

Effective Elimination of Hazardous Chromium (VI) Using Periodic Elements and Contemporary Adsorption Methods by Using Magnesium Ferrite Nanoparticle: A Review

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Abstract

A well-known hazardous metal and top contaminant in wastewater is hexavalent chromium. The two forms of most commonly found chromium are chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). Leather tanning, cooling tower blow-down, plating, electroplating, rinse water sources, anodizing baths etc. are the main sources of Cr (VI) contamination. The Cr (VI) is not only non-biodegradable in the environment but also carcinogenic to living population. It is still difficult to treat Cr contaminated waste water effectively, safely, eco-friendly, and economically. As a result, many techniques have been used to treat Cr (VI)-polluted wastewater, including adsorption, chemical precipitation, coagulation, ion-exchange, and filtration. Among these practices, the most practical method is adsorption for the removal of Cr (VI) from aqueous solutions, which has gained widespread acceptance due to the ease of use and affordability of the equipment and adsorbent. It has been revealed that Fe-based adsorbents' oxides and hydroxides have high adsorptive potential to lower Cr (VI) content below the advised threshold. Fe-based adsorbents were also discovered to be relatively cheap and toxic-free in Cr (VI) treatment. Fe-based adsorbents are commonly utilized in industry. It has been discovered that nanoparticles of Fe-, Ti-, and Cu-based adsorbents have a better capacity to remove Cr (VI). Cr (VI) was effectively removed from contaminated water using mixed element-based adsorbents (Fe-Mn, Fe-Ti, Fe-Cu, Fe-Zr, Fe-Cu-Y, Fe-Mg, etc.). Initial findings suggest that Cr (VI) removal from wastewater may be accomplished by using magnesium ferrite nanomaterials as an efficient adsorbent.

Keywords

Chromium (VI), Periodic Elements, Adsorption, Elimination, Magnesium Ferrite

1. Introduction

Chromium is one of the most significant elements on Earth. It is a micronutrient for mammals and plants as well. It is related to glucose tolerance limit and is essential in animal and human nutrition for normal carbohydrates metabolism [1] [2]. Cr is found in air, water and soil that means in all spheres of the environment, and it is a common element that makes up the 17th most abundant element in the earth's mantle and crust. A French chemist named Vauquelin discovered it in Siberian red lead ore (crocoite) in 1797. Finland, India, Kazakhstan, Philippines, South Korea, and Zimbabwe are naturally abundant with chromium [3]. Chromium is a transitional element. The periodic chart places it in group VIB and period 4 respectively. This group's other components include molybdenum (Mo), tungsten (W), and seaborgium (Sg). Because of the atomic configuration of the outer shell, there are some parallels in the properties of the elements. Its ground state electrical configuration is identical to that of $[\text{Ar}] 3d^5s^1$. It has two stable forms Cr (III) and Cr (VI) [4]. Chromium is in position 24 on the periodic table. Vanadium is before and manganese is after it. The atomic weight of Cr is 51.996 gmol^{-1} and is the 21th most abundant element of earth's crust [5]. Its density is 7.19 gcm^{-3} (20°C) and electronegativity is 1.6. It has a boiling temperature of 2672°C and a melting point of 1907°C . Its ionic and Vander Waals radii are 0.127 nm (+3) and 0.061 nm (+6), respectively. Six isotopes of chromium exist in nature. The first, second, and last shells had ionization energies of 651.1 kJmol^{-1} , $1590.1 \text{ kJmol}^{-1}$, and $2987.0 \text{ kJmol}^{-1}$ respectively [6]. Oxidation states of chromium range from -2 to $+6$ condition. Many stable and unstable compounds contain chromium. Chromium exists in two stable forms: trivalent Cr (III) and hexavalent Cr (VI). Cr (III) in soil and water as well as in organic matter is less poisonous and less mobile. Cr (VI) is toxic and poisonous. It forms Chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) with the association of oxygen. The value of Cr found in blood is 2.8 to 45 microns gram/liter [7]. Chromium occurs in the soil in the range of 5 to 1000 ppm. The concentration of Cr in plants varies from plant to plant [1]. Due to its use as a raw ingredient in the tannery of leather, electroplating, metal polishing, magnetic tapes, pigments, electrical or electronic equipment, and catalysis, among other industries, chromium plays a significant role. Leather industries are the main factor contributing to the high level of Cr entering the biosphere. It accounts for 40% of industrial use. But Chromium (VI) is toxic even at low concentrations. The health of humans is impacted by chromium (VI), which is teratogenic and carcinogenic. The World Health Organization has set a range of 0.01 mg/L to 0.5

mg/L for the maximum amount of Cr that can be a pollutant [8]. An experiment demonstrates that Cr (VI) is a potent oxidant with a high redox potential between 1.33 and 1.38 eV, which is what causes the rapid and significant production of ROS (relative oxygen species) and this causes toxicity [4]. Cr (VI) can aggravate the respiratory tract, eyes, dermatitis, kidney damage, gastrointestinal problems, and lung cancer [9].

Researchers assigned to research Cr treatment and removal a high priority due to the harmful impacts of chromium. Precipitation is currently a financially viable therapy option [10] as well as electrochemical reduction [11], electrocoagulation [12], polymerization [13] and adsorption [14]. For the elimination of Cr (VI), adsorption emerges as the most well-liked and financially viable treatment method [15]. We must understand the fundamental chemistry of Cr(VI) in an aqueous media, including chemical speciation, oxidation and reduction, reaction kinetics, interaction with other elements, etc. before using the Cr (VI) treatment procedure [16].

The high toxicity of Cr (VI) and associated health issues have prompted much research on the substance. Although thousands of studies on Cr have been documented, only a small number have focused on its interactions with other elements in the periodic table. Knowing which periodic element has the greatest potential for removing Cr is essential when creating a new adsorbent. We looked at the performance of periodic elements as adsorbents as well as the reaction mechanism for each adsorbent. Also, we looked for the periodic element that adsorbs Cr the most effectively. A sizable amount of research data was tabulated and examined for this work. Also, information regarding the Cr commercially available adsorbents has been gathered and examined based on periodic elements. Consequently, this review information may be a valuable tool for scientists researching adsorptive Cr elimination techniques.

