A Staged Electrochemical–Cold Stabilization Strategy for Urban Fountain Water

Process Optimization, COD Reduction and Statistical Risk Stabilization

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Abstract

Urban fountain water is a low- to moderate-strength urban water matrix characterized by continuous recirculation, partial stagnation, atmospheric deposition and episodic biological inputs. Conventional maintenance practices, including chlorination, filtration and periodic refilling, can improve visible water quality but may not adequately control organic-load variability or avoid secondary chemical impacts. This study presents a staged treatment strategy combining controlled electrochemical oxidation with a subsequent temperature-driven stabilization phase. Electrochemical processing was performed in a batch system equipped with a boron-doped diamond (BDD) anode and a Ti/Pt cathode. The selected operational window was 6 V, 8.86 mA cm^{-2} and 15 min, with potassium iodide used as a conductivity-supporting additive and PVC evaluated as an auxiliary exploratory process material. The staged process decreased chemical oxygen demand (COD) from 45 to 11.65 mg L^{-1}, corresponding to a 74.2% reduction. A complementary statistical risk indicator, defined to account for both threshold exceedance probability and variability, decreased from 15.50 to 1.50, corresponding to a 90.3% reduction. The results indicate that deliberate process termination and low-energy post-treatment stabilization can improve both pollutant removal and operational reliability. The method is proposed as a practical and scalable concept for urban fountain water management, while further work should quantify microbial dynamics, possible by-products, microplastic release and full-scale energy demand.

Keywords: fountain water; electrochemical oxidation; boron-doped diamond; COD; potassium iodide; PVC; statistical risk; urban water management

1. Introduction

Urban fountains occupy an intermediate position between engineered recirculating water systems and open environmental water bodies. Their water quality is influenced by recirculation, intermittent stagnation, dust deposition, leaves, bird droppings, biofilm development and human activity. Although the organic load of fountain water is usually lower than that of municipal wastewater, its variability can cause aesthetic deterioration, odor formation, microbial proliferation and operational instability. Similar urban blue-space systems have been discussed as relevant to public health and urban well-being, provided that water-quality risks are properly controlled (Grellier et al., 2017).

Standard maintenance strategies include chlorination, mechanical filtration, algicide addition and periodic draining. These approaches are simple and widely used, but they may provide only short-term control of visible contamination. Chlorination can also generate disinfection by-products, while repeated draining increases water consumption. For urban fountain systems, the objective is therefore not only average organic-load reduction but also stable operation with low variability and limited chemical addition (Ale, 2009; Chowdhury et al., 2020).

Electrochemical advanced oxidation processes are attractive for this type of problem because oxidizing species can be generated in situ from the treated water matrix. In anodic oxidation using BDD electrodes, weakly adsorbed hydroxyl radicals and other reactive species can oxidize a broad range of organic compounds. BDD is particularly useful because of its high oxygen-evolution overpotential, chemical stability and strong oxidative capacity (Fernandes et al., 2016; Oliveira da Mota et al., 2015). Recent reviews emphasize the relevance of current density, electrode material, supporting electrolyte, mass transfer and energy demand when translating laboratory treatments to real water systems (Camacho-Cruz et al., 2020; Das et al., 2024).

Most electrochemical studies target highly contaminated industrial effluents, landfill leachates or pharmaceutical wastewater. In contrast, urban fountain water is a lower-strength matrix where overtreatment may be counterproductive. Excessive electrochemical exposure can increase energy use, promote secondary reactions or destabilize the measured COD profile. This makes controlled process termination a central design principle (Mollah et al., 2001; Prasetyaningrum et al., 2019).

The present study therefore proposes a staged strategy: electrochemical oxidation is first applied under a limited operational window and is then deliberately terminated, after which a low-temperature stabilization phase is used as a polishing step. The post-treatment stage is described here as temperature-driven stabilization rather than as a fully characterized biological treatment stage, because direct microbial community sequencing, ATP quantification or psychrophilic activity assays were not performed. This conservative wording reflects the experimental evidence available, while acknowledging that cold-adapted microbial systems can be relevant to low-temperature remediation contexts (Li et al., 2024; Prieto-Fernández et al., 2024).

The work addresses three practical questions: (i) whether a controlled electrochemical window can reduce COD in fountain water; (ii) whether a staged approach can reduce variability-associated risk; and (iii) which limitations must be considered before scale-up, especially regarding KI, PVC, energy demand and possible by-products.

