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Technologies for Removal of Chlorine Oxyanions from Water

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Abstract

Chlorate, perchlorate, and chlorite have become major challenges in drinking water treatment due to their environmental persistence and biological toxicity. With accelerating industrialization, pollution from these chlorine oxyanions in water bodies is worsening, urgently requiring the development of efficient and sustainable treatment technologies. However, existing technologies face limitations in selectivity, energy consumption, renewability, and large-scale applicability, with no single technology yet capable of comprehensively meeting these demands. This paper reviews multiple technologies including adsorption, membrane separation, ion exchange, biological reduction, chemical reduction, electrochemistry, and bioelectrochemistry. It delves into their mechanisms, influencing factors, and practical applications for removing perchlorate, chlorate, and chlorite. Overall, physicochemical technologies such as adsorption and membrane separation can deliver effective removal results in the short term. However, for long-term applications, electrochemical reduction and biological reduction technologies hold greater potential for development due to their lower energy consumption and simpler operating conditions.

Keywords

Drinking Water; Perchlorate; Chlorate; Chlorite; Removal Technology.

1. Introduction

For a long time, drinking water disinfection has been used to inactivate or suppress microbial populations in water. Chlorine dioxide (ClO_2) is commonly employed as a disinfectant because it generally reacts less with natural organic matter and bromide and produces fewer halogenated disinfection by-products-particularly chlorinated species-than chlorine[1]. However, ClO_2 disinfection produces harmful inorganic disinfection by-products. In water, chlorine dioxide rapidly decomposes to form chlorite (ClO_2^-), chlorate (ClO_3^-) and chloride (Cl^-), with chlorite constituting the largest proportion[2]. The presence of perchlorate is mainly attributable to anthropogenic sources, notably widespread use in military, aerospace, industrial manufacturing, and pyrotechnics production[3]. These inorganic chlorine oxyanions pose public health risks when present at elevated levels in drinking water. At sufficiently high doses, perchlorate can inhibit iodide uptake by the thyroid and may impair skeletal and central nervous system development in infants[4]. A study of 308 pregnant women found that environmental exposure to perchlorate negatively affected free thyroxine (FT4) levels in late pregnancy, potentially impairing fetal neurocognitive development[5].

The primary and most consistent finding from exposure to chlorite and chlorate is that oxidative stress induces alterations in red blood cells, impairing the blood's oxygen-carrying capacity and causing methemoglobinemia and hemolytic anemia[6]. In a long-term study, rats administered $NaClO_2$ or $NaClO_3$ in drinking water at doses up to 100 mg/L for one year exhibited changes in red blood cell morphology and osmotic fragility and developed mild hemolytic anemia[7].

Furthermore, chlorate, like perchlorate, is a goitrogen that can reduce iodide uptake via competitive inhibition, thereby leading to thyroid enlargement[8]. The potential health risks posed by chlorine oxyanions have drawn widespread attention from regulatory authorities both domestically and internationally; accordingly, investigating and discussing the occurrence of these oxyanions in drinking water and the available treatment technologies is essential. This paper presents the main methods for removing perchlorate, chlorate, and chlorite, including ion exchange, adsorption, membrane separation, chemical reduction, electrochemical reduction, and biological reduction. Overall, physicochemical techniques such as adsorption and membrane separation can deliver effective short-term removal, while electrochemical and biological reduction technologies show greater potential for long-term application.

2. Sources and Current Status

2.1 Natural and Anthropogenic Sources

Sources of chlorine oxyanion contaminants include both natural pathways and substantial anthropogenic activities. Chlorate and chlorite are primarily generated during drinking-water disinfection, especially when chlorine dioxide is used, where they form through its disproportionation in water; conventional disinfectants such as chlorine, hypochlorite, or ozone may also produce small amounts of these byproducts[9, 10]. In addition, process steps involving strong oxidants in industries such as pulp and paper, bleaching, textiles, agricultural herbicide application, and the food industry can discharge wastewater containing chlorate and chlorite[11, 12]. In the natural environment, chlorate is believed to form through photochemical processes analogous to those producing perchlorate, and it also occurs as a byproduct of microbial perchlorate degradation pathways[13]. In contrast, perchlorate originates from a more diverse array of sources. It is widely used in rocket propellants, pyrotechnics, explosives, fertilizers, and the electroplating industry, and constitutes a representative anthropogenic contaminant[14]. Atmospheric photochemical reactions in nature (for example, photochemical reactions between inorganic chlorine and ozone), volcanic eruptions, and stratospheric transformation of naturally occurring organochlorines such as methyl chloride can all lead to the formation of natural perchlorate[15-17]. In arid and semi-arid regions, strong evapotranspiration and scarce precipitation mean that perchlorate, owing to its poor sorption and high solubility, readily accumulates in the environment over long periods. The Atacama Desert in northern Chile is considered the world's largest natural perchlorate reservoir, with minerals extracted from the Atacama containing up to 1.8×10^6μg/kg of natural perchlorate[18].

2.2 Regulatory Limits and Current Status

Because chlorine oxyanions pose public-health risks, domestic and international drinking-water standards set different limits for chlorate, perchlorate, and chlorite. The U.S. Environmental Protection Agency (EPA) specify a maximum contaminant level goal (MCLG) for chlorine dioxide of 0.8 mg/L; perchlorate has an oral reference dose (RfD) of 0.0007 mg/Kg/day and is currently under evaluation for a maximum contaminant level (MCL); and the maximum contaminant level (MCL) for chlorite is 1.0 mg/L[19]. In the World Health Organization (WHO) drinking-water quality guidelines, a guideline value of 0.7 mg/L is recommended for both chlorate and chlorite[20]. EU drinking-water standards set limits for chlorate and chlorite at 0.25 mg/L. China's Standards for Drinking Water Quality (GB 5749-2022) also specify limits for these substances: chlorate 0.7 mg/L, chlorite 0.7 mg/L, and perchlorate 0.07 mg/L. By comparison, China's limit levels are broadly aligned with those of the WHO, though controls on perchlorate are relatively stricter, while the EU imposes more stringent requirements for chlorate and chlorite. This shows that both domestic and international authorities take these oxychlorine anion contaminants seriously, but there are differences among countries and regions in the risk-assessment approaches and safety thresholds used to set limits.