2. Sources of Chromium

2.1. Natural Sources

Cr is tightly bound in rocks especially in primary rocks and well crystallized Fe-oxides: In rocks, the average Cr content is 100 mg kg⁻¹. As shown in **Table 1**, the mean Cr concentration varies from rock to rock. The concentration varies from 1800 mg kg⁻¹ in ultramafic igneous rock to 200 mg kg⁻¹ in basaltic igneous rock, 120 mg kg⁻¹ in shales and clays, 100 mg kg⁻¹ in black shales, 35 mg kg⁻¹ in sandstone, 20 mg kg⁻¹ in granitic igneous rock, and 10 mg kg⁻¹ in limestone. Among the various compound of Cr, Chromite is the most prominent minerals that contains 32% FeO and 68% Cr₂O₃. Cr₂O₃ can be replaced with Al₂O₃, Fe₂O₃, MgO, Ca, and SiO₂. The Cr concentration in urban areas is 0.015 - 117 mgm⁻³ [17].

Commercial ore typically contains at least 45% chromium with a Cr: Fe ratio greater than 2.5L⁻¹ for metallurgical chromium [18]. Because most of the Cr ore cannot be concentrated, it is offered as FeCr₂O₄ by hand sorting. Ferrochromium is produced by electric furnace [19]. Cr associate with Mg and Ni form primary

Chromium deposit in ultramafic rocks or anorthosite rocks. Chromite is available in peridotites or anorthosite other ultramafic rocks. The process of Chromium deposits is magmatic segregations in ultrabasic rocks [20] [21]. Chromite is created either through early crystallization, cooling of the magma, or gravity liquid buildup stratiform and pod shape are two basic forms of Cr depositions. Montana and Bushveld are the example of stratiform deposition of Cr in South Africa [22]. Cr concentrations in Cr containing rocks are 1000 - 3000 ppm, but 200 - 500 ppm only in gabbro and granites [18]. Heavy metal accumulations in placer and beach deposition are the secondary deposition of Cr. In good condition, lateral soil has 50% Fe and 2% - 4% Chromium. FeCr_2O_4 is present in reddish-colored soil in ultramafic rocks [23] [24] Chromium has the hardness of 55 Mohs and it occurs in igneous rocks as well as sedimentary and metamorphic rocks [18]. Another green colored Chromium compound is Uvarovite. It is a garnet found in Chromium ore [25]. Chromdravite is another Chromium bearing minerals which is in tourmaline group [26]. Another bright green variety of mineral is Chrome diopside (Cr_2O_3). It contains small amount of elemental Chromium, chromium ore is the source of it [27]. Picotite is another Cr containing minerals. Chrome ochre contains 2% - 10.5% Cr_2O_3 and it is a bright color Chromiferrous clay. Lead Chromate which is called Crocoite is an economical Cr compound. It has the hardness of 2.5 - 3 Mohs. It is a conchoidal fractured mineral. It is rare but the first mineral to be extracted [28].

Table 2, also listed more forms of chromium, including fluorides (CrF_2 , CrF_3 , CrF_4 , CrF_5 , CrF_6), chlorides (CrCl_2 , CrCl_3 , CrCl_4), bromides (CrBr_2 , CrBr_3 , Cr), iodides (CrI_2 , CrI_3 , CrI_4), oxides (CrO_2 , CrO_3 , Cr_2O_3 , Cr_3O_4), sulfides (Cr_2S (Cr_2Te_3)). Strong oxide conditions allow chromium to exist in its CrO_4^{2-} state [18].

Table 1. Sources and concentration of Cr in nature.

Sources	Concentration
Ultramafic igneous rock	1800 mg kg ⁻¹
Basaltic igneous rock	200 mg kg ⁻¹
Shales and clays	120 mg kg ⁻¹
Black shales	100 mg kg ⁻¹
Sandstone	35 mg kg ⁻¹
Granitic igneous rock	20 mg kg ⁻¹
Limestone	10 mg kg ⁻¹
Fresh water	0.1 - 117 mg L ⁻¹
Sea water	0.2 - 50 mg L ⁻¹
Earth crust	0.1 - 0.3 mg kg ⁻¹
Air (urban)	0.015 - 0.03 mg m ⁻³
Air (rural)	59 × 10 ⁻⁶ mg m ⁻³

source: [17].

Table 2. Major chromium containing minerals in nature.

Minerals	Chemical Composition	Cr (%)	Natural Occurrences
Chromite	Cr ₂ O ₃	68.4%	Ultramafic rocks
Ferro Chromium	FeCr ₂ O ₄	2% - 4%	Ultramafic rocks
Uvarovite	Ca ₃ Cr ₂ (SiO ₄) ₃	20.78%	Chromium ores
Chromdravite	NaMg ₃ (Cr ³⁺ Fe ³⁺) ₆ (BO ₃) ₃ Si ₆ O ₁₈ (OH) ₄	20.99%	Clay carbonate rocks
Chrome diopside	Cr ₂ O ₃	-	Chromium Ores
Picotite	(Fe, Mg) (Al, Cr) ₂ O ₄	0.01%	Igneous rocks
Chrome ochre	Cr ₂ O ₃	2% - 10.5%	Chromium ores
Crocoite	PbCrO ₄	16.09%	Ultramafic rocks

Source: [18]

2.2. Anthropogenic Sources

In recent decades, significant amounts of Cr have been released into the natural environment by various human activities such as steel production, smelting, electroplating, tanning, printing, dyeing, papermaking, textile, fertilizer, and pesticide manufacturing etc. [29] [30] [31]. Among these sources, iron and steel manufacturing factories are the main anthropogenic sources of Cr emissions worldwide [32]. These discharged waste residues into the natural environment severely contaminated the soil and water bodies with Cr (VI) [33] and the estimated global discharge rates into soils and water are 896 and 142 metric tonnes/year, respectively [34]. On the other hand, industrial cooling towers and road dust release fugitive chromium that are the most important sources of Cr [35]. A large percentage of Cr is released from phosphate fertilizers [36]. Numerous anthropogenic sources are shown in **Figure 1**.

According to Ross (1994), Chromium contamination from anthropogenic sources is categorized into five major groups [37]. These are (a) discharge of industrial waste, comprising sewage and sewage sludge as well as solid waste [38]; (b) disposal of solid wastes, particularly near coal-fired power plants, including garbage, coal, and fly ash [29]; (c) chromium in roadside soils resulting by asbestos-containing brake linings in automobiles and aerosols [18]; (d) emissions of chromium into the atmosphere from the manufacture of metals and chemicals as well as the burning of fossil fuels (gas, oil, and coal) [18] and (e) inappropriate usage of phosphorus fertilizers that contain substantial amounts of Cr. [39]. Phosphate fertilizers contain approximately 30 - 3000 mg kg⁻¹ toxic chromium that is a major source of Cr pollution [40].

