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Brief review of the history and characteristics of the acid tar-contaminated site Predajná I and the potential application of electrochemical oxidation for the remediation of surface waters from uncapped lagoons

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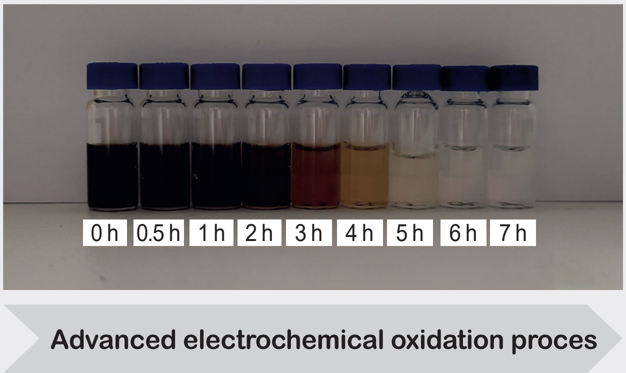
Abstract: Historical disposal of acid tars from Petrochema refinery operations has resulted in persistent environmental hazards arising from the open acid-tar lagoons. These lagoons accumulate strongly acidic, highly contaminated waters enriched with organic compounds and heavy metals, posing significant risks of overflow and contamination of surrounding soils and groundwater. To mitigate these risks, electrochemical advanced oxidation using boron-doped diamond electrodes (BDD) was investigated as a treatment method for the contaminated surface water. Laboratory experiments demonstrated progressive degradation of organic pollutants, with chemical oxidation demand (COD) and total organic carbon (TOC) reductions of up to 94 % after four hours. Sulfonated compounds were oxidatively cleaved, releasing sulfate ions, while oxalate formed as a transient intermediate before complete conversion to CO_2 and water. Instantaneous current efficiencies reached ~90 % and specific energy consumption 25 kWh per kg of COD removed in the initial current-limited stage, decreasing at higher currents due to mass transport limitations and side reactions. These results highlight the potential of electrochemical oxidation to achieve near-complete mineralization of persistent organics, and provide a sustainable solution for the remediation of acid-tar-contaminated waters at legacy industrial sites.

Key words: acid tar lagoons, electrochemical oxidation, boron-doped diamond BDD

Graphical abstract



Highlights

- Acid-tar lagoons at Predajná site contain highly acidic, organic- and metal-rich waters, posing ongoing environmental risks.
- Electrochemical oxidation using a boron-doped diamond (BDD) anode achieved up to 99.6 % COD reduction and near-complete mineralization of persistent organics.
- The proposed treatment offers a sustainable, waste-free, and environmentally friendly solution for continuous remediation of contaminated lagoon waters.

Introduction

Acid tars are black- to brown-colored, highly viscous residues produced during crude-oil processing and are characterized by extremely low pH (approx. pH 0.8–2) and a strong, acrid odor. They arise as by-products of three major industrial operations: benzole refining, oil re-refining, and white-oil production, all of which historically relied on concentrated sulfuric acid for feedstock purification (Milne et al., 1986; Nancarrow et al., 2001; Speight, 2014). The treatment of petroleum products with strong acids has been practiced for decades in petroleum chemistry. However, the management of the resulting spent acid sludge remains a significant environmental and operational challenge, prompting ongoing efforts toward its recovery, treatment, and reuse (Hadadi & Moradi, 2019; Leonard & Stegemann, 2010). Throughout the 20th century, waste acid tars were commonly disposed of in unengineered pits or natural depressions near production sites. They were often mixed with other wastes and left without treatment or isolation. This practice created acid-tar lagoons that remain a lasting environmental burden.

Apart from the co-disposed waste, acid tars typically comprise water, sulfuric acid and a broad spectrum of organic compounds that remain soluble in concentrated sulfuric acid. These residues contain numerous toxic and environmentally relevant constituents, including saturated and unsaturated aliphatic and cyclic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), organic acids such as sulfonic, carboxylic, and aromatic acids, as well as trace to moderate concentrations of heavy metals (Leonard et al., 2010; Milne et al., 1986).

The physical properties of acid tars further complicate their management. Their viscosity is strongly temperature-dependent: at elevated temperatures acid tars become more fluid and mobile, whereas at lower temperatures they can solidify. Reported bulk densities typically range from 1,020 to 1,430 $kg\cdot m^{-3}$ (Hao & Smith, 2005; Nichol, 2000) exceeding those of typical coal tars (approximately 1,140–1,250 $kg\cdot m^{-3}$ (PubChem, 2025), primarily due to their high sulfuric acid content (density of 98 % H_2SO_4 = 1,840 $kg\cdot m^{-3}$).

At uncapped acid-tar lagoons, an overlying aqueous phase that is highly acidic and enriched in sulfate ions is frequently observed, as reported for the contaminated Predajná site in Slovakia. This surface water layer is formed primarily through atmospheric precipitation and is sustained by the low permeability of the underlying acid tar matrix, which restricts infiltration and drainage (Adzimová et al., 2023; Knapcová & Samešová, 2017). The partial solubility of acid tars in water is attributed, to the presence of sulfonic acids and other polar sulfur-containing compounds, such as sodium dodecyl sulfate (SDS) that exhibit surfactant-like properties, thereby enhancing the transfer of organic constituents into the aqueous phase (Bhoi et al., 2015).

Production and Disposal of Acid Tars in Petrochema plant

The petroleum refinery in the municipality of Dubová, located in the Banská Bystrica Region of central Slovakia, was established in 1938 as a state-owned enterprise and later operated under the name Petrochema (Ďurigová, 2001). The facility was initially designed to process crude oil of Slovak and Czech origin. During the Second World War, the refinery suffered extensive damage as a result of aerial bombing (Šumichrast, 2014).

At the Petrochema plant, acid tars were generated as by-products of treating petroleum fractions with concentrated sulfuric acid. This refining step was employed to remove unsaturated hydrocarbons and heterocyclic compounds from heavy lubricating-oil fractions, enabling the production of white oils used in medicinal, cosmetic, and specialized lubrication applications. In addition, sulfonation technology was particularly applied for the synthesis of alkyl-sulfonate detergents (Hrušková et al., 2013; Samešová et al., 2007).

Chemical production waste from Petrochema rafinery was deposited in two lagoons situated within the rafinery premises. The larger lagoon occupies an area of 8,680 m^2, while the smaller covers 2,440 m^2, together providing an estimated storage capacity of approximately 100,000 m^3. Two additional acid-tar disposal sites are situated approximately 3.5 km east of the refinery, near the municipality of Predajná. The Predajná I landfill was constructed in 1963, currently covering an area of 10,577 m^2 and containing an estimated 100,000 m^3 of acid waste. The Predajná II landfill, built in 1973, occupies an area of 5,700 m^2 and stores approximately 50,000 m^3 of acid tar (Adzimová et al., 2023; Paluchová et al., 2008). A location of acid-tar deposits in relation to the municipality Predajná is provided in Fig. 1. Documentation of the current landfill conditions is shown in Fig. 2a.

