

Review

Critical Review of Cr (VI) Removal Technologies from Water and Wastewater

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Abstract

Hexavalent chromium (Cr (VI)) contamination of water resources constitutes a major environmental and public health issue due to its high toxicity, mobility, and carcinogenic properties. This review examines recent advances in Cr (VI) removal technologies from water and wastewater, with emphasis on membrane-based separation processes and adsorption approaches. Conventional treatment methods, including chemical precipitation, ion exchange (IX), electrocoagulation (EC), electrodeionization (EDI), bioremediation, and photocatalysis, are comparatively discussed in terms of removal efficiency, operational limitations, and applicability. In parallel, sustainable adsorbent materials derived from biomass and agricultural waste are evaluated as environmentally friendly and cost-effective alternatives for chromium removal. The role of functional groups, adsorption mechanisms, and redox interactions involved in Cr (VI) reduction and immobilization is also analyzed. Attention is given to membrane technologies, such as reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED), and ultrafiltration (UF) after surface modification with the incorporation of nanomaterials and/or the application of Layer-by-Layer (LBL) assembly techniques, which enhance selectivity, permeability, and antifouling behavior. The reviewed studies demonstrate that advanced membrane systems and bio-based adsorbents can achieve high chromium removal efficiencies while supporting sustainable water treatment practices. Overall, the combination of membrane technologies with functionalized materials represents a promising direction for the development of efficient and environmentally sustainable Cr (VI) remediation systems capable of meeting increasingly strict regulatory limits.

Keywords: hexavalent chromium; membrane separation; adsorption; nanomaterials; Layer-by-Layer assembly; water treatment; Cr (VI) removal



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1. Introduction

Water pollution is a major global challenge that threatens both human health and the environment, while simultaneously reducing access to clean water due to climate change and the increasing demand for agricultural production [1]. Particularly, hexavalent chromium (Cr (VI)) contamination has become a significant environmental and public health concern because of its high toxicity, mobility, and carcinogenicity. Growing industrial activities, along with naturally occurring chromium-bearing geological formations, have contributed significantly to the widespread presence of Cr (VI) in groundwater and surface

water systems. Its persistence in these water sources, along with increasingly stringent regulatory limits, has created an urgent need for efficient and sustainable removal technologies.

Although numerous studies and review articles have investigated individual Cr (VI) treatment technologies, comprehensive comparative assessments of treatment performance, operational requirements, energy consumption, chemical demand, sludge generation, scalability, and technology readiness remain limited. Therefore, this review critically evaluates conventional and emerging Cr (VI) removal technologies, highlighting their strengths, limitations, practical applicability, and future development prospects.

Growing attention has focused on developing efficient and sustainable technologies for Cr (VI) removal from aqueous environments. Among the most promising approaches are membrane-based separation processes and adsorption techniques. Modified ultrafiltration membranes have attracted considerable interest because of their enhanced removal efficiency and lower energy requirements compared to conventional membrane systems. At the same time, the use of adsorbent materials derived from food waste, such as fruit peels and shells, has gained increasing attention as an environmentally friendly and cost-effective strategy aligned with circular economy principles. The following sections examine the fundamental chemistry of chromium and present the conventional treatment approaches in comparison with advanced membrane and adsorption technologies, as well as emerging hybrid systems for efficient Cr (VI) removal from water and wastewater.

Hexavalent Chromium

Chromium (Cr) is one of the most common heavy metals detected in water resources, especially in groundwater systems. Its presence can originate from both natural and anthropogenic sources [2]. In nature, chromium mainly occurs as chromite ($\text{Fe}_2\text{Cr}_2\text{O}_4$), an iron-chromium oxide mineral commonly associated with ultramafic and ophiolitic rocks [3]. Natural sources mainly include ophiolitic rocks, which contribute to the enrichment of groundwater with hexavalent chromium, Cr (VI) [4–6]. The most significant anthropogenic sources are industrial activities such as leather tanning, metal electroplating, mining, paint and pigment manufacturing, cement production, and the use of chromium-containing phosphate fertilizers [7]. Chromium exists in several oxidation states; however, trivalent chromium, Cr (III), and hexavalent chromium, Cr (VI), are of greatest environmental significance due to their relative stability in the environment. These two forms differ substantially in their physicochemical properties and in their chemical and biochemical reactivity [8].

Hexavalent chromium, Cr (VI), exhibits high mobility in the environment and is particularly toxic. Its high solubility across a wide pH range facilitates transport through soils and aquifers, increasing the risk of groundwater contamination [9,10]. It can readily penetrate cell membranes and cause harmful intracellular effects and is associated with various forms of cancer [11]. Short-term exposure to high concentrations may cause irritation and ulceration of the skin and stomach, while long-term exposure can lead to dermatitis, liver and kidney damage, circulatory and nervous system disorders, and even death at sufficiently high doses [12]. In contrast, trivalent chromium, Cr (III), is much less toxic than Cr (VI) and is almost insoluble at neutral pH. Cr (III) is considered an essential trace element for human health, as it helps regulate glucose, cholesterol, and lipid metabolism, and toxic effects occur only at very high concentrations [13].

The major natural and anthropogenic sources of Cr (VI), its release into the environment, transport through surface water and groundwater systems, and the main human exposure pathways are illustrated in Figure 1. Cr (VI) contamination may originate from both geogenic and anthropogenic activities and can subsequently migrate through environmental compartments, ultimately affecting drinking water resources and human health.

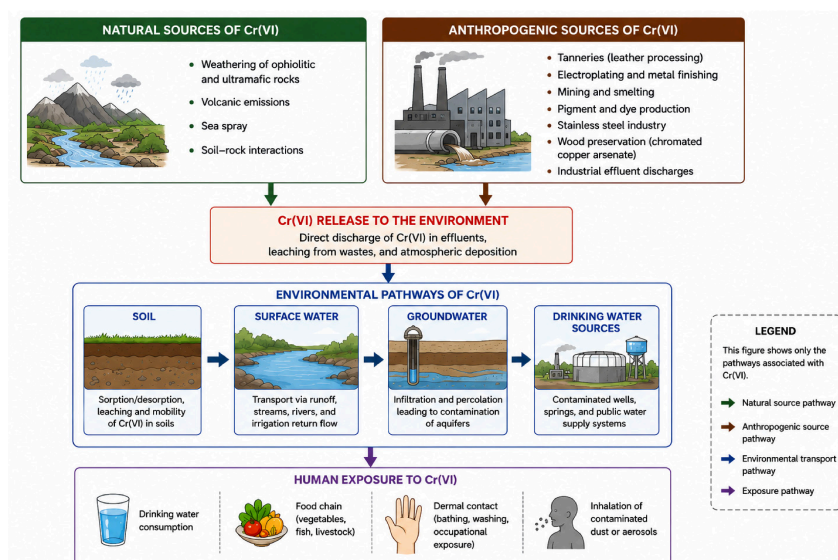


Figure 1. Sources, environmental pathways, and exposure routes of hexavalent chromium (Cr (VI)).

The main forms of hexavalent chromium present in aqueous solutions are $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , H_2CrO_4 , and HCrO_4^- . The distribution of these species depends on several factors, including solution pH, total chromium concentration, the presence of oxidizing or reducing agents, redox potential, and the kinetics of oxidation-reduction reactions [9]. The corresponding Pourbaix diagram for chromium in aqueous solution is shown in Figure 2. The chromium Pourbaix diagram is particularly relevant for water treatment applications because it illustrates the pH and redox conditions governing the stability, mobility, and interconversion of Cr (VI) and Cr (III), which directly influence removal efficiency and process selection. Furthermore, chromium undergoes continuous oxidation-reduction transformations in the environment. Trivalent chromium, Cr (III), may be oxidized to Cr (VI) in the presence of manganese oxides under oxidizing conditions, whereas Cr (VI) can be reduced back to Cr (III) by organic matter, microbial activity, and other reducing agents naturally present in soils and sediments. These redox reactions strongly influence chromium mobility, bioavailability, and toxicity in groundwater systems [14,15].

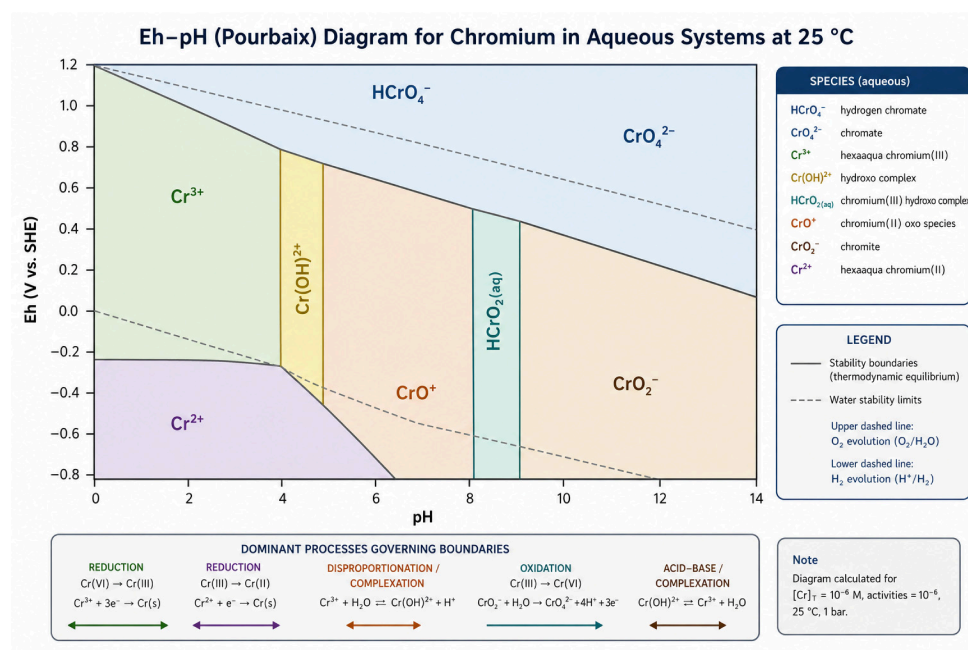


Figure 2. Pourbaix diagram of Cr in aqueous solution.

As shown in Table 1, Cr (VI) contamination is a global issue affecting developed and developing countries. Although the dominant contamination sources vary by region, industrial activities such as tanning, electroplating, mining, and pigment production remain the main anthropogenic contributors. Additionally, natural weathering of ophiolitic and ultramafic formations has been identified as an important geogenic source in several countries, including Greece, Italy, Mexico, and parts of the United States. These diverse contamination pathways necessitate the development of robust and adaptable treatment technologies capable of meeting increasingly stringent regulatory limits.

Table 1. Country-Specific Cr (VI) Extent, Policies, and Treatment Technologies.