3. Chemistry of Chromium

Chromium was first found as a mineral of Pb as Crocoite (PbCrO₄). It is widely used as powerful coloring pigment. Chromium is a naturally occurring element found in rock, soil, water, volcano dust, etc. The main source of Cr is primary

rock and its derivatives and well crystallized Fe-Oxides [41]. Vauquelinite ($\text{CuPb}_2\text{Cr}_2\text{O}_4\text{PO}_4\text{OH}$), tarapacaite ($\text{K}_2\text{Cr}_2\text{O}_4$), bentorite ($\text{Ca}_6(\text{CrAl})_2(\text{SO}_4)_3$), and crocoite (PbCrO_4) are minerals found in serpentine or ultramafic rocks. Chromite (FeCr_2O_4) is a kind of chromium ore. Chromium exists as natural minerals, co-precipitates with manganese, aluminum, and iron oxides, and is ingested by soil particles as hydro-oxides [41]. Chromium exhibits several forms in the various Eh-P^H seen in Figure 2. In the environment, Cr mostly takes the forms of Cr^{3+} , $\text{Cr}(\text{OH})_2^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$, and $\text{Cr}(\text{OH})_5^{2-}$, and it easily reacts with oxygen, hydroxide, sulfate, and organic matter to generate insoluble chromium. Because of this, Cr(VI) is easily found in waters as CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$, with chromate or dichromate acting as a potent oxidant [42].

Chromium has an electronic configuration of $[\text{Ar}] 4s^1 3d^5$. Cr with high spin has an oxidation stages ranging from -2 to $+6$. Chromium is an element of d block that's why it exhibits different kinds of physical and chemical properties. Cr (VI) shows CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- and H_2CrO_4 in different situations and Cr (III) shows Cr^{3+} , CrO^+ , $\text{Cr}(\text{OH})_2^+$, CrO_2^- , HCrO_2 etc. in solution [44]. Some possible oxidation reduction is given below in Table 3.

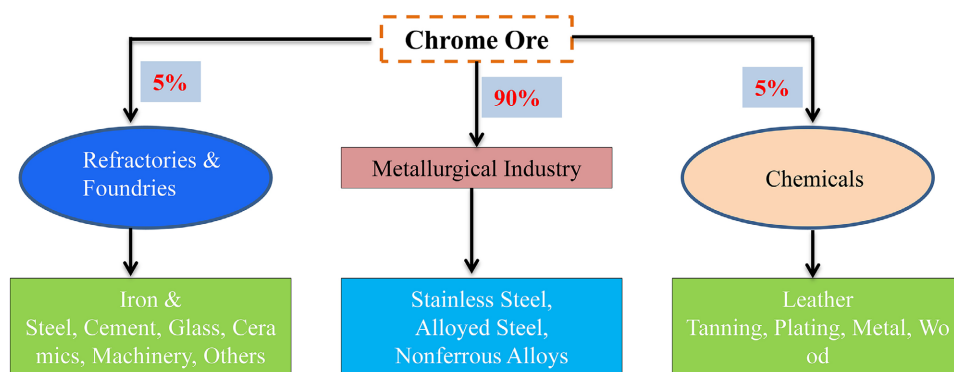


Figure 1. Percentage of use of chromium in different industries (Dhal *et al.*, 2013) [29].

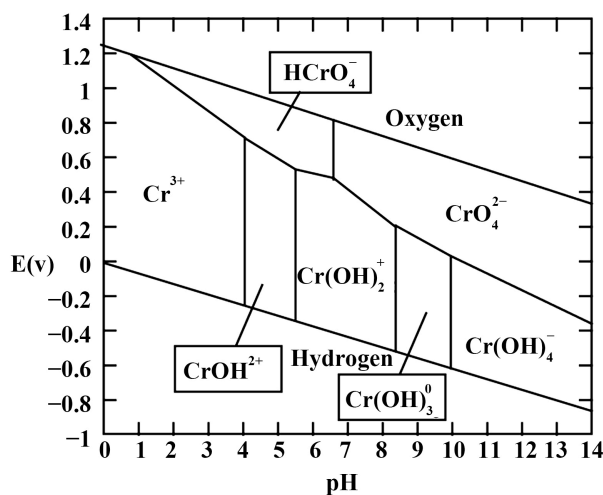


Figure 2. Chromium's Eh-pH phase diagram [43].

Table 3. Possible oxidation/reduction reactions, as examples.

Reaction	E ^(b)
(A) $2\text{Cr}^{3+} + 5\text{H}_2\text{O} + 3\text{O}_3 \Leftrightarrow 2\text{CrO}_4^{2-} + 10\text{H}^+ + 3\text{O}_2$	0.87
(B) $2\text{Cr}^{3+} + 2\text{H}_2\text{O} + 3\text{H}_2\text{O}_2 \Leftrightarrow 2\text{CrO}_4^{2-} + 10\text{H}^+$	0.58
(C) $3\text{MnO}_2 + 2\text{Cr}(\text{OH})_3 \Leftrightarrow 3\text{Mn}^{2+} + 2\text{CrO}_4^{2-} + \text{H}_2\text{O} + 2\text{OH}^-$	1.328
(D) $2\text{Cr}^{3+} + 3\text{H}_2\text{O} + 2\text{MnO}_4^- \Leftrightarrow \text{Cr}_2\text{O}_7^{2-} + 6\text{H}^+ + 2\text{MnO}_2$	0.35
(E) $2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Mn}^{3+} = \text{Cr}_2\text{O}_7^{2-} + 6\text{H}^+ + 6\text{Mn}^{2+}$	0.18
(F) $2\text{Cr}^{3+} + \text{H}_2\text{O} + 3\text{PbO}_2 \Leftrightarrow \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + \text{Pb}^{2+}$	0.13
(G) $\text{HCrO}_4^- + 3\text{V}^{2+} + 7\text{H}^+ \Leftrightarrow \text{Cr}^{3+} + 3\text{V}^{3+} + 4\text{H}_2\text{O}$	1.45
(H) $\text{HCrO}_4^- + 3\text{Fe}^{2+} + 7\text{H}^+ \Leftrightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} + 4\text{H}_2\text{O}$	0.56
(I) $2\text{HCrO}_4^- + 3\text{H}_2\text{S} + 8\text{H}^+ \Leftrightarrow 2\text{Cr}^{3+} + 5\text{H}_2\text{O} + 3\text{S}$	1.18
(J) $2\text{HCrO}_4^- + 5\text{H}^- + 3\text{HNO}_2 \Leftrightarrow 2\text{Cr}^{3+} + 5\text{H}_2\text{O} + 3\text{S}$	0.35
(K) $2\text{HCrO}_4^- + 5\text{H}^+ + 3\text{HSO}_3^- \Leftrightarrow 2\text{Cr}^{3+} + 5\text{H}_2\text{O} + 3\text{SO}_4^{2-}$	2.115
(L) $2\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-} + \text{R}_3\text{CH} \Leftrightarrow \text{Cr}^{3+} + \text{R}_3\text{COH}$	-
(M) $2\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-} + \text{RCH}_3 \Leftrightarrow \text{Cr}^{3+} + \text{RCH}_2\text{OH}$	-
(N) $2\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-} + \text{RCHO} \Leftrightarrow \text{Cr}^{3+} + \text{RCOOH}$	-
(O) $2\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-} + \text{PAH} \Leftrightarrow \text{Cr}^{3+} + \text{Quinones}$	-
(P) $2\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-} + 3\text{HCOOH} \Leftrightarrow 2\text{Cr}^{3+} + 3\text{CO}_2$	-
(Q) $2\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-} + 2\text{CH}_3\text{CH}_2\text{OH} \Leftrightarrow 2\text{Cr}^{3+} + 2\text{CH}_3\text{COOH}$	-

