

Chromium (VI) Removal from Waste Water using Low-Cost Adsorbent-Review

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Abstract:- Heavy metal contamination in water is one of the world's most severe environmental and ecological issues. Mining, agricultural, and industrial activities contribute to stream heavy metal contamination. The Environmental Protection Agency has classified chromium as one of the most toxic and hazardous metals. Chromium is removed from aqueous solutions and industrial effluents in various ways. Various adsorbents are utilized to remove Cr(VI) metal from wastewater. The removal of chromium from wastewater using adsorbents has seen significant advances in efficiency and cost. However, the recycling of utilized adsorbents received little attention. When the chromium concentration is low (1–100 mg/l), current approaches to extract chromium ions from wastewaters are costly and unsuccessful. As a result, developing alternative technologies is critical right now. Adsorption system that uses dead biomass to collect chromium in wastewater can be utilized to replace traditional processes for chromium contamination remediation. adsorbents are made from biomass that are present in abundance as waste is a step toward a prospective method because of its high absorption capacity and low-cost raw material source. This review article will discuss various agricultural waste-based adsorbents and their regeneration techniques for the effective removal of Cr(VI) from the aqueous solution in an cost effective and ecofriendly approach.

Keywords:- Adsorption, Low-cost sorbent, Chromium (VI) removal, adsorbent regeneration, eco-friendly adsorption.

I. INTRODUCTION

Water is a critical and necessary component for living organisms. Water quality is under threat as a result of economic growth, population growth, and climate change, which all contribute to widespread and severe degradation of the water bodies. Around 1% of groundwater is available for human consumption, including drinking, agricultural activities, construction, industrial applications, power plant operation, and so on. Unfortunately, human activities such as population increase, industrialization, and domestic and agricultural activities have harmed the earth's biosphere since the industrial revolution, and the quality of our resources is rapidly deteriorating (Xu, 2014). Almost four billion people are associated with severe water scarcity for at least one month each year, and half of the world's population could be affected by water scarcity by 2025 (UNICEF 2021). Heavy metal gets released into the environment in large quantities in the discharged by industries. Untreated wastewater contains heavy metals and

metalloids is the leading cause of water pollution, with up to 90% of untreated wastewater goes into water bodies around the world (UNEP and UN Habitat 2010). Heavy metal ions contamination in untreated wastewater is one of the most serious threats to the quality of the world's groundwater (Gupta et al., 2021; Lian et al., 2019; Nakkeeran et al., 2018). Wastewater from Industries release high toxic metals such as cadmium, lead, cobalt, chromium, and arsenic into water bodies, causing environmental harm. The harmful effects of contamination on individuals and the environment are determined by the length of exposure, the rate of toxicity, and the dosage amount. Chromium (Cr) is one of the most toxic heavy metals. The oxidation states trivalent Cr(III) and hexavalent Cr(VI) represent the existence of chromium in the environment (Karimi et al., 2012). The maximum acceptable concentration of heavy metals highlighted in the Table 1 shows the highest value of heavy metals that can be acceptable by various health and environment agencies (Gautam et al., 2016; Gopalakrishnan et al., 2015).

Metals	Conc (mg/L)
Chromium	0.05
Nickel	0.05
Iron	0.3
lead	0.1
Mercury	0.001
Cadmium	0.01
Arsenic	0.050

Table1: Acceptable concentration of some toxic heavy metals in drinking water (Binkley and Simpson, 2003)

Chromium exists in the water in two states out of which hexavalent chromium (Cr-VI) anions is more poisonous and poses a bigger threat to the quality of water and the ecosystem, due to its solubility and mobility under ambient environmental conditions. Its long-term exposure can impact humans and the ecosystem negatively. Various agencies have declared chromium exposure to be carcinogenic can lead to stomach and lung cancer, as well as epigastric, nausea, diarrhoea, vomiting, and haemorrhage. Further details can be seen in **Table 2**. Hexavalent chromium compounds, such as Ca, Zn, Sr, and Pb chromates, are highly water-soluble, poisonous, and carcinogenic. In addition, chromium compounds are utilized to treat ulcers that are slow to heal. Chromate chemicals have also been shown to degrade DNA in cells (Gupta et al., 2021; Tumolo et al., 2020). The highest acceptable safe levels for Cr(VI) in water and agricultural soils, according to the Environmental Protection Agency (EPA), are 0.05 and 0.1 parts per million, respectively.

Exposure	Mode	Health hazards
Air	Breathing	Nasal irritation, ulcers, cancers of the respiratory tract, tuberculosis, coughs and colds.
Water	Drinking and eating	Stomach cancer, epigastric, diarrhea, and pneumonia.
Dermal	Skin penetration	Dermatitis, skin irritation, and skin diseases.

Table 2: Exposure of Hexavalent (Cr) and diseases(Das and Singh, 2011)

II. MODE OF THE RELEASE OF CHROMIUM (CR) AND WATER POLLUTION

Chromium is an economically essential mineral for Industrial activities. Chromium (Cr-VI) is widely used in chromium plating industries such as metallurgy, electroplating, paints, pigments, and leather tanneries due to its exceptional anti-corrosive and tanning qualities. They have the potential to be poisonous and cancerous. Chromium contamination enters in water by natural and anthropogenic sources(Tumolo et al., 2020).Chromate rocks are the natural source of Chromium which release chromium

by oxidation of chromites and commercial activities like mining, chromate processing, metals industries, and tanning processing waste are the major anthropogenic source of Chromium contamination in environment (He and Li, 2020). Untreated waste water from Chromium plating industries is the major source of chromium contamination in water bodies. Waste effluent also causes soil contamination as chromium ions accumulate in the soil through the agricultural irrigation, and related activities(Thakur et al., 2021).Different chromium content of the wastes is enlisted in **Table 3**.

Sources	Contamination
Combustion of fuel	Cr(III)
stainless steel industries process	Cr(III),Cr(VI)
Chromium chemicals manufacturing	Cr(VI)
Electroplating	Cr(VI)
Tanning process	Cr(III),Cr(VI)
Production of Dyes, Paints, and Pigments	Cr(III), Cr(VI)
Industrial wastes disposal and coal ash	Cr(III),Cr(VI)

Table 3: Source of chromium (Cr) and water contamination(Banchhor et al., 2017).

Chromite ore production is the first step in the synthesis of chromium compounds, which has been steadily declining for the past 20 years due to environmental concerns. South Africa, Kazakhstan, India, and Turkey are the top four producers of chromite ore. Indian chromite reserves account for about 2% of global resources. Odisha possesses nearly 98% of India's total proven chromite (Cr-ore) reserves, with the Sukinda Valley contributing 97% of totalChromite deposit(Mishra and Sahu, 2013). The starting

substance for all industrial chromium compounds is sodium dichromate. The second most valuable industrial chromium compound, chromic acid is utilized to make wood preservatives and metal polishing operations. Chromium sulfate (leather tanning) and chromium oxide are two other chromium compounds (metallurgical, refractory, and pigment application). Different application of the chromium compounds is noted in Table 4.

Industrial applications	Compound form of Chromium(Cr)
Anti-corrosive agent (chrome, spray coatings)	Zinc chromate($ZnCrO_4$), Calcium chromate ($CaCrO_4$), Sodium chromate ($CrNa_2O_4$) and other chromates of Barium, and Strontium.
Tanning of leather products	Ammonium dichromate
Wood-preservatives	Chromium trioxide (CrO_3)
Stainless Steels	Ammonium dichromate [$(NH_4)_2Cr_2O_7$], Potassium dichromate ($K_2Cr_2O_7$), and chromates of sodium, and potassium.
Paints, Dyes, and plastic, Pigment	Barium chromate, Zinc chromate, Calcium chromate, and Lead Chromate Potassium dichromate ($K_2Cr_2O_7$), and chromates of Lead, sodium, and calcium.