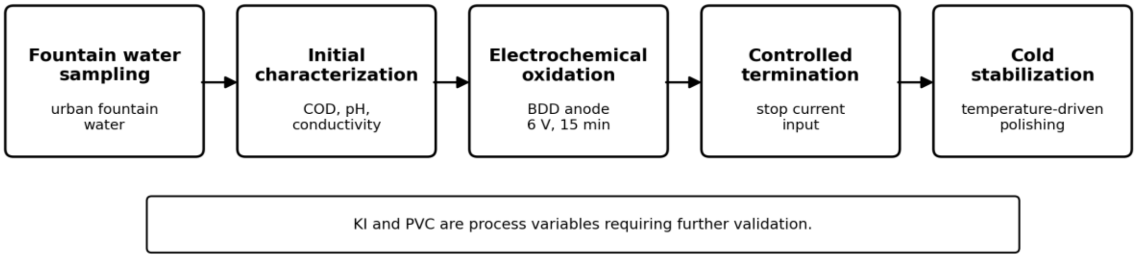

Figure 1. Clean process-flow schematic for the staged treatment strategy. The figure separates measured operations from interpretive limitations and avoids treating the cold stage as a fully proven biological process.

2. Materials and Methods

2.1 Water sampling and initial characterization

Water samples were collected from an operational urban fountain located in Northern Greece. The system is representative of small urban recirculating water features exposed to atmospheric deposition, biological debris and intermittent stagnation. Sampling followed a triplicate protocol using three one-liter samples collected under comparable operational conditions. COD was selected as the primary organic-load indicator because it integrates dissolved and suspended oxidizable matter and is widely used for non-specific organic contamination in water and wastewater analysis (Bazrafshan et al., 2013; Geerdink et al., 2017). Additional descriptors included pH, temperature, electrical conductivity, salinity, total dissolved solids and oxidation-reduction potential.

2.2 Electrochemical reactor and operational window

Electrochemical treatment was carried out in a batch reactor equipped with a BDD anode and a titanium/platinum cathode. A direct-current power supply was used to regulate the applied voltage and current density. Preliminary screening of voltage, current density and treatment duration indicated that COD removal did not improve monotonically with increasing treatment intensity. Instead, a limited operational window was required to obtain COD reduction without destabilizing the system. The selected operating condition was 6 V, 8.86 mA cm^{-2} and 15 min. This condition was retained as the core treatment window because it achieved the strongest combination of COD reduction, limited exposure time and acceptable process stability.

Parameter	Revised value / description	Purpose in the study
Water matrix	Urban fountain water, Northern Greece	Low-strength recirculating urban water
Sampling	Three one-liter samples	Representative physicochemical assessment
Anode	Boron-doped diamond (BDD)	Generation of strong oxidizing species
Cathode	Ti/Pt	Electrochemical counter-electrode
Applied voltage	6 V	Selected operational window
Current density	8.86 mA cm^{-2}	Selected operational window
Treatment duration	15 min	Controlled termination point
KI addition	1.5 g initial addition; additional 3 g tested	Conductivity support; concentration effect assessed
PVC	Auxiliary exploratory material; not retained as final water component	Interfacial/process-effect exploration
Post-treatment stage	Low-temperature stabilization phase	Polishing and variability stabilization
Microbial measurements	Not directly measured	Limitation explicitly stated

Table 1. Experimental and interpretive parameters included in the revised manuscript.

2.3 Role of potassium iodide

Potassium iodide was added to support conductivity and charge transfer during electrochemical oxidation. The initial addition was 1.5 g, while additional KI was explored to evaluate whether higher electrolyte loading improved the process. The results indicated concentration-dependent behavior: moderate addition supported treatment, whereas excessive addition or prolonged electrochemical exposure in the presence of KI was associated with lower efficiency or greater variability. The inhibitory effect is therefore described operationally, based on COD response and variability, rather than as a fully resolved mechanistic toxicological effect. Because iodide can participate in electrochemical oxidation chemistry, future work should quantify iodine species and iodinated by-products (Verwold et al., 2021).

2.4 Role of PVC

PVC was evaluated as an auxiliary process material during the electrochemical stage. It is not proposed as a standard water-treatment reagent, a target pollutant or a permanent component of treated water. Its role is interpreted conservatively as exploratory and interfacial. Because no microplastic-release test, polymer-mass balance or polymer-aging analysis was performed, the revised discussion treats PVC as a limitation requiring further validation before any field-scale application.

2.5 Cold stabilization phase

After electrochemical treatment, electrical input was terminated and the water entered a low-temperature stabilization phase. In the revised manuscript, the term “cold biological treatment” has been replaced or qualified as “temperature-driven post-treatment stabilization” unless explicitly discussed as a hypothesis. This avoids overclaiming because ATP, microbial-load measurements, psychrophilic activity assays and community sequencing were not performed. The stabilization phase is interpreted as a combined physicochemical and potential biological equilibration step.

