

Synergistic treatment of chloride and mine-impacted water using ultraviolet/hydrogen peroxide

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Abstract: Paper presents the preliminary concept of salinity reduction in mine water by advanced chloride ions oxidation. New methods and technologies of salinity reduction are crucial in the context of mine water management strategies. These strategies are now the area of concern of coal mining entrepreneurs responsible for saline discharges into environment, which should be significantly reduced or eliminated to meet legal requirements. The study presents the effectiveness of standalone ultraviolet/hydrogen peroxide (UV/H₂O₂, no iron catalysts) as a robust, simpler alternative to complex, multi-stage hybrid systems, e.g., ultraviolet/persulphate (UV/PS) or photo-Fenton) in real, high-salinity mine water. Contrary to the assumption that chloride strictly inhibits oxidation, findings indicate that at high salinity, UV/H₂O₂ maintains high organic degradation efficiency (above 90% in complex matrices). While UV/PS can achieve higher removal in some cases (e.g., up to 99% for chlorinated contaminants at 600 mJ·cm⁻²), UV/H₂O₂ is highlighted as more environmentally sustainable, as persulphate production contributes a larger environmental footprint than H₂O₂. The advanced chloride ion elimination method is a promising solution for mitigating the impact of saline water on water resources generated by coal mining during the transition period. This approach utilises UV/H₂O₂ for direct photolysis and hydroxyl radical (•OH) oxidation, with results showing high efficiency (>90% degradation) on recalcitrant organic contaminants even in complex matrices, demonstrating its effectiveness against chloride inhibition.

Keywords: advanced oxidation processes (AOPs), chloride ions, mine water, mine water management, salinity reduction, ultraviolet/hydrogen peroxide (UV/H₂O₂)

INTRODUCTION

Underground coal mining necessitates the dewatering of pits and the discharge of saline mine waters into the environment, which can exert pressure on surface waters in terms of both quantitative and qualitative parameters (Janson, 2024). A significant impact is the pollution of river water and the increase in salinity-causing compounds, including chloride ions (Cl⁻). Concentrations of chloride ions in mine waters directly relate to depth of exploitation and dewatering levels. Rózkowski (2000) reports a marked increase in water mineralisation with depth in the Upper Silesian Coal Basin (USCB, Pol.: Górnośląskie Zagłębie Węglowe). This pattern results from vertical hydrogeochemical zoning and reduced exchange between deep and infiltrating waters under natural conditions. Mining operations and intensive

dewatering have significantly disrupted this system. The expansion of mining workings has increased hydraulic connectivity between aquifers, promoting migration and mixing of waters with different mineralisation levels. Nevertheless, the overall trend of increasing salinity with depth persists. In Polish USCB chloride concentrations range from 1 g Cl⁻·dm⁻³ to 140 g Cl⁻·dm⁻³ (mineralisation range from 2 g·dm⁻³ to 230 g·dm⁻³) on depths of dewatering 300–1,250 m below ground level respectively.

Quantity of mine water in Polish coal mines range from 0.5–78 m³·min⁻¹, therefore the discharges of these loads of chlorides may reach 5,500 Mg·day⁻¹ which affects the chemical status of surface water bodies in the Upper Silesia, with electrolytic conductivity (EC) up to 4,000 μS·cm⁻¹ in the water downstream (Janson, Gzyl and Banks, 2009). Due to legislative requirements (Ustawa, 2017) and tightening of regulations in the

future – EC of river waters defined as good status must meet the limit of $690 \mu\text{S}\cdot\text{cm}^{-1}$, management of saline mine waters requires new advanced methods of reduction chlorides in mine waters, while discharges without treatment may be no longer possible. Existing methods of reducing chloride ion concentration (reverse osmosis) are characterised by high electricity consumption, carbon dioxide emissions, and generation of waste concentrates. Advanced oxidation processes (AOPs) represent promising strategies for reducing harmful substances, including chlorides (Asefon, 2025). In particular, the combination of ultraviolet (UV) light and hydrogen peroxide (UV/H₂O₂) can potentially reduce chlorides from mining waters with relatively lower energy demand. Nevertheless, this solution has not been implemented at an industrial scale, limiting the ability to compare its energy demand with mature technologies such as desalination or reverse osmosis.

Although the UV/H₂O₂ process in AOPs has been extensively studied for the removal of various pollutants, a research gap remains in the systematic study of chloride reduction from mine water using only hydrogen peroxide and UV light.

