

Article

The Electrochemical Reaction Kinetics during Synthetic Wastewater Treatment Using a Reactor with Boron-Doped Diamond Anode and Gas Diffusion Cathode

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Abstract: A system of boron-doped diamond (BDD) anode combined with a gas diffusion electrode (GDE) as a cathode is an attractive kind of electrolysis system to treat wastewater to remove organic pollutants. Depending on the operating parameters and water matrix, the kinetics of the electrochemical reaction must be defined to calculate the reaction rate constant, which enables designing the treatment reactor in a continuous process. In this work, synthetic wastewater simulating the vacuum toilet sewage on trains was treated via a BDD-GDE reactor, where the kinetics was presented as the abatement of chemical oxygen demand (COD) over time. By investigating three different initial COD concentrations ($C_{0,1} \approx 2 \times C_{0,2} \approx 4 \times C_{0,3}$), the kinetics was presented and the observed reaction rate constant $k_{obs.}$ was derived at different current densities (20, 50, 100 mA/cm²). Accordingly, a mathematical model has derived $k_{obs.}$ as a function of the cell potential E_{cell} . Ranging from 1×10^{-5} to $7.4 \times 10^{-5} \text{ s}^{-1}$, the $k_{obs.}$ is readily calculated when E_{cell} varies in a range of 2.5–21 V. Furthermore, it was experimentally stated that the highest economic removal of COD was achieved at 20 mA/cm² demanding the lowest specific charge (~7 Ah/g_{COD}) and acquiring the highest current efficiency (up to ~48%).

Keywords: kinetics; electrochemical reaction; rate constant; electrolysis system; boron-doped diamond electrode; gas diffusion electrode



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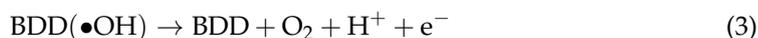
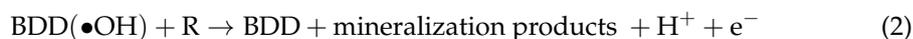
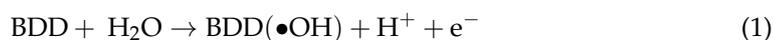
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1. Introduction

Studying the kinetics of the electrochemical mineralization of organic pollutants in wastewater is one of the most important research aspects helping to define the reaction rate constant (k), which is very essential in the matter of reactor design and optimization of the operating parameters. The residence time in the reactor can be readily defined if the value of k is known. Accordingly, the reactor volume can be obtained through the flowrate of the treated wastewater achieving a certain removal efficiency [1]. This arrangement is very beneficial for discharged wastewater on public transport services such as trains or cruise ships, where the wastewater properties change significantly according to the passenger numbers and travel time during the day.

Using boron-doped diamond electrodes (BDD) as an anode in the electrolysis cells to mineralize organic pollutants has drawn more attention in the last decades [2–8] due to the generation of hydroxyl radicals ($\bullet\text{OH}$), which completely degrades water organics to CO_2 with zero-discharge and without the formation of toxic by-products. Those distinctive features are missing in other wastewater treatment methods, such as ozone, that forms undesired by-products [9] or biological treatment processes that produce sludge in considerable amounts. $\bullet\text{OH}$ generated at the BDD surface mineralizes organics (R) in the

electrolyte, according to reaction Equations (1) and (2), while the energy-wasting undesired reaction (3) leads to oxygen evolution due to mass transport limitations [10].



A combination of BDD as anode with a gas diffusion electrode (GDE) in the same electrolysis cell showed higher effectivity to remove organic pollutants from wastewater, as more reactive species are released at low energy consumption [11,12]. These oxygen-reactive species contribute to mineralizing organics in the electrolyte solution, as well as $\bullet\text{OH}$ released at the BDD surface [13,14]. Produced by reduction of oxygen at GDE according to Equation (4), H_2O_2 decomposes by $\bullet\text{OH}$ generating more oxygen reactive species such as $\bullet\text{O}_2\text{H}$, $\bullet\text{O}_2$, $\bullet\text{OH}$, $^1\text{O}_2$ [15–17].



The electrochemical mineralization of organics relates to the operating parameters in the electrolysis cell [18]. For example, the physico-chemical properties of the electrolyte [19] can increase or diminish the mineralization efficiency, which is affected by other effectors such as conductivity [20] and type of organics [21]. Current density and cell potential also play a very important role to determine the efficiency of the electrolysis system. Regarding the other operating parameters, increasing the current density can promote the mineralization rate and consequently the efficiency, as the $\bullet\text{OH}$ generation rate will be effectively accelerated [22]; however, it depends on the types of organics aimed to be degraded [23]. The application of very high current density leads to the formation of side products, such as oxygen, through the reaction of oxygen evolution (Equation (3)), decreasing the current efficiency, because reactive species are wasted without promoting the mineralization of the organic [24]. Treating the vacuum toilet sewage generated on trains or cruise ships is an environmental matter which has gained more attention from many suppliers during the last two decades [25]. This sewage is a kind of low-diluted blackwater with high organics concentration ($\text{COD} = 3350\text{--}25,800 \text{ mg/L}$ and $\text{BOD}_5 = 3750\text{--}7424 \text{ mg/L}$), according to Wasielewski et al., 2016 [26]. Different treatment methods have been investigated to deal with such sewage, including a continuously stirred tank reactor (CSTR), an up-flow anaerobic sludge blanket (UASB), and a membrane bioreactor (MBR), but they need much more space than available on the mentioned transition means [27]. Place shortage and production of sludge has forced industry to look for other alternatives. Electrolysis systems can be an optimal choice due to their small occupation size and zero-discharge property [15]. Other methods to treat vacuum toilet sewage were investigated by Haupt et al., 2019 [11] to compare the removal effectivity of organics and the related energy demand. For this goal, Haupt et al. investigated ozonation, peroxone, and BDD-GDE reactor as treatment methods.

