

Removal of chromium from industrial effluents using nanotechnology: a review

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Abstract The presence of chromium in industrial effluents has become a huge problem worldwide as hexavalent chromium is highly toxic to animals due to its ability to generate reactive oxygen species in cells. The trivalent state of chromium, on the other hand, is significantly less toxic and also serves as an essential element in trace amounts. When industries such as electroplating, tannery, dyeing and others release their effluents into water bodies, hexavalent chromium enters the food chain and, consequently, reaches humans in a biomagnified form. Many remediation processes for removal of hexavalent chromium have been researched and reviewed extensively. These include chemical reduction to trivalent chromium, solvent extraction, chelation and adsorption, among others. It has been generally concluded that adsorption (and/or subsequent reduction) of hexavalent chromium is the best method. However, relatively little is known about the potential of using nanoparticles as adsorbents for the removal of hexavalent chromium from industrial effluents. This method of nanoremediation is more effective than conventional remediation methods and is cost-effective for the industry in the long run. This article reviews the various remediation methods of hexavalent chromium, with emphasis on the field of nanoremediation.

Keywords Chromium toxicity · Remediation · Nanotechnology · Industrial effluents

Introduction

Chromium has widespread applications in various industrial processes such as electroplating, printing, dyeing, tanning and metallurgy. However, improper disposal of effluents from these industries results in environmental pollution [1–3]. This has fatal consequences on the environment, plants and animals as it exerts carcinogenic, mutagenic and teratogenic effects and causes tissue damage [4].

Chromium most commonly occurs in trivalent/Cr(III) and hexavalent/Cr(VI) states [5]. While the trivalent state of chromium is an important trace element, its hexavalent state is non-essential and toxic to animals [6] and may cause dermatitis, lung cancer, kidney and gastric damage, irritation to respiratory tract and eyes [7]. Continuous accumulation of toxic Cr(VI) along food chains often leads to biomagnification, putting humans at great risk [8].

The global requirement of water for industrial uses has been increasing by leaps and bounds. However, abuse of this valuable resource and adequate lack of timely treatment often lead to water pollution, resulting in its scarcity. To overcome this problem, industries need to adopt several technologies of water purification, for use in manufacturing processes. There are many conventional processes currently in use for remediation of Cr(VI) from industrial effluents. These processes mainly involve immobilisation of Cr(VI) and/or reduction of toxic Cr(VI) to the less-toxic Cr(III). The latter can be achieved chemically by means of a variety of sulphur or iron-based compounds, such as Fe(II) [9], amorphous FeS₂ [10], calcium polysulphide (CaS_x) [11], sodium thiosulphate (Na₂S₂O₃) [12] and many more. The major disadvantage of chemical reduction is the generation of a huge amount of toxic sludge. Some other methods of Cr(VI) removal include membrane filtration,

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solvent extraction, leaching [13, 14] and electrokinetic procedures [15, 16]. These methods, though commonly used, have certain limitations. The major disadvantage of such conventional treatment methods is the high cost, which dissuades many industries from adopting any remediation methods.

Another commonly used method involves the adsorption of Cr(VI) onto various surfaces like titanium dioxide, goethite, activated carbon, zeolites and many more. In some cases, reduction to Cr(III) may follow. Biosorption is a subdivision of adsorption, in which Cr(VI) is adsorbed onto biomaterials found in abundance in nature, like microbial biofilms [17, 18]. Adsorption is considered to be an effective method due to the low initial cost, flexibility in design and ease of operation [19]. Moreover, adsorption does not involve the formation of any secondary wastes such as sludge.

In this context, nanoparticles have gained prominence as adsorbents of Cr(VI). While choosing suitable nanomaterials for environmental remediation, the characteristics usually explored are size, solubility, surface area, surface charge and surface chemical composition [20]. Having large surface areas and being highly stable, nanoparticles have demonstrated themselves to be excellent adsorbents for environmental remediation [19]. Due to their high catalytic activity, some nanoparticles, such as nanoscale zero-valent iron, are capable of reducing Cr(VI) to Cr(III). Moreover, using nanoscale zero-valent iron does not produce intermediate by-products, which are usually observed when bulk Fe powders are used [21]. This review describes the various methods used for remediation of Cr(VI) with special emphasis on the rapidly emerging field of nanoremediation.

Chromium in industrial effluents

The hexavalent state of chromium, which exists primarily as the tetrahedral chromate ion in aqueous solution (CrO_4^{2-}), is able to penetrate cellular membranes using various permeases, and this penetration of membrane occurs 500–1000 times more effectively than the trivalent form [22, 23]. Once inside the cell, Cr(VI) is reduced enzymatically and/or non-enzymatically to the reactive intermediates, Cr(V), Cr(IV) and Cr(III) [24], which are capable of generating reactive oxygen species (ROS) [25]. Under physiological conditions, overproduction of ROS causes damage to cellular proteins, lipids and DNA [26].

Industries such as electroplating, tannery, paints, petroleum and dyeing contain Cr(VI) in their effluents [1]. For example, textile industries use synthetic dyes to impart colour to raw materials or products. These dyes contain many toxic heavy metals, especially chromium [27–29].

Examples of other industries contributing to Cr(VI) pollution are summarised in Fig. 1 [1, 30].