Studies published between 2007 and 2025 (according to the Scopus database) on the use of H₂O₂ for salinity reduction have primarily addressed the Fenton process and its modifications (Filice *et al.*, 2022; Ma *et al.*, 2022; Yang *et al.*, 2025). In contrast, other works (Yoon *et al.*, 2023; Loreti Hupsel *et al.*, 2024; Wu *et al.*, 2024; Lan *et al.*, 2025) have examined H₂O₂ or UV/H₂O₂ as a preliminary treatment of mine water or as a part of hybrid systems, but never as a standalone process. It is worth to add that Lan *et al.* (2025) provide a computational approach to optimising systems, while Yoon *et al.* (2023) provides a biological approach to isolating microbes. In this context, the novelty of this work lies in the direct application of UV/H₂O₂ for the potential reduction of chlorides from mine-impacted water as a standalone process.

Most researchers have focused on entirely different water matrices (or only on deionised water alone), as well as on other types of pollutants. Most studies omit the specific composition of wastewater and focus on generating oxidising radicals to remove usually single contaminants. Hence, a key aspect of this work is the utilisation of the specific composition of mine water, characterised by a high chloride ion concentration, to generate oxidising radicals, such as $\bullet\text{Cl}$, $\bullet\text{Cl}_2^-$ and $\bullet\text{ClOH}^-$.

MATERIALS AND METHODS

This conceptual study demonstrates the potential applicability of UV/H₂O₂ as an alternative to currently used reverse osmosis (RO), electrodialysis (ED), multiple effect distillation (MED) or multi-stage flash distillation (MSF).

The salinity of mine water from underground coal mines is mainly related to chloride ions. Noteworthy is the fact that highly saline mine waters are dominated by chloride ions with a low proportion of other interfering ions. In drained coal mining areas in Poland, there is a general tendency for water mineralisation to increase with depth, with the composition of anions evolving along a sequence typical of the Silesian coalfields: $\text{HCO}_3^- \rightarrow \text{SO}_4^{2-} \rightarrow \text{Cl}^-$ (Janson, Gzyl and Banks, 2009). The idea presented in this paper is to exploit the properties of saline mine waters rich in chloride ions toward using these ions to generate

oxidising radicals such as $\bullet\text{Cl}$, $\bullet\text{Cl}_2^-$ and $\bullet\text{ClOH}^-$ (Djaballah *et al.*, 2023), with simultaneous reduction of chloride concentrations in mine waters.

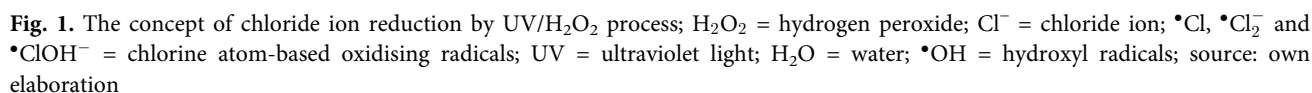
RESULTS AND DISCUSSION

IMPLICATIONS

Chloride ions play a key role in advanced oxidation reactions, although they are considered as interfering ions. Hence, in Advanced oxidation processes (AOPs), interfering ions such as NO_2^- , NO_3^- , CO_3^{2-} and Cl^- are avoided or removed from purified solutions. Interfering ions can impair the oxidation process, causing, for example, the absorption of radiation (required to activate catalysts) or reacting with oxidising radicals, such as hydroxyl or sulphate radicals, thereby producing less reactive species (Zhao *et al.*, 2025). Advanced oxidation processes are widely used in the degradation of organic matter, but there is a limited amount of research on their application to the removal of chloride from saline industrial wastewater. The redox potential of Cl_2/Cl^- is 1.36 V. Advanced oxidation processes can produce highly reactive $\bullet\text{OH}$ with a redox potential of 2.8 V (Haynes, 2016; Wang *et al.*, 2024). Therefore, they can also ensure sufficient redox potential for Cl^- oxidation. Besides generating the $\bullet\text{OH}$ radicals, these techniques can also directly oxidise Cl^- via O_3 , electron transfer, and $\bullet\text{SO}_4^-$ radicals. The NaOH solution can absorb the post-process gas (Cl_2). Alternative methods for absorbing Cl_2 in industrial practice include lime, which can be used depending on the desired end products. The Cl_2 neutralisation system must address both safety requirements and absorption efficiency. For safety reasons, the process must be sealed, properly ventilated, and constructed with chemically resistant components. Continuous monitoring of parameters such as pH, oxidation-reduction potential, and chlorine gas detector is required. The absorption system should be designed to achieve an efficiency greater than 99.9%. Oxidising radicals have a short half-life ($t_{1/2}$), so they should not have a significant negative impact on the environment. For example, the $t_{1/2}$ of the $\bullet\text{SO}_4^-$ radical is equal of $3.0\cdot 10^{-5}$ – $4.0\cdot 10^{-6}$ s, while that of the $\bullet\text{OH}$ radical is equal of $2.0\cdot 10^{-8}$ s. The $t_{1/2}$ of other radicals is shorter at 10^{-9} – 10^{-4} s (Zhu *et al.*, 2019).

