



Efficiency enhanced electrochemical treatment of industrial wastewater by quasi-division

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We present a novel method for treating real life industrial wastewaters containing different kind of organic contaminants, utilizing a quasi-divided cell setup that enhances total organic carbon (TOC) and chemical oxygen demand (COD) elimination efficiency. Three distinct wastewater streams were analyzed, containing various organic pollutants, including nitriles, amines, and dissolved cyanides. Degradation efficiencies of up to 99 % for both TOC and COD were achieved using a newly slit spacer that facilitates quasi-division, effectively reducing the hindrance of reductive back reactions by minimizing the cathode surface area. The innovative design of two plate electrodes, combined with the newly developed spacer, simplifies the scaling process for industrial applications by addressing the challenges of integrating quasi-division into conventional electrochemical flow systems with wires as the smaller electrode. Also the undivided cell setup simplifies the periphery infrastructure of a technical plant to one cycle. Additionally, we explored the impact of sulfate on treatment efficiency, finding that peroxodisulfate species generated in situ at boron-doped diamond anodes significantly enhance our degradation rates. This study introduces a promising approach for TOC elimination and cyanide oxidation simultaneously, demonstrating strong potential for industrial application due to its simplicity in regard to engineering the electrochemical reactor and periphery infrastructure.

1. Introduction

Almost every chemical process generates industrial wastewater, which often contains contaminants hazardous for both, nature and humans. One class of contaminants that needs to be eliminated from industrial wastewater are substances that are not biodegradable and may accumulate over time [1]. Therefore, treatment of industrial wastewater is often necessary prior to emission into the environment [2]. Commonly employed wastewater treatment processes revolve around microbiological degradation of contaminants. The biological treatment features are often limited in applicability, if organic pollutants are present in such wastewater [2]. In particular, organic species with high resistance to oxidative degradation require more aggressive treatment. There are various mature methodologies for wastewater treatment, which can be employed for the elimination of stable organic pollutants. These processes include membrane technology for separating

pollutants from water, the Fenton technology and ozonolysis for the oxidative decomposition of organics, in addition to classical incineration among others [1–7]. All of these methods exhibit significant disadvantages: Membranes are prone to fouling and lose stability when exposed to aggressive chemicals [1,8,9]. Additionally, the membrane divides the wastewater stream into two sub streams, with the concentrate requiring further treatment, typically by incineration resulting in increased carbon dioxide emission [1]. Despite being comparably cost-effective in the elimination of poorly oxidizable substances, the Fenton process requires strict safety standards for H₂O₂ management and generates a high salt load including iron and other chemicals necessary for pH adjustments [4,10–13]. Lastly, ozonolysis entails the handling of hazardous gases and is comparably energy intensive. Thus, more sustainable processes are heavily sought after.

In the past years, electrochemistry has evolved to an emerging technology for sustainable chemical processes [14–18]. Electrochemistry has found widespread application in the production of organic

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Nomenclature

Abbreviations

BDD	Boron doped diamond
COD	Chemical oxygen demand
PP	Polypropylen
PTFE	Polytetrafluorethylen
RCS	Reactive chlorine species
RSS	Reactive sulfur species
TOC	Total of carbon

