



Removal of Hexavalent Chromium From Waste Water- A Review

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Abstract-

Hexavalent chromium (Cr(VI)) contamination in wastewater poses a significant threat to human health and the environment due to its carcinogenic and toxic nature. This review aims to provide a comprehensive overview of various methods employed for the removal of hexavalent chromium from wastewater, emphasizing recent advancements and challenges.

The review begins by elucidating the sources and adverse effects of Cr(VI) contamination, highlighting the urgency of effective remediation strategies. Subsequently, it explores conventional treatment methods such as chemical precipitation, coagulation-flocculation, and ion exchange, while underscoring their limitations in terms of cost, sludge production, and efficiency. In response to the drawbacks of conventional methods, the review extensively covers emerging technologies and advanced materials for hexavalent chromium removal. Advanced oxidation processes, membrane filtration, and biological treatment methods are discussed, shedding light on their potential in achieving higher removal efficiencies and minimizing environmental impact. Furthermore, the incorporation of nanomaterials and composite materials for Cr(VI) adsorption and reduction is thoroughly examined, emphasizing the role of nanotechnology in enhancing treatment performance. The review also addresses the challenges associated with the scalability, stability, and cost-effectiveness of these novel technologies. Additionally, regulatory aspects and the global scenario of hexavalent chromium contamination are discussed, emphasizing the need for stringent guidelines and international collaboration to address this environmental concern. The economic feasibility and sustainability of various removal techniques are evaluated to provide a holistic perspective on their practical applicability.

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INTRODUCTION

The earth's crust contains a comparatively large amount of the transitory metal chromium. Chromium can be in one of two oxidation states: +6 or +2. Cr(VI) and Cr(III) are the most stable and, as a result, the prevalent forms. In ultramafic igneous and metamorphic rocks, Cr(III) is a mineral that is frequently found in soil. Stable and highly affine to particle surfaces is Cr(III). Because Cr(III) hydroxide is a salt that dissolves sparingly, its

mobility is restricted. Manganese oxides are the sole substances that can cause Cr(III) oxidation in soil. Cr(III) is an essential component of life, used in the digestion of lipids, amino acids, and carbohydrates, and is far less hazardous than Cr. Human activity is the primary source of Cr(VI) in the environment. A wide spectrum of industrial activities involves the use of chromium, among them, are electroplating, leather tanning, mineral processing, metallurgical processes, mining,



paints, pigment, and glass. Cr(VI) is an oxidant, it is reactive and mobile since it is not adsorbed in most sediment, particularly after pH. Cr(VI) is highly toxic, mutagenic, teratogenic, and carcinogenic. It causes many health effects on humans such as renal impairment, neutral cell injury, liver dysfunction, and stomach ulcers. Chromium chemistry in soils is well studied. Cr(VI) has an affinity to water, is not sorbed in most sediments, and migrates above neutral pH. Organic matters, particularly those having sulfhydryl groups and humic and fulvic acids, reduce Cr(VI). It is also reduced by ferrous iron (Fe^{2+}) and S^{2-} . The above information indicates the need for control and treatment of chromium-laden wastewaters at the source. There are various techniques used for the treatment of chromium in wastewaters. Among them are ion exchange, adsorption using a wide spectrum of natural and waste material, membrane processes such as electrodialysis, electro-ionization used separately or coupled with ion exchange, and biological treatment using bacteria, fungi, yeast, or algae, all suffering from the production of high amounts of contaminated waste material, sludge, or concentrate

Hexavalent chromium (Cr(VI)) contamination in wastewater is a pressing environmental issue with profound implications for public health and ecological well-being. Chromium, a naturally occurring metal, exists in various oxidation states, with hexavalent chromium being a particularly hazardous form due to its carcinogenic and toxic properties. The widespread use of chromium in industrial processes, such as metal plating, leather tanning, and textile manufacturing, has led to the discharge of Cr(VI) into water bodies, posing a significant threat to ecosystems and human populations.

