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Review Article

Removal of hexavalent chromium from wastewater using different biological processes combined with conventional approaches: A Review

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Abstract

Chromium is released into the environment by industrial and commercial processes. Due to their toxicity, they induce serious human disorders. Traditional physiochemical approaches are being replaced by biological Cr-removal, which is a cost-effective, long-term technology. Biological Cr-removal has been investigated extensively in resistant microorganisms (such as yeast, bacteria, fungus and algae). To cope with chromium toxicity, microbes have developed several strategies. Biotransformation, bioaccumulation and biosorption are some of the strategies that can be used to get rid of heavy metals. The present review is focused on recent breakthroughs in integrating/combining biological or natural processes with additional methods already in use which have a lot of potential for future research and could be used to treat trivalent chromium and hexavalent chromium contaminated water in an environmentally benign and cheapest way in the near future.

Keywords: Chromium; bioremediation; electrochemical remediation; integrated techniques; wastewater

1. Introduction

The existing state of industrial and developing activity is disrupting those natural materials which are found in nature and flow or introducing foreign substances into the environment (Faisal and Hasnain, 2004). Heavy metals/loids, radionuclides, explosives, agrochemicals, petroleum hydrocarbons, and Halogenated solvents are examples of environmental pollutants that pose a major hazard to the ecosystem and are destroyed badly. Many heavy metals (HMs) like Zinc (Zn); Arsenic (As); Copper (Cu); Lead (Pb); Mercury (Hg); Cadmium (Cd); Nickel (Ni); Iron (Fe); Manganese (Mn)) are widely employed in various industries and emitted in large quantities with their effluents. These contaminants enter the environment either directly or indirectly. For most living organisms, a few metals such as Mg, Cu, Mn, Co, and Zn are micronutrients; however, this is not true for all living things, and raising concentrations over their admissible limits produces toxicity. HMs may have an important function in metabolic activity as micronutrients. HMs are easily absorbed or ingested by organisms due to their high solubility in the aquatic media (Tahir et al., 2017). Because of their long half-lives after entering the food chain, severe toxicity, and persistence in nature, they pose many dangers to living species (Manorama et al., 2016; Singh et al., 2017). HMs can enter the food chain in a variety of ways, including leaking wastewater into groundwater, drinking dirty water, and using wastewater to irrigate crops (Ali et al., 2015; Jamali et al., 2007; Mondal et al., 2017), and significant threat to people and other species after accumulating in the living organism. As a result of their widespread use and toxicity, heavy metals have deposited a slew of environmental and human health problems, making them a pressing issue to address now (Dhankar and Hooda., 2011; Mishra and Malik., 2012). Controlling hazardous chemicals, particularly toxic HMs, has been a major emphasis over the previous four decades. There is an insistent requirement for cost-effective and efficient approaches to treating HMs-contaminated industrial wastewater at the moment. Ion exchange, adsorption, chemical coagulation, reduction, membrane filtration, precipitation, are some of the traditional procedures used to remediate Heavy metal polluted wastewater. Most of these approaches, however, are unsuccessful at removing HMs below 100 mg/L, resulting in secondary contamination. Their high cost and lack of environmental friendliness limit their use, necessitating the development of other, more cost-effective, and environmentally friendly methods for treating HMs-contaminated wastewater (Barakat, 2011; Fu and Wang, 2011). Bioremediation, which involves using bacteria, fungus, and plants to remediate wastewater, has received a lot of attention in the recent three to four decades (Dhankar and Hooda, 2011). Although all heavy metals are found in the earth's crust, chromium is regarded as a particularly dangerous and toxic heavy metal because, unlike other metals, chromium toxicity is determined by its possible oxidation states rather than the total available amounts in the environment. In industrial effluents, chromate and dichromate are commonly found (Chen et al., 2019; Sakthivel et al., 2016). Chromium is a transitional element and lies in the d-block of the periodic table and its atomic number is 24. It is widely utilized in the textile, leather tanning, dyeing, paint and pigment, and electroplating industries (McGrath and Smith, 1990). Hexavalent chromium and trivalent chromium are two major states of chromium, respectively. Cr(VI) is easily accessible due to its high solubility at neutral pH, but trivalent chromium has lower solubility at neutral pH, limiting its ability to cross cell membranes (Malaviya and