The purpose of this study is to investigate the treatment efficiency of organic pollutants, measured as COD and contained in synthetic wastewater, using an electrochemical BDD-GDE reactor. Different values of current density and initial COD concentration were tested. Experimental data were used to describe the kinetics of the electrochemical oxidation depending on COD degradation under the dominant operating conditions, aiming to calculate the related values of the rate constant. A mathematical model to determine the rate constant depending on the desired cell potential value was also proposed.

2. Materials and Methods

The investigated synthetic wastewater (SWW) used to simulate the real vacuum toilet wastewater was developed in cooperation with a train toilet operator [11]. The efficiency and the kinetics of the electrochemical treatment were presented through COD elimination

over the experiment time. All conditions, including pH and temperature, were kept the same as that of the vacuum toilet wastewater on trains, to meet the real treatment conditions. The used SWW included different organic sources where glucose was the main organic source, contributing to 96% of the whole COD concentration. To test the effect of the initial COD concentration ($COD_{int.}$) of SWW on the electrochemical mineralization of organics, the original COD concentration of SWW ($C_{0,1}$ of $\sim 4410 \pm 17$ mg/L) was diluted to $C_{0,2} = 2267 \pm 99$ mg/L and $C_{0,3} = 1175 \pm 13$ mg/L, whereby the electrolyte conductivity σ was reduced from $\sigma_{0,1} = 8.58 \pm 0.24$ to $\sigma_{0,2} = 4.62 \pm 0.12$, and $\sigma_{0,3} = 2.49 \pm 0.06$ mS/cm, respectively.

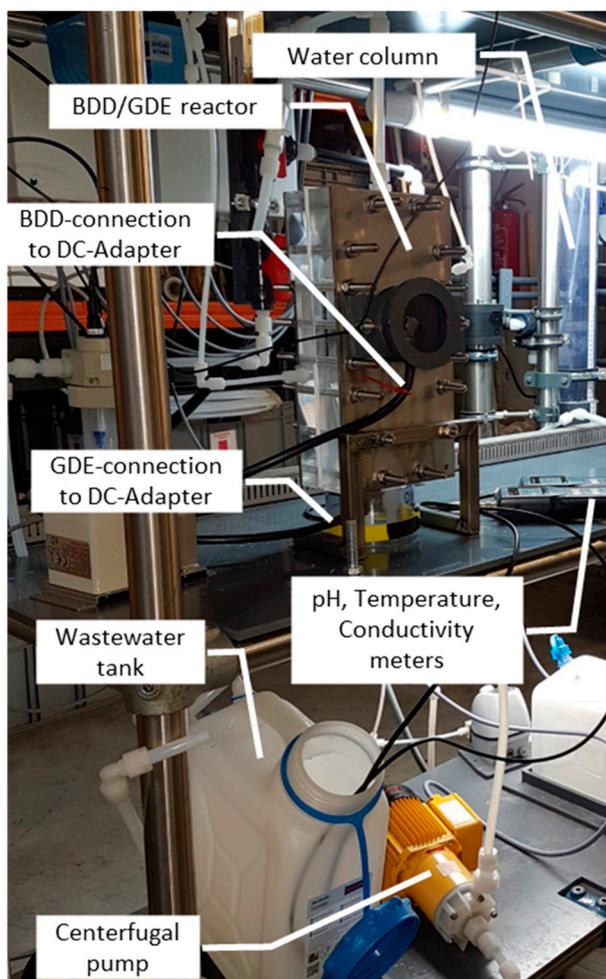
2.1. Experimental Set-Up

All experiments were conducted using the experimental setup shown in Figure 1a. The SWW as feed was stored in a tank of 3 L. A centrifugal pump (Schmitt Kreiselpumpen GmbH & Co. KG, Ettlingen, Germany) was used to supply the reactor at a flow velocity of 0.23 m/s, from the bottom to the top. The BDD-GDE reactor had flow channels to ensure homogeneous electrolyte flow in the reaction zone (10 cm \times 10 cm). The flow rate profile between both electrodes at the highest flow velocity (0.23 m/s) in the current BDD-GDE reactor was simulated using the computational fluid dynamics (CFD) software and presented in Figure 1b. Air, containing oxygen, needed for the GDE to generate H_2O_2 , was provided through a back compartment behind the GDE and its pressure was adjusted to approximately 35 mbar via the following water column. The current was supplied in three different densities 20, 50, and 100 mA/cm² by a TDK Lambda power supply (Gen 20–76; Tokyo, Japan), which also enabled controlling both voltage and current applied at the electrolysis reactor. Each current density was investigated at the three different concentrations ($C_{0,1}$, $C_{0,2}$, and $C_{0,3}$) for 4 h, while COD, pH, temperature, voltage, and current were measured over the time of the experiment. A pH-, temperature- and conductivity meter (Windaus-Labortechnik GmbH & Co. KG, Clausthal-Zellerfeld, Germany) was used for these measurements.

