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Hazardous Consequences and Management of Heavy Metals in Sewage Sludge: An Overview

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Abstract: ***Natural substances called heavy metals (*****HMs*****) can build up in the environment over time and are dangerous even in small amounts, posing a danger to the ecosystem and human health. Certain metals can infiltrate the wastewater treatment system and eventually accumulate in the sludge produced during the treatment process. Due to its interaction with industrial and household effluents, sludge, a by - product of sewage water treatment, is known to contain significant quantities of toxic metals. Sludge can contain*** **HMs** ***from several sources, such as industrial discharges, domestic wastewater, and agricultural runoff. In this review, the presence of*** **HMs** ***in sludge, and several treatment methods, consisting of physical, chemical, and biological processes have been developed, as have the regulations and guidelines controlling their disposal and usage were discussed. The selection of an appropriate treatment procedure, on the other hand, is dependent on the individual features of the sludge and the target metals. Sludge, if not managed properly, may leach*** **HMs** ***into the environment, damaging water, soil, and food crops. Proper*** **HMs** ***management in sludge is critical for reducing environmental and health concerns and promoting long - term sustainability.***

Keywords: HMs, sludge, toxicity, wastewater treatment, regulatory bodies

1. Introduction

The deposition of suspended solids during sewage treatment operations results in the semisolid residual material known as sewage sludge [1]. Sludge from various industries contains organic chemicals, trace metals, micronutrients, macronutrients, microbes, organic micro - pollutants, and parasitic organism eggs [2]. Although adding nutrients and organic matter to the soil using sewage sludge may be advantageous, the presence of pathogens, HMs, and other pollutants makes this practice risky [1]. Out of which HMs are metallic substances having relative densities equal to or greater than that of water [3]. With the expansion of industry and human activity, HMs have become more common in wastewater. Examples include the plating and electroplating industry, herbicides, power sources, silk industry, mining sector, Bioreactors with fluidized beds, metal rinsing procedures, tanning industry, the industry of metal smelting, textile sector, paper manufacturing, petrochemicals, and electrolysis applications. They are non - biodegradable and may cause cancer [4], [5]. Also, HMs migrate through the water - soil contact and the water - atmosphere interface [6]. Therefore, HMs poisoning of the environment from Sediment with untreated wastewater from numerous sectors is a global environmental hazard [7]. Figure 1 depicts the primary sources of distinct HMs ions.

Figure 1: Numerous sources of HMs in sludge

HMs over permitted limits frequently have negative impacts on people, other creatures, and the environment [8]. Particularly in developing nations, wastewater containing HMs ions such as As (III) /AS (V), Pb (II), Cd (II), Ni (I), Cr (III) /Cr (VI), Zn (II), Cu (II), Hg (I) /Hg (II), and Co (II) is increasingly discharged directly or indirectly into streams, lakes, rivers, or oceans [9]. The two most reliable international organizations, the WHO and United States Environmental Protection Agency (USEPA), have determined somewhat different values for the maximal contamination measure or permitted limitations of several HMs ions in drinking water. The US EPA and World Health Organization (WHO) rank arsenic (As) as the highest - priority hazardous element. The WHO and several environmental protection organizations established the acceptable threshold for drinking water at 0.01 mg/L. The USEPA has nonetheless designated Pb as a priority contaminant. The highest permissible contamination level (MCL) of lead ions in drinking water has been established at a very low level of 0.015 mg/L although the WHO specifies a limit of 0.05 mg/L. [10] - [12]. However, the WHO recommends safe Pb levels of 0.01 and 0.1 ppm in agricultural soils and wastewater, respectively [13]. The permitted limit of Cr (VI) for drinking water is 0.05 mg/L and 0.1 mg/L for industrial effluents released into surface water, respectively [11], [14].

The USEPA has set a 2 ppb maximum limit for Hg (II) in drinking water and has categorized mercury as a priority contaminant [10], [12], However, the WHO recommends 0.001 parts per billion (ppb) of mercury in wastewater and soils for agricultural use [15] and 0.05 ppm [16]. Further, USEPA has designated cadmium (Cd) as a potential human carcinogen and raised the acceptable drinking water level to 0.005 mg/L [10] - [12], slightly different from the WHO has established 0.003 ppm as the acceptable limit for Cd in agricultural soils and wastewater [17].

