Recent Advances in Biomass-Based Waste Materials for the Removal of Chromium (VI) from Wastewater: A Review

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Highlights

• Cr(VI) is more toxic because of its carcinogenic effects in humans.
• Adsorption is a very effective and helpful method for the removal of Cr(VI).
• The modified adsorbents are found more effective in comparison to unmodified adsorbents.
• Biomass-based waste materials could be good alternatives for Cr(VI) removal.

Abstract

Hexavalent chromium (Cr(VI)) is a critical pollutant with high toxicity, even at trace concentrations. Cr(VI) is possibly carcinogenic and mutagenic and can produce serious health issues. Hence, it is necessary to remove Cr(VI) from the water before releasing it into the environment. Currently, numerous removal techniques were used. Adsorption is the best method compared to others because it is simple, cheap, highly efficient, and can be used in water having trace concentrations of contaminants. Biomass-based waste materials (BMWs) are found as far better adsorbents than commercially and other available adsorbents. In this study, the existing Cr(VI) removal techniques are reviewed and, a broad range of current research studies of Cr(VI) removal from water by using BMWs are evaluated. This review can be helpful to develop a more efficient, cheap, reliable, and environmentally benign bio-adsorbent. It is obvious after the literature review given herein that BMWs exhibited potential adsorbents for the removal of Cr(VI). Also, the chemically modified adsorbents exhibited a higher adsorption capacity than unmodified adsorbents.

Keywords: Cr(VI), Water, BMWs, Adsorbents, Adsorption

Introduction

The water quality is affected mainly by organic contaminants and heavy metals. Heavy metals in water cause widespread harm to human health. The metallic elements having a density greater than 5.0 g/cm³ are called heavy metals. The most common heavy metals are Cd (8.65 g/cm³), Cr (7.14 g/cm³), Co (8.90 g/cm³), Cu (8.95 g/cm³), Pb (11.34 g/cm³), and Hg (13.53 g/cm³). Among the toxic heavy metal ions, chromium has a significant impact on the aquatic environment. Chromium, an element having trivalent [Cr(III)] and hexavalent [Cr(VI)] as the most stable species. Hexavalent species is usually found in oxyanion as chromate (CrO₄²⁻) or dichromate (Cr₂O₇²⁻). Trivalent chromium is an essential element for living organisms, while Cr(VI) is more hazardous due to its carcinogenic effects [1]. The Cr(VI) is soluble in the aquatic environment of a wide pH range. It is considered the 16th most hazardous pollutant due to its carcinogenic and teratogenic properties [2,3]. Heavy metals including chromium are more potent to toxicity than other organic pollutants due to their non-biodegradable nature [4]. Chromium enters
into the aquatic environment through natural sources such as geochemical activity, rock and soil weathering, and anthropogenic sources, including various industrial activities such as tanneries, electroplating, textile processing, alloying, wood preservative, dying, pesticides, and fertilizer production. The most significant release of Cr(VI) occurring from industrial sources. Naturally, it occurs as crocoite (PbCrO₄), chrome ochre (Cr₂O₃), and ferric chromite (FeCr₂O₄) deposits [5].

Chromium as a metal is biologically inert and does not produce toxic effects in humans. Cr (III) and Cr(VI) have different toxicity, mobility, and bioavailability. Cr(III) is an essential element needed for normal carbohydrate and lipid metabolism in humans. Its deficiency can cause slow removal of sugar from the blood. Cr(III) and insulin together balance the glucose level in the blood. Hence, it utilizes as a dietary supplement, usually as chromium (III) chloride, chromium (III) polynicotinate, or chromium(III) D-phenylalanine [6]. However, in an excess amount or long-term exposure, it is toxic. Cr(VI) is much more lethal than Cr(III) because Cr(VI) compounds are usually highly soluble, mobile, and bioavailable than Cr(III) compounds [7]. Even trace level concentrations of Cr (VI) in drinking water can endanger human health. Compounds of Cr(VI) are potent oxidants. The toxicological impact of Cr(VI) arises from the possibility of free diffusion through cell membranes. In the cell, it oxidizes biomolecules and forms free radicals during the reduction of Cr(VI) to Cr(III). Thus formed Cr(III) inside a cell in a significant amount may cause other adverse effects because of its high affinity to bind various organic compounds that inhibit some metalloenzyme systems [8,9]. Cr(VI) affects physiology, concentrating in the food chain, causes several disorders in human health such as vomiting, bleeding, disturbances, and ulcer in the stomach, kidney, and liver damages, skin rash, weakened immune system and can even lead to sudden death[10,11]. Based on its acute lethal effects on human health, WHO and USEPA promulgated the maximal contamination limit for Cr(VI) in drinking water not to exceed 0.05 mg/L and in industrial effluents is 0.25 mg/L [11,12]. The necessity of its removal from the natural environment arises due to its high desolation rate in the wide pH range of the aqueous phase, non-biodegradable, and obviously due to its toxic nature.