Environmental risks and hydrogeological context

The tar dumps are situated on Middle Triassic dolomites of the Choč Nappe (Ostrolucký et al., 1982). The surrounding and underlying bedrock consists predominantly of sedimentary carbonate rocks, chiefly dolomite and dolomitic limestone, with an estimated thickness of several tens of meters (Polák et al., 2003a; Polák et al., 2003b). The deposition of acid tars and other chemical wastes directly into carbonate bedrock without bottom sealing poses a significant environmental risk. Hydrodynamic tests indicate that the permeability of the bedrock beneath the tar dumps is low to very low (Pirman & Potyš, 1997). Nevertheless, the hydrogeological environment is highly heterogeneous, with preferential groundwater flow occurring along open fractures, caverns, and karst channels associated with zones of karstification and tectonic disturbance (Ostrolucký & Gálisová, 1986). Historical records indicate that during landfill filling, acid tar infiltrated the heterogeneous bedrock and migrated through the dam body, resulting in contamination of the surrounding groundwater (Auxt et al., 2020; Jánová, 2019).

After landfill closure in 1976, the lagoons remained exposed to surface water infiltration, leading to the formation of a persistent water layer within the landfill. This contaminated water exhibits seasonal fluctuations driven by precipitation, snowmelt, and runoff from surrounding slopes, increasing the risk of overflow from the landfill margins and subsequent contamination of surface and groundwater, soils, and other environmental compartments (Adzimová et al., 2023; Jánová, 2019). The uncontrolled disposal of hazardous materials at these sites underscores the severe environmental challenges associated with historical refinery operations. Notably, both Predajná landfills are situated within the protection zone of the Low Tatras National Park (Knapcová et al., 2017).

Geological survey and remediation efforts

The Predajná I and II landfills are classified as confirmed, high-priority environmental burdens due to persistent contamination: *BR (015) Predajná – skládka PO Predajná I (SK/EZ/BR/73) and BR (016) Predajná – skládka PO Predajná II (SK/EZ/BR/74)*.

Since 2016, the State Geological Institute of Dionýz Štúr (SGIDŠ) has been conducting monitoring of Predajná I and II landfill sites as part of the project Geological

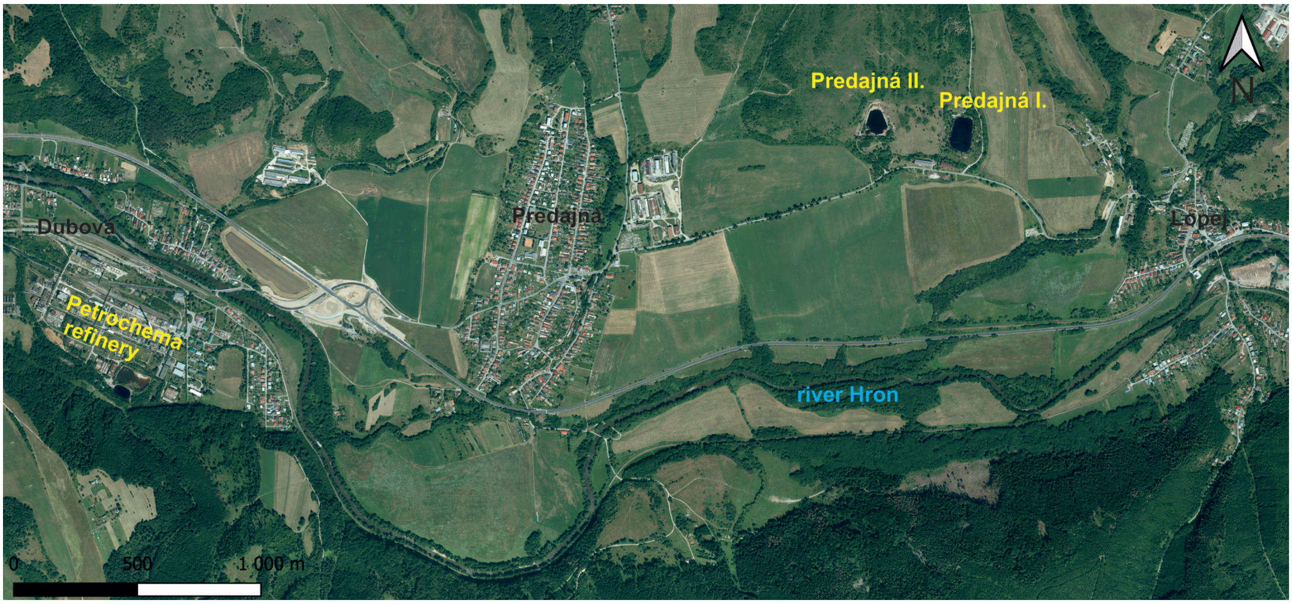


Fig. 1. Location of acid tars lagoons in relation to the municipality of Predajná and former Petrochema Dubová plant

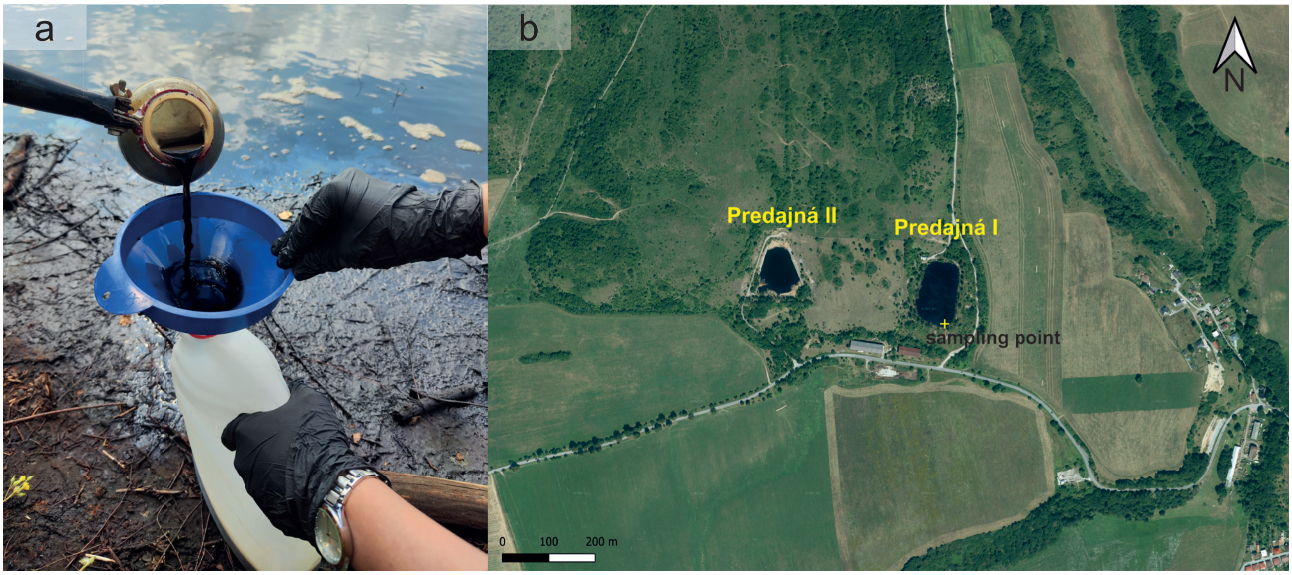


Fig. 2. Sampling of the acid-tar surface water (a), sampling point location (b)