The maximum allowable level of zinc ions in drinking water is set at 5.0 mg/L by the WHO and USEPA. Additionally, the USEPA considers 1.3 mg/L to be the maximal allowable Cu ion content in drinking water, although the WHO recommends 1.5 mg/L [10], [12]. Drinking water, inland surface water, and irrigation water all have cobalt acceptable limits of 1, 0.05, and 0.01 mg/L, respectively. The maximum allowable content of nickel (Ni) in industrial discharge effluent is 2 mg/L, but it should be less than 0.1 mg/L in drinking water, according to WHO rules [10]. Hg, Cd, and Pb are a few of the HMs that have gained more attention in recent years [18]. Moreover, the Complete Ecological Remediation Compensation and Liability Act (CERCLA) states that the maximum permitted concentrations of certain HMs in water were 0.01, 0.05, 0.01, 0.015, 0.002 and 0.05 mg/L for Ar, Cd, Cr, Pb, Hg and Ag, respectively [19].

2. Obstacles due to the presence of HMs in sludge

The ecological balance of the aquatic environment can be negatively impacted by HMs pollution entering rivers, and the variety of aquatic life is constrained as pollution levels grow [20]. The natural processes and anthropogenic contribute significantly to the build - up of HMs in water. Other natural causes of HMs contamination in water include water - rock contact, water interaction with soil, and wet and dry deposition of air salts. However rapid urbanization and industrialization are examples of human drivers of water contamination [21]. HMs are naturally present in the soil, but geologic and human processes raise their concentration to detrimental levels to both animals and plants [22]. The presence of HMs in surface and sub - surface water pollutes soil, and contamination increases when mined ores are left on the ground surface for hand dressing [23]. It has been demonstrated that HMs contamination hurts agricultural plant physiological functions. They frequently resulted in decreased dry matter build - up and plant growth. Moreover, high HMs deposition in agricultural soils frequently causes substantial HMs absorption by crops, endangering the quality and safety of food [24]. Direct intake or contact with polluted soil, the food chain, drinking contaminated groundwater, phytotoxicity, reduced food quality, decreased land usability for agricultural production leading to food insecurity, and issues with land tenure, HMs contamination of soil may pose risks and hazards to the ecosystem and humans [25], as illustrated in Figure 2.

