Sensing of chemical oxygen demand (COD) by amperometric detection – Dependence of current signal on concentration and type of organic species

Samira Lambertz
Friedrich Schiller University Jena

Marcus Franke
Friedrich Schiller University Jena

Michael Stelter
Friedrich Schiller University Jena

Patrick Braeutigam (✉ patrick.braeutigam@uni-jena.de)
Friedrich Schiller University Jena

Research Article

Abstract

The standard method for the determination of chemical oxygen demand (COD) with $K_2Cr_2O_6$ uses harmful chemicals, has a long analysis time, and cannot be used for on-site online monitoring. Therefore, it is necessary to find a fast, cheap, and harmless alternative. The amperometric determination of COD on boron-doped diamond (BDD) electrodes is a promising approach. However, to be a suitable alternative, the electrochemical method must at least be able to determine the COD of water samples independently of the contained substances. Therefore, the current signal as a function of various organic materials was investigated for the first time. It was shown that the height of the signal current was dependent on the type of organic matter in single substance solutions and that this substance dependency increases with the amount of COD. Those findings could be explained by the mechanism proposed for this reaction showing that the selectivity of the reaction is dependent on the ratio of the concentration of the hydroxyl radical and the organic species. We give an outlook on how to improve the method to increase the linear working range, avoid the signal variance and how to further explain the signal variance.

Introduction

Increasing industrialization, usage of more chemical products and the climate crisis are all factors that in the long run lead to a conflict of water usage and are a threat to natural water bodies (Goel, 2006). One way to meet this potential danger and protect the natural resource water is water monitoring and treatment. (Quevauviller et al., 2007) (Shannon et al., 2008) However, many classical methods for the analysis of wastewater use toxic chemicals which leads to waste production, increase in the costs of the analysis and the need for specialized personnel for performing the analytical procedure.

An important sum parameter that is widely used in water monitoring is the COD (Pisarevsky et al., 2005). The COD measures the amount of oxygen that is needed to mineralize the organic content of a given water sample defined by standard reaction conditions. It can be used to monitor the quality of water bodies, access the degree of contamination in wastewaters and control wastewater treatment plants (Awe et al., 2016).

The standard method to determine COD uses potassium dichromate ($K_2Cr_2O_6$) or potassium permanganate ($KMnO_4$) as oxidant(Boyles, 1997). Both are toxic and dangerous for the user and the environment. The usage of $K_2Cr_2O_6$ is to be faded out in the future due to it being a treat to the environment and thereforeis part of several regulations (ECHA, 2015). In addition, the standard method uses other toxic chemicals ($HgSO_4$, H_2SO_4, Ag_2SO_4), has a high energy consumption due to a long heating and is time consuming (~4 h), making it unsuitable for in-time measurements and also giving it a higher impact on climate change(Ji Li et al., 2018).

COD is mentioned as a mandatory parameter in various laws and is therefore part of standard procedures in many countries. The German federal law states that the COD must be measured whenever wastewater is discharged into surface waters. (Ordinance on Requirements for the Discharge of Wastewater into

Waters, German Federal Law) That is also stated in other state laws (e.g. USA, EU)(Urban Waste Water Treatment Directive, Annex I: Discharge requirements) (US EPA The Water Quality Standards Regulation). Therefore it is necessary to find a sustainable alternative to the standard method that can also be used in other applications like real-time monitoring and control of sewage treatment plants(Geerdink et al., 2017).

A way to avoid the usage of toxic chemicals is to switch to methods that work without toxic chemicals like optical or electrochemical methods (Su et al., 2007). Among the research that has been conducted in finding alternative methods for the determination of COD there have been non-oxidative and oxidative methods. A non-oxidative method is the spectrophotometric method which correlates absorbance of water samples with the COD. However, the COD is only indirectly determined, the method has to be calibrated and no conclusion about the actual oxidizability can be drawn. The wide range of oxidation based methods that have been investigated include some that are based on advanced oxidation processes (AOPs): the photocatalytic method, the photoelectrocatalytic method and the electrocatalytic method. (J. Li et al., 2018)

For the electrocatalytic method the research is mainly focused on finding suitable electrode materials (Gutierrez-Capitan et al., 2015) (Cheng et al., 2011) (Zhou et al., 2012) and establishing an electrochemical method. The most promising electrode material for the determination of COD is BDD which has been investigated by several groups (Bogdanowicz et al., 2012) (Kondo et al., 2016) (Wang, Li, Yang, et al., 2012) (Wang, Li, Zhang, et al., 2012) (Yu et al., 2007) (Kondo et al., 2014) (Yu et al., 2009). The electrochemical determination of COD on BDD electrodes is based on the oxidation of the organic compounds by hydroxyl radicals which are produced on the electrode surface having a high overpotential for oxygen evolution (Chang et al., 2008). Those hydroxyl radicals are supposed to react with organic matter in an unselective way making it possible to determine all kinds of organic substances (Lee & Von Gunten, 2010).

Methods that have been used for the determination of COD with BDD electrodes are amperometric and coulometric methods. The amperometric method is more applicable for real-time analysis as it has a much shorter analysis time. It is instrumentally simple, fast and does not use any toxic chemicals. It can easily be automated which means avoiding staff cost and making it usable for wastewater treatment plant monitoring and control. It has already been explored in several studies (Wang, Li, Yang, et al., 2012) (Wang, Li, Zhang, et al., 2012) (Yu et al., 2007) (Yu et al., 2009). A summary of the studies investigating this approach with their stated working range, the chemicals used to validate the method and some comments why that is not applicable to real world analysis can be found in Table 1.

Table 1: Published amperometric methods using BDD electrodes with their corresponding linear working range, studied substances and comments.

Authors	Linear working range	Substances studied	Comments
Yu et al. (Yu et al., 2007)	20 – 9,000 mg/L COD	Glucose, KHP, Glutamic acid, phenol, p-Nitrophenol, salicylic acid, cysteamine, oxalic acid, acetic acid	• Calibration was only conducted between 0 – 120 mg/L • Validation with the same substances that were used for calibration
Yu et al. (Yu et al., 2009)	2 – 175 mg/L COD	Glucose, KHP, Glutamic acid, phenol, p-Nitrophenol, salicylic acid, cysteamine, oxalic acid, acetic acid	• Validation with the same substances that were used for calibration • Validation only in the range of 0 – 100 mg/L
Wang et al. (Wang, Li, Zhang, et al., 2012)	19.2 – 11,600 mg/L COD	Glucose, KHP	• Calibration was only conducted between 0 – 120 mg/L • Only two organic substances were used
Wang et al. (Wang, Li, Yang, et al., 2012)	0 – 23.200 mg/L COD	Glucose, KHP	• Calibration was only conducted between 0 – 250 mg/L • Only two organic substances were used

While these papers show satisfactory results, one can criticize that it was not considered if there is a dependency of the signal current on the organic species. Only a few chemicals were used to evaluate the method. The methods were optimized and calibrated using one organic substance or a mixture of different organic substances with a constant composition. No attention was paid to the dependence of the signal on the composition of the sample. This means that the established methods are only applicable for the tested substances and samples. As the COD is a sum parameter, it should be applicable to all water contents that are oxidizable by strong oxidants like $K_2Cr_2O_6$. Until now, it is unknown if it is possible to analyze the COD independent of the organic substance.