survey of selected environmental burdens in Slovakia (Kordík et al., 2023). Between 2021 and 2023, an additional comprehensive geological survey was carried out at both sites, following up the results of previous works, with the aim of ensuring a detailed survey of both landfills and assessing the risks of these environmental burdens (Adzimová et al., 2023). As part of this survey, surface water samples were collected from the water body present at the Predajná I landfill. This water, representing a mixture of landfill leachate and rainwater, is characterized by a brownish coloration and a pronounced organic or petroleum-like odor. Chemical analyses revealed several characteristic properties (Adzimová et al., 2023). Extremely low pH values (1.0–1.9), high specific electrical conductivity (average 1,710 $mS \cdot m^{-1}$), very high TOC concentrations, reaching up to 5,457 $mg \cdot L^{-1}$ elevated concentrations of metals were confirmed, including Al, Fe, Mn, As, Sb, Cd, and V, along with high sulfate concentrations and high surfactant concentrations reaching (1,130 $mg \cdot L^{-1}$). Significant petroleum-derived substances were identified as NEL UV (614 $mg \cdot L^{-1}$), along with elevated concentrations of dichlorobenzene.

These results confirm that the surface water within the landfill exhibits extreme acidity, a high organic load and elevated levels of both inorganic and organic contaminants, emphasizing the ongoing environmental risks associated with uncontrolled leachate accumulation.

In September 2021, Vodohospodárska výstavba, š. p., State-owned Enterprise, acting under the authority of the Ministry of the Environment of the Slovak Republic, prepared a Technical and Safety Supervision Program for the Dubová water structures, including the Predajná I and II tar lagoons (Kasana et al., 2021). As part of this program, the Slovak Hydrometeorological Institute (SHMÚ) monitors the water levels in both lagoons continuously. In spring 2022, at the Ministry's request, the company deployed a mobile facility to pump and treat top water from Predajná I, representing a critical intervention to reduce immediate environmental risks (TASR, 2022a).

The applied technology combined on-site chemical treatment with subsequent biological treatment at a municipal wastewater treatment plant. Approximately 800,000 liters of highly acidic, tar-contaminated water were successfully removed and treated, temporarily mitigating the risk of dam overflow.

The treatment process involved several sequential steps: extraction of contaminated water by pumping, chemical neutralization and coagulation, separation of generated sludge by flotation and sedimentation, and transfer of pre-treated water to the municipal wastewater treatment plant. The resulting non-hazardous sludge was disposed of at an authorized landfill (TASR, 2022b).

This treatment technology relies on separation processes that remove pollutants from the aqueous matrix without substantial chemical modification. However, the approach inevitably produces waste sludge that must be handled safely or landfilled. The sludge still contains both the extracted contaminants and the chemical agents used to induce precipitation and coagulation. Even after stabilization, such sludge may retain substantial amounts of toxic substances and therefore represents a potential long-term environmental risk.

Advanced electrochemical oxidation

This work focuses on developing a continuous treatment technology for tar-lagoon surface water to reduce the volume of contaminated water and thereby minimize the risk of overflow from containment dams. Given the complexity, toxicity, and persistence of the contaminants present, electrochemical advanced oxidation processes (EAOPs) were selected as the primary treatment method (Chaplin, 2014)

In an electrochemical cell, strong oxidizing agents are generated both at the electrode surfaces and within the bulk solution from species naturally present in the electrolyte. These oxidants include reactive oxygen species (hydroxyl radicals $\bullet OH$, with $E^0 = 2.73$ V), active chlorine species and other highly reactive intermediates formed through the electrolytic decomposition of water molecules or dissolved ions (Ferro et al., 2000). Due to their high oxidative potential, hydroxyl radicals readily attack organic contaminants, facilitating their transformation and ultimately promoting complete mineralization to carbon dioxide and inorganic end products (Martínez-Huitle et al., 2015).

The performance of various electrode materials for electrochemical water treatment has been extensively investigated (Comninellis, 1994; Kraft, 2007; Martínez-Huitle, 2014). In EAOPs, an effective anode material should exhibit a low overpotential for the oxidation of the target pollutant while maintaining a high overpotential for undesired side reactions, thereby minimizing energy losses and maximizing degradation efficiency (Martínez-Huitle et al., 2015; Panizza & Cerisola, 2005). Boron-doped diamond (BDD) is an exceptional electrode material that exhibits the widest electrochemical potential window reported for any known electrode, defined as the potential range that can be applied before the onset of electrolyte oxidation or reduction at the electrode surface (Martínez-Huitle et al., 2015).

Electrochemical treatment enables the degradation and mineralization of organic contaminants without the addition of chemical reagents, as oxidation reactions are driven solely by electrical energy. Consequently, electrochemical processes are widely regarded as environmentally friendly technologies, with the electron itself functioning as a clean, safe, and highly efficient reagent (Comninellis, 1994; Comninellis et al., 2014; Comninellis et al., 2008; Muff, 2014).

Materials and Methods

Sampling

A surface-water sample was collected in June 2025 by point sampling near the shoreline from the upper water layer formed within the landfill lagoon Predajná I (Fig. 2a, b). The water level in the lagoon was stirred and mixed over a range of approximately 5 m to ensure a homogeneous sample collection as much as possible. The composition of the surface water in the lagoon varies throughout the year in response to seasonal factors. Thus, the sample collected for laboratory-scale experiments represents the composition of surface water in the summer, or warmer period. Sampling was conducted with permission and under the supervision of a Petrochema refinery officer. Field parameters, including temperature, pH, oxidation-reduction potential (ORP), and electrical conductivity (EC), were measured in situ using calibrated portable instruments in accordance with standard field sampling protocols (STN-ISO-5667-4 2018).

Chemical analyses

Total organic carbon (TOC) in both the untreated and electrochemically treated samples was determined by the combustion method using a Vario TOC Cube analyzer (Analysensysteme GmbH, Germany).

Chemical oxygen demand (COD_{Cr}) was determined using LCK400 test kits (Hach Lange GmbH). Samples were digested with a solution of $K_2Cr_2O_7$ and H_2SO_4 at 150 °C for 120 min. COD concentrations were subsequently measured using a Hach Lange DR 3900 spectrometer.

Anion and cation concentrations were determined by ion chromatography using a Dionex ICS-5000 system (Thermo Fisher Scientific, Sunnyvale, CA, USA) equipped with electrolytic eluent generators, suppressed conductivity detection, and UV detection.

Metal and metalloid concentrations were analyzed using flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS; Varian AA240FS and AA240Z).