Singh, 2016). Due to their inherent ability to soak up pollutants as nutrients, such as HMs, microorganisms may thrive in practically any adverse environment. Microorganisms are capable of not only accumulating or adsorbing HMs but also of converting hazardous HMs into non-toxic or less-toxic species. The mobilization and immobilization potential of metal ions has been investigated in a wide range of microbes, resulting in a wide range of metal ion accessibility to plants (Birch., 1990; Bachofen., 1990; Deng et al., 2013; Rhee et al., 2014). Fungi/bacteria have been found to have high resistance /tolerance to HMs and to be the dominating species in polluted water bodies and other ecosystems and environments. Accumulation and resistance properties of bacteria/fungi are the most important factors to consider when deciding whether or not to use them in bioremediation (Gola et al., 2016; Mishra and Malik, 2012). Mycoremediation is the term used to describe the use of growing fungi in the remediation process (Fomina et al., 2017; Holda et al., 2016; Mondal et al., 2017; Sriharsha et al., 2017; Tahir et al., 2017). Enzymatic detoxification, active/passive absorption, adsorption on their exterior cell structures, precipitation on the cell surface, permeability barrier exclusion, efflux pumps, and cellular object modification are all mechanistic strategies used by microorganisms (algae, bacteria, and fungi) for metal resistance (Bruins et al., 2000; Cao et al., 2018; Dang et al., 2018; Kumar et al., 2019; Merroun et al., 2001; Yin et al., 2011; Zhang et al., 2005). Fungi/bacteria use one or a combination of the fundamental pathways to achieve elimination, resistance/tolerance, and homeostasis in the presence of HMs.

2. Distribution of chromium in the world

The global distribution grade chromium resources are more than twelve billion tonnes, with the majority of resources (95%) being found in Zimbabwe (6%), Kazakhstan (5 percent) and South Africa (84%),. India is ranked fourth on the list, with other countries such as Brazil, the United States, Russia, Canada, Finland, and others accounting for the remaining 3% of the total. However, according to 2009 figures, India is the world's second-largest producer of chromite ore. India's chromite deposits account for two percent of the world's overall resources (Das and Singh, 2011). Odisha is home to around 98.6% of the country's chromite deposits, with 95 percent of those discovered in the Sukinda valley, which is located in Cuttack. The state's Jajpur districts Andhra Pradesh, Tamil Nadu, Goa, Karnataka, Jharkhand, and Maharashtra have the remaining resources, with Jammu & Kashmir, the Andaman and Nicobar Islands, Nagaland, and Manipur having extremely few. Deposits of chromite can be found spread over particular locations in India known as 'belts.' The Sukinda, Ramagiri, and Bhalukasuni—Nilgiri chromite belts are in Odisha, Chandrapur, and Sindhudurg in Maharashtra, Janaram block, Konayyapalem block, Linganapetta block, Sriramgiri block, and Kondapalli block in Andhra, Jojohatu—Roroburu in Jharkhand, Bhandara in Nagpur (Das et al.,2021).

3. Chromium in the environment

Rock weathering, erosion, comets, volcanic eruptions, and forest fires are environmental chromium sources that are completely natural; nevertheless, many man-made activities give inputs account for the abundance of the chromium in the ecosystem. Cr deposits can be found in anorthosite rocks or ultrabasic rocks that are closely related in soil. Chromite can be found in anorthosites, ultramafic rocks and peridotites with a few exceptions. Almost all chromium deposits occur as masses, lenses, or dissemination as a result of magmatic segregation in ultrabasic rocks. During magma cooling, chromite is generated either through later gravitational liquid buildup or early crystal setting. Pod-shaped and Stratiform (or layered) chromite deposits are the two most common types. Forest fires, volcanic activity, meteoric dust, windblown sand, and sea salt spray or particles are all resources of natural Cr released into the environment, though only volcanic eruption and windblown sand activities are significant (Barnhart et al., 1997).

Anthropogenic activities have elevated the global chromate content in solid/liquid waste to dangerous levels, and the fact that chromate is tenacious and accumulative exacerbates the problem. Metal finishing, iron, petroleum refining, leather tanning, stainless steel industries, and chrome electroplating for chrome alloy production, polluted waste dumping sites, pulp processing and wood preservation, paint and pigment manufacturing, asbestos lining erosion, textile and fertilizer manufacturing, aerosol secretion from chemical industries and incineration units, ferrochrome production, nuclear coolants (i.e., biocide), water cooling (Cheung and Gu., 2007). *etc* are the anthropogenic activities responsible for chromate in the environment.

4. Remediation strategies for Cr contaminated soil /water

Environmental experts must figure out how to lower Cr(VI) to combat the damaging effects of Cr(VI) on the environment and human health. A variety of traditional physicochemical methods has been used for the detoxification of Chromium (Elahi et al.,2020), in the environment.

4.1. Physical parameters

4.1.1. Ion exchange/ Ion flotation

Ion exchange technology is widely used for the chemical separation of noble metal ions. Ion exchange has been widely used for recovering and removing metal ions from dilute aqueous solutions. Ion flotation is the separation technology. In this process, an ionic collector is utilized to transport a non-surface active colligend ion of the opposite charge from the bulk solution to the solution vapor interface (Shao et al., 2019).

