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Treatment of Industrial Waste Water Containing Heavy Metal Ions by Non-Conventional Methods

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Abstract: *Heavy metals are recognized as the most significant environmental concern, since they are a major source of wastewater pollution. Human activities and industrialization have mostly resulted in the discharge of heavy metal-containing pollutants into water resources, contaminating them and endangering the health of humans and the environment. Many studies on wastewater treatment procedures such as precipitation, evaporation, ion exchange, membrane processes, and electroplating have been done. However, these traditional methods are costly, non-renewable and produce secondary pollutants. We concentrated on biosorption in this review because it is thought to be the most promising alternative strategy for eliminating hazardous metal ions from water sources. Biosorption is a physical process that employs ion exchange, surface complexation and precipitation to use less expensive alternative biological materials as biosorbents. Various biomasses including microorganisms (bacteria and fungi), algae and plant products have been used as biosorbents for metal biosorption. Biosorption with local microbiota has inspired considerable interest in the removal of harmful heavy metals from wastewater without creating any detrimental consequences in recent years. Microorganisms, particularly fungi (both live and dead), have been recognized as a potential class of low-cost adsorbents for heavy metal ion removal in solution. The biosorption behavior of fungal biomass attracts the attention due to its numerous advantages; consequently, additional study is required to completely exploit it in wastewater treatment.*

Keywords: Wastewater, Heavy Metal, Chitosan, Adsorption, Membrane

I. INTRODUCTION

Water is the basis of all life. All living organisms, and in fact the entire ecosystem, are completely depend on the availability of water [1]. Although water is the basis of life for everyone, it is becoming an increasingly scarce and changing natural resource for millions of the world's population [2]. Concerns about water pollution are increasing day by day, because it harms people's health and well-being. Both human and natural activities have the potential to pollute water. Natural sources can be found in microbial activities, geological structures, and natural contaminants present in water supplies. On the other hand, anthropogenic causes are related to human activities such as industrial scale manufacturing process operations, agricultural fields, inappropriate waste disposal and inadequate sewage systems. They pollute water resources, endangering their safety and purity [3]. Pollution disrupts the natural balance of water and affects the environment, economy and health. Contaminants include heavy metals, chemicals, as well as microbial contaminants that damage aquatic ecosystems and render water unusable. Heavy metal pollution is a global concern [4,5]. Heavy metals, which belong to the group of high-density elements, including metals and metalloids, cause concern due to the increase in their concentration in the natural environment as a result of anthropogenic activities [6]. Most heavy metals are toxic to human life even in small amounts [7]. At concentrations higher than a few µg/l, heavy

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metals damage internal organs and tissues by affecting the normal development and functioning of organs in the human body by various mechanisms such as enzyme denaturation, ion exchange, and protein inactivation [8]. Heavy metals can cause diseases such as gastrointestinal, kidney, cardiovascular systems, including cancer, liver and kidney diseases, melancholia and osteoporosis. Heavy metal pollution can affect plant metabolism and growth [9]. Toxic heavy metals must be removed from wastewater before being released into the environment. Recently, numerous approaches have been put forward in the field of creating cheaper and more effective technologies to both reduce the amount of wastewater produced and improve the quality of treated wastewater. Recent researches include electrocoagulation (EC), adsorption using synthetic and natural adsorbents, application of magnetic field, advanced oxidation processes, membranes, etc. Attention has been paid to special methods for the removal of heavy metal ions. A complete description of heavy metal removal methods from wastewater resources has not yet been established. Therefore, the present review comprehensively and critically discusses the available technologies for efficient removal of heavy metal ions from wastewater. In addition, it should be considered that the most suitable methods are preferred based on the cleaning efficiency, chemicals/adsorbents added, initial concentration, optimum treated pH value and other processing conditions.

Heavy Metals in Wastewater:

Depending on their properties, these metals are divided into four categories: I. Toxic heavy metals (eg Hg, Cr. Pb, As, Sr, Si, Ag and Ti); II. Radioactive metals (eg Tc, U, Rn, Th, Ra and Am); III. Metabolically important metals (eg Mo, K, Ca, Fe, Ni, Cu and Zn); IV. Metal detection of biological efficacy (eg Ge, Sb, Te, Po and B) [11]. Currently, the recent research trend is more focused on the removal of type 1 and 2 metals and their reuse for various efficient purposes [12]

Currently, wastewater containing heavy metals is directly or indirectly discharged into the environment. Due to their toxicity and non-biodegradability, they tend to accumulate in the living organism and therefore can cause numerous diseases and disorders [20, 21]. Several acute and chronic toxic effects of heavy metals damage various body organs. Gastrointestinal and renal dysfunction, nervous system disorders, skin lesions, vascular damage, immune system dysfunction, birth defects, and cancer are examples of the toxic effects of heavy metals [22, 23]. Some regulations have been made to minimize the effects of hazardous chemicals on humans, other living things and the environment. This includes limits on heavy metal concentrations and the concentrations that may be present in discharged wastewater. Table 1 summarizes the acceptable limits of various heavy metals according to the requirements of the World Health Organization (WHO) and the United States Environmental Protection Agency.