The release of several industrial effluents containing Cr(VI) into water bodies exposes aquatic life to this toxic and corrosive element. It readily gets accumulated and consequently biomagnified in the species at the top of the aquatic food chain, viz, fishes [31]. This phenomenon manifests itself physically in fishes in the form of an increased mortality, erosion of scales, discolouration, mucous secretion, irregular swimming and disruption of their osmoregulatory functions [8, 32].

As a result, Cr(VI) enters the terrestrial food chain and reaches humans in highly biomagnified amounts. This leads to several health problems such as damage to liver and kidney, carcinogenesis (mostly lung cancer), genotoxicity, neurotoxicity, immunotoxicity, asthma, skin ulcerations and many more [6, 33–35]. Rats intraperitoneally injected with Cr(VI) have been reported to develop both structural and functional anomalies of the pituitary and thyroid glands [36]. Potassium dichromate, administered subcutaneously into rats, had led to accumulation of chromium mainly in the renal cortex [37] and had caused cellular degradation of the proximal convoluted tubule and formation of hyaline casts in the lumen of renal tubules [22]. Hence, there is an urgent need to develop an effective technique for chromium remediation from wastewater.

Conventional processes for chromium remediation

Like all heavy metals, Cr(VI) cannot be completely removed from the environment. However, its toxicity can be reduced (by reduction to the trivalent state), or it can be adsorbed onto a surface to be dumped at a different site, or a combination of both approaches may be used.

The various conventional methods of Cr(VI) remediation have been reviewed by Kalidhasan et al. [38], and these methods have been summarised and are compared in Table 1 [39–69].

The conventional chemical reduction method comprises of two steps—the reduction of Cr(VI) to Cr(III) by a reducing agent, at an acidic pH, and the precipitation of Cr(III) as an insoluble hydroxide at an alkaline pH. The chemical reductant can be any sulphur-based or iron-based salt. These two steps can be combined into a single step by the electrochemical addition of ferrous ion, rather than the addition of a ferrous salt (FeSO_4 or FeCl_2) which necessitates the use of an acidic and an alkaline pH, making it a two-step process. The removal of Cr(VI) by the former can be illustrated using the following reaction [70]:

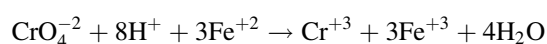
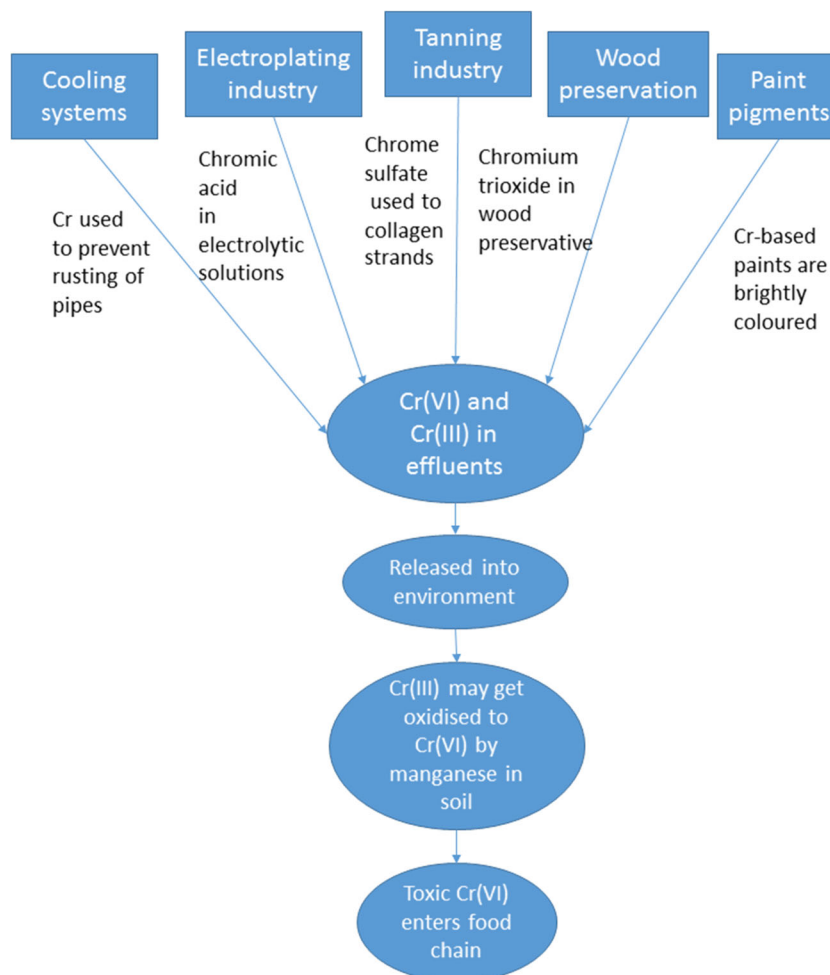


Fig. 1 Various industries release Cr(VI) in their effluents



The major limitation of this method is the formation of toxic solid sludge during the precipitation of Cr(III) [38]. Moreover, in the treatment of soil contaminated by Cr(VI) from industrial effluents, the chemical reduction method is disadvantageous as the contaminated soil needs to be physically mixed with the reducing agent, making the entire process labour-intensive. An alternative method which can be used in this situation is electrokinetic remediation, which involves passing of low-voltage direct current through the soil, thus providing in situ remediation [16]. The toxic metals move towards the electrodes, primarily by electromigration. This method can be further enhanced by using metal chelators such as citric acid and polyaspartic acid [15].