2.6 Energy-demand estimate

Specific energy consumption was estimated from the standard expression E ($kWh\ m^{-3}$) = ($U \times I \times t$) / Vtreated, where U is the applied voltage, I is current, t is treatment time in hours and Vtreated is treated volume in cubic meters. Because the original records report current density but not a fully standardized active electrode area for scale-up, the manuscript reports a transparent normalized estimate. For example, assuming 8.86 $mA\ cm^{-2}$, 10 cm^2 effective electrode area, 6 V, 15 min and 1 L treated volume, the specific energy demand is approximately 0.133 $kWh\ m^{-3}$. This value should be treated as a preliminary laboratory-scale estimate, not a final engineering value.

3. Results and Discussion

3.1 COD reduction

The initial COD of the fountain water was 45 $mg\ L^{-1}$. After the selected electrochemical window and subsequent stabilization, COD decreased to 11.65 $mg\ L^{-1}$. This corresponds to a 74.2% reduction, demonstrating that short electrochemical exposure combined with stabilization can reduce organic load in a low-strength urban water matrix. The result is consistent with the broader use of electrochemical oxidation for organic-load removal, while the low-strength matrix and short treatment time distinguish the present application from typical wastewater-focused studies (Fernandes et al., 2016; Camacho-Cruz et al., 2020).

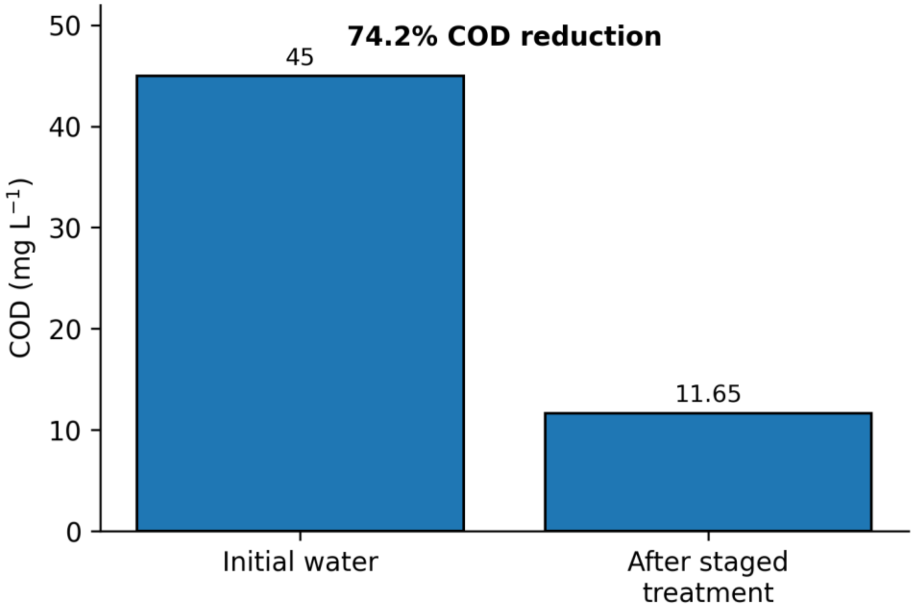

Figure 2. COD before and after the staged treatment strategy.

3.2 Statistical risk stabilization

Mean COD reduction alone does not fully describe fountain-water performance because short-term fluctuations can create operational and aesthetic problems. The revised manuscript therefore retains the statistical risk indicator as a complementary metric. The indicator combines threshold-exceedance probability with COD variability, following the general principle that risk assessment should combine probability and consequence rather than rely only on mean values (Ale, 2009). Under the staged treatment, the risk indicator decreased from 15.50 to 1.50, equivalent to a 90.3% reduction. Entropy- and distribution-based measures have previously been used to describe uncertainty and divergence in environmental datasets, supporting the use of complementary variability descriptors when conventional averages are insufficient (Lin, 1991; Charles et al., 2022).