Polycyclic aromatic hydrocarbons (PAHs) were extracted from 20 mL water samples using CHROMABOND® Easy solid-phase extraction (SPE) columns (Macherey-Nagel). The analytes were eluted sequentially with 2 mL of methanol followed by 2 mL of acetone. The combined eluates were evaporated by nitrogen gas stream, and the resulting residue was reconstituted in acetonitrile prior to chromatographic analysis. Quantitative and qualitative analyses of PAHs were performed using a Dionex UltiMate 3000 RS liquid chromatograph (Thermo Fisher Scientific) equipped with a diode array detector (DAD 3000-RS) and a fluorescence detector (FLD 3400-RS). HPLC separation was achieved on a Nucleosil 100-5 C18 PAH column (250 × 3 mm, 5 µm, 100 Å; Macherey-Nagel).

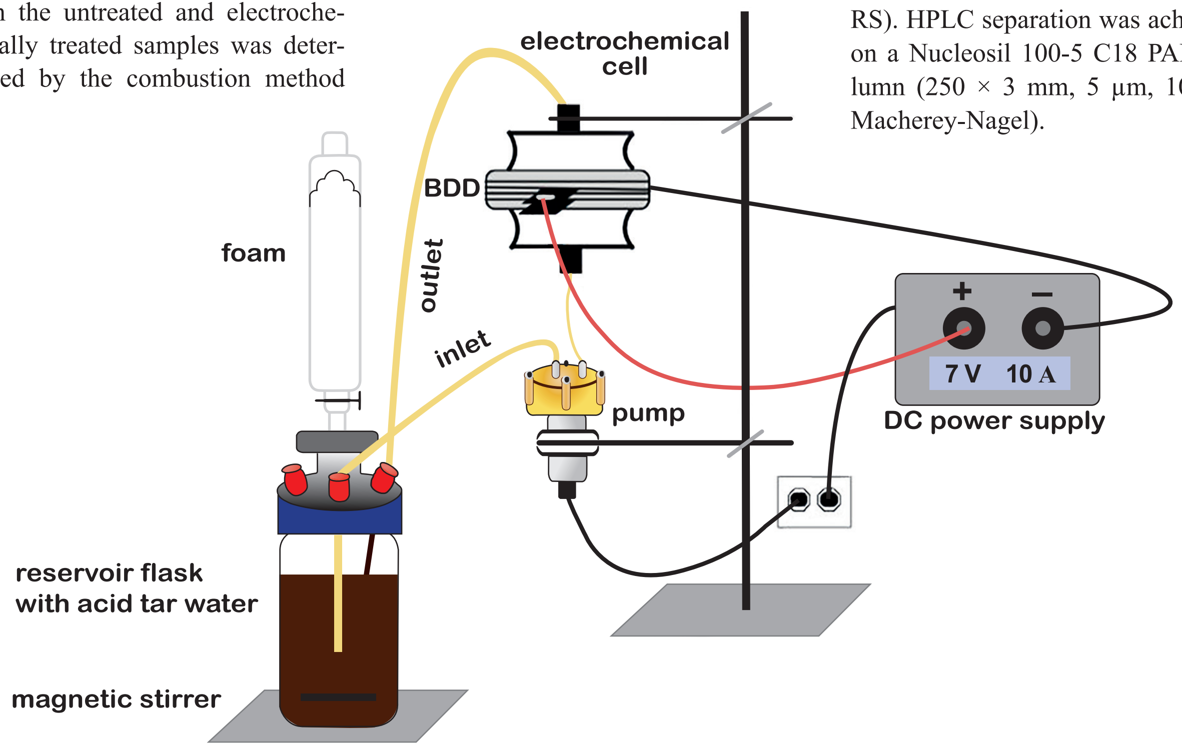


Fig. 3. Schematic representation of the experimental setup used for electrochemical treatment

Additional organic compounds were analyzed using a Bruker Q-TOF Compact mass spectrometer (Bruker Daltonics GmbH, Germany), either by direct injection or following SPE and ultra-high-performance liquid chromatography (UHPLC) separation.

Electrochemical treatment

Electrochemical treatment was carried out in batch mode with continuous recirculation of wastewater through the electrochemical reactor (Fig. 3). Wastewater was pumped upward from a thermostated reservoir through the non-divided electrochemical cell and subsequently returned to the reservoir, forming a closed-loop system. The reactor consisted of a four-electrode stack comprising two BDD anodes and two BDD cathodes arranged alternately. Each electrode was circular, with a diameter of 5 cm, corresponding to a geometric surface area of 19.635 cm^2. Wastewater flowed directly through the electrode apertures and inter-electrode gaps, maximizing fluid-electrode contact and enhancing mass transfer efficiency. The process was conducted at a constant temperature of 25 °C, and a flow rate of 3 L·min^{-1}. The system was powered by a regulated DC supply operating under galvanostatic control, with real-time monitoring of current and voltage via an ammeter and voltmeter. Laboratory tests were performed in accordance with the experimental conditions specified in Table 1.

Tab. 1

Experimental conditions for laboratory tests

Name of the test	**Time** [h]	**Voltage** [V]	**Current** [A]
T-01	4	6	10
T-02	7	9	12

Tab. 2

Selected chemical parameters of surface water sampled from the Predajná I lagoon

COD [mg.L^{-1}]	**TOC** [mg.L^{-1}]	**pH**	**Na^+** [mg.L^{-1}]	**NH_4^+** [mg.L^{-1}]	**K^+** [mg.L^{-1}]	**Mg^{2+}** [mg.L^{-1}]	**Ca^{2+}** [mg.L^{-1}]	**Cl^-** [mg.L^{-1}]	**SO_4^{2-}** [mg.L^{-1}]	**NO_2^-** [mg.L^{-1}]	**NO_3^-** [mg.L^{-1}]
19,300	5,588	1.04	125.6	19.53	25.65	170.3	175.9	34.8	8,133	0.32	3.87

Tab. 3

Concentrations of metals and metalloids in surface water from the Predajná I lagoon

Fe [mg.L^{-1}]	**Al** [mg.L^{-1}]	**Mn** [mg.L^{-1}]	**Zn** [mg.L^{-1}]	**Cu** [mg.L^{-1}]	**Pb** [μg.L^{-1}]	**Cr** [μg.L^{-1}]	**As** [μg.L^{-1}]	**Ni** [μg.L^{-1}]	**Sb** [μg.L^{-1}]	**Co** [μg.L^{-1}]	**Cd** [μg.L^{-1}]
72.4	37.1	2.13	1.70	1.22	446.3	221	82.3	69.7	54.8	16.4	5.60

Tab. 4

Concentrations of polycyclic aromatic hydrocarbons (PAHs) in Predajná I lagoon surface water: native sample, sample after 4 h of electrochemical treatment at 10 A, and after 7 h at 12 A. Indication (ID) and intervention (IT) criteria according the Directive of the Ministry of the Environment of the Slovak Republic 1/2015-7.Values represent mean ± standard deviation (SD), calculated from four independent experimental measurements (n = 4).