Country/Region	Extent of the Cr (VI) Problem	Relevant Policies, Standards & Guidelines	Technologies Used for Removal	Reference
United States (California, North Carolina)	Heavy anthropogenic groundwater plumes linked to aerospace, defense, and industrial legacy sites, combined with localized geogenic leaching from ultramafic rock weathering.	US EPA Standards: Total Cr Maximum Contaminant Level (MCL) set at 100 µg/L. California State Water Resources Control Board-SWRCB: Enforces strict, specific 10 µg/L MCL solely for Cr (VI) to mitigate chronic public health risks.	Strong-base and weak-base Ion Exchange resins. Reduction–Coagulation–Filtration systems utilizing Fe (II) as a reducing agent.	[16]
China (e.g., Changhua, industrial provinces)	Severe soil and deep aquifer contamination zones resulting from rapid industrial manufacturing, historical chromium slag heaps, and unregulated chemical dumping.	National Standard (GB 5749): Limits total chromium in potable water to 50 µg/L. GB 8978: Classifies Cr (VI) as a highly restricted Class I industrial effluent requiring pre-treatment (0.1 mg/L cap).	In situ Chemical Reduction via subsurface injection of nano-zerovalent iron (nZVI). Permeable Reactive Barriers (PRBs) for plume containment.	[17–19]
India (e.g., Hazaribagh, Chhattisgarh, Sembattu)	Critical surface and groundwater pollution caused by the direct, unchecked discharge of toxic effluents from clusters of leather tanneries and electroplating units.	IS 10500: Enforces a drinking water threshold of 50 µg/L for total chromium. Central regulatory shift toward mandating Zero-Liquid-Discharge (ZLD) configurations.	Large-scale batch Chemical Precipitation using ferrous sulfate FeSO ₄ and lime. Low-cost Adsorption utilizing functionalized agricultural biomass and eco-friendly microalgal materials.	[20,21]
Greece (e.g., Asopos Basin, Thiva, Euboea)	Complex environmental intersection of historical industrial discharge into surface basins and high geogenic concentrations leaking from indigenous ophiolitic/ultramafic rocks.	EU Drinking Water Directive: Limits total Cr to 50 µg/L, with legislative amendments trending toward a stricter 25 µg/L cap. ECHA REACH Regulation: Strict oversight on industrial chromate utilization.	Hybrid Coagulation/Ultrafiltration (UF) membrane units. Active boundary control via localized hydraulic containment (Pump-and-Treat systems).	[22]
Other Regions (Italy, Mexico, Morocco, Algeria)	Natural geogenic background in volcanic aquifers (Italy, Mexico) alongside severe surface river contamination from urban/tannery cluster runoffs (Morocco, Algeria).	Baseline alignment with the World Health Organization (WHO) international drinking water guidelines of 50 µg/L for total chromium.	Energy-intensive Reverse Osmosis (RO) and Nanofiltration for direct ion separation. Electrochemical Coagulation (EC) using iron sacrificial anodes.	[23]

In Greece, chromium occurrence in groundwater is strongly associated with the presence of extensive ophiolitic formations. Weathering and erosion of ophiolites have enriched

sedimentary formations with alteration products, contributing to the presence of Cr (VI) in groundwater systems near ophiolitic terrain [24]. The highest Cr (VI) concentrations are typically found in shallow porous aquifers. The contamination of the Asopos River, which became widely known in 2006, is the most characteristic case of Cr (VI) pollution in Greece. Studies within the river basin reported concentrations reaching up to 80 µg/L in both surface and groundwater resources used for drinking water supply [24]. Other investigations revealed substantial spatial variability in chromium concentrations, with values up to 180 µg/L. Initially, these elevated concentrations were mainly attributed to industrial activities in the region, where large quantities of chromium are used. However, more recent studies [4,5] suggest that chromium occurrence may also have a natural origin, as minerals such as chromite, Fe-chromite, chromium-bearing goethite, and silicate minerals have been identified within the Asopos basin. Nevertheless, anthropogenic activities may further enhance the mobilization and persistence of geogenic chromium through changes in groundwater hydrodynamics, irrigation practices, alkaline conditions, and industrial waste disposal [25]. The interaction of water with ultramafic rocks and soils, including serpentinite, dunite, and ophiolitic formations, has also been shown to generate elevated Cr (VI) concentrations in other parts of the world, including Mexico [25], California [26], Zimbabwe [27], Italy [3], Brazil [28], Japan, and Indonesia [29].

The study by Kaprara et al. (2015) [24] analyzed drinking water samples collected from several regions of Greece near ophiolitic formations. The samples originated from different groundwater aquifer systems [24]. The highest Cr (VI) concentrations were detected in areas such as Asopos, Thebes, Evia, Vergina, and Anthemountas. Similarly, high concentrations were also recorded in other regions, including Agios Dimitrios in Kozani, where chromium levels exceeded 100 µg/L. This phenomenon has been linked to the operation of lignite-fired power plants of the Public Power Corporation (PPC), which generate fly ash enriched with heavy metals, including chromium [30].

Elevated chromium concentrations are associated with porous aquifers containing weathering products of ophiolitic rocks, while the large specific surface area of fine-grained ophiolitic material further enhances chromium release. The revised European Union Drinking Water Directive (Directive (EU) 2020/2184) significantly reduced the permissible concentration limit for hexavalent chromium, setting a maximum of 25 µg/L with mandatory implementation by 2036. The previous limit, which remains valid until then, is 50 µg/L of total chromium [31]. In Greece, the maximum permissible limit for inland surface water, such as rivers and lakes, is 3 µg/L (Government Gazette 1909/B/08-12-2010, Annex I, Part B) [32]. The reduction in these regulatory limits highlights the urgent need to develop efficient water treatment technologies capable of producing water with extremely low Cr (VI) concentrations, even below 3 µg/L.

2. Conventional Cr (VI) Removal Technologies

A wide range of methods for chromium (Cr) removal from wastewater has been reported in the literature, most of which are particularly effective at high chromium concentrations. Recent treatment techniques generally focus not only on chromium removal but also on chromium recovery for potential reuse [33].

The most frequently applied methods include chemical reduction–precipitation, ion exchange, adsorption, electro-driven treatment processes, and various membrane-based technologies, such as UF, RO, NF, and ion-exchange membranes (IEMs) [16].

Among these technologies, chemical reduction-precipitation and membrane separation processes are considered particularly widespread and effective for industrial-scale applications [9].

2.1. Chemical Reduction-Precipitation

Chemical reduction-precipitation processes are among the most established methods for Cr (VI) treatment because they simultaneously detoxify chromium by reducing it to Cr (III) and enable its removal via hydroxide precipitation. This process reduces Cr (VI) to Cr (III) under acidic conditions (low pH), followed by the precipitation of Cr (III) as an insoluble hydroxide under alkaline conditions. The reduced Cr (III) mainly precipitates as Cr (OH)₃ or Fe_xCr_{1-x}(OH)₃. Iron- and sulfur-based reducing agents, such as sodium metabisulfite (Na₂S₂O₅) and ferrous sulfate (FeSO₄), are commonly used for this purpose [32].

One major drawback of this method is the generation of sludge during the chromium precipitation stage. To reduce Cr (VI) to Cr (III) at pH values below 3, sodium hydroxide (NaOH) or lime [Ca(OH)₂] is typically added to raise the pH to 9.5–12.5, thereby facilitating Cr (III) precipitation [30]. In addition, iron- and sulfur-containing compounds, such as calcium polysulfide (CaS_x) and sodium thiosulfate (Na₂S₂O₃), have demonstrated effective chromium removal performance. Reported chromium removal efficiencies of 49% and Cr (VI) reduction efficiencies of 65% have been achieved in iron-carbon constructed wetland systems containing biochar and iron oxides, achieving significantly improved performance compared to control systems [34–36].

Chemical reduction-precipitation remains one of the most mature and widely implemented technologies for treating Cr (VI)-contaminated industrial wastewater streams. Under optimized operating conditions, Cr (VI) removal efficiencies exceeding 90–99% are commonly reported, particularly for wastewater with high chromium concentrations and adequate pH control [37]. The process is attractive due to its operational simplicity, relatively low capital cost, and ease of implementation at industrial scale. However, its practical application involves significant chemical consumption for both chromium reduction and pH adjustment, as well as the generation of substantial quantities of chromium-containing sludge that require further handling and disposal. In addition, treatment performance may be affected by wastewater composition, dissolved oxygen levels, and pH fluctuations. Compared with emerging adsorption- and membrane-based technologies, chemical reduction-precipitation alone is generally less effective at achieving the ultra-low residual chromium concentrations required for drinking water applications. Nevertheless, it remains one of the most practical and economically viable solutions for bulk chromium removal from industrial effluents and is frequently employed as a primary treatment step prior to polishing processes such as adsorption, ion exchange, or membrane filtration [38].

2.2. Ion Exchange

Ion exchange is considered a mature and highly selective treatment technology, particularly suitable for removing low Cr (VI) concentrations and for applications requiring compliance with stringent drinking water standards. Chromium removal through ion exchange has been extensively investigated [39,40]. Cation exchange resins are effective for the removal of Cr (III), whereas anion exchange resins are suitable for Cr (VI) removal. Strong-based anion exchange resins, in which chloride ions (Cl[−]) serve as the exchangeable anions, are most used for Cr (VI) removal.

Theoretically, anion exchange using synthetic resins is considered highly suitable for chromium removal because chromate ions (CrO₄^{2−}) are among the most strongly preferred anions in natural water. Various ion exchange resins have been used for chromium removal from aqueous systems, including strong-base anion resins such as Amberlite IR, IRA-900, and DOWEX 1; weak-base anion resins such as Amberlite IR-67RF, IRA-94, DOWEX MA43, and MAC3; as well as cation exchange resins including Amberlite IR-120, IRN77, and SKN1 [41].

Due to the positive charge of Cr (III) and the negative charge of Cr (VI), a dual ion exchange system may be particularly effective when both chromium species coexist in water samples. In such systems, a cation exchange resin is first employed for Cr (III) removal, followed by an anion exchange resin for Cr (VI) removal. In an industrial electroplating application in Illinois (USA), wastewater was initially passed through a column containing the cation exchange resin Amberlite IR-120 to remove iron, nickel, trivalent chromium, and other cations, and then through a second column containing the anion exchange resin Amberlite IRA-402 for the removal of hexavalent chromium, fluoride, and other anions [41].

