

Removal of Cr(VI) from aqueous solution using Madhuca Longifolia as plant-based Biosorbent

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Abstract : This study investigates the efficacy of Madhuca lonifolia(mahua) extract as a sustainable, eco-friendly biosorbent for the remediation of highly toxic Hexavalent Chromium [Cr(VI)] from contaminated aqueous solutions. Spectroscopic characterization of the extract revealed the presence of alpha-amyrin acetate and vitamin C, which provide them electron-rich functional groups essential for the remediation process. Experiments evaluating the effect of initial Cr(VI) concentrations demonstrated a nearly quantitative removal efficiency (>90%) at lower concentrations (10-20 ppm), which are typical of industrial wastewater. While the percentage of removal slightly declined at higher concentrations (50—100 ppm) due to the saturation of active reducing sites, the absolute adsorption capacity (mg/g) increased in accordance with the Langmuir adsorption model. The primary mechanism for removal was identified as a dual-step reduction-adsorption process: Cr(VI) is first reduced to the less toxic Cr(III) by the extract's ester and carbonyl groups, followed by the stable complexation and capping of Cr(III) ions with the oxidized organic products. UV-Vis spectroscopy successfully validated this mechanism by monitoring the distinct 225 nm Cr(VI) peak. Ultimately, this research establishes Madhuca lonifolia(mahua) extract as a highly effective, non-toxic, and viable botanical alternative to harsh chemical precipitation methods for the development of low-cost water filtration systems.

Keywords: Hexavalent Chromium Remediation, Madhuca lonifolia(mahua) Extract, Biosorption, Green Chemistry. UV-Vis Spectroscopy, Reduction-Adsorption, Water Filtration.

Chapter - 1 Introduction

1.1 INTRODUCTION

The rapid growth of the global population has significantly increased industrial activities, reducing the availability of clean water. Water is one of the most pressing environmental concerns, making obtaining safe and affordable clean water increasingly challenging. Heavy metal contamination in water is also a major concerns, arising from both natural and human activities. Both industrial processes and natural phenomena, such as weathering of metal rich rocks, forest fire, and volcanic eruptions.[1] In the contemporary era, the intersection of rapid industrial growth and environmental sustainability has become one of the most critical challenges facing global society. As nations strive for economic advancement through sectors such as metallurgy, textiles, and chemical manufacturing, the unintended consequence has been the systemic degradation of aquatic ecosystems. Among the various pollutants identified by environmental scientists, heavy metals

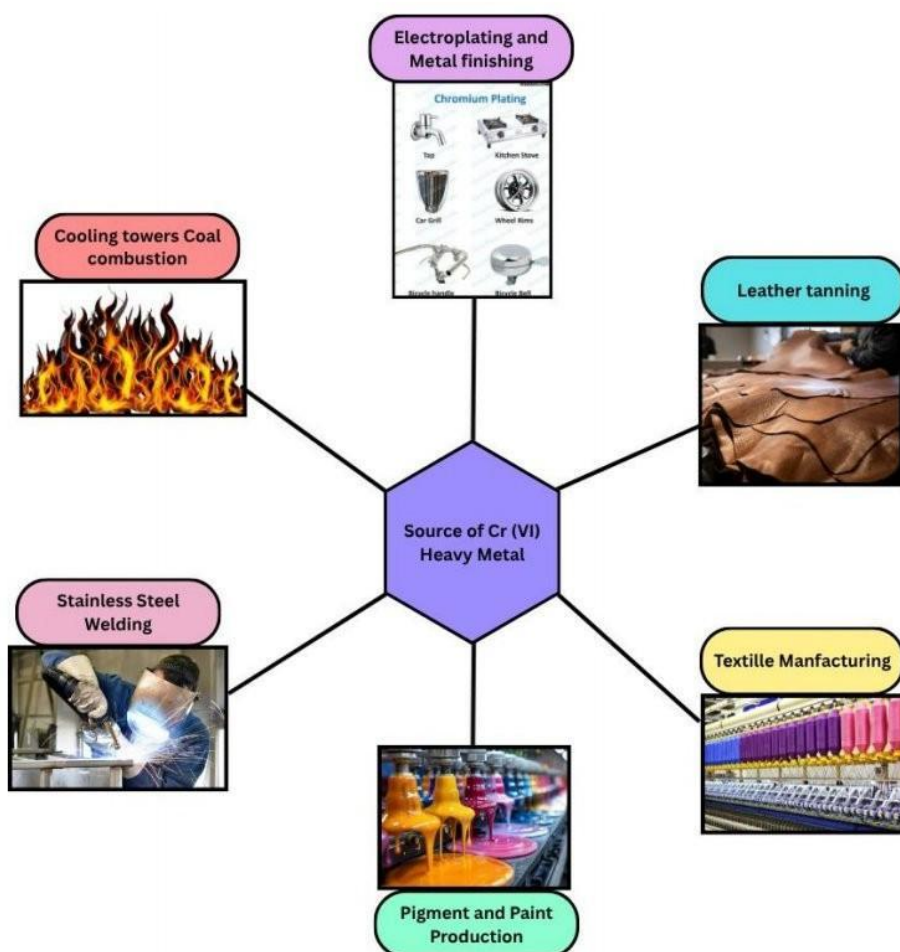


Fig 1. Source of Cr (VI) Heavy Metal [1]

represent a category of extreme concern due to their persistence, non-biodegradability, and profound toxicity even at trace concentrations. Unlike organic pollutants, which can be broken down by microbial degradation or chemical oxidation over time, heavy metals are elemental. They cannot be destroyed; they can only be transformed from one oxidation state to another or sequestered from the environment. This persistence leads to bioaccumulation the process by which toxins build up in the tissues of living organisms and biomagnification, where the concentration of the metal increases as it moves up the food chain, eventually reaching humans in lethal doses. Within this context, the removal of toxic metals from water bodies is not merely an engineering goal but a fundamental necessity for the preservation of public health and biological diversity.[23]

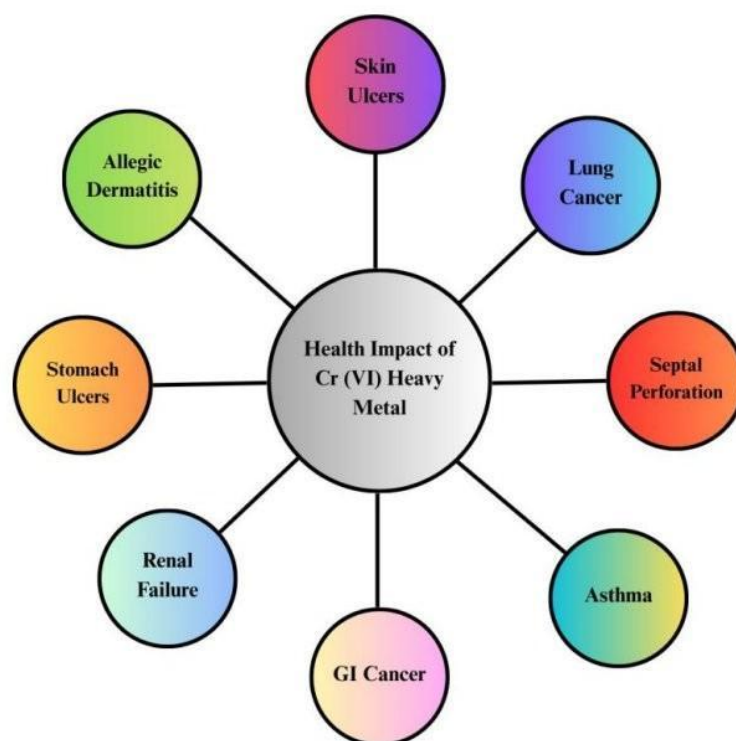


Fig. 2 Health impact of Cr (VI) heavy metal [1]

1.2. Chromium: A Dual-Faced Environmental Threat

Chromium (Cr) is a transition metal that serves as a quintessential example of how chemical speciation dictates environmental impact. In nature, chromium primarily exists in two stable oxidation states: Trivalent Chromium [Cr(III)] and Hexavalent Chromium [Cr(VI)]. The behavior, mobility, and toxicity of these two forms are starkly different.[23]

- **Trivalent Chromium [Cr(III)]:** Generally considered the less hazardous form. It is relatively immobile in soil and water and is even recognized as an essential micronutrient for human insulin function and glucose metabolism at very low levels.
- **Hexavalent Chromium [Cr(VI)]:** This form is the primary target of environmental remediation. Cr(VI) is highly soluble across a wide pH range, allowing it to leach easily into groundwater. It is a potent carcinogen, mutagen, and teratogen. Due to its structural similarity to essential sulfate and phosphate ions, Cr(VI) can easily cross biological membranes via non-specific ion channels. Once inside the cell, it undergoes intracellular reduction, releasing reactive oxygen species (ROS) that cause catastrophic DNA damage and organ failure.
- Industrially, hexavalent chromium is indispensable in leather tanning, electroplating, wood preservation, and pigment production. However, the discharge of untreated or poorly treated industrial effluent has led to concentrations in many water bodies that far exceed the World Health Organization (WHO) limit of 0.05 mg/L.[23]

Table 1 Comparison of Cr (III) VS Cr (VI) [23]

Property	Cr (III)	Cr (VI)
Types	Trivalent chromium	Hexavalent Chromium
Solubility in water	Low	High
Membrane permeability	Poor	Easily crosses cell membranes
Characteristics	Poorly absorbed	Highly soluble, easily absorbed
Redox activity	Stable, not a strong oxidizer	strong oxidizing agent
DNA/ protein interaction	Binds after intracellular reduction	Causes DNA damage via ROS and direct action
Biological role	Essential trace element	No known beneficial role
Toxicity	Low	High
Regulatory status	Supplement form (e.g. Cr picolinate)	Carcinogenic (IARC Group 1)

Table 2 Mechanisms of Cr (VI) toxicity [23]

Step	Description
Cellular uptake	Cr (VI) enters cells via non-specific anion channels (similar to sulphate and phosphate transport).
Intracellular reduction	Cr (VI) is stepwise reduced to Cr (V) and Cr (IV) and ultimately to Cr (III) within the cell, producing ROS during each reduction.
ROS generation	Hydroxyl radical are the result of the formation of superoxide (O_2^-) and H_2O_2 , which generate oxidative stress and DNA damage.
Cr (III) binding	Cr (III) binds covalently to DNA, Ribonucleic acid (RNA), and protein, leading to mutations, DNA cross-linking, and impaired cellular function.
Genotoxicity and carcinogenicity	DNA strand breaks, chromosomal aberrations, and interference with DNA repair enzymes may lead to mutagenesis and cancer.
Inflammation and apoptosis	Cr(VI) can activate NF- κ B and p-53 pathways, resulting in apoptosis, inflammatory response, and cytotoxicity.

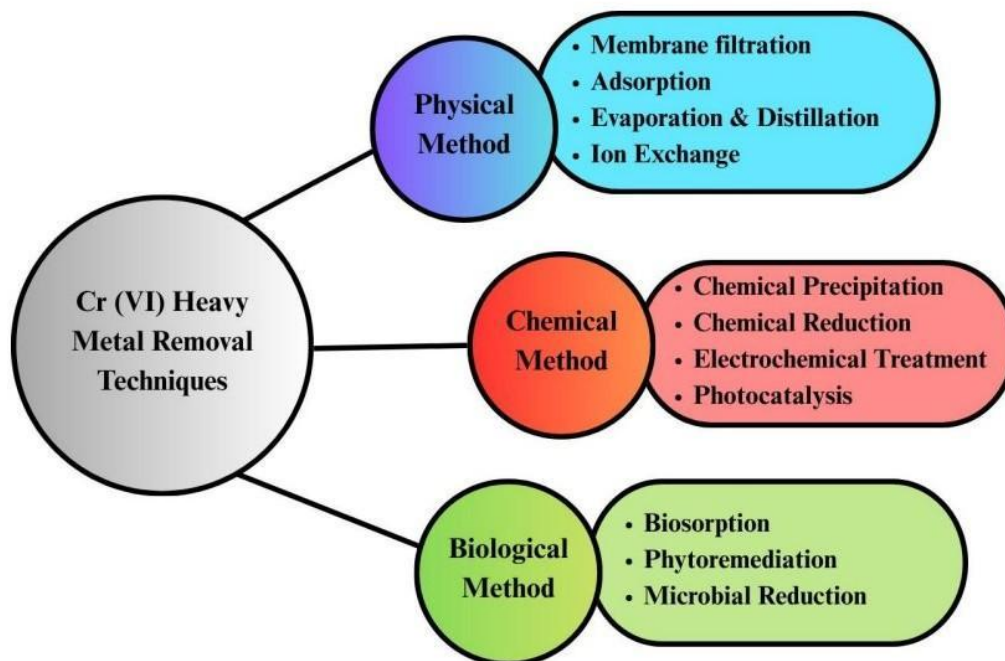


Fig. 3 Cr (VI) heavy metal removal techniques [1]

Table 3 : Mechanism of Cr (VI) removal by plant based biosorbents [23]

Mechanism	Description	Typical functional group	Cr species
Adsorption	Cr (VI) ions physically bind to the surface of biosorbents	-OH, -COOH, lignin, cellulose	Cr (VI)
Ion exchange	Exchange of native ions (e.g. H ⁺ , Na ⁺) on the biosorbent surface with Cr (VI) species	-COOH, -OH	Cr (VI)
Electrostatic attraction	Attraction of negatively charged Cr (VI) species to positively charged biosorbents surfaces	Protonated -NH ₂ , -OH groups	Cr (VI)
Reduction (Cr(VI)-Cr(III))	Cr (VI) is reduced to Cr (III) by electron-donating groups (phenolic), often followed by Cr (III) binding.	Phenols, tannins, flavonoids	Cr (VI)
Chelation/complexation	Formation of Coordinate bonds between Cr ions and ligand present in the biosorbent	-COOH, -NH ₂ , -OH	Cr (III)
Surface complexation	Covalent-like interaction of Cr (VI) with reactive surface sites	Modified -OH, -COOH	Cr (VI)
Micro precipitation	Formation of insoluble Cr (III) species (e.g., Cr(OH) ₃ at or near the biosorbent surface	Local pH increase	Cr (III)
Hydrogen bonding	Stabilising secondary interactions between Cr species and biosorbent functional group	-OH, -NH	Cr (VI)
Physical entrapment	Cr (VI) ions get trapped in the porous structure of the biosorbent	Porous structure	Cr (VI)

