# 1. General Introduction:

## 1.1. Context of the Thesis

Heavy metal pollution in soil and water is one of the major problems faced by numerous countries all over the world. Heavy metals are naturally existing components of the Earth's crust, and their abundance varies substantially from place to place. However, human-induced activities, is a major contributing factor in the high quantities of heavy metals discovered in the ecosystem [10] and a better understanding of these sources and their associated risks can help in controlling the heavy metal pollution in the environment. Rapid population increase, urbanisation, and industrial development all contribute to an exponential rise in annual trash .and the most common method of disposal of waste in poor nations, as well as in some industrialised nations, is to dump the non-segregated solid waste in municipal landfills. The main issue with municipal landfills is their potential for causing pollution as a result of the leachate they produce which seeps through the subsoil and into the surface and groundwater. Residents, particularly in the urban and semi-urban areas are negatively impacted by this unmanaged waste management through contaminated soil, water and agricultural produce contaminated with extremely dangerous chemicals such as heavy metals.

Pollutants from landfills can be broadly categorized into two major types: organic and inorganic. Organic contaminants include chemicals used in industry, volatile organic compounds, herbicides, insecticides, and food processing residues. In contrast, inorganic water contaminants encompass metals, fertilizers, and acidity from industrial discharges, many of which are hazardous and carcinogenic [17]. Among the various pollutants in wastewater, toxic heavy metals are particularly significant due to their detrimental impact on the aquatic environment. The discharge of these metals into the environment threatens water quality and aquatic ecosystems, posing severe risks to human health. Recognized metallic contaminants in wastewater, industrial effluent, and sewage sludge include arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn). Despite often being present in trace amounts, these substances pose significant dangers due to their tendencies for bioaccumulation and biomagnification [5]. Heavy metals are classified into essential and non-essential categories. Essential heavy metals, such as copper (Cu), manganese (Mn), zinc (Zn), cobalt (Co), chromium (Cr), nickel (Ni), and iron (Fe), play crucial physiological and biochemical roles in plants and animals and are integral to many essential enzymes. Conversely, non-essential heavy metals are extremely hazardous, capable of causing damage ranging from acute to chronic.

## 1.2. Toxicological aspect of studied heavy metal pollution on human health and environment:

Heavy metals are defined as metals with a specific gravity larger than 5 g/cm³ (Bakshi et al., 2018). Among the heavy metals released from landfills, non-essential elements such as lead (Pb) and cadmium (Cd) pose significant health risks to humans. Pb exposure has been linked to severe health issues, including lung cancer, mental impairment in children, anemia, and kidney failure. Cadmium is known to be carcinogenic, hepatotoxic, neurotoxic, and toxic to the kidneys. These metals are dangerous to living beings even at low concentrations, contributing to metabolic problems, particularly in species consuming food from plants and crops grown in contaminated soil or

drinking contaminated water [2]. To properly assess the eco-toxicological impact of heavy metals on human health and the environment, it is essential to consider all hazards associated with these pollutants through various routes of exposure (oral, inhalation, and dermal). The associated risks, quantified through Hazard Quotients (HQ), should be calculated for water, air, and soil to perform an integrated human health risk assessment (HHRA).

Germination studies are carried out in heavy metal remediation to understand how heavy metals affect the germination of seeds and the growth of seedlings:

- **Assess the effects of heavy metals on seed germination**
  Heavy metals can reduce the germination rate of seeds or damage seedlings. For example, exposure to cadmium and lead can inhibit germination, delay germination time, and retard seedling growth.
- **Understand how heavy metals affect physiological processes**
  Heavy metals can affect other physiological processes, such as photosynthesis.
- **Determine the toxicity of heavy metals**
  The toxicity of heavy metals is often concentration dependent. For example, zinc can be a cofactor for enzymes, but too much zinc can inhibit germination and change the structure of plant roots.
- **Isolate stress tolerant bacteria and fungi**
  Germination studies can help identify bacteria and fungi that are tolerant to heavy metals.