Various methods, such as electro-dialysis, membrane technology, redox reaction followed by precipitation, ion exchange, and adsorption are applied to eliminate(VI) from the aquatic environment [13,14]. Requirements for the high energy and expensive instruments, lacking metal removal completion, toxic waste sludge, and disposals, etc., are the reasons which limit the use of most of the options mentioned above [15-18]. The adsorptive method of removal is the most widely used method for the removal of heavy metal pollutants, including Cr(VI), from the wastewater due to the availability of cheaper materials for the production of low-cost adsorbents [19,20]. Trace concentrations of the metals can even remove by adsorption, which proves this method more beneficial than conventional methods. Despite the usefulness of the adsorbents, they have some disadvantages like low adsorption capacities or long adsorption equilibrium times [21,22]. Therefore, it is crucial to pursue for novel effective adsorbents. This review focuses on the comparative study of the use of readily available agricultural byproducts as effective adsorbents for removing Cr(VI) from the aquatic environment.

Recently, several review papers on removing Cr(VI) from water and wastewaters by adsorption process have been published [23-25]. Most of the reviews focused only one specific type of adsorbents such as carbon nanotubes[26], activated carbon derived from biomass [27], carbonaceous nanomaterials [28], microporous polymers [29], silica-based materials [30], chitosan-based nanocomposite [31], magnetic iron oxides [32], nanoparticle-based adsorbent [33,34], polyaniline-based materials [35], metal-organic framework (MOF) derivatives and their composites [36], and natural minerals [37]. This study offers a significant and thorough review on removing Cr(VI) from water by using biomass-based waste materials (BMWs) as adsorbents, especially those that have emerged in recent years. This review aims to pursue the adsorbents that are less expensive and to examine their efficacy for removing Cr(VI) ions from contaminated water.

**Chromium (VI) Removal Method**

Several methods are used to remove Cr(VI), such as ion exchange, chemical precipitation, coagulation, membrane separation, electro-coagulation, reverse osmosis, etc. Due to their high cost and minimal practicability, these processes of removing Cr(VI) are not applicable. Instead, the adsorption techniques, due to their low cost and high efficiency, are most used though searching for the most efficient adsorbent is still on.

**Ion exchange method**

It is the physio-chemical process used for the last few decades based upon the exchange of cation with the metal ion in wastewater. This process involves a reversible exchange of ions between solid and liquid phases, which has received significant
attention for removing Cr(VI). Having inexpensive nature and capability of selective metal removal, natural zeolites are used as mediums for ion exchange reactions. In most cases, synthetic ion exchange resins are used. Effect of pH, variation of the solution, expensive synthetic resins, and non-usability on a large scale are the disadvantages of this process [38,39]. Various ion exchange resins such as synthetic Dowex 2-X4 ion exchange resin [40], Ambersep 132 [41], Amberlite XAD-4 (MAX-4) [42], Diaion CR11, and Amberlite IRC86 [43] were studied for Cr(VI) removal from aqueous solutions.

**Chemical precipitation method**

This process is an easy, inexpensive, commonly used one. Chemical reagents like lime, alum, and limestone reacted with the metal ion to form the precipitation, which was later filtered. The requirement of large amounts of reagents, high cost for the disposal of remaining sludge are the disadvantages of this process [44,45].

**Coagulation**

In this process, coagulates such as ferric and aluminium chloride form the colloids with the metal ion. The removal in this process is determined by the pH of the solution, initial metal ion concentration, and concentration of coagulant used. Although used on a larger scale, the expensive coagulants and problems in the sludge disposal are the disadvantages of this process [46,47].