Chapter - 2 Review Literature

1. Abimbola Oluwatayo Orisawayi, et al., (2026)

This review evaluates the effectiveness of sodium alginate, cellulose, and *Moringa oleifera* composites in removing heavy metals like Cr (VI) from contaminated water. A comparative analysis reveals that Cr(VI) adsorption capacity by different bio based composite of *Moringa Oleifera* like Amino - functionalized sodium alginate aerogel, carboxymethyl cellulose/alginate acid hydrogels, carbonized composite manganese cross linked sodium alginate and alginate/reduced graphene double- network hydrogel beads respectively 678.67 mg/g, >750 mg/g, 104.50 mg/g and 72.5 mg/g. [1]

Mechanism of Cr(VI) removal :

- 1. Ion Exchange:** Carboxyl groups in alginate and hydroxyl groups in cellulose facilitate the exchange of ions with metal cations.
- 2. Surface Complexation:** Metal ions bind to the surface of the adsorbent through the formation of complexes with active functional groups such as hydroxyl, carboxyl, and phenolic moieties.
- 3. Electrostatic Attraction:** The negative charge of certain biopolymer surfaces attracts positively charged metal ions.
- 4. Redox Transformations:** Some composites, particularly those containing metal oxides or nanoscale zero-valent iron (nZVI), can reduce toxic chromium species to less toxic or immobilized forms.
- 5. Coagulation/Flocculation:** *M. oleifera* seeds contain bioactive cationic proteins that act as natural coagulants, binding and aggregating dissolved metal ions. [1]

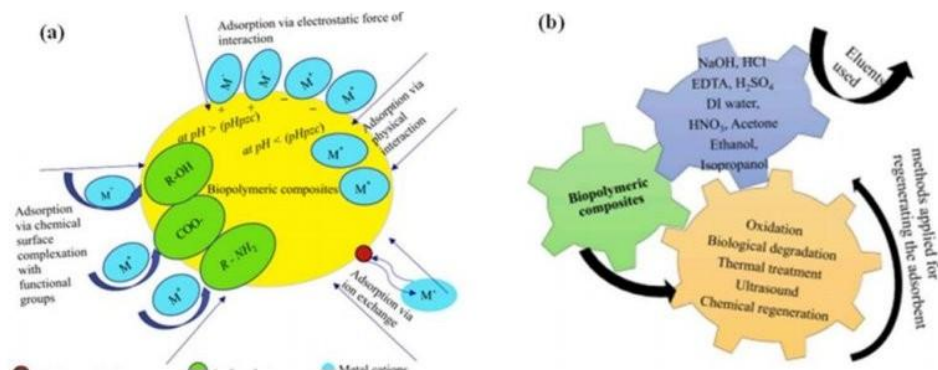


Fig. 4 (a) Proposed adsorption mechanism of biopolymeric composites for heavy metal removal, and (b) regeneration methods and chemicals used for biopolymeric composites during the adsorption-desorption process (adapted with permission, Licensed under Elsevier's terms). [1]

2. Juturu, R., et al., (2025)

The study focuses on developing a sustainable, magnetic adsorbent that can be easily recovered from water. By modifying *Acacia falcata* biomass with orthophosphoric acid (OPA) and embedding it with magnetite nanoparticles, the researchers created a material with a high surface area (472.98 m²/g) and excellent magnetic responsiveness. The adsorbent demonstrated high efficiency and reusability, maintaining strong performance over five regeneration cycles.[2]

Table 4 Experimental parameters and result [2]

Parameter	Experimental Condition / Result
Initial Concentration Cr(VI)	10 ppm - 100 ppm
Adsorption Capacity	114.09 mg/g at 303 K.
pH Condition	pH: 2.0. Removal efficiency 85.45% at pH 2, dropping to 20.31% at pH 12
Temperature	293 - 323 K.
Reaction Time	5 - 180 minutes.
Adsorbent Dosage	0.1 to 0.5 g/L.

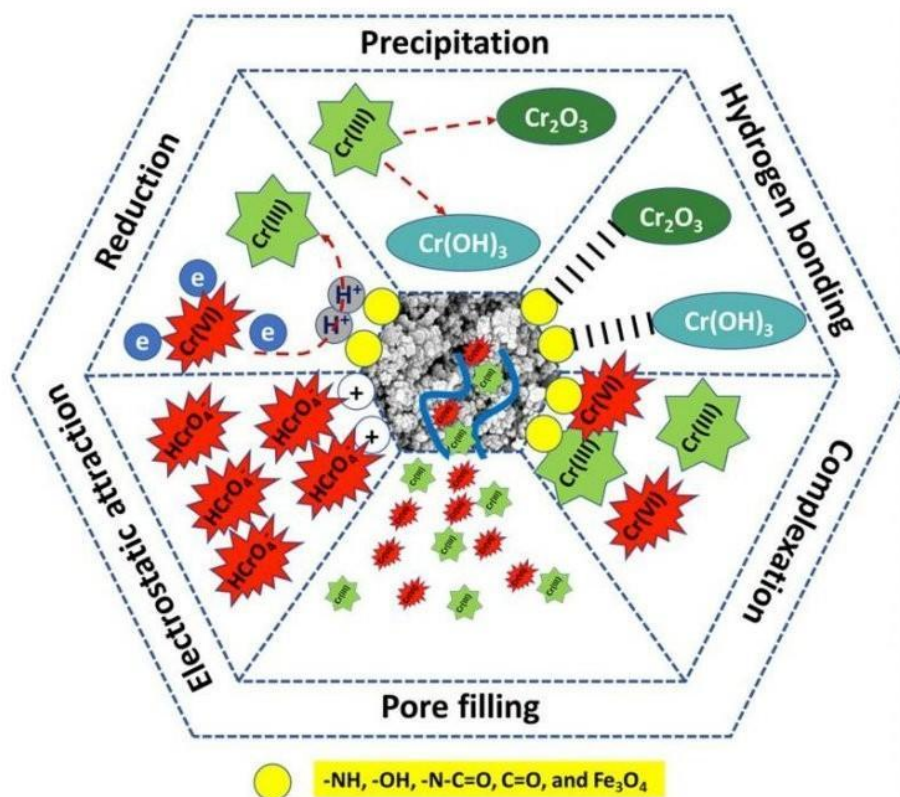


Fig. 5 Cr (VI) removal technique [2]

Mechanism of Chromium Removal: The removal of Cr(VI) by Af-MAC involves a multi-step chemical and physical process.

- **Electrostatic Attraction:** At low pH (pH 2), the surface of the Af-MAC becomes protonated (positively charged) because the solution pH is below the material's zero-point charge (pH{ZPC} = 6.96). This creates a strong attraction to anionic chromium species like HCrO_4^- .
- **Adsorption-Reduction:** Surface functional groups (such as hydroxyl, carboxyl, and phosphorus-containing groups) facilitate the reduction of toxic Cr(VI) to the less toxic Cr(III). XPS analysis confirmed that approximately 37% of the adsorbed chromium on the surface was Cr(III).
- **Surface Complexation:** The resulting Cr(III) ions form complexes with the oxygenated functional groups on the carbon surface or are precipitated as chromium oxides/hydroxides within the porous structure.
- **Pore Filling:** The high porosity and mesoporous structure (3.01 nm pore diameter) of the material allow for the physical entrapment of chromium ions. [2]

3. Atiang', S. et al., (2025)

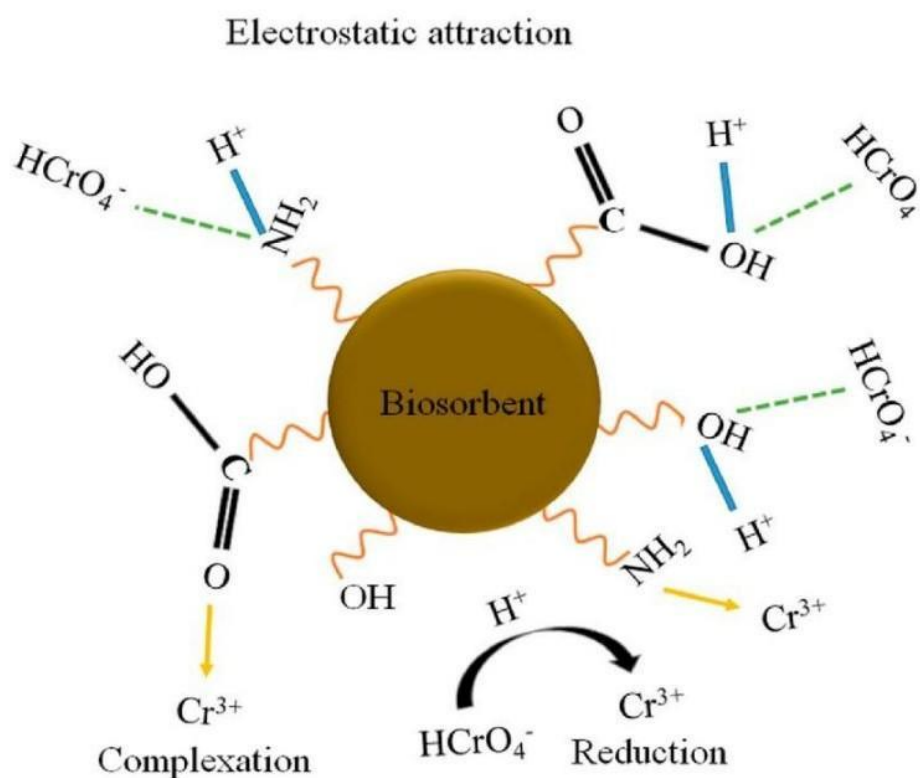
The paper evaluates various strategies for decontaminating wood waste and the surrounding environmental matrices (water and soil). It highlights that while wood incineration or landfilling were common past practices, they lead to the release of toxic elements into the air and groundwater. The review advocates for a combination of **chemical extraction** (using organic/inorganic acids or chelating agents) and **bioremediation/phytoremediation** as more sustainable, circular-economy-friendly approaches to recover metals and clean the environment. This review focuses on the "valorization" of agricultural and natural waste - such as fruit peels, shells, and leaves-converting them into effective adsorbents for hexavalent chromium Cr(VI). The study highlights that natural adsorbents are superior to synthetic ones due to their biodegradability, abundance, and the presence of diverse surface functional groups (carboxylic, hydroxyl, and amino groups) that naturally have a high affinity for heavy metals. The paper emphasizes the shift toward "Green Chemistry" to replace expensive and energy-intensive treatment methods like ion exchange and membrane filtration. [3]

Table 5 Experimental parameters and result [3]

Parameter	Experimental Result
Initial Concentration	10 ppm -200 ppm
Max Adsorption Capacity	20 mg/g to 150 mg/g
Temperature	25 °C - 30 °C
pH	2-3
Reaction Time	120 - 180 minutes.

Mechanism of Cr(VI) Removal:

- **Acid Leaching & Solubilization:** In wood waste treatment, strong acids (H_2SO_4 , HNO_3) or organic acids (Citric, Oxalic) provide protons (H^+) that break the chemical bonds between the wood fibers and the chromium, moving the metal into a liquid phase for collection.
- **Adsorption-Reduction:** In water treatment, Cr (VI) is attracted to positively charged sites on



adsorbents (Electrostatic Attraction). It is then reduced to the less toxic and less mobile Cr (III) by electron-rich functional groups (like hydroxyl or carboxyl groups).

- **Phytoremediation/Biosorption:** Certain plants and microbes secrete organic acids and enzymes that chelate chromium, allowing it to be taken up by roots (phytoextraction) or bound to the cell walls of fungal biomass.[3]

4. Haron H., et.al., (2025)

This review focuses on the "valorization" of agricultural and natural waste such as fruit peels, shells, and leaves converting them into effective adsorbents for hexavalent chromium (Cr(VI)). The study highlights that natural adsorbents are superior to synthetic ones due to their biodegradability, abundance, and the presence of diverse surface functional groups (carboxylic, hydroxyl, and amino groups) that naturally have a high affinity for heavy metals. The paper emphasizes the shift toward "Green Chemistry" to replace expensive and energy-intensive treatment methods like ion exchange and membrane filtration. [4]

Table 6 Experimental parameters and result [4]

Parameter	Experimental Result
Initial Concentration	10 ppm -200 ppm
Adsorption Capacity	30 mg/g to 120 mg/g
Temperature	25 °C - 45°C
pH	1-3
Reaction Time	60 - 180 minutes.
Absorbent dosage	1 g/L - 5 g/L

Mechanism of Cr(VI) Removal: The removal of Cr(VI) using natural adsorbents is a complex process involving simultaneous physical and chemical interactions.

- **Electrostatic Attraction:** At low pH, the adsorbent surface is saturated with H⁺ ions (positively charged). This creates a strong attraction for the anionic chromium species (HCrO₄⁻ or Cr₂O₇²⁻) dominant in wastewater.
- **Adsorption-Coupled Reduction:** This is the primary chemical pathway. The Cr(VI) ions bound to the surface are reduced to the less toxic **trivalent chromium (Cr(III))** by gaining electrons from the organic functional groups (lignin, cellulose, and tannins) in the natural biomass.