Symbols

A	Ampere
j	Current density
V	Voltage
Wh	Watt hour

compounds—known as electrosynthesis [19–21]. Additionally, electrochemistry can be utilized for highly efficient, oxidative decomposition of organic substances in aqueous media, a process, which can be extended to the treatment and disinfection of different kinds of wastewaters [4,12,13,15]. The electrochemical treatment of industrial wastewater involves the generation of highly reactive oxidizing species at the anode, which can eliminate various organic pollutants [3,6,22–25]. Boron-doped diamond (BDD) is the most efficient electrode material for this purpose, due to its high overpotential for oxygen evolution and its ability to generate highly reactive hydroxyl radicals in aqueous media [12,22–24,26–31]. Inorganic chlorides or sulfur species can be added to enhance the effect of the so-called cold combustion [24,26,27]. In this process, chloride is oxidized to reactive (oxo)chlorine species (RCS) and sulfur to reactive (per)sulfate species (RSS) [6]. Both species exhibit an utmost oxidizing power and support the degradation of organic pollutants [7,24,26–28,32–34]. Compared to other oxidative wastewater treatments, electrochemistry is more resource efficient and sustainable based on the in-situ generation of oxidizing species [7,15,32]. In the work of Canizares et al. [3], the three oxidative methods of Fenton, ozonolysis, and electrochemical treatment were compared regarding their efficiency in degrading various organic pollutants and in terms of operational and investment costs. The electrochemical approach proved to be the most efficient method, especially in heavily polluted wastewater, and was able to compete well with the operational costs of the Fenton process for many pollutants [3,26,35].

The experimental investigations presented here were conducted with the aim of developing a highly efficient, long-term stable and sustainable process for the treatment of industrial wastewater contaminated with organic pollutants resistant towards conventional biological treatment options. Therefore, the focus was on reducing environmentally harmful chemicals and ensuring the sustainability of the method. Additionally, the technology had to be amenable to varying wastewater composition from different industrial production plants and at various timepoints across the production lifecycle.

To enhance the applicability of our treatment system in industrial settings, we exclusively tested real effluent streams from chemical production. These wastewaters contained a diverse range of contaminants, including nitriles, amines, ketones, and free cyanides. Our objective was to develop a process that not only improves the biological degradability of these contaminants but also effectively removes residual cyanides. A key consideration was to maintain simplicity in reactor design, minimizing the peripheral infrastructure required for the treatment plant. Consequently, we conceived an undivided cell setup, streamlining the engineering requirements to a single cycle. This innovative approach addresses the challenge of maintaining sufficient oxidation power while suppressing undesirable reductive side or back reactions. By focusing on

an uncomplicated system architecture, we aim to facilitate the integration of our treatment process into existing industrial frameworks, thereby enhancing its feasibility and operational efficiency. This study underscores the potential of our undivided cell design as a practical solution for the treatment of complex real life industrial wastewaters.

2. Materials and methods

2.1. General description of the experiments

The various wastewater samples (see Table 1) were tested in a laboratory facility using a semi-batch process. For this purpose, 300 mL of wastewater were continuously cycled through an electrochemical cell until the designated treatment time was achieved. During the treatment, samples were taken, and the volume was kept constant by addition of water. The samples were analyzed for COD, TOC changes, and, if applicable, cyanide content. Initial experimental investigations identified BDD as a suitable and long-term stable anode material, and a Pt strip welded onto tantalum as the best cathode material. For detailed information, please have a look at the supporting information.

2.2. Wastewater characterization

The real life industrial wastewater was provided by Evonik Operations GmbH and the main compounds are listed in Table 1. All Wastewaters had a caustic pH due to the inorganic bases.

3. Results

The experimental investigations were initiated with an attempt of treatment the different wastewater streams employing conventional electrochemical conditions. A classic flow cell with a BDD anode and a platinum on tantalum cathode was applied and very limited lowering (under 15 % TOC and COD elimination) in the contaminant concentration was obtained. Since a membrane for enhancing oxidation proved unfeasible, due to the limited stability of classic separators at the current densities required in wastewater treatment, a solution without a separator was required. In classical electrosynthesis, a technique called quasi-division was previously demonstrated to improve overall cell oxidative power. The basic concept of quasi-division is a kinetic limitation of undesired transformations occurring at the counter-electrode, thereby improving the overall cell-efficiency [36]. Generally, this is achieved by using a cell design with significant cell surface difference between the working and counter-electrode. Employing quasi-division was envisioned for the treatment of stable organic pollutants found in common industrial wastewater. With a tremendously undersized cathode surface area likely resulting in shielding of the electrode and restriction of undesired processes to the bulk. To test this concept, quasi-division was applied in wastewater treatment: Two plate electrodes were utilized in the optimized cell setup with restriction of the cathode surface by a polymer spacer with a slit (see Fig. 1). The plate electrode design allowed for simpler cell setup and the use of various electrode materials with easily available dimensions. The spacer material was either polypropylene or PTFE.