Table 4: Hexavalent Chromium [Cr(VI)] utilization in various industries

Source: Das and Mishra 2009

In the recent decade, various industries established in India, and waste generated from tanning industries increases the load of proper wastewater treatment. Due to improper treatment and waste discharge in water bodies, the concentration of chromium increases in the water bodies, and soil lead to excess contamination that accumulates in the environment.India is a developing country that has natural reserves resource, a market, and favorable land policies for the manufacturing plants installation that attracts investors

and industrialists to establish their setup in India, which contributes to improving the economic conditions.Although, Government has strict norms for the waste disposal due to untreated waste water discharging from industries water sources degrading their quality. Industrial waste effluent disposal contribute majority/severe of Cr(VI) contamination in water and environment worldwide (Nakkeeran et al., 2018).Because of the high Cr levels in the tanning Indian economy, it is one of the most polluting industries in India.

Tamil Nadu, West Bengal, Uttar Pradesh, and Gujrat are the epicenters of these industries. They contribute roughly 2000-3000tons Cr to the environment, contaminating water basins in the process. The Cr concentration in effluent varies

between 2000 and 5000 mg/L in wastes(Dhal et al., 2013).**Figure 1.** showcase the sources of chromium in the water bodies.

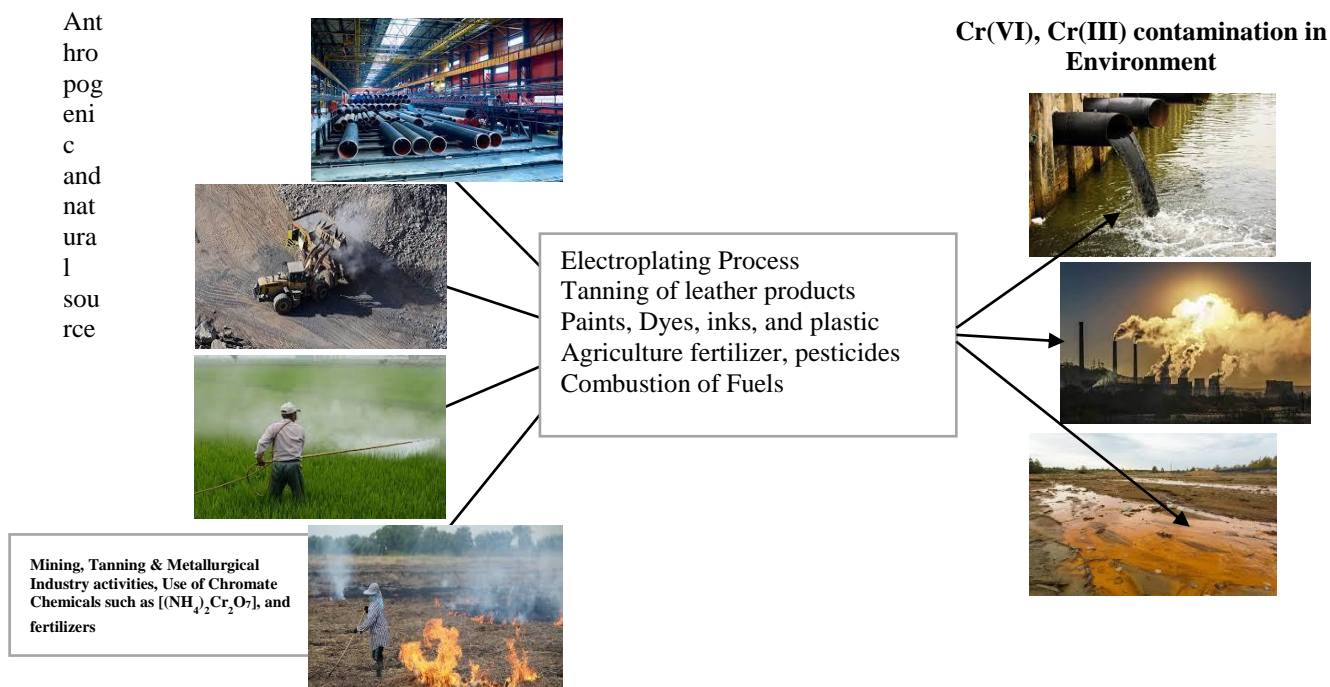


Fig. 1: Sources of chromium (Cr) and contamination in Environment

Some cities facing the serious issue of chromium heavy metal contamination of ground water. Chromium levels over the permitted limit have been reported in numerous residential and industrial areas across India. Sukinda valley, Orissa is one of the world's ten most chromate polluted cities. It generates a significant quantity of mining waste and causes serious health and environment problems in the area(Kumar Yadav et al., 2018).Ranipet is a town in Tamil Nadu, One of India's most chromium polluted zones, with roughly two hundreds tanneries and other small-scale chemical companies dominating the area(Tamma Rao et al., 2013). Extremely untreated waste is discharged from tanneries' nearby water bodies, thus the water in Thandalam and Manianpattu lakes had become so polluted with chromium that it was no longer fit for human consumption.Uttar Pradesh, Kanpur is known for its tanneries and companies that produce basic chrome sulfate.

Its eastern part has around 350 tanneries, these tanneries alone produce around 1500 metric tonnes of chromium sulfate waste each year (Mohan et al., 2011).In 1997, the Central Pollution Board of India reported Cr(IV) levels in Kanpur, India, that were up to 250 times higher than the WHO's permitted level (0.05ppm).Chennai, Water samples were taken from the Bengaluru region surrounding the industrial cluster, which covered 1.4 km² and was relatively close to the residential area. The results revealed that 54 percent of the samples were contaminated and unsafe for domestic use, The maximum chromium contamination values found in area indicating that the ground water is becoming alarmingly contaminated.is 1.41-1.48 mg/l(Shankar, 2009). The compilations of different areas of chromium pollution across India and the concentration therein is noted in Table 5.

State/Teritary	Area	Source of samples	Max. (mg/L)	Reference
Andhra Pradesh	Medak	Ground and surface water, effluent	0.07	(Krishna et al., 2009)
Himachal	Solan	Drinking water	1.07	(Singh and Sharma, 2020)
Jammu&Kashmir	Udhampur	Groundwater	0.14	(Kumar et al., 2018)
Maharashtra	Thane	Groundwater, soil	0.03	(Bhagure and Mirgane, 2011)
Orissa	Jajpur	Near mines residential area	2.48	(Naz et al., 2016)
Punjab	Ropar, Bathinda	Pumps, Tube wells	0.25	(Kumar et al., 2021; Sharma et al., 2019)
Tamil Nadu	Ranipet	Surface water	1.31	(Srinivasa Gowd and Govil, 2008)
UttarPradesh	Kanpur	Groundwater	33.8	(Singh et al., 2012)
Uttarakhand	Nainital	Water pumps, wells, and springs	0.01	(Jain et al., 2010)

Table 5: Concentration of Chromium(Cr) in Indian states.

In Indian perspective such pollution hampers a bigger population and its dire need to attend such aspect of importance with due care. We have to learn from the past wherein one such example is the chromium pollution by Pacific Gas and Electric Company (PG&E) that poses us to rethink on the chromium pollution and impact it can make it to the wider population. Based on our research and literature evaluation, the objective of this review is to investigate the existing bio-adsorbents for removing chromium from wastewater and their potential applications. Despite multiple techniques available for the removal and remediation, resourceful removal through ecofriendly solution remain at the heart of the solution. adsorbents stands out as a effective and novel solution that will cater the existing problem and provide the environment friendly option. Such technologies has to be scaled up and taken to the industrial level but the first part is the understand the effectiveness and the feasibility of adsorbents. The current review will provide the holistic picture on the applicability of adsorbents for the removal of chromium and the gaps where the scientific community can contribute.