- **Surface Complexation/Chelation:** The newly formed Cr(III) cations are then immobilized through the formation of stable complexes with oxygen-containing functional groups (like carboxyl and hydroxyl) on the adsorbent surface. [4]

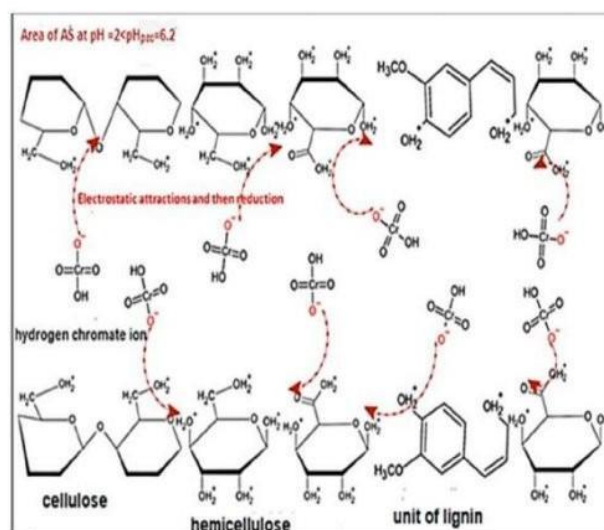


Fig. 7 Removal of Cr(VI) [4]

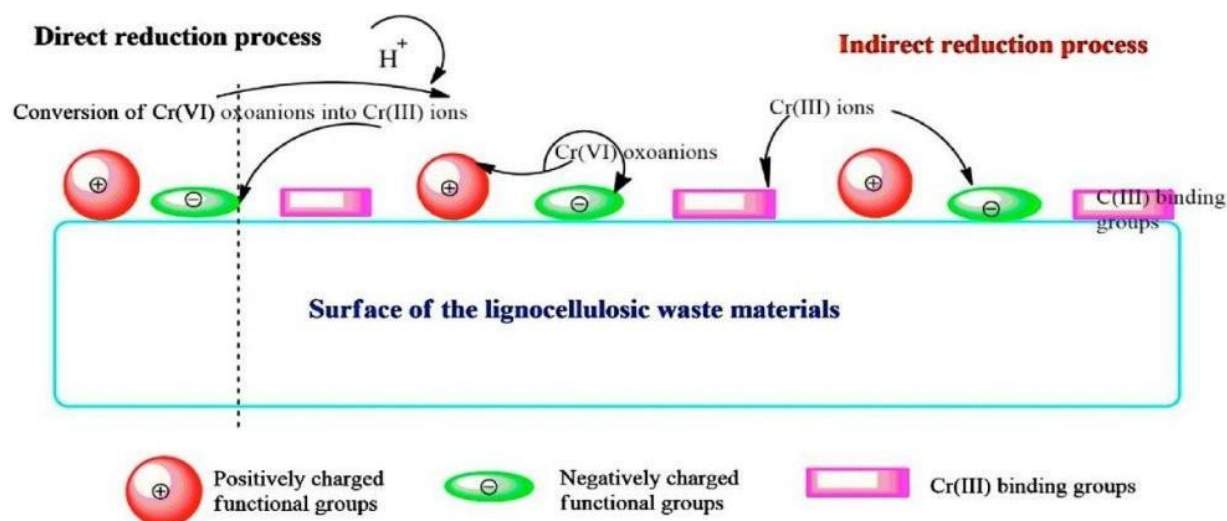


Fig.8 Removal of Cr(VI) by waste materials [4]

5. Metta,S. R. & Sahu, (2025)

The study focuses on the synthesis of a magnetic activated carbon (MAC) derived from the waste shells of **marigold flower straw**. The biomass was carbonized and impregnated with iron oxide to impart magnetic properties, allowing for easy separation from treated water using an external magnet. The research demonstrates that this biogenic magnetic carbon is a highly efficient, low-cost, and reusable adsorbent for the removal of toxic hexavalent chromium (Cr(VI)) from synthetic wastewater. [5]

Table Experimental parameters and result [5]

Parameter	Experimental Result
Initial Concentration	10 ppm -100 ppm
Max. Adsorption Capacity	53.19 mg/g 303 K
Temperature	303 K, 313 K, 323K
pH	2
Reaction Time	120 minutes.
Absorbent dosage	0.1 g/50ml
Order of Reaction	2 nd

Mechanism of Cr(VI) Removal: The removal of Cr(VI) by the marigold-derived magnetic activated carbon involves a synergistic mechanism.

I. Electrostatic Attraction: At the optimal **pH of 2.0**, the surface of the MAC is highly protonated (positively charged). This creates a strong electrostatic attraction for the negatively charged chromium species, primarily HCrO_4^- .

II. Reduction: The carbon framework and functional groups (such as hydroxyl and carbonyl) act as electron donors, reducing the toxic **Cr(VI)** to the less toxic **Cr(III)**.

III. Complexation: The newly formed Cr(III) cations are then immobilized on the surface through coordination with the oxygen-containing functional groups or by being trapped within the pores of the activated carbon.[5]

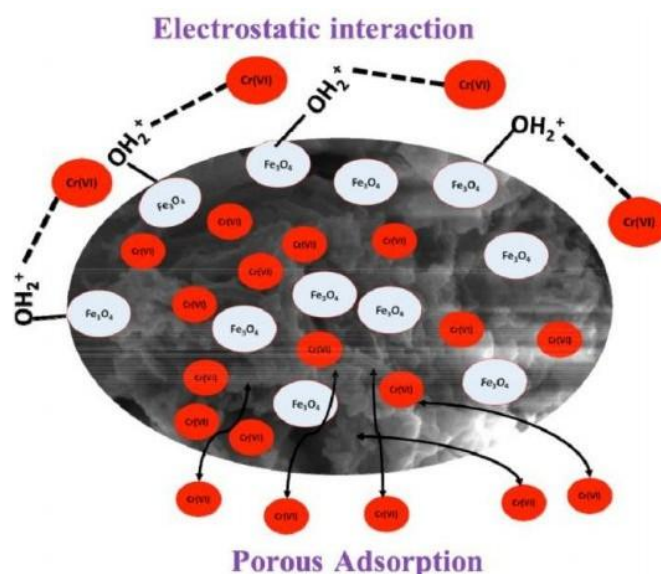


Fig. 9 Removal of Cr(VI) [5]

6. Xie, S. (2024)

The research highlights that industries like leather tanning and mining release non-biodegradable heavy metals that accumulate in the food chain. While conventional methods (e.g., ion exchange or membrane filtration) exist, they are often expensive and produce toxic secondary sludge. Biosorption utilizes **dead biomass** derived from plants, algae, fungi, or agricultural waste—to bind these metals through various functional groups on their surface. The review emphasizes that biosorption is cost-effective, efficient even at low metal concentrations, and eco-friendly.

Adsorption Capacity: Biosorbents like agricultural waste, rice husk, and citrus peels have a high binding affinity for heavy metals due to functional groups like carboxyl, hydroxyl, and amino groups. For example, sugarcane bagasse and rice straw show a zinc adsorption capacity of 0.12 mg/g at highly acidic condition of 60 minutes reaction time. [6]

Table Experimental parameters and result [6]

Biosorbent	Optimal pH	Adsorption Capacity (mg/g)	Contact Time (min)
Banana Peel Powder	2.5	30.5	60
Tea Waste	4	23.1	60
Rice Husk Ash	2	15.7	120
Moringa oleifera Pods	4	33.8	80
Coconut Shell (Activated)	2	48.3	90
Chlorella vulgaris (Algae)	2	45.6	90

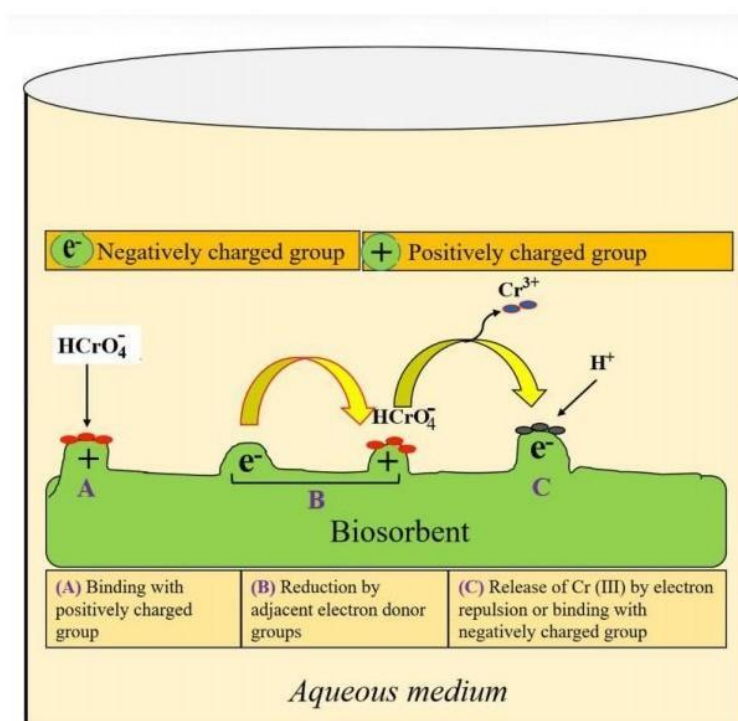


Fig. 10 Removal of Cr(VI) [6]

Mechanism of Cr(VI) Removal:

Electrostatic Binding: Negatively charged Cr(VI) ions (such as HCrO₄⁻) are initially attracted to and bind with **positively charged groups** on the surface of the biosorbent.

Reduction: The Cr(VI) ions are subsequently reduced to the less toxic **trivalent chromium Cr(III)** through electron transfer from functional groups on the biomass.

Complexation/Precipitation: The resulting Cr(III) ions may then be captured through surface complexation or ion exchange with other functional groups like carboxyl or hydroxyl. [6]

7. Pandey, K., Saharan, B. S., Kumar, R., Jabborova, D., & Duhan, J. S. (2024).

The paper highlights that hexavalent chromium [Cr(VI)] is a highly toxic and carcinogenic industrial byproduct from sectors like electroplating and leather tanning. While traditional physical and chemical methods (e.g., ion exchange, reverse osmosis) are effective, they are often expensive and produce secondary pollutants. The review advocates for **bioremediation** - specifically using bacteria, fungi, algae, and agricultural waste due to its high efficiency in diluted solutions and

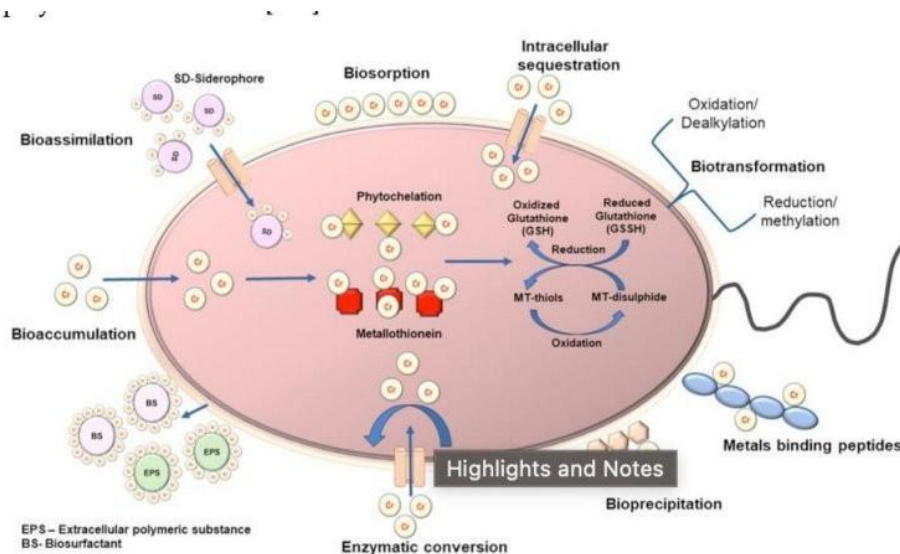


Fig.11 Reaction Mechanism of Cr(VI) Removal by bacterial remediation [7]

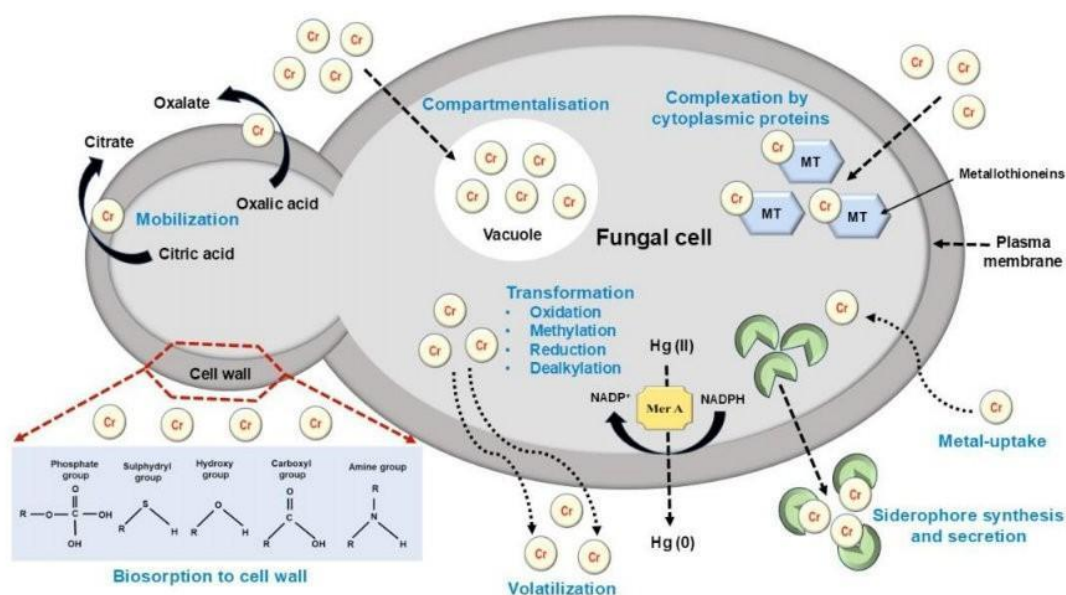


Fig.12 Reaction Mechanism of Cr(VI) Removal by Fungal Cell [7]

potential for metal recovery. Initial concentration is taken range of 2 ppm to 500 ppm and starting 2 hr. of reaction time 99% of chromium is removed and total reaction time is 72-96 hrs.[7]