Table 1

Wastewater components: Listed are the main compounds of the wastewater originating from the production plant.

Wastewater	Main compounds	Approximate TOC
1	Dinitrile, HCN, inorganic salts like phosphates	15,000 g/L
2	Cyclic diamine, HCN, sodium hydroxide, ammonia	2000 g/L
3	Cyclic nitriles, HCN, sodium hydroxide	4000 g/L

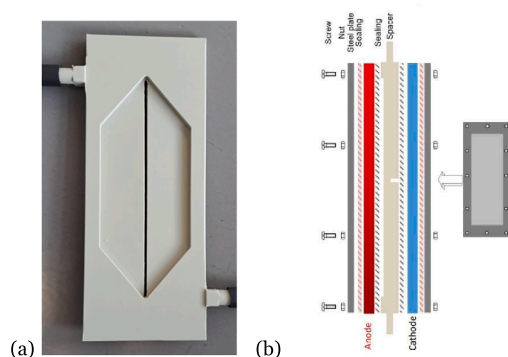


Fig. 1. (a) PP Slit spacer real image and (b) technical side view cell setup. Slit spacer (a) was used for all quasi-divided experiments and the technical sketch (b) shows the implementation within the cell setup.

3.1. Efficiency test of the quasi division introduced by the spacer developed

Evaluation of the impact by quasi-division on COD/TOC elimination was conducted by treatment of wastewater stream 1 in a comparative experiment with conventional electrolysis and a quasi-divided setup. The wastewater was electrolyzed at a BDD anode and platinum on tantalum as cathode for 2 h at 3 A ($37,5 \text{ ma/cm}^2$). By using the quasi-division, the elimination of COD was increased from 14 % to 25 % and the elimination of TOC from 11 % to 20 %, respectively. This represents a 1.8-fold increase in efficiency displayed in Fig. 2, almost doubling the elimination. Consequently, quasi-division was used in all subsequent studies.

3.2. Reaction time dependency of the electrochemical quasi-division elimination of TOC and COD

Following initial optimization of the cell setup to boost the oxidation of the organic pollutants, the generality of the treatment process was evaluated using three different wastewater streams with varying levels of contaminants. Wastewater stream 1 contained a dinitrile as the main organic contamination; wastewater stream 2 contained cyclic diamines, and wastewater stream 3 contained a cyclic nitrile. All wastewater streams contain low levels of cyanide in the range of 3 to 72 ppm. Because of the presence of residual sodium hydroxide or ammonia, wastewater streams 1 and 3 exhibited sufficient conductivity and an alkaline pH. In case of wastewater stream 2 sodium hydroxide was

added to enhance electrical conductivity without affecting the initial pH. To evaluate the relationship between the treatment duration and the degradation rate, samples were taken at different times. These samples were plotted in a graph of elimination rate against treatment time. A linear relationship between the treatment time and elimination of organic contaminants was found (see Fig. 3). Thus, the required treatment time can be determined via a linear function depending on the desired degree of elimination.

3.3. Influence of the pH on the treatment efficiency in all three wastewater streams

To investigate the effect of pH on treatment efficiency, concentrated sulfuric acid was added to the wastewater resulting in a pH of 7. In addition, sodium sulfate was included when necessary to increase conductivity. By adding small amounts of sulfuric acid until pH neutralization (up to 2 mL concentrated sulfuric in 300 mL wastewater to reach pH 7), the treatment efficiency was significantly improved (see Fig. 4). All other parameters, e.g. current density, voltage, treatment time and anode material were kept constant. Additionally, the same batch of wastewater was used as a reactant in both experimental series. The elimination rates were increased by approximately 300 %. In wastewater stream 1, the COD elimination was improved from 18 % to 97 %, and the TOC elimination from 13 % to 79 %. In wastewater stream 2, adding sulfuric acid resulted in an increase in COD elimination from 24 % to 85 %, and the TOC elimination efficiency was improved from 18 % to 78 %. In the wastewater stream 3, the COD elimination reached 98 % instead of 24 %, and the TOC elimination improved from 4 % to 98 %.