Table 1: Permissible limits for various heavy metals remaining after wastewater treatment according to the requirements of the World Health Organization and the US Environmental Protection Agency (USEPA)

Heavy Metals	Permissible limits (WHO) µg/L	Permissible limit (USEPA) µg/L
Arsenic	500	
Mercury	1	0.03
Cadmium	3	10
Lead	10	6
Chrome	50	50
Nickel	20	200
Zinc	5000	–
Copper	3000	–

II. BIOSORPTION

One of these crucial processes, known as biosorption, requires a more strongly bonded solid phase (the biosorbent) and a liquid phase (often water) containing dissolved sorbed material (sorbate: metal ions) (Dhankhar & Hooda, 2011). It is regarded as a quick phenomenon of non-growing passive metal sequestration; this is the process whereby inert biological materials or materials derived from biological sources passively absorb harmful substances. Several biomaterials, including microorganisms (bacteria, mold, and yeast), algae and plant byproducts have been studied for their biosorption capabilities and indicated significant potential for metal precipitation from water (wastewater or water resources) (Petersen et al., 2005). Microorganisms such as bacteria and fungi are thought to be efficient suppliers of biosorbents (Wang & Chen, 2009). These biosorbents have metalsequestering capabilities and may be utilized to reduce heavy metal ion concentrations in solution from ppm to ppb (Abbas et al., 2014).

This efficiency is due to the makeup of the cell wall and the functional groups involved in metal binding. Many microorganisms remove heavy metals by surface adsorption, which involves metals accumulating on the cell surface and interacting with functional groups on the cell surface such as carboxyl, amine hydroxyl, phosphate and sulfhydryl groups (Das et al., 2008; Kisielowska et al., 2010). Biosorption happens under a range of physiochemical parameters such as temperature, pH and the presence of other ions. Because of its quick kinetics, it can treat enormous amounts of wastewater. Biosorption employs naturally rich renewable biomaterials that are inexpensive to create and reduce the need for extra costly chemicals, which generally cause disposal and space issues (Zaki et al., 2022).

Biosorption provides excellent selectivity for the recovery and elimination of heavy metals. Furthermore, biosorption has a cheap capital investment and operating cost, and it can handle a variety of mixed wastes and heavy metals (Aktan et al., 2013). Finally, biosorption has increased the recovery of bound heavy metals from biomass while decreasing the amount of hazardous waste created (Aksu & Dönmez, 2001). However, biosorption has two major drawbacks: metal desorption needed because of ongoing use regardless of metal value, and early saturation occurring when all metal interaction sites are used up (Tabaraki et al., 2013). The biosorbent's adsorption characteristics are uncontrollable by biology and are formed during pre-growth (Colak et al., 2011).

Biosorption Mechanism

Several methods have been reported for the biosorption-based removal of dangerous chemicals. Metabolism-dependent or -independent categories were established (Veglio & Beolchini, 1997). While, metabolic activities are required for bioaccumulation, biosorption occurs without metabolic involvement (Volesky, 2007; Chojnacka, 2010). In contrast to the active process of bioaccumulation, the passive biosorption process may be completed in a shorter amount of time. Biosorption is a multistep process that includes adsorption, chelation/complexation, ion exchange and surface precipitation (Farooq et al., 2010; Bilal et al., 2018). The biosorption mechanisms are shown in Fig. (1) and discussed as follows:

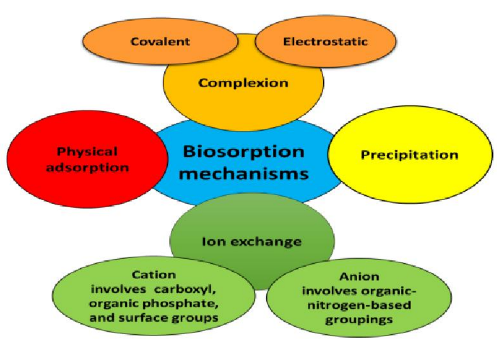

Fig1: Schematic diagram involving biomass biosorption mechanisms.

A. Ion Exchange

Different functional groups on the surface of biomass are hypothesized to facilitate ion exchange as the major mechanism of biosorption. Polysaccharides present in microorganism cell walls are metal ion exchange sites due to the

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polysaccharide's opposing charge (Chojnacka, 2010; Vijayaraghavan & Balasubramanian, 2015). Cell walls of different species have different compositions; for example, bacterial cell walls are composed of peptidoglycan; fungal cell walls are composed of chitin, and algal cell walls are composed of alginate and sulfonated polysaccharides (Bilal et al., 2018).