4.1.2. Membrane filtration

Membrane filtration is a sophisticated and widely used technique for dealing with heavy metal-polluted wastewater. It is widely utilized because of various advantages, including semi-permeability, low chemical and space requirements, and excellent adaptability (Kumar et al., 2021).

4.1.3. Adsorption

Adsorption is a term used to describe the process of different materials that are now being researched for the removal of pollutants from industrial effluent. Adsorption is widespread used because of its inexpensive cost, ease of use, and simple design. Adsorption is a physical phenomenon in which molecules cling to the surface of a solid substance through physical or chemical connections (Kumar et al.,2021). Many types of materials have been identified as having a strong potential for removing a wide spectrum of organic and inorganic pollutants, including nano, activated carbon, agro-waste ash, agro waste biochar, zeolite, micro, and meso particle, low-cost agriculture originated material, nanotubes, nanofibers, nanoparticle assisted membrane, nanocomposites, and others (biochar, activated carbon *etc*).

4.2. Chemical parameters

4.2.1. Electrocoagulation

Electrocoagulation (EC), which differs from traditional coagulation, offers a wide range of applications in wastewater treatment (Ye et al., 2016; Un et al., 2017). An EC unit is made up of an electrolytic cell that has cathode and anode metal electrodes and is tenuously connected to a direct current (DC) control source. The EC process includes cation release from the "Sacrificial electrode," hydrogen production at the cathode, and coagulant synthesis via aggregation of released cations in the system solution (Un et al., 2017; Ye et al., 2016; Lu et al., 2016; Grace et al., 2019).

4.2.2. Electrodialysis

Ionic species are commonly removed and recovered from contaminated water using the electrodialysis (ED) method. An electrostatic force generated by the electric potential between cathode and anode transports ions from a solution across an ionic membrane (Santos et al., 2019; Gurreri et al., 2020). The use of solid membranes to remove heavy metals, such as Cr(VI), has been extensively researched.

4.2.3. Electrodeionization

The electrodeionization (EDI) method eliminates ions from the solution by supplying electricity between the cathode and anode (Coman et al.,2013; Grace et al., 2019). Ion exchange and electrodialysis are combined in EDI. A hybrid approach that combined ED and ion exchange membrane resin was employed for chromium recovery (Gabli et al., 2020, Zhang et al. 2014).

4.2.4. Electrochemical reduction

Electrochemical reduction (ECR) of Cr(VI) to Cr(III) has been extensively described as the process of removal of Cr(VI) or Cr(III) from polluted wastewater. In one study, a single-chambered cell with a titanium anode was used to reduce Cr(VI) indirectly and precipitate Cr (III) (Yao et al., 2020; Hu et al., 2017). The reduction of Cr(VI) increases as the pH of the solution decreases, whereas the precipitation of Cr(III) decreases. It was also discovered that during the reaction mechanism, the Ti anode might corrode, producing Ti_2 and Ti_3, which makes a free-electron accessible for Cr(VI) reduction.

4.3. Bioremediation

Microorganisms play a significant role in regulating Cr biogeochemical activity in contaminated soil and polluted water body. Microbial remediation is the sustainable technique of eliminating Cr(VI) from wastewater and soil immobilization by sorbing, accumulating, and transforming microbial activity. Many researchers have studied the applicability of this technology to Cr(VI) contamination due to the benefit of bioremediation in terms of its low cost and low risk of secondary pollution. Cr-resistant microbes in contaminated soils or wastewater can reduce Cr toxicity through various methods. Many studies have looked into precise procedures including various microorganisms, including their capability for Cr remediation and the variables that affect the process (starting biomass, pH, and concentration). It is necessary to select certain algal, bacterial, and fungal species to apply Cr-contaminated soils and wastewater due to changes in soil type, hydrogeological circumstances, soil and water resource utilization, Cr species and concentrations, and spatial distribution in contaminated regions (Fan et al., 2018; Georgieva et al.,2020; Liu et al., 2018; Qu et al., 2020; Wong et al., 2018).

4.3.1. Bacteria

In bacteria, chromosomal resistance is achieved through mechanisms such as hexavalent chromium removal, DNA repairing, free radical detoxifying activities, and processes related to sulfur or iron homeostasis. From the perspective of bioremediation, the microbial reduction of Cr(VI) to Cr(III) is particularly intriguing because it could be regarded as a new chromate resistance mechanism. Thermus, Shewanella, Agrobacterium, Enterobacter, Deinococcus, Escherichia, Pseudomonas, Bacillus, and other species have been identified as Cr-tolerance bacteria with strong Cr(VI) removing capability. Both chromate-resistant and non-resistant strains have been shown to decrease chromate, but the latter's growth is severely hindered at higher chromate concentrations (Khoubestani et al., 2015; Kwak et al., 2015; Nemr et al., 2015). This revels that is a bacterial feature high tolerance and resistance, as well as an ability to convert Cr(VI) to Cr (III), which is particularly important for a successful bioremediation method.

