Review of Literature

2. Introduction:

Urbanization is rapidly accelerating in low-income countries, leading to overpopulation in cities within little- and lower-middle-income regions [12]. This surge, driven by population growth, industrialization, and changing lifestyles, has exacerbated the issue of solid waste management, with most waste currently being disposed of in open pits or landfills [11]. Due to underdeveloped waste management systems, many sites in these regions have become heavily polluted over recent decades. Urban ecosystems face significant risks of soil and water contamination from the toxic effects of salinity, heavy metals, and organic pollutants found in old landfills [8]. Additionally, the recycling and disposal processes can release hazardous substances, threatening public health and the environment.

2.1. Landfill leachates:

Landfill leachates, formed when rainwater percolates through waste dumps, are major contributors to groundwater pollution, posing significant threats to groundwater quality [2]. These leachates can leach large quantities of toxic metals, contaminating soil, surface water, groundwater, and sediment. Heavy metal contamination of agricultural soils near landfill sites has become a global environmental concern [13]. A study by Bora et al. (2020) on a specific landfill site revealed severe soil contamination with cadmium (Cd) and lead (Pb), with ecological risk indexes indicating a high potential ecological impact for Cd and a low to moderate impact for Pb. Furthermore, metals such as chromium (Cr), lead (Pb), nickel (Ni), and cadmium (Cd) were identified as potentially carcinogenic to both children and adults, although no significant non-carcinogenic risks were detected for the analysed metals [10].

2.2. Types of pollutants in leachate and its pollution indices:

Heavy metals such as cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), and copper (Cu) accumulate in soil, changing its chemical composition and increasing the risk of groundwater contamination [5]. Numerous studies have demonstrated the detrimental effects of heavy metals on human health in a number of different ways with kids being more vulnerable to such effects [10,6,9]. In order for local municipal governments to take the appropriate measures, it is vital to evaluate the potential health hazard posed by heavy metals in soil and ground water of landfill sites. Thus, for the reasons stated above, it is vitally important to observe the hazardous metal contents in the nearby environments (water and soil) of landfill sites to prevent the detrimental effects to human population. Effective monitoring and assessment of soil and groundwater heavy metal contamination, as well as quantifying vulnerable zones for preventive measures, rely on the use of pollution indices. These quality indices are simple scientific systems for categorizing the quality of soil and water. The Heavy Metal Pollution Index (HPI) is a tool used to estimate the degree of heavy metal pollution in a water body [3]. Another method, the Contamination Index (CI), summarizes the overall consequences of water pollution [1]. Additionally, the Heavy Metal Evaluation Index (HEI) was developed to provide a comprehensive assessment of the presence of heavy metals in water bodies, similar to the HPI and CI [4]. For quantifying soil pollution, tools such as individual indices and complex indices utilize metal concentrations in soils and reference data from literature. In this study, the Leachate Pollution Index (LPI) is used to estimate the leachate contamination potential of landfill sites. This quantitative tool allows for the uniform reporting of leachate pollution data from landfill sites [7].

2.3. Effects of heavy metals on human health:

Major sources of heavy metal introduction into the environment are industrial processes, automobile emissions, mining activities, battery manufacturing, fossil fuels, metal plating, and electronic industries. The extensive use of chromium (Cr) in leather tanning, metallurgy, electroplating, and other industries has resulted in the subsurface release of aqueous chromium at numerous sites. An appropriate concentrations of metals like chromium (Cr), nickel (Ni), and zinc (Zn) are vital to a variety of biochemical and physiological functions in plants and animals. Thus, they form essential components of numerous critical enzymes and are involved in a variety of oxidation-reduction processes [40]. However, presence of heavy metals above threshold values negatively impacts plant and human health. Lead (Pb), classified as prevalent toxic metal with potential to impact the environment and cause health problems, is known to enter the food chain through drinking water and crop irrigation. The bones are predominant sites of Pb accumulation in the human body, thus engendering haematopoiesis and anaemia, in addition to being neurotoxic and carcinogenic. Cd which gains access through inhalation can potentially elicit chromosomal abnormalities, apart from being mutagenic and teratogenic. High doses of Ni is implicated in nephrotoxic and carcinogenic activities; besides causing diseases of the cardiovascular and central nervous system [33,35]. Environmental exposure to Chromium (Cr-VI)-containing substances has been linked to multi-organ toxicity in humans, including kidney impairment, allergy and asthma, and respiratory cancer [33,35]. For estimation of heavy metals in our study, inductively coupled plasma mass spectrometry (ICP-MS) was chosen from the available technologies, to enable detection of low levels of chemicals found in water samples [33].