Mechanism of Cr(VI) Removal :

- I. **Adsorption (Passive Binding):** Metal ions initially bind to the cell walls of the microorganisms. This is facilitated by functional groups such as **carboxyl, hydroxyl, amino, phosphate, and sulphonate groups**.
- II. **Bioreduction:** Once adsorbed, the highly toxic and water-soluble **Cr(VI)** is enzymatically reduced to the less toxic and less soluble **Cr(III)**. This reduction is often catalyzed by chromate reductase enzymes.
- III. **Intracellular Uptake & Complexation:** Some organisms utilize metal-binding proteins (e.g., **siderophores**) or release **extracellular polymeric substances (EPS)** to trap the metal ions and prevent them from harming the cell's internal environment.
- IV. **Translocation (in Plants):** In rhizoremediation, microbes help convert insoluble chromium into soluble forms that plants can then uptake and store in their tissues (phytoextraction) [7]

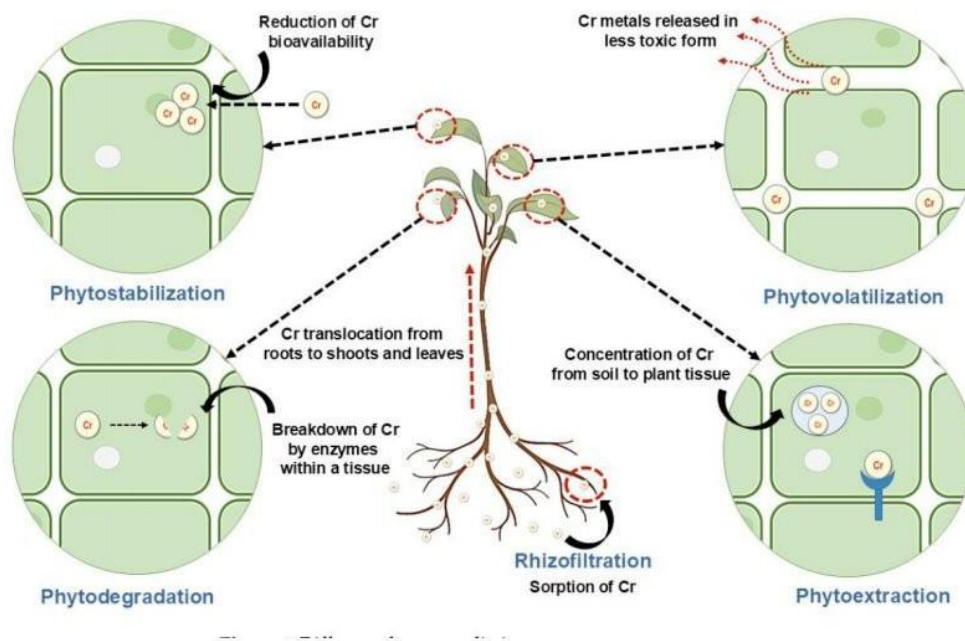


Fig.13 Reaction Mechanism of Cr(VI) Removal by Plant Cell [7]

8. Islam, M. M et.al., (2023)

The review provides a holistic overview of conventional and emerging technologies for chromium remediation. It discusses the chemical behavior of chromium, noting that Cr(VI) is highly soluble, mobile, and carcinogenic, whereas Cr(III) is less toxic and less mobile. The paper evaluates several removal methods, including chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, and especially **adsorption/biosorption**, which is highlighted as one of the most cost-effective and efficient techniques for large-scale application. [8]

Table: Experimental parameter and results of chromium removal [8]

Parameter	Experimental Result
Max. Adsorption Capacity	10%
Temperature	160 °C
pH	7-10
Reaction Time	120 minutes.
Order of Reaction	1 st

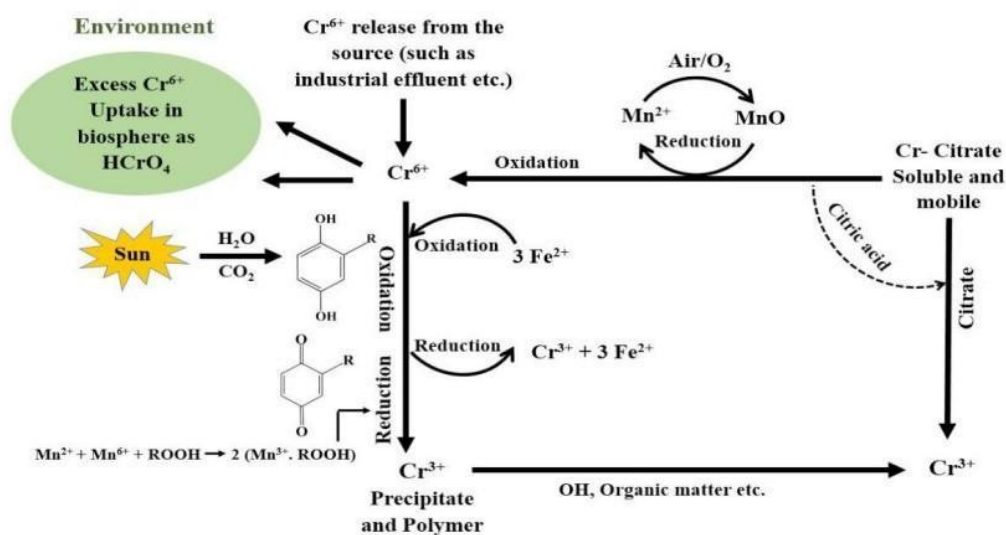


Fig.14 Reaction Mechanism of Cr(VI) Removal [8]

Mechanism:

1. **Electrostatic Attraction:** Under acidic conditions, the positively charged surface of the adsorbent attracts negatively charged Cr(VI) ions (HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$).
2. **Adsorption-Reduction:** This is the most critical step. Functional groups on the adsorbent surface (like hydroxyl, carboxyl, or amino groups) donate electrons to reduce Cr(VI) to Cr(III).
3. **Complexation/Chelation:** The resulting Cr(III) cations are then bound to the surface through coordination with functional groups or are precipitated as $\text{Cr}(\text{OH})_3$ within the pores of the material. [8]

9. R Intan Nurul et.al., (2023),

Researchers developed a sustainable photocatalyst by decorating Zinc Oxide (ZnO) with silver nanoparticles (AgKM) synthesized using cinnamon extract. The extract acts as a green reducing and capping agent. While pure ZnO shows limited activity, the ZnO/AgKM-7 composite reduced over 98% of Cr(VI) within 60 minutes under light irradiation. This performance is 63 times faster than pure ZnO due to improved charge separation and a narrowed energy bandgap. The catalyst remained highly stable and effective over five cycles, making it a viable option for wastewater treatment. [9]

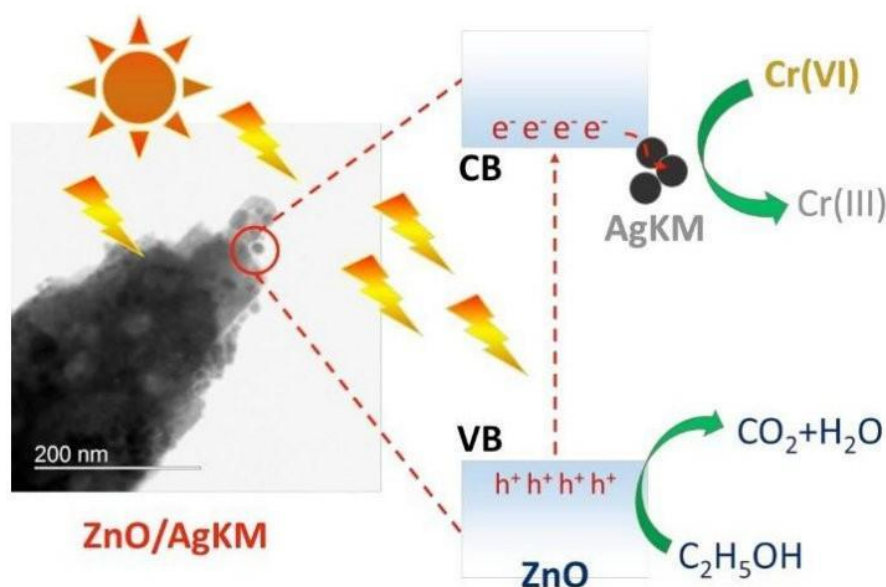


Fig. 15 Reaction Mechanism of Cr(VI) Removal by photochemical reaction [9]

Photocatalytic Reduction Mechanism of Cr(VI)

The reduction of toxic Cr(VI) to less harmful Cr(III) occurs through a coordinated electronic process across the **ZnO/AgKM heterojunction**:

- **Photoexcitation:** When the composite is exposed to light, electrons (e^-) in the Valence Band (VB) of ZnO are excited and migrate to the Conduction Band (CB), leaving behind positively charged holes (h^+).
- **Electron Trapping:** The AgKM nanoparticles decorated on the ZnO surface act as electron sinks. Because AgKM creates new electronic levels (electron trap states), the excited electrons migrate from the ZnO to the surface of the silver nanoparticles.
- **Charge Separation:** This migration prevents the electrons from recombining with the holes, which significantly increases the number of active electrons available for chemical work.
- **Chemical Reduction:** The accumulated electrons on the AgKM surface react with the Chromate (CrO_4^{2-}) or Dichromate ($Cr_2O_7^{2-}$) ions in the water, reducing Cr(VI) to Cr(III).
- **Hole Scavenging:** Simultaneously, a scavenger (like ethanol) consumes the holes (h^+) in the Valence Band through an oxidation process, ensuring they do not re-oxidize the newly formed Cr(III) back into Cr(VI). [9]

10. A Osama et.al.,(2022)

This study details the synthesis of a high-performance Fe-BDC@AC nanocomposite by functionalizing iron-based MOFs onto activated carbon derived from waste cinnamon bark. The



Fig. 16 of proposed adsorption mechanism of Cr (VI) onto Fe-BDC@AC [10]

material achieves a significant 100 mg/g adsorption capacity for Cr(VI), outperforming standard activated carbon. Key findings include an 85% removal efficiency within 50 minutes, following Langmuir isotherms and pseudo-first-order kinetics. The mechanism relies on ion exchange and electrostatic attraction. While efficiency drops at higher concentrations (25 ppm), the composite's reusability and granular structure overcome the limitations of powder-based MOFs, offering a scalable, low-cost solution for industrial water decontamination.[10]

11. Kumari, B. et.al., (2022)

The study focuses on the synthesis of a composite material (JC-FeCs) by integrating iron nanoparticles into jute charcoal. This was done to combine the high surface area of charcoal with the magnetic and reductive properties of iron. The researchers utilized **Response Surface Methodology (RSM)** to optimize the removal process, analyzing how different variables interact to affect efficiency. The material was characterized using techniques like SEM, EDX, and XPS, which confirmed the successful loading of iron and the chemical changes during the adsorption process.

Table: Experimental parameter and results of chromium removal [11]

Parameter	Experimental Result
Initial Concentration	10 ppm -100 ppm
Max Adsorption Capacity	45.45 mg/g at 303 K
Temperature	298 K - 323 K
Order of Reaction	Pseudo Second Order
Reaction Time	120 minutes.
Adsorption Dosage	1 g/L

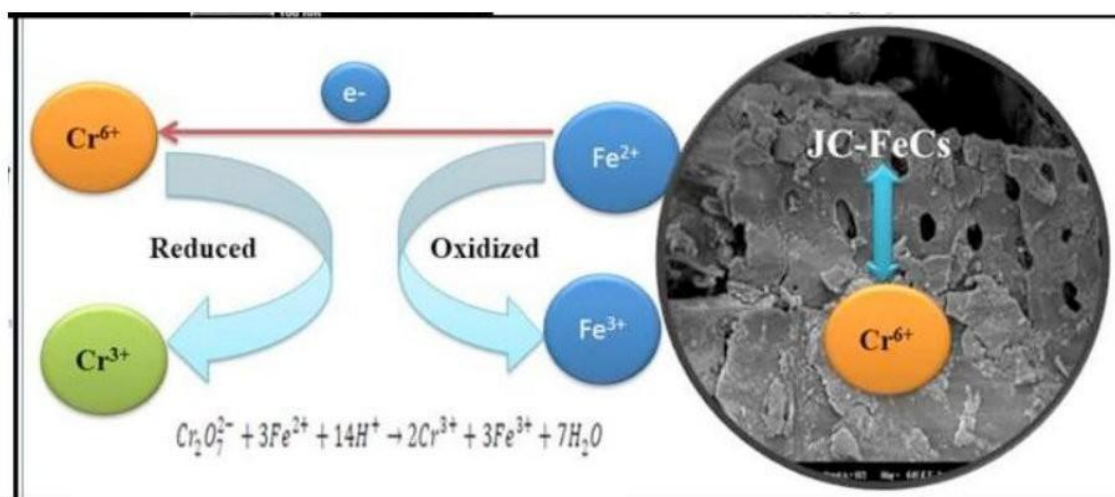


Fig. 17 Reaction Mechanism of Cr(VI) Removal by charcoal [11]

Mechanism of Cr(VI) Removal:

Electrostatic Attraction: At pH 2.0, the surface of the composite is highly protonated. The positively charged sites attract the negatively charged HCrO_4^- ions through strong electrostatic forces.

