenols in the brewing water and top-fermented wheat beers.

From repetitive cyclic voltammograms in Fig. 1, it can be deduced that the electrode reactions of the 2-CP, 2,6-DCP, and 2,4,6-TCP at carbonaceous electrodes in an aqueous environment are irreversible. Within scan rate study for each chlorophenol recorded at 10, 50, 100, 200, 300, 400, and

500 mV/s (*vs.* Ag│AgCl│3 mol/L KCl), it was observed that the anodic peak current response (I_p^a) linearly ($R^2 \geq 0.9952$) increased with the square root of the scan (v). For this finding, diffusion-controlled electrochemical oxidation reaction can be accepted. Here, it is necessary to mention that each cyclic voltammogram was recorded on a newly restored GCPE surface due to subsequent reactions.

Except for 2,4,6-TCP, for which an electrochemical-chemical (EC) reaction mechanism has been proven, all other chlorophenols are directed with electrochemical-chemical-electrochemical (ECE) reaction mechanism, whereas amounts of subsequent products formed from their anodic oxidations decrease with the increasing number of chlorine atoms on the benzene ring and polarisation rate.

In the first anodic scan (solid cyclic voltammograms in Fig. 1), only one intense oxidation peak is seen, the peak potential of which shifts to more positive values with decreasing pH of the working medium. This phenomenon is related to two-electron oxidation during which cation intermediates are formed (*28*). These reactive intermediates undergo subsequent nucleophilic addition of water to form *ortho* and *para* quinones, which can be reversibly reduced to the corresponding chlorinated dihydroxyphenols. This fact is proven by a pair of redox couples in subsequent cycles (dash and dotted cyclic voltammograms in Fig. 1).

>> Fig. 1 <<

As evident from the proposed anodic oxidation pathway of 2-CP in Fig. 2, *ortho* and *para* positions on the benzene nucleus must not be occupied to form the above-mentioned chlorinated quinones. However, well distinguishable two redox pairs of 2,6-DCP (see Fig. 1I), although it has both *ortho* positions occupied by chlorine atoms, show that the electrochemical behaviour of chlorophenols is much more complex. Apparently, chlorine atoms can be replaced by hydroxyl groups, when chlorine is released in the form of HCl (*29*), and/or dimers are formed by the coupling of phenoxy radicals (*30*). The formation of such an electrochemically inactive dimer can be considered as a product of the anodic oxidation of 2,4,6-TCP because it did not provide any subsequent peaks in the second and third cycle. These findings indicate that chlorine atoms are not replaced by hydroxyl groups during the anodic oxidation of 2,4,6-TCP when a 2,4,6-trichlorophenoxy radical is formed which undergoes a coupling reaction (*31*).

>> Fig. 2 <<

Possibilities of simultaneous voltammetric determination of chlorophenols

As proven from the electrochemical behaviour of chlorophenols at GCPE, all investigated chlorophenols provide one oxidation peak that could be used for electroanalytical purposes.

Generally, it can be assumed that voltammetric analysis should be performed on virgin electrode surface due to subsequent reactions of their oxidation products. Because a carbon paste electrode meets two basic requirements, namely polarization in anodic potential window and simple renovation of the electrode surface (*15*), its different analogues and modifications with carbon nanomaterials were examined in electrochemical detection of chlorophenols in brewing water and several top-fermented wheat beers and using square wave voltammetry.

Unfortunately, an admixture of MWCNTs or RGO into CPE or GCPE, respectively, did not cause the expected narrowing of the anodic peak of 2-CP, as shown in Fig. S1 (see Supplementary materials). Another option to achieve the desired separation of individual chlorophenols in the mixture was to optimize the SWV parameters. Despite setting very low values of the potential step (2.5 mV) and frequency (4 Hz), which allowed obtaining well-defined shapes of their anodic peaks, it was not possible to distinguish individual chlorophenols in their equimolar mixtures. Values of their anodic peak potentials (E_p^a) depending on the pH, which are listed in Table S1, confirm this statement.

In addition, it was experimentally found that their peak current response significantly depends on the composition of the working medium. As documented by results obtained from calibration measurements in Fig. S2, in the environment of brewing water (unbuffered working medium), the peak current area (A_p) decreases with the number of chlorine atoms on the benzene nucleus because chlorine is an electron-withdrawing group. Thus, the acidic character of chlorophenols increases with a higher number of substituted chlorines.