## 1.3. Techniques for the removal of heavy metals from polluted water:

Industries such as refineries, mining, tanneries, electroplating, fertilizers, textiles, and dyes have employed conventional methods like membrane filtration, solvent extraction, ion exchange, reverse osmosis, oxidation, and chemical precipitation to remove heavy metals from wastewater. However, these techniques often produce toxic chemical sludge, exhibit incomplete metal removal, have low efficiency, and require high energy and reagent input [12,3,7]. Consequently, there is a need for cost-effective, safe, and efficient alternatives. Adsorption has emerged as a superior technology for pollutant removal due to its low cost, ease of adsorbent replacement, high efficacy, minimal sludge production, and operational simplicity. This method is especially suitable for heavy metal removal as it is both regenerative and economical. Recently, there has been a shift towards using eco-friendly biosorbents from agro-wastes for heavy metal remediation. Adsorption using biocomposites offers a promising, cost-effective, and environmentally friendly solution with advantages like low operation cost, minimal or no toxic sludge generation, short operating times, ease of preparation, no need for supplementary nutrients, and the potential for metal recovery [3,12]. Agro-industrial wastes, rich in cellulose, lignin, and other functional components such as lipids, proteins, hemicellulose, and various functional groups, have shown excellent potential as adsorbents for heavy metals, thus contributing to a circular economy. Specifically, sugarcane bagasse, a byproduct of the widely cultivated Saccharum officinarum in regions like Brazil, India, China, Mexico, and South Africa, is composed of approximately 42% cellulose, 25% hemicellulose, and 20% lignin [14,15], making it a promising candidate for heavy metal adsorption.

Agricultural wastes are showing promise as inexpensive and efficient adsorbents, including corn stalks, rice trash, peanut shells, straw, sawdust, and sugarcane bagasse (Dey et al., 2021). Green adsorbent development has drawn a lot of attention lately because of its low cost, non- toxicity, and renewability. Sawdust and sugarcane bagasse, in particular, have shown outstanding adsorbent qualities due to their widespread availability. Its cell wall also contains hydroxyl groups, cellulose, and lignin—all of which are capable of exchanging ions. Additionally, these functional groups offer a large adsorption surface area, which facilitates the effective removal of heavy metal ions. According to studies, conductive polymer such as PAni has been utilized to coat natural fibres because of its ability to absorb metal ions [9]. Due to their unique topologies, functional groups, and straightforward manufacturing process, conducting polymers have garnered a lot of interest in pollutant adsorption. Through complexation and ion-exchange mechanisms, they can get rid of heavy metals. In recent years, the polymer polyaniline (PAni) has been investigated for its potential as a heavy metal adsorbent. An attractive property of PAni, a conducting polymer containing a terminal amine ($-NH_2$) group, is its large surface area, changeable surface chemistry, ideal pore size distribution, stiffness, and cost-effective regeneration. Some researchers have tried coating sawdust and sugarcane bagasse with PAni to improve their sorption capacities. Because of its affordability, versatility, and eco-friendliness, it is also seen as a promising polymer for coating natural fibers.

Due to its porous structure, ion exchange capabilities, regenerability, and abundance of amine/imine groups, PAni has the highest adsorption capacity. Due to their wide availability, low cost, environmental friendliness, and favourable mechanical qualities, lignocellulose materials have received a lot of interest recently when it comes to their use as adsorbents for wastewater purification. An effective and cost-effective method to enhance the characteristics and applicability of PAni is to cover the surface of the lignocellulose biomass with PAni polymer. PAni-based composites have shown good water contaminant uptake efficiency in this field, including PAni/chitosane, polyaniline-modified chitosan embedded with ZnO-Fe3O4, PAni/sawdust, PAni/jute fibre, PAni/nylon-6, and PAni/argan nut shell [4].

When conductive polymers are doped with sulfates and phosphate groups, they acquire essential properties that facilitate the incorporation of cations into their framework, subsequently attracting negatively charged ions such as fluoride. These conductive polymers can be further enhanced by impregnating them with high molecular weight polymers like polyethersulfone (PES), polysulfone (PSF), and cellulose acetate (CA) to create composites (Mishra et al., 2022). Characterization of the resulting polyaniline (PAni) biocomposites employs techniques such as powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). This coating technique can significantly

enhance the adsorption capacity of materials like sawdust and sugarcane bagasse for heavy metal ions in aqueous solutions, making it a more practical and cost-effective approach to addressing water pollution.