The aim of this study is to advance the research on the amperometric determination of COD with BDD electrodes to make it suitable for water monitoring systems and for the monitoring and management of wastewater treatment plants.

A necessary step to establishing the proposed method in real life applications is to investigate the dependency of the organic substance on the signal current as it should be applicable for all kinds of waste waters with different compositions. Therefore, the dependence of the signal current on the organic species was investigated for the first time. Six diverse organic compounds (citric acid, glucose, acidic acid, sucrose, ascorbic acid, malonic acid) were investigated over a wide COD range (10 mg/L to 10,000

mg/L). They were used in single substance samples to avoid leveling out of the signal variation between different compounds. Statistical methods (Analysis of variance (ANOVA), Tuckey Test) and non-linear regression were used to further describe the concentration dependent signal variation. A model was created explaining the signal variation depending on the concentration using the underlying reaction mechanism showing that the signal variation depends on the ratio of the concentration of hydroxyl radicals and organic substances.Based on these results, possible improvements of the method were derived. Finally, a calibration of the method was conducted to find out in which working range and with which precision the method can be used.

Material And Methods

Chemicals and samples

All chemicals were used as provided and are listed in Table 2 including provider and purity.

Table 2: Used chemicals and specifications

Chemical	Purchased by	purity
Na_2SO_4	Merck	$\geq 99\%$
H_2SO_4	VWR	100%
D(+)-Glucose monohydrate	Carl Roth	$\geq 99,5\%$
Citric acid	VWR	100%
Acidic acid	Merck	100%
D(+)-Sucrose	Roth	$\geq 99,5\%$
L(+)-Ascorbic acid	Roth	$\geq 99\%$
Malonic acid	Sigma-Aldrich	99%

All solutions were prepared using freshly filtered ultrapure water ($\sigma \leq 0.055$ µS/cm, TOC < 5 ppb; GenPure Pro, Fisher Scientific). The electrolyte was prepared using 0.1 M Na_2SO_4 and 0.1 mM H_2SO_4.
 For the preparation of the COD samples, a 10,000 mg/L COD stock solution was prepared with the theoretical amount of organic species for the given COD. The calculation can be found in the Online Resources (S1). The organic species were dissolved in the electrolyte. All other COD sample solutions were prepared as dilutions from the stock solution with the electrolyte as solvent. The solutions containing organic substances were stored at 7° C before usage.

Experimental setup

The experimental setup consisted of a three-electrode measurement cell, a stirrer and a potentiostat. The exact geometry of the custom-made Teflon electrochemical cell (Volume 17 ml) (Fig. 1) can be found in the Online Resources (S2).

A commercial BDD electrode (5 μm diamond on Niobium, coated on both sides, 8 mm diameter, DiaCCon) was used as working electrode, an Ag/AgCl (3M NaCl) electrode (RE-1S Reference electrode (Ag/AgCl), ALS) as reference electrode and a platinum wire as counter electrode (Diameter 0,5 mm, Length 10 mm, Purity 99,95 %, Polymet). The geometry of the electrodes and their corresponding mounting can be found in Online Resources (S3). The electrochemical cell was connected to a potentiostat (Versastat 3F, Princeton Applied Research) for the electrochemical measurements. The solution was stirred using a stirrer (IKA Nanostar 7.5 digital stirrer) that was connected to a custom agitator shaft. The exact geometry of the agitator shaft can be found in the Online Resources (S4).

Electrochemical method

All experiments were done following the same procedure. Before starting the measurement, the electrochemical cell was filled with 12 ml of electrolyte. The stirrer was started with a stirring speed of 100 rpm. The amperometric measurement method was started. It consisted of an activation step with a potential of 3 V vs Ag/AgCl (3M NaCl) for 30 s. After that the potential was set to 2.4 V vs Ag/AgCl (3M NaCl) for 170 s. After a waiting period of 110 s 5 ml of the sample solution was added to the measurement cell. The current measured at 2.4 V vs Ag/AgCl (3M NaCl) was used for the calculation of the signal current. All experiments were executed at room temperature in a triple determination.

Data analysis

Calculation of the signal current

The current signal was calculated from the current-time curve using several data processing steps:

1. Smoothing of the data by using a moving average function
2. Calculating the average over the background current
3. Subtracting the average of the background current from the signal current
4. Calculating the average of the reduced signal current

The calculated average of the reduced signal current was used as the current signal. The data processing was done using a KNIME® workflow that can be found in the Online Resources (S5).

Statistical methods

The statistical calculations that were used in the data evaluation were done with OriginLab Pro. An ANOVA was used to evaluate if the signal current for different organic substances showed a significant difference. Subsequently, the Tuckey Test was used for those data sets that showed a significant difference between the groups. It determined which of the groups exactly showed the significant

difference, resulting in subgroups with similar mean values. All tests were done using a significance level of 0.05. The calibration curve was evaluated comparing the adjusted R^2 for different concentration ranges. The concentration range with the highest adjusted R^2 was chosen as the working range.

Results And Discussion

Dependence of the electrochemical oxidation at BDD electrodes on the type of organic compound

A necessary step in establishing the amperometric method for determining COD is to check whether there is a dependence of the current signal on the organic substances in the water sample. Since COD is a sum parameter, it must be possible to apply the method independently of all water constituents and thus the current signal must be independent of the organic substances. The compounds used here were selected from a wide range of chemicals used in COD sensor studies and derived substances. The final substances were selected from a larger group of chemicals by preliminary testing to achieve the greatest possible variation between signals. Measurements were made using sample solutions of each compound. In a real water sample, a mixture of different organic compounds and other species is present. This could lead to a compensation of the signal between different species which is avoided here by using single compound samples to simulate extreme situations where only readily or poorly oxidizable compounds are present. No non-organic water components were used to avoid overlapping effects on the signal current, since this study focuses only on the organics.

To determine the dependence of the electrochemical oxidation at BDD electrodes on the type of organic compounds, current-time curves were recorded for six distinct species (ascorbic acid, acetic acid, glucose, malonic acid, sucrose, citric acid) at four different COD values (10 mg/L, 100 mg/L, 1,000 mg/L, 10,000 mg/L) (Fig. 2).