Table.2.1. Comparison between different countries metal contamination of landfill leachate, soil and ground water

Country	Sample type	Metal concentration								References
		Pb	Cd	Ni	Cr	Cu	Zn	Mn	Co	
Nigeria	Leachate	3.00±1.04	7.12±4.80	2.42±2.31	1.50±0.91	NA	23.88±14.40	NA	NA	[62]
	Soil	1.89±0.79	0.29±0.36	0.63±0.45	4.19±3.37	NA	0.22±0.39	NA	NA	[62]
Western Saudi Arabia	Leachate	0.029	0.029	0.697	1.503	0.048	110	73.08	1.681	[63]
	Ground water	0.027±0.047	0.004±0.006	0.006±0.011	0.064±0.032	ND	0.061±0.101	0.007±0.028	0.013±0.023	[63]
	Soil	4.52±5.45	0.1±0.16	16.82±7.69	16.16±8.27	20.44±7.08	69.13±25.6	164.73±46.65	9.3±4.47	[63]
Southwest-Nigeria	Ground water	0.05 ± 0.01	0.04 ± 0.01	0.03 ± 0.02	0.02 ± 0.01	0.05 ± 0.03	0.08 ± 0.04	NA	NA	[65]
	soil	0.66 ± 0.04	0.43 ± 0.02	0.29 ± 0.02	0.37 ± 0.03	0.89 ± 0.04	1.05 ± 0.06	NA	NA	[65]
China	Soil	52.22±9.09	32.85±0.73	28.98±7.5	68.51±13.96	32.85±10.95	110.77±33.4	NA	NA	[66]
Turkey	Soil	6.93±3.7	0.56±0.47	67.04±67.86	58.54±50.66	36.55±15.64	36.14±11.85	NA	8.63±5.59	[66]
Iran	Leachate	2.17	0.32	3.36	NA	0.37	NA	1.95	NA	[67]
	Soil	1.02	0.07	2.83	NA	0.86	NA	33.92	NA	[67]
Gurugram, India	Ground water	0.023	0.029	NA	NA	0.4	0.25	0.288	NA	[67]
Kerala, India	Soil	2.86	0.569	0.539	0.321	4.659	5.721	1.809	NA	[64]
	Ground water	<0.001	<0.001	<0.001	<0.001	0.002	0.11	<0.001	NA	[64]
Assam, India	Soil	4.053±0.990	0.021±0.010	1.888±0.170	3.86±0.27	3.564±0.712	9.091±1.333	62.868±21.436	0.779±0.115	This study
	Ground water	0.0570.025	ND	0.260±0.026	0.36±0.03	0.230±0.026	4.318±4.217	40.015±65.643	0.177±0.045	This study
	Leachate	1.737±0.636	0.007±0.006	3.387±0.933	20.89±3.77	9.051±6.206	6.769±1.528	125.930±11.402	5.788±1.278	This study
WHO	Drinking water	0.01	0.005	NA	0.1	1.5	5	NA	0.01	
	Soil	0.3-10	0.01-0.7	0.1-5	0.002-0.2	1_-12	12_-60	NA	NA	
	Waste water	0.01	0.003	0.02	0.05	NA	NA	NA	NA	
US EPA	Drinking water	0.015	0.005	NA	0.05	1.3	5	NA	NA	
	Soil	200	0.48	72	11	NA	NA	NA	NA	
	Waste water	0.006	0.01	0.2	0.05	NA	NA	NA	NA	
India CPCB	Inland surface water	0.1	2	3	0.1	NA	NA	NA	NA	