Source: [42].

The adsorption and desorption processes are crucial for determining the most effective method of removing Cr. Adsorption describes the process by which a solid matrix removes solutes from water forming bond Cr makes many compounds and stay in environment. But suitable substitute and net electric charge can remove Cr from the crystals and lattice [42].

4. Chromium Concentration in Soil, Water and Air

Cr is an element which is persists in all sphere of environment including soil, air and water. The concentration of Cr in soil varies from 5 mgkg⁻¹ to 1500 mgkg⁻¹ depending on the parent material [45]. Approximately 0.1 to 117 micronL⁻¹ is found in fresh water [4] but the concentration is 0.2 - 50 micronL⁻¹ in the sea water. The concentration of Cr varies from time to time in the atmosphere and it is nearly 5.0 × 10⁻⁶ - 1.2 × 10⁻³microngramm⁻³. The Cr found in soil mostly is trivalent form. So, the chromate form is not naturally produced, it is directly or indirectly inputted by human [46] in soil. Input may cause by dumping of Cr bearing liquid or solid, waste water from industry, chromium mud, ferrochromium, chromium planting bath etc [42]. In the USA, the limit for Cr is 25.9 gmkg⁻¹ of soil per hectare and 14.6 gL⁻¹ of groundwater. Due to industries more Cr is in-

truded in soil water and air [4]. Soil Cr concentration increases by Cr containing Phosphate fertilizer. For example, the National Research Council of Canada (1976) estimated that the chromium concentrations in phosphate fertilizer are roughly 30 - 3000 mg kg⁻¹.

5. Toxicity of Chromium

Cr (VI) and Cr (III) are the two most widely available forms of chromium. In comparison to Cr (III), Cr (VI) is the most poisonous. When this Strong oxidant Cr (VI) passes through human tissue, it produces chromate which is impassable to membrane [42]. Cr have been released from steel factories, electroplating, tanneries, paintings, dyeing, paper making, textiles, fertilizer and pesticides manufacturing factories. Once again, the anthropogenic source of Cr is the iron and steel industry. The waste from tanneries contains a lot of Cr into the rivers, ocean, reservoir etc. [17]. As illustrated in **Figure 3**, Cr contamination can induce skin rash, weakened immune system, nose irritations, nose bleeding, ulcers, allergic reactions, kidney and liver damage, genetic material alteration, and even death [9].

6. Adsorption Processes as Chromium Elimination Technology

There are many technologies of Cr removal around the world. The technologies can be divided into two sub divisions. They are Conventional technologies and advanced technologies shown in **Figure 4**.

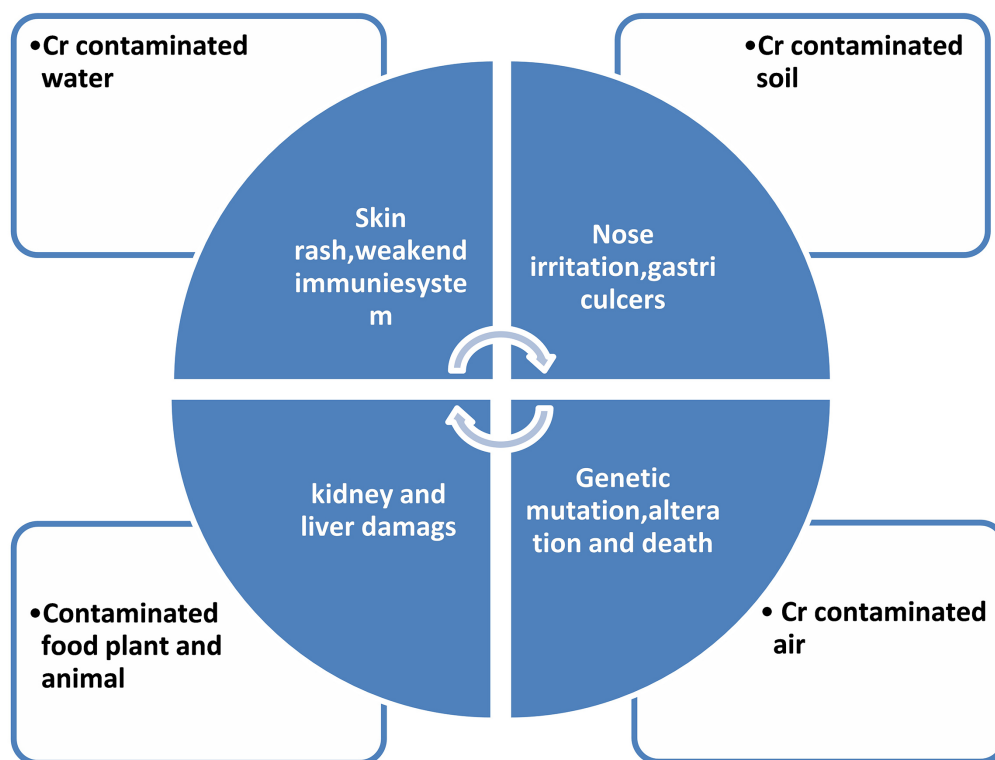


Figure 3. Human exposure route and effects of chromium toxicity in human health.