Adsorption is the most effective and economical solution to remediation of Cr(VI), especially if it is coupled with proper regeneration of the adsorbent [71]. Activated carbon (AC) is one such highly effective adsorbent, which resembles granular or powder charcoal and possesses high porosity, internal surface area and mechanical strength. AC is especially useful in remediation of low concentrations of

effluent stream. However, commercially available ACs are not economically feasible, and hence, any material with a high organic content and low inorganic content can be used for manufacturing of AC [72]. For example, AC developed from Tamarind wood activated with zinc chloride has shown 99% efficiency in removal of Cr(VI) from wastewater [72]. AC prepared from Fox nutshell and activated by zinc chloride showed a maximum Cr(VI) removal efficiency of 99.08% at a pH of 2 [73]. Under the conditions of pH 2, biomass dose 2.5 g/100 ml and equilibrium time of 150 min, AC prepared from mango kernel and activated with H_3PO_4 reported a maximum Cr(VI) removal rate of 7.8 mg/g [74].

Another adsorption method is the use of silica-based adsorbents, which has both reduction and sorption capabilities in a single solid [75]. Mostly prepared by the sol-gel process, these adsorbents consist of a silica backbone and attached functional organic groups capable of complexing with the concerned metallic ion [76]. The presence of hydroxyl groups in the silica gel allows for easy modification for effective performance [77]. These adsorbents

Table 1 Conventional remediation methods of Cr(VI)

Sl. no	Process name	Type of process	Comments	References
1.	Liquid–liquid extraction	Physical	Amine-based extractants (hard bases), preferably long-chain quaternary ammonium or tertiary amine-based compounds, typically chosen. Examples include tribenzylamine in toluene, tetrabutylammonium bromide (pH 1.0) in dichloromethane and liquid Aliquat-336 (methyl trioctylammonium chloride) in isoamyl alcohol	[39–44]
2.	Reduction to Cr(III) using bisulphate and subsequent precipitation using lime or alkali	Chemical	Recovery of precipitated Cr(III) possible using H ₂ SO ₄ Excessive sludge produced during precipitation, making overall process costly	[45]
3.	Adsorption	Physical	Most commonly used method Adsorption surfaces include peroxide-modified titanium dioxide, goethite, zeolite, chitosan and waste slurry and also include inorganic cationic materials, such as zeolites modified with quaternary ammonium surfactants, activated carbon enriched with nitrogen and magnetic lignin composite adsorbents	[46–51]
5.	Solid-phase extraction	Physical	Solid adsorbents may be inorganic (silica, alumina, activated carbon, clays, ceramics) or organic (cellulose, graphene oxide). High selectivity, high pre-concentration factor, ability to regenerate and capability to treat large volumes of wastewater at once	[52]
6.	Polymer-based chelating ion exchangers	Physicochemical	Anionic resins with a quaternary amine as the attached group (R ₄ N ⁺ Cl ⁻) used for Cr(VI) removal from acidic medium. Modified polystyrene divinylbenzene (PSDVB) resins can also be used	[53]
7.	Adsorption by biopolymers	Physical	Include cellulose, chitosan, chitin, lignocellulose and lignin	[54, 55]
8.	Adsorption by hybrid clay material	Physical	Organomodified clays such as natural red clay modified by hexadecyltrimethylammoniumbromide, acid-activated tetrabutylammonium kaolinite, cetylpyridiniumbromide-modified montmorillonite and dodecylamine-modified sodium montmorillonite (NaMMT) Biopolymer–clay composites such as cellulose with NaMMT Graphene oxide, in combination with TiO ₂ or sand to form composites EDTA-reduced graphene oxide	[56–63]
9.	Polycrystalline haematite	Physicochemical	Iron displays the ability of physical adsorption of Cr(VI) and its reduction to Cr(III)	[64]
10.	Biomass	Biological	Adsorption of Cr(VI) on dead fungal biomass (<i>Aspergillus sydoni</i>) Reduction of Cr(VI) to Cr(III) using algae such as <i>Chlorella miniata</i> , certain cyanobacteria, <i>Microbacterium liquefaciens</i> immobilised in polyvinyl alcohol, <i>Neurospora crassa</i> , and many more species	[65–69]

are considered advantageous as they possess a defined pore geometry, large surface area, high porosity, good mechanical strength, high thermal resistance, stability in a wide range of pH, and are insoluble in water, environmentally benign and cost low [78, 79]. Kumar et al. [80] used aniline formaldehyde condensate (AFC) as the functional organic group to be attached on the silica backbone and reported 85% removal of Cr(VI) and 70% removal of total chromium (Cr(VI) and Cr(III)), while also reporting