**Electrodialysis method**

It is a membrane separation technique to transport ions aided under electrical potential across the membranes [48,49]. Based on the methods and the size of the metal ion present, different types of membranes are used to remove the metal ion. Although having advantages like the use of fewer amounts of chemicals and the formation of less amount of sludge, the high maintenance, and operational cost are its drawbacks [50].

**Reverse osmosis**

It was a promising membrane technology used to remove the Cr(VI) by using the semi-permeable membrane [51]. In this process, pressure is applied in the concentrated part followed by the movement of water to a more dilute part, and metal ions are washed away with water. High operational and maintenance expenses and the requirement for increased power for the pressure are the drawbacks of this process [52].

**Adsorption process**

This process involves the accumulation of metal ions or adsorbate on the surface of the adsorbent, creating a layer. This process is extensively used because of its low cost and high efficiency. It has some disadvantages too, such as: in some cases, involvement of increased prices to prepare the suitable adsorbent, chemical regeneration, and loss during this process [53,54]. Because of the high price, low efficiency, use of excessive chemicals, production of toxic and non-eco-friendly sludge, and disposal of the sludge, the use of conventional methods of removal of Cr(VI) is limited. Preferentially, being simple, affordable, highly productive and efficient, and low cost, the adsorption method of removing Cr(VI) metal ions is mainly used [54]. Aside from the adsorption process, the search for a suitable adsorbent is essential too. For the selection of a suitable adsorbent, the cost factor is the important one. With the cost factor, the adsorbents should be widely available and should require little processing. Biomass-based waste materials (BMWs) present a better and inexpensive alternative for adsorbents [55].

**Adsorbents for Removing of Chromium (VI)**

Having high surface area and various functional groups, commercially available adsorbents like graphene, activated carbon, and carbon nanotube act as efficient adsorbents for removing Cr(VI) metal ions from the wastewater, however, they are expensive [56–58]. Zeolites, clays, and silicious materials are low-cost, widely available, and able to modify the adsorption characteristics, natural materials are used in the adsorption [59–61]. Using bio-adsorbents like chitins and chitosan, yeast, fungal biomass, and bacterial biomass, the Cr(VI) remove from wastewater [62,63].

**Biomass-based adsorbents**

Because of their low-cost, eco-friendly nature, vast abundance, and high efficiency, the use of low-cost adsorbents has gained colossal popularity to purify water contaminated by heavy metals. Generally, the categories of these adsorbents include
agricultural byproducts, animal waste, forest waste, industrial waste, etc. Despite the effectiveness of the commercially available activated carbon in the adsorption of heavy metal ions, its expensiveness limits its use. Hence, it is necessary to develop the adsorbents which are readily available at a relatively low cost, that can be widely employed for the adsorption of heavy metal ions, including Cr(VI), from the aqueous environment. Although agricultural byproducts are comparatively less effective than commercially available activated carbons, their low cost and high abundance have made them a better option. Agrarian byproducts are composed of starch, sugar, lignin, cellulose, pectin, etc. Several functional groups such as hydroxyl, aldehyde, and ketone groups present in many adsorbents. These qualities of the adsorbents have made them more efficient for the removal of pollutants [64–67].

Fruit peels are readily available from juice industries, which are solid wastes. Mohammed et al. used pomegranate peel as a natural adsorbent for the adsorption of Cr (VI) ions from industrial wastewater. The authors reported that the experimental data best fitted for the Langmuir isotherm model. They determined the metal removal efficiency to be 90%, with the most excellent adsorption capacity of 9.45 mg/g [68]. Galil et al. observed the maximum adsorption capacity for Cr (VI) onto H_2SO_4 treated pomegranate peel to be 28.28 mg/g at the pH of 3.0. They used the batch adsorption technique to study the influence of various operating factors such as pH, initial concentration, contact time, and biosorbent dose. The equilibrium data fitted best to the Langmuir model, and the kinetics of the process better explained by the pseudo-second-order model [69].