III. SCOPE OF REVIEW

Despite the fact that various adsorbents have been tested and used for the removal of Cr(VI) from wastewater, there is a need to compile and analyze the available options for Cr(VI) contamination remediation to guide researchers for future work in this domain. This article addresses the need by highlighting the various chromium removal techniques and materials investigated by researchers. The review focuses on the bio-adsorption and development of various adsorbents, the material's performance, and its reusability to determine its applicability and economic viability. In this review, all significant work done by researchers on the removal of hexavalent chromium Cr(VI) from wastewater has been addressed.

IV. CHROMIUM REMOVAL TECHNIQUES

Many approaches to elimination of chromium such as chemical precipitation(Hintermeyer et al., 2008), Ion exchange(Tiravanti et al., 1997), Electro-coagulation (Ayub et al., 2020; Thirugnanasambandham and Shine, 2018), Reverse Osmosis(Membrane) Technique(Ranganathan and Kabadgi, 2011), foam flotation(Shojaei and Khoshdast, 2018), Electrolysis(Chaudhary et al., 2003), and Electrochemical(Lakshmipathiraj et al., 2008; Li et al., 2018). These approaches have been identified, but there are limitations such as being expensive, taking considerable intake of chemicals, sludge formation and requiring incomplete elimination. Adsorption is suitable and efficient mechanism that utilized for treating toxic Chromium ions from wastewater (**Figure 2**). Since it allows for design flexibility, quality treated effluent, reversible mechanism, and the reusability of adsorbent, the adsorption approach is emerging as a promising alternative techniques for the decontamination of heavy metals(Fu and Wang, 2011). Bio-adsorption also promotes green technologies through various chemical transformations, oxidation-precipitation, and oxidation-reduction reactions(Jiang et al., 2020).Adsorption is the greatest method for removing chromium from wastewater out of all the other options. The approach has many distinguishing characteristics, including being very successful, eco-friendly, requiring minimal chemicals, and having the simplest design. The reusability of adsorbent material, low operating costs, better selectivity for specific metals of interest, extraction of heavy metals from effluent regardless of toxicity, quick operation time, and no creation of potentially harmful sludge as a secondary pollutant are all advantages of bio-adsorption technology(Acharya et al., 2018).

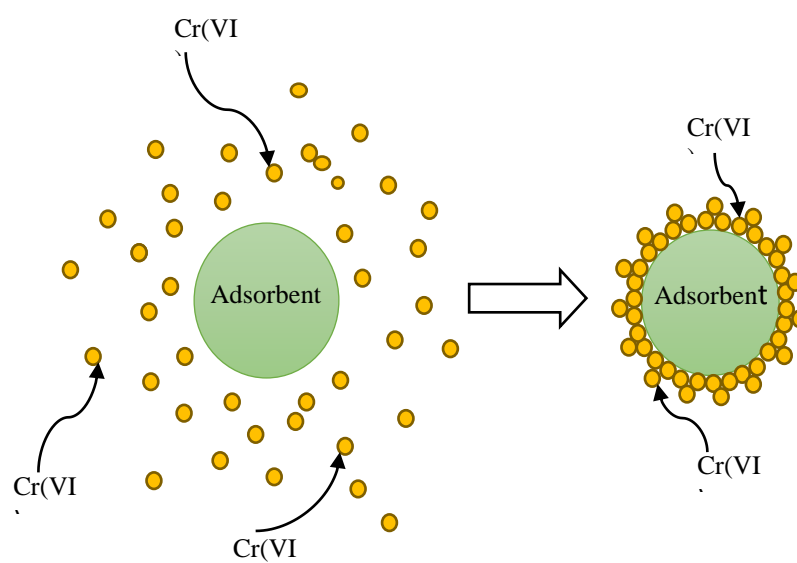


Fig. 2 : Adsorption Mechanism

Among all the methods, adsorption is best suited and inexpensive which can be utilized to decontamination of Chromium from wastewater. There are numbers of adsorbents used for chromium removal some of them are produced commercially or naturally occur or agricultural waste materials. Commercial adsorbents are those that are manufactured on a big scale for a profit, such as activated carbon, silica gel, alumina, and other expensive materials. Natural adsorbents are inexpensive and can be extracted from organic material. However, in the elimination of Chromium Ion from wastewater, cost analysis is a crucial consideration for selecting an adsorbent. The price of the adsorbent determines the overall cost of the process. According to data activated carbon is approximately 400-500 Rs/kg, whereas the price of bio adsorbent materials is 4.4–36.89 Rs/kg, which is significantly less than the traditional adsorbent (Gupta and Babu, 2008). Although, regeneration of adsorbent is also an important factor in the significance of the process implementation, The efficacy of adsorbent is determined by its regeneration following metal desorption (Gupta et al., 2000).

V. OVERVIEW OF CHROMIUM ADSORBENT

In the recent decade, a wide variety of materials are tested, and reported by researchers for Chromium removal from wastewater that are traditional or adsorbent. Here is discussed in detail some highlights adsorbent utilized for the Chromium removal from wastewater and water remediation.

VI. ADSORBENTS FOR THE ADSORPTION OF CHROMIUM

Wide research relating to the adsorption process for chromium reduction has been reported in the literature. The adsorption onto activated aluminum (Rajurkar et al., 2011), H₂SO₄ treated activated carbon (Hintermeyer and Tavani, 2017), Silica (Sivakumar, 2015), Iron Oxide/Mesoporous Silica Nanocomposites (Egodawatte et al., 2015), Aluminum oxide hydroxide (Bedemo et al., 2016), Iron oxide magnetic nanoparticle (Shahriari et al., 2014), PEI-silica nanocomposite (Choi et al., 2018), Polyacrylonitrile-based porous carbon (Feng et al., 2018), Carboxymethyl cellulose modified Fe⁰ composite (Yu et al., 2020), Nanoscale zero-valent metal (Li et al., 2016), Calcium alginate as biopolymer (Pandey et al., 2007), Surface Modified Nanozeolite (Tashauoei et al., 2010), Zeolite/Chitosan Hybrid Composite (Meiling Pang et al., 2015), Amino-functionalized nano-Fe₃O₄ magnetic polymers (H. Shen et al., 2012), Multi-walled CNTs (Kumar Krishna et al., 2015), functionalized and non-functionalized CNTs (Mubarak et al., 2014), Cross linked hydrazide-based polymers (Dautoo et al., 2017), Different natural Nanoporous Materials (Maheshwari and Gupta, 2015), and Carboxymethyl cellulose-stabilized Fe⁰ nanoparticles (Wang et al., 2010). Nano Technology is an emerging field of science which also utilized in adsorption of heavy metals. Nanomaterials are efficient for recovery of the chromium ions from aqueous phase due to their large surface area, stability, mesoporous structure, and affinity towards metal ions (Gopalakrishnan et al., 2015). Magnetics nano oxides and zero-valent iron nanoparticles are widely utilized for

chromium removal from wastewater (X. L. Chen et al., 2019; Hua et al., 2012).