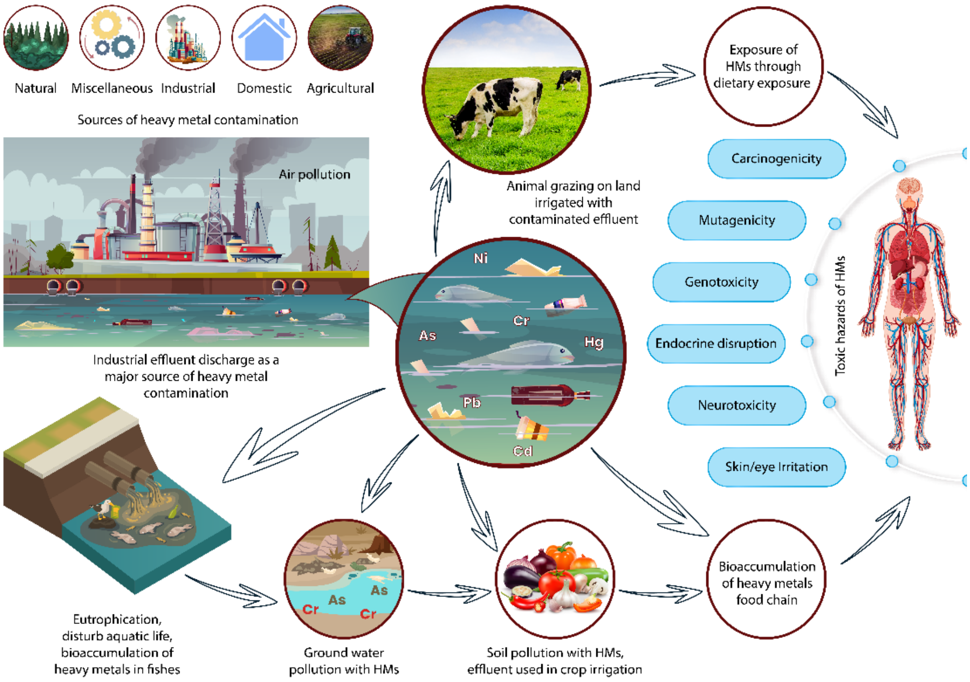

Figure 2: Various issues due to presence of HMs in sludge

Modeling of risk assessment is broken down into four stages: evaluation of exposure, evaluation of toxicity (dose - response), evaluation of hazards, and evaluation of risk. Humans are exposed to HMs in three different ways: directly by ingestion, inhalation through the mouth or nose, and absorption through exposed skin [26]. The HMs often enter the body by cutaneous absorption and ingestion after being exposed to water. For each identified route, the average daily dosage of contaminants is assessed to determine exposure. Reference doses (RfD) for noncarcinogenic chemicals are established using a dose - response analysis, whereas slope factors (SF) for carcinogenic substances are derived using the USEPA's Integrated Risk Information System (IRIS) database [23]. HMs consumption has frequently been associated with a variety of health issues, including intrauterine development abnormalities, immunological compromise, nutritional deficiency, altered psychosocial behavior, and many more [27]. HMs poisoning in the human body reduces energy levels, interferes with brain function, and interferes with the functioning of several various organs, including the liver, kidneys, lungs, and brain, in addition to affecting blood composition. The physical, neurological, and musculoskeletal functions may be hampered if exposure to HMs is prolonged. Also, because of conditions including Parkinson's disease, muscular dystrophy, Alzheimer's disease, and multiple sclerosis. Prolonged exposure to some HMs and their compounds may potentially result in the development of cancer [28]. Minamata, an organic mercury poisoning illness, is brought on by the presence of several HMs. These HMs pose a risk to both the animals and human population that drink the water when they bioaccumulate in the water [29].

3. Role of various regulatory bodies for the management of HMs in sludge

The presence of HMs in sludge endangers both human health and the environment. A lot of regulatory agencies throughout the world are looking at the detrimental consequences of HMs in sludge. The European Union has adopted several rules and directives about the usage and disposal of sludge [30]. For instance, the Water Framework Regulation of the EU places restrictions on the amount of HMs that can be incorporated into sludge before it is applied to agricultural land [31]. To use wastewater, including sludge, safely in agriculture, the WHO has established guidelines. The highest level of HMs in sludge that can be spread on land is constrained by these regulations [32]. For the usage and disposal of sludge in Canada, the Canadian Council of Ministers of the Environment has published recommendations. The maximum amounts of HMs in sludge that can be spread on agricultural land are constrained by these regulations [33]. The United States Environmental Protection Agency has made provisions for the management and disposal of hazardous wastes, including sludge, across the country. The maximum quantities of HMs in sludge that can be applied to land are regulated by these rules [34]. Occupational safety and health is the responsibility of the Occupational Safety and Health Administration. To safeguard employees who, handle HMs - containing sludge, the government has issued restrictions [35]. The Department of Agriculture is in charge of regulating the application of sludge as fertilizer. The agency has set laws and recommendations for the use of sludge in agricultural areas to ensure the preservation of human health and the environment [36]. The maintenance of public health is the responsibility of the Department of Health and Human Services. To safeguard the public's health, the agency has prepared recommendations for the secure processing and disposal of HMs - containing sludge [37]. In India, the Ministry of Environment, Forest and Climate Change has set rules for the management and disposal of sludge, including restrictions on the levels of HMs that can be applied to agricultural land. The management of environmental concerns within each state has been delegated to State environmental agencies. For the management of HMs in sludge, they are in charge of implementing federal laws and guidelines as well as drafting state - specific regulations and standards [38].