In water surveys conducted in many parts of the world, chlorate, perchlorate and chlorite are frequently detected. In Malta, ClO_4^- concentrations in stormwater runoff following the dry-summer fireworks period can exceed 110 μg/L, indicating the persistent impact of fireworks on perchlorate contamination[14]. In California, perchlorate was detected in 96 drinking-water systems and 395 wells[21]. In Canada, a survey of 16 drinking-water treatment plants using hypochlorite as the disinfectant found chlorate in treated water at all sites, at concentrations ranging from 0.002 to 0.96 mg/L[22]. In tap-water samples from Tokyo and surrounding areas, ClO_4^- concentrations reached up to 37 μg/L, while drinking water on India's west coast ranged from 11.4 to 69.2 μg/L[23, 24]. In Hengyang, Hunan Province, China, surface waters exhibited relatively high average perchlorate concentrations, and chlorate (ClO_3^-) and chlorite (ClO_2^-) were also detected, with maximum concentrations of 343 μg/L and 44.4 μg/L, respectively[25]. A drinking-water survey in Emilia-Romagna, Italy, showed relatively high exposure levels of chlorite and chlorate, with mean concentrations of 427 ± 184 μg/L and 283 ± 79 μg/L respectively[10].

These contaminants are widely distributed in drinking water, groundwater and surface runoff across different countries and regions, with concentrations in some areas even exceeding several hundred to several thousand micrograms per liter, and they often co-occur with ions such as nitrate and bromate, further exacerbating water-quality risks. Because oxychlorine compounds are highly soluble and environmentally persistent and are difficult to remove by conventional treatment processes, long-term exposure has been associated with thyroid dysfunction, hematologic toxicity and potential teratogenic effects. Consequently, effectively reducing oxychlorine levels in water has become an urgent priority for protecting drinking-water safety and has driven the exploration and innovation of various treatment technologies targeting these contaminants.

3. Removal Technologies for Chlorine Oxyanions

3.1 Adsorption

3.1.1 Activated Carbon Adsorption

Adsorption is one of the most frequently used approaches in research and practice for removing oxychlorine anions. Activated carbon- both granular activated carbon(GAC) and powdered activated carbon (PAC) is widely adopted because of its high specific surface area, well-developed pore structure, and established engineering applications. Activated carbon technologies remove perchlorate, chlorate and chlorite from water through mechanisms of physical and chemical adsorption. Its surface features abundant micropores and mesopores that can retain pollutants via van der Waals forces, electrostatic attraction, and other interactions. In addition, the surface of activated carbon contains numerous functional groups that can chemically interact with the ions of chlorine oxyanions, thereby further enhancing removal performance.

GAC has been employed in drinking water treatment plants to remove organic matter, residual chlorine, and odorous compounds, and its use has been extended to the removal of various anionic pollutants. Research on adsorption for perchlorate (ClO_4^-) is the most advanced; numerous experiments indicate that it can exhibit appreciable adsorption capacity under certain conditions, whereas reports on the removal of chlorite (ClO_2^-) and chlorate (ClO_3^-) are relatively limited, mainly remaining at the laboratory scale or under specific operational conditions.

Activated carbon is the earliest and most commonly used adsorbent for removing perchlorate, and researchers tend to employ modification methods to enhance its adsorption performance and capacity. After appropriate surface modification, it has been demonstrated to be competitive for perchlorate adsorption. One study showed that granular activated carbon (GAC) loaded with cetyltrimethylammonium bromide (CTAB) exhibited the best performance under acidic conditions. As the CTAB content increased from 0.023 mmol CTAB/g GAC to 0.135 mmol CTAB/g GAC, the K value in the Freundlich adsorption model increased from 0.071 to 0.19 mmol/g, indicating a marked enhancement in perchlorate adsorption capacity. When the solution pH was controlled at 2–3, the maximum perchlorate uptake on GAC-CTAB reached 0.36 mmol/g[26]. Another experiment showed that $FeCl_3$-impregnated granular activated carbon could achieve the simultaneous adsorption of perchlorate and bromate. The adsorption capacity for ClO_4^- may increase in the presence of BrO_3^-; the maximum Langmuir adsorption capacity increased from 0.179 mmol/g (without BrO_3^-) to 0.256

mmol/g/ (with 0.2 mmol/L BrO_3^- at pH 6.0)[27]. Krishnan et al. [28] further demonstrated that acid-modified GACs, including phosphoric acid-treated GAC (GAC-PH) and acetic acid-treated GAC (GAC-AA), achieved the highest removal efficiencies at pH 1. At 303 K, the maximum adsorption capacities of GAC, GAC-AA, and GAC-PH were 20.1, 37.5, and 44.0 mg/grespectively. Overall, modified activated carbon significantly outperforms pristine GAC in terms of removal efficiency, adsorption capacity, and operational lifetime.

Research on the removal of chlorate and chlorite by activated carbon is limited. In a continuous-flow experiment conducted in 1994, the removal amounts of ClO_2^- and ClO_3^- reached 162 mg ClO_2^-/g(influent concentration:2.3 mg/L and 4.9 mg ClO_3^-/g (influent concentration: 5.0 mg/L), respectively; however, the empty bed contact time (EBCT) used in this experiment was only 0.18–0.35 min, far shorter than that required in practical engineering applications. [29]。 Cases of modified activated carbon targeting the adsorption of $ClO_2^-$and ClO_3^- are also very scarce. Recent research has shown that granular activated carbon modified with cetylpyridinium chloride (CPC@GAC1) exhibits significantly enhanced adsorption performance for chlorate and chlorite, achieving ≥99% removal of ClO_2^- and 80% removal of ClO_3^- within 2 hours, realizing excellent removal efficiencies[30].