56% recovery of chromium from the adsorbent in the presence of NaOH. The protonated amino (–NH₂) groups of AFC may electrostatically attract CrO₄²⁻, lead to reduction of Cr(VI) to Cr(III) and form bonds with Cr(III) for their adsorption. Similarly, polyaniline (PANI) can form coordinate bonds with the metal ions and reduce Cr(VI) to Cr(III) by surface chemical reaction. These PANI/silica composites have shown a maximum adsorption capacity of 63.41 mg/g at an equilibrium

concentration of 50 mg/l [77]. The silica backbone can also be modified by ionic liquids, imidazolium-based ones being an attractive option. The imidazolium ring can be covalently bonded onto silica, linked by alkyl group chains (provided by silane-coupling agents). These alkyl branches can be attached to different positions of the imidazolium ring [81]. In a study by Whang et al. [82], imidazole-modified silica adsorbent with chloride as counter ion (SilprIm-Cl) was used to adsorb Cr(VI) with a maximum capacity of 47.79 mg/g (from an initial concentration of 150 mg/l) at pH of 2. Sulphonic acid-functionalised silica adsorbent was reported to remove Cr(III) (as CrAc_2^{+2}) at a rate of 72.8 mg/g at pH 3 [83]. Shevchenko et al. [84] studied the potential of bifunctionalised mesoporous silica, with the two functional groups chosen being thiol and sulphonic acid moieties. This adsorbent suffered from two main limitations—very little scavenging property of the material, and the weak interaction between Cr(III) cations and sulphonate groups. A few years later, Zaitseva et al. [75] explored another bifunctionalised silica adsorbent, with the functional groups being mercaptopropyl and ethylenediaminetriacetate. The former can reduce Cr(VI), while the latter can “scavenge” the Cr(III) present via complex formation. Microscale silica gel can also be used along with granular zero-valent metals as reductants. For example, granular zero-valent zinc was used along with the silica gel to satisfactory results. Silica gel prevents the formation of a passivating film on the surface of the zero-valent zinc particles [79].

An improvement over the conventionally used ion-exchange resins is the use of metal–organic frameworks (MOFs), which are essentially clusters of metal cations coordinately bonded to polytopic organic linkers. Kumar et al. [85] have efficiently reviewed the applications of MOFs in the removal of Cr(VI). Some examples include 1-ClO_4 , ABT.2ClO_4 , FIR-54, ZJU-101, $1'\text{-SO}_4$, Ag-3, SLUG-21 and many more. Taking it a step further, Hasan et al. [86] used a MOF-derived composite for this purpose. A Cu-based MOF, named HKUST-1, was subjected to single-step calcination at 550 and 650 °C under inert conditions. Under optimum conditions, it was able to reduce 200 mg/l of Cr(VI) within 15 min in the presence of HCOOH. A loss in its catalytic activity was observed after reusing it for four consecutive cycles.

Zeolites, also termed as molecular sieves, are hydrated aluminosilicate materials having three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra, giving it a connected cage-like or channel structure. The lattice has a net negative charge due to the isomorphous replacement of Si^{+4} by Al^{+3} , and this is balanced by the exchangeable cation (sodium, potassium or calcium) [87]. Zeolites do not have a strong affinity for Cr(VI) or Cr(III) since they exist as anions in aqueous phase. However, this can be changed by

suitable modification of the zeolite lattice. Natural zeolite can be modified by cationic surfactants, as reviewed by Jiménez-Castañeda and Medina [88]. Attachment of reductants, such as Fe(II), to natural zeolites allows for adsorption and subsequent reduction of Cr(VI). Such a system showed a Cr(VI) removal rate of 90 mg per kg of zeolite, but suffered from extensive leaching of iron [89]. Natural zeolite can also be coated with biofilms for Cr(VI) removal [90]. For example, NaY zeolite coated with a biofilm of *Arthrobacter viscosus* (a good exopolysaccharide producer) showed a Cr(VI) uptake rate of 3 mg/g of zeolite [87]. The biofilm is able to reduce Cr(VI) to Cr(III), which is retained in the zeolite by ion exchange. Habiba et al. [91] prepared a chitosan/polyvinyl alcohol/zeolite composite for Cr(VI) removal. To reduce swelling of chitosan-based adsorbents by strengthening them, polyvinyl alcohol (PVA) was used, while reusability of the adsorbent was improved by the addition of zeolite. This composite adsorbent reported a Cr(VI) adsorption capacity of 450 mg/g.

Several bacteria of the *Pseudomonas*, *Bacillus*, *Enterobacter*, *Deinococcus*, *Shewanella*, *Agrobacter*, *Escherichia*, *Thermus* genera are resistant to Cr(VI) and can be used for Cr(VI) remediation [17, 92–95]. Many mechanisms for this have been proposed, such as generation of Cr(V) by bacterial enzymes mediating transfer of an electron to Cr(VI) and reduction of Cr(VI) to Cr(III) by bacterial chromate reductase [93]. However, bacteria in the form of planktonic cells are ineffective in Cr(VI) remediation as high concentrations of Cr(VI) can kill the cells. On the other hand, bacteria in the form of biofilms exhibit an increased tolerance to Cr(VI) and better settlement [18, 68]. Moreover, biofilms allow easy separation of the treated liquid from the biomass [18]. As has been appropriately noted by Pan et al. [17], more research needs to be focused on the immobilisation of Cr(III) obtained after reducing Cr(VI) by biofilms, as the insoluble Cr(III) can form organo-Cr(III) complexes, which become toxic for cells in high concentrations. Biosorption is an advantageous technique as it costs less, is highly effective, does not have any toxic side effects, the biosorbent can be rebuilt, and the adsorbed metal can be recovered for possible later usage [96].