VII. GRAPHENE BASED MAGNETIC ADSORBENTS

Many researchers have developed composite to enhance the performance of adsorbent including, amino functionalized magnetic graphene composite materials (Guo et al., 2014). In comparison to magnetic adsorbents (Fe@Fe₂O₃ core-shell nanowire) FCSNs reported adsorption capacity 7.78 mg/g (Ai et al., 2008), functionalized graphene with Fe(III) oxide (Fe₃O₄) composite had a greater adsorption capacity of 17.29 mg/g (Guo et al., 2014). Magnetic MnFe₂O₄ nanoparticles coated with chitosan composite was prepared and utilized for the hexavalent chromium removal at the concentration 0.6-1 mg/L shows removal capacity of 35.2 mg/g (Xiao et al., 2013). Magnetite-PEI-MMT composite demonstrated for Cr(VI) treatment shown adsorption capacity of 8.8 mg/g (Larrazza et al., 2012). For the decontamination of Cr(VI) from wastewater, Iron (Fe⁰) nanoparticles (NPs) have proven to be extremely effective at removing Cr(VI) contaminants from the wastewater. From a dilute solution of 10 mg of Cr, 100 % Cr(VI) was converted to Cr(III) using CMC as a stabilizer for nZVI (Wang et al., 2010). The production of iron(III)-Chromium(III) hydroxide on nanoparticles surface is the main drawback of utilizing nZVI. Another disadvantage of employing nZVI particles is that they are difficult to remove from treated water. nZVI was also synthesized on a magnetic Fe₃O₄/graphene nanocomposite to address both of the stated disadvantages, and it showed an 83.8% Cr(VI) removal effectiveness (Lv et al., 2014). Graphene Oxide composite studied for the reduction of Cr(VI) to Cr(III) and reported that acid-induced reaction takes place as a result of Graphene Oxide-Nickel Ferrite Composite, a metallic catalyst (Bhowmik et al., 2014). Ferrite-based graphene nanocomposite synthesized and reported for the removal of Chromium (IV) ions, exhibited adsorption capacity of 68.85 mg/g. Study revealed that removal of Cr(VI) ions was favorable at higher acidic pH, and decreased with the increase in pH. The desorption study revealed the stability of adsorbent up to five cycles (Santhosh et al., 2017). The reduction of Cr(VI) from aqueous solution studied on graphene oxide synthesized from graphite and isotherm results revealed the adsorption capacity of 1.22 mg/g. The highest removal (92.8%) was found to be accomplished at an acidic pH-4. The regeneration study of graphene oxide adsorbent revealed 56.20% desorption after one cycle (Mondal and Chakraborty, 2020). Cr(VI) adsorption was discovered to be a spontaneous, endothermic, and entropy-driven process using thermodynamics (Mondal and Chakraborty, 2020; Santhosh et al., 2017). Magnetic nano Fe⁰ based composite demonstrated for the decontamination of Cr(VI) from leachate and simulated water. In this study, a 1-5 percent bentonite-supported Fe⁰NPs composite of bentonite was prepared, and batch experiments with the selected BFe⁰NPs for simulated and leachate wastewater were performed. The Cr(VI) reduction was reported greater than 90% at pH-2 for both wastewaters and decreased significantly as the pH value increased. Within the first 10 minutes, the Cr(VI) removal reaction was quite fast, and

reached at 85 % for both the wastewaters (Wang et al., 2018). A styrene-based ion exchange resin D201 is used as a carrier to load nZVI particles and removal of chromium from simulated Cr(VI) water demonstrated, reported

excellent adsorption capacity of 123.10 mg/g for the 50mg/L Cr(VI) with 100% removal efficiency. The electrostatic attraction helps Cr(VI) to reduce to Cr(III) and form $Cr_xFe_{1-x}(OH)_3$ co-precipitation (Gao et al., 2020).

Adsorbent's	Initial Conc. (mg/L)	pH	Dose (g/L)	Contact time (min)	Adsorption Capacity (mg/g)	Removal Percentage	Reference
Graphene Oxide-Nickel ferrite Composite	1000	4	0.1- 2.5	120	45	-	(Lingamdinne et al., 2016)
Nanoscale Fe ⁰ (nZVI) assembled on Fe ₃ O ₄ /graphene	40-100	3	-	120	101	83.80	(Lv et al., 2014)
Diethylaminoethyl methacrylate onto graphene oxide	-	1.1	-	45	82.4	93.0	(Ma et al., 2016)
Nanoscale zerovalent Fe supported on graphene nanosheet	15-35	3	1	90	-	70.0	(Li et al., 2016)
Graphene oxide	2.6-104	5	0.25	-	92.65	>90	(Yang et al., 2014)
Graphene oxide from graphite	80	4	0.01	60	1.22	92.80	(Mondal and Chakraborty, 2020)
Graphene sand composite	20	1.5	10	90	2859	93.0	(Dubey et al., 2015)
Modified graphene with cetyltrimethylammonium bromid	50, 100	2	400	60	21.57	98.2	(Wu et al., 2013)
Graphene modified with Acrylonitriledivinylbenzene	30	2	0.6	420	101.2	80	(Duranoğlu et al., 2010)

Table 6: Chromium remediation using graphene and their modified composite

VIII. CARBON NANOTUBES BASED ADSORBENTS

Carbon nanotubes also utilized for the wastewater treatment process. Because of their chemical stability, surface area, and well-organized mesopores adsorption capabilities, carbon nanotubes are also good option for heavy metal rejection (Gupta et al., 2011; Mubarak et al., 2014). Composite Magnetic Iron oxide with multiwall carbon nanotube obtained removal of 88% at pH-6. The advantage of this work is that the contamination removal controlled by using magnetic process. The study also

revealed that Cr adsorption on composites is substantially influenced by contact time, agitation speed, and pH (Gupta et al., 2011). Chemical, thermal, and biological treatment of adsorbent can improve adsorption capability to a larger extent. Thermal treatment by microwave heating to create carbon nanotubes for the analysis of chromium(III) removal evaluated the greatest removal was 24.45mg/g with a 95.5% efficiency at pH-8 (Mubarak et al., 2016). Other studies on CNT based adsorbents are enlisted in Table 7.

Adsorbent's	Initial Conc. (mg/L)	pH	Dose (g/L)	Contact time (min)	Adsorption Capacity (mg/g)	Removal Percentage	Reference
Modified and nonmodified MW-carbon nanotubes	1	7	150	120	0.5	18.0	(Tawabini et al., 2010)
CNTs-activated alumina composite	100	2	2.5	240	264.5	>95.0	(Sankaramakrishnan et al., 2014)
Magnetic CNTs doped by Nitrogen	12.82	8	0.2	720	638.56	>97.0	(Shin et al., 2011)
CNTs supported by activated carbon	0.50	2	40	60	9	72.0	(Ali Atieh, 2011)
Multi wall CNTs-iron oxide composite	20	6	0.1-2	10,60	-	88.0	(Gupta et al., 2011)
CNTs functionized using HNO ₃ acid and KMnO ₄	1	9	0.1	120	2.48	87.60	(Mubarak et al., 2014)
CNTs produced using microwave heating	2	8	9	60	24.45	95.0	(Mubarak et al., 2016)

Table 7: Chromium remediation using CNTs and their modified composite

IX. BIO-MATERIAL BASED ADSORBENTS

According to the data of the investigations, it appears that extracting Chromium ions using low-cost adsorbents material is becoming increasingly advantageous, especially in the long run (Bhattacharya et al., 2008). In recent years, some modifications and treatments have been done on natural raw materials in order to improve their efficiency, thus increasing the adsorption capacity or the selectivity (Dakiky et al., 2002; Khalil et al., 2021). Because

of its porous nature and large internal surface area, activated carbon is also a reliable chromium adsorbent (Anirudhan and Sreekumari, 2011). It can be made from a variety of agricultural wastes. This is due to the fact that some materials are readily available, i.e., they exist naturally or can be found in agricultural and wastes, and they can be utilized as low-cost adsorbent materials. Various biological waste material and vermiculite utilized to remove the Crions from tannery effluent (Sumathi et al., 2005). Studies shows that the natural wastes are highly effective Cr(VI)