Fig. 2 shows that not only the absolute value of the current signal increases as one would expect for a concentration-dependent sensing method but also the variation between the current values for the different organic species at different COD values. While the variation between the current signals is low at 10 mg/L and 100 mg/L, there is a visible deviation at 1,000 mg/L and even more at 10,000 mg/L.

The calculated current signal for the different organic species at different COD values is shown in Fig. 3.

The average current signal increases with increasing COD but so does the range of the current signals and the deviation between the signal for the different species.

A one-way ANOVA was performed to evaluate if the difference between the current signal of the distinct species is significant at different COD values. The detailed ANOVA calculations can be found in the Online Resources (S6).

The ANOVA calculations show that the difference between the average signal current is not significant for 10 mg/L COD (p = 0.05). For all the other COD values there is a significant difference between the

current signals.

Subsequently a Tukey Test was conducted for the current signals at 100 mg/L, 1,000 mg/L and 10,000 mg/L. While the ANOVA only determines if there is a significant difference between the compared groups (in this case the different organic compounds), with the Tukey Test the groups that show a significant difference can be found at the stated significance level (p = 0.05).

The resulting groups of organic compounds with no significant difference of the current value are listed in Table 3.

Table 3: Groups with significantly different signal currents resulting from the Tuckey Test with a significance level of 0.05.

COD	Resulting groups			
10 mg/L	Ascorbic Acid, Malonic Acid, Glucose, Sucrose, Acetic Acid, Citric Acid			
100 mg/L	Ascorbic Acid, Malonic Acid, Glucose, Sucrose, Acetic Acid	Glucose, Sucrose, Acetic Acid, Citric Acid		
1,000 mg/L	Glucose	Sucrose, Ascorbic Acid	Citric Acid, Malonic Acid	Malonic Acid, Acetic Acid
10,000 mg/L	Ascorbic Acid	Sucrose, Glucose	Citric Acid	Malonic Acid, Acetic Acid

For the 100 mg/L COD samples two groups can be built that either contain all the compounds but citric acid or all the compounds but malonic acid and ascorbic acid. For 1,000 mg/L COD and 10,000 mg/L COD the comparison of the groups showed that the higher oxidized compounds that only contain carboxylic groups (citric acid, malonic acid, acetic acid) were clustered together as are the lower oxidized compounds that also contain other functional groups (ascorbic acid, glucose, sucrose).

The data shows that the current signal is highly dependent on the organic species and the difference between the current signals increases with increasing COD, meaning that the dependency can be described by different functions for the different organic substances. The variation between different organics is significant for all COD values above 100 mg/L. The Tukey test was used to divide the data into groups containing the compounds with significantly different current signals. The groups can be used to draw a preliminary conclusion on whether the chemical structure of the organic compound influences the current signal, although this is very limited due to the small sample size. For 100 mg/L, only citric acid shows a lower current signal, which could be explained by the fact that it is already highly oxidized. In contrast, malonic acid and ascorbic acid show a higher signal current compared to the other compounds. They have quite different structures, so no statement can be made at this point as to why they differ so much. For 1,000 mg/L and 10,000 mg/L it is not possible to find a correlation between the structure and the average current since the compounds used are quite different. It is noteworthy that the average current for acetic acid, malonic acid, and citric acid does not increase significantly from 1,000 mg/L COD to 10,000 mg/L COD. This could mean that the electrode is already saturated at 1,000 mg/L COD.

Concentration dependent current signal from the electrochemical oxidation of different organic species at BDD electrodes

To investigate the course of the current signal over a wide COD range it was recorded depending on the COD for different organic compounds (Fig. 4).

Fig. 4 shows that the course of the curve is dependent on the organic species, and that it is not linear over the whole COD range investigated here and can be fitted by a non-linear equation that can be derived from the mechanism:

$$y = a(k_2 x \cdot k_1)/(k_2 x + k_1) \qquad (1)$$

a, k_1 and k_2 were calculated from the fit data (Table 4).

Table 4: Fit coefficients from the nonlinear fit of the COD-dependent signal current.

Organic compound	a	k_1	k_2
Acetic acid	0.0025	0.089	2.36×10^{-4}
Glucose	0.0058	0.088	9.74×10^{-5}
Malonic acid	0.0062	0.027	2.49×10^{-5}
Ascorbic acid	0.0027	0.125	3.55×10^{-4}
Sucrose	0.0058	0.064	1.97×10^{-4}
Citric acid	0.0055	0.048	1.46×10^{-4}

While a and k_1 are in the same order of magnitude for all organic compounds, k_2 varies over different orders of magnitudes.

The data from Fig. 4 can also be fitted linearly. Therefore, it is divided into three parts (Fig. 5).

It is known that the oxidation of organic compounds at BDD electrodes follows a two-step mechanism (Martinez-Huitle & Ferro, 2006):

$$BDD() + H_2O \leftrightharpoons BDD(OH) + H^+ + e^- \qquad (2)$$

$$BDD(OH) + R \rightarrow BDD() + CO_2 + H_2O \qquad (3)$$
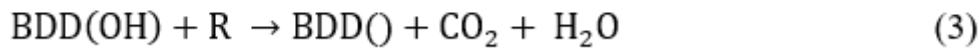
In the first step, hydroxyl radicals are formed from water at the BDD electrode (Eqn. 2), which then react with an organic compound in the second step (Eqn. 3). When the organic compound is completely oxidized, the reaction products are CO_2 and water. From this mechanism, an equation describing the concentration dependence of the current can be derived under various assumptions (Popović & Johnson, 1998):

$$I_{tot} = 2zF\Gamma(k_2 c_R \cdot k_1)/(k_2 c_R + k_1) \qquad (4)$$

Here, k_1 is the reaction constant for the forward reaction of Eqn. 2, while k_2 is the reaction constant of Eqn. 3. c_R is the concentration of the organic species, z is the number of electrons transferred, Γ is the coverage of the electrode, and F is the Faraday constant. z and Γ are assumed to be constant during the process.

Eqn. 4 was simplified to Eqn. 1, which was used to fit the data in Fig. 4.

$$y = a(k_2 x \cdot k_1)/(k_2 x + k_1) \qquad (1)$$

The good agreement of the data with the fit is an indication that the reaction taking place can be well described by the mechanism. However, the fit only works for the data up to 2,000 mg/L. This could be due to the assumptions made in deriving the equation, which do not work for higher concentrations. One of the assumptions is the steady state for the formation of the hydroxyl radical. At high concentrations of organic compounds, the reaction of hydroxyl radicals with organic compounds is so fast that they cannot be replaced immediately by new ones. This could be the reason why the equation does not work at higher concentrations.