The initial cost of most adsorbents is high, especially if they need to be pre-treated. However, in the long run, these techniques are cost-effective. Also, using greener techniques such as biomass reduces the initial cost of chemicals to a great extent [38].

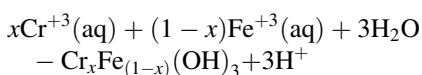
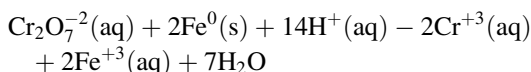
The major disadvantage of bulk adsorbents is the generation of enormous mass transfer resistance due to large surface areas and large diffusion lengths [97]. Thus, use of adsorbents with nanofeatures allows higher accessibility of the industrial effluent to the adsorbent, leading to higher efficiency.

Remediation using nanotechnology

Out of the many adsorption processes discussed above for the remediation of Cr(VI), nanomaterials possess certain properties which make them an ideal adsorbent. These include a suitable particle size, large surface area, accessible pores and high stability [19]. Moreover, due to their extremely small size, they can be easily transported through a water body simply by Brownian motion, without the aid of any external force. As a result, the nanoparticles remain suspended longer to establish an in situ remediation zone [98]. These nanoparticles can be synthesised by various physical, chemical and biological processes, and the adsorptive capacity of the particle varies according to the method of production.

Nanoadsorbents for chromium remediation

Zero-valent iron nanoparticles (nZVI) have become one of the most used metal nanoparticles for environmental remediation of Cr(VI). Since the redox potential of chromium is much more positive than that of Fe^0 , it reduces the hexavalent form of chromium to its trivalent form (itself getting oxidised to Fe^{+3}), which then precipitates along with Fe^{+3} on the surface of the nanoparticles [99–101]. This can be illustrated using the following chemical equations [102]:



Ion-exchange resins can be used as supporting material for the nZVI particles. While conventional ion-exchange resins can remove either a cation or an anion, resin-supported nZVI can eliminate both forms. Such resin-supported nZVI have been reported to remove Cr(VI) with an efficiency of 84.4% at optimal conditions [103]. Using carboxymethyl cellulose (CMC) as a stabiliser for nZVI, 100% of Cr(VI) was reduced to Cr(III) from a solution containing 10 mg of Cr(VI)/l [104]. A major problem of using nZVI particles is the formation of a Fe(III)–Cr(III) (oxy)hydroxide film on the surface of the nanoparticles, rendering the surface passive, as it does not allow the Fe^0 particles at the core to react with the Cr(VI) particles on the surface. This problem is usually overcome by cementing a second metal (preferably inert, such as Ag, Cu, Ni, Pd, Co) on to the surface of the transition metal, thus preventing the formation of the self-inhibiting film [105, 106]. Such bimetallic combinations, for example nZVI/Cu, demonstrate pseudo-first-order kinetics or Langmuir–Hinshelwood first-order kinetics [105, 107]. The second metal acts

as an electron shuttle between the two metal systems, thus forming a catalyst. It also protects the surface of nZVI from corrosion [106]. Another drawback of using nZVI particles is that their removal from treated water is tedious. This can be overcome by using magnetised nZVI nanoparticles, i.e. nZVI nanoparticles coated with magnetic Fe_3O_4 nanoparticle which could be removed easily with the help of an external magnetic field [108]. Such ZVI- Fe_3O_4 nanocomposites form a heterogeneous Fenton-like system [109, 110], which showed an increase in Cr(VI) removal efficiency from 48.8% (using bare n Fe_3O_4) to 96.4% (using nZVI- Fe_3O_4 nanocomposites) in 2 h [19]. nZVI has also been assembled on magnetic Fe_3O_4 /graphene nanocomposites to tackle both the drawbacks mentioned above, and it shows a Cr(VI) removal efficiency of 83.8%, following pseudo-second-order kinetics [111]. Use of ultrasound technology contributes to an increase in the available surface area and induces new reactive sites for the reduction reaction of Cr(VI) [112].

Formic acid is an organic and non-toxic reducing agent that reduces Cr(VI) to Cr(III), while itself getting converted to CO_2 and H_2 , which can be recycled for industrial purposes. This reaction occurs in the presence of metallic heterogeneous catalysts, namely graphene oxide-supported Ni nanoparticles [113], TiO_2 -supported Pd nanoparticles [114], Pd nanoparticles supported on amine-functionalised SiO_2 [115], among others. More recently, 3D urchin-shaped monometallic palladium was used as a nanocatalyst for the detoxification process of Cr(VI)-contaminated industrial effluents using formic acid. It was found that the rate of detoxification process could be enhanced by exposure to light of appropriate intensity. Further, this nanocatalyst exhibited stable catalytic activity even after six cycles of reaction [116].

