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Applicability of Agricultural Wastes for Heavy Metals Bio Remediation- A Low-Cost Approach

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Abstract:- Heavy metals are toxic recalcitrant compounds, present in many industrial effluents like tannery industry, electroplating industry and more. Industrial sector develops whole world and contributes to welfare of the country and supports every country gross domestic product (GDP). To protect our environment from toxic compounds and carcinogenic heavy metals without compromising on environmental health, new eco-friendly adsorbents must be implicated in treatment of industrial discharges. The agriculture wastes from both domestic and large-scale sectors majorly dumped in landfills, which further pollutes the environment, so these agriculture waste can be further utilized for its metal sequestration property and can be used for heavy metals bio-remediation. This study shows that agriculture waste such as saw dust, brans, cobs, pulps, fruits flowers, adsorbed up to 98 % of the heavy metals. This study supports sustainable development goals and recommends using agriculture wastes, an eco-friendly green technology, for safeguarding our environment from further secondary pollution.

Keywords: *agriculture waste, heavy metals, wastewater, industrial effluents.*

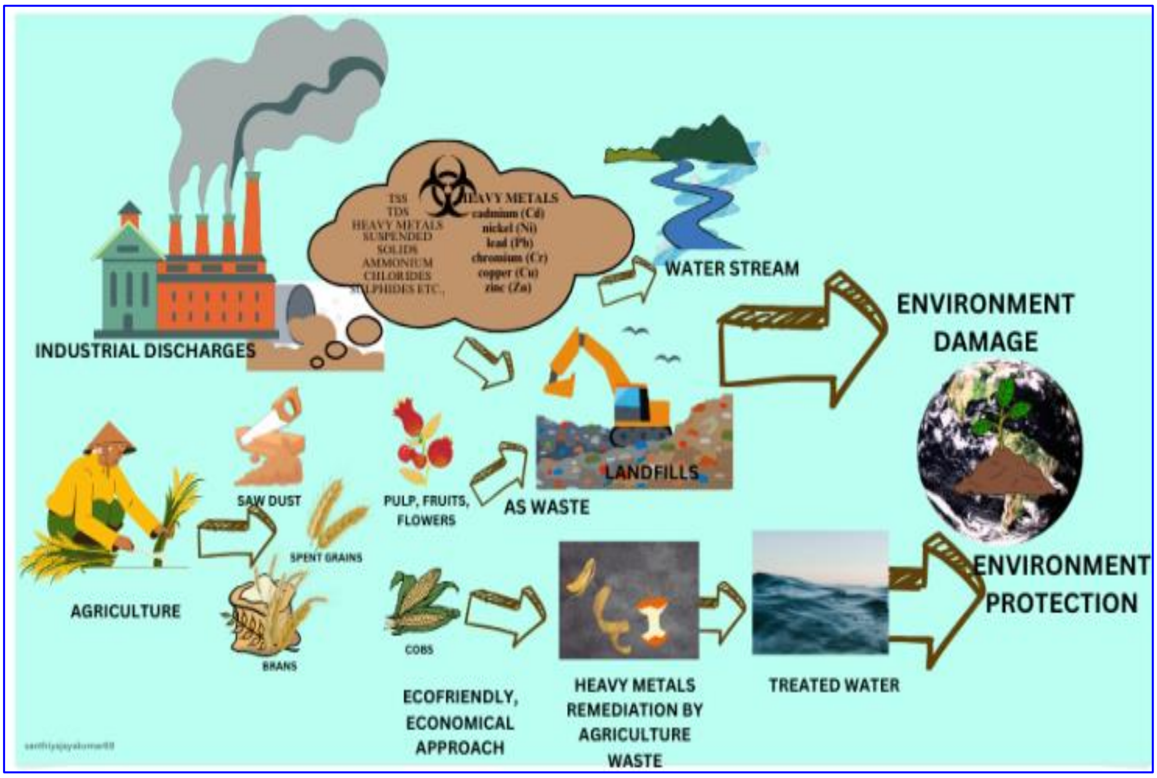

Fig 1: graphical abstract

1. Introduction

Whole world is exposed to toxic industrial effluents, dyes, hazardous chemicals, mutagenic heavy metals, biological agents and radioactive elements as per the surveys conducted by Public Health Services of several nations(Narayanan et al., 2016). Heavy metals have high atomic density, atomic weight, and has constant and bio-accumulation normality, so they are toxic even in very low doses. Heavy metals get exposed into the water stream and environment naturally, by soil and rock leakage or anthropogenically, by discharging unprocessed industrial discharge to rivers. Industrialization accounts for growth of whole world as it greatly contributes to GDP, but problems arisen by improper treatment of industrial discharges and distorts environment and also contributes to global warming(Sharmila & RM., 2018). Though many regulations were mandated by different countries, the contamination of the toxic compounds in all stages of food chains proves the contamination of water streams by untreated or partially treated industrial discharges. Biosorption uses industrial wastes, agricultural wastes, biological organisms and other polysaccharide materials to absorb metals and toxic substances. Wastewater treatment must be designed to dispose the industrial effluents without harming humans or the environment so, agricultural wastes have been used in man-made products/processes for generations due to their light weight and density, better mechanical strength and flexibility (Saikia et al., 2017) for waste water treatments. In 2015, the UN proposed global goals for the sustainable water management, good sanitation and potable water for people, but according to the UN World Water Development Report 2020, damaging water sources puts the 6th Sustainable Development Goal of the 2030 agenda at risk (Gómez-Aguilar et al., 2022). Agricultural wastes can recover or remove heavy metals even at low quantities as it contains lignin, cellulose, hemi-cellulose, pectin, phytic acid, and many proteins which has functional groups to adsorb metal cations (Saraswat & Rai, 2010). The natural fibers can be used as immobilizing carrier for biological systems (Kalaiarasu et al., 2024) and can act as adsorbent of contaminations at same time. In this study low-cost, reusable, ecologically safe, locally available agricultural waste, which is majorly disposed in landfills or burned were reviewed for heavy metals bioremediation.

2. Objectives

Agricultural wastes proved to adsorb about 99 % of heavy metals, so implicating agriculture waste, an eco-friendly technology for heavy metals bioremediation improves agriculture and agriculture-based industry and heavy metals removal from environment without any chemicals at low cost over other methods.

3. Methods