adsorbent. According to previous studies, there is a growing interest in studying alternative materials that can be used as low-cost adsorbents (Mohan and Pittman, 2006). These include Orange Peel activated by K_2CO_3 (TOMUL et al., 2017), Iron nanoparticles embedded orange peel pith (López-Téllez et al., 2011), lignin (N. Chen et al., 2019; Lalvani et al., 2000), sugarcane bagasse bio-polymeric beads (Kumar et al., 2020), silica gel/Polyaniline composite (Karthik and Meenakshi, 2014), Coconut husk (Tan et al., 1993), Modified walnut shells (Altun and Pehlivan, 2012), Walnut, hazelnut, and almond shell (Pehlivan and Altun, 2008), Groundnut shell (Bayuo et al., 2019), Wheat bran (Kaya et al., 2014), Natural and calcined rice husks (Sugashini and Begum, 2015), Acid activated rice husk and potato peel (Vunain et al., 2021), Rice bran (Singh et al., 2009), Tamarind wood (Acharya et al., 2009), Rice husk (Ghosh et al., 2018), activated carbon (Mohan and Pittman, 2006), Coconut shell carbon (Babel and Kurniawan, 2004), Walnut shell activated carbon (Nethaji and Sivasamy, 2014), Activated carbon from waste bamboo (Dula et al., 2014), Hazelnut Shell Activated Carbon (Kobya, 2004a), Marine green macroalga *Ulva fasciata* (Shobier et al., 2020), Marine bacteria (Vijayaraj et al., 2020), Bacterium MNU16 (Upadhyay et al., 2017), Succinic acid treated sugarcane bagasse (Garg et al., 2009), Immobilized fungal cells (Bai and Abraham, 2003), Eggshell (Abatan et al., 2020), Biochars (Y. S. Shen et al., 2012), Magnetic biochar derived from bagasse (Liang et al., 2020), Sawdust from rubber trees (Karthikeyan et al., 2005; Ma et al., 2020), Hazelnut carbon (Kobya, 2004b), Coconut sawdust (Selvi et al., 2001), Fe(III)-impregnated Sugarcane bagasse (Zhu et al., 2012), and Formaldehyde treated rosewood sawdust (Garg et al., 2004). The utilization of low-cost adsorbents such as waste materials is attractive because it also helps to reduce waste disposal expenses. Moso and Ma bamboo-derived activated carbon achieved nearly 100% and 91.7% removal effectiveness for the Cu^{2+} , Cd^{2+} , and Cr^{3+} heavy metals, after single and twice adsorption activation, respectively (Lo et al., 2012). An effluent sample with a Chromium concentration of 184.8 mg/L was run through columns with various adsorbent mediums, with adsorbents and vermiculite being determined to be the most effective at removing hexavalent Chromium. The blend of vermiculite and coir pith results in a significant reduction in total Chromium concentration (184.8–4.48 mg/L) (Mani Tripathi and Chaurasia, 2020). Alkaline KOH activated carbon synthesized from the waste of Bamboo (*Oxytenanthera abyssinica*) and tested for the hexavalent chromium removal from aqueous solution reported 98.28% of adsorption efficiency and 59.23 mg/g capacity at pH-2 (Dula et al., 2014). Sugarcane bagasse was activated with zinc chloride to produce microporous nano carbon. MNSAC had a sorption capacity of 277.78 mg/g as determined by the Langmuir isotherm model. The regeneration of the used adsorbent studied, and the maximum removal of Cr(VI) ion was around 93.60%, 82.40%, and 64.10% reported in the consequent three cycles (El Nemr et al., 2021). Maize straw biochar-supported nanoscale iron (Fe^0) (MSB-nZVI) composite prepared to demonstrate the remediation of Cr (VI) decontamination from soil (saline-alkali, pH 8.6–9.0, Cr 341 mg/kg). The Cr

(VI) removal reported was 70.7 mg/kg at pH 2.5 with the 99% efficiency, and the pH variation study reveals 0.6–1.7 mg/kg Cr (VI) removal at pH ranges 4.0–8.0 and indicates that the saline-alkali environment inhibited the Cr (VI) remediation efficiency. Kinetics study determined pseudo-second-order model reveals that the remediation of Cr (VI) is controlled by the chemical process, adsorption, reduction, and coprecipitation (Wang et al., 2019). An adsorbent derived from mango and jackfruit seeds used to demonstrate Cr(VI) removal capacity over the pH range from 5 to 11 for simulated water reported an equilibrium capacity of 5.2 and 2.23 mg/g with 94 to 92% efficiency, respectively (Giri et al., 2021). The Eucalyptus bark/maghemite composite of *Eucalyptus camaldulensis* was investigated for the removal of Cr(VI) from an aqueous solution and 0.1 g adsorbent found efficient to remove 70 mg/g at pH-2 and 30 °C. Furthermore, ECMC reported 99 and 93.46% removal efficiency from 10 and 50 mg/L solution, respectively (Erkurt et al., 2018). β -cyclodextrin chitosan modified biochar composite was observed (206 mg/g) at pH-2 (Huang et al., 2016). MgO-coated biochar composite was prepared from sugarcane by treating it with diluted H_2SO_4 and at 550 °C and reported 54.64, and 62.89 mg/g capacity for both the adsorbent, it also found that the acid activated MgO-composite still had good regeneration ability and maintained a high Cr(VI) removal efficiency (>57%) even after four-time regeneration (Xiao et al., 2018). The adsorption of Cr(VI) onto the Polypyrrole/calcium rectorite clay was observed pH-dependent, and the removal efficiency of Polypyrrole/Ca-REC composite reported was much higher than Polypyrrole homo-polymer. The Langmuir isotherm data were fitted well and reported 714.30–833.34 mg/g at 25–45 °C (Xu et al., 2019). The batch adsorption method was used to evaluate Cr(III) removal from aqueous phase solutions. Adsorption capacity of orange peel activated with potassium carbonate was higher than that of both original orange peels and activated with phosphoric acid adsorbents, adsorption tests have revealed that more than 80% of the Cr(III) ions are eliminated (TOMUL et al., 2017). A one-step mild hydrothermal approach used to generate waste peanut hull-derived nitrogen-doped spherical carbons (WPHSC). The resulting carbon spheres have adsorption removal efficiencies of over 99.5 % for 100 mg/L Cr(VI), with residual concentrations of less than 0.5 mg/L. WPHSC has an adsorption capacity of 181.82 mg/g at its highest. This comprehensive study broadens the range of renewable raw materials that can be utilized to make carbon spheres, which have a great potentiality in the treatment of Cr(VI) wastewater (Jiahao and Weiquan, 2020). The kinetic and equilibrium behavior of eggshell as an adsorbent for Cr(VI) ion recovery from wastewater has shown that when the dose of adsorbent was changed from 5 to 25 g for every 100 mg/L of solution at pH-6, the adsorption of Cr(VI) improved from 44.80 to 60.96% (Abatan et al., 2020). Modified clinoptilolite zeolites were used as adsorbents to remove chromium from an aqueous solution. Using clinoptilolite/MgO, the removal of Cr(VI) was 81.07 % reported. Furthermore, when compared to the Langmuir isotherm, the experimental data is well suited to the Freundlich isotherm model. The desorption results reveals that regeneration may be accomplished by utilizing