The fitting parameters a, k_1, and k_2 describe the prefactor and kinetic constants of the reaction, respectively. a and k_1 should be similar for all organic compounds because they describe the formation of hydroxyl radicals on the BDD surface, which is independent of the organic compound. As expected, they are of the same order of magnitude for all organic compounds. k_2 describes the reaction between the hydroxyl radical and the organic compound. This reaction is selective and k_2 varies between different orders of magnitude. The linear fit of the data shows different linear ranges. Each of them is dominated by a different reaction:

Small concentrations: $k_1 \gg k_2 c_R$

The determination of COD is independent of the type of organic species. The excess of produced hydroxyl radicals at the electrode over the organic species is so high that every molecule reaching the electrode is directly oxidized. The reaction rate depends only on the total concentration of the organic species since this determines the rate of hydroxyl radical production. It is possible to determine the COD independently of the species contained in this range.

Medium concentrations: $k_1 \approx k_2 c_R$

The total reaction constant is affected by both processes: the production of the hydroxyl radical and the reaction of the organic species with the hydroxyl radical. Since the rate of hydroxyl radical production is similar to the rate of reaction with the organic species and there is no excess of either process, the reaction is selective towards different organic compounds and the different species show different current signals. It is not possible to determine the COD independently of the substances contained in this range, but it can be determined if a calibration for the specific composition is available.

High concentrations: $k_1 \ll k_2 c_R$

The concentration of the organic species is so high that any hydroxyl radical generated is immediately consumed, and the generation of hydroxyl radicals becomes the rate-determining step. The current is independent of the concentration of organic species and does not increase with the amount of organic species present because the electrode is already saturated. It is not possible to determine the COD in this range.

Fig. 6 shows the processes taking place dependent on the concentration range.

While the mechanism used to describe the reaction is a good and simple approach for some general conclusions, several simplifications have been made. Important factors not considered in this simplification are the formation of radicals other than the hydroxyl radical and the incomplete oxidation of the organic compounds.

Since different radicals have different oxidation potentials and have different lifetimes and mobility within the cell, they can affect the selectivity of the reaction (Farhat et al., 2015) (Lee & Von Gunten, 2010). A better knowledge of the type and amount of radicals formed could contribute to the understanding of the reactions taking place and could be used to influence them. Thus, the dependence of the current signal on the organic species could be reduced.

Incomplete oxidation of organic compounds could also lead to underestimation of COD. Theoretically, complete oxidation of the organic compounds to CO_2 is expected in the mechanism, which is a prerequisite for the correct determination of COD. COD can only be correctly determined if all organic compounds and their intermediates are included in the reaction. If the final product for some compounds is not CO_2, the COD will be underestimated (Mascia et al., 2007).

The data show that oxidation of some compounds is easier than others. As shown in the literature, the relationship between the structure of a compound and its reaction can be modeled (Jiang et al., 2017). This would help to determine what types of wastewater can be determined using the method described. Knowing the relationship between the structure and the signal current can also help optimize the method and could be used to predict the scope of the method.

In summary, the results of this section show that the reaction occurring in the sensor can be described by the mechanism used in the literature, although there are limitations due to the simplifications used. The organic compounds are oxidized by the hydroxyl radicals electrochemically formed on the BDD surface. The change in signal current depends on the ratio between the organic compounds and the hydroxyl radicals. The method only works independently of the organic species if the concentration of the organic compounds is much lower than the amount of hydroxyl radicals formed.

Determination of the working range for the determination of COD independently of the organic species

To determine the working range in which the determination of the COD is possible independently of the organic species, a calibration curve was created between 0 and 400 mg/L COD using the mean and

standard deviation of the signal current from the individual measurements of the organic species (Fig. 7).

The calibration curve shows two linear working ranges for 25 - 150 mg/L and for 200 - 400 mg/L. The standard deviation for all organic compounds becomes larger at higher COD values because the dependence of the current signal on the type of organic species increases. Therefore, the higher linear working range for 200 - 400 mg/L is not included in the linear working range for compound-independent determination of the COD.

The precision of the calibration was calculated from the standard deviation of the measurements for all organic species. It was calculated by   with the precision p, the standard derivation of the current signal s_y and the slope of the calibration curve m. This resulted in a precision of 30 %.

Since the variation of the current signal for different organic species depends mainly on the ratio between the amount of hydroxyl radicals and organic compounds, one way to increase the linear range of the method is to increase the amount of hydroxyl radicals present while keeping the COD of the sample the same. In the context of general process optimization, this can be done by increasing the surface area of the electrode without increasing the volume of the measuring cell and the sample volume.

This can be done, for example, by using a porous working electrode so that there is a larger active surface area on the same geometric area. Since the hydroxyl radicals are only on the electrode surface, more effective mixing would result in a higher ratio of hydroxyl radicals to organic compounds in the bulk medium. This could be achieved by using an ultrasonic mixer instead of a mechanical stirrer.

Similarly, it is possible to reduce the amount of organic compounds while maintaining the same amount of hydroxyl radicals. Therefore, a thin film cell with a minimal amount of sample would be a possible approach.

In summary, COD can be determined with a precision of 30% in the linear range of 25 - 150 mg/L, independent of the organic species.

Conclusion

In this paper, the dependence of the current signal on the organic species in the amperometric determination of COD is described for the first time. The variation of the current signal depends on the COD quantity and increases with increasing COD. While COD can be determined independently of the organic species up to about 150 mg/L, the dependence of the current signal on the organic species makes it impossible to determine COD above 150 mg/L independently of the organic species.

The dependence on the organic species can be explained by the mechanism of the reaction, which consists of two reactions: the formation of hydroxyl radicals on the BDD surface and the reaction of the hydroxyl radicals with the organic compounds. Depending on the amount of organic compounds in the measurement cell, one of the two reactions dominates. At low concentrations, there is an excess of

hydroxyl radicals, so that any organic compound can be oxidized unselectively. At intermediate concentrations, the amount of hydroxyl radicals is similar to the amount of organic compounds, so the reaction is selective. At high concentrations, there is an excess of organic compounds so that the electrode is saturated and the current does not increase with increasing concentration. To increase the working range in which all organic compounds can be oxidized non-selectively, the ratio between the electrode surface area and the COD must be increased.

To determine a compound-independent linear working range, the calibration curve was constructed from the individual measurements of single-substance samples of various organic compounds. A linear working range of 25 mg/L - 150 mg/L can be achieved with a low detection limit of 25 mg/L and a precision of 30%.