The literature review involved critical searches of several academic databases, including JSTOR, Google Scholar, Scopus, Web of Science and Science Direct, and several academic databases used with keywords such as “agriculture wastes”, “heavy metals”, “industrial effluents”, “wastewater treatment”, “biosorption”

4. Agriculture wastes for heavy metals sequestration

4.1 Saw dust

Saw dust is an inexpensive biosorbent produced as a waste in large quantities at sawmills by various process such as cutting, grinding, drilling, sanding, or pulverizing wood with a saw or other tools, sawdust column removes heavy metal ions from both industrial and laboratory waste water. As saw dust majorly contains lignin and cellulose, it can be used as recalcitrant heavy metals sequestering adsorbent from industrial effluents or metals contaminated water streams for safe disposal in environment. In a study conducted by Logeswari *et al.*, about 81 % of Cr adsorbed at 1-200 ppm doses and 62.5 % of Cr adsorbed at 2-250 ppm doses in 200 minutes, and further increase in adsorption noted with increase in contact durations (Logeswari et al., 2013). The study conducted by Sharma and Foster showed oven dried saw dust had maximum adsorption at 40 and 100 mg/L of Cr at pH 2.0 and about 39.7 mg/g Cr was adsorbed at 1000 mg/L dosage of Cr at pH 2 (Sharma & Forster, 1994). Dakiky and coauthors showed about saw dust optimally adsorbed about 53.5 % of Cr at 30°C, in pH 2 within 2 hr contact time at initial Cr dosage of about 8g/L) (Dakiky et al., 2002). Memon and his coworkers investigated caustic treated Deodar Cedrus sawdust for Cd removal, and recorded highest Cd reduction at pH 5 and rapid adsorption observed at lower adsorbate dose than higher dose and lower temperature, indicating the process to be exothermic (Memon et al., 2007). Formaldehyde treated P. sylvestris sawdust showed increased level of stabilization and also prevented COD release by releasing polyphenols, metals like Pb and Cd were rapidly removed within 20 minutes at pH 5 (Taty-Costodes et al., 2003). The inexpensive formaldehyde treated meranti tree sawdust processed into fine powder has good potential to adsorb aqueous Pb and Cd removal (Ahmad et al., 2009). Acetone and NaOH treated larch sawdust adsorbed about 2.71, 2.22, 2.35, 3.19 mg of Cu, Cd, Ni, Pb respectively (Chung et al., 1999). Plants saw dust selectively adsorbed different metals such as Cu, Ni adsorbed by oak, Cd adsorbed by pine and Pb adsorbed by alder saw dust respectively (Anees Ahmad et al., 2007), while in another study modified oak sawdust adsorbed about 3.220 mg/g of Cu (Argun et al., 2007). Mangifera indica (Mango tree) saw dust adsorbed maximum Cu within an hour at pH 6.0, which further increased on increasing contact time, sawdust dose and decrease in particle size, and increased salinity (Ajmal et al., 1998). Maple tree saw dust is a promising heavy metals adsorbent from untreated industrial wastewater and can be reused. Maple sawdust have maximum adsorption of Ni (Shukla et al., 2005) and Cr (Yu et al., 2003b) at pH 9.0, but heavy metals uptake depends on the initial sorbent and sorbate dosage, time of contact, and pH. In study conducted by Henderson et al., untreated wood sawdust significantly absorbed Cu and Ni at both high and low metal concentrations (Henderson et al., 1977). Teak saw dust rapidly absorbed 52% of Cr at pH 3, within an hour and reached saturation with 88 % (Sumathi et al., 2005). African beech sawdust adsorbed about 1.913, 0.804, 4.357, 1.354, 1.058 mg/g while Chemically treated African beech sawdust adsorbed about 0.854, 1.122, 5.249, 1.955, 1.689 mg/g of Al, Fe, Cu, Zn, Pb, respectively (Abdel-Ghani et al., 2013). Linden sawdust adsorbed about 0.350, 1.900, 1.425 mg/g of Fe, Cu, Zn respectively (Božić et al., 2009). Hevea Brasiliensis saw dust adsorbed about 3.452 mg/g of Cu (Kalavathy & Miranda, 2010) and poplar sawdust adsorbed 2.540 mg/g of Cu and fir sawdust adsorbed 2.350 mg/g of Cu (Šćiban et al., 2006). As many studies reviewed in this paper, this paper shows that saw dust mainly adsorbed Cu than another metals the specifications of heavy metals adsorption by saw dust, the saw dust from different plants adsorbed Cu mainly due to the functional groups present in lignin and cellulose.