However, when working in buffered media with its elevated ionic strength, it was able to achieve relatively comparable sensitivity (~0.045 μA V L/μmol) for all investigated chlorophenols regardless of the type of working electrode used. Since all equations of linear regression were characterized with a statistically insignificant y-intercept (lower than ~0.0005 μA V), the standard addition method could be offered for voltammetric determination of the total amount of chlorophenols, which could be expressed as the concentration equivalent of the most occurring 2,6-DCP.

Voltammetric analysis of brewing water

The brewing water is considered a crucial component in the beer-making process because its chemical composition can significantly affect the flavour and quality of the beer. The brewing water usually contains essential minerals (calcium, magnesium, sodium, and potassium) and common ions, including bicarbonate, sulfate, and chloride. In contrast, chlorine and chloramines can lead to beer aftertaste, and therefore need to be removed or neutralized before brewing. When chlorinating tap water, phenols form intensely smelling chlorophenols. This is the main reason why chlorophenols can be found in brewing water.

In this study, the use of a slow scan rate (v) of 10 mV/s and potential amplitude (E_{ampl}) of 25 mV allowed to sufficiently distinguish the anodic peak of any chlorophenol from the baseline signal of tap water (dash square wave voltammograms in Fig. S2) even for a concentration of 0.1 µmol/L. Repeatability, defined as a measure of the ability of the method to generate similar results for multiple preparations of the same sample, was evaluated in a model analysis of brewing water spiked with 1 µmol/L of each chlorophenol. A value of relative standard deviation (RSD) of 3.1 % for five (N=5) repetitions was achieved.

Unfortunately, it was experimentally confirmed that their simultaneous determination in a mixture is not possible to carry out by direct anodic oxidation. This fact is demonstrated in Fig. S3, where voltammetric records for individual chlorophenols and their mixture are shown. Thus, it can be concluded that this approach allows only the sum of all chlorophenols present in the brewing water to be quantified, which could be expressed as a concentration equivalent of 2,6-DCP.

Voltammetric analysis of wheat beers

Generally, insufficiently removed chlorine can potentially generate unwanted chlorophenols during the fermentation phase of the brew. Because beers usually contain high amounts of naturally occurring phenolic substances, the application of direct anodic SWV cannot be considered as in the case of brewing water. For this reason, the cathodic reduction of anodically oxidised chlorophenols was at least tested as a possibility for their selective voltammetric detection in the complex matrix of wheat beers. During the potentiostatic oxidation of 2,6-DCP, the working solution was stirred to increasing the amount of accumulated oxidation product. Since the pH of beer in practice is most often in the range of 4.3-4.7, the wheat beer samples enriched by 1 µmol/L 2,6-DCP content were differently diluted using 0.1 mol/L AcB (pH 4.5).

Fig. 3a shows that 2,6-DCP can provide up to three cathodic peaks at +0.841, +0.487, and +0.272 V if it would previously be potentiostatically oxidized at +1.4 V for 120 s. Surprisingly, the cathodic peak at +0.487 V was not observed for all beer samples, whether diluted (blue dash voltammogram in Fig. 3a) or not (black dash voltammogram Fig. 3b). The magnitude of this cathodic signal depended on the concentration of 2,6-DCP, while it was not possible to detect lower contents than 50 µmol/L 2,6-DCP in the undiluted beer samples.

Fortunately, it was possible to detect and quantify even 1 µmol/L of 2,6-DCP content in the model sample through further investigation and partial optimisation of electrochemical detection, especially by setting the SWV operating parameters. Furthermore, it was also found out that φ=5 % EtOH has a statistically significant effect on the height of the reduction peak in cathodic stripping voltammetry (Fig. S4a), in contrast to direct anodic voltammetry, where this effect is negligible (Fig S4b). This phenomenon can be attributed to the higher solubility of 2,6-DCP in aqueous-ethanol mixtures, and hence to its lower tendency to accumulate on the surface of GCPE by polar/nonpolar interactions affected also by electrostatic interactions by applying a positive deposition potential (E_{dep}). Either way, this electrochemical study suggests that a stripping voltammetric method for the selective determination of 2,6-DCP in beers could be developed in the near future.