2.4. Effects of heavy metals on seed germination:

Heavy metal contamination significantly reduced seed germination and plant growth. Soil remediation procedures should be utilised to reduce heavy metal contamination in soil to increase seed germination and plant growth [14]. Cadmium's impacts on seed germination and seedling growth in rice were investigated in a study. Cadmium significantly decreased seed development and germination. To increase rice seed germination and seedling growth, the authors advise using soil management practises to reduce cadmium pollution in soil [19]. Another study looked at how lead affected mung bean seed development and germination. Lead significantly affected seed germination and early seedling growth. The authors recommend that lead contamination in soil be monitored and minimised to promote seedling development and germination in mung bean [20]. One study found that chromium affects tomato seed germination and seedling growth. The authors discovered that chromium significantly decreased seed germination and seedling growth. To increase tomato seed germination and seedling growth, the authors advise using soil management practises to limit chromium contamination in soil [21]. Copper was found to have some effect on cucumber seedling development and germination in another investigation. The authors discovered that it had a significant impact on seed germination and seedling growth. The authors advocate employing soil management practises to decrease copper pollution in the soil to promote seedling development and germination in cucumber [15]. Seed germination is an important process that is influenced by several environmental factors, including the presence of leachate in the soil. Leachate is a liquid that forms when water flows over landfill rubbish, and it contains a variety of organic and inorganic chemicals that may inhibit seed germination. The study made use of petri dishes loaded with filter paper that had been saturated with either pure water or varying amounts of landfill leachate. They discovered that in the presence of landfill leachate, the percentage of germination and root and shoot lengths of cowpea seeds were significantly reduced, with larger amounts of leachate having a greater inhibitory effect [18]. Similarly, one study investigated the effect of municipal landfill leachate on wheat seed germination and growth (*Triticum aestivum L.*). The researchers employed petri dishes containing filter paper that had been wet with varied concentrations of leachate to determine that leachate dramatically lowered the germination percentage and root and shoot lengths of wheat seeds, with larger concentrations of leachate having a bigger inhibitory effect [16]. Another study looked at the effect of municipal landfill leachate on maize seed germination and growth (*Zea mays L.*). The researchers used petri dishes with filter paper moistened with either distilled water or different concentrations of leachate to discover that leachate significantly reduced the germination percentage and root and shoot lengths of maize seeds, with higher concentrations of leachate having a greater inhibitory effect [17].

2.5. Treatments for remediation of heavy metals:

Leachate treatment is crucial because it eliminates pollutants, safeguarding the environment and the general public's health. A variety of methods, including coagulation, chemical precipitation, reverse osmosis, membrane filtration, photo-remediation, ion exchange, and adsorption, have been developed for the removal of heavy metal pollution in order to minimize its adverse impacts. There are several reasons why maintaining the cleanliness of our water is crucial: fisheries, habitats for wildlife, leisure activities, quality of life, and health concerns. As a result, there is a lower chance of water contamination and the development of diseases that affect the water, conserving the ecology and natural resources.

