



Review

The journey traversed in the remediation of hexavalent chromium and the road ahead toward greener alternatives—A perspective



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ABSTRACT

The discharge of heavy metals from industrial wastewater beyond the permissible limit causes serious pollution to the environment. In this regard, chromium that is discharged from electroplating, tannery and dye industrial effluents poses a major health hazard in view of the carcinogenic and genotoxic nature of hexavalent chromium. It is imperative to devise effective remediation strategies to detoxify chromium keeping in view the USEPA regulatory limit. This review deals with the environmental occurrence, remediation methods and future perspectives in the sequestration of hexavalent chromium [Cr(VI)] from wastewater. Remediation methods such as solvent extraction, adsorption using polymeric resins, clays, biopolymers, biomass, activated carbon and graphene oxide are discussed with respect to their removal efficiency, regenerability, adsorption capacities and other characteristics. Considerable emphasis is laid on the utility of chelating adsorbents and ionic liquid impregnated adsorbents for the remediation of chromium from tannery and electroplating wastewater. The review examines published data in last few years concerning the removal of toxic Cr(VI) with a critical evaluation on the merits and demerits of each of the processes and the road ahead towards formulating more effective strategies.

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1. Introduction

The phenomenal advancements in science and technology over the last decade have witnessed the applicability of metals and its alloys for diverse applications. However, the improper disposal of the metal ions can affect the environment significantly. The wastewater originating from various industries (textiles, dyes, tannery, electroplating etc.) contain a significant amount of metals such as chromium, lead, cadmium, arsenic, mercury etc. These

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are typically referred to as 'Heavy metals' with an atomic density greater than 6 g cm^{-3} . Heavy metal pollution is an environmental problem [1] in view of their toxicity even at parts per billion levels.

In retrospect, there are several methods that are very useful for heavy metal detoxification [2]. Nevertheless, it is vital to understand the efficacy of these methods and there is always a growing need to address the problems associated with some of the existing processes and devise improved strategies for remediation. This aspect should be evaluated from pilot scale treatment to large scale operations in order to ensure that the final discharge of the metal ions is within the standard permissible limits. Separation techniques such as reverse osmosis [3], chemical precipitation [4], ion exchange [5], membranes [6], liquid–liquid extraction (LLE) [7] and solid phase extraction (SPE) [8] are widely utilized for sequestration of metal ions. Novel electrochemical techniques [9] involving biopolymer electrodes are also quite effective to extract metal ions from water. After achieving the required degree of selectivity, these separation techniques are coupled to various sensitive analytical detection methods such as spectrophotometry, inductively coupled atomic emission spectrometry (ICP-AES), inductively coupled mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry.

Each of the above methodologies has their own merits. Nevertheless, some of the above mentioned methods are associated with high operational costs, limitations in scale up operations and sludge disposal problems. Among these, LLE and SPE are used quite extensively and play a crucial role in metal ion separations and removal at diverse concentrations ranging from parts per million to billion levels.

Chromium is an important transition element that yields brilliant colored compounds and is one of the key ingredients in precious gem stones such as emeralds and ruby [10]. Chromium based catalysts are also used for polymerization of ethylene [11]. Hexavalent chromium is genotoxic, carcinogenic [12,13] and the reaction of Cr(VI) with ascorbate and hydrogen peroxide results in the accumulation of hydroxyl radicals thereby causing damage to the DNA [14]. Electroplating and tannery industries [15–17] are the major sources of chromium contamination and the USEPA has stipulated a limit of 0.1 mg L^{-1} in water [18].

Hence, the remediation of chromium(VI) contaminated effluents is of considerable importance in the view of its threat as a potentially toxic heavy metal ion [19,20]. This review presents an outlook on the environmental occurrence, remediation techniques and future perspectives with regard to the removal of hexavalent chromium Cr(VI) from wastewater. Techniques such as liquid–liquid extraction, solid phase extraction using polymeric resins, clays, biopolymers, biomass, activated carbon and graphene oxide are compared with regard to their removal efficiency, regeneration, adsorption capacity and other features. The importance of chelating and ionic liquid impregnated adsorbents for the remediation of chromium from tannery and electroplating wastewater is also discussed. Considering the merits and demerits associated with various methods, the road ahead towards devising improved methodologies is also suggested from a greener perspective.