Weak-base anion exchange resins are commonly used for the removal of chromate ions under acidic conditions and are typically regenerated with stoichiometric amounts of sodium hydroxide (NaOH). In contrast, strong-base anion exchange resins are preferred for removing trace chromate concentrations from tap water under neutral pH conditions and are regenerated with 5–8% sodium chloride (NaCl) solutions. Regeneration efficiency can be further improved by adding NaOH, which converts the resin from the HCrO_4^- form to the more stable CrO_4^{2-} form.

Ion exchange, regarded as one of the most effective technologies for the removal of low Cr (VI) concentrations, achieves removal efficiencies above 90–99% and produces treated water that complies with stringent drinking water standards [40]. Compared with chemical precipitation, ion exchange generates significantly less solid waste and enables selective chromium recovery through resin regeneration. The main limitations of ion exchange processes include the need for frequent resin regeneration and concentrate disposal, potential resin fouling, and interference from competing ions present in water, all of which may reduce chromium removal efficiency [41]. Moreover, operational costs associated with resin replacement, regeneration chemicals, and concentrate management can become substantial, particularly at large treatment scales [42]. Furthermore, the presence of competing anions such as sulfate, nitrate, bicarbonate, and chloride may reduce resin selectivity and efficiency under real wastewater conditions. Consequently, ion exchange is particularly attractive as a polishing technology for drinking water treatment and low-strength wastewater, whereas its application to highly contaminated industrial effluents is often limited by regeneration requirements and operating costs.

2.3. Adsorption

Adsorption is one of the most versatile and extensively investigated technologies for Cr (VI) removal from water and wastewater due to its operational simplicity, relatively low energy requirements, and the wide range of available adsorbent materials. The process relies on materials with high specific surface area, such as activated carbon, zeolites, specialized minerals, and engineered sorbents, which can attract and retain chromium species from aqueous solutions. During adsorption, Cr (VI) ions are immobilized on the surface of the adsorbent, resulting in their effective removal from the treated water [43]. Because of its flexibility and ease of implementation, adsorption is frequently employed as a polishing or complementary treatment step alongside other water purification technologies [44].

It should be noted, however, that Cr (VI) removal by adsorbent materials does not always occur through a purely adsorption-based mechanism. In many systems, particularly those containing iron-bearing phases, biochar, activated carbon, and engineered nanomaterials, chromium removal involves a combination of adsorption, surface-mediated reduction in Cr (VI) to Cr (III), and subsequent immobilization or precipitation of the reduced species [45]. Consequently, reported Cr (VI) removal efficiencies should be interpreted with caution, as different studies may involve fundamentally different removal pathways and chromium speciation outcomes.

A wide variety of adsorbent materials have been developed using natural, synthetic, and biologically derived precursors. Among these, layered double hydroxides (LDHs) represent an important class of adsorbents. LDHs are anionic clay-like minerals consisting of positively charged hydrotalcite-like layers separated by interlayers containing inorganic anions and water molecules. Due to the relatively weak interactions within the interlayer space, these materials exhibit efficient anion-exchange capabilities, providing high flexibility and adsorption capacity for chromate species [46].

Silica-based (SiO_2) adsorbents constitute another important category of chromium sorbents. These materials are typically synthesized using sol–gel methods and consist of a silica framework functionalized with active surface groups capable of forming complexes with metal ions. As a result, silica-based materials can simultaneously promote chromium reduction and adsorption within the same solid matrix [47].

Nanomaterials have emerged as a particularly promising class of advanced adsorbents due to their high specific surface area, tunable surface chemistry, and enhanced reactivity. Representative examples include nanoscale zero-valent iron (nZVI), graphene-based composites, magnetic iron oxides, and functionalized metal oxide nanoparticles. Many of these materials have demonstrated excellent Cr (VI) removal efficiencies under laboratory conditions. Nevertheless, challenges associated with material stability, regeneration, recovery, and large-scale implementation continue to limit their practical application. A more detailed discussion of nanomaterial-based adsorption systems is provided in Section 2.4.

Among the various adsorption materials, activated carbon remains one of the most widely applied and economically attractive options for Cr (VI) removal [48,49]. Activated carbon has a highly developed porous structure, large specific surface area, and tunable surface chemistry, enabling high adsorption capacity and selectivity. In recent years, considerable attention has focused on activated carbons produced from low-cost agricultural and biological residues, including rice husks, coconut shells, algae, and aquatic plants, which have demonstrated highly satisfactory chromium removal performance [49,50]. Adsorption efficiency depends strongly on operating conditions such as solution pH, temperature, and the nature of surface functional groups. Furthermore, competing ions such as sulfate, nitrate, chloride, and phosphate, as well as dissolved organic matter, can significantly reduce adsorption performance under real wastewater conditions by competing for active sites and influencing chromium speciation [51–53].

Maximum Cr (VI) removal is generally achieved under acidic conditions (pH 2–4), where HCrO_4^- species predominate and are more readily adsorbed through electrostatic attraction and surface-mediated reduction to Cr (III). Under these conditions, removal efficiencies frequently exceed 80–99%, depending on the adsorbent type and operating parameters [54–56].

The regeneration of saturated adsorbents is a critical factor influencing the economic and environmental sustainability of adsorption processes. For activated carbon, hydrogen peroxide (H_2O_2) has attracted significant interest as a regeneration agent because it is a strong oxidizing agent capable of decomposing adsorbed organic and inorganic contaminants through the formation of hydroxyl radicals ($^{\bullet}\text{OH}$) without requiring elevated temperatures or highly toxic chemicals [57]. In addition, H_2O_2 -based regeneration is considered environmentally friendly because its decomposition products are water and oxygen.

Recent studies have shown that regeneration efficiency can be further enhanced through advanced oxidation processes such as Fenton oxidation ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), UV/ H_2O_2 systems, and ultrasound-assisted treatments, which promote increased hydroxyl radical generation and improve restoration of adsorption capacity [58,59]. Depending on operating conditions, regeneration can recover approximately 80–95% of the original adsorption capacity. However, repeated regeneration cycles may gradually alter the pore structure of

activated carbon or lead to the loss of active surface sites, highlighting the need to optimize regeneration protocols.

Overall, adsorption offers several advantages over alternative Cr (VI) treatment technologies. Energy consumption is generally lower than that of pressure-driven membrane processes because adsorption does not require significant hydraulic pressure or electrical input during operation [56,60]. Compared with chemical precipitation, adsorption typically generates less sludge and is particularly well suited for polishing applications and compliance with stringent drinking water standards. Bio-based adsorbents and agricultural waste-derived activated carbons provide attractive sustainability benefits, whereas engineered nanomaterials often offer superior adsorption capacities and faster kinetics.

Despite these advantages, adsorption performance remains highly dependent on solution chemistry and wastewater composition. Variations in pH, the presence of competing ions, and complex wastewater matrices can substantially reduce removal efficiencies compared to those reported in laboratory studies [51–53]. Additional challenges include adsorbent regeneration, long-term stability, secondary waste management, and overall economic feasibility [60]. Furthermore, many promising adsorbent materials reported in the literature have been evaluated primarily using synthetic solutions rather than real industrial wastewaters, making direct comparisons of adsorption capacities and removal efficiencies difficult [54,55]. While conventional adsorbents such as activated carbon are already commercially available and widely implemented, many engineered nanomaterials and bio-based adsorbents remain at the laboratory or pilot scale. Therefore, future research should focus on long-term stability, regeneration performance, techno-economic assessment, and validation under realistic operating conditions to facilitate large-scale implementation of adsorption-based Cr (VI) treatment systems [60].

2.4. Nanomaterials

Nanotechnology-based approaches for Cr (VI) removal rely on engineered nanomaterials with dimensions typically ranging from 1 to 100 nm. These materials exhibit unique physicochemical properties due to their high surface area-to-volume ratio, quantum-scale effects, and abundant reactive surface sites. As a result, nanomaterials have attracted considerable attention for water treatment applications, particularly for improving adsorption capacity, selectivity, and reactivity toward heavy metals and other contaminants [61].

A wide range of nanomaterials has been investigated for Cr (VI) remediation. These include nanoscale zero-valent iron (nZVI) systems such as ZVI-Fe₃O₄ and ZVI-Fe₃O₄/graphene composites; noble metal- and transition metal-based catalysts including Ni, Pd/TiO₂, and Pd/functionalized SiO₂ systems; metal oxide nanoparticles such as Fe₃O₄, γ -Fe₃O₄ (often surface-modified with polydopamine), ZnO, TiO₂, WO₃, cerium-based nanoparticles, CoFe₂O₄, and MnO₂/Fe₂O₃/MWCNT composites; as well as polymeric nanocomposites, ionically modified nanoparticles, and membrane-integrated nanostructures [32]. The adsorption performance of these materials strongly depends on synthesis methods, surface functionalization, particle size, and dispersion stability, all of which determine the accessibility of reactive sites.

Among these systems, magnetic and surface-functionalized nanoparticles have been widely studied due to their ease of separation and tunable surface chemistry. For example, ionically modified magnetic nanoparticles functionalized with phosphonium silane have been shown to enhance Cr (VI) removal through electrostatic attraction between negatively charged chromate species and positively charged surface sites [53]. In addition to adsorption, partial reduction in Cr (VI) to Cr (III) may occur on the nanoparticle surface due to electron-donor groups and the high redox potential of Cr (VI). X-ray photoelectron spectroscopy (XPS) analyses have confirmed the coexistence of Cr (VI) and Cr (III) on

treated nanoparticle surfaces, indicating that coupled adsorption-reduction mechanisms are often involved. In some cases, Cr (III) may be partially released back into solution depending on surface charge interactions and solution chemistry.

Nanoscale zero-valent iron (nZVI)-based materials represent another extensively studied class of Cr (VI) adsorbents. Their high reactivity is attributed to their large specific surface area, abundant active sites, and efficient electron transfer capabilities. Reported mechanisms typically involve a sequence of adsorption, surface-mediated reduction in Cr (VI) to Cr (III), and subsequent precipitation or immobilization of the reduced species. These combined processes are often confirmed through spectroscopic techniques such as XPS, which reveal changes in chromium oxidation states during treatment.

In addition, hybrid nanostructures such as iron oxide nanoparticles embedded in chitosan matrices have demonstrated effective Cr (VI) removal from aqueous systems [57]. In these composites, electrostatic attraction between protonated functional groups and anionic chromate species, together with ion-exchange processes, plays a dominant role in contaminant uptake. Overall, the efficiency of nanomaterial-based adsorption is governed by physicochemical parameters including particle size, surface area, surface charge density, solubility, and functional group composition.

The superior performance of nanomaterials in Cr (VI) remediation is primarily attributed to their exceptional physicochemical characteristics, including high surface area, tunable porosity, surface functionalization capability, and strong binding affinity for metal ions. These features enable simultaneous adsorption, catalytic reduction, and in some cases precipitation within a single material system, leading to reported Cr (VI) removal efficiencies frequently exceeding 90–99% under optimized laboratory conditions [61,62]. Compared with conventional adsorbents, nanomaterials also exhibit faster kinetics due to the increased availability of reactive surface sites.