The adverse effects of hexavalent chromium exposure, including respiratory problems, skin irritation, and increased cancer risk, underscore the critical need for effective wastewater treatment strategies. Traditional methods for chromium removal, such as chemical precipitation and ion exchange, have limitations in terms of cost, efficiency, and the generation of secondary pollutants. As a result, there is an increasing emphasis on exploring and developing advanced technologies and materials that offer improved performance and environmental sustainability.

This comprehensive review seeks to examine and synthesize the existing knowledge on the removal of hexavalent chromium from wastewater. The aim is to provide a holistic understanding of the various treatment methods, ranging from conventional to cutting-edge technologies, and to highlight recent advancements, challenges, and opportunities in this field. By doing so, this review aims to contribute to the development of innovative and sustainable solutions to address the persistent issue of hexavalent chromium contamination in wastewater.

The subsequent sections of this review will delve into the sources and impacts of hexavalent chromium contamination, explore conventional treatment methods and their limitations, and comprehensively discuss emerging technologies, advanced materials, and nanotechnology-based approaches. Regulatory considerations, global perspectives on chromium contamination, and the economic feasibility of removal techniques will also be addressed. Through this comprehensive exploration, we aspire to offer valuable insights that can guide researchers, environmental engineers, and policymakers in devising effective strategies for the removal of hexavalent chromium, ultimately contributing to the protection of water resources and human health.

ELECTROCOAGULATION PROCESS

Cr(VI) may be converted to Cr(III) in the electrocoagulation process (i) at the cathode or (ii) at the anode surface in an acidic environment. After then, Cr(III) precipitates as $\text{Cr}(\text{OH})_3$ when it co-precipitates with metal hydroxides. Additional removal mechanisms include (i) the specific adsorption of Cr(VI) through surface complexation reactions and direct complexation with soluble and insoluble metal hydroxides (or oxyhydroxides), respectively, and (ii) adsorption through electrostatic attraction and electrical neutralization between charged metal hydroxides and Cr(VI). Depending on the metal of the sacrificial electrode iron or aluminum one or more of these mechanisms is in charge of removing chromium via the electrocoagulation method. Thus, in the subsequent subsections, chromium removal procedures will be presented individually for each electrode material. Coagulation and flocculation techniques are used to remove suspended solids from the effluents. The



separation efficiency of suspended particles depends on particle size, shape, and density. Suspended solids with similar surface charge repel each other and remain suspended in water. Coagulation and flocculation enhance particle collision, neutralize surface charges, and grow floc by sedimentation. Coagulants neutralize the negative surface charges present on non-settleable solids and create micro flocs of small suspended particles. Agitation disperses coagulant and promotes particle collisions and adequate coagulation. Contact time in the rapid-mix chamber is typically 1 to 3 min. Flocculation increases the particle size from micro flocs produce larger flocs called pin flocs. Flocculation contact times range from 15 or 20 min. The mixing velocity is gradually decreased to prevent flocs from being torn apart. Coagulation techniques precipitate low soluble compounds like hydroxides, sulfides, and carbonates. A colloid is a suspension of atoms or molecules whose density is equal to water density. These particles are unable to settle down because of low density. The coagulation treatment method increases the density and removes these colloidal particles. Coagulation efficiency depends on the type of coagulant, coagulant dosage, pH, temperature, alkalinity, and mixing conditions. In this method, chemical reagents or inorganic flocculants like $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and $FeCl_3$ and derivatives of these materials such as poly aluminum chloride and poly ferric chloride are flocculants used in the wastewater treatment process. Ferric ammonium sulfate (FAS) produces large amount of sludge which precipitates during sedimentation stage of the coagulation process. The coagulation process is known to treat cadmium, chromium, nickel, and zinc. The sludge may be recovered, recycled, and used again. Coagulation/flocculation is efficient for eliminating heavy metals from wastewater. Coagulation produces secondary solid contaminant in the form of flocs and sludge. The added chemical solvents are low reusable that is harmful to both the human and the environment.