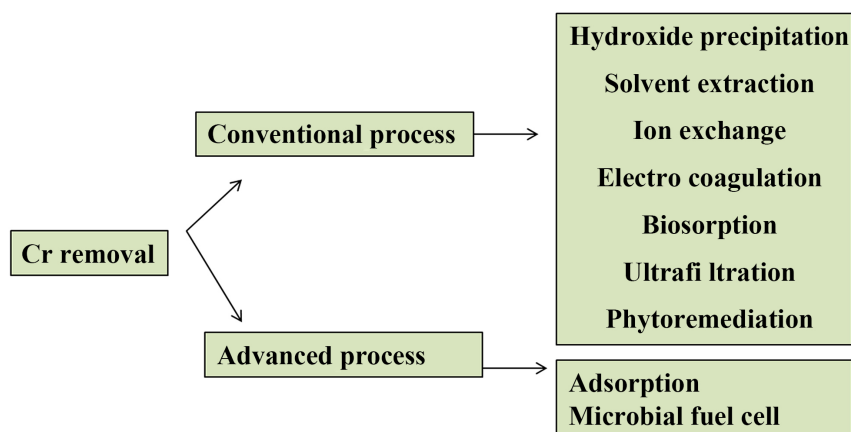


Figure 4. Different technologies involved in chromium removal from water.

The conventional technologies are hydroxide precipitation [47], solvent extraction [13], ion exchange [47] [48] electro coagulation, biosorption, and ultrafiltration [47] as shown in **Figure 3**. These technologies are widely used all over the world from the past. Although the effectiveness of these methods has been amply demonstrated, they have certain drawbacks due to their high energy requirements and inability to lower the amount of concentration that is needed [49]. The conventional method seems unsuitable for treating Cr bearing water due to lack of space. Moreover, the conventional method may not always be able to reduce the Cr concentration as low level as required by these processes. These processes are not feasible economically as well as technically.

Adsorption processes are the best suitable and promising advance techniques for metal removal as like Cr [49]. Various adsorption processes including synthetic polymer-based adsorbents, natural poly-based adsorbent, bio-adsorbents, carbon-based adsorbents, silica-based adsorbents, graphene based adsorbents, hierarchical porous carbon adsorbents, nanomaterial based adsorbents has been used for the removal of Cr [47]. Nanomaterials are in high demand for industrial applications such as water treatment and the removal of Cr because they are very effective, versatile, economically viable, ecologically friendly, and recyclable [50]. Numerous adsorption processes of chromium elimination technology are shown in **Figure 5**.

Technology based on magnesium ferrite nanomaterials may be used to removal of chromium from water. The use of magnesium ferrite nanomaterial for the removal of Cr from water and waste water has, however, received very little research too far.

7. Periodic Components Found in Chromium Elimination Adsorbents

For adsorption and adsorption design, adsorption mechanism is important. It is important to understand the efficiency and sustainability utilization at a large scale. Surface complexation, ion exchange, chelation, van der Waal force, acid-base interaction, covalent bonding, diffusion, and proton displacement should all be concerns while an adsorption process is in operation [49]. Adsorption process is go-

verned by its interaction between adsorbate and adsorbent. Different strapping, such as sodium hydroxide, sodium chloride, sodium nitrate, and sodium sulphate, are used to remove extracted chromium (VI), but these processes are not very efficient for removing Cr due to their high energy requirements, pricey equipment, insufficient metal removal monitoring systems, and production of toxic sludge [18]. Adsorption techniques have gained attention in recent years for the efficient removal of Cr. To select adsorbent for Cr removal, it is important to collect elements data. It will help to predict and find out the proper adsorbent. We, therefore organize the elements focusing on chemical properties of elements as an adsorbent.

7.1. s-Block Components in the Elimination of Chromium

The *s*-block elements are found in Group IA and Group IIA of the periodic table. These elements consist of an electrical configuration of ns^{1-2} . The electron of outer shell is in *s*-orbital that's why they are called *s*-blocked elements. Hydrogen (H), Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), and Francium (Fr) are the elements that make up Group IA. Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba), and Radium (Ra) are all members of Group IIA [44] [51]. Other forms of chromium include Cr_2O_7 and CrO_4^{2-} , which when combined with certain metals from the *s*-block create extremely water-soluble compounds that are poisonous (Table 4). Cr form Sodium dichromate ($Na_2Cr_2O_7$) and sodium chromate (Na_2CrO_4) with Na which is two industrially important salts because they are used in tannery dyeing industries etc. Cr form K_2CrO_5 reacting with potassium.

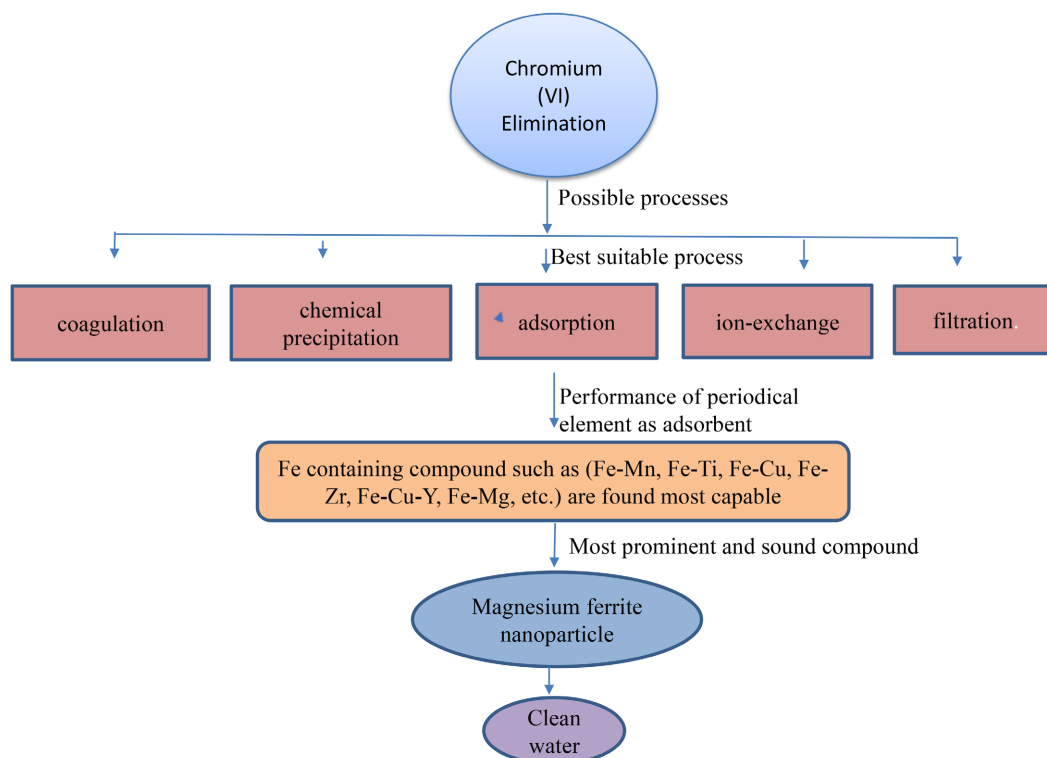


Figure 5. Adsorption processes as efficient chromium removal technology.