0.35MNaCl(Rahimi and Mahmoudi, 2020).The pyrolysis procedure was followed to the preparation of nanoporous activated carbon from wasted coffee using potassium hydroxide (KOH). The diffusion–chemisorption model was shown to be the best suited kinetic model. This experiment resulted maximum capacity of 109mg/g at pH-3 for Cr(VI) concentration 54.5ppm solution(Asimakopoulos et al., 2020).A simple hydrothermal approach was used to produce the PEI functionalized magnetic montmorillonite clay (MMT-Fe₃O₄-PEI), Cr(VI) had the highest adsorption capacity of 62.89mg/g(Fayazi and Ghanbarian, 2020).Tobacco petiole biochar prepared by pyrolysis at different temperatures and demonstrated for remove Cr(VI) and achieved results shows that TPBC300 efficiently remove 66.7% of Cr(VI) and 21.10% total Chromium from electroplating wastewater (Zhang et al., 2018).Magnetic Biochar prepared from different biomass using iron salt steel pickling waste reported that out of all four biomass sugarcane derived biochar shows Cr(VI) reduction capacity of 43.12mg/g at 30 °C (Yi et al., 2019).Corn straw biochar derived at various temperature and then modified with UV irradiation and demonstrated to study the Cr(VI) removal ability. Adsorption study results shows that the UV-modification exhibited excellent Cr(VI) removal ability 20.04 mg/g as compare to biochar 1.11mg/g (Peng et al., 2018).Magnetic biochar functionalized with Fe₂O₃ and Fe₃O₄ followed by pyrolysis of bagasse prepared from bagasse to study the chromium removal behavior and mechanics, results achieved shows the max. capacity was 29.08 mg/g at 25 °Cwith 99.9% of efficiency for the 0.012g/L dose of adsorbent which was higher than other biochar (Liang et al., 2020). Chromium(VI) elimination from wastewater was achieved with 99% effectiveness using zinc chloride activated Tamarind wood(Acharya et al., 2009). Nutshell treated with zinc chloride and activated carbon revealed 99.08% efficacy, adsorption capacity 43.45 mg/g for chromium(VI) detoxification at pH-2(Kumar and Jena, 2017a).Another experiment done with H₃PO₄ activated nutshell activated carbon to investigate Cr(VI) adsorption at a starting concentration of 35 mg/L at pH-2.0, maximum adsorption of 74.95mg/g was observed(Kumar and Jena, 2017b).

Rice husk organic wastes could be good substitute for chromium metal adsorbent. It has metal affinity due to its functional group, and distinct physiochemical and biological properties, making it ideal for activated carbon. This material has a surface morphology,chemically stable, and high strength(Alam et al., 2020).Silica from rice husk ash had been extracted by the sol–gel technique(Adam et al., 2006). when chromium removal was demonstrated using raw rice husk silica and modified iron incorporated silica obtained from rice husk, modified silica showed significantly greater adsorption (63.69mg/g)(Oladoja et al., 2013).Rice husk was studied in both its native and modified forms (activated rice husk carbon by ozone) to investigate chromium adsorption and compare the findings, with the Ozone treated rice husk reporting much better capacity than the raw material(Bishnoi et al., 2004). Modified rice husk to produce activated carbon by treating it with ozone reported removal of Chromium removal capacity about 86%(Sugashini and Begum, 2015).Rice husk can also be

pyrolysis to produce biochar, a carbon-rich substance that can be utilized as a Chromium adsorbent due to its absorption capabilities. Pyrolysis-modified rice husk had a 95 percent Chromium(VI) removal capability(Agrafioti et al., 2014).Since coconut contains hydroxyl and carboxyl functional groups, coconut waste utilizing as an adsorbent for the decontamination of heavy metals. It could be good option for the adsorbents generation.Studies found that raw coconut coir pith was able to remove roughly 94 percent of chromium with a capability of 1.204mg/g(Sumathi et al., 2005).modified coconut adsorbents were more efficient than raw adsorbents, In this study, they used hexadecyltrimethylammonium bromide surfactantto modify coconut coir pith to improve efficiency, and reported threshold Crcapacity 76.3 mg/g at optimal pH-2(Namasivayam and Sureshkumar, 2008). This shows that the adsorption ability of the raw bio adsorbent was much increased. It is estimated that using coconut coir pith and created biochar resulted in a 70% increase in Chromium removal(Y. S. Shen et al., 2012).Calcium Chloride activated Coconut shell (0.5-10nm size spherical Dia.) powdered adsorbent synthesized and utilized to study the chromium (VI) adsorption at pH range from 1 to 10. This study reported higher removal efficiency 99.2% at pH-2 and 30 °C (Bal and Bhasarkar, 2021).As an adsorbent, wheat bran was also used. It's inexpensive, biodegradable, and made out of organic functional groups and has a surface area of 441m²/g that can able to capture heavy metal ions(Singh et al., 2009). Adsorptive removal on wheat bran reported 89%, with a capacity of 93 mg/g(Farajzadeh and Monji, 2004). Different acids treatments utilized to improve the removal capability of wheat bran(Al-khalidi et al., 2015).

X. MARINE BASED ADSORBENTS

Some others biological materials also tested for the demonstrated chromium removal or reduction from wastewater such as Alga, Bacterial cell, dead cell, and their derived adsorbent, which are showing good affinity to reduce the noxious chromium contamination from aqueous solution.Marine derived materials also a good source of adsorbent due to its low cost, eco-friendliness, and promising adsorbent quality. The raw alga *Ulva fasciata* was shown high removal efficiency of Cr(VI) ions from its aqueous solutions.The ability of a marine green macroalga (*Ulva fasciata*) derived adsorbent investigated and utilized to remove Cr(VI) from solutions of 10 and 20 mg/L, this study evaluates that the Cr(VI) was fully eliminated from the solutions after only 5 minutes of contact at pH-1 (Shobier et al., 2020). Microalgal adsorbentsprepared by after chemical, and thermal treatment, and studied for the Cr(VI) decontamination at various varying contions. Bio-sorption studyevaluatethat pyrolyzed microalga are more efficient, and shows100% of Cr(VI) removal. In column studied variation in dose from 0.125 to 0.20 g increase the efficiency 52.33 to 57.58%. Kinetics studies shows the monolayer adsorption with 23.98,25.19, and 24.27 mg/g capacities at temp. of 5,22, and 35 °C, respectively. Regeneration study reveals that 59.41% of Cr(VI) desorbed efficiently by using 0.1M NaOH and more than 97% of Cr(VI) was recoveredin the form of precipitated Barium Chromate within10 minby using BaCl₂ as a desorption

elluent (Daneshvar et al., 2019). This study reveals that the non living materials possess higher ability of Cr(VI) recovery than the raw living cells material. Magnetic biochar composite loaded with $\gamma\text{-Fe}_2\text{O}_3$ prepared from marine alga *Enteromorpha prolifera*, and studied for the removal of Cr(VI) which suited the Langmuir model of 88.17 mg/L and a removal efficiency reported 97.71%, for 100 mg/L of Cr(VI) (Chen et al., 2018). The ability of immobilized microalgae *Chlorella* with calcium alginate investigated to remove Cr ions from electroplating wastewater reported Cr(VI) 24.78 mg/L and Cr(III) 0.91 mg/L, and highest

efficiency of 50.28 percent at pH-3, with the cell density 1.54×10^6 cells/bead within 48hr (Elystia et al., 2020). Based on the findings of the published study, it can be inferred that isolated siderophore-producing marine bacteria are also capable of effectively lowering heavy metals pollutant loads from tannery wastewater. Microremediation is also a superior approach for chromium removal from tannery wastewater (Vijayaraj et al., 2020). The results for chromium remediation using bio-waste and their modified composite are compiled in **Table 8**.