HMs have several harmful impacts on living organisms, especially when consumed in quantities greater than those recommended by different regulatory bodies [39]. Nonetheless, governments of industrialized nations continue to present potential strategies for preventing and resolving HMs pollution through various regulatory organizations [40]. Almost 80% of the world's wastewater, according to UN Environment, is dumped into the environment without being treated, damaging lakes and rivers as well as fields where plants thrive [41]. These are only a few instances of regulatory agencies from different countries striving to address the negative effects of HMs in sludge. For handling and disposing of sludge, each nation and area may have its unique laws and regulations. To safeguard both human health and the environment, several regulatory organizations collaborate to guarantee the secure management, transportation, and disposal of sludge containing HMs [39].

4. Global awareness of the detrimental effects of HMs

Natural elements having a high density and atomic mass are known as HMs [42]. Iron, copper, and zinc are a few HMs that, in lower amounts, are necessary for life [43]. Some HMs, such as mercury, lead, and cadmium, are poisonous to people and can harm them severely even at low exposure levels [42]. As industrialization and human activities cause the discharge of HMs into the environment, HMs pollution has become a global issue [44]. These harmful chemicals can build up and endanger the ecosystem and human health by getting into the air, soil, water, and food [45]. Many health issues, including diabetes, neurotoxicity, asthma, inflammation, abnormalities of development and reproduction, and even cancer, can be brought on by HMs exposure [46]. Because their bodies are still growing and more susceptible to the toxic effects of these chemicals, children and pregnant women are more vulnerable to the negative effects of HMs [47].

HMs contamination is a significant issue in many regions of the world. For instance, industrialization and quick economic development in China have caused significant water and air pollution, with elevated levels of HMs including cadmium, chromium, arsenic, cobalt, copper, mercury, lead, nickel, and zinc in the environment [48]. With high levels of lead, mercury, and chromium in the water, air, and soil in India, HMs pollution from sectors like mining and metallurgy is a problem [49]. HMs pollution has spread throughout most of

Africa as a result of mining and industrial activities, with high quantities of lead and mercury found in soil, water, and food [50]. Over the world, initiatives are being taken to minimize pollution and spread knowledge of the negative consequences of HMs. People are being urged to take action to lessen their exposure to these harmful compounds as governments and organizations develop legislation and policies to restrict the discharge of HMs into the environment. For instance, people can opt to consume foods cultivated in regions with low levels of HMs contamination and refrain from using goods that contain HMs, such as lead - based paint. People, communities, and governments must work together to address HMs pollution and protect both human health and the environment from the detrimental effects of these toxic substances.

To mitigate the negative impacts of HMs in the environment and safeguard public health, India has adopted several actions. The Indian government has put laws in place to restrict the leakage of HMs into the environment. For instance, the National Ambient Air Quality Standards (NAAQS) established by the Ministry of Environment, Forest, and Climate Change specify the highest levels of HMs that are permitted in ambient air [51]. Similarly, to manage the processing, storage, and disposal of hazardous waste including HMs, the Central Pollution Control Board issued the Hazardous Waste (Management and Handling) Regulations, 1989, and, the Water (Prevention and Control of Pollution) Act, 1974 [52]. To track the ambient air quality across the nation, including the concentrations of HMs, the Central Pollution Control Board developed the National Air Quality Monitoring Programme (NAMP) [53]. Similar to this, the National Water Quality Monitoring Project (NWQMP) monitors the levels of toxic substances in the rivers and other water bodies of India [54]. The Government has started several awareness initiatives to inform the public of the dangers of HMs exposure and how to minimize it. For instance, the National Programme for Prevention and Control of Cancer, Diabetes, Cardiovascular Diseases and Stroke (NPCDCS) which includes education programs on the negative effects of HMs was introduced by the Ministry of Health and Family Welfare [55]. In India, studies on the negative consequences of HMs and the sources of their emission have also been supported by the government. For instance, the Ministry of Environment, Forest, and Climate Change has financed research on the causes of lead contamination in Indian towns and studies on the effects of HMs on human health [56]. In general, India has taken a variety of steps to lessen the harmful effects that HMs have on the environment and human health. To successfully manage and lessen the country's HMs pollution, additional efforts must be made.