2.6. Biosorbents for the removals of heavy metals:

Removing harmful metal pollutants from leachates using inexpensive and readily available materials is crucial [32]. Researchers have utilized biocomposites made from various plant by-products such as rice husk, banana peels, maize cob, orange peel, sawdust, and sugarcane bagasse for the adsorption of different pollutants. Adsorption mechanisms rely on solute hydrophobicity or high affinity between the solute and adsorbent, influenced by ionic attraction, van der Waals forces (physisorption), and chemical reactions (chemisorption). Eskandari et al. (2019) demonstrated that a PAni/chitin biocomposite prepared via a simple chemical route achieved over 80% removal efficiency for Pb (II) and Cd (II) ions at pH 6 [27]. Additionally, their PAni/SD composite, produced by surface polymerization of PAni on sawdust, proved feasible, spontaneous, exothermic, and reusable for seven successive runs with minimal loss in Cr (VI) adsorption performance, outperforming individual PAni and sawdust in Cr ion removal efficiency. Biosorption mechanisms include ion exchange, complexation, chelation, adsorption, and microprecipitation, with adsorption capacity dependent on functional groups on the adsorbent surface and adsorbate properties. Pretreating agricultural waste products—through drying, grinding, and chemical treatment—converts them into effective biosorbents. Polyaniline (PAni), an electrically conductive, environmentally stable, and inexpensive material with inherent redox properties and nitrogen-containing functional groups, enhancing its capacity for metal ion removal. The high adsorption capacity, selectivity, anion removal ability, and regeneration of PAni, attributed to doping-undoping mechanisms, make it highly viable. Synthesizing PAni biocomposites with biomass waste, rich in biopolymers, addresses PAni's low mechanical strength and processing limitations. Biocomposites offer an efficient, cost-effective, and environmentally friendly alternative for resource conservation, environmental remediation, and biomass waste management. Biomass waste, containing cellulose, hemicellulose, and lignin with functional groups like hydroxyl, carboxyl, and amino groups, supports the selective removal of toxic and useful metals from landfill leachate and groundwater via ionic exchange and electrostatic attractions. The application of conductive polymer biocomposites, such as PAni combined with similar or dissimilar materials, enhances their adsorption capabilities for various pollutants due to their unique physical and chemical properties [39].

Table.2.2. Comparison of biosorption capacities of different adsorbent on various types of pollutants.

Sl no	Key findings	Author name and year	Study area/Country	Absorbent types
1.	Application of polyaniline/activated carbon nanocomposites derived from different agriculture wastes for the removal of Pb (II) from aqueous media.	[24]	Egypt	Polyaniline/agricultural waste activated carbon (PANI/AC) composites.
2.	Green synthesis of iron nanoparticles using different leaf extracts for treatment of domestic waste water	[25]	Karnataka, India	Green synthesis of Murraya koenigii, Azadirachta indica and Magnolia champaca leaves
3.	Potential of polyaniline modified clay nanocomposite as a selective decontamination adsorbent for Pb(II) ions from contaminated waters; kinetics and thermodynamic study.	[36]	Iran	PANI/ clay nanocomposites.
4.	Synthesis of modified chitosan TiO2 and SiO2 hydrogel nanocomposites for cadmium removal.	[24]	Iran	Chitosan TiO2 and SiO2 hydrogel nanocomposites.
5.	The Impact of Silver Nanoparticles on the Composting of Municipal Solid Waste	[29]	Ohio	Polyvinyl-pyrrolidone(PVP) coated silver nanoparticles.
6.	Waste-Derived Nanoparticles: Synthesis Approaches, Environmental Applications, and Sustainability Considerations	[22]	Egypt	Metal and Metal Oxide Nanoparticles.
7.	Review on Applications of Nanoparticles in Landfill Leachate Treatment	[45]	Malaysia	Nanoparticles with Activated carbon.
8.	Removal of Mn(II) from groundwater by sugarcane bagasse and activated carbon (a comparative study): Application of response surface methodology (RSM)	[26]	Iran	Sugar cane Bagasse and activated carbon.
9.	Adsorptive Removal of Cd, Cu, Ni and Mn from Environmental Samples Using Fe3O4-Zro2@APS Nanocomposite: Kinetic and Equilibrium Isotherm Studies	[30]	South Africa	3-aminopropyltriethoxysilane(Fe3O4 -ZrO2@APS) nanocomposite