Despite these advantages, several challenges currently limit large-scale implementation. Nanoparticle aggregation can significantly reduce accessible surface area and thus lower adsorption efficiency, while recovery and separation of dispersed nanoparticles from treated water remain technically complex [63–65]. Furthermore, concerns related to long-term stability, environmental fate, ecotoxicity, and potential secondary pollution have not yet been fully resolved [66,67]. Although laboratory-scale studies consistently demonstrate high performance, relatively few nanomaterial-based systems have been validated at pilot or full scale.

Consequently, future development should focus on improving dispersion stability, enhancing regeneration and recovery strategies, reducing production costs, and systematically evaluating environmental safety. Advancing these aspects is essential to bridge the gap between laboratory success and practical large-scale deployment of nanotechnology-based Cr (VI) remediation systems.

3. Electro-Driven Processes

3.1. Electrodialysis

Electrodialysis (ED) is a membrane-based separation technology widely regarded as a promising approach for wastewater treatment and resource recovery. The process relies on the transport of ions through selective ion-exchange membranes under an applied electric field. In chromium remediation, ED has been extensively investigated for the removal and recovery of both Cr (III) and Cr (VI), particularly from industrial effluents such as electroplating and metal-finishing wastewater.

Early ED configurations used solid ion-exchange membranes arranged in multi-compartment cell systems, enabling selective separation and simultaneous recovery of chromium species [68]. More advanced configurations include two-stage electrodialysis sys-

tems, in which chromate ions are first concentrated under acidic conditions (predominantly as HCrO_4^-), followed by further separation based on ionic charge and valence differences, allowing discrimination between monovalent and divalent chromium species through controlled pH adjustment [69]. In addition, hybrid systems combining ion exchange and electrodialysis have been developed for the concentration and recovery of chromate from electroplating rinse waters [70]. Similar synergistic approaches have also been reported for metal-finishing and tannery wastewater, where solid membrane-based ED systems enhance chromium removal efficiency [45,51].

Beyond conventional solid membranes, ED with liquid membranes has been investigated as an alternative configuration. In this system, carrier-mediated transport within an organic phase is coupled with an externally applied electric field, which serves as the primary driving force for ion migration. Compared with solid ion-exchange membranes, liquid membrane systems may offer improved selectivity and permeability under specific operating conditions. However, process performance remains strongly dependent on membrane selectivity, feed composition, current density, and the presence of competing ions. Chromium transport is highly sensitive to oxidation state and speciation, both of which vary significantly with solution pH [71,72]. The application of an electric field further enhances ion transport and facilitates metal stripping from the organic phase, thereby improving overall separation efficiency [52,53].

Overall, ED offers several advantages for Cr (VI)-contaminated wastewater treatment, including high removal efficiency, reduced chemical consumption, and the potential for chromium recovery in concentrated streams. Reported removal efficiencies frequently exceed 90%, especially in hybrid systems combining electrodialysis with ion exchange or other membrane processes [68,69]. In addition, ED produces significantly less sludge compared with conventional chemical precipitation methods and supports resource recovery strategies through the reuse of concentrated chromium fractions.

Despite these benefits, electrodialysis performance is influenced by several operational limitations. Membrane fouling, scaling, and competition from coexisting ions can significantly affect process efficiency and increase maintenance requirements [71,72]. Energy consumption typically ranges from approximately 0.5 to 3.0 kWh m⁻³ for chromium-containing industrial wastewater, depending on feed composition, current density, membrane configuration, and recovery targets [73–75]. While energy demand is generally lower than that of pressure-driven processes such as reverse osmosis for moderately saline streams, it increases with higher conductivity and stricter separation requirements.

Electrodialysis is therefore particularly well suited for industrial applications involving relatively high chromium concentrations, such as electroplating, metal finishing, and tannery wastewater, where chromium recovery can offset operational costs. In contrast, its use in drinking water treatment is less common due to economic considerations and the availability of simpler polishing technologies. Although ED is a commercially mature technology, further improvements in membrane materials, fouling mitigation strategies, and process integration are required to enhance long-term stability and cost-effectiveness [71,75]. Compared with pressure-driven membrane processes, electrodialysis offers the unique advantage of selective ion recovery; however, it remains more sensitive to feed variability and membrane fouling, which continue to limit broader industrial deployment.

3.2. Electrodeionization

Electrodeionization (EDI), also known as continuous electrodeionization (CEDI), is a hybrid separation technology that combines ion-exchange resins with electrodialysis membranes to enable continuous ion removal and resin regeneration. The technology was developed in the late 1950s to address concentration polarization limitations in conventional

ED systems and to improve ion transport efficiency [54]. In a typical EDI setup, dilute compartments are filled with ion-exchange materials positioned between cation- and anion-exchange membranes. The ion-exchange resins provide highly conductive pathways for ionic transport while simultaneously enhancing mass transfer through their functional groups. This configuration significantly reduces concentration polarization effects and improves separation performance compared with conventional ED [55].

The synergistic combination of ion exchange and ED enables EDI systems to overcome the limitations of each individual technology. Studies have reported increases in ion separation efficiency from approximately 50% to 90% through the incorporation of ion-exchange materials within ED cells, demonstrating the effectiveness of this hybrid approach [55]. Unlike conventional ion-exchange systems, which require periodic chemical regeneration using acids or bases, EDI enables continuous in situ regeneration of the ion-exchange resins through the applied electric field. Consequently, chemical consumption and secondary waste generation are substantially reduced.

Although EDI was initially developed for ultrapure water production, its industrial application expanded significantly after commercialization in the late 1980s. The first successful production of ultrapure water using this configuration was reported in 1971, and subsequent technological developments incorporated advanced membrane materials and complementary processes such as ultraviolet (UV) irradiation [56]. Over the last decade, improvements in membrane performance, electrical efficiency, and system design have extended EDI applications beyond ultrapure water production to include the treatment of industrial wastewater streams containing toxic metals and inorganic contaminants.

Among these applications, the removal of chromium species has received considerable attention. Cr (VI) is particularly suitable for EDI treatment because chromate and dichromate ions can be effectively transported through anion-exchange membranes under the influence of an electric field. Reported Cr (VI) removal efficiencies frequently exceed 98%, highlighting the effectiveness of EDI as a chromium remediation technology [60,71]. Several studies have investigated the fundamental transport mechanisms governing chromium removal. For example, Bergmann et al. (2009) evaluated the performance of different ion-exchange resins for CrO_4^{2-} removal by examining transport numbers and conductivity characteristics [72], while Dzyazko et al. (2008) investigated diffusion coefficients of ion-exchange materials used in EDI systems [76].

Comparative assessments of ion exchange, ED, and EDI have consistently demonstrated superior performance for EDI. In one study, EDI achieved Cr (VI) removal efficiencies of up to 99.8%, outperforming both conventional ion exchange and ED systems [73]. Xing et al. (2009) further demonstrated stable continuous operation of an EDI process for more than 50 h, reducing chromium concentrations from initial values of 40 and 100 ppm to final concentrations of 0.09 and 0.49 ppm, respectively [74]. The corresponding energy consumption ranged from 4.1 to 7.3 kWh mol⁻¹ Cr (VI), illustrating the potential of EDI for high-efficiency chromium removal under continuous operating conditions.

An additional advantage of EDI is its ability to simultaneously remove and recover chromium. Alvarado et al. (2013) developed a continuous chromium treatment process integrating electrodeionization with ion exchange and demonstrated Cr (VI) removal efficiencies exceeding 98.5% under overlimiting current conditions [75]. During operation, the ion-exchange resin was continuously electro-regenerated, while chromium ions were concentrated in a separate compartment, enabling potential recovery and reuse. The reported energy consumption was exceptionally low (<0.07 kWh m⁻³), illustrating the potential economic advantages of optimized EDI systems. More generally, reported energy requirements vary considerably depending on feed composition, membrane properties, current density, water recovery targets, and system configuration. Nevertheless, several studies suggest that

optimized EDI systems can achieve lower specific energy consumption than conventional electrodialysis while maintaining superior chromium removal efficiencies [74,75].

Overall, EDI combines the high selectivity of ion exchange with the continuous operation and electro-driven regeneration capabilities of electrodialysis, making it one of the most effective technologies for Cr (VI) removal. Reported chromium removal efficiencies frequently exceed 98–99%, while the continuous electro-regeneration of ion-exchange resins minimizes chemical consumption and significantly reduces secondary waste generation [77–79]. Furthermore, the possibility of chromium recovery within the concentrate stream enhances resource efficiency and supports circular economy approaches for industrial wastewater management.

Despite these advantages, several challenges continue to limit the widespread implementation of EDI for chromium remediation. The technology is associated with relatively high capital costs, complex system design, and increased sensitivity to membrane fouling, scaling, and feed water composition [80]. Wastewaters containing elevated concentrations of suspended solids, organic matter, or competing ions often require pretreatment to maintain stable operation and prevent performance deterioration. In addition, although EDI is a commercially mature technology for ultrapure water production, its application specifically for large-scale Cr (VI) remediation remains comparatively limited, with relatively few full-scale industrial installations reported in the literature.

From a technology-readiness perspective, EDI can therefore be regarded as a mature and commercially established technology whose application to chromium remediation is still emerging. The process appears particularly attractive for the treatment of high-value industrial wastewater streams where chromium recovery, reduced chemical consumption, and stringent discharge standards justify the higher capital investment and operational complexity. Future research should focus on improving membrane durability, minimizing fouling and scaling, reducing energy requirements, and validating long-term performance under realistic industrial operating conditions [80].

3.3. Electrocoagulation

Electrocoagulation (EC) is an electrochemical water treatment technology that relies on the in situ generation of coagulant species from sacrificial metal electrodes. During operation, metallic ions released from the anode act as destabilizing agents, neutralizing the surface charges of dissolved and suspended contaminants and promoting their aggregation into larger flocs through charge neutralization and sweep coagulation mechanisms. Due to its operational simplicity, reduced chemical requirements, and relatively low sludge production, electrocoagulation has emerged as an effective alternative to conventional chemical coagulation for the treatment of contaminated water and wastewater [51].

Over the past several decades, the application of EC has expanded considerably in industrial wastewater treatment, particularly in Europe and South America [77]. The technology has been successfully applied to a wide range of industrial effluents, including mining wastewater, pulp and paper mill effluents [78], metal-processing wastewater, petroleum refinery wastewater, textile industry effluents, arsenic-contaminated foundry wastewater, nitrate-containing streams, tar and shale processing wastewater, restaurant wastewater, municipal wastewater, yeast-processing effluents, and drinking water treatment systems [79].