5. Multiple techniques used for the degradation of HMs in sludge

To remove HMs ions from diverse wastewater sources, numerous documented procedures have been developed. These techniques may be divided into adsorption, chemical, electric, membrane, and photocatalytic - based categories. The chemical, physical, and biological processes can all be used to break down HMs in sludge (see Figure 3). Chemicals and HMs ions interact to form precipitates that are insoluble during the chemical precipitation process. Filtration or sedimentation can be used to separate the developing precipitates from the water. After that, the treated water is decanted and properly released or recycled [57]. HMs are removed from the sludge using ion exchange resins. To remove contaminants from the sludge, the resins are made to preferentially bond with them [58]. Using an electric current to encourage the oxidation or reduction of HMs in the sludge and the production of non - toxic chemicals is known as an electrochemical treatment. The HMs are drawn to an electrode by the electric current, where they may be extracted [59]. In an oxidation and reduction process, HMs in the sludge are reduced or oxidized to generate less harmful forms using chemicals like hydrogen peroxide, ozone, or potassium permanganate [57]. To eliminate HMs particles, sludge is filtered by running through a filter [60]. The centrifugation entails spinning the sludge at a high speed to extract the HMs from the remaining sludge [61]. Heat the sludge to a high temperature during thermal treatment to make the HMs evaporate and leave behind a non - toxic residue. Using thermal techniques such as burning is a viable option [62]. Microorganisms are used in bioremediation to break down HMs in sludge. According to the variety of microbial agents used, this can be accomplished under either aerobic or anaerobic circumstances. These microbes are capable of transforming HMs into less harmful forms [63]. Plants are employed in the phytoremediation process to take the HMs out of the sludge. The plants absorb the HMs through their roots, where they are then stored in their tissues and prepared for harvest and disposal [64].

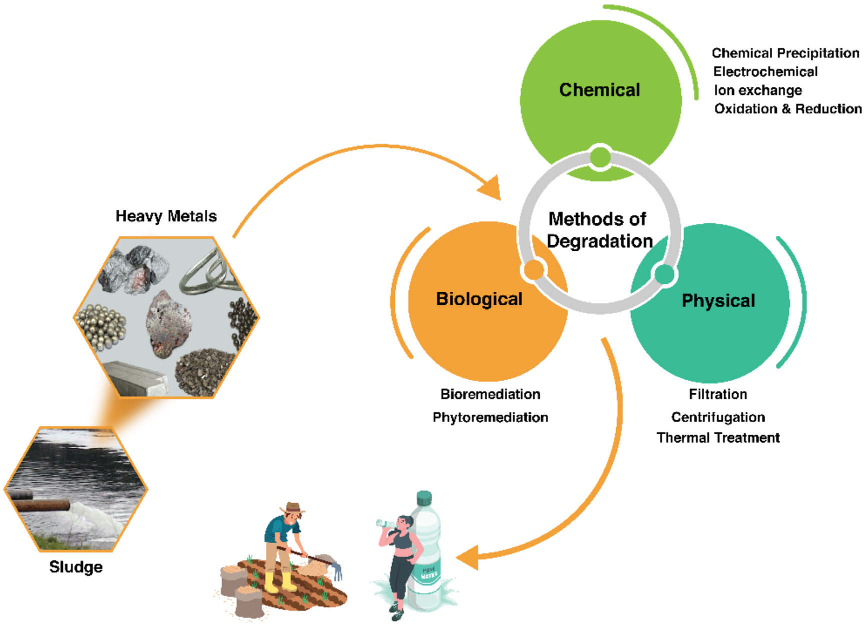

Figure 3: Different methods for HMs degradation in sludge

The best approach will depend on the particular circumstances and the kinds of HMs found in the sludge. Each of these strategies has benefits and drawbacks. Generally, the approach used will rely on the kind and quantity of HMs in the sludge as well as the environmental laws controlling its disposal.