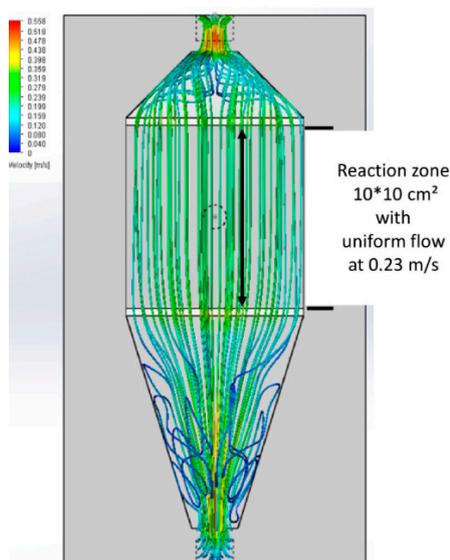
The electrolysis reactor had a combination of BDD and GDE without a separator (Figure 1c). In this reactor design, a BDD anode (type DIA-CHEM[®] by CONDIAS) was coupled with a carbon-based GDE (Printex L6 on Ag-plated Ni mesh; Covestro AG, Leverkusen, Germany). The printex catalyst was chosen for the GDE due to its high yield of H_2O_2 in acid and alkaline environments in comparison to other pure carbon catalysts. Detailed information on electrode characterization and manufacturing method was published by [12]. A PTFE-frame was located between both electrodes to seal the electrochemical reaction zone and keep a 3 mm distance.

2.2. Analysis and Calculations

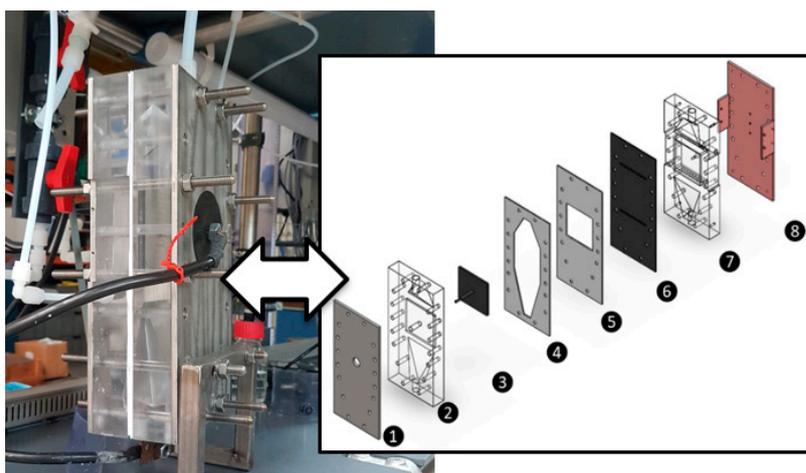
$NaHCO_3$ (Th. Geyer GmbH & Co. KG, Renningen, Germany) was used to destroy H_2O_2 generated during the process and existed in wastewater samples to avoid overestimation in the COD test [28,29]. The samples were prepared at the ratio 22.5 mol- $NaHCO_3$ /mol- H_2O_2 and were shaken at ambient temperature for 24 h by shaking the device (Edmund Bühler GmbH, Bodelshausen, Germany) before COD tests were carried out [30]. A rapid determination of H_2O_2 was conducted by test strips (Macherey-Nagel, Dürren, Germany) to ensure the total decomposition of H_2O_2 in wastewater samples before the COD test. COD was measured by cuvette tests (Macherey-Nagel, Dürren, Germany) and spectrophotometry (Nanoclor UV/VIS; Macherey-Nagel, Dürren, Germany) according to DIN 38 409-H41-1 [31].



(a)



(b)



(c)

Figure 1. (a) Experimental set-up with BDD-GDE reactor to treat synthetic wastewater (SWW); (b) CFD-flow schema at the highest flow velocity (0.23 m/s); (c) BDD-GDE reactor: (1) front metal plate; (2) anode half-shell; (3) boron-doped diamond (BDD) electrode; (4) thin PTFE frame of anode side; (5) thick PTFE frame of cathode side; (6) gas diffusion electrode (GDE); (7) cathode half-shell; (8) front metal plate of cathode side.

The organic mineralization effectivity of such an electrolysis system can be evaluated through the organics removal and current efficiency, in addition to the charge demand needed to mineralize a specific organic quantity. The specific charge demand (SCD) of the electrochemical mineralization can be calculated via Equation (5).

$$\text{SCD} = \frac{j \cdot A \cdot t}{V \cdot (\text{COD}_0 - \text{COD}_t)} \quad (5)$$

where SCD is the specific charge demand ($\text{Ah}/\text{g}_{\text{COD}}$), j is current density (mA/cm^2), A is the active area of electrodes (cm^2), t is experiment time (h), V is wastewater volume (L). COD_0 and COD are the chemical oxygen demand at $t = 0$ and the time point t , respectively. Both concentrations are given in g/L .

Current efficiency (CE), specified for the amount of electrochemically removed COD, can be obtained from the equation used by Panizza et al., 2019 [32], expressed in Equation (6).

$$\text{CE} = F \cdot V \frac{(\text{COD}_0 - \text{COD}_t)}{8 \cdot j \cdot A \cdot t} \quad (6)$$

where F is Faraday's constant ($96,485 \text{ C mol}^{-1}$).

Conducting the oxidation process under certain operating parameters and presenting the experimental data as $\ln \text{COD}_0 / \text{COD}_t$ proportioning linearly to the experiment time, the rate constant can be obtained as a slope of the linear plot of that direct proportionality. Accordingly, a mathematical model can be built on how the rate constant changes depending on the applied cell operation parameters [10]. Such a model can help to estimate the residence time in the reactor for a certain electrolyte at desired settings to achieve a certain removal efficiency, especially for wastewater with changed properties, such as that on public transport services (i.e., on trains). Accordingly, the reactor volume can be calculated beforehand to meet the maximal flow rate of the discharged wastewater.