Table 1. GAC or modified GAC adsorption methods used for chlorine oxyanions treatment

Adsorption materials	Findings	Maximum adsorption capacity	Adsorption model	Key references
GAC-CTAB	Under acidic conditions (pH 2–3), the performance is optimal; the perchlorate adsorption capacity increases markedly with the CTAB loading	0.36 mmol/g	Freundlich	[26]
FeCl3-impregnated GAC	Simultaneous adsorption of perchlorate and bromate can be achieved; in the presence of BrO_3^- at pH 6.0, the ClO_4^- adsorption capacity is enhanced.	0.256 mmol/g (BrO3−) 0.179 mmol/g (without BrO3−)	Langmuir	[27]
GAC/GAC-AA/GAC-PH	The highest perchlorate removal efficiency occurs at pH 1, and the adsorption capacity after modification is significantly superior to that of native GAC.	GAC: 20.1 mg/g、 GAC-AA:37.5mg/g、 GAC-PH: 44.0 mg/g	Not mentioned	[28]
GAC	In the continuous-flow experiment, ClO_2^- and ClO_3^- were removed, but the empty bed contact time (EBCT) was much shorter than that used in practical engineering applications.	162mgClO_2^-/g、 4.9mgClO_3^-/g	Not mentioned	[29]
GAC-CTAB	The adsorption performance for chlorate and chlorite is markedly improved, achieving ≥99% removal of ClO_2^- and 80% removal of ClO_3^- within 2 hours.	Not mentioned	Not mentioned	[30]

Activated carbon can achieve removal efficiencies of up to 99% for perchlorate, chlorate, and chlorite, with adsorption capacities typically ranging from 20 to 150 mg/g. However, its perchlorate removal is subject to certain limitations. Pristine GAC has limited adsorption capacity and must be modified with cationic surfactants, metal salts, or nitrogen functionalities to achieve significant performance enhancement; yet such modifiers often incur increased costs and potential risks of secondary pollution. Its removal efficacy is sensitive to solution pH, modifier dosage, coexisting ions, and interference from organic acids, making kinetics and breakthrough times difficult to control consistently. Regeneration is also constrained, as high-concentration regeneration solutions or spent carbon rich in perchlorate are difficult to handle. Moreover, the adsorption performance for other contaminants may be compromised after modification, increasing application uncertainty. Although activated carbon adsorption shows certain promise in laboratory settings, in practical engineering it is more often a temporary measure rather than a fundamental solution for perchlorate removal. Similar challenges exist for chlorate and chlorite removal; their treatment remains in the exploratory and optimization stage, and scaling up requires balancing adsorption capacity, durability, and cost-effectiveness.

3.1.2. Other Adsorbent Materials

In recent years, various organic, inorganic, and composite adsorbent materials have shown significant progress in the removal of oxyhalides. Chitosan and its derivatives possess abundant amino and hydroxyl groups, providing excellent potential for functionalization. Proton-crosslinked chitosan (PCLC) prepared by Xie et al. exhibited a maximum adsorption capacity of 45.455 mg g^{-1} at approximately pH 4; when treating a 10 mg/L perchlorate influent, the effluent perchlorate concentration could be stably maintained below 24.5μg/L, and the removal efficiency under acidic conditions was markedly superior to that in neutral systems[31]; Subsequent research found that glutaraldehyde-crosslinked quaternized chitosan salt (QCS) could maintain stable adsorption performance across the pH 4–10 range, with a maximum monolayer adsorption capacity of 119.0 mg/g, indicating that cationic modification can significantly enhance chlorate binding ability[32]. Based on this, Sowmya et al. prepared quaternary ammonium-functionalized crosslinked chitosan beads (QACB), further enhancing anion affinity. QACB maintained high perchlorate removal efficiency across a wide pH range (2–11), removed over 95% of perchlorate from brackish water, achieved a maximum adsorption capacity of 153.0 mg/g (initial concentration 1000 mg/L), and exhibited adsorption kinetics consistent with a pseudo-second-order model[33]. The adsorption mechanism of such materials is primarily attributed to the electrostatic attraction and ion exchange between the protonated amino sites and ClO_4^-.

In addition to organic adsorbents, inorganic sorbents have also attracted attention due to their structural stability and good regenerability. Carbon nanotubes (CNTs), with their high specific surface area and excellent surface chemical properties, have been applied to perchlorate removal studies. Fang and Chen compared the adsorption performance of pristine and oxidized carbon nanotubes for perchlorate (ClO_4^-), finding that the adsorption capacities followed the order multi-walled < single-walled < double-walled carbon nanotubes (DWCNTs); the saturation adsorption amount of DWCNTs reached 1.499 mg/g, and the maximum adsorption occurred at the isoelectric point pH (pH_IEP), indicating that the adsorption mechanism is not solely governed by electrostatic interactions[34]。 Hsu [35] found that the adsorption process of perchlorate on single-walled carbon nanotubes (SWCNTs) follows the Freundlich model, with an adsorption capacity of approximately 6 mg/g at an initial concentration of 20 mg/L. Lower temperature and reduced humic acid content facilitate perchlorate fixation because humic acid compresses the electrical double layer, thereby reducing surface potential and electrostatic interactions. Lou et al.[36] further compared the performance of SWCNTs with granular activated carbon (GAC) and found that GAC had a higher maximum adsorption capacity (28.21–33.87 mg/g) than SWCNTs (10.03–13.64 mg/g); however, SWCNTs exhibited stronger adsorption at low ionic strength and high initial concentrations, and their kinetics conformed to an enhanced Freundlich model.

Calcined layered double hydroxides (CLDHs) are widely used as adsorbents for anions in aqueous solutions and can also be applied to perchlorate removal. Yang et al. prepared MgFe–CO_3 layered double hydroxides (MgFe-LDH), with optimal synthesis conditions at a calcination temperature of 550 °C and a [Mg]/[Fe] ratio of 3. At pH 4–10 and a dosage of 33 g/L, MgFe-LDH nearly completely removed perchlorate at an initial concentration of 2000μg/L within 720 minutes[37]. Lv et al. achieved a maximum perchlorate adsorption capacity of up to 95 mg/g using CLDHs prepared by optimizing the Zn/Al ratio (Zn/Al = 2) and calcining at 500 °C[38].