Brans are the byproducts of the grains obtained from milling industries. Ogata et al. prepared virgin wheat bran and calcined wheat bran to remove Cr(VI). Adsorption isotherm and kinetic data best fitted the Freundlich and pseudo-second-order models, respectively [70]. The husk is also an agricultural waste collected from milling industries. Mullickle et al. carried out a comparative study on the capacity of Cr(VI) adsorption from water by activated carbon derived from rice husk with the commercial one. For this purpose, the rice husk sample was chemically modified with NaOH solution. They investigated the effects of operational parameters and reported the percentage removal of Cr(VI) at pH of 2.0 to be 91.23% for the rice husk-derived activated carbon. The pseudo-second-order model agreed well with the kinetic data, and the adsorption isotherm best fitted to the Langmuir isotherm model. The study revealed that the adsorption process was endothermic, and the equilibrium constant increased with increasing temperature [71].

Chakraborty et al. studied the adsorption of Cr(VI) ions from water using sawdust modified with formaldehyde. They investigated the effects of the parameters like pH, contact time, adsorbent dose, and initial metal ion concentration. The authors reported that the experimental data was better explained by the Freundlich isotherm model. The maximum adsorption of 100% was observed at pH 2.0, initial concentration of 10mg/L, and adsorbent dose of 4g/L. They reported the maximum adsorption capacity to be 8.84mg/g. The obtained data best fitted with a pseudo-second-order kinetic model, and the adsorption process was endothermic and spontaneous [53]. Li et al. studied the adsorptive removal of Cr(VI) from water by a walnut shell, chemically modified using diethylenetriamine. The study was carried out by the batch adsorption method. They reported the maximum adsorption of 50.1 mg/g at 303K with a solution pH of 3. The experimental data was better explained by the Langmuir isotherm model, and the data is better fitted with a pseudo-second-order kinetic model [72]. Lin et al. carried out the batch adsorption study using aminated rice straw grafted-poly (vinyl alcohol) to remove Cr(VI) from an aqueous solution. The authors reported that the experimental data was best supported by Freundlich isotherm and Elovich models. They found the maximum adsorption up to 140.39 mg/g at the pH of 2.0. The maximum adsorption was much more prominent than that of the unmodified rice straw (34.90 mg/g). The reaction was endothermic, and spontaneous [73].

Prabhakaran et al. reported the Cr(VI) adsorption capacity of spent tea and coffee dust. The Cr(VI) ions get reduced to Cr(III) ions, and the reduction of Cr(III) ions was found dependent on the pH of the solution. The maximum removal of chromium by tea and coffee dust was 44.9 mg/g and 39.0 mg/g, respectively, at the solution pH of 4.0. The experimental data is best described by Langmuir isotherm models [74]. Bhatt et al. prepared the charred sugarcane bagasse (CSB) by chemical modification of sugarcane bagasse with Conc. H_2SO_4. They used the batch adsorption technique to study the influence of parameters like pH, contact time, concentration, and doses of the adsorbent. The optimum pH was determined to be 1, following the pseudo-second-order kinetics. The adsorption % decreased with increasing initial metal concentration and a lower dose of adsorbent. Equilibrium adsorption was fitted the best with Freundlich adsorption isotherm [75].

Activated carbon (AC) can be synthesized by all carbonaceous materials. However, the product’s characteristics will alter based on the type of the raw material used, the nature of the activating agent, and the condition and activation processes. AC made from petroleum and coal by using multistep preparation process using of expensive and hazardous chemicals have the high
specific surface area and good adsorption capacity. Recently, biomass-based waste materials exhibited potential as precursor materials for the synthesis of AC, usually with comparable adsorption capacity with commercial activated carbons [71,76]. The use of biomass-based waste materials in AC preparation would not only help in solving the disposal problem but also help in reducing the cost of carbon preparation. It would provide a potentially inexpensive alternative to existing, extensively used, commercially available petroleum/coal-based activated carbons. AC produced from biomass-based waste materials was found to be the most effective adsorbent for the removal of Cr(VI) due to its high surface area, various surface functional groups, and microporosity structure. Thus, plenty of researches was carried on the adsorptive removal of Cr(VI) onto AC derived from different BMWs [76,77]. The particle size exhibited a vital role in adsorption efficiency. Besides, adsorption Cr(VI) on AC largely depends on its activation and pretreatment method [78]. Some of the BMWs bio-adsorbents used for the removal of Cr(VI) are presented in Table 1.