A typical electrocoagulation system consists of an electrolytic reactor equipped with one or more pairs of electrodes connected to an external power source. The simplest configuration uses a single anode–cathode pair immersed in wastewater, while mechanical mixing is often employed to maintain homogeneous suspension conditions. During electrolysis, oxidation reactions occur at the anode, resulting in electrode dissolution and the release of

metal ions, whereas reduction reactions take place at the cathode. Iron and aluminum are the most used electrode materials, either individually or in combination [80,81].

The generated metal ions undergo hydrolysis to form metal hydroxide species that function as coagulants and adsorbents. Pollutant removal occurs through a combination of coagulation, adsorption, precipitation, flotation, and electrochemical transformation processes. Simultaneously, electrochemical reactions promote hydrolysis, ionization, and free-radical generation, modifying both pollutant characteristics and solution chemistry. As a result, contaminants may be destabilized, transformed into less soluble species, or removed through sedimentation and flotation mechanisms [81,82].

For chromium-containing wastewater, iron electrodes are generally preferred because they provide a dual treatment mechanism. In addition to generating iron hydroxide flocs that facilitate coagulation, dissolved Fe (II) species can directly reduce toxic Cr (VI) to the less toxic Cr (III) form. The resulting Cr (III) species subsequently precipitate as chromium hydroxides or become incorporated into iron hydroxide flocs, enabling simultaneous chromium reduction and removal within a single treatment process [83,84]. This combined reduction-coagulation mechanism represents one of the major advantages of electrocoagulation compared with conventional physicochemical treatment methods.

Numerous studies have demonstrated the effectiveness of EC for Cr (VI) remediation. Investigations using synthetic chromium solutions at pH 3 and applied voltages of 20–40 V reported significantly higher removal efficiencies with iron electrodes than with aluminum electrodes [85]. Continuous Cr (VI) removal using Fe-based electrode systems has also been successfully demonstrated [86], while additional studies confirmed highly efficient chromium removal under acidic conditions and elevated applied voltages [87]. Furthermore, hybrid systems combining electrocoagulation with granular activated carbon (GAC) adsorption have shown enhanced chromium removal through the synergistic action of electrochemical reduction, coagulation, and adsorption processes [88].

Overall, EC has emerged as a highly effective technology for Cr (VI) removal, with reported removal efficiencies frequently exceeding 90–99% under optimized operating conditions [83,84,89,90]. The highest efficiencies are generally achieved under acidic conditions, where Cr (VI) reduction by dissolved Fe (II) species is thermodynamically favored. However, direct comparisons among published studies should be performed cautiously because treatment performance is strongly influenced by operational parameters, including initial chromium concentration, electrode material, current density, hydraulic retention time, reactor configuration, conductivity, and wastewater composition.

Compared with conventional chemical coagulation and precipitation processes, EC offers several important advantages. Coagulant species are generated in situ, reducing or eliminating the need for external chemical addition. Sludge production is generally lower and easier to dewater, while chromium reduction and removal can be achieved simultaneously within a single treatment unit. These characteristics simplify process operation and may reduce overall treatment costs for highly contaminated industrial wastewaters.

Despite its advantages, EC depends on electrical energy input and continuous electrode consumption, both of which contribute to operational costs. Electrode passivation, fouling, and scaling can reduce process efficiency over time and increase maintenance requirements [83,91]. Reported energy consumption values for chromium-containing wastewater typically range from approximately 0.5 to 8 kWh m⁻³, depending on current density, conductivity, treatment objectives, and reactor design [89–91]. Consequently, process optimization remains essential for improving economic performance and long-term operational stability.

From a practical perspective, EC is particularly attractive for the treatment of industrial effluents containing elevated chromium concentrations, such as electroplating, mining and

metal-finishing wastewater, where high removal efficiency can justify the associated energy requirements. Although several full-scale industrial applications have been reported, further optimization of electrode materials, reactor configurations, and hybrid treatment systems is required to improve competitiveness relative to advanced adsorption and membrane-based technologies.

Compared with adsorption processes, EC is generally better suited for the treatment of highly contaminated industrial wastewater streams, whereas adsorption technologies are often preferred as polishing steps to achieve stringent discharge limits and drinking water standards. Moreover, the application of EC in drinking water treatment remains relatively limited due to the need for post-treatment polishing, management of residual metal species, and greater operational complexity compared with adsorption or ion-exchange systems [83,91].

Overall, EC represents a mature and highly effective technology for Cr (VI) remediation, particularly when iron-based electrodes are used. Future developments should focus on improving electrode durability, reducing energy consumption, mitigating passivation phenomena, and integrating EC with complementary treatment technologies to enhance process sustainability and facilitate broader industrial implementation.

4. Bioremediation

Biological treatment technologies, commonly known as bioremediation, use the natural metabolic and physicochemical capabilities of living organisms to remove, detoxify, or stabilize chromium in contaminated environments [83]. These approaches employ microorganisms such as bacteria, fungi, algae, and cyanobacteria, as well as higher plants, and are widely regarded as environmentally friendly and cost-effective alternatives to conventional physicochemical treatment methods. Unlike many engineered technologies, bioremediation relies on naturally occurring biological processes and generally requires minimal chemical inputs and relatively low energy consumption.

Several biological mechanisms contribute to chromium removal. Biosorption is a passive process in which Cr (VI) or Cr (III) species bind to functional groups present on microbial cell walls, extracellular polymeric substances, or other biological surfaces without the expenditure of metabolic energy. In contrast, bioaccumulation is an active, energy-dependent process involving the transport and intracellular storage of chromium ions within living cells. Among the various biological pathways, bioreduction is generally considered the most important mechanism for Cr (VI) detoxification because it transforms highly toxic and mobile Cr (VI) into the less toxic and less mobile Cr (III) form [84]. This process is typically catalyzed by microbial enzymes, particularly chromate reductases, and is often followed by precipitation or immobilization of the resulting Cr (III) species.

Microbial remediation strategies therefore focus primarily on the biological reduction in Cr (VI). Numerous chromium-resistant bacterial and fungal strains have been isolated from contaminated environments and shown to tolerate Cr (VI) concentrations of several thousand milligrams per liter while maintaining substantial reduction activity [85]. Among the most extensively studied microorganisms are species belonging to the genera *Bacillus* [90–92], *Micrococcus* [90], *Rhodobacter* [93], and *Trichoderma* [94]. Under optimized laboratory conditions, these microorganisms have achieved Cr (VI)-to-Cr (III) conversion efficiencies ranging from 90 to 100% within periods of several hours to a few days. For example, complete reduction of 100 mg L⁻¹ Cr (VI) within 48 h has been reported using bacterial strains isolated from tannery wastewater [90], while removal efficiencies of 92–98% have been achieved in biological reactor systems [91,93].

In addition to bacteria and fungi, microalgae and cyanobacteria have demonstrated significant chromium removal capabilities through a combination of biosorption, bioac-

cumulation, and intracellular transformation mechanisms [95,96]. These organisms are particularly attractive because the resulting biomass may potentially be valorized for secondary applications such as biofuel production, thereby improving the overall sustainability of the remediation process.

The performance of microbial bioremediation is strongly influenced by environmental conditions, including pH, temperature, dissolved oxygen concentration, nutrient availability, and the presence of competing contaminants. Although biological systems generally exhibit much lower energy requirements than electrochemical or membrane-based technologies, treatment efficiencies observed under laboratory conditions may not be directly transferable to field applications due to the complexity of real wastewater matrices and fluctuations in environmental parameters. Furthermore, elevated Cr (VI) concentrations may inhibit microbial activity and compromise long-term process stability despite the high resistance exhibited by adapted microbial communities [97–99].

Phytoremediation represents a complementary biological approach that exploits the ability of plants to absorb, accumulate, stabilize, or transform chromium within contaminated soils, sediments, and water bodies. In phytoextraction processes, chromium is absorbed through plant root systems and translocated to above-ground tissues where it accumulates. Attention has been devoted to hyperaccumulator species capable of concentrating exceptionally high levels of metals within their biomass [89]. For example, *Callitriche cophocarpa* has been reported to accumulate up to 1274 mg Cr kg^{−1} dry biomass under suitable conditions [100].

Recent studies have demonstrated that the effectiveness of phytoremediation can be substantially enhanced through synergistic interactions between plants and microorganisms. The inoculation of plants with endophytic bacteria or mycorrhizal fungi often improves chromium tolerance, stimulates plant growth, and increases overall metal uptake. For instance, the combined application of *Trichoderma* and *Rhizomucor* fungi with King Grass increased chromium accumulation within plant tissues by approximately 64% and enhanced chromium removal from contaminated soil by 34% compared to uninoculated controls [94]. Similarly, bacterial inoculation of *Callitriche cophocarpa* significantly improved both plant health and Cr (VI) phytoextraction capacity [100]. These findings highlight the growing importance of integrated plant-microbe systems for improving biological remediation performance.

Despite these promising results, phytoremediation faces several practical limitations. Plant growth rates are inherently slow, treatment efficiency may vary seasonally, root penetration is limited to relatively shallow depths, and harvested biomass containing accumulated chromium requires appropriate management and disposal. Consequently, phytoremediation is generally considered more suitable for the long-term remediation of contaminated soils, sediments, and shallow groundwater than for the treatment of highly contaminated industrial wastewater streams [101–103].

Overall, bioremediation provides multiple pathways for chromium removal, including biosorption, bioaccumulation, reduction, immobilization, and phytoextraction. Reported Cr (VI) removal and reduction efficiencies frequently exceed 90% under optimized laboratory conditions, particularly when chromium-resistant microorganisms are employed [97–99]. Compared with conventional physicochemical treatment technologies, biological processes typically generate minimal secondary waste, require low energy input, and can often be implemented in situ, thereby reducing infrastructure requirements and environmental disturbance.

Nevertheless, the practical application of biological treatment remains constrained by relatively slow treatment kinetics, sensitivity to environmental conditions, and uncertainties associated with long-term process stability. In addition, management of chromium-

containing biomass and maintenance of active microbial communities remain important operational considerations [101–103]. As a result, bioremediation is generally most attractive for the treatment of contaminated soils, sediments, groundwater, and diluted waste streams, whereas physicochemical technologies are often preferred for highly concentrated industrial effluents requiring rapid and predictable treatment.

From a technology-readiness perspective, numerous laboratory-scale investigations have demonstrated the effectiveness of biological Cr (VI) remediation, while pilot- and full-scale applications remain comparatively limited. Future research should therefore focus on improving process robustness, enhancing microbial and plant tolerance to fluctuating environmental conditions, developing integrated plant-microbe remediation systems, and validating long-term performance under realistic field conditions. Such advances could facilitate broader implementation of bioremediation as a sustainable component of integrated chromium management strategies.