Table 4. Use of *s*-blocked elements in chromium removal.

Elements	Adsorbent	Characteristics	Efficiency	Reference
Na	Zeolite, Na(I)-montmorillonite	Good cation exchange capacities, easily synthesize in hydrothermal process but critical in gasification, low costing	Good adsorbent but very slow. Not much efficient.	[52]
K	Potassium hydroxide activated biochar	Highly porous and coarse structure, easily synthesize in hydrothermal process	Good and fast adsorbent but highly p^H dependent.	[54]
Mg	Magnesium Aluminum oxides, magnesium Zinc ferrites	Spinal properties, can form lattice	Very favorable for adsorption, ferrite nano particle is very efficient	[55]

Zeolite and Montmorillonite is a good adsorbent of Cr. Zeolite adsorption is fast but the synthesis process of zeolite is difficult. But the adsorption processes are slow. The average surface area of Na-montmorillonite is measured as 46.52 m^2/g and 8.24 nm. The surface area and average pore size of Na-montmorillonite is medium, which is owing to the considerably greater hydrated ion radius of Na (I) (0.246 nm). This adsorption process is relatively cheap [52] [53]. Potassium hydroxide (KOH) is used as an activator to remove Cr from dichromate in biochar adsorption removal process. This process is highly p^H dependent. If the p^H increases, the removal of Cr from $HCrO_4^-$ and $Cr_2O_7^{2-}$ decreases highly. By mixing converting corn straws (CCS) and KOH in a 1:4 weight-to-weight ratio and grinding the mixture in a quartz mortar, porous activated carbon adsorbents are created [54].

It is extremely advantageous for dichromate anions to bind to magnesium-zinc ($Mg_{1-x}Zn_xFe_2O_4$). The greatest adsorption capacity of the $Mg_{0.2}Zn_{0.8}Fe_2O_4$ sample is 30.49 mg/g. The $MgFe_2O_4$ sample, in comparison, had the lowest qads value (9.24 mg/g). It is therefore a promising adsorbent for Cr removal [55]. However, very limited research work is going on to prove the efficiency of *s*-block elements. Because of limited electron to share they have a limited scope of forming complex compound. But may be in future the researcher will be interested to work on it.

7.2. *p*-Block Elements in Chromium Elimination

The *p*-block elements have an electric configuration of ns^2np^{1-6} , The name “*p*-block elements” comes from the fact that the final electron of the outer shell enters the *p* orbital. Group VIIIA of inert gases normally don't interact with one another, other blocked elements which also include groups IIIA, IVA, VA, VIA, VIIA, and VIIIA. These blocks' constituent elements can be divided into metals and non metals. These two canonical states as well as chemical properties in aqueous solution are often characterized by physical properties of the elements in their condensed state, such as conductivity and crystal structure. In solid state, four elements are semiconductors. It's Si, Ge, Se, and Te. With the exception of

boron (B), group IIIA elements are metals. Tin (Sn) and Lead (Pb) are metals in Group IVA, while Germanium (Ge) and Silicon (Si) are semiconductors. Carbon (C) is a non metal. In Group VA, the nonmetals Nitrogen (N) and Phosphorus (P) are joined by the metalloids Arsenic (As), Antimony (Sb), and Bismuth. Group VIA includes the non metals oxygen (O), sulfur (S), and selenium (Se). Though Se is better said metalloid because of its both metallic and non metallic characteristics shown in **Table 5** [51].

The mechanical, thermal, and electrical characteristics of hexagonal boron nitride (h-BN) are unique. It has a big surface area polymer is created as well. Hexagonal boron has a variety of uses, including energy storage, plastic batteries, and optical storage, in addition to having excellent environmental stability, a high surface area, high porosity, ease of synthesis, and high conductivity. e h-BN@5% The adsorption efficiency of PANI was higher than that of the synthetic h-BN@1%. h-BN@%2 PANI and PANI hybrid composites [56].

Among the *p*-blocked elements Carbon is the most using element for the adsorption of Chromium (Cr) removal. Carbon element is using to remove Cr in different form like biochar, activated carbon, coal, humas, clay, fresh organic matter, maghemite, Seed shell and in some other forms shows in **Table 5**. Carbon has a high efficiency and surface area for performing as an adsorbent. Hexavalent chromium exists in the form of anion in solution. So novel C can remove it from waste water easily. But surprisingly, considerable elimination of hexavalent chromium is seen in the p^H range of 3 - 9. In contrast, the rate falls whether the p^H is high or low. Data reported at very high pH and low pH. It is a low-cost adsorbent and can get from easy way and cheap sources [34] [57] [58].

Table 5. Chromium adsorption by using *p*-block materials.

Elements	Adsorbents	Characteristics	Efficiency	References
B	Polyaniline-Boron nitrate compound or white Graphene.	Good porosity, good adsorbent, high pore space.	Fair adsorbent but P^H dependent	[56]
C	Novel carbon, activated carbon, biochar, fresh organic matter, humus, carbon nanotube, seed shell carbon.	Easily synthesized, good porosity, high surface area, abundant in nature, easily handle, good carrier	Good adsorbent, efficiently remove Cr from water	[43] [49] [50] [57] [59] [60] [61] [62]
Si	Silica sol-gel, Sodium metasilicate pentahydrate	Good surface area, good porosity, abundant, cheap	High potentiality when incorporating with sulphonic acid	[63]
Al	Metal organic framework, activated alumina	Good porosity, good aeration capacity,	Metal Aluminum is a good adsorbent but Alumina is not much efficient	[64] [65]
S	Sulphonic acid and S containing compound		Efficiently perform in Cr (III) removal but not for Cr (VI). Work as a catalyst.	[66]

Si form Sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) which remove Cr from water. On the other hand, silica sol-gel works as an adsorbent incorporate with sulphonic acid. Maximum uptake of Chromium (VI) by silica sol gel is 72.8 mg g^{-1} at pH [63] [66]. Alumina (nAl_2O_3) nano-particles were synthesized by sol-gel method for Cr (VI) removal. The process is feasible.