### Table 1: Adsorption capacities of various adsorbents for the removal of Cr(VI) ions from water

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Optimum pH</th>
<th>Adsorption capacity (mg/g)</th>
<th>Fitted isotherm model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pomegranate peel</td>
<td>-</td>
<td>9.45</td>
<td>Langmuir</td>
<td>[68]</td>
</tr>
<tr>
<td>H_2SO_4 treated pomegranate peel</td>
<td>3</td>
<td>28.28</td>
<td>Langmuir</td>
<td>[69]</td>
</tr>
<tr>
<td>NaOH treated rice husk</td>
<td>2</td>
<td>34.85</td>
<td>Langmuir</td>
<td>[71]</td>
</tr>
<tr>
<td>Formaldehyde treated sawdust</td>
<td>2</td>
<td>8.84</td>
<td>Freundlich</td>
<td>[53]</td>
</tr>
<tr>
<td>Diethylenetriamine treated walnut shell</td>
<td>3</td>
<td>50.1</td>
<td>Langmuir</td>
<td>[72]</td>
</tr>
<tr>
<td>Aminated rice straw</td>
<td>2</td>
<td>140.39</td>
<td>Freundlich</td>
<td>[73]</td>
</tr>
<tr>
<td>Waste tea leaves</td>
<td>4</td>
<td>44.9</td>
<td>Langmuir</td>
<td>[74]</td>
</tr>
<tr>
<td>Exhausted ground coffee waste</td>
<td>4</td>
<td>39</td>
<td>Langmuir</td>
<td>[74]</td>
</tr>
<tr>
<td>Gliricidia sepium Leaf Powder</td>
<td>2</td>
<td>35.71</td>
<td>Freundlich</td>
<td>[12]</td>
</tr>
<tr>
<td>H_3PO_4 activated Sugar cane bagasse</td>
<td>5</td>
<td>28.3</td>
<td>Langmuir</td>
<td>[79]</td>
</tr>
<tr>
<td>Conc. H_2SO_4 treated Grape waste</td>
<td>4</td>
<td>1.91 (mol/kg)</td>
<td>Langmuir</td>
<td>[80]</td>
</tr>
<tr>
<td>Mangifera Indica</td>
<td>3</td>
<td>320.07</td>
<td>Langmuir</td>
<td>[81]</td>
</tr>
<tr>
<td>Sakura waste</td>
<td>1</td>
<td>435.25</td>
<td>Langmuir</td>
<td>[82]</td>
</tr>
<tr>
<td>Eucalyptus camaldulensis seeds</td>
<td>1</td>
<td>51.93</td>
<td>Langmuir</td>
<td>[83]</td>
</tr>
<tr>
<td>Benincasa hispida peel</td>
<td>1</td>
<td>18.7</td>
<td>Freundlich</td>
<td>[84]</td>
</tr>
<tr>
<td>Sewage sludge biomass</td>
<td>2-10</td>
<td>1.87</td>
<td>Langmuir/Freundlich</td>
<td>[85]</td>
</tr>
<tr>
<td>H_3PO_4 activated apple peels</td>
<td>2</td>
<td>36.01</td>
<td>Freundlich</td>
<td>[86]</td>
</tr>
<tr>
<td>H_3PO_4 activated sugar beet bagasse</td>
<td>4</td>
<td>52.8</td>
<td>Langmuir</td>
<td>[87]</td>
</tr>
<tr>
<td>KOH activated Bermuda grass</td>
<td>2</td>
<td>403.2</td>
<td>Langmuir</td>
<td>[88]</td>
</tr>
<tr>
<td>Ozone activated rice husk</td>
<td>2</td>
<td>8.5</td>
<td>Freundlich</td>
<td>[89]</td>
</tr>
<tr>
<td>NaOH activated longan seed</td>
<td>3</td>
<td>169.5</td>
<td>Langmuir</td>
<td>[90]</td>
</tr>
</tbody>
</table>