10.	Selective removal of heavy metals from landfill leachate by reactive granular filters	[42]	Italy	Zero valent iron (ZVI), pumice, granular activated carbon (GAC) and a zeolite(Chabazite)
11.	The impact of nanoparticles on aerobic degradation of municipal solid waste	[27]	Turkey	TiO2 (AT) and Ag (AA) nanoparticles.
12.	Agricultural waste of sugarcane bagasse as efficient adsorbent for lead and nickel removal from untreated wastewater: Biosorption, equilibrium isotherms, kinetics and desorption studies	[28]	Nigeria	Sugar cane bagasse (SCB).
13.	Removal of Heavy Metals from Textile Wastewater Using Sugarcane Bagasse Activated Carbon	[30]	Malaysia	Sugar cane bagasse activated carbon (SBAC).
14.	Sugarcane Bagasse as an Efficient Biosorbent forMethylene Blue Removal: Kinetics, Isotherms and Thermodynamics	[38]	Brazil	Sugar cane bagasse (SCB).
15.	Stabilized landfill leachate treatment by sugarcane bagasse derived activated carbon for removal of color, COD and NH3-N – Optimization of preparation conditions by RSM.	[23]	Malaysia	Sugar cane bagasse derived activated carbon (SCAC).
16.	Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent.	[34]	India	Coal fly ash
17.	Enhanced heavy metals biosorption using chemically modifed chitosan coated microwave activated sugarcane baggage ash composite biosorbents	[35]	Switzerland	Chitosan and sugar bagasse ash
18.	Kinetic study of lead (Pb2+) removal from battery manufacturing wastewater using bagasse biochar as biosorbent	[37]	India	Bio char prepared from bagasse waste
19.	Development of Adsorbent from Sugarcane Bagasse for the Removal of Pollutants from Chrome Tanning Effluents	[38]	Bangladesh	Sugar cane bagasse.

2.7. Heavy metal remediation: Adsorption

It has been shown that heavy metals can be eradicated by a number of physical procedures, such as treating contaminated systems with the metals' physicochemical features by adsorption, electrokinetic approach, membrane filtering etc. Chemical precipitation, flotation, ion exchange, coagulation, and flocculation are all a component of the process. These methods are effective in removing heavy metals, but they require too many chemicals, which makes it difficult to dispose of sludge and raises the risk of secondary pollution. These procedures are exceedingly expensive, and energy-intensive, they often yield harmful consequences [60].

Adsorption is typically regarded as an effective procedure for wastewater treatment compared to other approaches due to various features. Adsorption can successfully remove a wide range of pollutants, including organic molecules (such as dyes, phenols, and pesticides), heavy metals, and even some inorganic compounds (Crini, 2006). Adsorption processes are relatively simple to build and operate. They do not require complex equipment or highly specialized knowledge, making them accessible for diverse sizes of operations, from tiny to big treatment facilities [48].

Minimal Sludge Production like biological treatment procedures, adsorption does not produce biological sludge, which lowers the need for subsequent sludge treatment and disposal. It also does not generate toxic by-products, making it an environmentally beneficial solution. The capacity to reinstate adsorbents minimizes the operational costs associated with regularly obtaining fresh materials [49].

Advantages Over Other Methods Compared to coagulation and flocculation, adsorption does not require the use of chemicals, eliminating the risk of chemical residues in treated water and the necessity for controlling chemical storage and handling. Adsorption creates less sludge compared to chemical precipitation processes, facilitating waste management. Adsorption is less impacted by hazardous compounds in the wastewater, which might limit biological treatment processes. It can be used to pre-treat wastewater before biological treatment to safeguard the microbial community. Adsorption processes are not subject to the oscillations and instabilities that might arise in biological systems due to variations in microbial activity or ambient circumstances [55].

2.8. Bio composite: a green and low-cost solution.

Biosorption is the removal of materials (metal ions, compounds etc) by inert, non-living biomass (materials from biological origins, agricultural waste) due to “high attractive forces present between the two [61]. Bio materials are more inexpensive and ecologically responsible solutions for the elimination of heavy metals contamination and for restoring the environment.

The advantages of using biomaterials for wastewater treatment due to its low cost and simplicity of usage, adsorption is one of these ways that is commonly used. It involves drawing impurities to the surface of an adsorbent substance and binding them there in order to remove heavy metals from water [51]. Salman et al. (2015) emphasize on the possible application of low-cost lignocellulosic material in heavy metal cleanup. In this study, they detailed about the binding process, relative uptake capabilities, the effect of change on increase in uptake capacities, equilibrium, kinetic and thermodynamic modelling involved [58]. They also said that there still remains a big barrier that prevents the industry from switching to the biosorption process in place of traditional technologies. Several recent publications utilized several inexpensive and locally abundantly accessible bio adsorbents to extract heavy metal from aqueous solution such as sawdust has the potential of removing Pb ions from the contaminated water was observed [53].