Sample		**Fluorene**	**Phenanthrene**	**Fluoranthene**	**Pyrene**	**Chrysene**
	unit	[μg.L^{-1}]	[μg.L^{-1}]	[μg.L^{-1}]	[μg.L^{-1}]	[μg.L^{-1}]
Native sample	average	4.53	**81.73**	4.35	19.75	**12.01**
	SD	0.87	5.55	0.33	0.13	1.19
After 4 h	average	0.95	8.70	0.50	0.50	**0.35**
	SD	0.07	0.42	0.00	0.00	0.07
After 7 h	average	0.55	3.70	0.25	0.15	0.15
	SD	0.07	0.57	0.07	0.07	0.21
ID		–	5	25	25	0.1
IT		**–**	**10**	**50**	**50**	0.2

Results

Surface water collected from the Predajná I lagoon, consisting of a mixture of landfill leachate and rainwater, exhibited a brownish coloration and a pronounced petroleum-like odor. The analytical results for the sampled water are summarized in Tables 2–4.

Electrochemical treatment of the surface water sample was carried out by continuous recirculation through the reactor using the experimental setup shown in Fig. 4. This configuration ensured multiple passes and repeated contact of the wastewater with the electrode surfaces. The electrodes were stable under both anodic and cathodic conditions, allowing periodic polarity reversal during each experimental run. For each experiment, 0.5 L of real wastewater was recirculated through the electrolytic cell using a pump operating at a constant flow rate of 3 L·min^{-1}. During electrochemical treatment, pronounced foam formation was observed, resulting from the high concentration of alkyl sulfonate surfactants present in the water (Fig. 4b). Foaming was most intense during the initial stage of the process, and gradually diminished with prolonged electrolysis as the surface-active compounds were progressively degraded and removed from the solution.

Hydroxyl radicals, generated at the anode are among the strongest oxidizing species known after fluorine and are widely employed in EAOPs for water treatment (Martínez-Huitle et al., 2015). These radicals react non-selectively with organic compounds in "R" aqueous media through hydroxylation, dehydrogenation, and electron-transfer mechanisms, resulting in the cleavage of aromatic rings, rupture of C–C bonds, and ultimately complete mineralization to CO_2 and inorganic products.

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD}(\bullet\mathrm{OH}) + \mathrm{H}_+ + e^- \qquad [1]$$

$$\mathrm{BDD}(\bullet\mathrm{OH}) + \mathrm{R} \rightarrow \mathrm{BDD} + \text{mineralization products} + e^- \qquad [2]$$

Parameters such as TOC and COD are commonly used as group indicators to evaluate the overall organic load in wastewater, particularly for complex matrices with unknown composition. During electrochemical treatment at applied currents of 10 A and 12 A, both COD and TOC exhibited progressive decreases, indicating efficient oxidation of organic compounds (Figs. 5a, b). In the initial two hours of treatment, COD declined almost linearly, reflecting a current-limited regime in which the rate of organic oxidation is controlled primarily by the applied

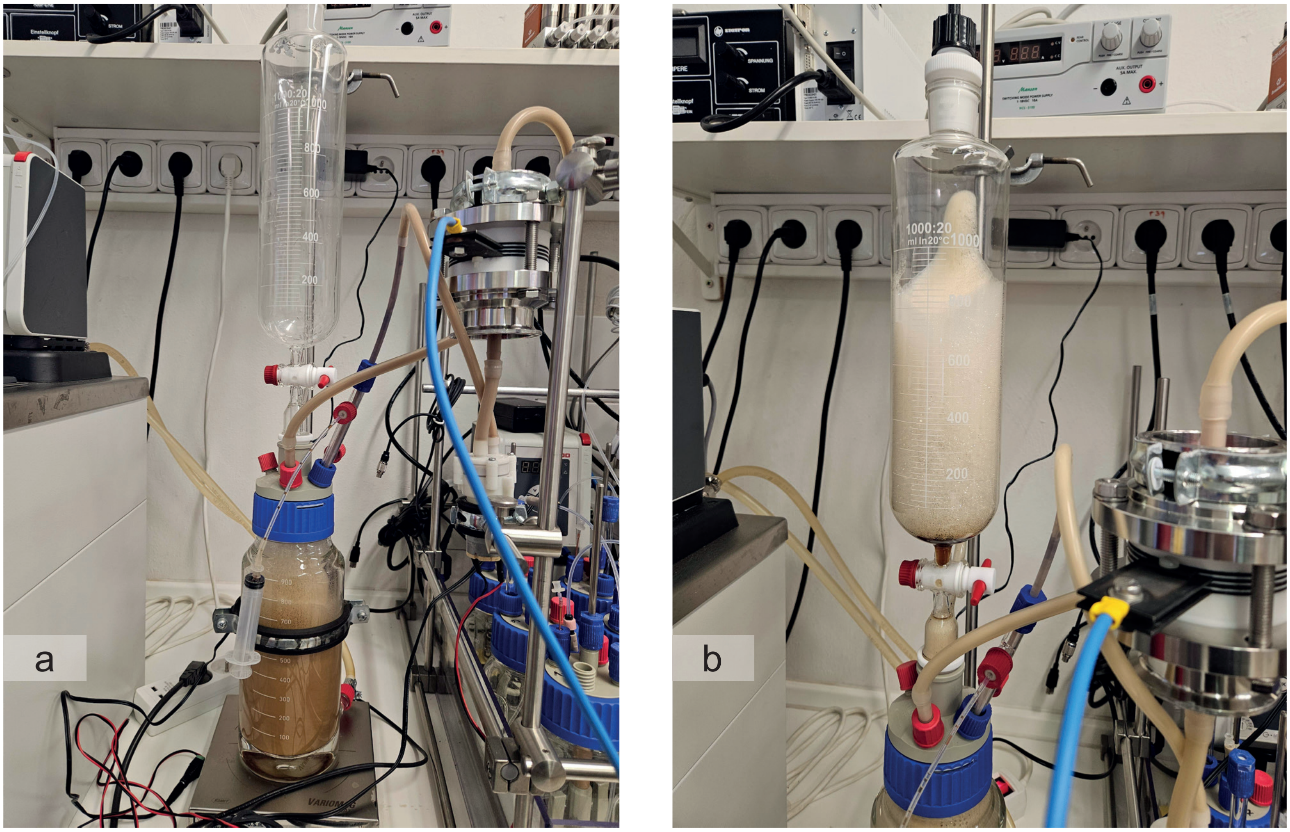


Fig. 4. Experimental setup for the electrochemical treatment (a). Foam formation observed during electrochemical treatment (b).