3.4. Highest elimination rates of COD in the developed reactor

Besides the significantly improved efficiency of the developed wastewater treatment process, the optimized conditions allowed for a reduction of the COD of all evaluated wastewaters below 100 ppm. Additionally, the process proved to be amenable to variations in the amount and type of organic pollution, as demonstrated by achieving below 100 ppm for both moderate initial COD of about 2000 ppm and heavily contaminated wastewater with a COD of 14,600 ppm, displayed in Fig. 5. Finally, it was demonstrated that electrochemical treatment is suitable as a single treatment option without requiring additional steps, e.g. biological degradation.

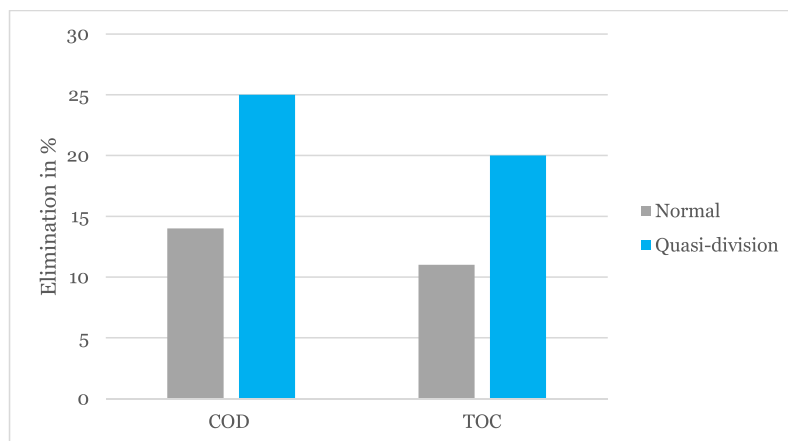


Fig. 2. Efficiency of the quasi-division: Comparison of TOC/COD elimination for wastewater stream 1 in a normal flow cell without quasi division and with a quasi-divided flow cell. Both experiments were executed with the same batch wastewater (300 mL) with a starting COD of 14,600 mg/l and a TOC of 5205 mg/l. As the anode BDD was used and as the cathode platinum on tantalum as support was employed.

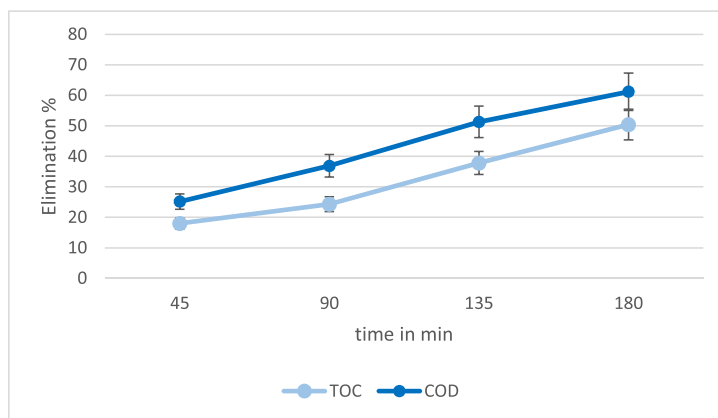


Fig. 3. Time dependent elimination: Treatment of wastewater stream 2 with added 50 mL 1 M NaOH with a BDD anode and cathode. The treatment was performed with 1 A (12,5 ma/cm²) for over 180 min and samples were taken in the course of the electrolysis. Error range 10 % due to sample taking while the experiment.