>> Fig. 3 <<

CONCLUSIONS

The present electrochemical study confirmed the impossibility of simultaneous voltammetric determination of phenol with chlorophenols and at the same time showed the hidden flaws of previously developed electroanalytical methods based on their anodic oxidation. It has been experimentally proven that only the total amount of chlorophenols can be determined using anodic SWV in soft drinking water, which is commonly used as brewing water. Nevertheless, it was possible to distinguish the artificial addition of 2,6-DCP even in the complex matrix of wheat beer using a cathodic SVW with potentiostatically controlled accumulation. This breakthrough finding could served as a basis for the development of selective and sensitive voltammetric methods applicable for such samples.

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CONFLICT OF INTEREST

All authors declare that they do not have any known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

SUPPLEMENTARY MATERIALS

All supplementary materials are available at: www.ftb.com.hr.

AUTHORS' CONTRIBUTION

S. Muriqi participated in the formal analysis, including preparation of carbonaceous composite electrodes with working solutions, sample pretreatment, and performance of voltammetric measurements. L. Červenka responsible for English language editing and providing appropriate level of English language. M. Sýs evaluated the measured data, coordinated the work of the whole scientific team, and wrote the final manuscript.

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Table 1. Overview of several voltammetric methods designed for determination of chlorophenols

Sensor	Analyte	Sample	Interferences	Reference
GCE/HP-β-CD-GNR	2-CP	Water	4-CP, 2,4,6-TCP	(*11*)
GCE/MWCNTs-DCP	2-CP	Water	PhOH, 4-CP, 2,4-DCP, 2,4,6-TCP	(*12*)
GCE/AuNPs@cMWCNT	4-CP	Water	PhOH	(*13*)
GPSZnH	4-CP	Water	no investigated towards other chlorophenols	(*14*)
CPE/Lap	2,4-DCP	Water	2-CP, 4-CP	(*15*)
GCE/MIPs/PRGO	2,4-DCP	Water	no investigated towards other chlorophenols	(*16*)
GCE/Dy_2O_3-Co_3O_4@CeO_2	2,6-DCP	Water	no investigated towards other chlorophenols	(*17*)
GCE/AlSiFe	2,6-DCP	Water	2-CP, 4-CP, 2,4-DCP, 2,4,6-TCP	(*18*)
BDDE	2,4,6-TCP	Beverages	no investigated towards other chlorophenols	(*19*)
GCE/Nafion/CuO	2,4,6-TCP	Water	no investigated towards other chlorophenols	(*20*)
ITO/SAM/AuNPs/HS-β-CD	2,4,6-TCP	Water	2-CP, 4-CP, 2,4-DCP	(*21*)

Abbreviations: AuNPs@cMWCNT; gold nanoparticle/carboxyl functionalized multi-walled carbon nanotube, BDDE; boron-doped diamond electrode, CPE/Lap; laponite modified carbon paste electrode, GCE; glassy carbon electrode, GPSZnH; graphite paste modified with metallosilsesquioxane, HP-β-CD-GNR; graphene nanoribbon functionalized with 2-hydroxypropyl-β-cyclodextrin, ITO/SAM/AuNPs/HS-β-CD; HS-β-cyclodextrin/gold nanoparticles composites modified indium tin oxide electrode, MIPs/PRGO; molecularly imprinted polymer with Carica papaya reduced graphene oxide, and MWCNTs-DCP; multi-wall carbon nanotube-dicetyl phosphate film