Table 2. Application of organic/inorganic adsorbents

Adsorption materials	Findings	Maximum adsorption capacity	Adsorption model	Key references
PCLC	Exhibited high adsorption capacity at approximately pH 4, reducing perchlorate influent of 10 mg/L to below 24.5μg/L, with superior removal efficiency under acidic conditions	45.455 mg/g	--	[31]
QCS	Stable adsorption across pH 4–10, and cationic modification significantly enhances perchlorate binding	119.0 mg/g		[32]
QACB	Maintained removal efficiency >95% over a wide pH range (2–11), capable of removing perchlorate from brackish water, with adsorption kinetics following a pseudo-second-order model	153.0 mg/g	Pseudo-second order	[33]
DWCNTs	Adsorption capacity exceeds that of SWCNTs and MWCNTs, with maximum uptake achieved at the isoelectric point pH, indicating the adsorption mechanism is not solely electrostatic	1.499 mg/g	--	[34]
SWCNTs	Adsorption conforms to the Freundlich model, with a capacity of approximately 6 mg/g; lower temperatures and reduced humic acid content favor adsorption	6 mg/g	Freundlich	[35]
SWCNTs vs GAC	GAC has a maximum adsorption capacity of 28.21–33.87 mg/g, higher than that of SWCNTs; however, SWCNTs demonstrate stronger adsorption at low ionic strength and high initial concentrations	GAC: 28.21–33.87 mg/g SWCNTs: 10.03–13.64 mg/g	Modified Freundlich	[36]
MgFe-LDH	pH 4–10, dosage 33 g/L, perchlorate at 2000 μg/L almost completely removed within 720 min	--	Pseudo-second order	[37]
CLDHs (Zn/Al=2)	Optimized Zn/Al ratio and calcination at 500 °C yielded a maximum adsorption capacity of up to 95 mg/g	95 mg/g	--	[38]

Research on novel adsorbents is currently focused primarily on perchlorate removal, with adsorption capacities ranging from single digits to 200 mg/g and removal efficiencies exceeding 95% under experimental conditions; most remain at the laboratory stage. Factors such as temperature, pH, adsorbent properties, dosage, and coexisting anions significantly affect ClO_4^- removal. To replace activated carbon in practical applications, these new adsorbents require further investigation in terms of adsorption performance, stability, and regenerability.

3.2 Ion Exchange Technology

Ion exchange (IX) technology is currently one of the most mature and commonly used methods for removing chlorate and perchlorate from drinking water and groundwater. Its core principle relies on the reversible exchange between the cationic/anionic exchange groups on functionalized resin surfaces and the oxyanions in solution, thereby achieving removal. Numerous studies have shown that ion exchange offers high selectivity and treatment efficiency, but its performance is influenced by various factors such as resin type, coexisting ions, pH, and temperature.

Research focusing on perchlorate is abundant. Pan et al[39] synthesized magnetized quaternary ammonium-functionalized bioresin (CS-MNB) using corn stalk as raw material. Under conditions of pH 4, flow rate of 5 mL/min, and bed depth of 2.15 cm, the maximum adsorption capacity for perchlorate reached 23.16 mg/g. The removal mechanism is primarily based on the ion exchange interaction between the quaternary ammonium groups and perchlorate ions, but the biosorbent regeneration efficiency was relatively low, ranging from 26% to 89%. Wu et al. [40] utilized biofilm magnetic ion exchange (BMIEX) material to achieve efficient removal under anaerobic conditions at approximately pH 6.8, attaining a removal rate of 99.4% (4 hours, initial concentration 10 mg /L), combining adsorption with biological reduction; however, the presence of NO_3^- and Cl^- is unfavorable for perchlorate reduction.

Table 3. Ion Exchange for the Treatment of chlorine oxyanions

Ion-exchange medias	Findings	Maximum adsorption capacity/Removal rate	Key references
CS-MNB	Under conditions of pH 4, flow rate 5 mL/min, and bed depth 2.15 cm, the maximum adsorption capacity is achieved, and the removal mechanism is ion exchange between quaternary ammonium groups and perchlorate	23.16 mg/g	[39]
Biofilm Magnetic Ion Exchange (BMIEX)	Under anaerobic conditions at approximately pH 6.8, the removal rate reaches 99.4% (4 hours, initial concentration 10 mg L^{-1}), combining adsorption with biological reduction; however, NO_3^- and Cl^- negatively affect the reduction process	99.4%	[40]
Commercial resin	Successfully removes perchlorate-enriched regeneration brine, with long-term removal efficiency remaining above 83%	83%	[41]
Dual-function resin Purolite A-530E	At an average 1 BV/min and influent ClO_4^- of approximately 860 μg/L, 36,000 to 38,000 BV of groundwater were treated, and resin performance showed no significant decay over two years	--	[42]
MIEX resin	Adsorption capacities for chlorate and chlorite are 525 mg/L and 398 mg/L, respectively, with optimal removal achieved near neutral pH	$ClO3^-$: 525 mg/L,80.4% ClO_2^-: 398 mg/L，70%	[43]

Ion exchange has accumulated extensive practical experience in perchlorate removal. Lehman et al. [41] employed commercial resins in a pilot plant to achieve continuous removal, and subjected the perchlorate-enriched regeneration brine to subsequent biological treatment; modeling demonstrated that ClO_4^- in the regenerated solution could be maintained below 500 μg/L, with long-term removal efficiencies exceeding 83%. Regarding long-term field operation, Gu et al.[42] reported the treatment of perchlorate-contaminated groundwater using the bifunctional resin Purolite A-530E. Under an average flow of 1 BV/min and influent ClO_4^- of approximately 860 μg/L, approximately 36,000 to 38,000 BV of groundwater were processed, and the resin performance showed no significant decline over two years.

Research on chlorate and chlorite removal is relatively limited. Yang et al.[43] investigated MIEX resin, which exhibited considerable adsorption capacity and a clear anion exchange mechanism. MIEX adsorption capacities for chlorate and chlorite were 525 and 398 mg/L, respectively, with optimal removal achieved near neutral pH. The maximum removal efficiencies for chlorate and chlorite were 80.4% and 70%, respectively. FTIR spectra indicated that the removal mechanisms of chlorate and chlorite on MIEX are based on anion exchange.

Ion exchange technology can achieve high removal rates of chlorate and perchlorate-ranging from 80% to 99%-without significantly altering the bulk water chemistry, while chlorate and chlorite removal efficiencies lie between 70% and 80%. Multiple studies have shown that resins with strong selectivity and good mass transfer performance offer advantages in trace-level scenarios. Nevertheless, challenges remain, including competition from coexisting anions, interference from active species such as sulfate radicals, and limited regeneration efficiencies of selective resins. The fundamental limitation is that ion exchange is an incomplete treatment method that generates high-concentration waste streams during the process, so perchlorate cannot be removed permanently. Resin regeneration thus remains the critical factor affecting the large-scale deployment and long-term stable operation of the process.

3.3 Membrane Filtration

Membrane filtration technologies can be divided into four categories: reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF) membranes, and electrodialysis. These membrane processes rely on the principle of semi-permeable membranes to prevent certain ions from passing through, thereby treating chlorate and perchlorate in water. However, it should be noted that reverse osmosis and electrodialysis do not discriminate among ions, so both technologies have the potential to remove all ions from the solution.