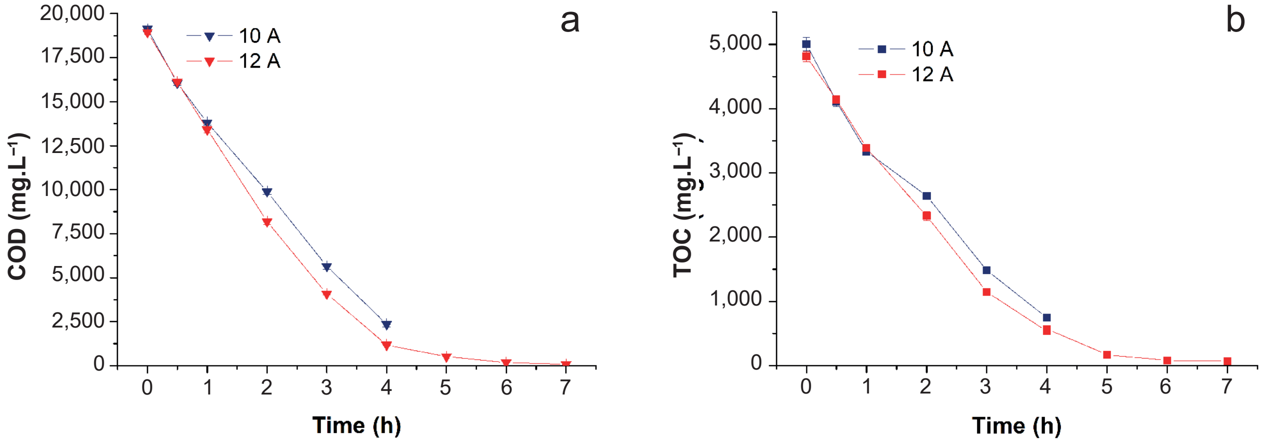


Fig. 5. Time evolution of (a) chemical oxygen demand (COD) and (b) total organic carbon (TOC) during electrochemical treatment at applied currents of 10 A and 12 A

current rather than mass transport. The COD degradation rates were 5,300 mg·L^{-1}·h^{-1}, and 5,500 mg·L^{-1}·h^{-1}, at 10 A and 12 A, respectively, with the instantaneous current efficiencies of approximately 90 % and 80 % (Fig. 6a). These results highlight the high effectiveness of BDD-based electrochemical oxidation for mineralizing organic pollutants, with slightly reduced efficiency at higher applied current due to enhanced side reactions.

In the subsequent stage, the degradation rates of both COD and TOC slowed, indicating the onset of mass transfer limitations as the concentration of readily oxidizable organic compounds declined and their transport to the electrode surface became the rate-limiting factor. After four hours of treatment, COD and TOC parameters were reduced by 87.7 % and 85.1 % at 10 A and by 93.9 % and 88.7 % and at 12 A, respectively, demonstrating the strong influence of applied current on degradation rates.

The electrochemical treatment also achieved substantial elimination of polycyclic aromatic hydrocarbons, with fluorene reduced by 79 % at 10 A and 88 % at 12 A, and other PAHs showing 90–99 % decreases (Tab. 4). Residual concentrations of monitored PAHs were generally below the indication criteria (ID) established by the Directive of the Ministry of the Environment of the Slovak Republic 1/2015-7, with the exception of chrysene, which remained at 0.15 µg.L^{-1}. These results indicate that EAOPs not only oxidize bulk organic matter, as reflected in COD and TOC removal, but also generate highly reactive radicals capable of breaking down recalcitrant and toxic compounds such as PAHs.

An important factor influencing the kinetics of electrochemical reactions is the transport of target compounds to the electrode surface, where the reactions take place. Current efficiency (CE) and specific energy consumption (EC) are key performance indicators for evaluating the effectiveness of electrochemical treatment processes for COD removal. CE reflects the fraction of the applied electrical current that is effectively utilized for target contaminant oxidation, while EC represents the electrical energy required per unit mass of COD removed (Muff, 2014). High CE values are generally associated with selective oxidation pathways (Zöllig et al., 2017) and limited parasitic reactions, whereas increased EC often indicates energy losses due to side reactions such as oxygen evolution (Panizza et al., 2008). Optimizing operating conditions to maximize CE while minimizing EC is therefore essential for improving the overall energy efficiency and practical feasibility of electrochemical COD removal.

Numerous studies (Aquino et al., 2014; Fóti et al., 1999; Panizza & Cerisola, 2005; Rodrigo et al., 2001; Xing et al., 2018) have reported near-complete mineralization of organic pollutants with current efficiencies approaching theoretical maxima under conditions where mass transport is not limiting. However, as electrochemical treatment progresses and organic concentrations decline, the instantaneous current efficiency (ICE) generally diminishes due to mass transport limitations and the increasing contribution of side reactions, such as oxygen and chlorine evolution (Kapałka et al., 2010). Under such conditions, diffusion of residual organics to the electrode surface becomes rate-limiting, and the probability of charge consumption in non-productive processes increases (Figs. 6a, b).

The instantaneous current efficiency (ICE) can be defined as the part of the current directly used for the oxidation of organic compounds. ICE during electrolysis can be performed from the decrease of COD by the means of the following eq. 3 (Muff, 2014; Panizza & Cerisola, 2009; Tsantaki et al., 2012):

$$\mathrm{ICE} = FV\,\frac{\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t}}{8I\,\Delta t} \qquad [3]$$

where F is the Faraday constant (96,487 C $\mathrm{mol^{-1}}$) V is the treated volume ($\mathrm{m^3}$), I is the applied current (A), t is the treatment time (h), COD is the chemical oxygen demand ($\mathrm{kg{\cdot}m^{-3}}$).

The specific energy consumption (EC), expressed as kWh per kg of COD removed, was calculated according to the following eq. 4:

$$\mathrm{EC} = \frac{UIt}{(\mathrm{COD}_0 - \mathrm{COD})\,V} \qquad [4]$$

where U is the average cell voltage (V), I is the applied current (A), t is the treatment time (h), COD is the chemical oxygen demand ($\mathrm{kg{\cdot}m^{-3}}$), and V is the treated volume ($\mathrm{m^3}$).

In aqueous solutions containing chlorides and sulfates, which are commonly present in natural waters and wastewaters, additional indirect oxidation pathways can occur. Chloride ions can be anodically converted into hypochlorous species, which act as secondary oxidants with relatively long lifetimes in solution. During treatment with BDD anodes, hypochlorite can be further oxidized to chlorate and perchlorate. Notably, BDD anodes exhibit a perchlorate formation potential that is approximately three orders of magnitude higher than that of other electrode materials tested (Bergmann et al., 2015; Kupka et al., 2017).

Sulfate may be electrochemically activated to sulfate radicals ($\mathrm{SO_4{\bullet}^-}$) and subsequently generate persulfate ($\mathrm{S_2O_8^{2-}}$) under certain current densities (Saha et al., 2022; Zuo et al., 2023). The formation of such highly oxidized species can enhance pollutant degradation (Saien & Jafari, 2022) but also contributes to anodic charge consumption that does not directly mineralize the target compounds, further reducing ICE at advanced treatment stages.

Sulfonated compounds constitute a major fraction of acid tars, including sulfonic acids and other sulfonated organic molecules such as aromatic sulfonates, sulfonated phenols, and thiophenes. Polyaromatic and heteroaromatic sulfonates are primarily formed during petroleum refining, where concentrated sulfuric acid reacts with unsaturated hydrocarbons, aromatic compounds and heterocycles (Speight, 2014). This sulfonation reaction introduces the sulfonic acid functional group ($\mathrm{-SO_3H}$) into the organic molecules, producing stable sulfonated compounds that are resistant to conventional chemical or biological degradation (Lin et al., 1999; Martins et al., 2011).