A conceptual framework for the elimination of chloride ions in advanced UV-hydrogen peroxide (H₂O₂) oxidation is shown in Figure 1. The radical generation occurs through the activation of H₂O₂ by a UV lamp ($\lambda = 254 \text{ nm}$). This wavelength corresponds to the maximum absorption of H₂O₂ (Parsa, Dhib and Mehrvar, 2024). The standard mechanism of radical generation follows Equations (1)–(4) – Table 1. During the UV/H₂O₂ process, the photolytic decomposition of each H₂O₂ molecule generates two $\bullet\text{OH}$ radicals.

The theoretical mechanism for Cl^- reduction in the UV/H₂O₂ process, as illustrated in Figure 2, involves a series of reactions in the presence of Cl^- ions described in Equations (5)–(11) (Jayson, Parsons and Swallow, 1973; Haag and Hoigné, 1985; Kläning and Wolff, 1985; Glaze, Kang and Chapin, 1987; Buxton *et al.*, 1988; Neta, Huie and Ross, 1988; Nowell and Hoigné, 1992; Hoigné, 1997; Yu, Bao and Barker, 2004). The kinetic rate constants presented here are based on conditions in dilute aqueous solutions (typically at 25°C and at low ionic



Reaction	Rate constant (M ⁻¹ .s ⁻¹)	Equation No.
$\text{H}_2\text{O}_2 \xrightarrow{\text{h}\nu} 2\bullet\text{OH}$	ΦI_o	(1)
$\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2^\bullet + \text{H}_2\text{O}$	$2.7 \cdot 10^7$	(2)
$\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2^\bullet + \text{H}_2\text{O}$	$7.5 \cdot 10^9$	(3)
$\text{H}_2\text{O}_2 \leftrightarrow \text{H}^+ + \text{HO}_2^-$	–	(4)
$\bullet\text{OH} + \text{Cl}^- \rightarrow \bullet\text{ClOH}^-$	$4.3 \cdot 10^9$	(5)
$\bullet\text{ClOH}^- + \text{H}^+ \rightarrow \bullet\text{Cl} + \text{H}_2\text{O}$	$2.1 \cdot 10^{10}$	(6)
$\bullet\text{Cl} + \text{OH}^- \rightarrow \bullet\text{ClOH}^-$	$1.8 \cdot 10^{10}$	(7)
$\bullet\text{Cl} + \text{H}_2\text{O} \rightarrow \bullet\text{ClOH}^- + \text{H}^+$	$2.5 \cdot 10^5$	(8)
$\bullet\text{ClOH}^- \rightarrow \text{Cl}^- + \bullet\text{OH}$	$6.1 \cdot 10^9$	(9)
$\bullet\text{Cl} + \text{Cl}^- \rightarrow \bullet\text{Cl}_2^-$	$1.4 \cdot 10^5$	(10)
$\bullet\text{Cl}_2^- + \bullet\text{Cl}_2^- \rightarrow 2\text{Cl}^- + \text{Cl}_2$	$9.0 \cdot 10^8$	(11)

strength). In systems with high salt concentrations, actual reaction rates may differ from the reported values due to ionic strength, activity, and changes in the radical species. Initially, Cl^- ion competes with other reactive species, mainly with the