Membrane filtration technology plays a crucial role in removing perchlorate from drinking water. Roach and Tush removed perchlorate from aqueous solutions using polyelectrolyte-enhanced ultrafiltration (PEUF). In a synthetic groundwater system containing 10.3 ppm perchlorate along with chloride and other ions, perchlorate separation still reached 95% even when competing anions were present at tenfold concentration[44]. Roach et al. compared the performance of poly(4-vinylpyridine) (P4VP) and poly(diallyldimethylammonium) chloride (PDADMAC) in perchlorate removal; owing to the stronger affinity of perchlorate for the protonated pyridine moieties of P4VP, the perchlorate rejection achieved was as high as 95.8%[44, 45]. Li et al.[46] developed a cationic MOF/hybrid ultrafiltration PVDF membrane (PVA/Cu-iMOFs/PVDF-0.05) that exhibits specific affinity for ClO_4^-, achieving up to 99.6% removal within a pH range of 3–10 even in the presence of multiple competing anions. Moreover, exhausted membranes can be easily regenerated in taurine solution for reuse, with negligible capacity loss. Sanyal et al. modified commercial NF membranes via layer-by-layer (LbL) self-assembly of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA). The modified membranes exhibited higher permeabilities than commercial BW30 and SW30 membranes-1.5 times that of BW30 and six times that of SW30-while achieving approximately 93% perchlorate rejection. Permeation selectivity was also improved, and ClO_4^- removal was governed primarily by size exclusion rather than purely charge repulsion[47].

Research on membrane filtration for chlorite and chlorate removal is limited, and these ions may even lead to membrane performance degradation. In studies on chlorate removal from skim milk, which is a complex matrix, NF achieved an average rejection rate of 38.8 ± 8.1% for ClO_3^-, significantly lower than the rejection rates for calcium, potassium, and lactose. In contrast, RO achieved a ClO_3^- rejection rate of 98 ± 0.5%[48].

Table 4. Applications of membrane technology

Membrane technologies	Findings	Removal rate	Key references
PEUF	In groundwater containing 10.3 ppm perchlorate and other ions such as chloride, perchlorate separation still reaches 95% even in the presence of competing anions at tenfold concentration.	95%	[44]
P4VP	Perchlorate rejection can reach 95.8% because perchlorate exhibits a stronger affinity for the protonated pyridine residues of P4VP than for PDADMAC.	95.80%	[44, 45]
Cationic MOF/mixed ultrafiltration membrane	Within the pH range of 3–10, a specific affinity for ClO_4^- enables up to 99.6% removal, and the membrane can be regenerated in taurine solution.	99.60%	[46]
NF（PAH、PAA）	The modified membrane shows higher flux than commercial BW30 and SW30 membranes—1.5 times that of BW30 and six times that of SW30—achieving around 93% perchlorate rejection, with size exclusion as the dominant removal mechanism.	93%	[47]
NF/RO	In skim milk, the average chlorate rejection is 38.8 ± 8.1%, much lower than for calcium, potassium, and lactose, whereas RO achieves chlorate rejection of 98 ± 0.5%.	NF: 38.8±8.1%、RO: 98±0.5%	[48]

In summary, membrane filtration demonstrates a certain capacity for rejecting oxychlorine species in drinking water treatment, achieving perchlorate removal rates of 95% or higher. Studies on chlorate and chlorite are relatively limited, although reverse osmosis shows good performance. Similar to ion exchange, the process essentially shifts oxyanion species from the mainstream to the concentrate stream, necessitating further treatment of the concentrate containing high ion concentrations; at the same time, issues such as membrane fouling and relatively high overall operating costs constrain large-scale standalone application. Therefore, in recent years it has become more common to couple membrane processes with adsorption/ion exchange, chemical or biological reduction units to synergistically achieve both mainstream separation and concentrate minimization.

3.4 Chemical Treatment

Physical removal technologies can effectively reduce oxychlorine in water, but they cannot fundamentally eliminate the risk. Oxychlorine salts are often merely transferred from the source water to another concentrated stream, which still requires subsequent treatment and safe disposal. To achieve a root solution, they must be converted into harmless chloride ions. In terms of environmental impact, chemical reduction is an eco-friendly method for perchlorate removal.

3.4.1. Chemical Reduction

Perchlorate is thermodynamically prone to reduction to chloride (Cl^-), but under environmental water conditions the reaction is kinetically limited. Its tetrahedral structure leaves the central chlorine atom surrounded by four oxygen atoms, resulting in a high activation energy that conventional reductants struggle to overcome in neutral water. Therefore, metal species or metal ions are required to strengthen the process and surmount this barrier.

Park et al. generated Ti(II) from Ti(0) under strongly acidic conditions and used it to reduce ClO_4^-. Compared with H_2SO_4, HCl was more effective in promoting degradation, with optimal perchlorate removal exceeding 90%[49]. Moore et al.[50] investigated perchlorate removal on iron surfaces and found that adding iron at 1.25 $g \cdot mL^{-1}$ achieved approximately 66% ClO_4^- removal within 336 hours. They also observed that increasing the temperature helps overcome the high activation energy barrier, significantly accelerating the reaction. Oh et al. [51] investigated elemental iron reduction of perchlorate under both microwave and conventional bulk heating and achieved 98% removal of aqueous ClO_4^- within 1 hour at 200 °C. Hori et al. studied pressurized hot water (PHW) decomposition of perchlorate and found that even heating to 300 °C in pure PHW produced negligible reaction; however, adding zero-valent metals greatly enhanced decomposition. The activity order was (no metal) $\approx$ Al $<$ Cu $<$ Zn $<$ Ni $\ll$ Fe, with over 99% removal achieved by combining iron powder and 150 °C heating, including successful treatment of water contaminated after the Albany, New York fireworks incident[52]. Additionally, Vellanki and Batchelor employed a sulfite/UV advanced reduction process (ARP) to reduce perchlorate, finding synergistic enhancement of ClO_4^- degradation with reaction rates increasing as pH, temperature, and sulfite concentration rose[53].