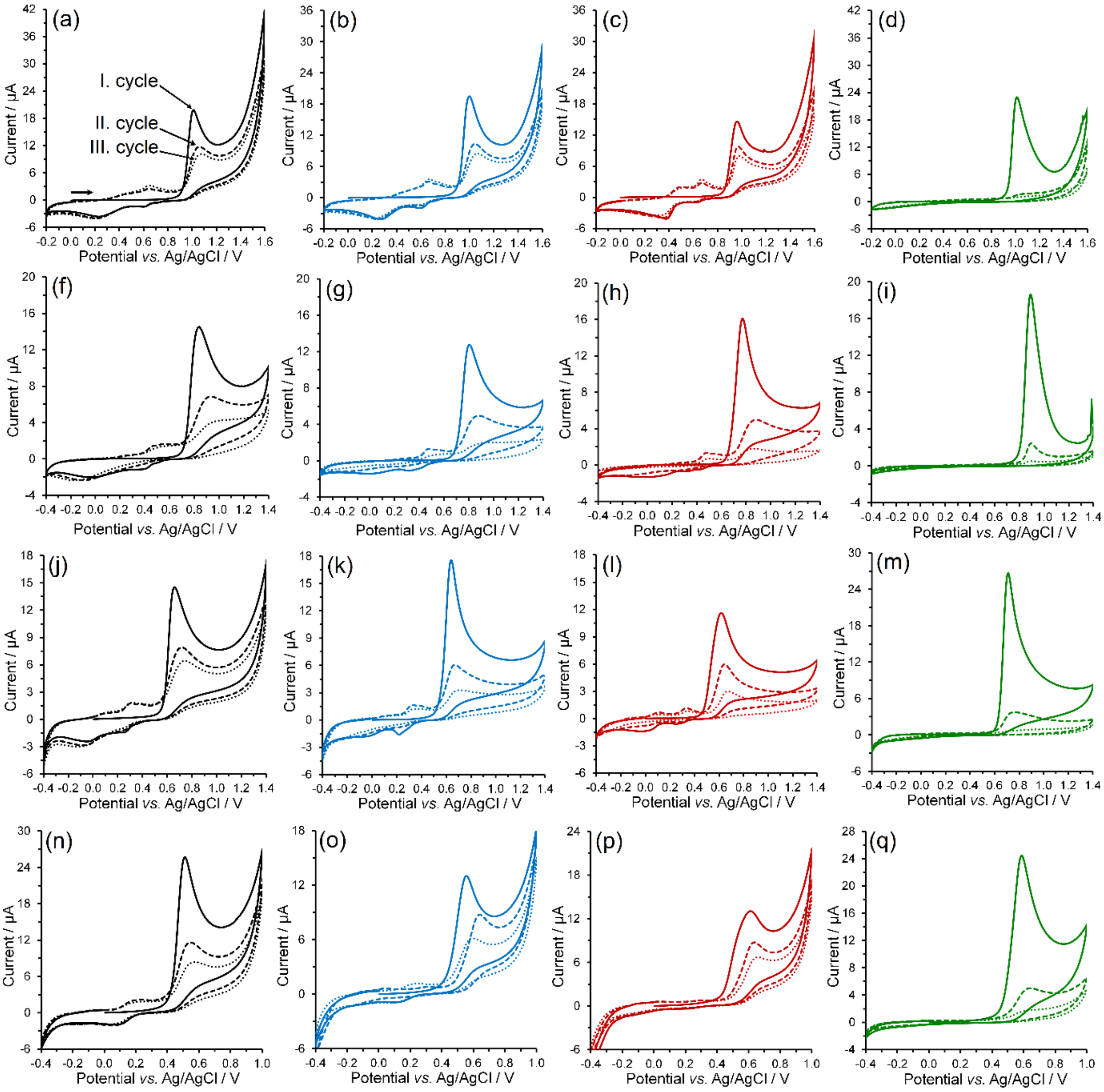

Fig. 1. Repetitive cyclic voltammograms (1st cycle; solid, 2nd cycle dash, and 3rd cycle dotted line) of 500 μmol/L PhOH (black), 2-CP (blue), 2,6-DCP (red), and 2,4,6-TCP (green cycles) recorded on GCPE in 0.1 mol/L HNO_3 (a, b, c, and d), AcB of pH 4.5 (f, g, h, and i), SPB of pH 7 (j, k, l, and m), and AmB of pH 10 (n, o, p, and q), all with φ=5 % EtOH content, at E_{step}=2.5 mV and v=50 mV/s