Abbreviations

COD, Chemical oxygen demand; BDD, Boron-doped diamond; ANOVA, Analysis of variance; AOP, advanced oxidation process

Statements And Declarations

The authors declare the following financial interests which may be considered as potential competing interests: Patrick Braeutigam, Samira Lambertz and Michael Stelter have patent #20848951.8 - 1001 pending to Friedrich-Schiller-Universität Jena.

Acknowledgments

Author Contribution statement

Samira Lambertz: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review& editing, Visualization, Project administration.

Marcus Franke: Writing – review & editing.

Michael Stelter: Resources, Supervision.

Patrick Braeutigam: Conceptualization, Resources, Supervision, Writing – review & editing

Funding statement

Data Availability statement

The data required to reproduce the above findings are available upon request.

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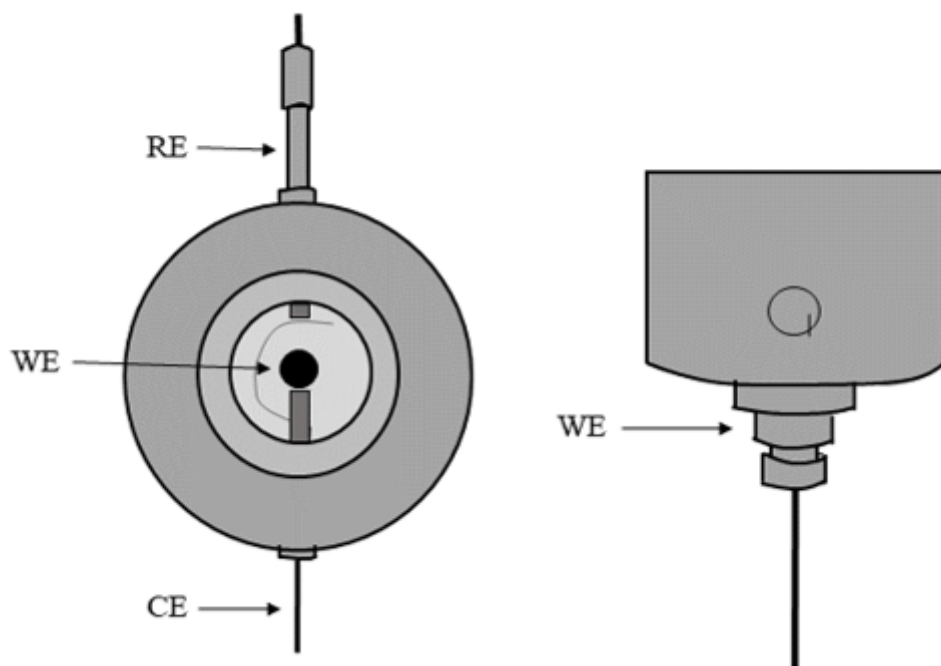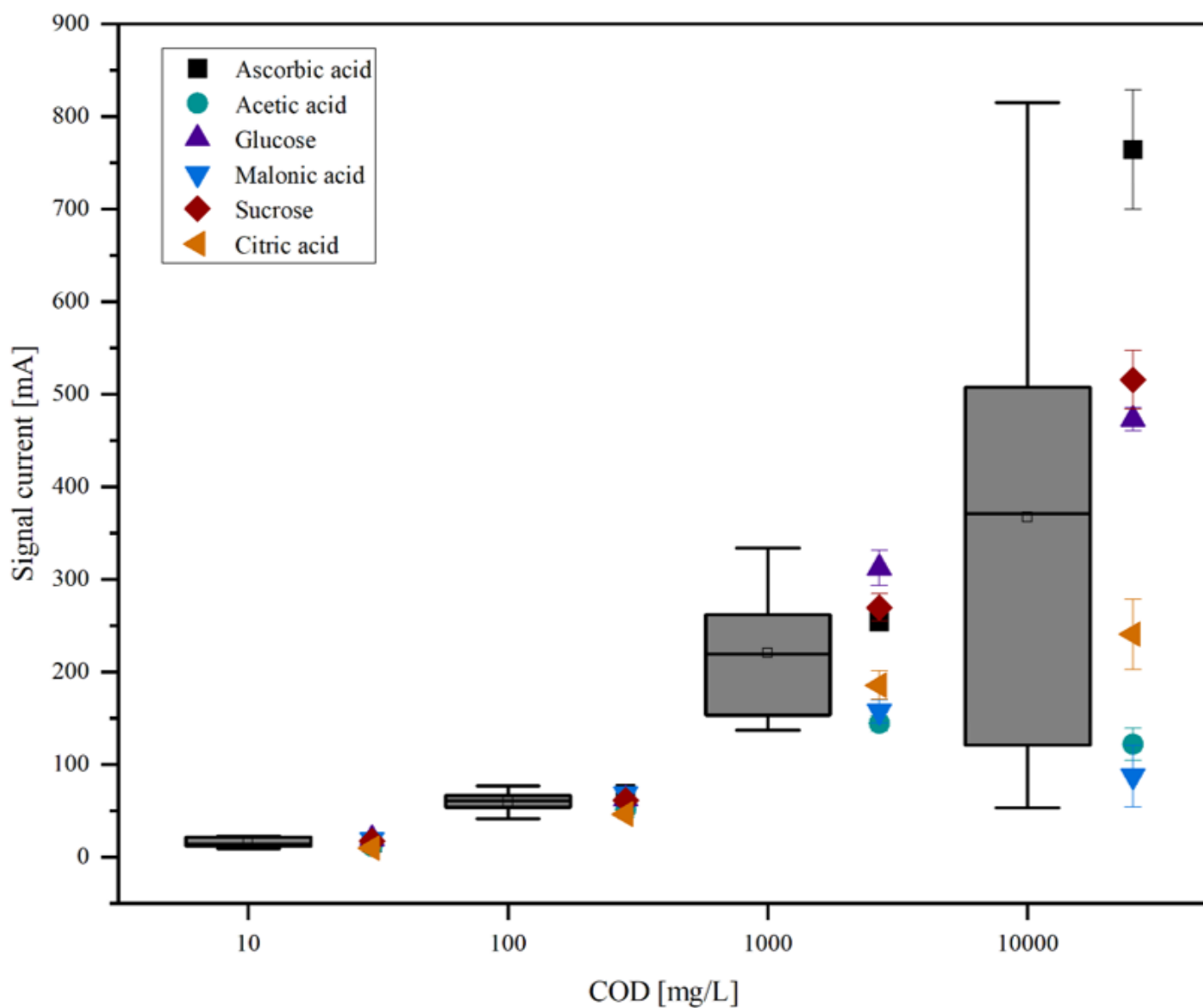
Figures