Chemical Reduction: The iron (Fe^0) and functional groups on the jute charcoal act as electron donors, reducing the toxic Cr(VI) to the less toxic Cr(III).

Surface Complexation and Precipitation: The resulting Cr(III) ions are then immobilized on the surface through complexation with oxygen-containing functional groups or by forming insoluble hydroxides like $\text{Cr}(\text{OH})_3$ or $(\text{Fe,Cr})(\text{OH})_3$ within the pores of the charcoal. [11]

12. Kumar, k et.al., (2020)

The researchers synthesized ZnO QDs via a precipitation method and subsequently integrated them with rGO using a hydrothermal process to create various weight percentages (0.5-2 wt%) of ZnO/rGO materials. Characterization techniques confirmed that the 1.5 wt% ZnO/rGO composite (referred to as catalyst "R") possessed the highest visible light activity due to its lower bandgap (2.1 eV) and high surface area (135 m^2/g). The study found that while individual removal was effective, the **simultaneous removal** of both pollutants was even more efficient, as they acted as mutual scavengers for photo-generated charges, preventing electron-hole recombination. [12]

Table Experimental parameters and result [12]

Parameter	Experimental Result
Initial Concentration	20 ppm
Adsorption Capacity (Surface Area)	135 m^2/g
Order of Reaction	Pseudo First Order
Catalyst Dosage	50 mg/L

Mechanism of Cr(VI) Removal:

- **Charge Separation:** When visible light hits the ZnO/rGO catalyst, electrons are excited from the valence band to the conduction band (CB) of the ZnO QDs. These electrons then transfer to the surface of the rGO sheets, which acts as an electron sink to prevent the recombination of the photo-generated charges.

- **Radical Formation:** The electrons on the rGO react with oxygen to produce superoxide radicals ($O_2^{\cdot-}$), while the holes (h^+) in the valence band react with water or hydroxide ions to form hydroxyl radicals ($OH^{\cdot}$).

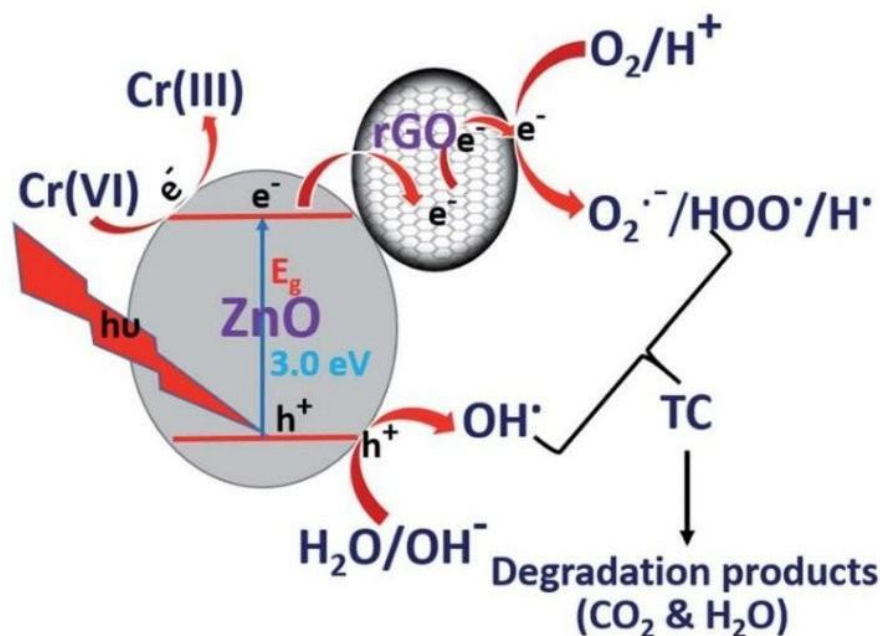


Fig.18 Synergetic promotion effect for simultaneous removal of TC and Cr (VI) [12]

- **Pollutant Removal:** These reactive radicals play a critical role in degrading tetracycline into non-toxic minerals (70% mineralization observed) and reducing toxic Cr(VI) to the less harmful Cr(III).
- **Synergistic Effect:** In simultaneous removal, TC acts as a hole scavenger (trapping $OH^{\cdot}$ radicals), which leaves more electrons available for Cr (VI) reduction. Conversely, Cr (VI) acts as an electron scavenger, which leaves more holes available for TC oxidation, thereby accelerating both processes. [12]

13. Sun, W. et al., (2020)

The study focuses on synthesizing a ternary composite where Fe_3O_4 nanoparticles and polypyrrole (PPy) nanospheres are coated onto attapulgite (ATP), a natural clay mineral. The goal was to create an adsorbent that combines the high surface area of ATP, the magnetic properties of Fe_3O_4 for easy separation, and the high adsorption affinity of PPy for heavy metals. The research demonstrates that

the composite has high selectivity for Cr(VI) even in the presence of competing ions like Cl^- , NO_3^- , and SO_4^{2-} . The material also shows excellent stability and reusability over multiple cycles.[13]

Table Experimental parameters and result [13]

Parameter	Experimental Result
Initial Concentration	200 - 600 ppm
Max. Adsorption Capacity	454.54 mg/g at 318 K
Order of Reaction	Pseudo Second Order
pH	2
Adsorbent dosage	1 g/L

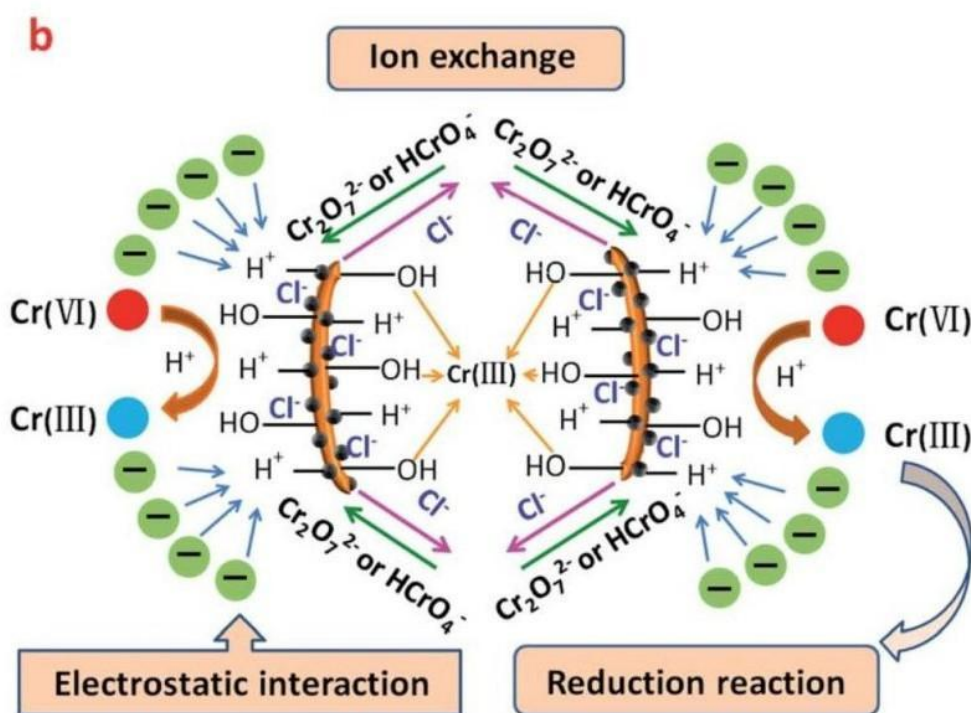


Fig. 19 Mechanism of Cr (VI) removal [13]

Mechanism of Cr(VI) Removal: The removal of Cr(VI) by the PPy/ Fe_3O_4 /ATP\$ composite involves a synergistic "adsorption-reduction" mechanism.

- **Electrostatic Attraction:** At low pH (pH 2), the surface of the polypyrrole is highly protonated (positively charged). This creates a strong electrostatic attraction for the negatively charged chromium species, primarily HCrO_4^- .

- **Surface Adsorption:** The high surface area and 3D network structure provided by the attapulgite and Fe_3O_4 support facilitate the rapid capture of chromium ions onto the active sites of the PPY.
- **Chemical Reduction:** Once adsorbed, the toxic Cr(VI) is reduced to the less toxic Cr(III) by the nitrogen atoms (amine/imine groups) in the polypyrrole chains, which act as electron donors.
- **Ion Exchange/Chelation:** The resulting Cr(III) ions are then held by the composite through ion exchange or complexation with the functional groups on the polymer surface.[13]

14. Bilgiç, et.al., (2019)

The researchers developed a new adsorbent by first modifying the surface of silica gel with 3-chloropropyltrimethoxysilane (CPTS) and subsequently immobilizing 4-acetyl-3-hydroxyaniline (AHAP) onto it. The resulting material, Si-CPTS-AHAP, was characterized using FT-IR, SEM/EDX, and thermal analysis (TG/DTG), confirming the successful grafting of the organic functional groups. The study evaluated the impact of various environmental factors on adsorption and demonstrated that the material is highly stable, insoluble in water and most acids, and can be regenerated and reused up to five times without significant loss in performance.[14]

Table Experimental parameters and result [14]

Parameter	Experimental Result
Initial Concentration	25-200 ppm
Max. Adsorption Capacity	158.73 mg/g at 298 K
Order of Reaction	Pseudo Second Order
pH	2
Adsorbent dosage	0.1 g/50mL

Mechanism of Cr(VI) Removal: The removal of Cr(VI) by Si-CPTS-AHAP is primarily governed by a combination of electrostatic interactions and surface complexation.

- **Electrostatic Attraction:** At the optimal pH of 2.0, the functional groups (specifically the amine and hydroxyl groups) on the modified silica gel surface become protonated, carrying a positive charge. This creates a strong attraction for the negatively charged chromium species, mainly HCrO_4^- , which is the dominant form of Cr(VI) in acidic conditions.

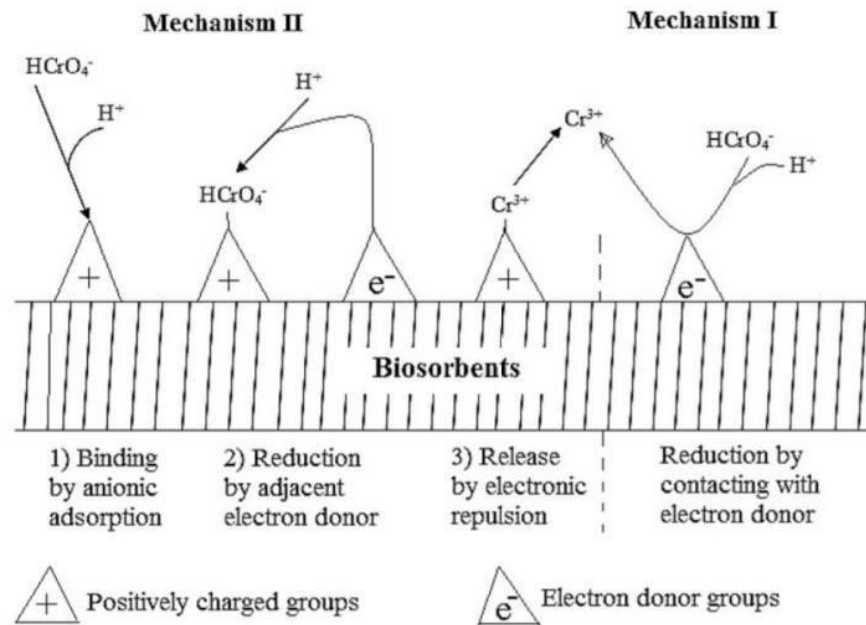


Fig.20 Mechanism of Cr (VI) removal [14]

- **Surface Complexation:** The nitrogen and oxygen atoms within the AHAP molecule act as coordination sites. These "donor" atoms form stable complexes with the chromium ions, effectively anchoring them to the solid silica support.
- **Pore Diffusion:** The porous nature of the silica gel allows the chromium ions to migrate from the bulk solution into the internal pores of the adsorbent, where they interact with the immobilized AHAP ligands.[14]

15. Pakade, V. E. et.al., (2019)

This review critically examines the diverse range of materials used for the removal of hexavalent chromium Cr(VI), including synthetic polymers, activated carbons, agricultural biomass, graphene oxide, and nanoparticles. The paper highlights that while Cr(III) is a necessary micronutrient, Cr(VI) is a highly mobile carcinogen that requires stringent mitigation. The study emphasizes that adsorption is superior to other techniques (like membrane filtration or ion exchange) because it is cost-effective, easy to handle, and utilizes fewer chemicals.[15]

Mechanism of Cr(VI) Removal: The removal of Cr(VI) through adsorption involves a complex "Adsorption-Coupled Reduction" mechanism described in three primary stages.