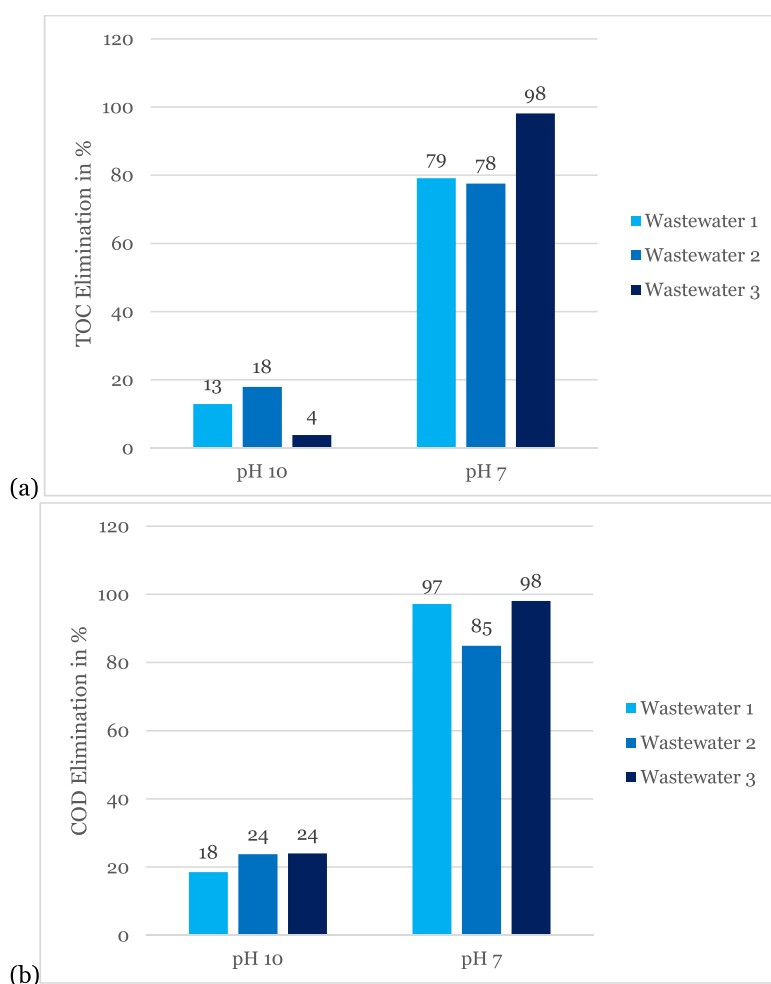


Fig. 4. Effect of neutralization prior to electrochemical wastewater treatment: The graphs show the TOC (a) and COD (b) elimination of all streams with pH 10 and 7. All wastewaters were treated with a BDD anode and either a BDD or tantalum supported platinum cathode. The spacer was a vertical PTFE plate. 300 mL of: Wastewater 1 was treated in both cases 270 min with 3 A (62,5 ma/cm²). Wastewater 2 was treated in both cases with 1 A (12,5 ma/cm²) for 180 min. Wastewater 3 was treated with 1 A (12,5 ma/cm²) 390 min. To adjust the pH concentrated sulfuric acid was added until a pH of 7 was reached. To remain the current density and voltage sodium sulfate was added to wastewater 2 until the same voltage was reached.

3.5. Examination of the role of peroxodisulfate as a mediator in the treatment

In order to delineate the origin of the improved electrochemical process efficiency under sulfuric acid addition, the effect of

electrochemical peroxodisulfate formation in presence of sodium sulfate or sulfuric acid was investigated. Therefore, 10 g of peroxodisulfate per 10 mL wastewater was added to all three wastewater streams and the TOC was measured before and after treatment without applying a current. A lowering in TOC was observed in all streams (see Fig. 6).