4.3.2. Fungi

Fungi are a vital part of the ecosystem, organically cleansing the environment due to their saprophytic qualities. They are used in a variety of industries, including food and beverage production. Furthermore, fungi are a collection of enzymes that might be used to clean up the environment by degrading organic pollutants (Kumar and Dwivedi., 2020; Singh and Dwivedi, 2020; Deshmukh et al., 2016; Singh et al., 2019; Grossart et al., 2019). Heavy metal buildup, detoxification, mineralization, transformation, and other processes involving Cr(VI) have all been extensively documented in fungus.

4.3.3. Yeast

Yeast is mainly used in fermentation and has the potential to remove a variety of contaminants. *Saccharomyces cerevisiae* which is Baker's yeast was immobilized on mango leaves and used for Cr(VI) . Even though it was extremely effective in the removal of Cr(VI) (Kumar and Dwivedi.,2020).

4.3.4. Algae

Algae have good biological characteristics such as high photosynthetic competency and a simple structure. They can develop in many difficult ecological situations such as heavy metal presence, nutrient stress conditions, high salinity, contaminated water streams, and high temperatures. Algae has been reported to create lipid, therefore it has a dual approach in terms of wastewater treatment and biomass generation for energy production (Leong and Chang, 2020; Moussa et al., 2018).

5. Biological processes combined with conventional approaches.

5.1. Biosorption

Biosorption is a physicochemical process that happens between metal species (sorbate) and biological material that is neutral, rapid, and reversible (biosorbent) (Ahluwalia and Goyal., 2007). It is a passive process that occurs regardless of whether active or inactive microorganisms are present. Using dead biomass has several compensations versus using living cells. It does not require the addition of fertilizers, is resistant to toxicity and poor working conditions, metal recovery is easier due to treatments that allow biomass regeneration, and the biomass itself is more cost-effective as an industrial waste product. Live cells, on the other hand, can acquire metals through a variety of mechanisms, including transport and extracellular complexes. Physicochemical and metabolic absorption mechanisms are not mutually exclusive. Physicochemical and metabolic absorption mechanisms may also play a role in the process. Metal recovery in live-cell processes can be difficult, especially if the metals have been compartmentalized or internally precipitated.

5.2. Biotransformation

The biotransformation of Cr(VI) is assumed to be a detoxifying mechanism since the Cr(III) of chromium is more stable and less toxic than Cr (VI). Many researchers identified extracellular chromate reductase activity in the supernatant of microbial cultures (Dey and Paul, 2016; Rath et al., 2014). Enzymatic reduction of Cr(VI) in bacteria (such as Pseudomonas, Bacillus, and Arthrobacter) could be due to soluble cytosolic proteins or insoluble cell membrane enzymes.

5.3. Bioaccumulation

The findings from algae, fungi, bacteria, and other plant-derived biomass were classified based on their ability to actively integrate metals into their cells from aqueous solutions (Gavrilescu, 2004; Cheung and Gu, 2007; Wang and Chen, 2009; Chojnacka et al., 2010). Metal absorption by microorganisms is influenced by the initial metal concentration as well as the contact time. It is a metabolism-dependent mechanism that only occurs in living cells and necessitates the use of energy to transfer Cr(VI) across the cell membrane. Cell development is hindered by high metal concentrations. Understanding how some microorganisms accumulate Cr(VI) is important for developing contaminant concentration, removal, and recovery procedures.

6. Conclusion:-

Microbes such as bacteria, yeast, algae, and fungi are commonly found in water bodies that absorb large amounts of industrial wastewater regularly. Microbes can use hazardous heavy metals in their metabolic pathways, such as fermentation, respiration, and co-metabolism, to generate energy for growth and development. These bacteria have developed amazing methods to maintain homeostasis and resistance to heavy metals in their poisonous environment. Biosorption, bioaccumulation, and biotransformation are all mechanisms that microbes can use to thrive in metal-contaminated environments. Microbe's abilities enable them to function well as biosorbents for heavy metal cleanup. Metal ions primarily break microbial cell biological membranes; however, these microbes have defence systems that assist them to battle the damaging effects of heavy metals. Microorganisms are a cost-effective and environmentally benign way to bioremediate a metal-contaminated environment. As a result, chromate-reducing microbes that can detoxify chromium by changing the valence of Cr(VI) to Cr(III) have proven to be promising candidates for *in situ* and on-site bioremediation.

Author contribution

Deepa Kannaujiya : conceptualization, collection of review literature , data analysis and interpretation, drafting of manuscripts, editing and finalization. Shikha : reviewing, editing, finalization, supervision.

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Conflict of interest

The authors report no conflicts of interest

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