Table 5. Application of chemical reduction

Reducing agent	Findings	Removal rate	Key references
Titanium (Ti)	Ti(II) generated under strongly acidic conditions facilitates ClO_4^- degradation, with H_2SO_4 proving more effective than HCl and achieving removal efficiencies exceeding 90%.	>90%	[49]
Fe	Adding 1.25 $g \cdot mL^{-1}$ of iron can remove approximately 66% of ClO_4^- within 336 hours, and raising the temperature accelerates the reaction.	66%	[50]
Fe	A one-hour reaction at 200 °C achieves 98% removal of aqueous ClO_4^-.	98%	[51]
Fe (PHW)	Even at 300 °C in pressurized hot water (PHW), ClO_4^- barely reacts, but the addition of zero-valent metals significantly enhances decomposition, with iron showing the highest activity.	>99%	[52]
Sodium bisulfite/UV	Advanced reduction processes (ARP) employing sulfite and UV effectively reduce perchlorate, with reaction rates increasing as pH, temperature, and sulfite concentration rise.	--	[53]
Fe^{2+}	Under pH 6.5–8.0, the reaction between Fe(II) and ClO_2^- is extremely fast, and a stoichiometric dose of about 3.31 mg Fe per mg ClO_2^- quantitatively reduces chlorite to chloride.	100%	[54]
VIII/IV	Catalytic reduction of ClO_3^- exhibits slow kinetics, but integrating vanadium (V) into conventional Pd/C catalysts enhances degradation activity.	--	[55]

Chlorite is chemically reactive and readily reduced to chloride; it can be rapidly and efficiently removed by ferrous iron under near-neutral conditions, whereas once chlorate is present in water, it tends to persist and is difficult to eliminate. The reaction between Fe(II) and ClO_2^- is extremely fast (approximately 5–15 seconds) at pH 6.5–8.0, and a stoichiometric dose of about 3.31 mg Fe per mg ClO_2^- can quantitatively reduce chlorite to chloride with minimal residual soluble iron. However, when the pH exceeds 8.0–8.5, Fe(II) readily hydrolyzes to $Fe(OH)_3$, reducing removal efficiency and necessitating dosing above the stoichiometric amount to compensate; when pH exceeds 9 and dissolved oxygen or organic carbon levels are elevated, the performance is further constrained. In engineering practice, a dosing window of 3.5–4.0 mg Fe per mg ClO_2^- is typically adopted to ensure complete removal[54].

The chemical reduction of ClO_3^- is more challenging. Gao et al. used palladium (Pd) nanoparticle catalysts and observed slow kinetics in catalyzing ClO_3^- reduction. By integrating vanadium (V) into the conventional Pd/C catalyst, they enhanced degradation activity, with the V(III)/V(IV) redox cycle identified as the primary mechanism for ClO_3^- reduction[55].

Chemical reduction can fully convert oxychlorine species-particularly perchlorate and chlorite-into harmless chloride, thereby mitigating the environmental risks of these contaminants, with removal efficiencies reaching up to 99%. However, the kinetic barriers for reducing perchlorate and chlorate remain substantial. In addition, key influencing factors such as natural organic matter, nitrate, and sulfate require further investigation. This approach is well suited for treating the high concentrations of perchlorate present in acidic regeneration streams generated by selective ion exchange columns.

3.4.2. Hydrogen Catalytic Reduction

Hydrogen (H_2), as a mild, clean, and inexpensive reductant, has demonstrated reduction potential toward oxychlorine species across various heterogeneous catalytic systems.

Findings regarding perchlorate removal via hydrogen reduction are primarily reflected in various metal surfaces and metal/support catalytic systems. Wang et al.[56] screened 78 metal catalytic systems in a pressurized reactor, and the results indicated that the Ti–TiO_2 surface exhibited the best performance for perchlorate removal using H_2. When the initial ClO_4^- concentration was 1 ppm (1000 ppb), removal efficiencies exceeded 90% within three days. H_2 also removed perchlorate via heterogeneous catalysis on activated carbon powder, achieving removal efficiencies of 88% or higher. Hurley and Shapley developed a Pd–Re heterogeneous bimetallic/activated carbon (Re/Pd–AC) system to facilitate the hydrogen-driven reduction of perchlorate. Pd adsorbs and dissociates H_2 to generate surface hydrogen atoms, which subsequently react with Re(VII)=O to reduce it to Re(V)(OH_2). Subsequent dissociation of the aqua ligand at the rhenium center creates vacancies capable of coordinating ClO_4^-, enabling Cl–O bond cleavage; Re(V) is then reoxidized to Re(VII)=O to complete the catalytic cycle. The resulting chlorate, chlorite, and hypochlorite ions are sequentially reduced to Cl^- and H_2O. This system drives ClO_4^- reduction at room temperature and atmospheric pressure[57].

Similar to the perchlorate removal strategy, Gao et al. constructed a Ru–Pd/C bimetallic/activated carbon catalyst under aqueous H_2 conditions to efficiently reduce chlorate (ClO_3^-). At 1 atm H_2 and 20 °C, Ru–Pd/C exhibited higher ClO_3^- reduction activity, achieving deep reduction of high-concentration (100 mM) ClO_3^- with a removal efficiency of 99%[58]. Lu et al. achieved highly efficient chlorate (ClO_3^-) removal using a Ru–Pd bimetallic catalyst supported on porous graphene (RuPd/PG). The system reached 99.9% ClO_3^- removal within 15 minutes and maintained stable, high activity over repeated cycles and when treating real water samples[59]. Sikora et al. developed a cellulose bead-supported palladium–platinum catalyst that shows promise for hydrogen-driven chlorate reduction. In batch reactions, Pd–Pt/CB alone reached 72% conversion, which increased by over 20% upon addition of iron oxide. Under continuous flow conditions, the Pd–Pt/CB–Fe_2O_3 catalyst reduced chlorate concentrations to zero in approximately 160 minutes[60]. The study compared three commercial activated carbon-supported 10 wt% Pd catalysts (10 wt% Pd/C). Under identical conditions, Cat-I and Cat-III achieved 93% and 91% chlorate removal, respectively, with

Cat-III showing superior reproducibility[61]. In another study, Pt/zeolite-catalyzed hydrogenation efficiently removed chlorate anions from flowing water; an acidic FAU zeolite with a low Si/Al ratio and approximately 1 wt% Pt introduced via ion exchange exhibited the highest activity. It was capable of simultaneously reducing chlorate and chlorite ions as well as chlorate[62].