2.9.Conductive polymers and its importance:

Conductive polymers, specifically polyaniline (PAni), polypyrrole (PPy), and polythiophene (PT), are used as ion exchangers and have shown promising results in removing heavy metals [56]. Laabd et al. (2017b) noted in his work that conjugated polymers, such as polyaniline (PAni), polypyrrole (PPy), polythiophene (PT), and its derivatives, have diversity of application fields, including electrical devices, hazardous gas sensors, rechargeable batteries, and wastewater treatment [50]. Conjugated polymers have favourable characteristics such as ease of synthesis, inherent non-toxicity, excellent electrical conductivity, good stability, and affordability. The primary elements behind this apparent interest in the utilization of polymers in waste water treatment are: The presence of a doping agent in the bio adsorbent provides valuable insights into the function of functional groups in the biosorption process [58].

Undoped PAni, a highly conductive polymer was placed in the sawdust to boost its absorption capability [53]. PAni is one of the most promising conjugated polymers because of its unique features, including its strong redox reversibility, biodegradability, biocompatibility, and ability to be produced in an aqueous solution. Although PAni has considerable potential, its commercial usage have been limited by its lack of processability. Consequently, adding PAni coating on a naturally occurring material can accomplish the purpose [56].

PAni is regarded as a superior conductive polymer when compared to others due to its important features and advantages. PAni possesses high electrical conductivity, which can be easily modified by doping and the oxidation state [59]. PAni offers remarkable environmental stability, keeping its conductivity even at ambient conditions. This stability is superior to many other conductive polymers which can breakdown more rapidly when exposed to air and moisture. PAni can be manufactured relatively easily and cost- effectively using chemical or electrochemical polymerization. The technique does not require tight conditions or highly expensive catalysts, making it more accessible for large-scale production [52]. Therefore, PAni is employed as a chemical modification agent in bio-composite to boost its absorption efficiency, reuse ability.

2.10. Adsorption studies:

2.10.1. Kinetic studies:

Kinetic adsorption models describe the mechanism of heavy metal ion adsorption by biosorbents, specifically the rate of biosorption during the removal of heavy metals from wastewater on an industrial scale, to optimize design parameters such as adsorbate residence time and reactor dimension [57]. Adsorption kinetics can be significantly affected by contact time, temperature, and concentration. Increased contact time permits more metal ions to interact with the sorbent material, increasing adsorption rates. Also, the concentration of metal ions in the solution can influence the rate of adsorption, with larger concentrations often resulting in faster adsorption kinetics.

Mishra et al., (2023) have done the kinetic modelling and found that Langmuir model provides more accurate representation of adsorption behavior of Pb uptake capacity onto PAni modified sawdust. Adsorption kinetics were studied during the research on PAni and PPy impregnated polyethersilfone based composite for defluoridation application by Mishra et al., (2022) and it was observed that it follows pseudo second order kinetic model [54].

The adsorption was better described by the pseudo-second order kinetic model followed by the Freundlich isotherm model in the removal of Cr (VI) and orange dye (OG) with the help of PAni modified almond shell and arginine-PAni doped walnut shell as mentioned [31]. In the sorption of Cd (II) from aqueous solution by rice husk, the pseudo-second order kinetic model agreed with the chemisorption as the rate-limiting mechanism. The equilibrium sorption isotherm tests were better represented by Langmuir model than the Freundlich model [7].

2.11. Regeneration studies

Mishra et al., (2023) have performed four cycles of regeneration, the removal efficiency of Pb ions at the first cycle was 50% and that it intensely decreased till the fourth cycle.

The desorption studies were also carried out to know the reusability and efficiency of the sawdust bio composite, this study was carried out for six cycles and it showed statured uptake capacity of fluoride after the first three cycles [54].

Hsini et al., (2020) further evaluated that PAni modified almond shell bio-composite could easily be regenerated with NaOH solution and efficiently be reused for the removal of Cr (VI) and OG dye from the aqueous medium [31].

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