On whole, each one of the operating parameters relatively contributes to controlling the electrochemical mineralization kinetics of the organics, which consequently determines the treatment efficiency. The kinetics can be experimentally investigated and graphically presented as COD degradation during the treatment time. Depending on what Schmidt, 2003 stated [33], most electrochemical reactions usually take place as a first-order reaction, which has the following mathematical form [34]:

$$k \cdot t = \ln \frac{\text{COD}_0}{\text{COD}_t} \quad (7)$$

where k is the rate constant (s^{-1}).

2.3. Results and Discussion

In the investigated BDD-GDE reactor, the effect of the different current densities (20, 50, and 100 mA/cm^2) at three different COD_{int} . ($C_{0,1} > C_{0,2} > C_{0,3}$) on the organics mineralization rate and specific charge demand was investigated. At all current densities, and after 4 h treatment, lower initial concentration showed a lower total removed COD (TR-COD) and consequently higher SCD, as shown in Figure 2a,b, respectively. Although $C_{0,1}$ is approx. 4 times higher than $C_{0,3}$, the TR-COD at $C_{0,1}$ was only 21–34% higher than that at $C_{0,3}$ at all current densities. Taking the TR-COD value (380 mg/L) at 20 mA/cm^2 and $C_{0,1}$ as a set-point, this value of TR-COD increased by 84% and 163% by the rising of the current density to 50 mA/cm^2 and 100 mA/cm^2 , respectively. For the other two concentrations, TR-COD also jumped 120% and 210% at $C_{0,2}$ and 74% and 186% at $C_{0,3}$ as the current density reached 50 and 100 mA/cm^2 , respectively.

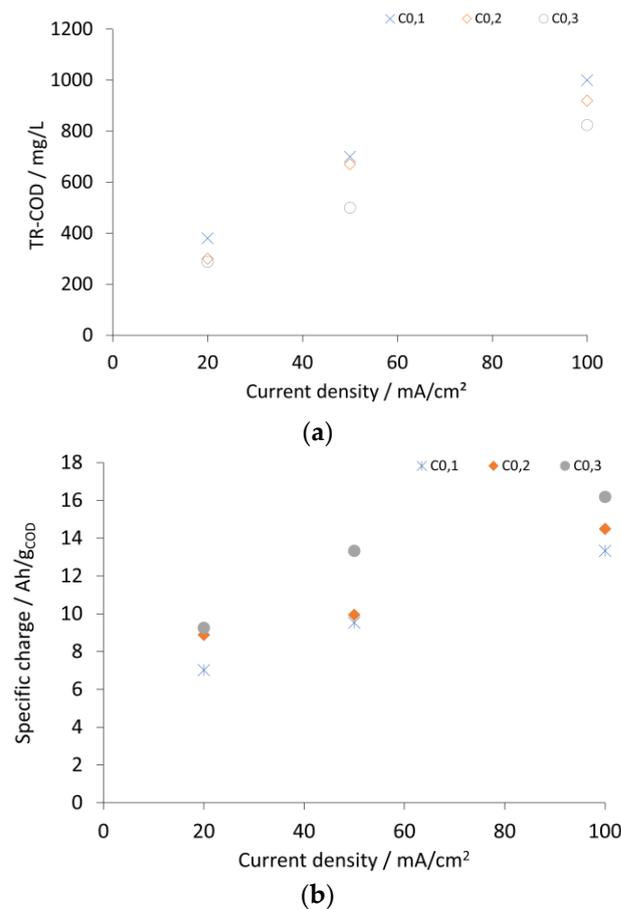


Figure 2. Influence of different $COD_{int.}$ ($C_{0,1} = 4410 \pm 17$ mg/L; $C_{0,2} = 2267 \pm 99$ mg/L; $C_{0,3} = 1175 \pm 13$ mg/L) on: (a) total removed COD (TR-COD) and (b) specific charge demand (SCD); at different current densities (20, 50, and 100 mA/cm²) after 4 h treatment.

The interpretation of this result is that the application of a higher current density generated more reactive species contributing to the electrochemical mineralization of organics in the BDD-GDE reactor, which means a higher generation rate of $\bullet OH$ radicals at the BDD surface. One portion of the generated amount of $\bullet OH$ radicals degraded more organics in SWW [35,36], whereas the other portion accelerated also the decomposition rate of H_2O_2 generated by GDE, providing the electrochemical mineralization once again with more oxygen-reactive species, such as $\bullet O_2H$, $\bullet O_2$, $\bullet OH$, 1O_2 . This agrees with the results reported by Muddemann et al., 2021 for the electrochemical degradation of phenol [12]. It is also important to mention that the H_2O_2 amount generated by the GDE in the reaction medium increases as well by increasing the current density [37]. This contributes to enhancing the quantity of the reactive species $\bullet O_2H$, $\bullet O_2$, $\bullet OH$, 1O_2 through the H_2O_2 decomposition by $\bullet OH$ radicals.

On the other side, the comparison between both effects of current density and $COD_{int.}$ increase on the TR-COD amount shows a dominant mass transfer limitation in the reaction medium which is hardly affected by changing the $COD_{int.}$, but is more affected by the applied current density. This result is close to that of [38], where mass transfer controlled the electrochemical mineralization rate at high current density and high reactants concentration.