METHODS OF ADSORPTION

The process of molecules being concentrated on the sorbent's surface is called adsorption. The molecules transition from the bulk phase to a semiliquid state when adsorbed in the pores. The ratio of the compound's solubility to concentration acts as the

driving force behind adsorption. Chromium metals are frequently removed from waterways and industrial wastewaters through adsorption. Suzuki (1990) provided a more thorough description and investigation of the adsorption phenomena, encompassing information on adsorption equilibrium and kinetics as well as the effects of various parameters like pH, temperature, and surface area. Adsorption offers significant advantages like low cost, availability, profitability, easy of operation and efficiency, in comparison with conventional methods (such as membrane filtration or ion exchange) especially from economical and environmental points of view (Hashem et al. 2007; Ravikumar et al. 2005; Allen et al. 2005; Mittal et al. 2005). A variety of natural and synthetic materials has been used as Cr(VI) sorbents, including activated carbons, biological materials, zeolites, chitosan, and industrial waste.

(i) Activated Carbon- The most studied adsorbent in adsorption of chromium is found to be the activated carbon derived from various sources (Mohan and Pittman 2006). Activated carbon adsorption seems to be an attractive choice for chromium removal both for its exceptionally high surface areas which range from 500 to 1,500 $m^2 g^{-1}$, well-developed internal microporosity structure as well as the presence of a wide spectrum of surface functional groups like carboxylic group (Chingombe et al. 2005). For these reasons, activated carbon adsorption has been widely used for the treatment of chromium containing wastewaters.

(ii) Biosorbents- Biosorption of chromium from aqueous solutions is relatively a new process that has proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of chromium ions from waste water streams (Volesky and Holan 1995; Lee and Volesky 1997; Kratochvil et al. 1998; Kratochvil and Volesky 1998; Basso et al. 2002; Pagnanelli et al. 2003; Volesky 2003; Park et al. 2006).

(iii) Modified Sorbents- Most of the adsorbents are not nearly effective at removing heavy metals like Cr(VI). Therefore, the adsorption capacities and the feasible removal rates must be substantially boosted by modification of the sorbent with suitable technique. For this reason, modification and impregnation techniques



were used to increase surface adsorption and, so, removal capacity and to add selectivity to sorbents.

(iv) Industrial Waste- Sorbents Industrial wastes can be used as low-cost adsorbents with capability to adsorb heavy metals. Iron(III) hydroxide is a waste from fertilizer industries and one of the principle sorbents of the oxyanionic pollutants such as phosphates, arsenates, and chromates in aqueous systems. It has been extensively investigated for removing Cr(VI) from wastewater (Namasivayam and Ranganathan 1993). It was reported that the maximum adsorption capacity of iron(III) hydroxide was found to be 0.47 mg of Cr₆₊/g at pH of 5.6.

(v) Chitosan- Another material shown to adsorb metals is chitin. Chitin is second only to cellulose in terms of abundance in nature and is found in the exoskeletons of crabs and other arthropods and in the cell walls of some fungi (Berkeley 1979). Chitin is also a waste product of the crab meat canning industry. Chitosan can be produced chemically from chitin and is found naturally in some fungal cell walls. The growing need for new sources of low-cost adsorbent, the increased problems of waste disposal, the increasing cost of synthetic resins undoubtedly make chitosan one of the most attractive materials for wastewater treatment.

TECHNIQUES FOR MEMBRANE FILTRATION

For the treatment of wastewater, membrane filtration has drawn a lot of interest. Membrane has the ability to eliminate heavy metals like Cr(VI). The following are some of the membrane filtration types that can be used for Cr(VI) removal: inorganic, polymeric, and liquid membranes. Hexavalent chromium treatment performance and the characteristics of some membranes.