Adsorbent's	Initial Conc. (mg/L)	pH	Dose (g/L)	Contact time (min)	Adsorption Capacity (mg/g)	Removal Percentage	Reference
Succini acid modified sugar cane bagasse	50.0	2	20	60	-	92.0	(Garg et al., 2009)
MgO-sugarcane composite	100	2	0.5	-	62.89	>74.0	(Xiao et al., 2018)
Activated sugarcane-bagasse by ZnCl ₂	77.50	8.5	6.85	60	-	>87.0	(Cronje et al., 2011)
Alkaline KOH activated Bamboo	100	2	10	120	59.23	98.28	(Dula et al., 2014)
Mango Kernel activated with H ₃ PO ₄	20-100	2	-	150	7.8	-	(Rai et al., 2016)
Maize straw Biochar supported Fe ⁰ composite	100	2.5	4	2880	-	>99	(Wang et al., 2019)
Tamarind	10	6.5	2	40	28.08	>89.0	(Acharya et al., 2009)
Iron incorporate rice hus- silica	50-300	2	2	120	63.69	71	(Oladoja et al., 2013)
Carbonized rice husk by ozone activation	50, 100	2	4	150	8.7-13.1	86	(Sugashini and Begum, 2015)
Impregnated rice husk with calcium and Iron	850	6.8	16	5760	-	95	(Agrafioti et al., 2014)
Coconut coir pith, HDTMA-Br Modified	20	2	6	90	76.3	96	(Namasivayam and Sureshkumar, 2008)
Coir pith and derived coconuts char	10-500	3	1	7200	70.4	70	(Y. S. Shen et al., 2012)
Calcium chloride treated Coconut shell	100-1000	2	20	120	16.39	99.2	(Bal and Bhasarkar, 2021)
Wheat bran	20	5	20	80	93	89.0	(Farajzadeh and Monji, 2004)
Sulphuric acid treated wheat bran	50, 100	1.5	2	300	133	99.90	(Özer and Özer, 2004)
Tartaric acid activated Wheat bran	52	2, 2.2	20	1440	5.28	90	(Kaya et al., 2014)
Green macroalga (<i>Ulva lactuca</i>)	5-50, 5-250	1	2	40	-	98	(El-Sikaily et al., 2007)
Sugarcane bagasse with Acinetobacter haemolyticus bacteria	10- 100	7	-	2880	-	>90	(Ahmad et al., 2013)
Prawn Shell	25-125	-	-	31.4	100	98	(Arulkumar et al., 2012)
Green Alga (<i>Ulva fasciata</i>)	10-200	1-9	0.05-0.25	60	2.9	99.4	(Shobier et al., 2020)
<i>Pterocladia capillacea</i> and its activated carbon (Marine red Alga)	5- 100	1	-	120	66	100	(El Nembr et al., 2015)

Table 8: Chromium remediation using various bio-adsorbents and their modified composite

All studies indicate that the natural wastes are highly efficient for Cr(VI) adsorbents that can be employed to reduce chromium concentrations in contaminated water (Mani Tripathi and Chaurasia, 2020). The efficiency of adsorbents can improve after the further modification by physical or chemical activation of natural waste materials.

XI. FACTOR AFFECTING THE ADSORPTION

Several factors can influence the adsorption and desorption efficiency of wastewater adsorbents. Concentration, Dosage, pH, contact time, and temperature. According to research data, The proportion of heavy metals removed depends on concentration, adsorbent dose, time, and the temperature (Sahu et al., 2009). The batch experiment

at room temperature an initial concentration 2ppm at pH 4.8carried out, the data shows that the adsorption is time dependent process, increasing in time will increases adsorption, initially 70% adsorption efficiency reveals within 30-40mins, which further increased and reached at94% and 92% in 120mins for the mango and jack fruit derived adsorbent, respectively (Giri et al., 2021).Adsorbent dose is one of the most significant factor for the chromium adsorption. The increase in dose increase the available surface area of the adsorbent to the adsorbate. The effect of dosesvariation of polypyrrole/ca-rec composite (0.25-2g) was investigated and data shows that Cr(VI) removal efficiency increased from 66.67% to 99.99% when the doses increases from0.25 g/L to 1g/L adsorbent, respectively(Xu et al., 2019). The adsorption study of Cr(VI) on Tamarind wood activated carbon studied and the effect of dose, initial

concentration, and time on Cr(VI) on % removal efficiency shows similar trends the adsorption capacities of Cr(VI) increased from 47 to 89%, at 20mg/L initial feed concentration when the adsorbent doses increases from 1 to 5 g/L at30 °C and pH 6.5. On the other hand, The percentage removal decreases with increase in initial Cr(VI) concentrationfrom 10 to 50mg/L. There was a decrease of 61 to 27%, 82 to 49%, and 88 to 63% adsorption efficiency of Cr(VI) for the doses 1, 2, and 3g/L adsorbent. respectively, at 30 °C and pH-6.5 (Acharya et al., 2009).Several research articles discussed on the removal efficiency of adsorbents and their effecting factorin their studies for various adsorbents Table 9summerizedsome factor that affecting the removal efficiency of biomaterial based adsorbent by various authors.

Factor	Observation	References
pH	pH influence on the adsorption depends on adsorbate properties. It improve the adsorption efficiency of positively charged metals but then decreases that of negatively charge metals or acidic dyes.	(Ahmed et al., 2019; Aranda-García and Cristiani-Urbina, 2019; Rajurkar et al., 2011)
Adsorbent particle size	Small particles sizes favarable and responsible for the increases biosorption because of the availability of higher surface area of the biosorbent. However, not suilable for the column adsorption due to its low mechanical strength and column clogging.	(Ahmed et al., 2019; Aranda-García and Cristiani-Urbina, 2019; Rajurkar et al., 2011)
Dosage	Reduction in the amount of pollutants absorbed per unit mass of adsorbent and then increases its percentage removal observed	(Rajurkar et al., 2011; Xu et al., 2019)
Contact Time	Metal removal efficiency increases until equilibrium reaches as contact time increases.	(Kar and Equeenuddin, 2019; Rajurkar et al., 2011)
Agitation	Adsoption rate increases by the fact that the agitation speed reduce its mass transfer resistance. However, the physical structure of adsorbent could be affected.	(Kumar and Jena, 2017b; Rajurkar et al., 2011)
Initial Concentration	It increases the amount of pollutants absorbed per mass of adsorbent but decreases the percentage removal.	(Acharya et al., 2009; Rajurkar et al., 2011)
Temperature	It increase the adsorption rate of pollutants by rising the surface activity and adsorbate kinetic energy, However,Itcould destroye physical structure of adsorbent.	(Kar and Equeenuddin, 2019; Rajurkar et al., 2011)
Impurities	If coexisting pollutant competes with targeted contaminat for binding sites or forms any complex with it, a higher amount of other toxins will decreses.	(Sdiri et al., 2012)

Table 9: Factor affecting the performance and removal efficiency of adsorbents

XII. REGENERATION AND RECOVERY OF ADSORBENT

One of the most significant issues is the reusability of the utilized adsorbent and the recovery of Chromium(VI). Metal-loaded adsorbents are harmful, and the utilized adsorbent will cause secondary contamination. It should be released into the environment once the metal has been fully recovered. For regeneration and reuse of bio adsorbents, many studies have utilized various regenerating agents such as acid, alkalis, and chelating agents.However, Only a few studies have been conducted on recovering wasted adsorbent and adsorbate before actual disposal. In nature, bio adsorbents are biodegradable materials. After being used as an adsorbent, it can be used to make bio-fertilizer for agricultural purposes. After a simple treatment with regenerating agent chemicals solution, it can be reused. Some material shows good regeneration and reusability after first usethis includes bio materials and their composite adsorbent.Desorption studies for the polysulfone-biomass

composite revealed that the biomass beads could be reactivated and reused more than 25 times, with a regeneration efficiency of 75–78% (Bai and Abraham, 2003). Cr (VI) was desorbed from metal-loaded chitosan without causing any physical harm to the adsorbent by using 0.1M H₂SO₄(Bhuvaneshwari et al., 2012). Sugarcane residue derived MgO-activated composite still showed good regeneration ability and maintained a high Cr(VI) removal efficiency (>57%) even after four-time regeneration (Xiao et al., 2018). The Polypyrrole/Ca-rectorite composite was reactivated and reused for up to three consecutive cycles without losing its original removal efficiency. The desorption of Cr(VI)-loaded composite was investigated using a 1M NaOH solution and sonicating for 1.5 hours, after which the solutions were filtered, and this is followed by adding the adsorbent to a 2M HCl solution and sonicating for 1.5 hours, after which the adsorbent was separated and dried. In first cycle lower desorption efficiency reported and 4.93% of Cr(VI) was extracted from

composite this is due to the reduction of adsorbed Cr(VI) to Cr(III) by electron-rich polymeric moieties after that desorption were 16.89,18.99% in second and third cycles, respectively. The removal efficiency of adsorbent for the chromium remains unchanged with more than 85% in the first three cycles(Xu et al., 2019).Groundnut husk powder reported 76.10% desorption of Cr(VI) by using 0.1M HCl and H₂SO₄ elutions. Although, desorption efficiency reduces by 20% after the consequent three cycle(Bayuo et al., 2020).Microporous sugarcane ZnCl₂activated carbon composite regeneration was studied using 0.1 M NaOH followed by 1M HCl and then hot distilled water washing and the maximum removal of Cr(VI) ion was 93.60%, 82.40%, and 64.10% recorded in the consequent three cycle(El Nemr et al., 2021). Different eluents tested on agro-waste adsorbent materials for regeneration were studied that remove chromium (III) from aqueous solution and reported that EDTA is a better and more efficient agent for desorbing