The positively mentioned effect of increasing current density on the TR-COD led to a charge loss outside the mineralization reaction, indicating an increase in the SCD value. The increase of current density from 20 to 100 mA/cm² increased the SCD by 90%, 63%, and 75% at $C_{0,1}$, $C_{0,2}$, and $C_{0,3}$, respectively. Conversely, the SCD decreased by 18%, 29%, and 24% at 20, 50, and 100 mA/cm² when $COD_{int.}$ is quadrupled from $C_{0,3}$ to $C_{0,1}$. The reason is that energy consumption increases by higher current density, causing electrons

(charge) transfer promoting acceleration of anodic polarization, and higher generation rate of $\bullet\text{OH}$ radicals [39]. The dominantly existing mass transfer obligates a portion of $\bullet\text{OH}$ to participate in some side (non-mineralization) reactions (i.e., oxygen evolution). The higher the current density is, the higher this participation in the non-mineralization reactions [40] which appears as an increase in SCD magnitude. Increasing the $\text{COD}_{\text{int.}}$ from $\text{C}_{0,3}$ to $\text{C}_{0,1}$ offers higher organic molecules that pick the generated $\bullet\text{OH}$ radicals via mineralization reaction and as a result lower the SCD slightly.

Charge loss due to side reactions can be also mirrored in Figure 3, by the diminishing current efficiency calculated depending on Equation (6), while the current density increases. Increasing current density (from 20 to 100 mA/cm^2) at the same conditions reduced the current efficiency by 47% (from 47.7% to 25.1%) at $\text{C}_{0,1}$ versus 40% and 43% for both $\text{C}_{0,2}$ and $\text{C}_{0,3}$, respectively. This reduction is attributed to the charge loss through the side reactions/products caused by mass transfer limitation. This result agrees with Zhang et al., 2013 who stated a diminishing current efficiency was due to the formation of side products [35].

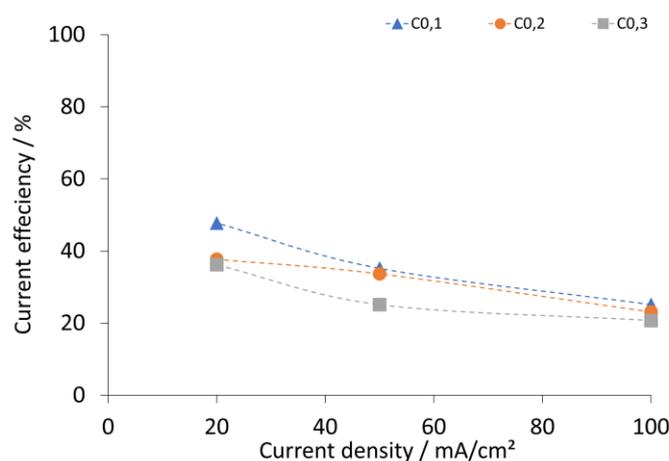


Figure 3. Current efficiency at different current density.

According to Equation (6), current efficiency is related to the TR-COD amount throughout the treatment process time (4 h), which is controlled by the kinetics conditions dominating in the reaction medium during the treatment. The kinetics presented as a timed COD concentration decreasing in the BDD-GDE reactor, as shown in Figure 4, whereby the pH decreased from 7 to 4 and the temperature increased from 10 to 34 °C during the 4 h treatment. It is assumed that the curves of the electrochemical reactions are fitted to the first-order pattern. Continued lines in Figure 4 present the measured COD concentration throughout the experiment time at 100 (a), 50 (b), and 20 mA/cm^2 (c).

At each current density, the COD concentration decreased over time in the approximately same pattern despite the different initial concentrations, whereas the stepwise decrease in current density from 100 to 50 and 20 mA/cm^2 at the same initial concentration softened the slope of the curves, indicating a lower degraded COD amount. The 4 h treatment agrees with the results in Figure 2a. Depending on Equation (7) for first-order reactions, $\ln(\text{COD}_0/\text{COD})$ shows a linear relationship to the experiment time at all current densities and $\text{COD}_{\text{int.}}$ values as shown in Figure 5a–c. As glucose content in the treated wastewater contributes to 96% of the whole COD, glucose was considered as the fingerprint COD source to simplify the deriving of the reaction rate constant. The slope of each curve refers to the value of the rate constant at the related conditions and shows that the rising of current density increased the value of the rate. The effect of increasing current density on the value of the rate constant can be illustrated by the activation of ascending the number of locations on the catalyst (electrode) surface reducing the activation energy of reactants and consequently increasing the rate constants [41,42].