4.2 Pulp, fruit, and flowers

Sugar industry is one of the most important agriculture-based industries, they produce sugar beet pulp as byproduct which can be used as adsorbent for heavy metals removal. sugar beet pulp is composed mainly of cellulose, pectin, pentozan, protein and lignin, which binds to metal cations due to carboxylic and phenolic groups. Sugar beet pulp can be utilized as a low-cost adsorbent because it can be used in its native state without recycling, at higher pH, surface of sugar beet pulp turned negative, so heavy metal adsorption was enhanced due to lesser competition between sodium ions and metal ions. In study conducted by Pehlivan et al., sugar beet pulp showed maximum Cu and Zn uptake at pH 5.5 and 6.0, respectively (Pehlivan et al., 2006). In another study oven dried sugar beet at higher doses removed 17.2 mg/g of Cr optimally at pH 2.0. with initial metals concentration of about 500 mg/L of Cr (Sharma & Forster, 1994). Inexpensive heavy metals sequestrant, beetroot fibers were used in a study conducted by Rima et al. showed 98, 92, and 90% of Pb, Zn, and Cu of heavy metals adsorption at pH 6.6 respectively (Rima et al., 2000). In study conducted by Elangovan et al. the untreated and sulfuric acid with NaOH treated palm flower (*Borassus aethiopum*) had maximum adsorption capacities of about 6.24 and 1.41 mg/g of Cr (III) and 4.9 and 7.13 mg/g of Cr (VI), respectively (Elangovan et al., 2008). According to Ahmad *et al*, palm fruit (*Elaies guineensis*) biomass can be used for the adsorption of toxic gases, heavy metals and other pollutants, in a study conducted by Salamatinia *et al*, oil palm fruits bunch efficiently removed Zn over oil palm bark (Salamatinia et al., 2007). Soda lignin from empty fruit branches isolated from black liquor generated from oil palm empty fruit bunches removed maximum aqueous Cu at pH 5, at an adsorbent dosage of 0.5 g and an agitation period of 40 minutes, following Freundlich isotherms (Sulaiman et al., 2010) in another study modified soda lignin had increased Pb ions adsorbing ability at increased contact time, pH, and initial metal ion concentration to remove aqueous Pb (II) ions and 80 % desorption achieved with HCl, HNO3, and EDTA solutions, so they can be reused without losing its initial adsorption capacity and adsorption followed pseudo-second-order kinetics, making oil palm empty fruit bunches economically feasible for aqueous heavy metals removal (Ibrahim et al., 2010). Oil palm industry produces fruits, trunks, fronds, leaves, empty fruit bunches, and shells as wastes that contains heavy metals sequestering hemicellulose, cellulose, and lignin structural components, as these wastes are rich in vitamin E (tocopherols, tocotrienols), carotenoids, phenolic acids, flavonoids, phytosterols they can be further utilized, but up to 65 % waste were disposed without further use. So, date palm-based adsorbents are the most promising adsorbents, so it can be utilized as heavy metals sequestrant. Corn (*Zea mays*), is a fruit that belongs to the *poaceae* family, in a study, untreated raw corn adsorbed about 200 mg/g of aqueous Cr at 300 K and followed pseudo-second order kinetic model and fitted Langmuir isotherm (Chen et al., 2011). The modified loofah sponge showed about 39 mg/g of aqueous Cr adsorption (Santhiya Jayakumar, Sharmila, 2024). So the pulp fruits and flowers can be used for heavy metals adsorption.