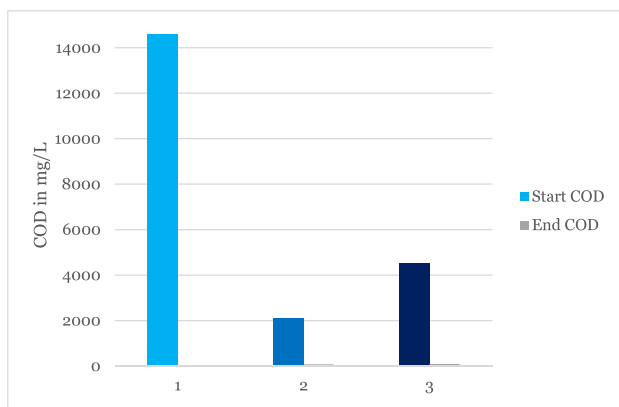


Fig. 5. Obtained elimination rates employing a quasi-divided cell setup under addition of sulfuric acid to improve treatment efficiency. All wastewaters were treated with a BDD anode, Tantalum supported Pt cathode and the vertical PTFE spacer. Wastewater 1 was treated for 390 min with 3 A (780 Wh/L, 62,5 ma/cm²); Wastewater 2 was treated for 270 min with 1 A (180 Wh/L, 12,5 ma/cm²); Wastewater 3 for 390 min with 1 A (220 Wh/L, 12,5 ma/cm²).

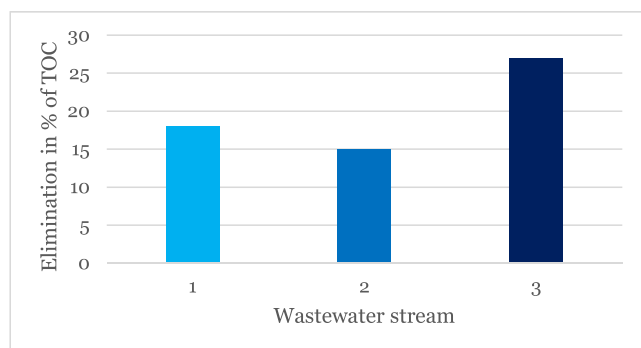


Fig. 6. TOC elimination achieved by peroxodisulfate treatment of wastewater streams 1–3 without electrolysis. 80 mL of the three wastewater streams were treated with 8 g of sodium peroxodisulfate and by stirring for 4 h.

Treatment with peroxodisulfate resulted in TOC elimination rates of 18 %, 15 % and over 25 % for wastewater streams 1, 2, and 3, respectively. This observation suggests the involvement of peroxodisulfate in the electrochemical wastewater treatment in the presence of sulfuric acid or sodium sulfate. The decrease in treatment efficiency compared to the

electrochemical treatment with sulfuric acid addition results from the lack of peroxodisulfate recycling, which is achieved during the electrolysis by anodic oxidation of sulfate. Therefore, catalytic amounts of sulfate ions are sufficient to obtain high elimination rates in the electrochemical environment.

This hypothesis was confirmed by replacing sulfuric acid in the electrochemical treatment of wastewater stream 2 with sodium sulfate resulting in comparable TOC elimination (see Fig. 7, 57 % with sulfuric acid vs. 53 % with sodium sulfate). The slight decrease in elimination efficiency demonstrates the importance of controlling the pH during the electrolysis. However, sodium sulfate lowers the corresponding terminal voltage and therefore has a lower energy demand (50 Wh/L) compared to sulfuric acid as an additive (70 Wh/L).