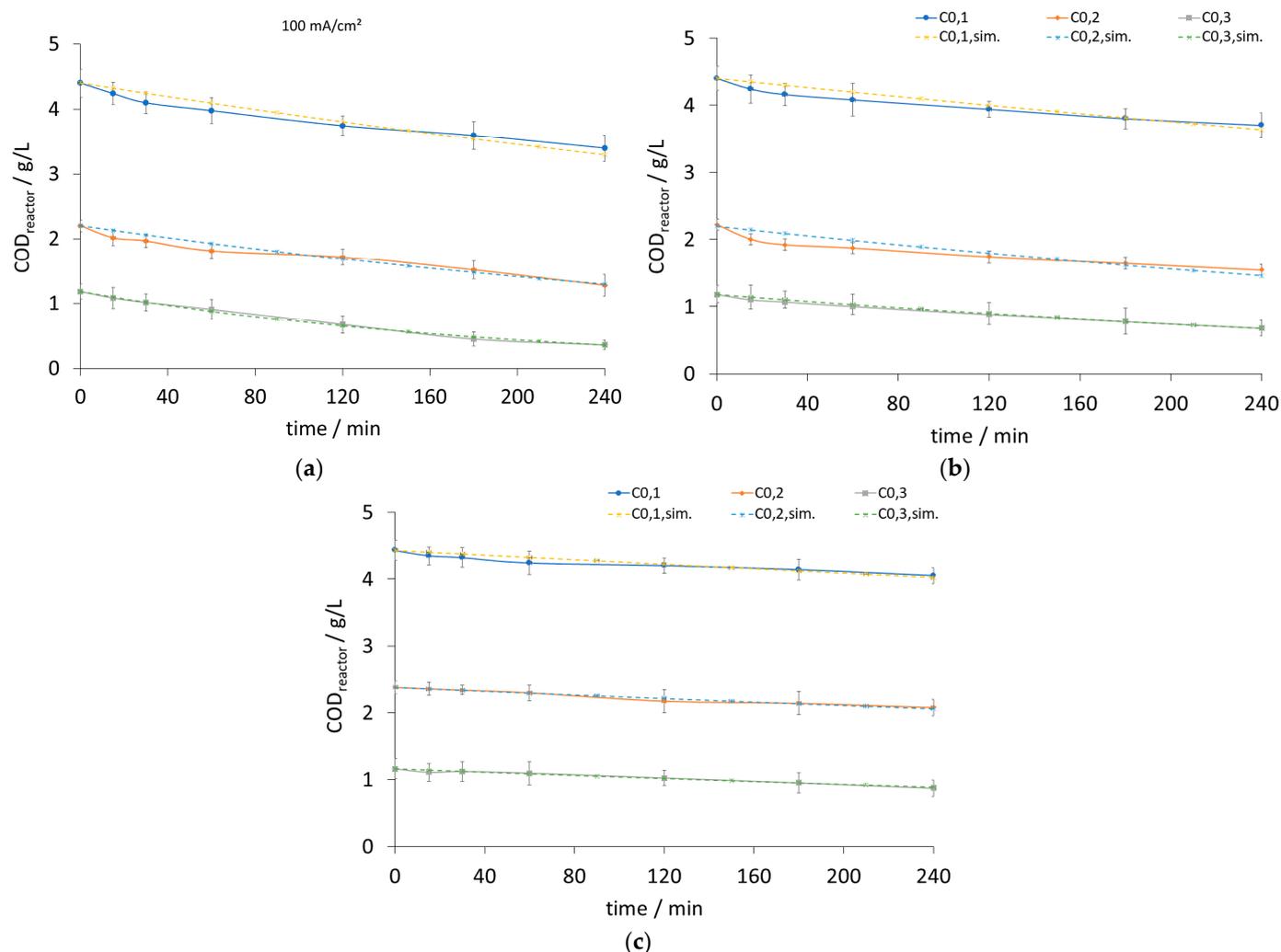


Figure 4. (a–c) COD concentration decrease at different current densities. The continued line is the measured value during the experiments. The dotted line is the theoretical value based on the rate constant calculated from measured values.

This proportionality of the rate constant is not only related to the current density but also the applied cell potential as stated by [33]. As mentioned, the dilution of the original solution ($C_{0,1}$) about 2-fold (generating $C_{0,2}$) and 4-fold (generating $C_{0,3}$) reduced the conductivity of both diluted solutions by an approximate extent from $\sigma_{0,1} = 8.58 \pm 0.24$ to $\sigma_{0,2} = 4.62 \pm 0.12$, and $\sigma_{0,3} = 2.49 \pm 0.06$ mS/cm, respectively, which increased the internal resistance in the treated wastewater. To overcome this difficulty and provide a certain charge input at different conductivities, an increasing initial potential ($V_{0,3} > V_{0,2} > V_{0,1}$) must be applied according to the decreasing conductivity ($\sigma_{0,3} < \sigma_{0,2} < \sigma_{0,1}$) as explained in Table 1.

This necessary increase in the cell potential was the reason for the value increase of the observed rate constant ($k_{obs.}$) which ranged in this work between 0.67×10^{-5} and $8.33 \times 10^{-5} \text{ s}^{-1}$. In the literature, $k_{obs.}$ showed very different values according to the organics to be treated and the treatment conditions. For example, it showed the value $2.4 \times 10^{-5} \text{ s}^{-1}$ at 18.90 mA/cm^2 for degrading ethidium bromide [35], $8.8 \times 10^{-5} \text{ s}^{-1}$ at 15 mA/cm^2 for the treatment of bisphenol A [43], whereas it was $1.9 \times 10^{-5} \text{ s}^{-1}$ at 15 mA/cm^2 during reducing COD of diluted raw leachate [44]. Comparably, $k_{obs.}$ showed a lower value ($1.83 \times 10^{-5} \text{ s}^{-1}$) at a current density of 20 mA/cm^2 for glucose degradation close to the current work, indicating that the natural structure of organics considerably controls the rate constant besides the effect of the current density and other parameters [45].

Table 1. Reaction rate constant k and initial potential V_0 at different electrolyte conductivities and current densities.

Current Density (mA/cm ²)	k [1/s]			Initial Potential V_0 [volt]		
	Conductivity [mS/cm]			Conductivity [mS/cm]		
	8.58 ± 0.24	4.62 ± 0.12	2.49 ± 0.06	8.58 ± 0.24	4.62 ± 0.12	2.49 ± 0.06
100	2.00×10^{-5}	3.67×10^{-5}	8.33×10^{-5}	8.03	14.3	20.9
50	1.33×10^{-5}	2.83×10^{-5}	3.83×10^{-5}	6.59	9.51	12.3
20	0.67×10^{-5}	1.00×10^{-5}	1.83×10^{-5}	4.24	4.85	7.8