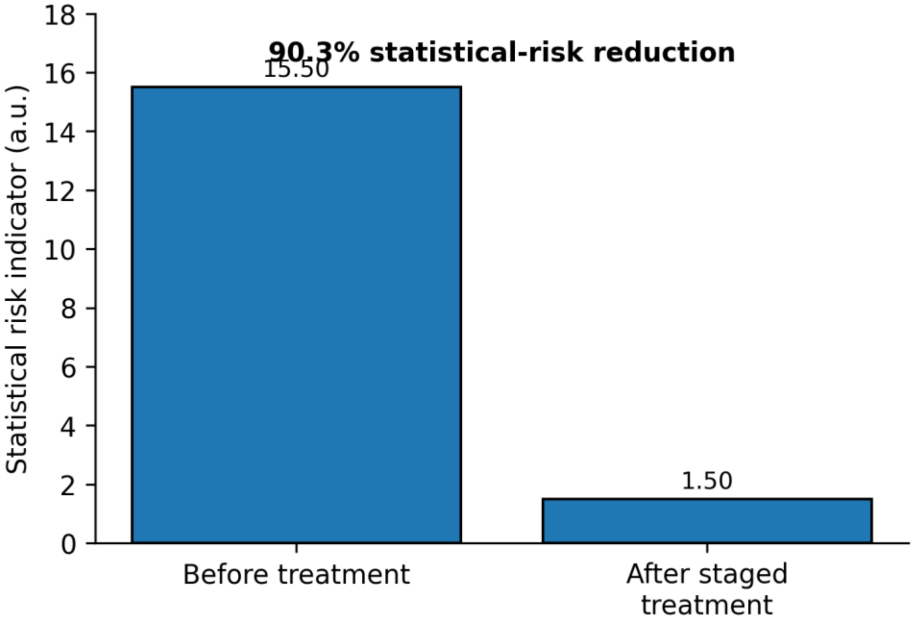

Figure 3. Reduction in variability-associated statistical risk after treatment.

3.3 Importance of controlled termination

A key interpretation of the dataset is that more electrochemical exposure is not necessarily better. In the thesis dataset, prolonged electrochemical exposure under non-optimal conditions was associated with strong COD increases, including reported values of 918 mg L^{-1} after 45 min and 528 mg L^{-1} after 90 min in one destabilized experiment. These data support the decision to emphasize a short, controlled 15 min treatment window rather than continuous intensification. The same practical warning has been highlighted in electrochemical treatment literature, where voltage, current density, pH, supporting electrolyte and treatment time can shift a process from beneficial oxidation to inefficient or secondary chemistry (Mollah et al., 2001; Prasetyaningrum et al., 2019).

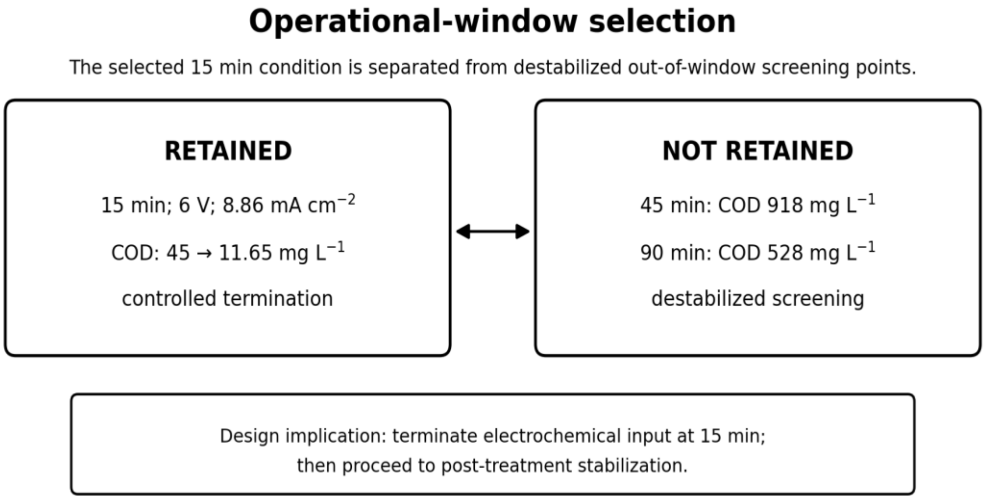

Figure 4. Clean operational-window decision figure. The retained 15 min condition is separated from later out-of-window screening observations to prevent overinterpretation as a normal time-response curve.

3.4 Mechanistic interpretation

The primary COD decrease is attributed to BDD-mediated electrochemical oxidation. At the BDD anode, water oxidation can generate weakly adsorbed hydroxyl radicals and other reactive oxygen species, which can attack oxidizable organic matter. KI may improve conductivity and participate in iodine-mediated oxidative pathways, but it also introduces the possibility of reactive iodine species and iodinated by-products. Therefore, KI is retained as an optimization variable and not presented as a universally beneficial additive (Oliveira da Mota et al., 2015; Verwold et al., 2021).

PVC is discussed as an exploratory auxiliary material. Its use may influence interfacial interactions, but the revised manuscript avoids presenting PVC as a proven adsorbent or standard treatment reagent. Additional controls are necessary to determine whether PVC releases particles or degradation products under electrochemical conditions.