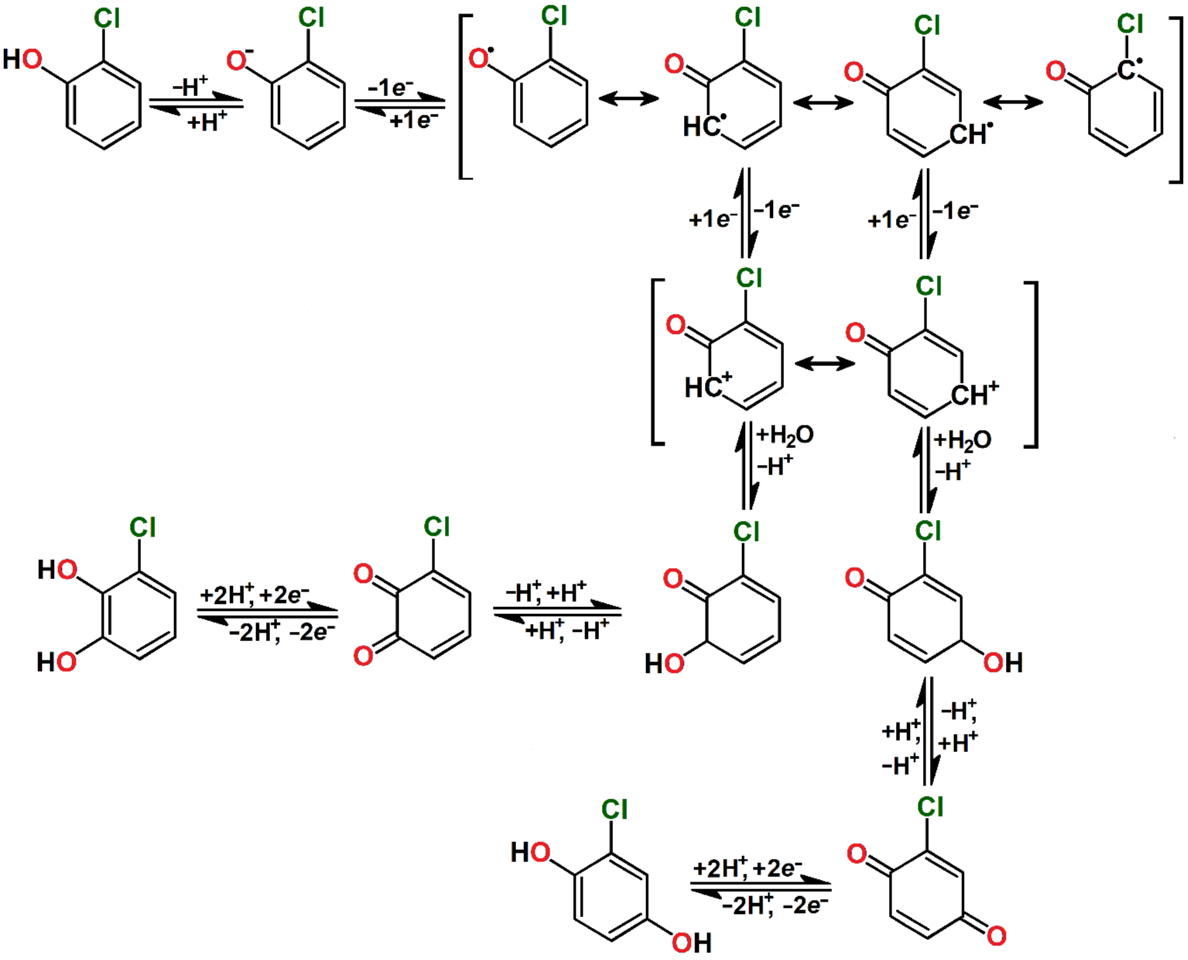

Fig. 2. Proposed electrochemical oxidation pathway of 2-chlorophenol

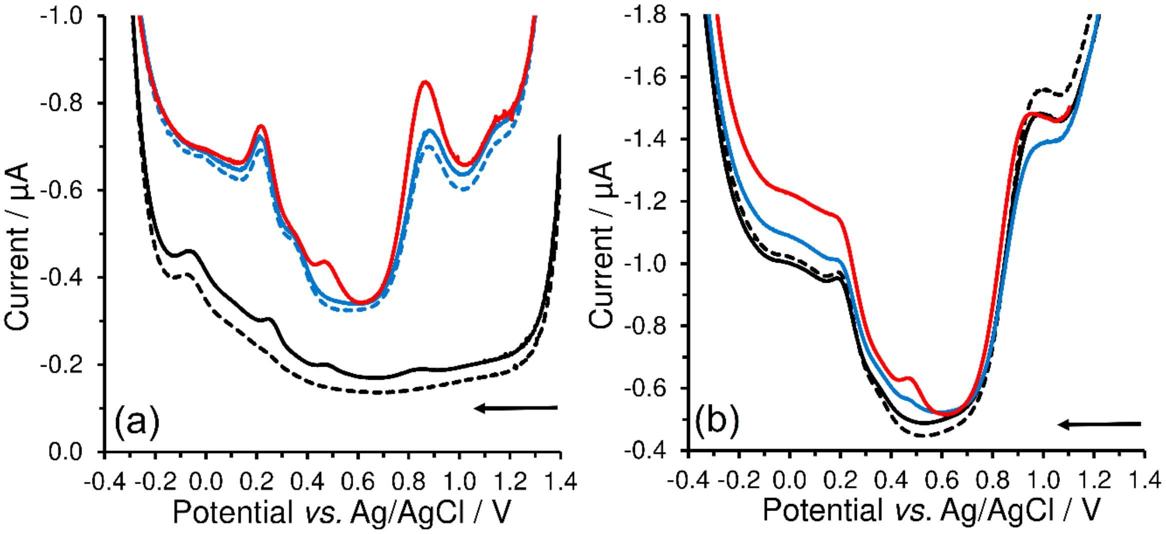

Fig. 3. Square wave voltammograms of 0.1 mol/L AcB (pH 4) without (dash black) or with 1 µmol/L 2,6-DCP (solid black), tenfold diluted Weizen without (dash blue) or spiked with 1 (solid blue) and 10 µmol/L 2,6-DCP content (a); square wave voltammograms of Paulaner Weißbier without (dash black) or spiked with 10 (solid