5. Photocatalysis

Photocatalysis is an advanced redox treatment technology that uses light energy, typically ultraviolet (UV) or visible radiation, to drive chemical reactions on the surface of semiconductor catalysts. In chromium remediation, photocatalytic processes primarily aim to reduce highly toxic and mobile hexavalent chromium (Cr (VI)) to the less toxic, less mobile, and less soluble trivalent form, Cr (III) [97,98].

The photocatalytic mechanism is based on the electronic properties of semiconductors. When a photocatalyst absorbs photons with energy equal to or greater than its band-gap energy, electrons are excited from the valence band to the conduction band, generating electron–hole (e^-/h^+) pairs [98]. These photogenerated charge carriers subsequently participate in oxidation–reduction reactions at the catalyst surface. The conduction-band electrons have sufficient reducing power to convert adsorbed Cr (VI) species into Cr (III), which is the principal pathway for chromium detoxification [99]. Simultaneously, the photogenerated holes act as strong oxidizing agents, reacting with water molecules or hydroxide ions to produce highly reactive hydroxyl radicals ($\cdot OH$) capable of degrading a wide range of organic contaminants [100]. As a result, photocatalytic systems offer the added advantage of simultaneously removing heavy metals and organic pollutants from wastewater.

The potential utilization of solar irradiation has made photocatalysis an attractive and rapidly evolving treatment technology, stimulating extensive research into visible-light-responsive photocatalysts beyond conventional UV-active materials such as TiO_2 [101,102]. Recent developments have focused on modifying semiconductor materials to improve light harvesting and suppress electron–hole recombination, thereby increasing the number of electrons available for Cr (VI) reduction. Strategies include elemental doping, heterojunction formation, and the development of composite and multifunctional materials. Representative examples include modified oxides such as N-doped TiO_2 [99] and $Ag/WO_3/rGO$ composites [102], sulfide-based photocatalysts including CdS/LDH [103,104], $BiOI/Bi_2S_3$ heterostructures [105], and SnS_2/GO composites [106], as well as more complex systems such as $Fe_3O_4@rGO@CdS/Bi_2S_3$ [107]. In addition, emerging classes of materials, including metal–organic frameworks (MOFs), covalent organic frameworks (COFs), MXene Two-Dimensional Materials (MXenes), and MXene-based composites, are increasingly investigated for Cr (VI) remediation applications [97,108].

Under optimized laboratory conditions, photocatalytic systems frequently achieve Cr (VI) reduction efficiencies exceeding 90–98% within periods ranging from several minutes to a few hours [103–105,107,109]. Certain visible-light-responsive heterostructures have demonstrated nearly complete chromium reduction within only 10–40 min of irradiation.

tion [106]. Successful treatment has been reported not only for synthetic solutions but also for real industrial wastewater streams [103]. Furthermore, multifunctional photocatalytic platforms capable of combining chromium reduction, adsorption, pollutant degradation, and contaminant sensing are currently under development, highlighting the growing versatility of this technology [109,110].

Photocatalysis is widely regarded as a promising treatment approach because it can utilize light energy to drive chromium reduction without the addition of chemical reducing agents. Compared with conventional chemical reduction and electrocoagulation processes, photocatalytic systems offer potential advantages such as lower chemical consumption, reduced sludge generation, and partial reliance on renewable solar energy [1–3]. Moreover, the simultaneous degradation of organic contaminants provides further benefits in treating complex industrial wastewaters.

Despite these advantages, several challenges continue to limit large-scale implementation. Photocatalytic performance is strongly influenced by operational parameters, such as pH, light intensity, catalyst dosage, dissolved oxygen concentration, and the presence of competing ions or natural organic matter in wastewater [4,5]. In addition, rapid electron–hole recombination, limited visible-light absorption by many conventional semiconductors, catalyst deactivation, and photocorrosion remain significant obstacles to practical application [6]. Although advanced heterostructures, doped semiconductors, MOFs, MXenes, and composite photocatalysts have substantially improved laboratory-scale performance, many of these materials have yet to be validated under long-term operating conditions or at pilot and industrial scales [3,7].

Consequently, photocatalysis is currently considered most suitable as a polishing or complementary treatment technology rather than a standalone process for highly concentrated Cr (VI)-contaminated effluents. Its greatest potential lies in the treatment of dilute wastewater streams and in integrated treatment systems where chromium reduction can be coupled with the degradation of coexisting organic pollutants. Future research should focus on improving visible-light utilization, enhancing catalyst stability and reusability, reducing material costs, and validating long-term performance under realistic wastewater conditions to facilitate large-scale implementation [4,6,7].

6. Pressure-Driven Membrane Technologies for Cr (VI) Removal

Membrane filtration technologies are widely recognized as highly effective systems for removing heavy metals from aqueous streams [111]. A membrane is a semi-permeable barrier that enables the selective separation of dissolved species based on physicochemical properties such as molecular size, shape, and charge. For chromium remediation, membrane-based processes are considered a sustainable and energy-efficient alternative to conventional physicochemical treatment methods, particularly for the selective removal of the highly toxic and mobile Cr (VI) species.

A wide range of membrane materials has been developed for water treatment applications. Polymeric membranes, including those based on polyamides, polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE), are widely used due to their chemical resistance, mechanical stability, and ease of fabrication. In addition, carbon-based nanomaterials such as graphene and carbon nanotubes have attracted significant attention because of their high permeability and tunable selectivity. More recently, composite membranes—including polymer–ceramic, polymer–metal, and nanocomposite structures—have been developed to combine the advantages of different material classes, thereby enhancing permeability, selectivity, fouling resistance, and overall operational lifetime [111].

Membrane processes applied for chromium removal include ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [53,112]. These technologies differ primar-

ily in pore size and separation mechanism, which directly determine their suitability for specific chromium species and wastewater characteristics. UF is generally used to remove particulate-bound or complexed chromium species, while NF is effective for rejecting both Cr (VI) and Cr (III) under suitable operating conditions. RO membranes, with their dense selective layer, provide the highest rejection efficiency and are typically used for highly contaminated streams or when stringent effluent quality is required. Performance can be further improved through membrane modification; for example, chemical modification of polyacrylonitrile (PAN)-based UF membranes has been shown to significantly enhance Cr (VI) removal efficiency [113]. In industrial applications, commercially available UF systems have achieved chromium removal efficiencies exceeding 95% in electroplating wastewater treatment [53].

Overall, membrane-based technologies are among the most efficient options for treating chromium-contaminated water, as they consistently achieve high removal efficiencies and produce high-quality effluents suitable for reuse or even potable applications. Reported chromium rejection rates commonly exceed 90–99% for nanofiltration and reverse osmosis systems, as well as for optimized ultrafiltration-assisted processes [61–63]. In addition to removal, membrane systems enable the concentration of chromium in the retentate stream, facilitating recovery and resource reuse strategies.

Despite these advantages, several operational challenges limit large-scale implementation. Membrane fouling, concentration polarization, and scaling significantly affect long-term performance and increase maintenance requirements. Furthermore, concentrate disposal and membrane replacement costs remain important economic constraints [64,65]. Energy demand also strongly depends on membrane type, with reverse osmosis requiring substantially higher pressure and energy input compared with ultrafiltration and nanofiltration. As a result, membrane processes are often integrated with pretreatment or post-treatment steps to improve stability, reduce fouling, and enhance overall process economics [61,64].

In summary, membrane filtration offers a highly effective and mature platform for chromium removal, combining high separation efficiency with the potential for water reuse and metal recovery. However, continued improvements in antifouling materials, process integration, and energy optimization are essential to further enhance its competitiveness in large-scale chromium remediation applications.

6.1. Ultrafiltration Membranes

Since their initial industrial deployment in the 1970s, UF membranes have undergone continuous development and are now widely recognized as a safe, cost-effective, and scalable separation technology for a broad range of contaminants in water and wastewater treatment applications.

Ultrafiltration is a pressure-driven process in which hydrostatic pressure forces water through a semi-permeable membrane, enabling the separation of solutes primarily based on molecular size. The separation performance is determined by the membrane's molecular weight cut-off (MWCO) and is further influenced by solute shape, charge, hydrodynamic conditions, and membrane–solute interactions [114]. The dominant mechanism in UF is size exclusion; however, surface interactions may also contribute to solute retention or, in some cases, reduce efficiency.

In the context of chromium removal, conventional ultrafiltration membranes have limited ability to directly reject dissolved Cr (VI) species (HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$), as these ions are significantly smaller than typical membrane pore sizes. Consequently, Cr (VI) removal cannot be effectively achieved through size exclusion alone. To overcome this limitation, several enhanced and hybrid approaches have been developed, including polymer-

enhanced ultrafiltration (PEUF), micellar-enhanced ultrafiltration (MEUF), adsorption-assisted ultrafiltration, surface-modified membranes, and coagulation-ultrafiltration integrated systems [66,67]. These strategies improve chromium removal by promoting complexation, adsorption, or entrapment of chromium species within larger aggregates that can be retained by the membrane.

The expansion of UF technologies in recent decades has been strongly driven by increasing demand for selective, low-cost, and energy-efficient separation processes. This growth has also been supported by greater environmental awareness, water scarcity, and increasingly stringent regulations governing water quality and industrial effluents [115].

UF systems offer several operational advantages, including relatively low transmembrane pressure requirements, reduced energy consumption, and easier scalability compared with tighter membrane processes such as nanofiltration and reverse osmosis. When combined with enhancement strategies such as polymer or surfactant addition, or adsorption-based integration, Cr (VI) removal efficiencies often exceed 90–95% [116,117]. In addition, UF systems generally have lower capital and operational costs, as well as reduced membrane replacement expenses.

However, despite these advantages, UF alone is insufficient for effective removal of dissolved chromium species due to the inherent size limitation of chromate ions. As a result, chemical complexing agents, adsorbents, or membrane surface modifications are often required to achieve satisfactory performance [67,116]. Furthermore, membrane fouling, concentration polarization, and the potential generation of secondary waste from additives such as polymers or surfactants may negatively affect long-term process sustainability [117].

From an application perspective, UF is most suitable as a pretreatment or as part of hybrid treatment systems, rather than as a standalone technology for chromium removal. In contrast, nanofiltration and reverse osmosis are generally preferred when stringent discharge standards or drinking water quality requirements must be met, due to their higher rejection efficiency for dissolved ionic species.

Overall, UF is a mature and economically attractive membrane technology that plays an important role in integrated chromium removal systems. Its greatest potential lies in combination with chemical or physical enhancement strategies that overcome its intrinsic limitations while maintaining low energy demand and operational simplicity.