During electrochemical treatment, sulfonated compounds undergo oxidative cleavage by radicals generated at the anode, breaking the C–S bonds and releasing sulfate ions ($\mathrm{SO_4^{2-}}$) into the solution (dos Santos et al., 2024; Lai et al., 2025; Lu et al., 2022).

The formation of sulfate reflects the mineralization of sulfonated organics and serves as a direct indicator of the treatment efficiency for this class of persistent pollutants. Sulfate concentrations increased steadily during the first three hours of treatment (Fig. 7a), confirming the progressive degradation of sulfonated compounds and the effective conversion of these highly stable organosulfur species into inorganic products. After three hours, the sulfate concentration in the electrolyte reached a plateau, indicating that the bulk of the sulfonated compounds had been destroyed. In the subsequent phase, a slight decrease in sulfate concentration was observed, likely due to its further conversion into persulfates under the strongly oxidizing conditions within the reactor. The ability to mineralize sulfonated compounds is particularly significant, as these

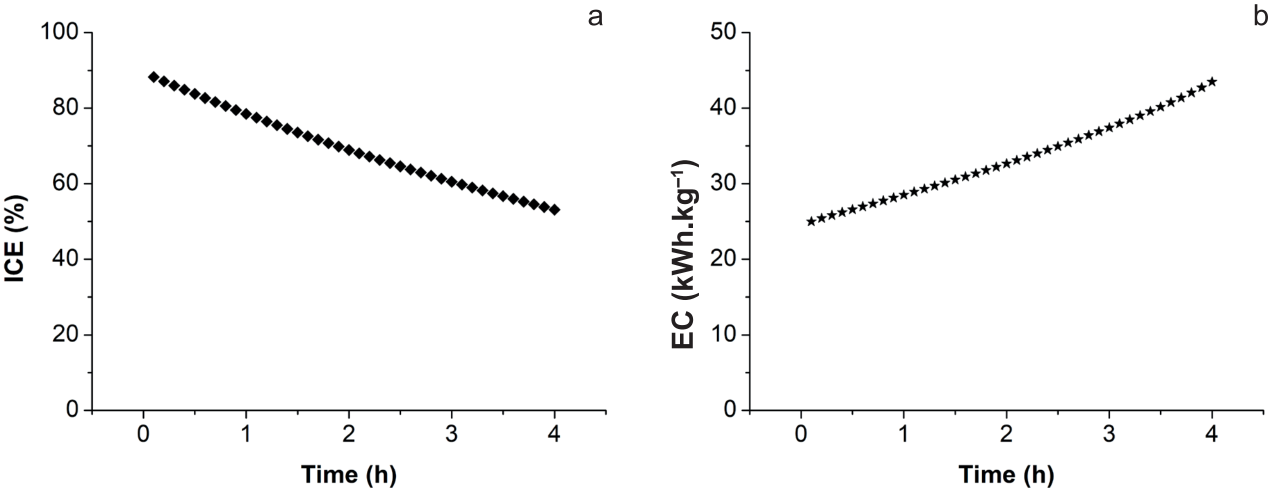


Fig. 6. Time evolution of (a) instantaneous current efficiency and (b) specific energy consumption (kWh per kg of COD removed) during electrochemical treatment of wastewater at an applied current of 10 A.

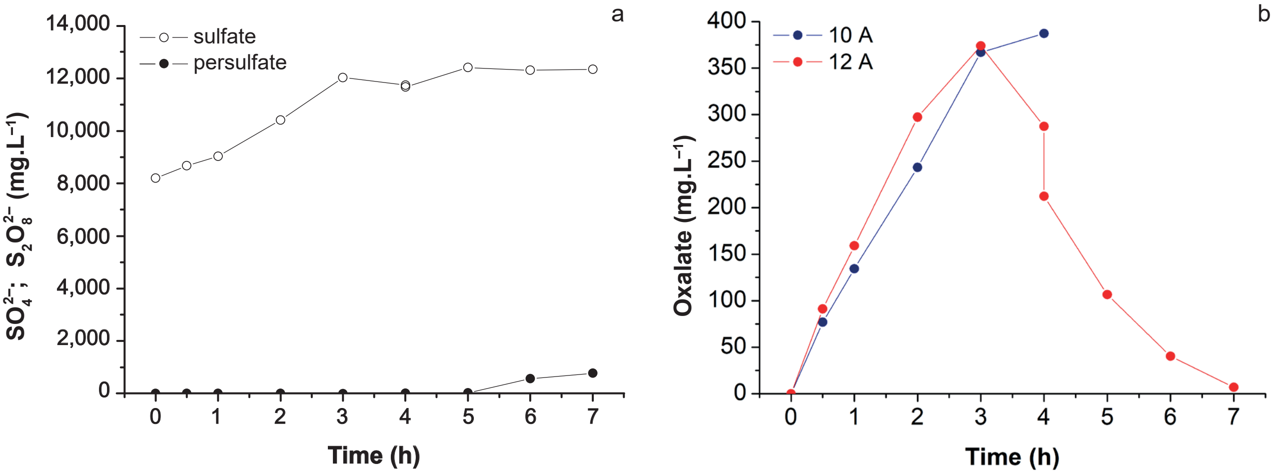


Fig. 7. Time evolution of (a) sulfate and persulfate anion concentrations during electrochemical treatment at an applied current of 12 A, and (b) oxalate concentration during electrochemical treatment at applied currents of 10 A and 12 A.

species are otherwise resistant to conventional wastewater treatment, highlighting the advantage of electrochemical advanced oxidation processes for the remediation of acid tar-contaminated water.

EAOPs can attain complete mineralization of contaminants to CO_2 given sufficient contact time, during which strong oxidants are continuously generated at non-active anodes (Panizza et al., 2008). The oxidation of aromatic compounds tends to yield short-chain carboxylic acids that are non-toxic and can easily be biodegraded (Brillas et al., 2000). Figure 6b illustrates the concentration profile of oxalate during electrochemical treatment. During the first three hours, oxalate concentration increased reaching a maximum of approximately 375 mg·L^{-1}, indicating its accumulation in the electrolyte. Oxalic acid is frequently observed as the main and final intermediate for the catalytic and electrochemical oxidation of a wide range of organic compounds (Martínez-Huitle et al., 2004; Scialdone et al., 2009a; Scialdone et al., 2009b).

Oxalic acid (HOOC–COOH) is a low-molecular-weight dicarboxylic acid that commonly forms as an intermediate during the oxidative degradation of complex organic matter, including carbohydrates, lignin, humic substances, and petroleum-derived organics. Its formation is observed in both biological and chemical oxidation processes (Gadd et al., 2014).

During the oxidative breakdown of complex organics, such as phenolic compounds, aromatic hydrocarbons and sulfonated organics, oxalic acid is relatively stable due to its small molecular size and resistance to mild chemical oxidation. Consequently, it often accumulates transiently in advanced oxidation treatment systems, including ozonation, photocatalysis, Fenton oxidation, and electrochemical advanced oxidation processes (Nakagawa & Yamaguchi, 2012). Oxalate is frequently observed as the final intermediate during anodic oxidation of a wide range of organic compounds on DSA electrodes (Scialdone et al., 2009a).