3.6. Proposed electrode reactions in the quasi-divided reactor with sulfate mediation

With this result in hand we propose electrode reaction like shown in Fig. 8 [37]. A suppression of direct reductions of the oxidants, products or organic contaminants is achieved by the smaller surface area of the cathode. Since the wastewater is an aqueous solution we are proposing classic hydrogen evolution reaction here. We confirmed this by measuring the hydrogen qualitative with a sensor during some experiments. In the literature two main oxidative decomposition pathways of organic contaminants are proposed. The direct anodic mineralization from the organic contaminants to their oxidized products. The other pathway is the mediated oxidative mineralization via oxidants. The radical oxidants are generated from the water and the sulfate. These radicals can then either directly oxidize the organic contaminants or prior react to stable oxidants [37].

3.7. Cyanide elimination in the developed reactor

Lastly, the removal of cyanide from the wastewater samples was investigated. In particular, dissolved cyanide poses a significant challenge for chemical and biological treatment options. It was envisioned that the developed wastewater process can be tuned to allow for simultaneous TOC and cyanide elimination. Employing the developed setup, it was found that treating cyanide containing wastewater streams at basic to neutral pH resulted in almost complete removal of the cyanide (see Fig. 9). Staying at basic or neutral pH proved to be crucial in order to prevent emission of dissolved cyanide as hydrogen cyanide. Additionally, it was observed that the degree of cyanide removal was independent of the starting concentration (Fig. 9) with a reduction from 72 ppm to 1 ppm and 3 ppm to 0.1 ppm for wastewater streams 3 and 2,

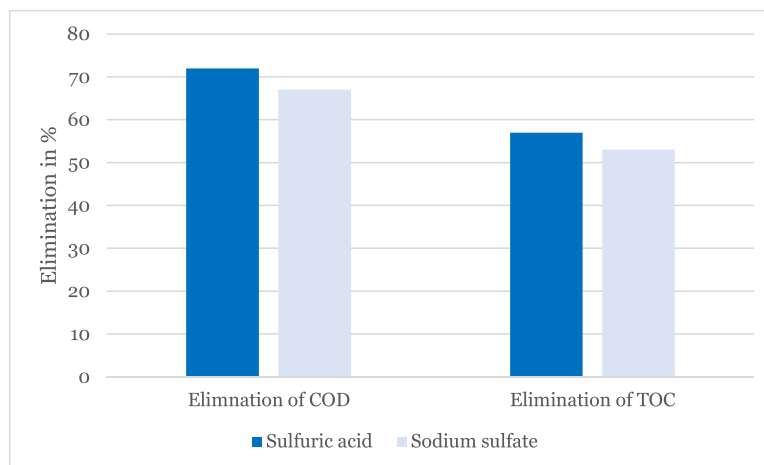


Fig. 7. Comparison of elimination in TOC and CSB with sodium sulfate and sulfuric acid as additive. The wastewater 2 was electrolyzed 2 h with 1 A (12,5 ma/cm²) and the wastewater was taken from the same batch. The energy demand was 70 Wh/L with sulfuric acid and 50 Wh/L with sodium sulfate as an additive.

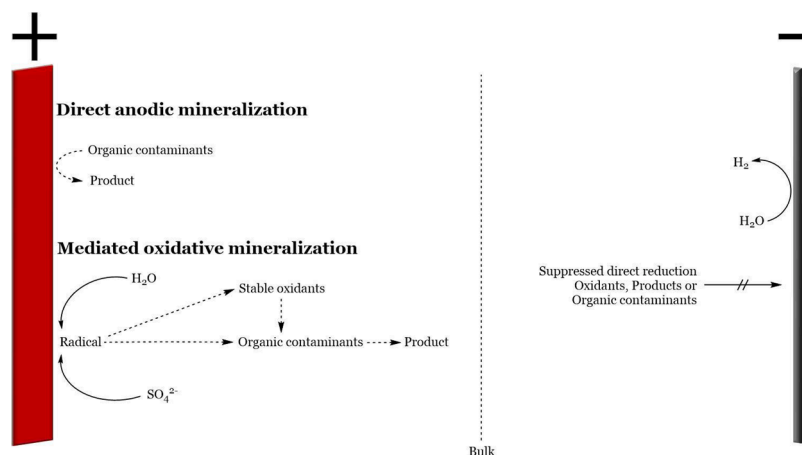


Fig. 8. Proposed electrode reactions: Shown is the BDD initiated radical generation and mediated mineralization of organic contaminants as well as the direct anodic mineralization in a quasi-divided cell setup, with sulfate additives [37]. Also the proposed suppressed reductive side reaction via the quasi division at the cathode is pictured.