Figure 1

Three-electrode measurement cell containing working electrode (WE), reference electrode (RE) and counter electrode (CE)
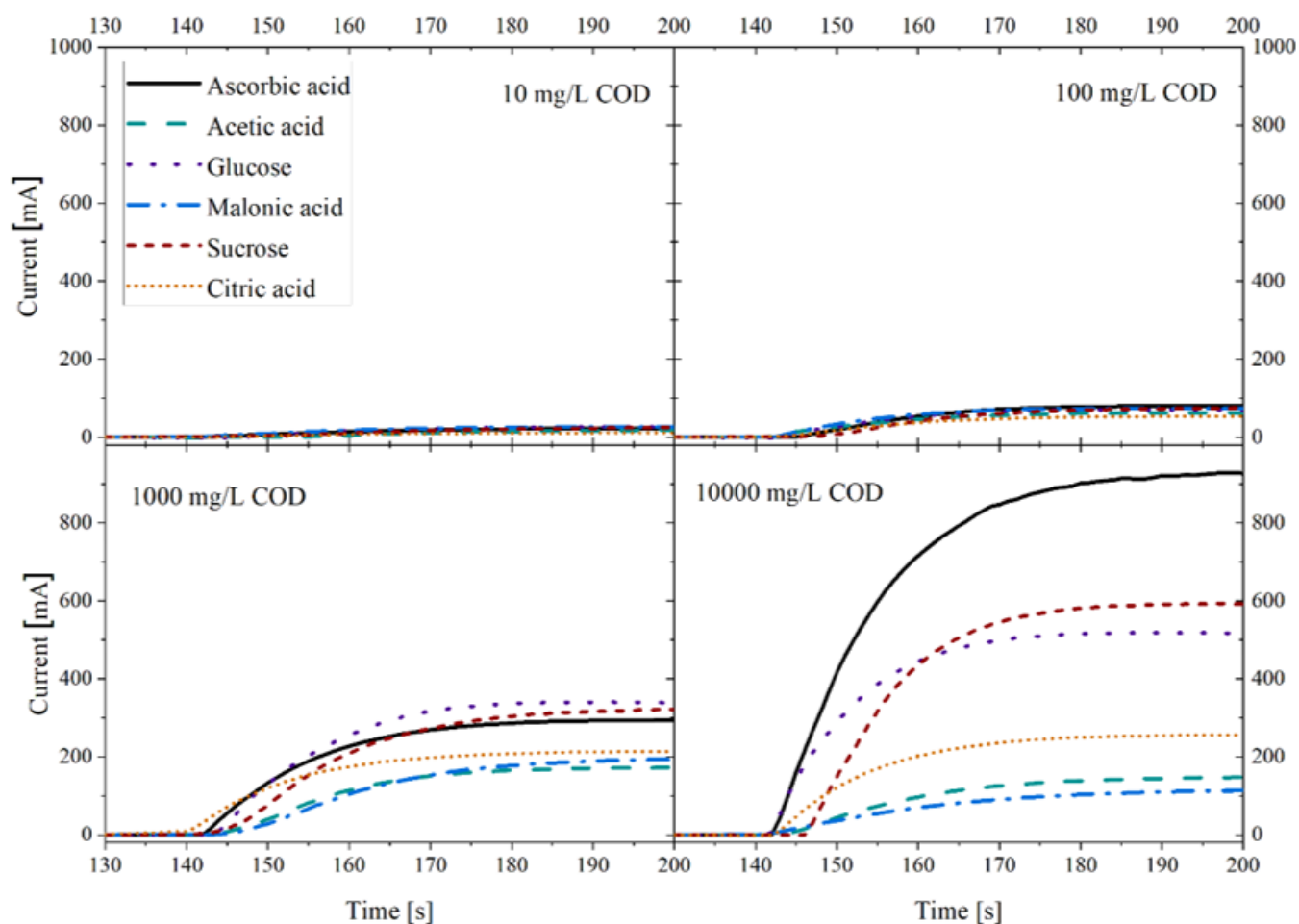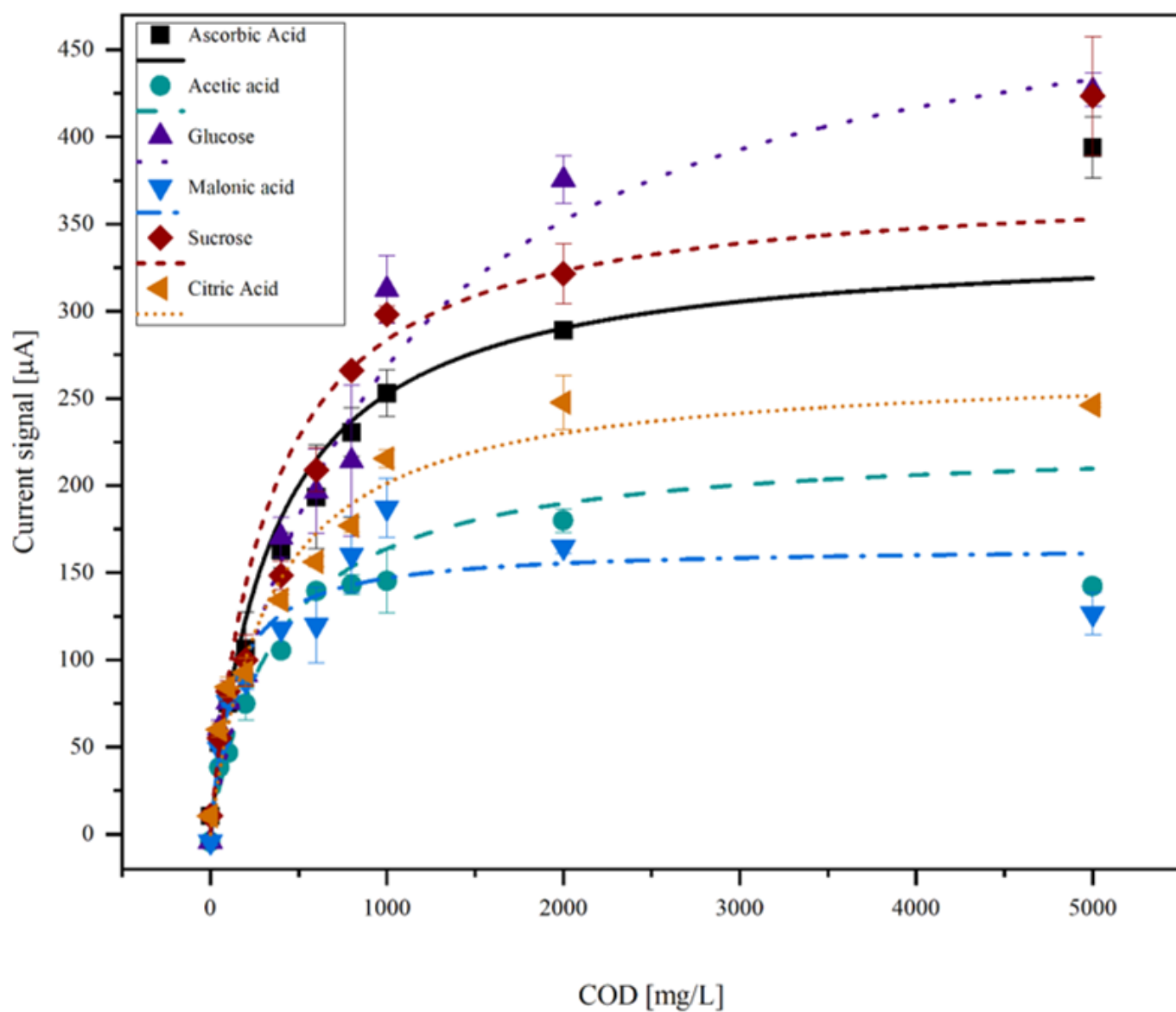
Figure 2