black) 50 (solid blue), and 100 µmol/L 2,6-DCP content (solid red line) (b); all recorded on GCPE at E_{dep}=+1.4 V, t_{dep}=120 s, t_{eq}=5 s, E_{step}=−2.5 mV, E_{ampl}=−25 mV, and f=4 Hz

SUPPLEMENTARY MATERIALS

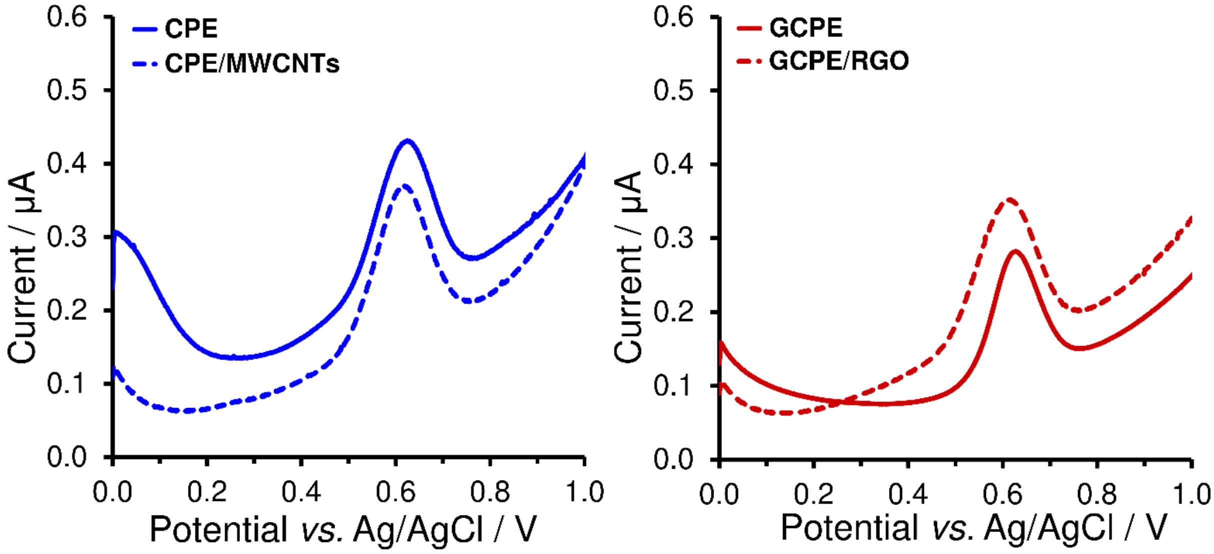

Fig. S1. Square wave voltammograms of 0.5 µmol/L 2-CP obtained in 0.1 mol/L AcB (pH 4) with φ(EtOH)=5 % at different carbonaceous composite electrodes in brewing water at E_{step}=2.5 mV, E_{ampl}=25 mV, and f=4 Hz