Adsorption isotherm generally provides information about adsorption behaviour between the adsorbent and adsorbate and the surface properties of the adsorbent. Generally, two typical isotherm models, Langmuir and Freundlich models, were fit the experimental adsorption data and assessed the isotherm performance. Most biomass-based adsorbents reported to follow Langmuir adsorption isotherm, and few of them reported to follow Freundlich Adsorption. Better fit with the Langmuir isotherm model indicates that Cr(VI) ions from monolayer on a homogeneous surface of the adsorbents without interaction between
adsorbed molecules and all the adsorption sites are energetically equivalent [68-71, 79-83]. However, the Freundlich isotherm model considers multilayer adsorption of Cr(VI) on the heterogeneous surface of the adsorbents, and the adsorption energy exponentially decreases on completion of the adsorption sites of adsorbents [46,66,86]. The mechanism of adsorption of metal ions includes chemisorption, surface adsorption, adsorption–complexation, ligand exchange, and microprecipitation[25]. The proposed possible interactions between Cr(VI) and adsorbents [91] are adsorptions through electrostatic attraction between Cr(VI) anion and positive functional groups of adsorbent and adsorption of Cr(VI) followed by complete reduction to Cr(III). The reduction is carried out by the donation of electrons from donor atoms such as O, S, and N of the adjacent functional group of adsorbents during Cr(VI) adsorption. The mechanism of biosorption of hexavalent chromium onto AC was reported as the reduction of Cr(VI) to Cr(III) on the adsorbent surface, followed by Cr(III) [25,80,91].

Biomass-based adsorbents exhibit satisfactory % removal of Cr(VI) to the commercial adsorbents but are still lower than the conventional methods. However, in developing countries like Nepal, biosorption is considered to be an effective water treatment method compared to conventional methods due to its simplicity and flexibility of design, ease of operation and maintenance, cheap, minimal sludge generation, the potential for regeneration, and can be used in water having trace level of contaminants.

The chemistry of Cr(VI) and the effect of pH

Chromium exists in several oxidation states ranges from 0 to VI. However, only Cr(III) and Cr(VI) are stable to exist in the environment. The Cr(III) is the most stable oxidation state. Hexavalent chromium forms various species such as \( \text{Cr}_2\text{O}_7^{2-} \), \( \text{HCr}_2\text{O}_7^- \), \( \text{CrO}_4^{2-} \), \( \text{HCrO}_4^- \). The relative proportions of Cr(VI) are dependent on both pH and total Cr(VI) concentration which was shown in Figure 1 [92].

![Fig 1: Chemical equilibrium speciation of Cr(VI)](image)

In a basic medium, at pH > 6, it forms chromate ion \( \text{CrO}_4^{2-} \) ion. In an acidic medium, at pH between 1 and 6, \( \text{HCrO}_4^- \) and \( \text{Cr}_2\text{O}_7^{2-} \) ions are in equilibrium, but \( \text{HCrO}_4^- \) is the prevalent species as shown in Figure 1. At pH < 1 the main species is \( \text{H}_2\text{CrO}_4 \) [80,93]. The main equilibriums for the Cr(VI) species in water are reported below [94,95]:

\[
\text{H}_2\text{CrO}_4 \rightarrow \text{H}^+ + \text{HCrO}_4^- \quad K_1 = 0.37 \quad (1)
\]

\[
\text{HCrO}_4^- \rightarrow \text{H}^+ + \text{CrO}_4^{2-} \quad K_2 = 3.2 \times 10^{-7} \quad (2)
\]

\[
2\text{HCrO}_4^- \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \quad K_3 = 35.5 \quad (3)
\]

Cr (VI) in acidic solution exhibits a very high positive redox potential which indicates that it is highly oxidizing in the presence of electron donating species [80,96].
\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad \text{E}^o = 1.33 \text{ V} \quad (4)
\]

However, the \text{CrO}_4^{2-} ion in alkaline solution is much less oxidizing:

\[
\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3 (s) + 5\text{OH}^- \quad \text{E}^o = -0.13 \text{ V} \quad (5)
\]

In a more alkaline solution the reduction of \text{CrO}_4^{2-} generates \text{OH}^- against a gradient. This destabilizes \text{Cr(III)} compared to the \text{Cr(VI)} resulting in a decrease in the redox potential with the increase in basic strength [97].