Current-time curves for the described electrochemical method at different CODs (10 mg/L, 100 mg/L, 1.000 mg/L, 10.000 mg/L) and for different organic compounds (ascorbic acid, acetic acid, glucose, malonic acid, sucrose, citric acid)
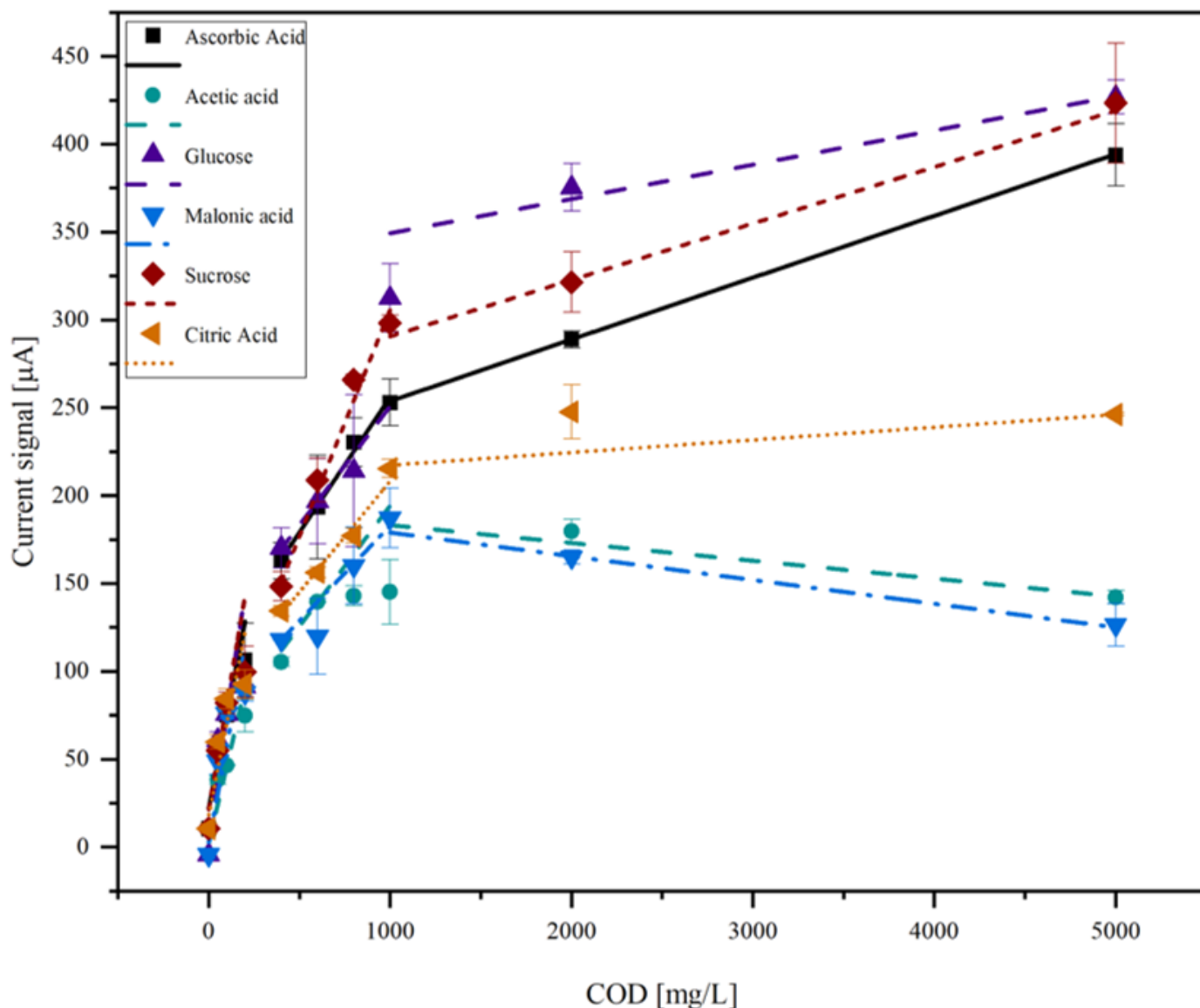
Figure 3

Signal currents for several organic species (ascorbic acid, acetic acid, glucose, malonic acid, sucrose, citric acid) at different COD values (10 mg/L, 100 mg/L, 1,000 mg/L, 10,000 mg/L). The signal currents are shown as a boxplot and as individual measurements

Figure 4

COD-dependency of the current signal for different organic species (acetic acid, glucose, malonic acid, ascorbic acid, sucrose, citric acid) in the COD range from 0 mg/L to 5,000 mg/L. The data was fitted using the following equation: $y = (ak_1k_2x)/(k_1+k_2x)$, which can be derived from the reaction mechanism

Figure 5

COD-dependency of the current signal for different organic species (acetic acid, glucose, malonic acid, ascorbic acid, sucrose, citric acid) in the COD range from 0 mg/L to 5,000 mg/L. The data was fitted linearly