4.3 Cobs

Corncobs produced in tonnes as agriculture-based industry waste that is incinerated as it has no commercial value, but many studies proved that it has heavy metals sequestering so it can be used for heavy metals bioremediation and affordable alternative to commercial ion-exchange resins (Hawthorne Costa et al., 1995). In Henderson *et al* study large size untreated corncob removed very less percentage of aqueous Cu and Cd (Henderson et al., 1977). Nitric or citric acid treated corn cobs showed 5.1 mg/g of Cd (II) adsorption at pH range 6–8, which showed about 3.8-10.8 times increased adsorption in the modified corncobs, further adsorption increased on increasing temperature, at low pH desorption occurs so it can be reused for further usage (Leyva-Ramos et al., 2005). In study conducted by Jain *et al* the untreated corncob adsorbed 16.2 mg/g of Pb, NaOH treated corn cobs has increased Pb adsorption up to 43.4 mg/g (Tan et al., 2010) and 79.2mg/g of Zn adsorption also noted when phosphoric acid modified corncobs used (Jain et al., 2016). Graft co-polymerization modified corncobs absorbed 90% of aqueous Cd at pH 3-7, and adsorption increased with adsorbent dose and fitted both Langmuir and Fruendlich models (Zheng et al., 2010a; Zheng et al., 2010b). In another study, oven dried maize cobs showed higher adsorption of about 13.8 mg/g of Cr at pH 2.0, with optimum dosage of about 500 mg/L and adsorption increased on lower dosage of Cr at pH 2.5 (Sharma & Forster, 1994). Modified cobs showed highest adsorption for Cd over other metals and proved to adsorb many heavy metals from simulated heavy metals so it can be used for heavy metals contaminated waste water treatment.

4.4 Brans

Brans are seeds shell produced majorly by flour factory byproduct, which is a lignocellulosic waste so that can be used for heavy metals adsorption. Sulfuric acid modified wheat bran absorbed Cu ions within 30 minutes at pH range 3.5-5.0, and further adsorption increased with increase in temperature. In another study, wheat bran adsorbed about 101.0 mg/g of maximum Cd adsorption was noted within 4 hours contact time at pH 5.4, 25 °C with removal efficiency of 86.2 % and initial dose of 100 mg/L and followed Langmuir isotherm and reaction was exothermic in nature (Özer et al., 2004; Özer & Pirinççi, 2006). In study conducted by Nameni *et al* wheat bran adsorbed 87.8 % Cr at pH 2.0 and adsorption increased with lower Cr dose and higher adsorbent doses (Nameni et al., 2008). Wheat bran showed different adsorption capacity at different temperature, within an hour, 69, 80.7, 87.0 mg/g of maximum Pb adsorption noted at 20, 40, and 60 °C, respectively and reaction showed endothermic adsorption (Bulut & Baysal, 2006). In study conducted by Singh *et al*, wheat bran adsorbed 87.15 % of Cd at pH 8.6, 20°C, with an initial concentration of 12.5 mg/L and followed mono layer adsorption and was adsorption reaction was exothermic and spontaneous in nature (SINGH et al., 2006a). In a study, wheat brans showed maximum adsorption of 15.71 mg/g for Cd (Nouri et al., 2007) and acid treated wheat brans showed 5.28 mg/g of Cr adsorption So, wheat bran has been successfully used as the adsorbing agent for removal of many heavy metal ions from aqueous solutions (Kaya et al., 2014). Rice bran is outer layer of rice, produced in tones as a by-product of the rice milling industry, so there are disposable problems, as brans are granular in structure, insoluble in water, chemically stable and locally available, the hemicellulose B in rice brans had highest adsorption capacity for metal ions vs. hemicellulose A and c present in rice brans (Hu et al., 2010), so it can be considered for heavy metals sequestration. In study conducted by Montanher *et al.*, rice bran showed Cd (II), Cu (II), Pb (II) and Zn (II) adsorption within 10 minutes contact time and increasing rice bran concentration from 1-20 g/L showed decreased heavy metal removal and followed freundlich isotherm model (Montanher et al., 2005). Rice bran showed maximum adsorption of about 21 mg/g of aqueous Cu and formaldehyde modified rice husk increased maximum adsorption further by 23 % (Joseph et al., 2019). In a study, rice bran was tested for lead adsorption and showed maximum adsorption of about 416.61 mg/g of aqueous Pb adsorption and had 74.54 % of Pb removal efficiency (Fatima et al., 2013). Phosphoric acid treated rice brans had maximum adsorption of 102 mg/g of aqueous Ni at pH 6, with initial concentration of 100 mg/L, adsorbent dosage of 0.25 g and metal adsorption decreased with decrease in pH and reactions followed both Langmuir and Freundlich isotherms (Zafar et al., 2007) and in another study NaOH treated rice brans showed 153.6 mg/g of maximum adsorption for Ni metals (Zafar et al., 2015). In a study rice bran were tested for Pb adsorption and showed maximum adsorption of about 416.61 mg/g of aqueous Pb adsorption with 74.54 % of Pb removal efficiency (Fatima et al., 2013). Hexane defatted rice brans absorbed Cr, Co, Ni, Zn, Cu at 82.5, 63.5, 52.8, 93.7, 82.4 % respectively, where Zn was absorbed the most (El-Said et al., 2010). So, environmentally friendly rice bran in natural or modified forms can be efficiently used as adsorbent for all toxic pollutants and heavy metal ions. Maize bran had a maximum removal efficiency of 98.4% for aqueous Pb at pH 6.5 and 20℃ with initial concentration of 100 mg/L and followed Langmuir isotherm model and reactions were spontaneous and exothermic in nature (Singh et al., 2006), in another study maize showed maximum Cr adsorption of about 312.52 mg/g of adsorption (Hasan et al., 2008). So, Brans effectively adsorbed Pb over other metals and many studies reported showed it can be used for all types of metals removal.