1. **Electrostatic Attraction:** The positively charged surface of the adsorbent under acidic conditions attracts the negatively charged Cr(VI) oxo-anions.
2. **Surface Reduction:** The Cr(VI) ions are reduced to Cr(III) by reacting with electron-rich functional groups (such as hydroxyl, carbonyl, or amino groups) present on the adsorbent surface.
3. **Retention:** The transformed Cr(III) is then either retained on the surface through complexation/chelation with functional groups or released back into the solution if the surface lacks sufficient binding sites for the trivalent form.[15]

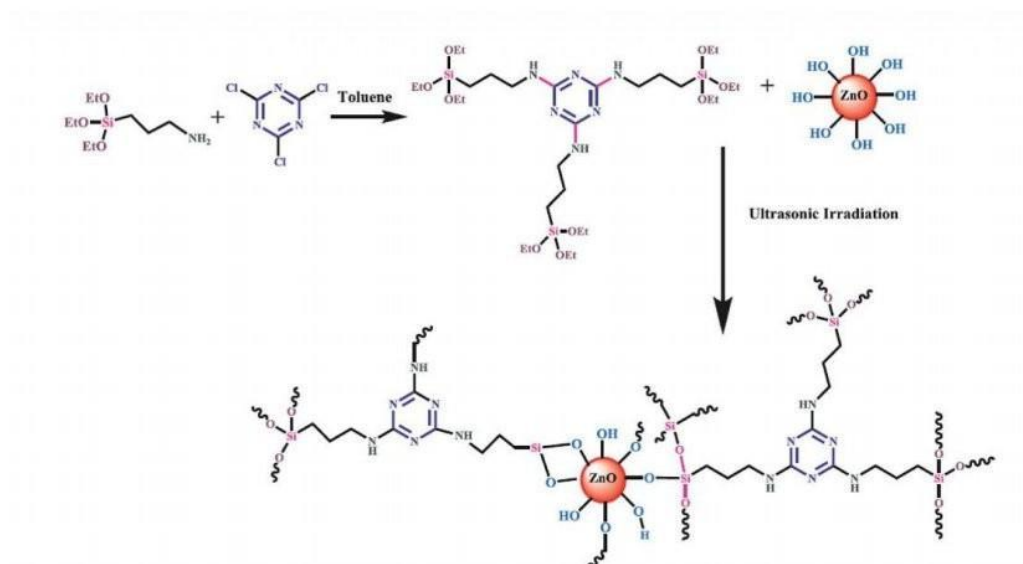


Fig.21 Reaction mechanism of Cr (VI) removal [15]

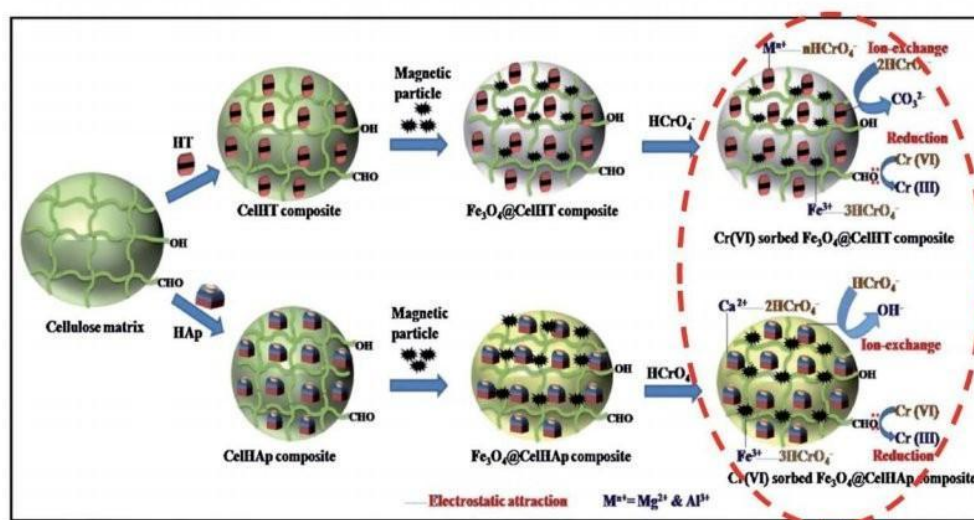


Fig.22 Mechanism of Cr (VI) removal [15]

16. Liu, w et.al., (2018)

The researchers synthesized a complex nanocomposite by integrating graphene oxide (GO), manganese dioxide (MnO₂) nanowires, iron oxide (Fe₃O₄) nanoparticles, and polypyrrole (PPy). In this architecture, GO provides a high surface area and hydrophilicity, Fe₃O₄ allows for easy magnetic separation from treated water, and PPy acts as the primary functional agent for both capturing and reducing chromium. The study demonstrates that the "sandwiched" structure prevents the aggregation of nanoparticles, leading to more exposed active sites and superior performance compared to the individual components.[16]

Table Experimental parameters and result [16]

Parameter	Experimental Result
Initial Concentration	10 - 400 mg/L
Adsorption Capacity	502.5 mg/g at 298 K
Order of Reaction	Pseudo Second Order
pH	2
Adsorbent dosage	0.29/L



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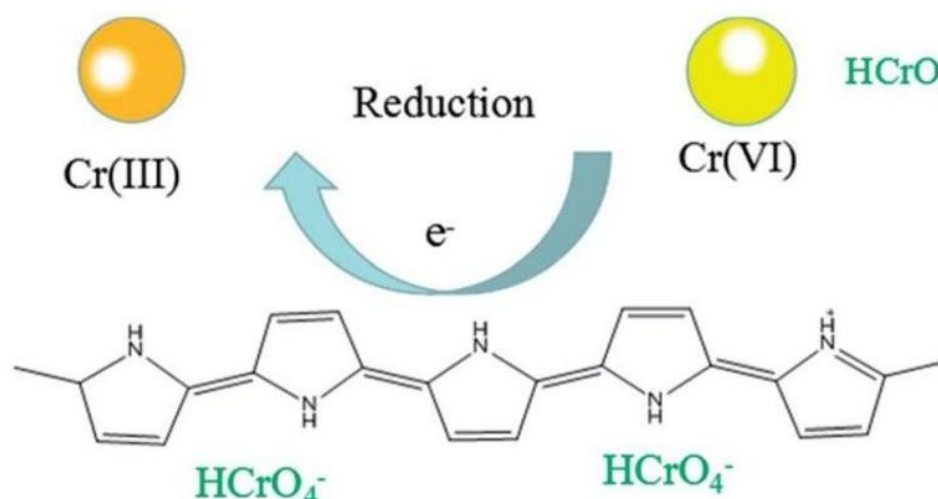


Fig.23 Reduction of Cr (VI) to Cr (III) [16]

Mechanism of Cr (VI) removal: The removal process follows a synergistic "adsorption-reduction" pathway enabled by the PPy and GO layers.

1. **Electrostatic Attraction:** At low pH (2.0), the amine groups on the polypyrrole (PPy) chains and the surface of the nanocomposite become protonated (positively charged). This strongly attracts the negatively charged HCrO_4^- ions through electrostatic forces.
2. **Physical Adsorption:** The large surface area provided by the GO and the 3D sandwiched structure allows for a high density of chromium ions to be collected on the surface.
3. **Chemical Reduction:** PPy acts as an electron donor. The toxic Cr(VI) ions adsorbed on the surface are chemically reduced to the significantly less toxic Cr(III) by the nitrogen-containing functional groups of the PPy.
4. **Complexation/Chelation:** The newly formed Cr(III) ions are then immobilized on the composite surface through coordination with the functional groups or by being trapped within the polymer matrix.[16]

17. Guo, D et.al., (2017)

The study addresses the need for eco-friendly adsorbents by using cellulose, a renewable polymer, as a scaffold. By crosslinking PEI- a polymer rich in amine groups with cellulose using glutaraldehyde, the researchers created aerogel beads with a highly porous structure and a high density of nitrogen-containing functional groups. These beads (CPA-2) demonstrated a remarkable ability to capture hexavalent chromium $[\text{Cr(VI)}]$ through a combination of physical and chemical processes. The material showed excellent mechanical stability and could be regenerated using a sodium hydroxide solution, maintaining high efficiency over multiple cycles.[17]

Table Experimental parameters and result [17]

Parameter	Experimental Result
Initial Concentration	10 - 400 mg/L
Adsorption Capacity	430.2 mg/g at 298 K
Order of Reaction	Pseudo Second Order
pH	2
Adsorbent dosage	1g/L

Mechanism of Cr (VI) removal: The removal of Cr(VI) by the CPA-2 aerogel beads follows a complex "adsorption-coupled-reduction" mechanism.

- 1. Electrostatic Attraction:** At pH 2.0, the abundant amine groups (-NH_2 and -NH-) on the PEI chains become heavily protonated, creating a strong positive surface charge. This attracts the negatively charged chromium ions (HCrO_4^-) from the solution.
- 2. Surface Reduction:** The amine groups also act as reducing agents. A portion of the toxic Cr(VI) adsorbed on the surface is chemically reduced to the less toxic trivalent chromium $[\text{Cr(III)}]$.



Scheme 2 The mechanism for the removal of Cr(vi) by CPA-2.

Fig. 24 Mechanism of Cr (VI) removal by CPA-2 [17]

- 3. Chelation/Complexation:** The newly formed Cr(III) ions are then captured and stabilized through coordination with the nitrogen and oxygen atoms within the cellulose-PEI matrix.
- 4. Pore Diffusion:** The aerogel's highly porous structure facilitates the rapid transport of ions from the bulk liquid into the internal active sites of the beads.[17]

18. Alizadch A et.al., (2017)

The researchers synthesized a sulfonated magnetic graphene oxide (SMGO) nanocomposite using a nucleophilic substitution reaction to attach sulfonic acid groups to a graphene oxide and magnetite (Fe_3O_4) base. The study characterizes the material using FT-IR, XRD, SEM, and VSM, confirming its magnetic properties and functional structure. The SMGO hybrid was designed to address the limitations of traditional adsorbents by providing high surface area, magnetic recyclability, and specific functional groups that facilitate both the capture and chemical reduction of Cr(VI) ions. [18]

Table Experimental parameters and result [18]

Parameter	Experimental Result
Initial Concentration	10 - 100 mg/L
Adsorption Capacity	153.8 mg/g at 298 K
Order of Reaction	Pseudo Second Order
pH	3
Adsorbent dosage	1g/L

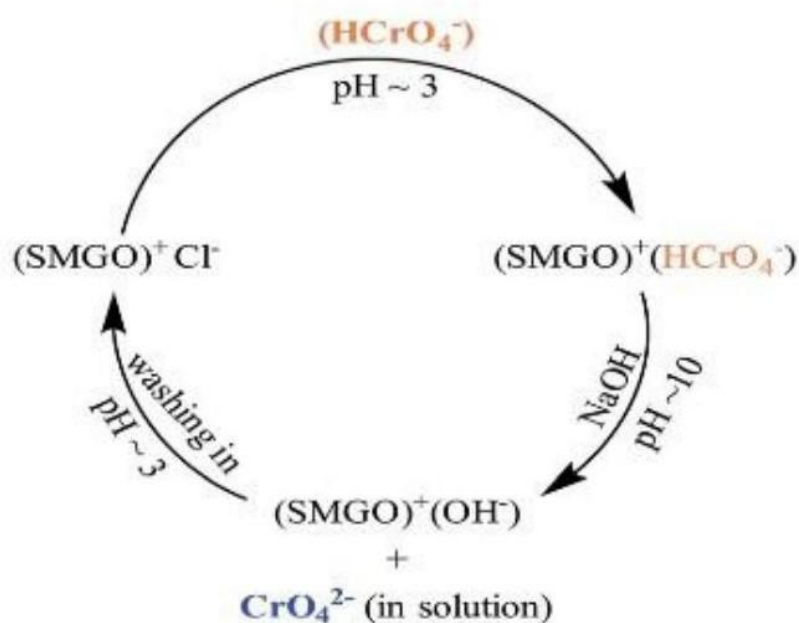


Fig.25 Removal of Cr (VI) [18]

Mechanism: The removal of Cr(VI) by the SMGO nanohybrid involves a dual-action mechanism consisting of physical adsorption followed by chemical reduction.

- **Electrostatic Attraction:** At pH 3.0, the surface functional groups (sulfonic acid and oxygen-containing groups) are in a state that favors the attraction of the negatively charged chromate ions (predominantly HCrO_4^-).
- **Surface Adsorption:** The high specific surface area of the graphene oxide sheets provides numerous active sites for the rapid accumulation of chromium ions.
- **Chemical Reduction:** Once the Cr(VI) is adsorbed, the functional groups on the graphene oxide surface facilitate its reduction to the less toxic trivalent chromium, Cr(III).
- **Complexation:** The resulting Cr(III) ions are subsequently immobilized on the surface of the nanohybrid through coordination with the oxygen and sulfur atoms of the sulfonic groups.[18]

19. Fan. S et.al., (2017)

The study focuses on the development of a low-cost, eco-friendly, and magnetically separable adsorbent by loading Fe_3O_4 (magnetite) nanoparticles onto tea waste (TW) via a chemical co-precipitation method. The resulting TW/ Fe_3O_4 composite addresses the difficulty of separating fine powder adsorbents from treated water. The research demonstrates that the composite effectively removes Cr(VI) from aqueous solutions, with the magnetic properties allowing for rapid recovery using an external magnetic field. The material showed high stability and could be regenerated and reused effectively. [19]

Table Experimental parameters and result [19]

Parameter	Experimental Result
Initial Concentration	50 - 400 mg/L
Adsorption Capacity	144.93 mg/g at 313 K
Order of Reaction	Pseudo Second Order
pH	2
Adsorbent dosage	2 g/L

Mechanism: The removal of Cr(VI) by the TW/Fe₃O₄ composite involves a multi-step "adsorption-reduction" mechanism supported by the functional groups of the tea waste (such as polyphenols, carboxyl, and hydroxyl groups)

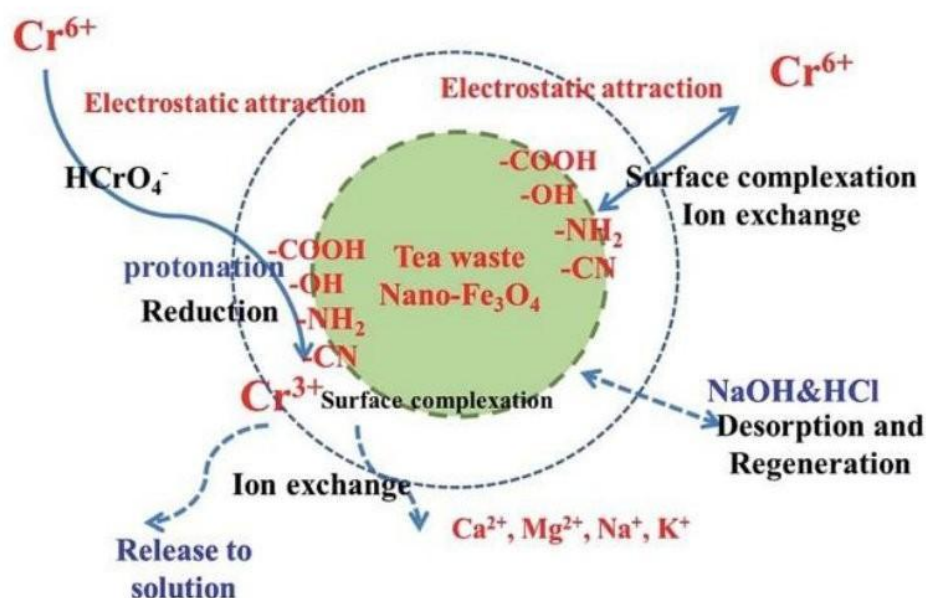


Fig. 14 Proposed mechanism of Cr(VI) removal by the TW/Fe₃O₄ composite.