6. Effectiveness of various methods used for HMs removal in sludge

Many industrial and municipal wastewater treatment operations can produce sludge that can assemble HMs. HMs may endanger both human health and the environment if they are not properly controlled. As a result, HMs are removed from sludge using a variety of techniques [65]. The category and concentration of the HMs, the features of the sludge, and the treatment objectives can all affect how successful these approaches are. Chemical precipitation is the process of adding chemical agents to the sludge to create insoluble metal hydroxides that may be removed by sedimentation or filtering. HMs including lead, chromium, and mercury can be eliminated with this technique [66]. Ion exchange involves substituting alternative ions that have a greater affinity for the exchange resin for the HMs ions in the sludge. With this technique, HMs including copper, cadmium, and zinc may be effectively removed [23]. To bind the HMs ions in the sludge, adsorption is used. Activated carbon, zeolites, and other organic or inorganic substances can be used as adsorbent materials. HMs including lead, cadmium, and mercury may be successfully removed with this technique. By utilizing a semi - permeable membrane, HMs ions are separated from the sludge during membrane filtration. The membrane might be reverse osmosis, microfiltration, or ultrafiltration membrane. With this technique, HMs including arsenic, chromium, and nickel may be effectively removed [59]. In biological treatment, the HMs in the sludge are biodegraded or immobilized utilizing microorganisms [67]. HMs removal with this technique may be successful for removing cadmium, lead, and zinc. The efficiency of various techniques for removing HMs from sludge might also differ based on several variables. To accomplish the specified treatment objectives and guarantee the safe disposal or reuse of the sludge, a mix of these techniques could be required.

7. Degradation mechanism of HMs in sludge

Depending on the treatment process, several HMs removal mechanisms can be applied in sludge. Chemical precipitation entails introducing chemicals like sodium hydroxide, lime, or ferric chloride to the sludge. Insoluble metal hydroxides are created when HMs ions in the sludge undergo chemical reactions. These hydroxides can then be filtered or sedimented out of the water. The process that separates the HMs from the sludge involves the creation of a solid precipitate [68]. Ion exchange entails replacing the HMs ions in the sludge with ions that have a greater affinity for the exchange resin. The HMs ions are drawn to the ion exchange resin by electrostatic forces. Adsorption is the process of employing adsorbent materials to bind HMs ions in the sludge. In the procedure, hydrogen bonds, van der Waals forces, or ion exchange are used to chemically or physically attach the HMs ions to the surface of the adsorbent material [23]. In membrane filtration, the HMs ions are separated from the sludge using a semi - permeable membrane. The mechanism is the size exclusion of the HMs ions from flowing through the membrane pores [69]. In biological treatment, the HMs in the sludge are biodegraded or immobilized by microorganisms. The mechanism at play is the metabolic activity of the microbes, which can convert the HMs ions into less harmful forms or immobilize them within the biomass. Moreover, the methodology utilized to remove HMs from sludge might differ depending on the kind of treatment used and frequently involves interactions between the treatment agents and the HMs ions in the form of physical, chemical, or biological processes [70].

8. Limitations of various methods used for HMs degradation in sludge

For the degradation of HMs in sludge, a variety of techniques are utilized, and each technique has advantages and disadvantages. The addition of chemicals in sludge to create insoluble metal hydroxides that can be easily removed from the sludge, such as lime, ferric chloride, or alum, is called aqueous precipitation [71]. The primary drawback of this approach is that it can only get rid of metals that produce insoluble hydroxides, and it might not work for all HMs. Adsorption is the process of removing HMs from the sludge by utilizing substances like activated carbon, zeolites, or chitosan [59]. The primary drawback of the bioremediation method is that the microbes may need a long time to break down the HMs, and environmental variables like temperature, pH, and oxygen supply may have an impact on how well they work [72]. Using an electric current, HMs in the sludge are removed by electrochemical treatment. The primary drawbacks of this approach, however, include the possibility that it may not work for all HMs and the potential energy input [57]. The main disadvantage of the thermal approach, however, includes the possibility that it may not be efficient for all HMs, the potential energy requirements, and, emissions of greenhouse gases [73]. Ion exchange uses substances like resins to convert HMs ions in the sludge into lighter ions like sodium or hydrogen ions. The drawback of this approach is that not all HMs may be removed using it, and the ion exchange materials may saturate and need to be changed [74]. When selecting a remediation strategy for HMs in sludge, it is crucial to thoroughly consider the inadequacies and disadvantages of each approach.