Although commercially available UF membranes have demonstrated Cr (VI) removal efficiencies exceeding 95% under specific operating conditions, removal efficiency alone does not fully determine process performance or practical applicability. The development of nanomaterial-functionalized and Layer-by-Layer (LBL) membranes is driven by several additional objectives, including enhanced selectivity for chromium species, improved permeability and water flux, reduced membrane fouling, greater chemical stability, broader pH operating ranges, lower energy requirements, and increased membrane lifespan. Many advanced membrane materials are also designed to facilitate chromium recovery, improve performance in complex industrial wastewater containing competing ions, and reduce long-term operational costs. Therefore, interest in nanomaterials and LBL membrane architectures extends beyond marginal improvements in removal efficiency and focuses on improving the overall sustainability, robustness, and economic viability of chromium treatment systems. The Layer-by-Layer (LBL) assembly technique, based on the sequential deposition of polyelectrolytes, has emerged as a promising approach for membrane fabrication through the alternating deposition of cationic and anionic polyelectrolytes in aqueous media onto supporting substrates [63]. A schematic representation of the LBL assembly process is shown in Figure 3.

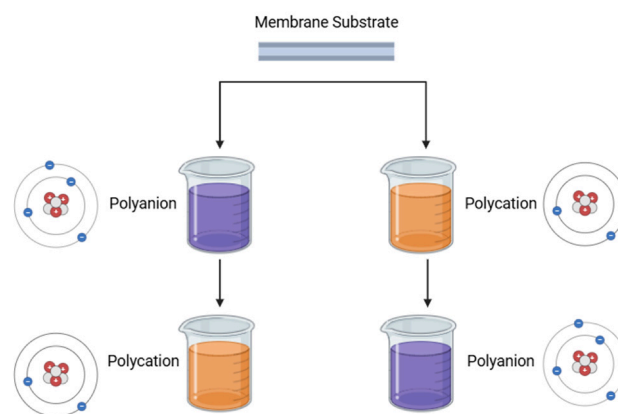


Figure 3. Membrane fabrication process via Layer-by-Layer (LBL) technique.

In this technique, the membrane substrate is alternately immersed in polycation and polyanion solutions, allowing the adsorption of polyelectrolytes onto its surface. After each deposition step, the membrane is rinsed with water to remove excess polyelectrolytes and facilitate the rearrangement of previously adsorbed layers [64,65]. The combined deposition of one anionic and one cationic polyelectrolyte forms a polyelectrolyte bilayer. Multiple bilayers can be formed through repeated deposition cycles. Using water as a solvent makes LBL technology environmentally friendly and sustainable, since harmful organic solvents are avoided [66,67]. Cationic and anionic polyelectrolytes have long linear polymeric chains that form interconnected nanochannels, enabling selective water transport with high permeability [63]. The wide variety of available polyelectrolytes allows precise control over charge density and pore size within these nanochannels, ensuring ionic selectivity [116].

Furthermore, LBL membranes exhibit significant antifouling properties due to their hydrophilic surface characteristics, which reduce pollutant adhesion. Electrostatic repulsion between the membrane surface and similarly charged foulants further inhibits contaminant adsorption [118]. LBL membranes also demonstrate antibiofouling behaviour, mainly attributed to strong interactions between their multifunctional groups and the nanomaterials incorporated into their structure [118].

The versatility and tunability of membranes fabricated via the LBL technique make them highly promising for a broad range of advanced separation applications. The Layer-by-Layer (LBL) assembly technique offers exceptional flexibility for membrane design because membrane surface charge, thickness, pore structure, hydrophilicity, and selectivity can be precisely controlled through the sequential deposition of polyelectrolyte layers [116,118]. Consequently, LBL-modified membranes have demonstrated significant improvements in Cr (VI) rejection, water permeability, antifouling behaviour, and membrane stability compared with many conventional membrane fabrication approaches. The use of aqueous processing conditions further enhances the environmental sustainability of the technique.

Despite these advantages, several limitations remain. The fabrication process often involves multiple deposition and rinsing cycles, which may increase production time and manufacturing costs. The long-term stability of multilayer structures under highly acidic, alkaline, or high-salinity operating conditions also remains an important consideration for industrial deployment [119]. Most studies evaluating LBL membranes for chromium removal have been conducted at laboratory scale, and relatively limited information is available regarding long-term operation under realistic wastewater conditions. Therefore, further research is required to improve scale-up strategies, membrane durability, and economic competitiveness prior to widespread commercial adoption.

6.2. Nanofiltration Membranes

To bridge the gap between the low rejection rates of conventional ultrafiltration and the high energy demands of reverse osmosis, nanofiltration (NF) membranes have emerged as a highly efficient alternative. Characterized by a loose, non-porous structure or sub-nanometer pore sizes, NF membranes typically have a MWCO ranging from 200 to 1000 Da [120]. Unlike ultrafiltration, which relies almost exclusively on physical sieving, the separation of hexavalent chromium in NF systems is governed by a complex interplay between steric hindrance and electrostatic interactions, most notably described by Donnan exclusion [121].

Because NF membranes generally have a negatively charged thin-film composite (TFC) polyamide surface layer, their ability to reject Cr (VI) is strongly influenced by the pH and ionic strength of the feed water. Under neutral to alkaline conditions, dissolved hexavalent chromium shifts predominantly into divalent chromate CrO_4^{2-} anions. The high negative charge density of these divalent ions intensifies electrostatic repulsion against the membrane surface, enabling NF systems to consistently achieve Cr (VI) removal efficiencies between 95% and 99.7% [121]. However, process efficiency can decrease in highly acidic streams, where Cr (VI) shifts toward less charged or protonated species, such as HCrO_4^- , weakening the Donnan exclusion effect. To address this limitation, recent research has focused on modifying membrane matrices to create permanently, highly negatively charged nanocomposite membranes that maintain superior rejection rates across a much wider pH operating window [122].

From an operational perspective, NF offers a compelling balance of high selectivity and moderate economic viability. It operates at significantly lower hydrostatic pressures than reverse osmosis, resulting in reduced energy consumption and lower capital costs for industrial facilities [120]. In circular economy configurations, NF is highly valued for its ability to selectively fractionate ions. For instance, in metal finishing and chromium plating rinse water, NF membranes can achieve near-complete heavy metal rejection while allowing certain monovalent salts to pass through, yielding a purified permeate stream suitable for direct industrial reuse [121,123]. Nevertheless, NF systems remain vulnerable to membrane fouling and concentration polarization, and managing the resulting chromium-rich retentate stream continues to be a core challenge for long-term process sustainability [120].

6.3. Reverse Osmosis Membranes

When absolute containment of heavy metals and the production of ultra-pure drinking water are required, Reverse Osmosis (RO) is one of the most effective membrane-based barriers for removing dissolved heavy metals and ionic contaminants. Operating via a solution-diffusion mechanism rather than pore-based sieving, RO membranes feature an extremely dense, non-porous active polyamide layer [120]. This structure serves as an unyielding barrier against almost all dissolved inorganic solutes and heavy metal ions, regardless of their specific speciation state, molecular size, or surface charge [121].

In comparative performance assessments, RO systems consistently deliver the highest and most reliable Cr (VI) retention rates, routinely exceeding 99.0% to 99.9% [121,122]. This makes RO exceptionally well-suited for treating highly concentrated industrial effluents, such as car shock absorber factory wastewater, or for ensuring compliance with stringent municipal drinking water standards where residual chromium concentrations must be virtually undetectable [121]. To optimize this process, multi-stage hybrid configurations often use ultrafiltration or nanofiltration as a selective pre-treatment stage before the RO stage [120]. This dual-membrane approach significantly reduces the extreme operational

demands on the RO elements, stabilizes overall permeate flux, and protects the sensitive dense layers from catastrophic failure [120].

Despite delivering near-perfect decontamination, RO is the most energy-intensive and costly membrane technology discussed [115,116]. Overcoming the immense osmotic pressure of concentrated heavy metal streams requires substantial hydrostatic pressure, which increases electricity demands and operational expenditures compared to UF and NF. Furthermore, RO membranes are highly susceptible to inorganic scaling and mineral fouling [120]. Hardness ions, such as calcium and magnesium, along with suspended organic matter, readily precipitate onto the dense membrane surface, causing a rapid decline in water flux and necessitating aggressive, frequent chemical cleaning cycles that quickly degrade the membrane material. Finally, the generation of a highly concentrated, hazardous liquid brine stream remains a major environmental drawback. Unlike hybrid UF systems that produce manageable sludge, the disposal of RO brine requires complex downstream handling, such as evaporation or crystallization, to achieve true zero liquid discharge (ZLD).

6.4. Critical Assessment of Membrane Technologies

Membrane-based technologies are among the most effective options for Cr (VI) removal because they consistently provide high rejection efficiencies and can achieve very low residual chromium concentrations. Nanofiltration typically achieves Cr (VI) removal rates above 95%, while reverse osmosis frequently exceeds 99% rejection, making these technologies particularly suitable for drinking water production and industrial water reuse applications [120,121]. Compared with conventional precipitation and adsorption processes, membrane systems generate less solid waste and offer superior effluent quality.

However, membrane fouling, concentration polarization, membrane replacement costs, and the management of chromium-rich concentrate streams remain significant operational challenges [120,121]. In addition, energy requirements increase substantially from ultrafiltration to nanofiltration and especially to reverse osmosis due to the higher operating pressures involved. Consequently, although membrane technologies provide excellent treatment performance, their economic feasibility strongly depends on wastewater characteristics, recovery targets, and concentrate disposal strategies. Hybrid treatment configurations that combine adsorption, precipitation, or electrochemical processes with membrane filtration are increasingly being investigated to improve overall process sustainability and reduce operating costs [122,123].

7. Comparative Assessment of Cr (VI) Removal Technologies

The wide range of technologies available for Cr (VI) removal makes direct comparison difficult, as each process operates through different mechanisms and targets specific treatment objectives. Conventional technologies such as chemical precipitation, ion exchange, and adsorption are generally mature and widely implemented, while advanced processes, including electrochemical, biological, photocatalytic, and membrane-based systems, often offer improved performance, selectivity, or resource recovery potential. However, these benefits are frequently associated with increased operational complexity, higher energy requirements, or increased capital costs.

In addition, reported Cr (VI) removal efficiencies should be interpreted with caution because experimental conditions, chromium speciation, wastewater composition, and performance metrics vary considerably among studies. Therefore, the comparison in Table 2 is intended to provide a qualitative overview of the main advantages, limitations, energy requirements, technological maturity, and typical application fields of the most widely studied Cr (VI) removal technologies, rather than a strict quantitative ranking.