7.3. *d*-Block Elements in Cr (VI) Elimination

The elements with the electrical configuration of $ns^{(1-2)} nd^{(1-10)}$ are *d*-blocked elements. These elements obtain a *d* orbital in its shell. Some *d*-blocked elements are Fe, Cu, Mn, Zn, Ni, Ti, etc. [51]. The research data shows that these elements are good adsorbent of Cr (VI) from water. As summarized in Table 6, *d*-blocked element's active cation site easily absorb the anionic Chromium compound chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). These elements, which have high porosity, high surface area, and good adsorptive efficiency, have promising performance as adsorbents for removing Cr(VI) from water, as shown in Table 6 [6]. Jiang *et al.* (2013) found good adsorption capacity in the removal of Cr (VI) from water.

d-blocked elements like Fe, Mn, Zn, Ni, Ti have some special characteristics that are magnetic, photo-catalytic, catalytic, variable oxidation number etc [44] specially Fe has a magnetic characteristic which helps to remove Cr(VI) efficiently. Some of Fe adsorbents are Fe-Mn binary oxide [70] maghemite [69], Fe chloride [68], Fe-Mg oxide [55], Fe-Zn oxide [55], Fe hydroxide [67], Fe-biochar [70] etc.

Table 6. Chromium removal using *d*-block elements.

Elements	Adsorbents	Characteristics	Efficiency	References
Fe	Magnetite (Fe_3O_4), Maghemite ($\gamma\text{-Fe}_2\text{O}_3$), $\alpha\text{-Fe}_2\text{O}_3$, etc.	Have magnetic characteristic, high surface area, easy separation, recovery, inexpensive, eco-friendly	Excellent adsorption capacity	[61] [67] [68] [69]
Mn	manganese (II) chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$)	High surface area (even up to $7000 \text{ m}^2 \text{ g}^{-1}$), high/tunable porosity, and a variety of pore shapes and functions	Good adsorption efficiency in cheap rate	[70] [71]
Zn	Magnesium zinc ferrite $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$	High adsorption capacity in definite pH magnetic characteristics	Good adsorbent	[71]
Ni	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, N,N-dimethylformamide (DMF)	Limited adsorption capacity, environment friend I and low-cost adsorbent	Increases the rate and amount of adsorption	[72] [73]
Ti	Titanium Oxides (TiO_2), Metatitanic acid ($\text{TiO}(\text{OH})_2$), layered titanium oxide (LTO)	Possess photo-catalytic activity, more surface area, are nontoxic, are corrosion-resistant, and are stable	Spontaneous adsorption by nano particles dependent when form oxides	[74] [75] [76]

7.4. *f*-Block Elements in Cr (VI) Elimination

An element having electronic configuration in *f*-group in the outer shell in electron is *f*-block element [51]. Some *f*-blocked elements are La, Ce, Nd, Sm, Ho, Er, Th, U and Gd, etc. [77]. Because *f*-block elements can exist in several oxidation states, their nature is exceedingly complex [78]. The usage of *f*-block components in the Cr treatment process is currently quite restricted. A typical rare earth element is lanthanum (La), which is one of the seventeen chemical elements in the periodic table that share properties with highly active metals according to the international union of pure and applied chemistry (IUPAC). According to the researcher, lanthanum can significantly activate with some adsorbents to remove Cr, Ni, Ti, Mn, Zn and Cu. All of these harmful metal concentrations were much lower than what was required by the Municipal treatment's guidelines for the purity of drinking water. The maximal adsorption capacity in the Langmuir isotherm process is 16.5810 mg/g [79]. Another *f*-blocked element is Gadolinium. The optical performance and surface area of the synthesized sensor material are improved by the inclusion of gadolinium. The photoluminescence spectrum of the doped sample reveals strong fluorescence intensity, proving that this material is suitable for fluorescence applications. For the elimination of Cr (VI), gadolinium oxide (Gd_2O_3 , MW 362.50) is employed. Using fluorescence quenching and an adsorption approach, the novel gadolinium ion-doped boehmite based fluorescent nano sensor (MFNS) is a potential adsorbent of hexavalent chromium ions [80]. In light of these kinds of findings, the application of *f*-block elements revealed a novel strategy for the successful removal of Cr (VI) from water.

7.5. Periodic Elements for Chromium Adsorption in Nanoparticles

There are so many methods for heavy metal adsorption. Among these methods, nanoparticles are one the better technique for heavy metal adsorption, which is a new study field in toxic heavy metal removal. Nanoparticles are a stable in nature and are not harmful. Due to their high surface area and insolubility in water, they may be suitable adsorbents for the removal of pollutants from polluted water, as indicated in **Table 7** [81]. Iron (Fe) based nanomaterial successfully and arbitrarily eliminated the Cr^{6+} species from the aqueous medium during the adsorptive process. The coexistence of other cations, such as Mg^{2+} , Ca^{2+} , Ni^{2+} , and Cu^{2+} has a little impact on the adsorption of Cr^{6+} ions. By raising the pH of water, the adsorptive separation capacity is diminished. The major species of Cr^{6+} are CrO_4^{2-} and $Cr_2O_7^{2-}$ at pH 6 - 7.5 and $HCrO_4^-$ and CrO_4^{2-} in the pH range of 2-6 respectively. The reduced adsorptive separation of Cr^{6+} species reported in **Table 7** is a result of electrostatic repulsion brought on by the higher pH [16]. TiO_2 -based nanoparticles are also used in Cr (VI) removal because they are less toxic, chemically stable, and low-cost. Ti-based adsorbents have photocatalytic activity which adsorb Cr (VI) [76]. Other than this B, Mn Zn nano compound are also efficient in removing Cr from water by adsorption processes [56].

Table 7. Adsorption removal of Cr (VI) by nanoparticles and nano composites.

Elements	Morphology	Adsorption Isotherm	Adsorption Capacity, mg/g	Reference
Graphene-coated Fe ₂ O ₃	Iron oxide nanoparticles with graphitic carbon coating	Freundlich	352.1	[16]
GO/chitosan/ferrite	Nanocomposite	Langmuir	270.3	[16]
α -Fe ₂ O ₃	Nanocomposite	Freundlich	-	[81]
FeOOH /AlOOH /MultiWall Carbon NanoTubes	Nanoparticles	Langmuir	-	[57]
MMCs: MIL-100 (Fe)	Iron oxide magnetic particles;	Freundlich	45	[82]
Fe ₃ O ₄ / grapheme	Nanocomposite	Langmuir	280.6	[16]
PAN-CNT/TiO ₂ -NH ₂	Composite nanofibers		714.27	[9]
Fe ₃ O ₄ /polyacrylonitrile	Fibrous morphology	Langmuir	684.9	[16]
h-BN@5%Pani hybrid composite	Hybrid composite	Langmuir	133.34	[56]
[16] Fe ₃ O ₄	Nanoparticle	Freundlich	11.13	[49]
MnO ₂ /Fe ₃ O ₄ /O-MWC NT	Nanocomposite	Langmuir	186.9	[16]
a-MnO ₂ -NH ₂ -rGO	Hybrid	Freundlich	307.0	[16]