If the electrooxidation process is maintained for a sufficient duration, oxalate is further oxidized to carbon dioxide and water, achieving complete mineralization. This is evidenced by the gradual decrease in oxalate concentration observed after more than three hours of treatment at 12 A (Fig. 7b). In aqueous media, oxalic acid can also combine with cations such as sodium, calcium, magnesium, ferrous iron, or potassium to form oxalate salts, which are sparingly soluble. The combined trends in COD, TOC, PAHs, sulfate, and oxalate demonstrate the effectiveness of BDD-based electrochemical advanced oxidation in achieving near-complete mineralization of complex organic pollutants in acid tar-contaminated waters.

Conclusions

Acid-tar lagoons from historical Petrochema refinery operations represent a persistent environmental hazard due to the accumulation of highly acidic, organic- and metal-rich leachates. Surface water from the Predajná I landfill exhibited extreme acidity, elevated TOC and COD, as well as high concentrations of sulfate, metals, and sulfonated organics, confirming the ongoing environmental risks associated with uncontrolled leachate accumulation.

Previous immediate mitigation via on-site chemical neutralization and coagulation successfully removed a substantial fraction of contaminants from the aqueous phase, producing stabilized sludge for safe disposal (Vodohospodársky podnik, š. p.). However, such type of sludge still contains toxic substances and represents hazardous waste. Therefore, this approach does not achieve complete mineralization and generates secondary waste that requires careful handling.

Electrochemical advanced oxidation using BDD electrodes proved highly effective for the mineralization of complex and persistent organic compounds in lagoon water. Laboratory tests showed a reduction in total organic carbon and chemical oxygen demand of 88.7 % and 94 %, respectively, after four hours of electrolysis, and 98.5 % and 99.6 %, after seven hours, respectively. The strong correlation between bulk organic load reduction and PAH degradation suggests that EAOPs can effectively target complex mixtures of dissolved organics, combining generalized oxidation with effective destruction of persistent pollutants.

Sulfonated compounds were efficiently converted to sulfate, while oxalate, formed as an intermediate, was further oxidized to CO_2 and water during extended treatment. The observed trends in TOC, COD, sulfate, and oxalate provide insights into reaction kinetics, mass transport limitations, and intermediate dynamics, highlighting the ability of BDD-based EAOPs to overcome the limitations of conventional chemical treatments. Overall, electrochemical treatment represents an essentially waste-free and environmentally friendly approach for the continuous remediation of contaminated lagoon water, offering a safer and more sustainable alternative to conventional physicochemical methods. Pilot experiments will be the subject of further study. It is potentially possible to consider some flow-through or batch systems using alternative energy sources directly on site, without the need for electricity.

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Stručný prehľad histórie a charakteristika lokality Predajná, kontaminovanej kyslým dechtom, a potenciálne využitie elektrochemickej oxidácie na sanáciu povrchovej vody z otvorených lagún

Kyslé gudrónové smoly sú odpad, ktorý vznikal pri spracovaní ropných frakcií a rafinácii recyklovaných ropných produktov kyselinou sírovou. V areáli bývalého podniku Petrochema Dubová a na súvisiacich skládkach Predajná I a II sa tento odpad ukladal na miesta bez adekvátneho technického zabezpečenia. Skládky gudrónov patria medzi najzávažnejšie environmentálne záťaže, spojené s chemickým priemyslom 20. storočia. Kyslé gudrónové smoly sa vyznačujú vysokou koncentráciou kyseliny sírovej, tenzidov, polycyklických aromatických uhľovodíkov, sulfonovaných organických látok a kovov. V dôsledku atmosférických zrážok sa na povrchu lagún vytvorila silne kyslá vodná fáza obohatená o sulfáty a organické látky, ktorá predstavuje dlhodobý zdroj kontaminácie okolitého prostredia.

Skládky Predajná I a II sa nachádzajú v oblasti s karbonátovým podložím tvoreným dolomitmi a dolomitickými vápencami a sú situované v ochrannom pásme Národného parku Nízke Tatry. Absencia potrebnej izolácie umožnila infiltráciu kontaminovaných výluhov do horninového prostredia a podzemnej vody, čo sa potvrdilo geologickým prieskumom. Sezónne kolísanie hladiny povrchovej vody v lagúnach v závislosti od zrážok a topenia snehu zvyšuje riziko pretečenia hrádzí a šírenia kontaminácie do okolitého prostredia. Tieto aspekty poukazujú na potrebu výskumu účinných sanačných opatrení, zameraných predovšetkým na bezpečné a dlhodobo udržateľné nakladanie s takto kontaminovanou vodnou fázou.

Predmetom tohto článku bolo posúdenie potenciálnej aplikácie a účinnosti elektrochemickej pokročilej oxidačnej metódy založenej na aplikácii elektród z diamantu dopovaného bórom (BDD) na dekontamináciu povrchovej vody z lagúny Predajná I. Experimenty sa realizovali vo vsádzkovom režime s recirkuláciou. Odpadová voda sa zo zásobnej temperovanej nádoby čerpala obehovým čerpadlom do externého okruhu s prietokovým elektrochemickým reaktorom a následne sa vracala späť do zásobnej nádoby. Táto konfigurácia umožňovala kontinuálny prietok odpadovej vody cez reaktor a opakovaný kontakt s povrchom elektród. Výsledky laboratórnych testov preukázali vysokú účinnosť procesu. V priebehu štyroch hodín elektrolýzy sa znížila koncentrácia celkového organického uhlíka (TOC) a hodnota chemickej spotreby kyslíka ($CHSK_{Cr}$) o 88,7 %, resp. 94 % a po siedmich hodinách elektrolýzy o 98,5 %, resp. 99,6 %.

V procese elektrochemickej oxidácie sa štiepili sulfonované organické zlúčeniny a následne sa uvoľňovali sírany. Ako stabilný medziprodukt bol identifikovaný oxalát, ktorý sa pri dlhšom čase pôsobenia elektrochemicky generovaných oxidačných činidiel ďalej mineralizoval na oxid uhličitý a vodu. Ďalšie produkty rozpadu zložitých chemických zlúčenín stále podliehajú laboratórnym testom. Dosiaľ dosiahnuté výsledky potvrdzujú, že elektrochemická oxidácia s využitím elektród z BDD predstavuje perspektívny, environmentálne prijateľný a bezodpadový spôsob využiteľný na sanácie silne kontaminovanej vody aj v gudrónových lagúnach. Na rozdiel od konvenčných chemicko-fyzikálnych postupov, táto technológia umožňuje vysoký stupeň degradácie perzistentných organických látok bez vzniku sekundárneho nebezpečného odpadu. Elektrochemické pokročilé oxidačné prístupy by tak mohli prichádzať do úvahy ako súčasť komplexných sanačných prístupov pri riešení tejto environmentálnej záťaže na Slovensku.

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