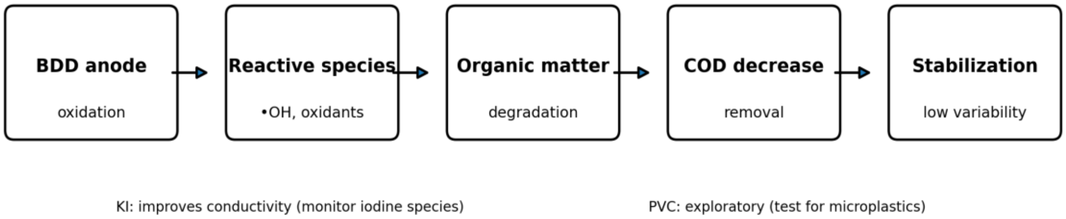

Figure 5. Conservative mechanistic scheme for the BDD/KI/PVC treatment interpretation.

3.5 Comparison with hybrid and conventional methods

Approach	Strength	Limitation relative to fountain-water use
Chlorination	Low cost and familiar operation	Possible disinfection by-products; limited COD-focused stabilization
Mechanical filtration	Simple particulate removal	Limited effect on dissolved organics
Electro-Fenton + biological treatment	Strong oxidation and biodegradability improvement	More complex reagent/pH control
BDD + UV	High oxidative capacity	Higher energy and equipment demand
Present staged BDD + cold stabilization	Short treatment time, COD reduction, variability stabilization	Needs by-product, microbial and scale-up validation

Table 2. Practical comparison of the revised treatment strategy with conventional and hybrid options.

Hybrid methods such as electro-Fenton, biological polishing and BDD-based advanced oxidation can provide high removal efficiency, but they often require additional operational control or higher energy input (Mumtaz et al., 2024). The present approach is therefore positioned as a low-complexity concept for small urban water features rather than as a replacement for intensive industrial wastewater treatment.

3.6 By-products, safety and limitations

The presence of iodide requires explicit by-product consideration. Electrochemical oxidation of iodide can generate active iodine species, and in natural organic matter-containing waters this may increase the relevance of iodinated disinfection by-products. The present study did not quantify iodate, periodate, total iodine species or iodinated organic by-products; therefore, the revised manuscript identifies these analyses as required before field implementation (Verwold et al., 2021). Possible chlorine or mixed oxidant formation also depends on the chloride content of the water matrix. Because the fountain-water ionic composition was not fully resolved for by-product prediction, future work should include chloride, iodide/iodate speciation and adsorbable organic iodine screening.

The PVC component is also a limitation. Before any practical deployment, the material must be assessed for mass loss, surface degradation and potential microplastic release. This revision therefore reframes PVC as a research variable rather than a recommended operational material.

4. Practical relevance and scale-up considerations

The practical contribution of the method is not only COD reduction but also the demonstration that low-strength urban water may benefit from limited electrochemical exposure followed by stabilization. This design principle could reduce energy use compared with prolonged advanced oxidation while avoiding routine chemical overdosing. The preliminary normalized energy estimate of approximately 0.133 kWh m^{-3} under assumed 1 L and 10 cm^2 conditions suggests that the process may be compatible with small fountain systems. However, this value must be experimentally remeasured at pilot scale using recorded current, electrode area, hydraulic residence time, electrode spacing and real recirculation flow.

Scale-up should prioritize modular treatment loops installed in the fountain recirculation line rather than one-time batch treatment. A practical pilot should monitor COD, TOC, pH, conductivity, ORP, temperature, microbial indicators, iodine species, possible chlorine species and particle release from any auxiliary material.

5. Conclusion and future research

This revised manuscript presents a staged electrochemical–cold stabilization strategy for urban fountain water. Under the selected 6 V, 8.86 mA cm^{-2} and 15 min operational window, COD decreased from 45 to 11.65 mg L^{-1}, corresponding to a 74.2% reduction. The complementary statistical risk indicator decreased by 90.3%, supporting the value of variability control in addition to mean COD removal.

The revised interpretation is intentionally conservative. The post-treatment stage is described as temperature-driven stabilization rather than as a fully proven biological process, because direct microbial activity data were not obtained. KI and PVC are also treated as optimization and limitation variables rather than as fully validated field reagents.

Future work should include microbial-load and ATP measurements, 16S rRNA sequencing or comparable community analysis, iodine and chlorine by-product monitoring, microplastic-release testing, TOC measurement, pilot-scale energy quantification in kWh m^{-3} and long-term recirculation trials under real fountain operation. These additions would convert the present laboratory concept into a stronger field-ready treatment protocol.

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