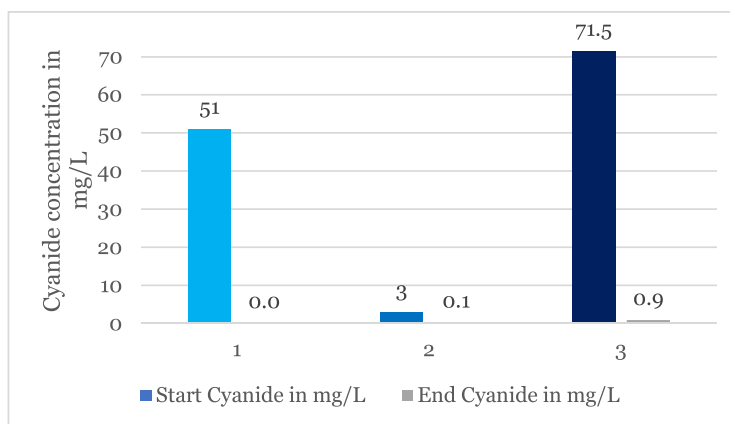


Fig. 9. Removal of cyanides: From wastewater stream 1–3 using the developed treatment process. All wastewater streams were treated at an alkaline pH to prevent the evaporation of HCN. At all experiments BDD was the anode and BDD or tantalum supported platinum the cathode. Wastewater 1 270 min with 5 A (900 Wh/L, 62,5 ma/cm²); Wastewater 2 was treated 180 min with 1 A (90 Wh/L, 12,5 ma/cm²); Wastewater 3 270 min with 1 A (150 Wh/L, 12,5 ma/cm²). This experiment was conducted in an alkaline pH with no additives in 1 and 3 and 50 mL of 1 M NaOH in 2, to avoid HCN release due to acidic pH.

respectively.

4. Conclusions

In conclusion, a highly efficient treatment method for diverse wastewater composition was established based on a quasi-divided cell setup with a newly designed spacer. Employing quasi-division was found to be crucial for allowing the elimination of highly stable organic pollutants with simultaneous removal of dissolved cyanide. By testing different concentrations of organic load and cyanide in addition to varying composition of different wastewater streams, the broad applicability of the quasi-divided setup developed was demonstrated. Optimizing the starting pH significantly improved the treatment efficiency. Given the necessity of neutralizing organically contaminated wastewater with sulfuric acid prior to biological treatment or emission to the environment, no additional additives were required. The established process demonstrates the suitability of electrochemistry employing quasi-division in combination with sulfate additives as a sustainable and efficient option for the treatment of diverse wastewater streams allowing for the simultaneous elimination of organic contaminants and residual cyanide. This method enables compliance with environmental limits while lowering them to a minimum without the use of biological treatment processes.

CRediT authorship contribution statement

L. Lennartz: Investigation, Conceptualization, Visualization, Methodology, Data curation, Project administration, Writing – original draft. **J.B. Metternich:** Conceptualization, Visualization, Project administration, Writing – original draft. **T. Stadtmüller:** Investigation, Conceptualization, Visualization, Writing – review & editing. **L. Jonescheit:** Investigation. **P. Stenner:** Supervision, Conceptualization, Writing – review & editing. **S.R. Waldvogel:** Supervision, Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Siegfried R. Waldvogel reports was provided by Max-Planck-Institute for Chemical Energy Conversion. Siegfried R. Waldvogel reports a relationship with Max-Planck-Institute for Chemical Energy Conversion that includes: employment and funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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