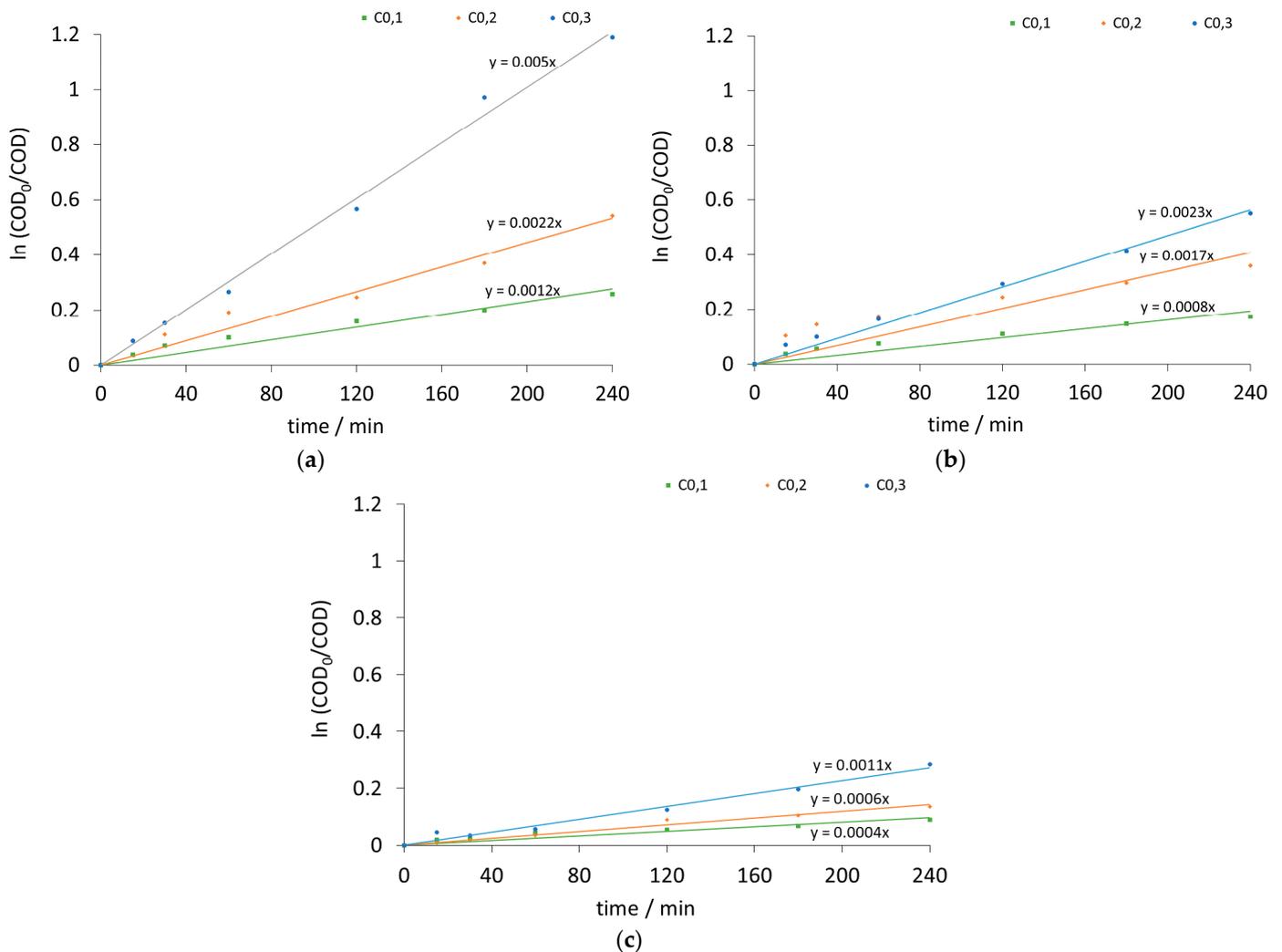


Figure 5. Kinetic curves of the electrochemical reaction as a first-order reaction at different current densities: (a) at 100 mA/cm²; (b) at 50 mA/cm²; (c) 20 mA/cm², and different concentrations: $C_{0,1}$ (square), $C_{0,2}$ (diamond), and $C_{0,3}$ (circle).

To validate the obtained values of the rate constant listed in Table 1, they were used in the kinetics equation of the first-order reaction (Equation (7)) to theoretically calculate COD concentration profiles in the reactor over time. The theoretical values are presented in Figure 4a–c as dotted lines. Regarding the standard deviation, the theoretical values are fitted to the experimental ones for glucose mineralization by BDD-GDE reactor very well. Depending on values listed in Table 1, three models at three different current densities

are graphically represented in Figure 6a which provides a wide range of cell potential to calculate the rate constant.