Several metal oxide nanoparticles have also been used for the remediation of heavy metals, especially Cr(VI). Besides being used as nanocomposites as discussed above, magnetite (Fe_3O_4) nanoparticles can also be used individually for removal of Cr(VI) from wastewater [117]. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) coated with polydopamine (a catecholamine) showed a Cr(VI) removal efficiency of 97% at pH of 3 [118]. ZnO nanoparticles were used as photocatalysts for the reduction of Cr(VI) to Cr(III) in the presence of solar radiation [119, 120]. Such photocatalytic reduction experiments have also been carried out on TiO_2 [121, 122] and WO_3 [123]. The mechanism of photocatalysis is based on the principle of semiconductor solid catalysis, wherein electrons move from valence band to conduction band on being stimulated by light of appropriate wavelength. The charge carriers on the surface of the catalysts (such as O_2) take up the electron promoted to the conduction band, and the O_2^- thus formed engages in redox reactions with the adsorbed pollutants. The resulting electron deficiency in

the valence band is fulfilled by H₂O [124]. Cerium oxide nanoparticles stabilised with hexamethylenetetramine were able to remove Cr(VI) with 96.5% efficiency, and after the treatment process, the nanoparticles could be centrifuged out of the water, while chromium could be desorbed using NaOH [125]. Taking it a step further, the ability of hydrous cerium oxide nanoparticles to adsorb Cr(VI) was also investigated, which yielded positive results [126]. The potential of CoFe₂O₄ nanoparticles (synthesised in a cost-effective manner) for remediation of Cr(VI) from wastewater released from a printing press was quantified to be 67%, with no major loss of adsorption capacity up to three reaction cycles [127]. In a novel approach, manganese dioxide/iron oxide/acid oxidised multi-walled carbon nanotube magnetic nanocomposites (MnO₂/Fe₃O₄/o-MWCNTs) were used for Cr(VI) removal from wastewater. Apart from being highly efficient in this purpose, Cr(VI) can be desorbed and the adsorbent may be regenerated by using an alkali. However, the efficiency of Cr(VI) adsorption efficiency reduces to 85% after five cycles of reuse of these nanotubes [128].

Ionically modified nanoparticles have also been studied for applications in the field of nanoremediation. Magnetic Fe₃O₄ nanoparticles were modified by phosphonium silane, which enhanced their adsorption capacity of Cr(VI) at optimum pH. However, desorption of chromium from these modified nanoparticles using NaOH was poor [129]. Aminosilicate-functionalised titanium dioxide nanotubes modified with gold nanoparticles supported on EDAS (EDAS/(TiO₂ NTs-Au)_{NCM}) photocatalytically reduce Cr(VI) to Cr(III) (using oxalic acid as electron donor) with 77% efficiency. Light induces interfacial charge transfer from the (TiO₂ NTs)_{NCM} to Cr(VI) through the gold nanoparticles, which act as sinks for the photogenerated electrons [130].

To overcome the problem of mass transfer resistance in the case of bulk adsorbents, nanoparticles can be embedded in the bulk materials, thus facilitating the contact of contaminants to large surface area and encouraging internal mass transfer. This was achieved by the synthesis of a magnetic zeolite/polypyrrole composite, which consisted of magnetic zeolite (embedded with magnetic Fe₃O₄ nanoparticles) mixed with the organic polymer polypyrrole. This adsorbent showed a removal efficiency of 99.99% when the pH was 2 and the initial Cr(VI) concentration was 300 mg/l [97]. A similar study was conducted by using chitosan as the polymer instead of polypyrrole, and a removal efficiency of 98% was reported at pH 2 and initial Cr(VI) concentration of 200 mg/l [96]. A cross-linked silica gel/chitosan-g-poly(butyl acrylate) nanocomposite showed a maximum Cr(VI) adsorption capacity of 55.71 mg/g [131]. While bulk iron sulphide (FeS) has been used as a chemical reductant in the

remediation of Cr(VI), FeS nanoparticles show higher reactivity due to larger surface area. These nanoparticles can be stabilised using CMC, and biochar can be used as a mechanical support to disperse the nanoparticles. Such a composite adsorbent showed a Cr(VI) adsorption capacity of 130.5 mg/g at a pH of 5.5 [132].

As previously mentioned, TiO₂ is a good candidate for photocatalytic reduction of Cr(VI). Addition of carbon nanotubes (CNTs) to the photocatalytic material increases its adsorption capacity and electron-conducting ability [133]. Polymer-based composite materials (incorporation of semiconductor nanoparticles in polymeric nanofibers) are being explored to improve the recovery of the photocatalytic powder from treated solutions after the completion of reaction [134]. Polyacrylonitrile (PAN) is widely used for producing the polymeric nanofibers [135]. In a recent study, composite nanofibers of PAN and multi-walled CNTs were synthesised and were further cross-linked by amino-modified TiO₂ nanoparticles. When irradiated with visible light, this system showed complete photoreduction of Cr(VI) after 30 min. It underwent five cycles of adsorption–desorption before its photoreduction efficiency decreased by 3% [136].

Nanoparticles can also be applied on membranes used to enhance removal of chromium ions from an aqueous solution. For example, the polysulphone (Psf) membrane is widely used for this purpose. To increase the hydrophilicity of the membrane, it was doped with SiO₂ nanoparticles (PSf/SiO₂), thus enhancing the chromium flux through the membrane [137].