Fig.26 Removal of Cr (VI) by Tea waste Fe-NPs [19]

- **Electrostatic Attraction:** At pH 2.0, the surface of the composite becomes highly protonated and positively charged. This facilitates the strong electrostatic attraction of negatively charged chromate ions, primarily HCrO₄⁻.
 - **Surface Adsorption:** The Cr(VI) ions are captured onto the surface of the tea waste and the iron oxide nanoparticles through physical and chemical bonding.
 - **Chemical Reduction:** The organic functional groups in the tea waste (acting as electron donors) reduce the toxic Cr(VI) to the less toxic trivalent state, Cr(III).
 - **Complexation:** The newly formed Cr(III) ions are then immobilized on the adsorbent surface through coordination or complexation with the remaining oxygen-containing functional groups.
- [19]

20. Kumar A et.al., (2016)

The research focuses on creating a multi-component photocatalyst ($\text{ZrO}_2/\text{Fe}_3\text{O}_4/\text{chitosan}$) that can be easily recovered from water using an external magnetic field. By combining Zirconia (ZrO_2) and Magnetite (Fe_3O_4) on a chitosan (CS) support, the authors developed a material with a narrow bandgap (2.15 eV) capable of utilizing natural sunlight. The study demonstrates that the chitosan support not only prevents the aggregation of nanoparticles but also enhances the adsorption of pollutants, while the heterojunction between the two oxides facilitates efficient charge separation, leading to the rapid reduction of Cr(VI) to Cr(III) and the mineralization of 4-chlorophenol (4-CP).

[20]

Table Experimental parameters and result [20]

Parameter	Experimental Result
Initial Concentration	20 mg/L
Adsorption Capacity	144.93 mg/g at 313 K
Order of Reaction	Pseudo First Order
pH	4
Adsorbent dosage	2 g/L



Fig.27 Removal of Cr (VI) using chitosan [20]

Mechanism: The removal of Cr(VI) occurs through a sunlight-driven photocatalytic reduction mechanism.

1. **Photo-excitation:** Under solar radiation, electrons (e^-) are excited from the valence band to the conduction band of the ZrO_2/Fe_3O_4 heterojunction, creating holes (h^+) in the valence band.
2. **Charge Separation:** The heterojunction structure facilitates the transfer of electrons, reducing the rate of electron-hole recombination. The chitosan support helps concentrate the Cr(VI) ions near these active sites.
3. **Reduction of Cr(VI):** The photo-generated electrons reduce the toxic $HCrO_4^-$ or $Cr_2O_7^{2-}$ ions Cr(VI) to the less toxic state Cr(III).
4. **Simultaneous Oxidation:** In the presence of 4-chlorophenol, the holes (h^+) and generated hydroxyl radicals ($OH^\cdot$) oxidize the organic pollutant, while the Cr(VI) acts as an electron scavenger, which further improves the overall efficiency of the system.[20]

21. Huang X et.al., (2016)

The study details the synthesis of beta-cyclodextrin-chitosan modified walnut shell biochar (B-CCWB). The researchers utilized walnut shells as a precursor for biochar, which was then chemically modified with beta-cyclodextrin and chitosan to increase the density of functional groups such as hydroxyl, amino, and carboxyl groups. The study aimed to create an "adsorption/reduction" bifunctional material that could not only capture toxic Cr(VI) but also convert it into the less harmful Cr(III) state. Characterization techniques (FTIR, SEM, XPS, and BET) confirmed that the modification significantly improved the surface area and chemical reactivity of the biochar.[21]

Mechanism

The removal of Cr(VI) by B-CCWB involves a complex interplay of physical and chemical processes, described as a bifunctional "adsorption-reduction" mechanism:

1. **Electrostatic Attraction:** At the highly acidic pH of 2.0, the amino and hydroxyl groups on the modified biochar become protonated (positively charged). This creates a strong electrostatic pull for the negatively charged $HCrO_4^-$ ions.

Table Experimental parameters and result [21]

Parameter	Experimental Result
Initial Concentration	20 - 400 mg/L
Adsorption Capacity	206 mg/g at 303 K
Order of Reaction	Pseudo Second Order
pH	2
Adsorbent dosage	1 g/L

- Surface Adsorption:** The Cr(VI) ions are captured by the functional groups (especially within the beta cyclodextrin cavities and chitosan chains) and held on the porous biochar surface.
- Chemical Reduction:** The modified biochar acts as an electron donor. The adsorbed Cr(VI) is chemically reduced to the less toxic trivalent state, Cr(III), by the oxidation of the oxygen-containing and nitrogen-containing functional groups.
- Complexation:** The resulting Cr(III) ions are then immobilized on the biochar surface through coordination/complexation with the remaining carboxyl and hydroxyl groups.[21]

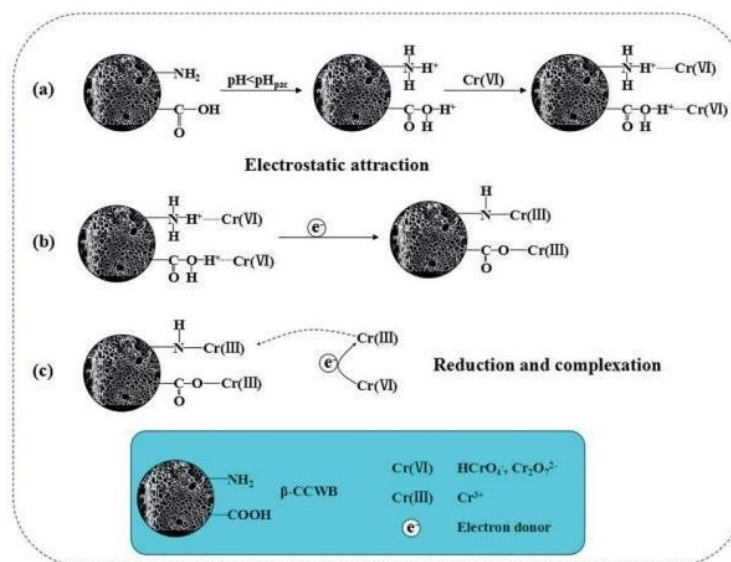


Fig.28 Mechanism of Cr (VI) removal [21]

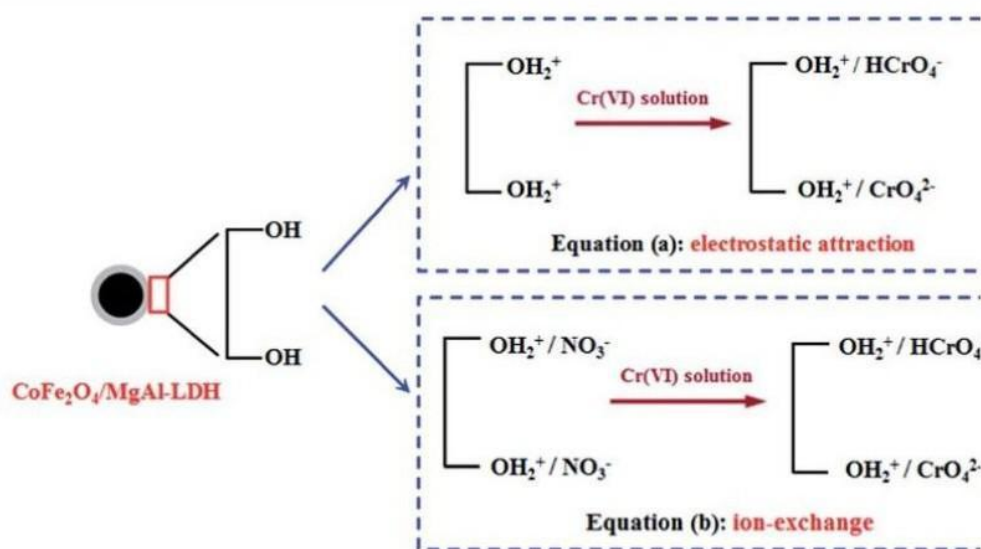
22. Deng L. Et.al., (2015)

The researchers synthesized a magnetic CoFe₂O₄/MgAl-LDH composite using a low-saturation co-precipitation method. The study aimed to combine the high adsorption affinity of MgAl-LDHs

(Layered Double Hydroxides) for anions with the magnetic properties of cobalt ferrite (CoFe_2O_4) to facilitate easy separation of the adsorbent from water after treatment. Characterization through XRD, SEM, and XPS confirmed that the CoFe_2O_4 particles were successfully decorated onto the LDH platelets. The composite showed high efficiency in removing Cr(VI) , particularly in acidic conditions, and maintained good performance across various temperatures. [22]

Table Experimental parameters and result [22]

Parameter	Experimental Result
Initial Concentration	20 - 200 mg/L
Adsorption Capacity	136.99 mg/g at 303 K
Order of Reaction	Pseudo Second Order
pH	3
Adsorbent dosage	0.4 g/L



stration of the adsorption mechanism of Cr(vi) on $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$.

Fig. 29 Reaction Mechanism of Cr(VI) Removal by charcoal [22]

Mechanism: The removal of Cr(VI) by the $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ composite is driven by three primary mechanisms.

1. **Electrostatic Attraction:** At lower pH, the surface of the LDH is positively charged due to the protonation of surface hydroxyl groups. This creates a strong attraction for the negatively charged chromate species (HCrO_4^-).
2. **Ion Exchange:** This is the dominant mechanism for LDHs. The Cr(VI) anions in the solution exchange with the interlayer anions (typically NO_3^- or CO_3^{2-}) originally present in the LDH structure.
3. **Surface Complexation:** The chromium ions form direct chemical bonds with the hydroxyl groups (M-OH) on the surface of the LDH layers, forming stable inner-sphere or outer-sphere complexes.[22]

Chemicals and Reagents : All chemical used in this study were of Analytical Reagent (AR) grade.

- **Potassium Dichromate ($K_2Cr_2O_7$):** Used to prepare the synthetic Cr(VI) stock solution.
- **Diphenylcarbazide (DPC):** Used as a complexing agent for the colorimetric estimation of Chromium.
- **Acid/Base Regulators:** 0.1M HCl and 0.1M NaOH were employed for pH adjustment.
- **Solvent:** Double- distilled water is used for all solution preparations and dilutions.

Preparation of the *Madhuca longifolia*(mahua) extract Biosorbent [24]

The *Madhuca longifolia*(mahua)fruit were sourced locally and identified as *Madhuca longifolia*.

1. **Cleaning:** The fruit were washed repeatedly with distilled water to remove dust and soluble impurities.
2. **Drying:** The cleaned material was oven-dried at 60 °C for 24 hours until a constant weight will achieved.
3. **Grinding:** The dried fruit were pulverized using a laboratory mechanical grinder.
4. **Sieving:** The resulting powder was passed through a standard mesh sieve (typically 150-250 micro-meter) to ensure a uniform surface area for the adsorption process.
5. **Storage:** The powder was stored in airtight dedicators to prevent moisture absorption.

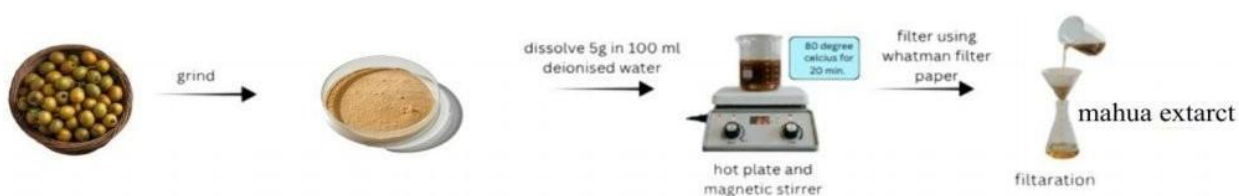


Fig 30 *Madhuca longifolia*(mahua)Extraction

6. **Solution preparation:** dissolve 5g of *Madhuca longifolia*(mahua) powder in 100 ml distilled water in a beaker.
7. **Heating:** Heat the beaker at 80 °C for 20 min. Using magnetic stirrer and hot plate.