Cr (III) from agro-waste materials(Bernardo et al., 2009).In adsorbents regeneration process BaCl₂ also good agent for the desorption of Cr from aqueous phase using barium chloride Cr (VI) ions react with BaCl₂ and form yellow colored Barium chromate solid precipitates that can be more valuable industrial applications(Mikhaylov et al., 2018).

Reusability of used adsorbent not only helps to select the best suitable inexpensive techniques, but also reusability of adsorbent materials helps to manage the environment pollution. Untreated adsorbent causes secondary pollutant to environment. Here is some techniques which utilized to regenerate the adsorbent as well as to recover the valuable chromium metal from the adsorbent for the further industrial utilization. **Table 10** highlights the reported usage of various regeneration agents for biomaterial based adsorbent regeneration by various authors.

Adsorbent's	Conc./Removal efficiency	Agents used	RE%	Observations	Reference
Immobilized fungal biomass (Rhizopus nigricans)-Polysulfone beads	101.5mg/g, 500mg/l	0.01N NaOH, NaHCO ₃ and Na ₂ CO ₃	78.0%	Effective recovery of bound Cr(VI) ions from biomass-polysulfone beads can be regenerated and reused upto 25 times	(Bai and Abraham, 2003)
Maghemite Nanoparticles	97.3% at initial 50mg/l	0.01M NaOH	87.70%	Sodium hydroxide solution found most effective.	(Hu et al., 2005)
Nonviable cyanobacterium Nostoc muscorum biomass	22.92mg/g, at 25°C pH- 3	0.1M HNO ₃ and EDTA	90.0%	Desorption and recovery without affecting the binding sites.	(Gupta and Rastogi, 2008)
Polypyrrole composite	100% 100mg/l, pH- 1.5,	1M NaOH, 1M HCl	85.0%	Adsorbent regenerated upto three cycles,removal efficiency remains unchanged.	(Xu et al., 2019)
Agglomerates suspension of Fe(III) oxide/hydroxide nanoparticle	31.5mg/g,	NaOH and BaCl ₂	95.0%	BaCl ₂ precipitated the Cr as BaCrO ₄ Both Cr(VI) and regenerating agent were recovered for reuse.	(Zelmanov and Semiat, 2011)
Chitosan	6ppm, 99.25%	0.1H ₂ SO ₄ , 0.1M EDTA	99.0%	Without affecting removal efficiency of regenerated adsorbent. No physical damage of adsorbent.	(Bhuvaneshwari et al., 2012, 2011)
Groundnut powder	25mg/L	0.1M HCl and 0.1M H ₂ SO ₄ acid	76.0%	Cr(VI) adsorbed on the adsorbent surface recorded about 76.10 and 56%, respectively. Regenerated upto 5 cycles, efficiency reduction recorded by 20% after third cycle.	(Bayuo et al., 2020)
Iron Impregnated Sugar bagasse composite	50mg/L, 99.9% at pH-2	0.2M of NaOH, NaHCO ₃ ,and 0.2M HCl, and H ₃ PO ₄	80%	NaOH reported higher desorption Upto three cycles, regenerated adsorbent lost only 19.74 % of adsorption capacity.	(Liang et al., 2020)
Aniline formaldehyde condensate coated silica gel	200mg/l, 17mg/g	0.5N NaOH 0.5N NH ₄ OH	56.62%	40–84% of chromium was recovered from adsorbent	(Kumar et al., 2007)
PEI-Magnetic Composite	83mg/g, pH- 2,at 15 °C	0.02MNaOH	91.%	Regerated upto six cycles without losing much adsorption capacity	(Pang et al., 2011)
Porous graphene - CoFe ₂ O ₄ magnetic nanoparticles	2.5-100mg/L at 25 °C	NaOH	75– 80%	Metal-loaded composite agitated with 10 mL of 0.1M NaOH at 80 rpm for 3 h at 25 °C. Regeneration cycle was carried out upto five cycles.	(Santhosh et al., 2017)
Coffee Waste	70mg/g	Alkali	94.0%	Metal recovery considered using by recycling the adsorbent	(Kyzas, 2012)

Table 10: Chromium(VI) adsorbents reusability/regeneration techniques

XIII. PERSPECTIVE AND OPPORTUNITIES

The bio adsorbents introduced in this review which is utilized to demonstrate the Cr(VI) removal are low-cost, widely accessible agricultural waste adsorbents that could be a good substitute for commercially available adsorbents. Adsorbent removal effectiveness for metal extraction from wastewater has been observed to improve subsequent modification in various studies. However, relatively limited research has been done in this area. As a result, our long-term goals are to improve the removal efficiency of bio adsorbents through chemical modification, adsorbent regeneration, metal ion recovery, and commercial application of these bio adsorbents. The difficulty in removing heavy metals by adsorption is that it may require a considerable volume of adsorbent and additional reagents to regulate the pH to get the necessary adsorption results. Reusability, disposal, and final use of adsorbent are the main concern of adsorption process.

XIV. CONCLUSION

This research provides an in-depth analysis of the potential use of readily available agricultural waste for the elimination of chromium and other heavy metal contaminants from wastewater. Various researchers have studied a wide range of adsorbents to determine their maximum adsorption capabilities and regeneration techniques. Several studies indicate that alkali are efficient desorbing agents for chemically modified bio adsorbent and acids are efficient for desorbing bio adsorbent, EDTA is also highly efficient chelating agent for biomass desorption. However, only few studies are available on adsorption and desorption mechanism of adsorbent for Cr(VI). Adsorption is a cost-effective way for future perspective for Chromium heavy metal removal technique. The literature review shows that chromium can be absorbed/decontaminated by using bacteria, fungi, algae, plants, agricultural, and industrial wastes as an adsorbent. It's difficult to get a consensus on the optimal biomass for chromium biosorption because of the many and varied experimental circumstances, as well as the influence of many environmental elements. It is also indicated that the adsorption method has countless advantages for decontamination of chromium ions from wastewater. It is the cleanest water treatment technique. Nevertheless, further studies should be carried out to improve the adsorbents' applicability, regeneration, optimization and commercialization of suitable agricultural materials. Based on the study of various publications, this review evaluates that the use of biomass and their derived adsorbent are efficient and could be a promising way for an environment-friendly and economically feasible clean-up strategy for safer disposal of tannery wastewater.

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DECLARATIONS

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 - **Rajesh vanshpati-** Drafting the original draft manuscript, data collection. PG student (Environment and Management) in Chemical Engineering .
 - **Dr. J.K. Shrivastava-** Conceptualization, Writing-review and editing. Principal (UEC) and Professor in Department of Chemical Engineering, Ujjain Engineering College, Ujjain (M.P)-456006 (INDIA).
 - **Rakhi Baghel-** Review and editing. M.Tech- Chemical Engineering (Environment and Management).

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