The prevalent form of \text{Cr(VI)} at pH = 2 - 6 is \text{HCrO}_4^{-}. At this pH range, a large number of \text{H}^+ ions exists in the solution, and the surface protonation of the adsorbent leads to the formation of positively charged on the surface of the adsorbent. These positively charged surfaces of adsorbents interact with \text{Cr(VI)} anion by an electrostatic attraction so that prevalent species \text{HCrO}_4^{-} is strongly adsorbed onto the surface of the adsorbent. Hence, adsorption is more favorable in this pH range [96]. At higher pH, a high concentration of \text{OH}^- ions strongly compete with \text{CrO}_4^{2-} ions for the adsorption site, and thus, % adsorption of \text{Cr(VI)} sharply decreases at higher pH [80]. At pH < 2, even though the medium is strongly acidic, a very high concentration of \text{H}^+ ions is available, which can promote the reduction of \text{Cr(VI)} to \text{Cr(III)}. The cationic ions interact with the protonated surface of the adsorbent by electrostatic repulsion, and there is a competition between \text{H}^+ ions, \text{Cr(III)} species, and the adsorption surface active sites. Hence, the decrease in adsorption of \text{Cr(VI)} at very low pH is due to the reduction of \text{Cr(VI)} to \text{Cr(III)} [93]. The decrease in the rate of adsorption is due to the coexistence of \text{Cr}_2\text{O}_7^{2-} and \text{CrO}_4^{2-} with \text{HCrO}_4^{-} in the solution medium; thus, causing competition on the adsorption sites [98]. The chemistry of \text{Cr(VI)} is strongly dependent on pH. Table 2 reports the prevalent species of \text{Cr(VI)} at each pH range [99].

<table>
<thead>
<tr>
<th>pH</th>
<th>Prevalent species of Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>\text{H}_2\text{CrO}_4 (chromic acid)</td>
</tr>
<tr>
<td>2-4</td>
<td>\text{Cr}_2\text{O}_7^{2-} (dichromate)</td>
</tr>
<tr>
<td>4-6</td>
<td>\text{HCrO}_4^{-} (hydrogen chromate), \text{Cr}_2\text{O}_7^{2-} (dichromate)</td>
</tr>
<tr>
<td>6-8</td>
<td>\text{Cr}_2\text{O}_7^{2-} (dichromate), \text{CrO}_4^{2-} (chromate)</td>
</tr>
<tr>
<td>&gt;8</td>
<td>\text{CrO}_4^{2-} (chromate)</td>
</tr>
</tbody>
</table>

**Future Prospectives**

Biomass-based waste materials (BMWs) are a better alternative to the commercially available activated carbon for heavy metal removal from an aqueous environment. Due to their easy accessibility and economical and environmental friendliness, demand and uses of biomass-based adsorbents expected to rise shortly. Future studies must explore highly effective, cost-saving, and environment-friendly adsorbents that can easily regenerate from many operational cycles without significant loss of adsorption efficiency. In the future, the research should extend using the continuous column method on the natural wastewater and industrial effluents to enhance the large-scale application of the adsorbents. Further work needs to explore a cost-benefit analysis of the application of BMWs as adsorbents for the removal and recovery of \text{Cr(VI)} as well as other heavy metals.

**Conclusions**

Heavy metal pollution has been causing severe environmental issues around the globe. In an attempt to find the remedial action, numerous conventional techniques such as reverse osmosis, ion exchange, precipitation, coagulation, membrane separation, and adsorption methods are used for their removal. Among them, the adsorption method is found very practical and helpful for the purpose. Despite the higher efficiency of commercially available activated carbon, its high cost limits its use. It is hence economic and practical to use biomass-based waste materials due to their low cost, easy availability, easy separation, high adsorption capacity, and renewability. The chemically modified adsorbents are found more effective in comparison to unmodified adsorbents. Even though various research articles are available on biomass-based adsorbents, most of them are limited to batch-scale. There is no further scale-up of the process for the treatment of natural industrial wastewater. Hence, further research is...
necessary for this area. It is also reasonable to understand that advancement in the current modification methods to develop novel biomass-based adsorbents for removing Cr(VI) and other heavy metals from water is still an emerging field of research.

References