Table 6. H_2 reduction for chlorate oxyanion treatment

Catalyst	Findings	Removal rate	Key references
Ti–TiO_2	Perchlorate removal using H_2 in a pressurized reactor, with an initial ClO_4^- concentration of 1 ppm, achieved a removal efficiency of over 90% within 3 days.	>90%	[56]
Re/Pd–AC	In a gradient reactor, H_2 was dissociated to form atomic hydrogen, which reacted with Re=O to reduce ClO_4^-; 99% reduction was achieved within 5 h at room temperature.	99%	[57]
Ru–Pd/C	Under aqueous H_2 conditions, Ru–Pd/C exhibited efficient reduction of ClO_3^-, with a removal efficiency of up to 99% for 100 mM ClO_3^-.	99%	[58]
RuPd/PG	A chlorate removal efficiency of 99.9% was achieved within 15 min, while maintaining stable and high activity upon reuse and in real water samples.	99.90%	[59]
Pd–Pt/CB	In batch reactions, Pd–Pt/CB achieved 72% conversion, and the conversion increased by more than 20% upon addition of iron oxide; under continuous-flow conditions, the chlorate concentration was reduced to zero.	99.90%	[60]
10 wt% Pd/C	Among three commercial Pd/C catalysts, Cat-I and Cat-III achieved chlorate removals of 93% and 91%, respectively, with Cat-III exhibiting better reproducibility.	Cat-I: 93%、Cat-III: 91%	[61]
Pt/zeolite	An acidic FAU zeolite with a low Si/Al ratio and approximately 1 wt% Pt introduced enabled efficient simultaneous removal of chlorate and chlorite ions.	--	[62]

In summary, the hydrogen reduction of chlorate salts faces significant kinetic barriers and requires overcoming high activation energies. Introducing catalysts can significantly accelerate the reaction and shorten residence time, enhancing removal efficiency to levels of 90% or greater. However, this often comes with relatively stringent operating conditions and material costs. Currently, such processes are more suitable for small-scale or high-concentration wastewater. To apply them to large-scale drinking water treatment, much work remains. It is hoped that catalysts with low toxicity and low loading can be developed to operate stably over the long term under near-neutral pH and ambient temperature and pressure, reducing interference from coexisting ions and natural organic matter. Additionally, catalyst recovery and control of secondary metal residues should be well managed. The goal is to achieve a catalytic system that is efficient, low in toxicity, mild in conditions, and simple in post-treatment.

3.4.3. Electrochemical Reduction

Electrochemical reduction applies an electric current at the electrode surface to reduce perchlorate, chlorate, and chlorite in water, converting them into harmless chloride ions or lower-oxidation-state compounds. It can completely reduce perchlorate to chloride ions without the addition of chemical reductants, offering promising process prospects.

Wang et al. investigated the removal of high-concentration perchlorate and nitrate at Ti−water interfaces through an indirect electrochemical reduction process. Anodic polarization generated Ti(III)/Ti(II) in situ as strong reductants, reducing the initial 200 ppm perchlorate and 1000 ppm nitrate to below 20 ppb and 200 ppb, respectively, within 6–8 hours[63].

The conditions for electrochemical reduction of chlorate are relatively harsh. Han et al.[64] developed a Pd/C-MoOX/MF cathode, in which a molybdenum foil (MF) was oxidized to form amorphous MoOX and Pd/C particles were dispersed on its surface. Under optimal conditions of pH 2.0 and 3 V, the chlorate reduction efficiency reached 98.24%.

Similar to chemical reduction, the electrochemical reduction of chlorate salts remains constrained at engineering scales due to sluggish kinetics. Existing achievements are almost entirely derived from laboratory conditions, where removal efficiencies can reach over 98%, but there is a lack of pilot-scale and full-scale demonstrations. Reactions are mostly carried out in acidic media, leading to electrode corrosion and high power consumption during the removal process. Therefore, it is necessary to develop novel electrode materials and structures to improve current efficiency and selectivity.

3.4.4. Bioelectrochemical Reduction

In recent years, bioelectrochemical systems (BES) have gained attention as an electrochemical reduction method that combines pollutant remediation with sustainability. The core of BES is the use of electrogenic microorganisms as cathodic/anodic catalysts, which selectively reduce target pollutants by directing electron supply through an external circuit. BES does not rely on large amounts of organic/inorganic electron donors, thereby reducing the residual donor in the effluent that can lead to regrowth and disinfection by-products.

Butler et al. constructed a denitrifying biocathode in a microbial fuel cell that achieved a maximum removal flux of 24 mg/(L·d) without the need for a fixed potential or shuttle agents. When the influent pH briefly increased to 8.5 during days 297 to 300, complete removal of perchlorate was achieved[65]. Li et al. constructed a non-membrane microbial electrolysis cell using a polyaniline (PANI)-modified graphite cathode as the sole electron donor. On the modified graphite cathode, the biofilm enhanced the removal efficiency by 12% compared to the unmodified electrode, achieving nearly complete removal of perchlorate within 60 hours in the presence of the biocathode[66].

In summary, bioelectrochemical reduction is still in its infancy, with research primarily focused on the removal of perchlorate, achieving nearly 100% removal in long-term experiments. However, there is a lack of literature on the degradation of chlorite and chlorate. Although this technology offers a novel approach compared to traditional remediation methods for contaminated groundwater, it does not demonstrate significant advantages for the biological degradation of perchlorate, particularly in the treatment of large volumes of wastewater.

3.5 Biological Reduction

Bioreduction is primarily used for in situ remediation of groundwater and treatment of industrial wastewater, demonstrating great potential for large-scale applications. The principle is that certain microorganisms contain specific enzymes that can lower the activation energy required for the reduction of chlorates and perchlorates, allowing them to use these compounds as electron acceptors in their metabolism.