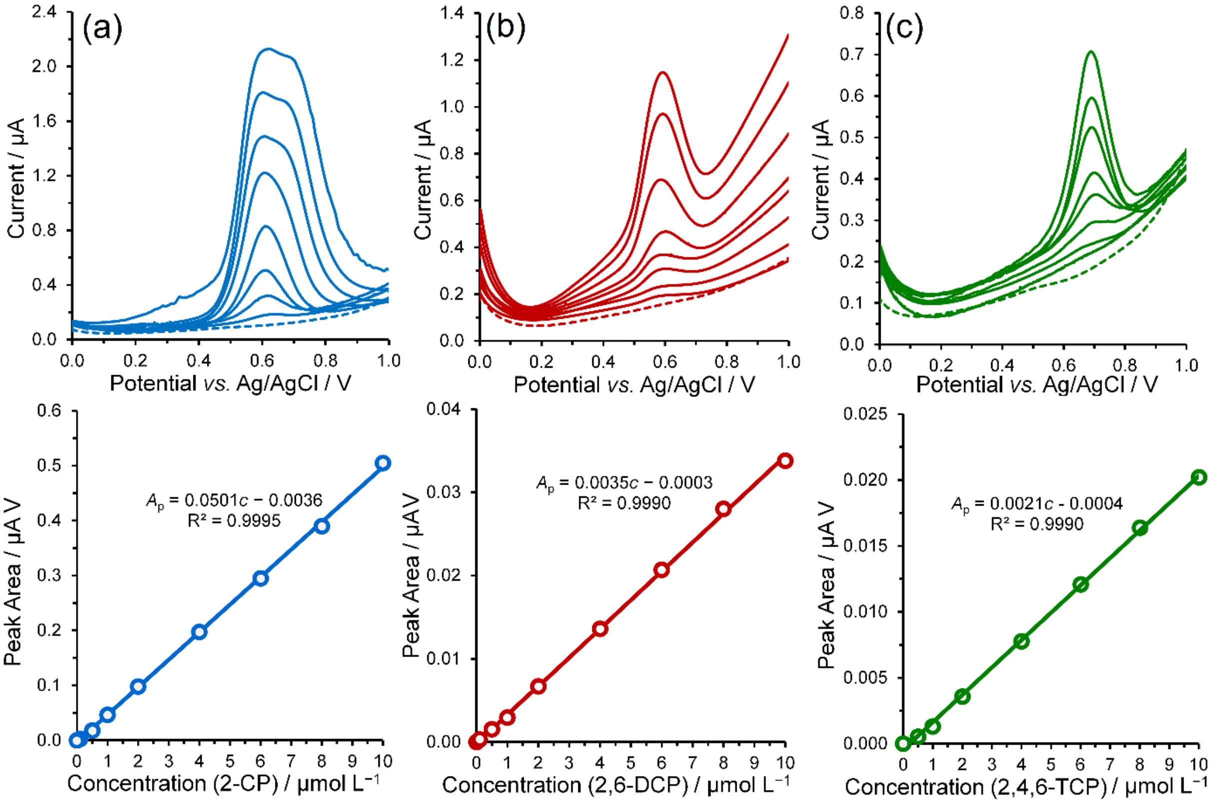

Fig. S2. Square wave voltammograms of 0 (0.1 mol/L AcB (pH 4) with *φ*=5 % EtOH; dash), 0.1, 0.5, 1, 2, 4, 6, 8, and 10 μmol/L (solid lines) 2-CP (a) 2,6-DCP (b), 2,4,6-TCP (c) obtained at GCPE, CPE/MWCNTs, and GCPE/RGO, respectively, in tap water at E_{step}=2.5 mV, E_{ampl}=25 mV, and *f*=4 Hz. The corresponding calibration curves are shown below