Limitations of nanoadsorbents

The major challenge in any remediation process is the disposal of the material containing concentrated Cr(VI) away from the treated water. In many of the remediation processes discussed here, Cr(VI) is reduced to its non-toxic trivalent form. Many methods have been proposed to dispose the nanomaterial containing concentrated adsorbed chromium. Several nanomaterials, such as titania, have been observed to improve the physicochemical properties of cement, mortar and concrete [138]. This fact can be used to immobilise the adsorbed chromium by using the titanium oxide nanoparticles in the preparation of mortar. The photocatalytically reduced Cr(III) was successfully immobilised in mortar with a specimen containing 15% titania powder by weight. Even after a period of 90 days, the leachate of chromium from such a mortar specimen was insignificant [139]. TiO₂ nanoparticles can also be immobilised on glass, stainless steel, silica films, ceramic particles and fibres [140–144].

This, however, does not solve all problems. Employing nanoremediation as a suitable alternative to conventional

methods of remediation is limited by the toxic effects exerted by the nanoparticles on the environment and to the people exposed to them. Moreover, an analysis of the cost of employing nanoremediation with respect to its efficiency is important before persuading industries to adopt this method. These two aspects have been discussed in detail below.

Toxicity of nanoparticles

It is believed that the toxicity of nanoparticles stems from their physicochemical characteristics, which includes their size, shape, surface area/volume ratio, chemical composition and surface chemistry [145, 146].

Rod-shaped cerium oxide nanoparticles have been shown to enhance pro-inflammatory and cytotoxicity responses in the RAW264.7 cell line [147]. Nanoparticles tend to get accumulated in the liver, kidney and lungs, where they exert their toxic effects. In the liver, these nanoparticles induce oxidative stress and may also trigger the inflammatory cytokines cascade, resulting in inflammatory cell chemotaxis and apoptosis [148, 149]. Xia et al. [150] proposed a hierarchical oxidative stress model which integrates the interlinked protective responses to nanoparticle toxicity. At the lowest tier of the hierarchy, the transcription factor Nrf2 induces various antioxidant and detoxification enzymes. The second tier involves pro-inflammatory responses, such as the activation of MAP kinases and NF- κ B cascade. At the highest tier, the electron transfer chain of the inner mitochondrial membrane is disturbed, and apoptosis is triggered by the increased permeability of the outer mitochondrial membrane. Xia et al. [150] also performed a comparative study on the cytotoxic effects of nanoparticles of TiO₂, ZnO and CeO₂. It was reported that, while TiO₂ nanoparticles did not elicit any cytotoxic effects under dark conditions, ZnO nanoparticles could induce spontaneous ROS production as an injurious response. Surprisingly, however, CeO₂ nanoparticles induced a protective response even though they generated ROS.

Nanoparticles have the ability to organise a protein corona around them, depending on particle size, curvature, shape, functionalised groups on the surface and free energy. This often leads to protein unfolding, thiol cross-linking, fibrillation and loss of enzymatic activity [151, 152]. Certain nanoparticles can also dissolve in the medium (or biological environment), leading to release of toxic ions. For example, ZnO nanoparticles dissolve under aqueous conditions, forming hydrated Zn⁺² cations, and this dissolution is accelerated under acidic conditions or in the presence of amino acids and peptides [153]. ZnO nanoparticles that reach the alveoli cause pulmonary inflammation through increased TNF- α , IL-6 and IL-8

production [154]. Linking Fe₃O₄ nanoparticles to neurodegenerative diseases, it was reported that Fe₃O₄ nanoparticles resulted in an increase in lipid peroxidation and ROS formation, along with elevated levels of mitochondrial enzymes and swelling (and corresponding decrease in respiration levels), TNF- α and caspase-3 (proapoptotic protein) activity [155]. Two-dimensional graphene oxide nanomaterials showed greatest rate of efflux of haemoglobin from suspended RBCs, while aggregated graphene sheets showed lowest haemolytic activity. Coating graphene oxide with chitosan, however, nearly eliminated haemolytic activity [156].

Water-solubilised aminoclay nanoparticles showed toxicity against eukaryotic microalga *Pseudokirchneriella subcapitata* at a concentration of 1.29 mg/l (possibly due to entrapment of the algal cells in the nanoparticle aggregations), but showed no inhibitory effect towards the marine bioluminescent bacteria *Vibrio fischeri* up to 25,000 mg/l [157]. Pereira et al. [158] studied the ecotoxic effects of various nanoparticles, including those of TiO₂, TiSO₄, CdSe/ZnS and many more, and reported the occurrence of toxic effects on *V. fischeri* and *Salmonella typhimurium*. A detailed toxicology investigation of CeO₂ nanoparticles revealed that the nanoparticles aggregated at a pH of 7.4, and showed no toxicity towards *Daphnia magna*, *Thamnocephalus platyurus* and embryos of *Danio rerio* up to concentrations of 1000, 5000 and 200 mg/l, respectively, but showed a significant toxicity towards *P. subcapitata* at concentrations of 2.6–5.4 mg/l [159]. Moreover, the stability and toxicity of CeO₂ nanoparticles is significantly affected by pH, natural organic matter and ionic strength. For example, the natural organic matter gets adsorbed to the surface of the nanoparticles, decreasing their bioavailability and, hence, reducing their toxicity [160]. Chen et al. [161] reported that CMC-stabilised nZVI showed more acute toxicity to larvae of *Oryzias latipes* (medaka fish) than bare nZVI and bare nFe₃O₄, arguing that CMC-nZVI led to increased hypoxia and increased production of ROS and aqueous Fe(II) than unsupported nZVI. The toxicity of ZnO nanoparticles against Gram-positive bacteria has long been exploited in their use as antibacterial agents. However, as reviewed by Ma et al. [162], they are also able to inhibit photosynthesis in *Anabaena flos-aquae*, cause cell death in *Euglena gracilis euglenoid*, affect root elongation of garden cress and even reduce biomass of wheat under field conditions. There are very few articles on the ability of nanoparticles to inhibit various enzymes secreted by soil-dwelling microbes. Silver nanoparticles can inhibit the activities of phosphomonoesterase, arylsulphatase, β -D-glucosidase and leucine aminopeptidase [163], while ZnO nanoparticles can inhibit the activities of acid phosphatase, β -glucosidase and dehydrogenase [164]. CeO₂ nanoparticles have been reported to inhibit urease and β -glucosidase,