B. Complexation or coordination

The complexion, also known as coordination, is the process by which cations attract molecules or anions that have a free electron pair. Coordination occurs between a central atom, anions or molecules with a heavy metal cation through a ligand. A "ligand atom" is a group of basic or nucleophilic atoms. Chelation is the process of generating a complex with multidentate ligands, which are bases containing more than one ligand atom (Abdia & Kazemia, 2015). Electrostatic interaction between a polymer released by bacteria and a metallic ion chelating agent leads to complexation or coordination. Metals may be removed from the solution through complex formation on the cell surface after interacting with active groups on the cell wall, including carboxyl, amino, thiol, hydroxy, and hydroxyl carboxyl (Sag & Kutsal, 2001). Electrostatic attraction exists between electron pairs in these chelating compounds (Gahlout et al., 2021).

C. Physical adsorption

The movement of ions from a fluid to a solid state is the physical adsorption. The process, which is often fast and highly reversible, may take place at the surface due to non-specific attraction forces (such as Van der Waals forces) or due to coulombic attraction forces between charged solute species and the adsorbing phase (Javanbakht et al., 2013). Since it is metabolically independent, this approach is particularly promising for treating enormous quantities of wastewater (Gahlout et al., 2021).

D. Precipitation

During precipitation, metal ions attach to the biosorbent's surface functional groups and either remain unaffected or taken up by the microorganism. Through sorptionprecipitation, metals may accumulate as organic or inorganic metal precipitates within cells or on cell walls (AjayKumar et al., 2009). According to Ahalya et al. (2003), the metabolic changes that take place in the cell following the metal's chemical contact with the cell surface may or may not have any bearing on the onset of precipitation (Javanbakht et al., 2013).

III. FACTORS AFFECTING BIOSORPTION

Biomass and metals are only two of the many factors that play a role in biosorption processes; environmental factors also play a role (Ghosh et al., 2016). The following are the primary elements that influence the biosorption process:

1. The pH values.

The pH of a solution influences the kind of biomass binding sites and metal solubility, as well as metal solution chemistry, functional group activity in biomass and metallic competition in biosorption processes (Deng & Wang, 2012). Metal biosorption has been demonstrated to be substantially pH-dependent in nearly every system examined, including bacteria, cyanobacteria, algae and fungi. Biosorption of metals such as copper, cadmium, nickel, cobalt and zinc is typically decreased at low pH levels owing to competition for binding sites between cations and protons (Deng &Wang, 2012). Metal ion removal from solutions is minimal at pH levels below 2; when the pH rises from 3.0 to 5.0, metal absorption rises. The appropriate pH level is crucial for achieving maximal metal sorption, and as the pH value rises, so does this capacity (Oyewole et al., 2018).

2. Temperature

The temperature has a substantial impact on the sorption process (Farooq et al., 2010). Thermodynamic parameters are altered by temperature change, which affects sorption capacity (Zeraatkar et al., 2016). The best temperature range for

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biosorption efficiency is between 20 and 35°C (Aksu & Dönmez, 2001). High temperatures such as 50 degrees Celsius may occasionally improve biosorption, but they can also permanently destroy live microbes, reducing metal absorption (Ahalya et al., 2003). Adsorption increases with decreasing temperature, which is generally due to exothermic absorption events.

IV. CONCLUSION

Without treatment, industrial wastewater is harmful to the environment. Because heavy metal ions are toxic substances discharged into the water, they must be removed from mining and other industrial effluents. Because traditional removal processes are costly, it is vital to seek low-cost, ecologically friendly substitute solutions. According to the aforementioned literature analysis, biosorption is the most cost-effective, economical, and ecologically acceptable way of eliminating heavy metals from home and industrial wastewater. Several biological materials can be used as heavy metal biosorbents. Microbial biomass is one of the most cost-effective and feasible methods of eliminating heavy metals from environmental solutions. Fungal biomass is as good as or better than other microbial adsorbents for the removal and recovery of metals from wastewater due to its greater flexibility under prolonged exposure to contaminants, and it can be easily recovered and reused. Some fungi can survive and thrive in environments with high levels of hazardous metal ions. The removal of metals over a broad pH and temperature range is one of the most attractive aspects of the fungal biosorption process. Fungi may interact with heavy metals via a variety of chemical forces due to the huge number of polysaccharides, proteins, and large functional groups in the fungal cell wall. As a result, future studies should focus on discovering and analyzing the potential of fungi that can tolerate high levels of hazardous metals for use in biosorption studies, which might replace current metal-removal methods. Consequently, biosorption technology gains advantages over traditional approaches and grows in popularity.

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