In the first area between 0 and 100 mg/L COD, the linear curves for all organic compounds overlap. In the second area between 100 and 1,000 mg/L COD the curves drift apart and show a significant dependency on the organic species. In the area between 1,000 and 10,000 mg/L the difference between different organic species becomes even bigger.
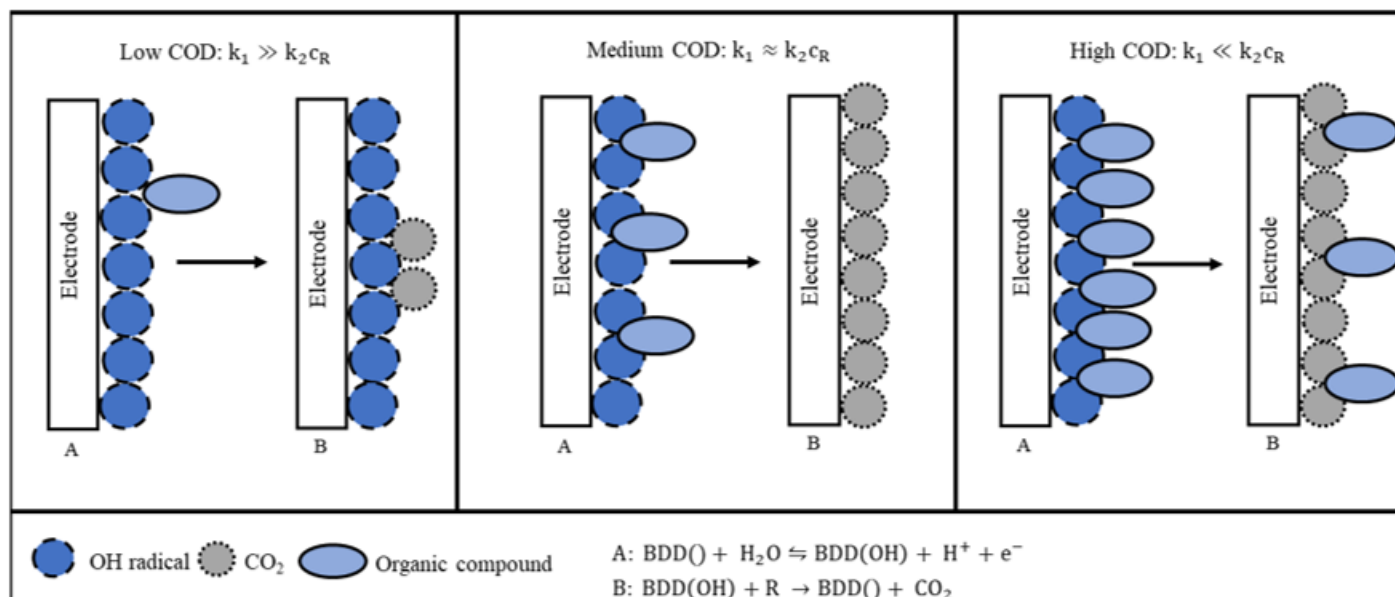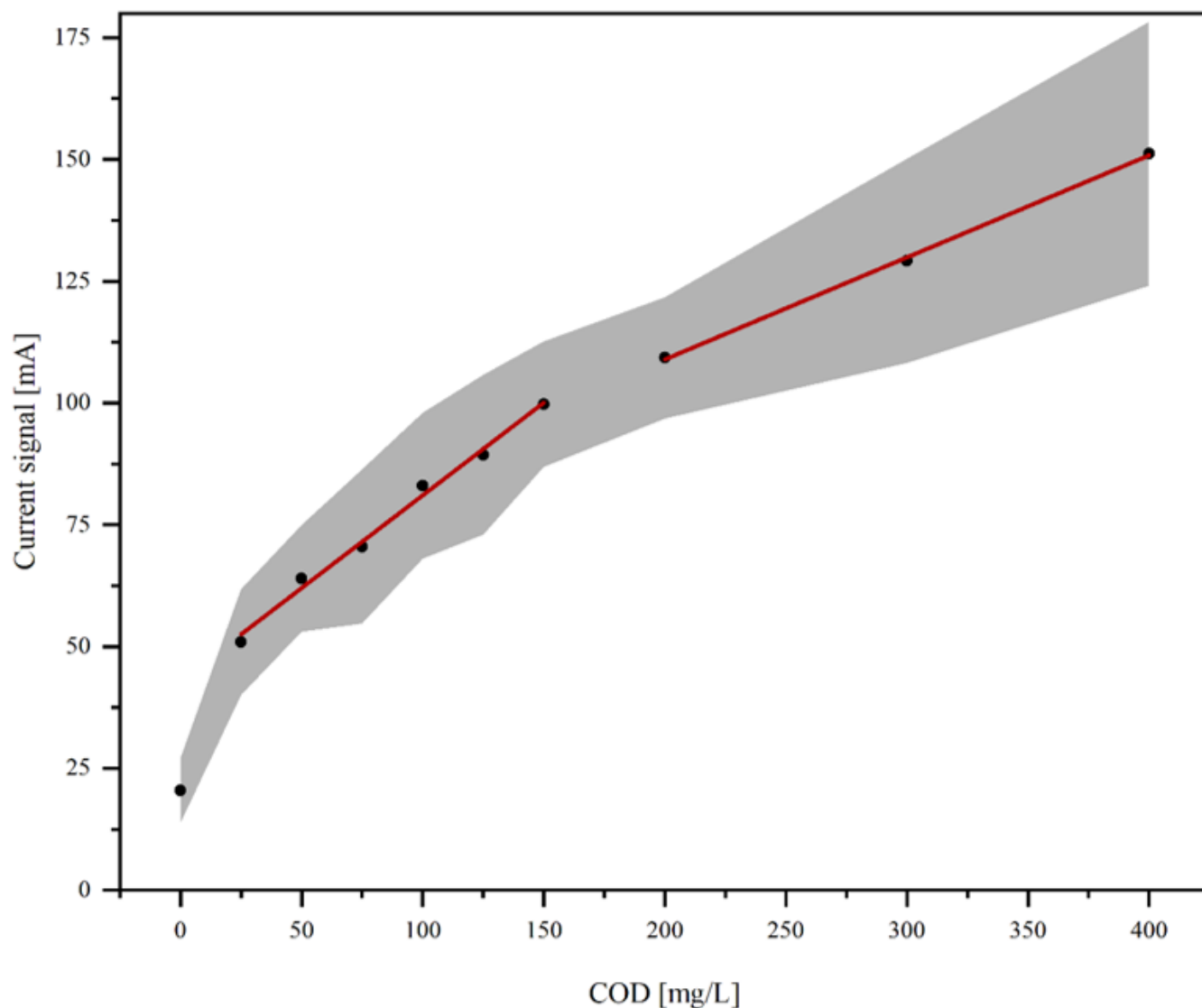
Figure 6

Processes at the electrode dependent on the amount of organic species in the wastewater sample for a low COD, medium COD and high COD. The electrode is shown after the formation of hydroxyl radicals and after the combustion of organic compounds.

Figure 7

Calibration curve for the determination of COD with the electrochemical method. The calibration curve was built using the average current of the individual measurements of all used organic species (black dots). The grey area shows the standard deviation of the individual measurements of all used organic species

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