8. Efficient Element for Chromium (VI) Adsorption

From the table no. 4, 5, 6 we can see that several elements like Na, C, Fe, Ti etc. are the good absorber of Cr. But all the elements are not efficient on the basis of pollutant concentration, time, cost and dependency depending on various factors etc. Among them Fe is the most promising element which are frequently used for the commercial purpose of Cr (VI) removal [82]. Fe has numerous forms which are used in Cr (VI) removal. But all the form are not feasible because separation of the adsorbent is not easy as well as cost effective [68]. Ferromagnetic adsorbents have drawn a lot of interest due to how easily they can be separated under magnetic fields. One of them is Fe₃O₄ nanoparticles. Conventional Fe₃O₄ is simple to make and effective in removing Cr (VI) by adsorption [82]. Some co existing cations make the separation of adsorbent such as (Mg²⁺, Ca²⁺, Ni²⁺, and Cu²⁺) etc. [16]. Fe-based adsorbents outperform other materials in removing Cr (VI) when the cost of research, availability, simplicity in separation, effectiveness, safe handling, and non-toxicity are taken into account. To create a more effective adsorbent for the treatment of Cr (VI), other elements (such as Ti, Cu, Mn, and Mg) can co-exist with Fe.

9. Factors Affecting Chromium (VI) Elimination

There were a number of components involved in removing chromium (VI) from waste water, which we categorized into direct factors and indirect factors. For Cr (VI) elimination, optimizing these elements could produce great results.

9.1. Direct Effect

The adsorption process is governed by a variety of variables, including surface area, charge, adsorbent's particle size, contact duration, temperature, pH, the amount of adsorbate and adsorbent, and interactions between adsorbent and adsorbate [16]. Cr (VI) removal rises when the pH is falling and falls when it is rising. And it might drop by as much as 50% [67].

9.2. Indirect Effect

Some indirect factor of Cr (VI) removal are cost and efficiency of regeneration of adsorbent [75], Scale-up possibilities of adsorbent [57], and cost of the study, scope of use, handling safety, and usage mindset, among other factors.

9.3. Economic Considerations for Chromium (VI) Elimination

The cost of individual adsorbent varies depending on the required amount in processing steps, local availability, treatment conditions, and recycle and life time considerations. The cost will vary depending on whether the adsorbents are made for developed, developing, or underdeveloped nations. Both as-received and after chemical alterations, several commercially available Fe-compounds, in particular nanomaterials of various oxides, have been employed for chromium adsorption. Costs associated with chemical alteration [75], however, are typically not disclosed in study publications. Additionally, the data supplied lacks consistency. The majority of publications solely discuss experiments and the separation of nanomaterials [43]. The list of some factors consider for the cost of Chromium (VI) removal are given below:

- 1) Modification process of adsorbent;
- 2) Locality of the research work;
- 3) Local availability of compounds [57];
- 4) Condition of Cr (VI) containing water;
- 5) Consisting exist data presented;
- 6) Source of sample water [43].

The cost of manpower, the availability of different adsorbents, the co-efficient of the adsorbent, and other considerations should also be taken into account while removing Cr (VI).

10. Recommendations for Future Research

Hexavalent chromium is mostly found in aqueous systems as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) compounds. It has ability to cause cancer and mutagenesis in living things. According to estimates, the optimum limit of Cr for

human body is 64 mg kg^{-1} [41]. Modern industries including metal finishing, leather tanning, wood preserving and electroplating widely use Chromium (VI). In general, the chromium concentrations released may be quite high, ranging from tenths to hundreds of mg/L. Strict wastewater discharge rules have been established in many nations because of the substantial environmental disturbance caused by the addition of Cr (VI) ions through industrial waste effluents into natural water bodies [83]. The use of metal oxide-based nanomaterials as adsorbents in lab settings with simulated wastewater has been extensively investigated. Flexibility is the key characteristic of metal oxides and their composites [16]. From the review of literature, it has been found that Fe-based adsorbents are the most popular and efficient adsorbent of Chromium (VI) treatment. Fe nanoparticles were applied effectively in the removal of hexavalent chromium from wastewater due to higher surface area and reactive hydroxyl surface sites [49]. The effectiveness of Fe was increased by using certain common co-existing ions as Na^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+} , NO_3^- , and Cl^- [16]. Among these, Mg^{2+} is a DNA forming element which is non toxic to health. So it can be a promising co efficient element. It is crucial to understand the periodic element's distinctive relationships as well as how this element holds Cr in order to improve the effectiveness of chromium removal via adsorption. Adsorption is now the most effective method for efficiently removing Cr, and Fe is a highly popular adsorbent for Cr (VI), according to study data. Future research may yield greater outcomes if Fe is combined with other periodic elements or chemical constituents.

11. Conclusion

Recent years have seen an increase in the use of heavy metals and metalloids like chromium (VI) due to rapid industrialization and human activities. Water sources are contaminated, which causes serious health hazards for people and other living things as a result of the direct and indirect release of harmful Cr (VI) into the environment. To eliminate Cr (VI), several procedures have been used. This review study explored the elimination of hazardous chromium (IV) using efficiently operating periodic elements and contemporary adsorption technology. As Chromium is an anion, it is typically adsorbed successfully by certain periodic elements such as C, Si, Fe, etc., which are largely used in Cr (VI) removal. Nonetheless, C and Si contain a lot of repulsive locations. In contrast, Fe, Ti, Cu, Zn, Mg, and Mn in the form of their oxides and hydroxide-based natural rock and minerals, laboratory-synthesized nanoparticles, and nanomaterials have high surface areas, high porosities, and evenly distributed pore spaces (macropores, pore, and micropores). Because they are cations and are widely available in nature, they are utilized as adsorbent to remove Cr (VI) from water. Especially, Fe-based adsorbent showed high positive sites in water and it has special characteristics like magnetism. So, it acts as an efficient and cheaper priced adsorbent for Cr removal from water. Again Fe-based adsorbents are chemically stable and safe during treatment. However, to enhance the adsorption performance the combination of Ti, Cu, Zr, Mn, Mg, and Ni elements with

their oxides and hydroxides are used. In addition, Fe-Mg based adsorbents performed efficiently to remove Cr from water in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). Recent literature data demonstrated that, in real applications, combinations of elements with suitable carrier materials might effectively remove Cr from wastewater.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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