2. Chromium chemistry

In acidic medium, hexavalent chromium exists as tetraoxohydrochromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) species and at alkaline pH, it is present as tetraoxochromate (CrO_4^{2-}) in solution. Hexavalent chromium is more mobile while the trivalent form is less toxic and strongly retained in the soil. However, it is probable for trivalent chromium to get oxidized to the hexavalent state due to the manganese oxides in the soil [21–25]. The properties of hexavalent and trivalent chromium are summarized in Table 1.

Table 1
Properties of Cr(VI and III).

Hexavalent chromium	Trivalent chromium
CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, H_2CrO_4 , HCrO_4^-	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ $[(\text{H}_2\text{O})_5\text{Cr}(\text{OH})]^{2+}$, $\text{Cr}(\text{OH})_3$
Higher mobility in acidic medium Genotoxic, carcinogenic	Less mobile in acidic medium Less toxic and serves as dietary supplement to regulate glucose metabolism

During the electronic waste recycling, the effluents discharged are a potential source of chromium pollution. Significant quantities of lead, mercury, cadmium, chromium, polyvinyl chloride (PVC) and flame retardants present in electronic components causes alarming threat to the environment. Guiyu, in China is one of the severely chromium polluted areas due to the presence of several electronic waste recycling sites [26]. The chromium-induced DNA damage of cord blood lymphocyte indicated that the concentration of umbilical cord blood chromium levels in neonates was as high as $300 \mu\text{g L}^{-1}$ and this exceeds the tolerance limit of hexavalent chromium significantly.

The chrome tannery wastewater which is another major source of pollution also contains as high as $500\text{--}1000 \text{ mg L}^{-1}$ of chromium [27]. Hence, understanding the chemistry of chromium and its toxicity are of prime importance in the development of effective remediation methods. An overview of some of the methods such as liquid–liquid extraction, chemical reduction and solid phase extraction are discussed in the following sections.

3. Overview of remediation methods

Liquid–liquid extraction (LLE) or more commonly referred to as solvent extraction (SX) is a versatile technique used in the extractive separation of metal ions. LLE plays a pivotal role in the separation of actinides for reactor fuel reprocessing in the nuclear industry [28]. In principle, LLE involves the distribution of metal ion between two immiscible phases. The distribution ratio, D which is essentially the ratio of concentration of metal ion in the organic to aqueous phase is a vital parameter to assess the efficiency of extraction. In this classical technique it is important to evaluate various aspects such as pH, third phase formation, use of relatively less toxic solvents, and above all regeneration and reusability of the metal extractants. All these factors are very essential to achieve a high distribution ratio for the desired metal ion.

The extractants are usually categorized into chelating and ion association systems. In acidic medium depending on the pH, chromium(VI) exists mostly in the form of HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$ anion. These anions are involved in the electrostatic interaction with cationic extractants. Cr(VI) is categorized as a hard acid interacts effectively with nitrogenous (hard base) compounds. Hence, typically the extractants for chromium are predominantly amine based [29,30] and owing to their bulky nature, they favor the uptake of chromium as an ion pair from the aqueous to organic phase through effective mass transfer. The amines that are useful are predominantly long chain quaternary ammonium or tertiary amine based extractants. With tertiary amines in acidic medium, the protonation of nitrogen favors coulombic interaction ($\text{R}_3\text{NH}^+\text{-HCrO}_4^-$ or $\text{Cr}_2\text{O}_7^{2-}$) with chromium. The facile extraction of Cr(VI) from wastewater as an ion-pair is possible using tetraphenylarsonium as well as phosphonium bromide using chloroform as the solvent [31]. With tetrabutylammonium bromide at pH 1.0, Cr(VI) is extractable into dichloromethane and the method was very useful to remove chromium from electroplating wastewater [32]. With tributylphosphate as a phosphorous containing extractant [33], Cr(VI) was extracted with 99.9% efficiency and 70% regeneration was achieved with 0.3 mol L^{-1} sodium hydroxide solution. The extraction of

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