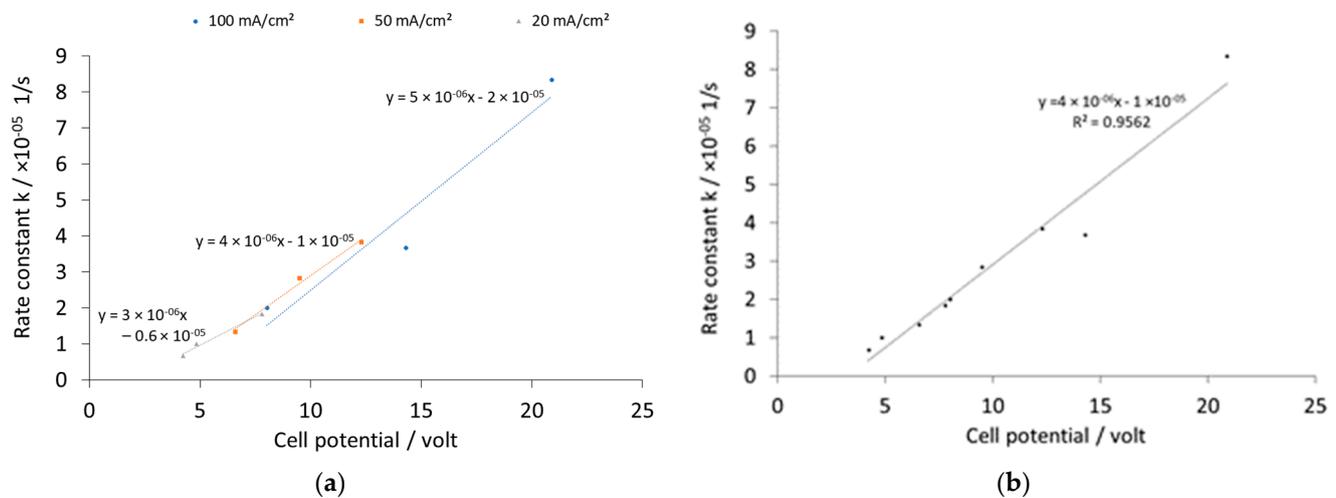


Figure 6. Three mathematical models (a) and its uniform model (b) to calculate the rate constant of glucose oxidation in BDD-GDE-cell on a wide range of current densities (20–100 mA/cm²) and cell potentials (5–20 V).

The three models at three different current densities (20, 50, and 100 mA/cm²) were assembled in one uniform model which is plotted in Figure 6b. This model allows calculating the rate constant of the electrochemical mineralization of organics in the SWW directly from the measured cell potential needed at a certain conductivity from the range of $2.49 \pm 0.06 - 8.58 \pm 0.24 \text{ mS/cm}$ to provide a certain applied current density ranging from 20 to 100 mA/cm². Indeed, changing the conductivity of the synthetic wastewater will just change the set-point value of the cell potential to meet the desired current density changing the rate constant. It means the rate constant can be directly and beforehand obtained from Equation (8) of the proposed model (Figure 6b) just by determining the cell potential.

$$k = 4 \times 10^{-6} \cdot E_{cell} - 10^{-5} \quad (8)$$

where E_{cell} is the applied cell potential at the BDD-GDE-cell (volt), whereby the model provides the value of k_{obs} on a range of $1 \times 10^{-5} - 7.4 \times 10^{-5} \text{ s}^{-1}$ when the E_{cell} varies from 2.5 to 21 V to provide a current density ranging between 20 and 100 mA/cm².

The validity of the model was mathematically checked on a cell potential range of 6–21 V and showed a maximal standard deviation $\leq \pm 20\%$ of the value of the rate constant calculated via the three models with different current densities (Figure 6a). Additionally, the R-squared value (95.6%) shows the model highly adapting to the k_{obs} values drawn from the experimental measurements. Therefore, it can be stated that the proposed model (Figure 6b) is derived and checked to deliver trustable values for organics mineralization in the investigated synthetic wastewater at the mentioned temperature, pH, conductivity, and current density limitations.

For electrochemical COD mineralization in raw leachate and according to the model of [44], k_{obs} reached $7.19 \times 10^{-5} \text{ s}^{-1}$, locating nearby the value $7.4 \times 10^{-5} \text{ s}^{-1}$, obtained in this work at close settings of both cell potential and current density. Such differences in k_{obs} values are mainly to be interpreted by the different physico-chemical properties of types of organics in the wastewater, which emphasizes the fact that a certain mathematical model must be derived for each type of wastewater, under certain limitations of operating parameters, to be able to determine the rate constant as precisely as possible.

3. Conclusions

In this work, different settings concerning current density and initial COD concentrations were investigated to study the performance of the electrolysis BDD-GDE reactor used to mineralize organics in synthetic wastewater, prepared to simulate real toilet wastewater collected on board trains. In addition, this study enabled us to derive a mathematical equation to determine the rate constant of the electrochemical reaction in advance, which mainly helps design an electrochemical reactor with high accuracy for real situations.

Increasing current densities improves the removal efficiency of the electrolysis BDD-GDE reactor more than increasing initial COD concentrations. For example, increasing the current density from 20 to 50 and 100 mA/cm² raised the TR-COD 84% and 163% (at C_{0,1}), 120% and 210% (at C_{0,2}), as well as 74% and 186% (at C_{0,3}), respectively. Conversely, using a higher initial COD concentration such as C_{0,1} (four times higher than C_{0,3}) helped increase the TR-COD by just 21–34%, depending on the adjusted current density at the BDD-GDE reactor.

Considering the energy side, the increase of current density from 20 to 100 mA/cm² increased the SCD by 90%, 63%, and 75% at C_{0,1}, C_{0,2}, and C_{0,3}, respectively. This means that the advancement in the quantity of mineralized organics was accompanied by a charge loss in the side reactions. Accordingly, the best current efficiency of the system is achieved at low current density (20 mA/cm²) ranging between 36–48%, depending on the adjusted COD_{int.} value, whereas it diminished to ~23% at all COD_{int.} values when the density increases up to 100 mA/cm².

Depending on the degradation of COD in the wastewater during the time of the electrochemical treatment, the reaction kinetics presented by the experimental measurements adopts the pattern of the first-order reaction. The experimental data of the different treatment runs enabled the derivation of a simple mathematical model to calculate the rate constant as a function of the cell potential. According to the model suited for the investigated synthetic wastewater and applied operating parameters, the observed rate constant k_{obs} ranges between 1×10^{-5} and $7.4 \times 10^{-5} \text{ s}^{-1}$ depending on a cell potential of 2.5 to 21 V.

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