(i) Inorganic Membrane- Inorganic membranes are one of the most important porous materials because of their high chemical and great thermal stability. Most of the ceramic and other inorganic membranes today are in the tubular configuration. Some studies have been done to remove Cr(VI) using inorganic membrane. Pugazhenthii et al. (2005) prepared supported non-interpenetrating modified ultra filtration carbon membrane by gas phase nitration using NO_x and amination using hydrazine hydrate. The membrane was used for the separation of Cr (VI) from the aqueous solution. It was found that the effective pore radius of the unmodified, nitrated, and aminated carbon

membranes are found to be 2.0, 2.8, and 3.3 nm, respectively. The water flux of the modified membrane, however, has been found to increase by two times compared to that for the unmodified membrane. Separation experiments on the chromic acid solution have been carried out using unmodified (giving 96% rejection), nitrated (giving 84% rejection), and aminated (giving 88% rejection) carbon membrane.

(ii) Polymeric Membrane- Polymeric membrane separation systems have nowa days become an important wastewater treatment technology, which facilitate the removal and recovery of pollutants as well as solvent, i.e., water. Aroua et al. (2007) removed Cr(VI) from aqueous dilute solutions using polymer-enhanced ultrafiltration (PEUF) process. Three water soluble polymers, namely, chitosan, polyethyleneimine (PEI), and pectin were used. The ultrafiltration studies were carried out using a laboratory scale ultrafiltration system equipped with polysulfone hollow fiber membrane. The effects of pH and polymer composition on rejection coefficient and permeate flux at constant pressure were investigated. It was reported that the solution pH was found to be the major factor which controls the rejection of chromium species. Muthukrishnan and Guha (2008) studied removal of Cr(VI) with different nanofiltration composite polyamide membranes for varying concentration and pH of the membrane feed solution. Two membranes were used for this investigation: one, a high rejection membrane (NFI) and the other, a low rejection membrane (NFII). The percent rejection of chromium was found to increase with the increase of feed solution pH. It has been observed that the effect of feed concentration on the percent rejection was quite low, but the nature of effect varies with the pH of the solution with a transition happening at above pH 7.0.

(iii) Liquid Membrane- High selectivity is one of the advantages of liquid membranes. There are two basic types of liquid membranes, emulsion liquid membrane (ELM), and immobilized liquid membrane (ILM), also called a supported liquid membrane (SLM). The emulsion liquid membrane uses surface forces to maintain a very thin yet stable immiscible membrane between the two miscible phases (Li and Calo 1992). Immobilized liquid membrane consists of a polymer support impregnated with a viscous solution of carrier. Many different types of polymer supports are available to prepare ILM including cellulose acetate reverse



osmosis membrane, microporous polypropylene ultra filtration membrane, polyvinylchloride filter, and hollow fiber membrane (Araki and Tsukube 1990). Liquid membranes have been proved to be an effective and inexpensive method with potential application for the removal of heavy metals. In this process, both extraction and stripping steps were combined in one stage, which led to simultaneous purification and concentration of the solute.

ELECTROCHEMICAL DISSOLUTION

To maximize the removal of heavy metal from contaminated wastewater, electrical potential has been utilized to modify the conventional chemical precipitation (Kurniawan et al. 2006). Some studies using electrochemical precipitation (ECP) was carried out for the removal of Cr(VI) from real electroplating wastewater. Kongsricharoern and Polprasert (1995) investigated the Cr(VI) removal from an electroplating wastewater using the ECP process. The ECP unit consisted of an electrolytic cell made of two steel plates representing anode and cathode. Cr⁶⁺ was in the range of 215–3,860 mg/l, and the pH was 1.5. The parameters varied during the ECP experiments were: electrical potential, hydraulic retention time, Cr⁶⁺ concentration, conductivity, and initial pH. It was found that the optimum ECP conditions are: electrical potential, 75 V; current, 4.8 A; hydraulic retention time, 50 min; initial pH, above 3.2. Under these conditions, the Cr⁶⁺ concentrations remaining in the effluent were less than 0.2 mg/l. The result is comparable to that of Kongsricharoern and Polprasert (1996), which also employed bipolar ECP for Cr(VI) removal using the same type of wastewater. Bipolar ECP was also technically applicable for 85% of Cr removal with an initial Cr concentration of 2,100 mg/l.