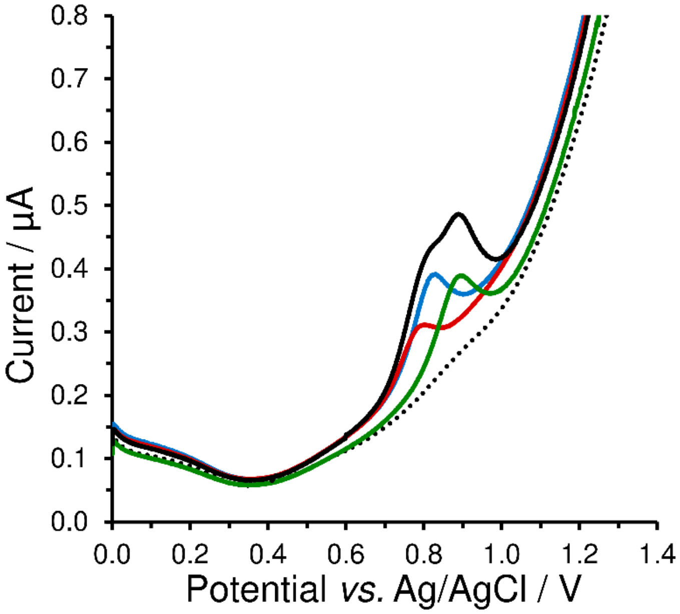

Fig. S3. Anodic square wave voltammograms of 0 (black dotted), 1 µmol/L (solid lines) 2-CP (blue) 2,6-DCP (red), 2,4,6-TCP (green), and their equimolar mixture (black curve) obtained at GCPE in 0.1 mol/L AcB of pH 4.5 at E_{step}=2.5 mV, E_{ampl}=25 mV, and *f*=4 Hz

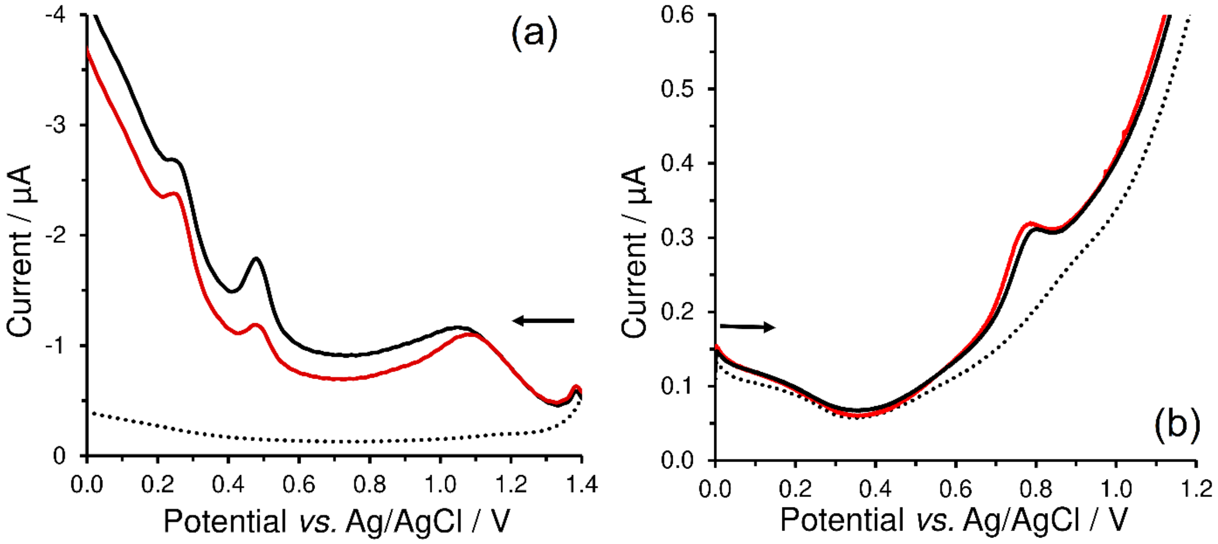

Fig. S4. Cathodic square wave voltammograms of 0 (dotted black) 1 µmol/L 2,6-DCP recorded on GCPE in 0.1 mol/L AcB (pH 4.5) without (solid black) and with (red curve) φ=5 % EtOH content at E_{dep}=+1.4 V, t_{dep}=120 s, t_{eq}=5 s, E_{step}=−5 mV, E_{ampl}=−25 mV, and *f*=60 Hz

Table S1. Overview of anodic peak potentials of phenol and chlorophenols depending on the pH of different working media

Working medium	pH	PhOH E_p^a (V)	2-CP E_p^a (V)	2,6-DCP E_p^a (V)	2,4,6-TCP E_p^a (V)
0.1 mol/L HNO_3	1.0	1.017	1.007	0.972	1.017
0.1 mol/L AcB	4.5	0.851	0.811	0.775	0.896
0.1 mol/L SPB	7.0	0.670	0.645	0.629	0.715
0.1 mol/L AmB	10.0	0.514	0.540	0.599	0.594

Abbreviations: AcB; acetate buffer, AmB; ammonia buffer, 2-CP; 2 chlorophenol, 2,6-DCP; 2,6-dichlorophenol, 2,4,6-TCP; 2,4,6-trichlorophenol, E_p^a; anodic peak potential, PhOH; phenol, and SPB; sodium phosphate buffer.