5. Conclusions

Agricultural waste was available in tonnes and are not utilized fully, as maximum amount is incinerated or dumped in the landfills. In this study many types of agricultural waste studied and the results from this review highlights the specific attraction of heavy metals by adsorbent is noted, different composition of adsorbents adsorbs different metals. The unmodified or modified agriculture waste, an enviro-technology has significantly removed about 99 % of heavy metals and many studies reported the multi metals adsorbing nature of adsorbents. The desorption of adsorbent studied, so this research highlights the agriculture waste, as efficient and valuable source for wastewater treatment than conventional approach. Industries and government can take the initiative to use this advanced enviro-technology to safeguard the future from secondary pollution. The cost is the major factor for improper discharge, so using this approach with conventional technology or using it as a new technology can make the process cheap and treatment with high standard results can be achieved. Introducing specific type of adsorbents is an add on feature as it can ensure adsorbing specific metals contaminated sites and effluents. Thus, agricultural waste, an environment based green technology can be further utilized in untreated or modified form as heavy metals for treating industrial effluents in eco-friendly manner in developing countries.

6. Further investigations

Many adsorbents must be studied and many studies showed single metal adsorption so, broad spectrum of heavy metals adsorption by adsorbents must be noted

In many studies adsorbents are used unmodified and studied only with synthetic heavy metals, so multi metals adsorption must be noted in real time tannery effluent

Many studies proved that adsorbent modifications improved metals adsorption, but cost-effective chemical modifications methods must be explored further for large scale application.

The mechanisms of heavy metals attachment to adsorbents and its thermodynamic isotherms are not explored in many studies so studies must be done for large scale implementation.

Using unmodified or modified adsorbent is an economically viable solution, but only batch approach is studied, so continuous system for industrial approach must be studied.

These further investigations must be studied to further improve this technology and thus agriculture waste as adsorbent can be glimpse of future.

7. Disadvantages

The adsorbent is seasonal, so rotation of adsorbent must be done based on season.

Setting up new agriculture waste-based plant, as a green methodology, must be taken into account by industries and government.

Training individuals and setting a new plant must be costly, and adaptation to new technology by public must also be noted.

The adsorbents sometime release color to the water, though non-toxic it may look unpleasant like groundnut peels, so waste water should be treated to remove color from solution.

Statements and Declarations

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Author contribution

The authors confirm contribution to the paper as follows: study conception and design: Santhiya Jayakumar; data collection: Santhiya Jayakumar; analysis and interpretation of data: Dr. K J Sharmila. Ms. Suganya K; draft manuscript preparation: Santhiya Jayakumar; supervision: Dr K J Sharrmila. All authors reviewed the results and approved the final version of the manuscript.

Competing interest

The authors, Mrs. Santhiya jayakumar, Ms. Suganya K, Dr K J Sharmila, declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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