To remove HMs from hazardous or polluted territory, a variety of clean - up approaches have been proposed and put into operation employing chemical, physical, and biological methods. The most often used traditional processes are excavation and landfilling [75], ion exchange, precipitation, hydrolysis, electrolytic technologies, leaching, chemical extraction, and polymer microencapsulation. Nevertheless, these methods are costly, sometimes impractical, and they don't specifically target metal - binding characteristics. However, the creation of hazardous waste, the high reagent need, and the unpredictable process of metal ion removal highlight some of the disadvantages of these processes. The majority of these approaches are worthless when the concentration of metal in the solution is less than 100 mg/L [19]. These physio - chemical methods are expensive, may not always be feasible, and also have general metal - binding characteristics [75].

9. How to improve the limitations of various methods used in HMs degradation?

The various approaches used to degrade HMs in sludge have several restrictions and downsides. The production of secondary pollutants is one of the primary drawbacks of chemical precipitation. The generation of secondary pollutants should be reduced by optimizing the pH, temperature, and dose of the chemical reagents in this technique [66]. The removal of HMs can also be improved further by adopting advanced oxidation processes (AOPs) [76]. Electrochemical therapy has a drawback in that it uses a lot of energy [77]. Using inexpensive electrodes and optimizing the electrode spacing and current density to lower energy usage are suggested ways to enhance this approach [78]. Also, the price of electrochemical treatment can be substantially reduced by utilizing alternative energy sources like solar or wind power [79]. The HMs sluggish rates of breakdown, particularly in sludge matrices with complex compositions, can be a barrier to bioremediation [67]. It is recommended to utilize genetically altered microorganisms with a stronger affinity for HMs to enhance this approach [80]. The effectiveness of the degradation can also be improved by adjusting the culture conditions, such as temperature, pH, and nutrient content. The poor adsorption capacity of the adsorbent materials is what restricts adsorption. It is advised to change the adsorbent material's surface to raise its surface area and boost its adsorption capability to improve this approach. The cost of the adsorption process can also be decreased by employing inexpensive and easily accessible materials, such as agricultural waste or industrial by - products. Fouling, which can decrease the permeate flux and raise energy costs, is one of the primary disadvantages of membrane filtering. It is advised to employ anti - fouling membranes or change the feed solution to lessen fouling to enhance this procedure. Furthermore, the efficiency of the membrane filtering process may be improved by modifying operational parameters such as pressure, flow rate, and temperature. Overall, using low - cost, locally accessible materials and exploring novel technologies like AOPs or genetically modified microbes are crucial to reducing the shortcomings and limits of these procedures.

10. Conclusion and Future Perspectives

The HMs poisonous nature and potential for harm to both human health and the environment make their presence in sludge a major cause for worry. Sludge is a useful resource for soil amendment and fertilizer, but it's crucial to properly control its HMs level to avoid contamination. By enacting stronger laws and recommendations for sewage water treatment plants, attempts have been made in recent years to lower the quantities of HMs in sludge. Research has also concentrated on creating cutting - edge HMs removal and sludge treatment methods. The employment of alternative treatment techniques including phytoremediation, bioremediation, and nanotechnology is one of the future options for handling HMs in sludge. Where bioremediation employs microorganisms to break down or detoxify contaminants, phytoremediation uses plants to absorb and eliminate HMs from polluted soil. Whereas, by adsorption or other methods, HMs may be removed from sludge using nanotechnology. Managing HMs in sludge is a constant problem, but with sustained study and innovation, there is promise for more efficient and long - lasting solutions to safeguard both human health and the environment.

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Conflicts of interest

The authors declare that there is no conflict of interest.

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