Literature data indicate a slight or negligible effect of Cl^- ions on the efficiency of the oxidation process, i.e., their presence does not adversely affect the kinetics of the oxidation reaction of pollutants. Kudlek, Dudziak and Bohdziewicz (2016) showed that the effect of chloride ions on oxidation efficiency in photocatalysis with titanium (IV) oxide is lower compared, for example, to CO_3^{2-} , HCO_3^- , and SO_4^{2-} ions. Zhang *et al.* (2024) indicated the negligible effect of chloride ions in the $\text{UV}/\text{H}_2\text{O}_2$ process. Ecer Uzun and Kabdaşlı (2024) proved that the presence of chloride ions can accelerate the mineralisation of some contaminants. Xiong *et al.* (2024) demonstrated the conversion of Cl^- ions into chlorine radicals by the electro-Fenton process. A study by Hu *et al.* (2021) revealed the essence of the reduction of Cl^- ions through the prior formation of $\bullet\text{Cl}$ i $\bullet\text{Cl}_2^-$ radicals. Yang *et al.* (2023) found that in the $\text{UV}/\text{H}_2\text{O}_2$, the presence of Cl^- ions promote the mineralisation of contaminants (total organic carbon, TOC), and above $\text{pH} = 5$, the rate of TOC removal increases. While pH of minewaters is mostly circumneutral (6.5–7.3) due to the presence of Triassic rocks in the USCB overburden which are buffering zone for acidic mine waters during flooding of the excavations or dewatering deeper Carboniferous strata where waters pH range from 5.3–6.0 and chlorides concentrations up to $100 \text{ g}\cdot\text{dm}^{-3}$ (Janson, Gzyl and Banks, 2009). Therefore, the sensitivity of the process on the pH range is relatively low. The $\text{UV}/\text{H}_2\text{O}_2$ advanced oxidation process promoted TOC removal and was effective even at Cl^- concentrations up to about $71 \text{ g}\cdot\text{dm}^{-3}$.

The potential reduction of Cl^- ions can be roughly compared to the theoretical reduction of Cl^- using sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$), as described by Dou *et al.* (2023). The

cited paper provides a mechanistic analogy rather than a direct confirmation of the expected efficacy of UV/H₂O₂. At high salinity, reactions involving •OH and •SO₄[−] radicals partially convert primary oxidising radicals into chlorine radicals. This transformation underpins the mechanistic analogy. The above-mentioned work is based on the concept of generating another strong radical – a sulphate radical (•SO₄[−]), with a redox potential of 2.5–3.1 V. Since the redox potential of the •SO₄[−] radical exceeds that of Cl₂/Cl[−], the theoretical reduction of Cl[−] is possible. The application of Na₂S₂O₈ oxidation was further validated by Hu *et al.* (2021). An efficiency of approximately 96% was achieved in the reduction of Cl[−] ions, with the remaining Cl[−] measured at a level of 0.158 g·dm^{−3}. This result demonstrates the significant role of •Cl and •Cl₂[−] radicals in Cl[−] reduction. However, a potential limitation of the above method may be the risk of secondary contamination with sulphates if reagent overdose or incomplete reaction occurs. In contrast, the UV/H₂O₂ concept utilises hydrogen peroxide, an environmentally friendly reagent that decomposes into hydrogen and oxygen atoms (Zhao *et al.*, 2021). In this approach, the thermodynamic threshold for the theoretical oxidation of Cl[−] to •Cl and •Cl₂[−] radicals are also exceeded in the case of the •OH radical ($E^0_{(•OH/H_2O)} = 2.8$ V). The theoretical chloride reduction efficiency is expected to be comparable to that reported by Hu *et al.* (2021), as both processes involve a similar radical mechanism. Simulating chlorate formation within high total dissolved solids (TDS) mine water environments indicate significant byproduct risks, particularly when employing aggressive disinfection (chlorine dioxide) or when high chloride levels are present in water treatment processes. Mine water often exhibits high sulphate and chloride concentrations (brackish, >1,000 mg·dm^{−3} TDS), which, when coupled with pH adjustment (lime), increases the risk of scaling and byproducts (Levanov *et al.*, 2019).

PROCESS COMPARISON

The overall environmental benefits of the UV/H₂O₂ method can be summarised as follows: limited generation of waste concentrate; the possibility of controlling H₂O₂ doses based on Cl[−] concentration; limited secondary pollution of the treated wastewater.

In contrast to the reverse osmosis (RO), the conceptual UV/H₂O₂ method does not generate waste concentrate. Such concentrate is typically classified as hazardous waste, which increases overall operational costs. The composition of mine water can fluctuate, affecting the efficiency of separation. In the physical separation process, it is crucial to select a technology suitable for the specific and stable composition of mine water. The UV/H₂O₂ process allows for precise control of reagent dosage for varying Cl[−] concentrations, which is a significant advantage of the process. The UV/H₂O₂ method uses UV light and H₂O₂; therefore, it does not contribute to secondary pollution of the treated wastewater, e.g., compared to the ultraviolet/persulphate (UV/PS) method.