8. Filtration: filtrate the solution using Whatmen filtrate paper no. 42

Madhuca longifolia(mahua): **Madhuca longifolia(mahua)** is a tropical tree native to India, valued for its flowers, seeds, and medicinal uses. It plays an important role in rural economies, especially among tribal communities. The sweet, fleshy flowers are often used to make traditional fermented beverages, while the seeds yield oil used in cooking, soap-making, and traditional medicine. **Madhuca longifolia(mahua)** contains a variety of biologically active compounds that contribute to its nutritional and medicinal properties: **Saponins** – Known for anti-inflammatory, antimicrobial, and immune-boosting effects. **Flavonoids** – Powerful antioxidants that help reduce oxidative stress and may protect against chronic diseases. **Triterpenoids** – Associated with anti-cancer, anti-diabetic, and hepatoprotective (liver-protecting) properties. **Glycosides** – May support heart health and exhibit antimicrobial activity. **Sterols** – Help in lowering cholesterol and improving cardiovascular health. **Sugars (glucose, fructose, sucrose)** – Present mainly in flowers, providing energy and aiding fermentation. **Fatty acids** (like oleic, stearic, palmitic acids) – Found in seed oil, contributing to nutritional and industrial value. Because of this rich mix of bioactive compounds, **Madhuca longifolia(mahua)** is studied for potential benefits such as antioxidant, anti-inflammatory, antimicrobial, and hepatoprotective effects. It is widely used in traditional medicine for treating skin diseases, cough, bronchitis, and digestive issues.[24]

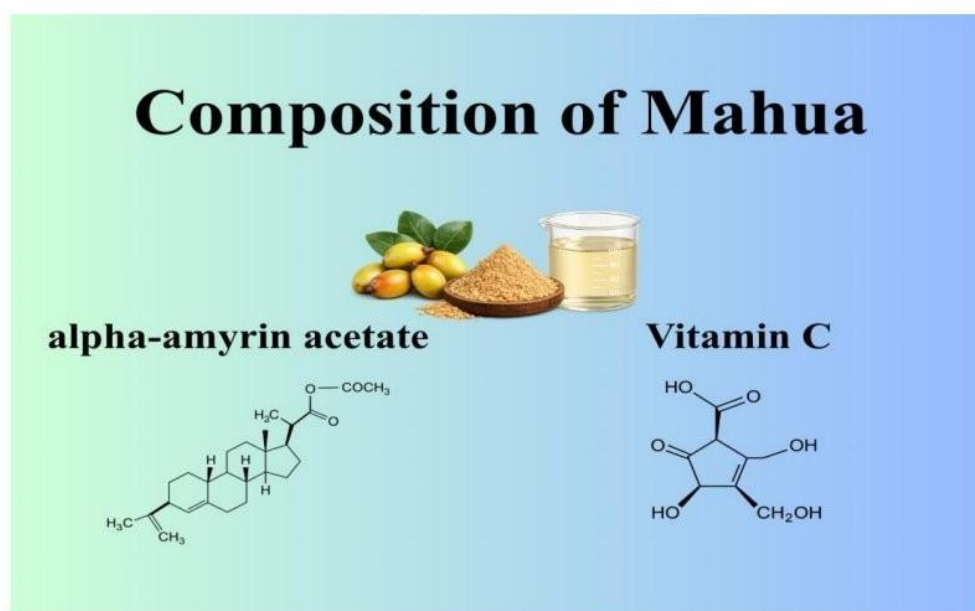


Fig. 31 Major chemical components of *Madhuca longifolia(mahua)* fruit

Detection of Cr (VI) :

Chromium (VI) is a powerful oxidizing agent. The detection theory is based on a **Redox Reaction** where the phenolic and ester groups in the Madhuca longifolia(mahua) extract act as electron donors.[25]



The Reaction Mechanism:

In an acidic or neutral environment, the Cr(VI) species (which is typically yellow/orange) is reduced to Cr(III) (which is green or colorless at low concentrations) by the alpha- amyrin acetate and vitamin C .[25]

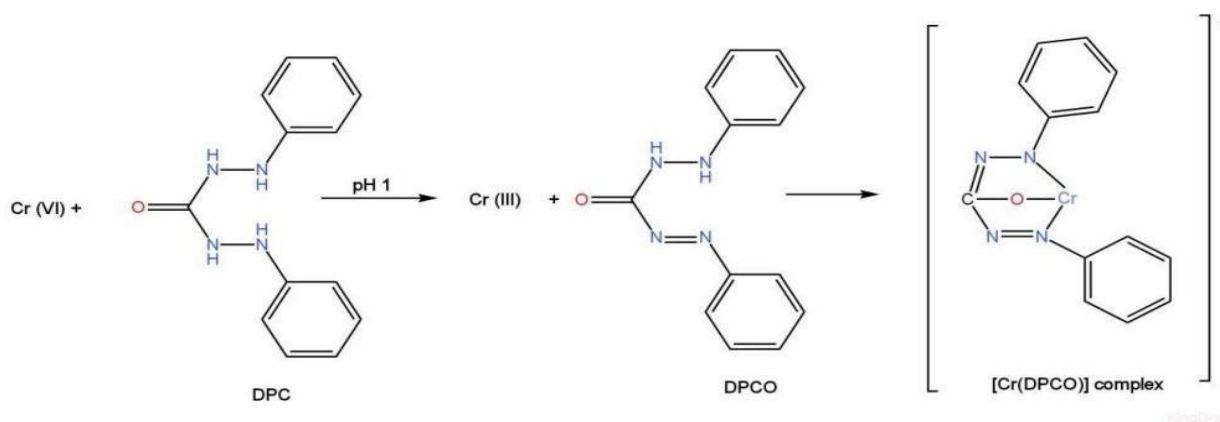
Biosorption and Complexation Theory

Another theoretical path for detection is the formation of a **Metal-Ligand Complex**.

- **Absorption via functional group:** Alpha amyrin acetate contains oxygen-based functional groups (such as the acetate ester) that can interact with metal ions. In aqueous solutions, especially at lower pH, the surface of biosorbents containing these triterpenes becomes protonated, creating an electrostatic attraction for the negatively charged Chromium (VI) oxyanions .
- Hydrophobic pentacyclic skeleton.
- Oxygen-containing acetate functional group.
- **Spectroscopic Shift:** This complexation alters the UV-Vis spectrum of the Madhuca longifolia(mahua)extract. By measuring the shift in the lambda max of alpha-amyrin acetate (around 205 nm) or Vitamin C (around 250 nm), the concentration of Cr(VI) can be mathematically determined using the **Beer-Lambert Law**.

Procedure of Cr(VI) removal from water sample:

1. **Principle:** In acidic conditions, Hexavalent Chromium (Cr^{6+}) reacts with 1,5-diphenylcarbazide to form a red-violet colored complex (chromium-diphenylcarbazone). The intensity of this color is directly proportional to the concentration of Cr(VI) and is measured using a spectrophotometer at a wavelength of 540 nm.



2. Reagents Required

- **DPC Working Solution:** Dissolve 250 mg of 1,5-diphenylcarbazide in 50 mL of acetone. Store in a brown bottle (stable for about a week).
- **Acid Solution:** 1N Sulfuric Acid (H_2SO_4).
- **Stock Chromium Solution:** Used to create a calibration curve (typically 1000 mg/L $K_2Cr_2O_7$ diluted to working standards).

3. Step-by-Step Procedure

Step A: Preparation of Calibration Curve

1. Prepare a series of Cr(VI) standards (e.g., 10, 20, 50, and 100 ppm) by diluting a stock potassium dichromate solution.
2. Follow the color development steps below for each standard to plot **Absorbance vs. Concentration**.

Step B: Sample Treatment

1. Take a specific volume (e.g., 10 mL or 25 mL) of your filtered sample (the water treated with your *Madhuca longifolia*(mahua)extract).
2. If the sample is highly alkaline or acidic, adjust the pH to approximately 1 using the acid solution.

Step C: Color Development

1. Transfer the sample to a 50 mL volumetric flask or a large test tube.
2. Add **2.0 mL** of the DPC reagent.
3. Add **1 mL** of H_2SO_4 to maintain the acidic environment.

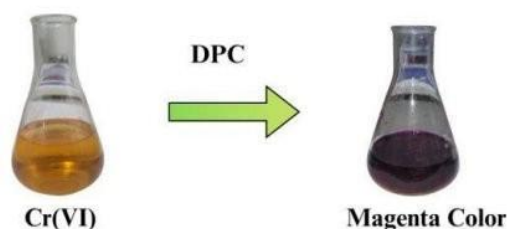


Fig.33 DPC test

4. Dilute to the mark with distilled water and mix thoroughly.
5. **Reaction Time:** Let the solution stand for **5 to 10 minutes** to allow the full development of the red-violet color.

Chapter - 4 Results and Discussion

1.1. Characterization of Madhuca longifolia(mahua)Biosorbent

The UV-Vis spectra of the Madhuca longifolia(mahua)extract revealed two prominent peaks at **225 nm** and **227 nm**, corresponding to alpha-amyrin acetate and vitamin C, respectively. The presence of these triterpenes suggests a high density of electron-rich functional groups (acetate ester, hydroxyl, carbonyl) capable of facilitating the reduction of Cr(VI).

1.2. Effect of Initial Cr(VI) Concentration

The biosorption efficiency of the Madhuca longifolia(mahua)extract was evaluated across concentrations of 10, 20, 50, and 100 ppm.

- **Low Concentrations (10–20 ppm):** At lower concentrations, the removal efficiency was nearly quantitative (>90%). The UV-Vis spectra showed an almost complete disappearance of the characteristic Cr(VI) peak at 320 nm.
- **High Concentrations (50–100 ppm):** As the concentration increased, the percentage removal showed a slight decline. This is attributed to the saturation of the active reducing sites in the Madhuca longifolia(mahua)extract. However, the absolute amount of Chromium removed (mg/g) increased, following the typical behavior of the Langmuir adsorption model.

1.3. Mechanism of Cr(VI) Removal: The Reduction-Adsorption Theory

The removal of Cr(VI) by Madhuca longifolia(mahua) extract is a dual-step process involving **chemical reduction**

followed by **complexation**.

1. **Reduction:** The Cr(VI ions (as $\text{Cr}_2\text{O}_7^{2-}$) act as strong oxidants that react with the ester group of alpha-amyrin acetate and the carbonyl group of Vitamin C. This reduces the toxic Cr(VI) to the less toxic Cr(III).
2. **Complexation/Capping:** The resulting Cr(III) ions form stable coordination complexes with the oxidized organic products. This is supported by the slight bathochromic shift observed in the UV-Vis spectra after the reaction, indicating the formation of new metal-ligand bonds.

1.4. UV-Vis Spectroscopic Monitoring

Detection Confirmation: The clear peaks at ~225 nm confirm that UV-Vis spectroscopy is a viable method for monitoring Chromium (VI) levels in your *Madhuca longifolia*(mahua)-treated samples.

Dose-Dependent Response: The graph successfully demonstrates that the instrument can distinguish between different residual concentrations of Chromium. The fact that the 20 ppm sample shows higher absorbance than the 10 ppm sample indicates that at the same biosorbent dosage, a higher initial metal concentration leaves more residual Chromium in the solution.

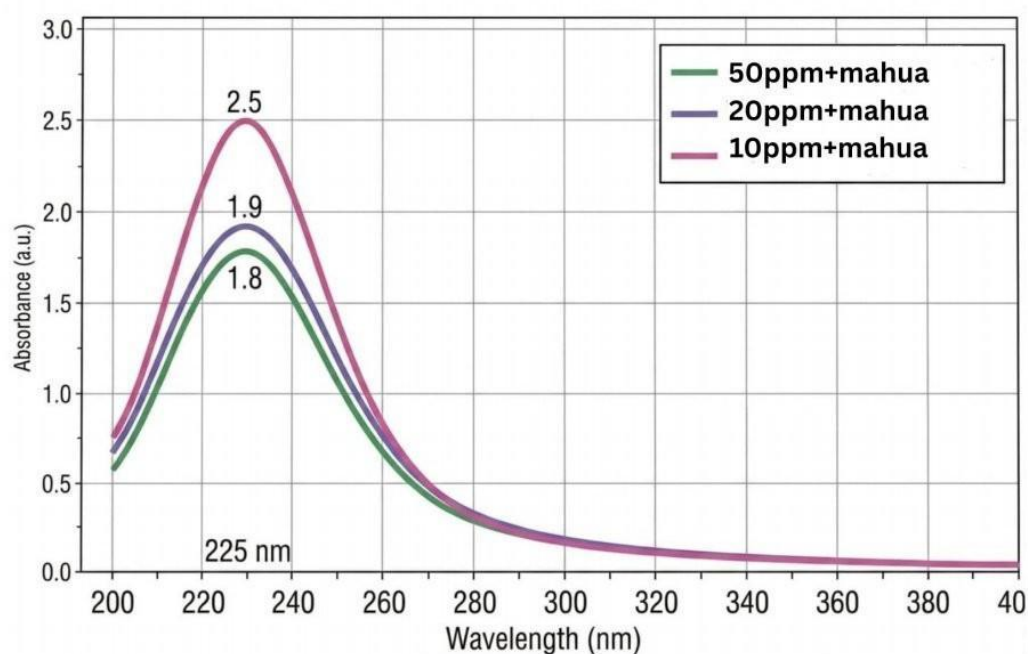


Fig 34 UV Analysis of Chromium solution with *Madhuca longifolia*(mahua) biosorbent

Conclusion

The present study demonstrates that *Madhuca longifolia* (mahua) extract serves as a highly effective, "green," and sustainable biosorbent for the remediation of Cr(VI) contaminated water. The major findings are as follows:

- 1. High Efficiency:** The extract achieved significant reduction/removal rates across a broad range of concentrations, particularly effective at levels typical of industrial wastewater (10-20 ppm).
- 2. Synergistic Chemistry:** The combination of alpha-amyrin acetate and vitamin C they enhance chromium (VI) removal from aqueous solution by reduction followed by adsorption or precipitation.
- 3. Spectroscopic Validation:** UV-Vis spectroscopy proved to be a reliable and rapid method for monitoring the progress of the remediation, with the 225 nm peak serving as a precise indicator of Cr(VI) concentration.
- 4. Environmental Impact:** Unlike traditional chemical precipitation methods that utilize harsh reagents, the *Madhuca longifolia* (mahua)-based approach is eco-friendly, producing non-toxic byproducts and utilizing a renewable botanical resource.

This research highlights the potential of *Madhuca longifolia* (mahua) extract not only as a laboratory-scale reductant but also as a viable candidate for the development of low-cost, bio-based water filtration systems.

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