Table 2. Comparative assessment of Cr (VI) removal technologies.

Technology/ Approach	Principle	Typical Cr (VI) Removal (%)	Advantages	Disadvantages	Sludge Generation	Operating Cost	Energy Demand	Suitable Concentration Range	Key Ref.
Chemical Precipitation	Reduction in Cr (VI) to Cr (III) followed by precipitation as insoluble hydroxides	90–99	Mature technology, simple operation, highly effective, scalable for industry	Large sludge production, chemical consumption, post-treatment often required	High	Low- Moderate	Low	Medium-High Cr (VI) Concentrations	[31–38]
Ion Exchange	Selective exchange of chromate ions with functional groups on resins	90–99	High selectivity, suitable for low concentrations, chromium recovery possible	Resin fouling, regeneration requirements, competing ions	Low	Moderate- High	Low	Low-Moderate concentrations	[39–42]
Adsorption	Surface adsorption and/or reduction in Cr (VI) on porous materials	80–99	Simple operation, low energy demand, versatile adsorbents	Strong pH dependence, regeneration challenges, performance reduction in real wastewater	Low	Low- Moderate	Low	Low-Moderate concentrations; polishing applications	[45–60]
Electrodialysis (ED)	Ion transport through ion-exchange membranes under electric field	>90	Simultaneous removal and chromium recovery, low sludge generation	Membrane fouling, scaling, sensitivity to competing ions	Very Low	Moderate	Moderate	Moderate concentrations, industrial wastewater	[68–75]
Electrodeionization (EDI)	Combination of electrodialysis and ion exchange with continuous resin regeneration	98–99.8	Very high removal efficiency, low chemical consumption, chromium recovery	High capital cost, complex operation, membrane fouling	Very Low	High	Moderate	Low-Moderate concentrations requiring high purity	[72–80]
Electrocoagulation (EC)	In situ generation of coagulants from sacrificial electrodes	90–99	Very high removal efficiency, low chemical consumption, chromium recovery	Electrode consumption, passivation, electricity requirements	Moderate	Moderate	Moderate	Moderate-High concentrations, industrial effluents	[83–91]
Bioremediation	Biosorption, bioaccumulation, bioreduction and phytoextraction	80–100	Environmentally friendly, low energy demand, in situ application possible	Slow kinetics, sensitive to environmental conditions, scale-up challenges	Very Low	Low	Very Low	Low concentrations, soils, groundwater	[90–103]

Table 2. Cont.

Technology/ Approach	Principle	Typical Cr (VI) Removal (%)	Advantages	Disadvantages	Sludge Generation	Operating Cost	Energy Demand	Suitable Concentration Range	Key Ref.
Photocatalysis	Photoreduction of Cr (VI) to Cr (III) using semiconductor catalysts under light irradiation	90–98	Solar energy utilization, minimal chemical requirements, simultaneous pollutant degradation	Catalyst deactivation, recombination losses, scale-up limitations	Very Low	Moderate	Low-Moderate	Low-Moderate concentrations; polishing applications	[97–110]
Ultrafiltration (UF)	Pressure-driven separation primarily through size exclusion	70–95	Low operating pressure, simple operation, suitable pretreatment step	Limited direct Cr (VI) rejection, membrane fouling	Very Low	Low	Low	Low-Moderate concentrations (often hybrid systems)	[114–117]
Nanofiltration (NF)	Size exclusion and Donnan electrostatic exclusion	95–99.7	High rejection efficiency, lower pressure than RO, partial ion selectivity	Membrane fouling, concentrate management	Very Low	Moderate	Moderate	Low-High concentrations	[120–123]
Reverse Osmosis (RO)	Dense membrane separation via solution-diffusion mechanism	99–99.9	Highest rejection efficiency, drinking-water compliance	High energy consumption, scaling, brine disposal	Very Low	High	High	Wide concentration range, highly contaminated streams	[120,121]
Nanomaterials	Adsorption, reduction and precipitation on engineered nanostructures	>90	Extremely high surface area, rapid kinetics, tunable properties	Recovery difficulties, stability concerns, limited commercialization	Very Low	Moderate-High	Low	Low-Moderate concentrations	[32,61–67]
Layer-by-Layer (LBL) Membranes	Polyelectrolyte multilayer assembly providing tunable nanochannels and charge selectivity	95–99	High selectivity, antifouling potential, tunable membrane properties	Mainly laboratory/pilot scale, fabrication complexity	Very Low	Moderate	Moderate	Low-Moderate concentrations	[63–67,117–119]

This comparative assessment highlights the trade-offs between removal efficiency, sustainability, operational complexity, and scalability that must be considered when selecting an appropriate treatment strategy for a specific application.

As shown in Table 2, no single technology can be considered universally superior for all Cr (VI) remediation scenarios. Conventional technologies remain attractive because of their simplicity, commercial maturity, and relatively low implementation costs. Among these, adsorption offers high flexibility and is frequently employed as a polishing step to achieve stringent discharge limits.

Advanced electrochemical technologies, such as electrodialysis, electrodeionization, and electrocoagulation, combine high removal efficiencies with the potential for chromium recovery. However, their performance depends strongly on electrical energy consumption, membrane or electrode stability, and wastewater composition. Among the advanced technologies reviewed, biological treatment processes generally exhibit the lowest energy requirements, whereas reverse osmosis represents one of the most energy-intensive options due to the high hydraulic pressures required for operation. Electrochemical technologies occupy an intermediate position, with energy demand strongly influenced by wastewater conductivity, current density, and process configuration.

Biological processes exhibit the lowest energy demand and excellent sustainability characteristics but typically suffer from slower treatment kinetics and greater sensitivity to environmental conditions. In contrast, photocatalytic systems can achieve rapid Cr (VI) reduction under optimized conditions, although large-scale implementation is limited by catalyst stability and light utilization efficiency.

Membrane technologies, particularly nanofiltration and reverse osmosis, provide some of the highest and most reliable chromium rejection efficiencies currently available. Nevertheless, membrane fouling, concentrate management, and energy consumption remain important operational challenges.

Emerging material-based approaches, including nanomaterials and Layer-by-Layer (LBL) membrane architectures, demonstrate considerable potential for future applications due to their tunable physicochemical properties and enhanced selectivity. However, most of these systems remain at the laboratory or pilot scale and require further validation under realistic operating conditions before widespread commercial implementation.

The selection of the most appropriate Cr (VI) treatment technology ultimately depends on site-specific factors, including chromium concentration, wastewater composition, treatment objectives, regulatory requirements, resource recovery potential, and economic constraints. Future research should focus on developing hybrid treatment systems that integrate adsorption, membrane separation, electrochemical processes, and advanced functional materials. Attention should be given to chromium recovery, reduction in energy consumption, membrane fouling mitigation, long-term material stability, and validation under real industrial wastewater conditions. The transition from laboratory-scale demonstrations to pilot- and full-scale applications remains one of the most important challenges in the practical implementation of next-generation Cr (VI) treatment technologies.

8. Conclusions

Hexavalent chromium contamination remains a critical environmental challenge due to its high toxicity, persistence, and mobility in aquatic systems. The literature reviewed in this study demonstrates that conventional treatment technologies, including chemical precipitation, ion exchange, and adsorption, can achieve significant Cr (VI) removal under appropriate operational conditions. Advanced electrochemical processes, such as electrocoagulation, electrodialysis, and electrodeionization, have further expanded the available treatment options. However, many of these methods are associated with limitations such

as sludge generation, high chemical consumption, membrane fouling, or reduced efficiency in complex water matrices.

Advanced treatment processes, particularly membrane-based technologies, have emerged as highly promising alternatives for efficient chromium removal. Among them, ultrafiltration membranes modified with functional materials, nanocomposites, and Layer-by-Layer (LBL) assemblies exhibit enhanced selectivity, permeability, antifouling behavior, and chromium rejection efficiency. In parallel, the use of sustainable adsorbents derived from biomass and agricultural waste offers environmentally friendly and cost-effective solutions aligned with circular economy principles.

Recent developments in nanotechnology, photocatalysis, and hybrid treatment systems further demonstrate the potential for achieving very high Cr (VI) removal efficiencies while reducing operational and environmental impacts. Nevertheless, large-scale implementation still requires further investigation into long-term membrane stability, regeneration efficiency, treatment cost, and performance under real wastewater conditions. The comparative assessment presented in this review highlights that no single technology is universally optimal for all Cr (VI)-contaminated water. The selection of an appropriate treatment strategy depends strongly on chromium concentration, wastewater composition, regulatory requirements, treatment objectives, and economic constraints. Conventional technologies remain attractive due to their technological maturity and relatively low implementation costs, whereas advanced membrane and electrochemical processes offer superior removal efficiencies and resource recovery potential at the expense of increased operational complexity and energy demand.

Future research should focus on the development of highly selective and fouling-resistant materials, improved adsorbent and membrane regeneration strategies, reduction in energy consumption, and validation of emerging technologies under realistic industrial operating conditions. Attention should be given to hybrid treatment systems that combine complementary removal mechanisms, thereby enhancing treatment efficiency, process sustainability, and resource recovery opportunities. Overall, the integration of advanced membrane technologies with functionalized materials, nanostructured adsorbents, photocatalytic systems, and bio-based treatment approaches represents a promising pathway toward the development of sustainable and resource-efficient water treatment systems. As environmental regulations become increasingly stringent, future Cr (VI) remediation strategies are expected to rely on hybrid and circular-economy-oriented approaches capable of simultaneously achieving high removal efficiencies, reduced environmental footprints, and enhanced resource recovery.

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Abbreviations

CEDI	Continuous Electrodeionization
COFs	Covalent Organic Frameworks
Cr	Chromium
Cr (III)	Trivalent Chromium
Cr (VI)	Hexavalent Chromium
EC	Electrocoagulation/Electrochemical Coagulation
ED	Electrodialysis
EDI	Electrodeionization
GAC	Granular Activated Carbon
IX	Ion Exchange
LBL	Layer-by-Layer Assembly
LDHs	Layered Double Hydroxides
MCL	Maximum Contaminant Level
MEUF	Micellar-enhanced Ultrafiltration
MOFs	Metal–Organic Frameworks
MWCO	Molecular Weight Cut-Off
MXenes	MXene Two-Dimensional Materials
NF	Nanofiltration
nZVI	Nano-zerovalent Iron
PAN	Polyacrylonitrile
PEUF	Polymer-enhanced Ultrafiltration
PPC	Public Power Corporation
PRBs	Permeable Reactive Barriers
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
UF	Ultrafiltration
UV	Ultraviolet Irradiation
WHO	World Health Organization
XPS	X-ray Photoelectron Spectroscopy
ZLD	Zero Liquid Discharge

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