Given that this approach presents a conceptual framework, detailed investigations into the potential formation of by-products should be carried out. In general, the minimised formation of reaction by-products is key advantage of AOPs (Silva, 2025); however, this benefit is typically realised only under precisely selected and controlled reaction conditions. Guan *et al.* (2020) demonstrated that no bromate or chlorate was detected in

UV/H₂O₂ system, in contrast to PS-based AOPs (ultraviolet/peroxydisulphate – UV/PDS and ultraviolet/peroxymonosulphate – UV/PMS). Furthermore, due to the greater number of reaction mechanisms in UV/PS compared to UV/H₂O₂, the probability of generating by-products is greater in the former (Zhang *et al.*, 2018). Effective control of oxidation by-products generation requires careful consideration of H₂O₂ dosage (mg·dm^{−3} or g·dm^{−3}), UV lamp power (W), UV dose (mJ·cm^{−2}), reaction time (min or h), and the influence of other interfering ions (Zhang, Sun and Yin, 2025). Operational monitoring of byproducts, including ClO₃[−] and ClO₄[−], typically involves both online monitoring (e.g., pH, oxidation-reduction potential, electrolytic conductivity – EC, UV₂₅₄, and free chlorine), as well as offline laboratory testing.

Currently, comparing the energy efficiency of the UV/H₂O₂ system with other commercial technologies remains challenging. However, specific technological components that affect electricity consumption can be compared. The UV/H₂O₂ system does not require large capacity reactors or batch-type mixers to achieve optimal contact between mine water and hydrogen peroxide. In practice, this is achieved with static mixers, which require no energy input, contain no moving parts, and are straightforward to maintain. In contrast to RO, the UV/H₂O₂ system does not use high-pressure pumps, which in highly saline waters significantly reduce energy efficiency. Electrical energy consumption is approximately 9 kWh·m^{−3} for RO, 6 kWh·m^{−3} for multi-stage flash distillation (MSF), and up to 3 kWh·m^{−3} for multiple effect distillation (MED). The UV/H₂O₂ system also does not require thermal energy, as is necessary in MSF and MED, which substantially reduces operational costs. For example, thermal energy consumption in MSF can reach approximately 20 kWh·m^{−3}, while in MED it is about 9 kWh·m^{−3} (Thi and Tóth, 2023). Basically, H₂O₂ activation occurs under the influence of an effective radiation dose from UV emitters. The effective radiation dose from UV emitters depends on factors such as the absorbance water and chemical composition of the water. The influence of these factors is typically evaluated through preliminary studies and requires pilot studies.

CONCLUSIONS

The use of advanced oxidation processes (AOPs) for potential salinity reduction in mine water is a promising alternative to conventional methods, such as reverse osmosis, electrodialysis, and thermal processes. This approach therefore warrants further investigation through laboratory-scale trials. The conceptual model facilitates understanding of the quantitative balance and conversion of Cl[−] in saline mine waters, as well as the associated risk of oxidation by-products formation. Perspective studies should focus on quantifying the fraction of Cl[−] that passes into the solid product with priority to batch kinetics on real mine water.

A comparative analysis of methods using H₂O₂ and persulphates will elucidate the relative reactivity of •OH and •SO₄[−] radical in highly saline mine waters. The proposed method offers practical potential for reducing chloride concentrations in saline mine waters and other chloride-rich environmental matrices. Advanced oxidation processes have been intensively developed in recent years. A promising technological direction involves integrating AOPs with renewable energy-driven electro-

lysis of mine water and green hydrogen production, thereby improving the economic efficiency and self-sufficiency of treatment plants. Comparing the concept between AOPs and conventional desalination processes, as well as robust estimation of by-products quantity, are further research challenges. Further in-depth development of the research should focus on enhancing the water environment in the context of the Water Framework Directive (WFD), as well as the increasing pressure on water resources associated with climate change, long-term droughts, and increasing salinity of surface waters. Mine-impacted rivers (surface water bodies), according to the WFD and the Polish Water Act Law, have established environmental goals in Water Management Plans that should be fulfilled and met by 2027. In these plans, in general, relevant requirements for the salinity of surface waters are stated as electrolytic conductivity (EC). In near future, the limits on industrial and mining discharges will be significantly decreased. The implementation of the proposed salinity reduction approach, facilitated by AOPs, is categorised as an advanced strategy for reducing water contamination. Forward-looking studies should consider the energy efficiency of this technology relative to conventional desalination treatments.

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CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

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