CONCLUSION

One of the most significant heavy metal contaminants in the world this century seems to be Cr(VI). Cr(VI), which is produced from industrial wastewater, is extremely hazardous and poses a major risk to the environment and public health. This review demonstrates how extensively researched and how many scientists are interested in the many methods for removing Cr(VI). Inconsistencies in the data presentation make it exceedingly difficult to compare different methodologies. The elimination of Cr(VI) was assessed under various circumstances, including pH,

temperature, ratios, and beginning chromium concentration. A variety of chromium-tainted water sources were utilized, including drinking water, tannery wastewater, ground water, electroplating wastewater, and synthetic industrial effluent. This increases the complexity and difficulty of pursuing comparisons. Thus, the comparison is limited to the benefits and drawbacks of the removal techniques that have been presented. Adsorption is a relatively novel method for chromium elimination. It has shown to be a helpful instrument in limiting the degree of metal contamination. The effectiveness of several activated carbon types in removing Cr(VI) was examined.

REFERENCES

1. Aggarwal, D., Goyal, M., Bansal, R.C., Adsorption of chromium by activated carbon from aqueous solution (1999) *Carbon*, 37 (12), pp. 1989-1997.
2. Ahalya, N., Ramachandra, T.V., Kanamadi, R.D., Biosorption of heavy metals (2003) *Research Journal of Chemistry and Environment*, 7 (4), pp. 71-79
3. K.C. Khulbe, T. Matsuura, *Appl. Water Sci.* 8 (2018) 19.
4. R. Mulyanti, Heru. Susanto, *Conf. Ser. Earth Environ. Sci.*, (2018) 142(1):012017 DOI: 10.1088/1755-1315/142/1/012017.
5. J Ilin Sadeghi, Papatya Kaner, Ayse Asatekin. *Chem. Mater.* 30 (2018) 21, 7328–7354 Publication.
6. Tetsuaki Nishida, Akane Morimoto, Yoshito Yamamoto, Shiro Kubuki. *Appl. Water Sci.*, 7 (2017) 4281-4286.
7. Muharrem. Ince, Olcay. Kaplan. Ince, *Water/Wastewater Treatment. Biochem. Toxicol. - Heavy Met. Nanomater.*, (2019)
8. A. Pohl, *Water Air Soil Pollution* 231 (2020) 503.
9. Tarekegn, M.M., Salilih, F.Z., Alemitu Iniyehu Ishetu, A.I., 2020. Microbes used as a tool for bioremediation of heavy metal from the environment. *Cogent. Food Agric.* 6, 1783174 <https://doi.org/10.1080/23311932.2020.1783174>.
10. Xia, S., Song, Z., Jeyakumar, P., Shaheen, S.M., Rinklebe, J., Ok, Y.S., Bolan, N., Wang, H., 2019. A critical review on bioremediation technologies for Cr(VI)- contaminated soils and wastewater. *Crit. Rev. Environ. Sci. Technol.* 49, 1027–1078.



12. M. Achak, F. Elayadi, W. Boumya, Am. J. Appl. Sci. 16 (3) (2019) 59.91
13. Khalid. Z. Elwakeel, Ahmed. M. Elgarahy, Ziya. A. Khan, Muath. S. Almughamisi, Abdullah. S. Al-Bogami, Mater. Adv.,1(2020) 1546-1574.
14. Muharrem. Ince, Olcay. Kaplan. Ince, Water/Wastewater Treatment. Biochem. Toxicol. - Heavy Met. Nanomater., (2019).
15. M.A. Agoro, A.O. Adeniji, M.A. Adefisoye, O.O. Okoh, Water 12 (2020) 2746.