while stimulating phosphatase activity. The former is attributed to the accumulation of ROS that damages the microbial cells, while the latter effect is due to either a shift in microbial community or due to the antioxidant property of CeO₂ nanoparticles [165]. These soil enzymes are markers of soil fertility and nutrient recycling via the various biogeochemical cycles of nature.

In a review by Niyas Ahamed [166], the ecotoxic effects of nZVI were summarised. It was noted that the toxic effect of iron is due to its catalytic activity towards production of ROS. While nZVIs can be used for environmental remediation, their dosage should not exceed the maximum permissible concentration before being detrimental to bacteria. Aquatic invertebrates, such as *Daphnia magna*, are very sensitive to certain nanoparticles. Germination of plants, such as *Zea mays*, is affected in the presence of silver nanoparticles.

However, the review [166] notes that supplementing the nanoparticles with bovine serum albumin reduces their toxic effects. Coating nZVIs with a biodegradable material also reduces their toxicity [166]. Similarly, biodegradable materials such as porous orange peel pith can be used as a supporting material for iron nanoparticles. This system has a Cr(VI) removal efficiency of 71% [167]. Another eco-friendly alternative available to industries is the green synthesis of nanoparticles using plant extracts and micro-organisms. CuO nanoparticles were synthesised using the extracts of *Citrus limon* (lemon juice) as a bioreductant and were used for Cr(VI) remediation [168]. The first biogenic nZVI were produced from tea (*Camellia sinensis*) polyphenols [169]. Since then, nZVI have been produced biogenically and investigated for Cr(VI) remediation. For example, nZVI particles were synthesised using the leaf extracts of *Eucalyptus globules*, and they showed a Cr(VI) removal efficiency of 98.1% in 30 min at a limited dosage of 0.8 g of nZVIs per litre of solution [170]. Iron-based nanoparticles were produced by reacting FeCl₃ with *Syzygium-jambos* (*L.*) *Alston* leaf extract, the latter being used as both reducing and capping agents. The Cr(VI) removal efficiency of the same, which was strongly dependent on temperature and pH, was 983.2 Cr(VI)/g Fe [171]. Sharma et al. [172] have reviewed the various methods of biogenic production of nanoparticles. Biogenic selenium nanoparticles, produced by employing *Bacillus* sp. as a reductant, are less toxic than synthetic selenium nanoparticles [173]. Even in the review by de Lima et al. [174], it was concluded that biogenic silver nanoparticles are much less genotoxic than chemically synthesised ones, while also noting that chemically capped nanoparticles induced severe cell damage in contrast to protein-capped silver nanoparticles, which showed no genotoxic effects.

Cost versus efficiency analysis of nanoremediation

From the above section, it is evident that besides the disposal problem, another major limitation of nanoremediation is the cost constraints. This problem can be addressed by improving the reusability of nanoadsorbents. Reusability of nanoparticles can be increased by immobilising them. For example, TiO₂ and ZnO nanoparticles were immobilised in poly(vinylidene difluoride)-co-trifluoroethylene to reduce their dispersibility, and it was observed that these nanoparticles could be used up to three cycles [175]. The dye-degradation efficiency of ZnO1000 (ZnO nanoparticles with particle size of 120 nm) was reported to decrease from 99.2 to 99.12% after four trials [176]. Further research is needed for the development of nanoparticles which retain their high adsorption capacity after multiple usages. Nanoparticles have a strong tendency to aggregate and are chemically unstable, thus limiting their application. To prevent this, a supporting material is used, many of which have been elaborated above. Supporting materials enhance the dispersity of the nanoparticles [177–180]. Use of a supporting material, however, raises the budget of the industry and may not always be an economic solution.

Future aspects

In today's society of unstable economy, industries are reluctant to spend adequate money on remediation processes. Industrialists should be made aware of such remediation processes and their benefits in the long run. The capital cost of cleaning industrial effluents may be high, but with the use of cost-effective techniques, such an investment may be profitable for the industry. Using greener and eco-friendly techniques, such as use of biogenic nanoparticles, reduces the cost even more with a simultaneous increase in efficiency. Future research should focus on developing less toxic, more efficient, cost-effective and increasingly reusable nanoadsorbents.

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