In this research work, doped and undoped PAni-coated sawdust and sugarcane baggage as bio-composites were employed for remediation of heavy metals from wastewater. Conductive polymers, namely polyaniline (PAni), polypyrrole (PPy), and polythiophene (PT)etc., are employed as ion exchangers because of unique redox property and have demonstrated encouraging outcomes in the elimination of heavy metals. Although PAni has great potential and has been widely used in various applications, its commercial uses have been hampered by its lack of processability, but the drawback has been overcome by making suitable dispersions of PAni. Consequently, applying PAni coating to a naturally occurring material can accomplish the goal [11]. Conductive polymers have emerged as promising candidates for environmental remediation applications due to their unique properties, including reversible redox property, high surface area, tunable surface chemistry, and facile synthesis. Polyaniline (PAni), in particular, has attracted significant interest for its excellent adsorption capabilities also because of the presence of N containing functional groups, towards various pollutants, including heavy metal ions. Sawdust and sugarcane bagasse, in particular, have shown outstanding adsorbent qualities due to their widespread availability. It’s cell wall also contains hydroxyl groups, cellulose, and lignin— all of which are capable of exchanging ions. Additionally, these functional groups offer a large adsorption surface area, which facilitates the effective removal of heavy metal ions. According to studies, PAni has been used to coat natural fibres because of its ability to absorb metal ions [9]. Researchers have tried coating sawdust and sugarcane bagasse with PAni to improve their sorption capacities. Because of its affordability, versatility, and eco-friendliness, PAni is also seen as a promising polymer for coating natural fibres. The application of this coating technique may improve sawdust and sugarcane baggasse's capacity to adsorb heavy metal ions from aqueous solutions, hence rendering it a more practical and economically viable means of tackling water pollution. Undoped PAni Refers to polyaniline in its neutral, non-conductive state. It is a polymer with alternating single and double bonds but lacks sufficient charge carriers to conduct electricity. Doped PAni Refers to polyaniline treated with a doping agent (e.g., an acid), which introduces charge carriers (protons) into its structure, making it conductive. This process transforms the polymer into its conductive state. The disadvantages of PANi  are Polyaniline can be brittle, making it difficult to use in flexible applications. Its conductivity decreases over time, especially when exposed to air or moisture..PAni does not dissolve easily in most solvents, which makes it challenging to process into desired shapes or forms.

### 1.4. Significance of the study

Despite the growing concern over soil and water pollution caused by unmanaged landfills, few studies have focused on the eco-toxicological and health risk assessments of landfill pollution in northeast India, as highlighted by the literature review. Alongside heavy metal pollution monitoring, the decontamination of heavy metals from wastewater is vital for environmental protection, public health, economic benefits, and scientific advancements. Remediation efforts are essential to safeguard food sources, prevent contamination of water bodies, and preserve ecosystems. In recent decades, the use of biocomposites for the remediation of heavy metals from wastewater has gained widespread recognition due to their numerous advantages, including low operational costs, eco-friendliness, short operating times, ease of preparation, no need for supplementary nutrients, potential for metal recovery, and availability. Utilizing agro-wastes for bioremediation not only addresses heavy metal pollution but also mitigates problems associated with improper agro-waste handling. Therefore, this research employs both doped and undoped polyaniline (PAni)-coated sawdust and sugarcane bagasse biocomposites for the remediation of heavy metals from wastewater.

### 1.5.Research objectives:

In light of the above discussion, we have mainly focussed on the following objectives for our research work.

Objective 1: Characterization of landfill leachate, groundwater and soil collected from open landfill sites in the Brahmaputra valley.

Objective 2: Characterization and application of PAni biocomposites (doped and undoped) for removal of toxic heavy metal from landfill leachate.

Objective 3: Assessment of the adsorption kinetics and equilibrium studies for the potential removal of toxic metals using polyaniline (PAni) biocomposite.

### 1.6.Research hypothesis

1. The characterization of groundwater and soil effected by leachate from open landfill sites in the Brahmaputra valley will reveal significant contamination with toxic metals.

2. The adsorption kinetics and regeneration studies of toxic metal removal using PAni biocomposites will demonstrate favorable properties, suggesting their potential as efficient adsorbents for environmental remediat

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