Microbial perchlorate reduction technology is already well developed and has been successfully demonstrated in numerous large-scale comprehensive studies. For ex situ bioremediation, fixed-bed and fluidized-bed biofilm reactors are the most mature applications. Choi et al. used glass beads and granular activated carbon (GAC) as support media in a fixed-bed biofilm reactor to assess the impact of dissolved oxygen (DO) concentration on microbial perchlorate reduction. The results indicated that in the glass bead reactor experiment with an influent ClO_4^- concentration of 50 μg/L, controlling the influent DO at 1 mg/L achieved complete removal, whereas a DO level of 3.5 mg/L only achieved partial removal; the chemical oxygen uptake of the biological activated carbon could buffer the impact of elevated DO. The BAC reactor using GAC as the carrier maintained complete perchlorate removal even during short-term exposure to DO at 8 mg/L, but with long-term exposure to 8.5 mg/L, both effluent ClO_4^- and DO gradually increased[67]. Giblin et al. employed a flow-through bioreactor to treat perchlorate in groundwater. At a flow rate of 1 mL min^{-1}, perchlorate concentration was reduced from 0.738 mg L^{-1} to below detectable levels; at 2 mL min^{-1}, 92% to 95% of perchlorate was removed. The removal efficiency could be further improved by increasing recirculation pumping[68]. Hatzinger et al. demonstrated at large scale using a GAC-based fluidized-bed reactor that groundwater influent containing perchlorate concentrations ranging from 2 to 4000 mg/L could be stably reduced to 4 µg/L, with continuous operation for two months and tolerance to relatively high nitrate levels[69].

Bioreactors capable of efficiently reducing chlorate and chlorite have also been studied. Functional bacteria reduce ClO_3^- to ClO_2^- via chlorate reductase (ClR) and then rapidly dismutate it to Cl^- and O_2 through chlorite dismutase (Cld). Chen et al. isolated a Gram-negative chlorate-reducing strain XM-1 that tolerates chlorate concentrations up to 200 mM and can utilize multiple carbon sources as electron donors, including glucose, L-arabinose, D-fructose, sucrose, glycerol, and sodium citrate. Enzymatic assays showed that ClR and Cld activities were detectable in cell extracts under both aerobic and anaerobic cultivation conditions[70]. Peng et al. developed a mixotrophic bioreactor that achieved simultaneous removal of As(III), ClO_3^-, and NO_3^-. Under mixotrophic conditions, As(III) was primarily removed by AsOB, while the other contaminants were mainly reduced by HB. With optimized hydraulic retention time (HRT) and influent COD conditions, removal efficiencies for all three contaminants exceeded 90%[71].

Table 7. H_2 reduction for chlorate oxyanion treatment

Findings	Removal rate	Key references
The chemical oxygen uptake capability of GAC buffers the impact of elevated DO, and the BAC reactor using GAC as the carrier maintained complete perchlorate removal even under short-term exposure to DO at 8 mg/L.	100%	>90%
In a flow-through bioreactor treating groundwater, perchlorate at 0.738 mg/L was reduced below detection limits at a flow rate of 1 mL/min; at 2 mL/min, removal efficiency reached 92%–95%, and increasing recirculation pumping further improved removal.	92%–95%	99%
Large-scale application of a GAC-supported fluidized-bed reactor could stably reduce groundwater ClO_4^- concentrations ranging from 2 to 4000 mg/L to 4 µg/L, with continuous operation for two months and tolerance to relatively high nitrate.	100%	99%
The Gram-negative chlorate-reducing strain XM-1 tolerated up to 200 mM chlorate, utilized multiple carbon sources, and exhibited detectable ClR and Cld activities in cell extracts under both aerobic and anaerobic conditions.	--	99.90%
A mixotrophic bioreactor achieved simultaneous removal of As(III), ClO_3^-, and NO_3^-, with removal efficiencies exceeding 90% for all three contaminants under optimized hydraulic retention time and influent COD conditions.	>90%	99.90%

Microbial perchlorate reduction has indeed been extensively researched, demonstrating removal efficiencies above 95% in many studies, and comprehensive demonstrations have validated its effectiveness. However, as you noted, introducing active microbial communities into drinking water systems faces significant public acceptance challenges, and microbial remediation has not been directly applied within drinking water treatment systems to date. Consequently, biological processes are better suited for controlled, longer-term operation in medium- to large-scale groundwater or wastewater systems where stable conditions can be maintained.

4. Conclusion and Future Prospects

Over the past decade, contaminants such as perchlorate, chlorate, and chlorite have garnered significant attention from researchers worldwide, particularly in relation to the development of treatment strategies addressing water pollution and ensuring water safety. This article reviews the common methods for removing perchlorate, chlorate, and chlorite from water, including adsorption, ion exchange, membrane filtration, chemical reduction, and biological reduction. Key areas still require further research to advance the efficient and environmentally friendly removal of these contaminants from real water bodies.

(1) Considering the relatively low concentrations of oxychlorine anions in natural waters, ensuring water quality through physical separation technologies is highly feasible. The physicochemical processes for removing ClO_4^- from drinking water and groundwater-such as ion exchange, adsorption, and membrane separation-are well-established, offering substantial adsorption capacities and removal efficiencies.

(2) Chemical/catalytic reduction can fully convert ClO_4^- to Cl^-, offering good environmental benefits and high removal rates, but it often requires strong reductants and (precious) metal catalysts, leading to stringent reaction conditions and environmental and cost constraints for drinking water applications. Electrochemical reduction can achieve degradation without added catalysts, yet its large-scale application is limited by power consumption and electrode corrosion.

(3) Anaerobic biological processes and bioelectrochemical systems have demonstrated stable and reproducible removal performance for high-concentration, high-flow-rate wastewater or groundwater, yielding relatively stable effluent quality; however, their direct integration into primary drinking water treatment processes remains constrained by public acceptance and health risk assessment requirements.

(4) Due to the chemical nature of chlorate, its removal is more challenging, and related research is relatively scarce. Electrochemical/hydrogenation reduction combined with heterogeneous catalysis currently represents the most promising pathway for deep removal of ClO_3^-, with multiphase bimetallic systems exhibiting significant activity and resistance to deactivation under neutral conditions.

(5) Chlorite is relatively reactive. In water treatment processes, source control and process management remain the primary measures to suppress the formation and accumulation of ClO_2^-. Chemical reduction using reductants such as ferrous iron proceeds rapidly and can be coupled with conventional coagulation and filtration. Attention should be paid to the potential formation of chlorate as a byproduct

(6) Overall, single technologies often suffer from drawbacks such as energy consumption, secondary pollution, limited material lifespan, or challenges in byproduct control, making process integration more practically feasible. Future research should particularly emphasize the collaborative application of physical, chemical, and biological degradation techniques. Synergistic mechanisms among photocatalysis, electrocatalysis, and bioelectrochemical processes could also provide key insights.

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