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# Utilization of Low-cost Agricultural Waste for Removal of Toxic Metals from Environment: A Review

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***Abstract-*** Rapid urbanization and industrialization are the leading causes of environmental pollution nowadays. Heavy metals are serious toxic pollutants in soil, water, and air environments. Anthropogenic activity including industrial waste and dust is a widely known source for metal pollution. Various techniques are being used including ion-exchange, membrane filtration, electrolysis, coagulation, flotation, and adsorption for the removal of heavy metals from the environment. However, these techniques have high operating cost, sludge generation and selectivity of metals. Among them, heavy metal removal by the plant is an eco-friendly, sustainable, rapid and economic process. The adsorbent capacity of metal ions by plant and its removal varies, depending on the nature of the plants, particle size, and metal concentrations. This review paper focuses on the idea of using various agricultural wastes for the removal of heavy metals and also a way to management of waste generated by agriculture field. In this context, agricultural biomass is the best technique for the removal of heavy metals and need to improve the utilization of agricultural waste as sustainable way.

***Keywords:*** *Toxic metals, Removal efficiency, Agricultural waste, Adsorbent, Plant tolerance power*.

## I. INTRODUCTION

Agricultural waste material including biomass burnt or naturally converted into organic fertilizer under favourable condition. But nowadays biomass produced from agricultural waste is used to generate energy and the effective utilization of agricultural waste is a good option to use as metal removal. For these efforts have been made and many more are underway, it requires guidelines concerning the utilization of agricultural biomass for a sustainable management tool for metal removal.

Toxic substances including heavy metals are hazardous to the environment, as they are non-biodegradable and toxic in nature [1]. Toxicity of metal poses many diseases in humans including cancer, nervous disorder, organ failure, growth reduction and abdominal pain [2-3]. The metals concentration in the environment is found due to the discharges of industrial effluents from many industries such as tanneries, textile, pulp, paper, chlore-alkali, electroplating, fertilizers, dying, battery manufacturing and mining operations which creates metal toxicity [4-5].

Removal of toxic metal from soil, water, and air environment uses various methods including ion exchange, chemical precipitation, membrane separation, electrochemical coagulation, photo-catalysis, reverse osmosis, electrodialysis, solvent extraction, evaporation, etc. [6-12]. These methods are expensive and not effective. Adsorption is an effective and attractive purification and separation technique used especially in the industry for water and wastewater treatment [13]. The process of adsorption is an advantage over other methods due to its sludge-free clean operation. The manufacturing and regeneration costs are very high [14]. Thus, the demand of the hour is a low-cost adsorption system for which some attempts have been made to find a low-cost alternative adsorbent with high efficiency.

In recent years, considerable attention has been given to study the application of agricultural waste materials for heavy metal removal. The use of agricultural wastes or lignocellulosic materials such as rice husk, sawdust, wheat straw, orange peels, baggase, peanut shells, etc. is an effective method due to their availability in abundance (naturally or as by-products from waste industry), low cost, being environmentally friendly, feasibility for physical and chemical modification, and good adsorption capacity of heavy metals from wastewater [15-16].

The purpose of this review paper is to collect information on the use of various agricultural wastes as a sustainable way to removal of metal and management of waste generated from the agricultural field. This paper also aims to review the applicability of plants for metal removal from the environment as it is a cost-effective and eco-friendly technique of metal removal.

## II. SOURCES OF HEAVY METALS AND ITS IMPACT ON AIR, WATER AND SOIL ENVIRONMENT

Heavy metal originates as a natural constituent of earth crust as well as from anthropogenic activity. Heavy metal persists in the environment and it cannot be degraded. Metals enter the body through food, air, and water and bio-accumulate over a period of time [17]. Sources of heavy metal differ from place to places. Minerals weathering, erosion, and volcanic activity are the most significant natural sources while for anthropogenic sources are mining, smelting, electroplating, use of pesticides and fertilizers as well as biosolids in agriculture, sludge dumping, industrial discharge, atmospheric deposition, etc. [18-19]. The most common and important heavy metals as a contaminant in the environment are As, Sr, Cs, U, Cd, Cr, Cu, Hg, Pb and Zn [20-21]. Some of these metals are micronutrients necessary for plant growth and development, such as Zn, Cu, Mn, Ni, and Co, while others have an unknown biological function, such as Cd, Pb, and Hg [22]. Heavy metal poses toxic effects on human health and causes several serious diseases. Elements with metallic properties and an atomic number >20 are the conventional definition of heavy metals. Naturally, metals are normal components in soils. However, in high levels, metals can be toxic for plants, animal and microbes [23]. The heavy metal pollutant is a substance causes negative effects on life and reducing the quality of the environment and eventually causing death. These types of substances present in the environment acceptable as tolerance limit. Hence, environmental pollution such as air, water, and soil, which may be poisonous or toxic and caused harmful effects on a living being. They are global problems that are a growing threat to the environment.

## III. HEAVY METAL REMOVAL EFFICIENCY OF AGRICULTURAL WASTE

Biomass of agriculture contains hemicelluloses, cellulose, lignin, protein, sugar, water, starch, and various functional groups, i.e., amine, aldehyde, hydrocarbons, keto group. Such properties enhance the efficiency of agricultural product and by-products in wastewater treatment. Agricultural biomass has properties viz. eco-friendly, wide availability, cheap in nature and material diversity. Some agricultural biomasses have been studied in the removal of toxic metal ions from aqueous solutions viz. stalk, husk, bagasse, fibre, shells, and straw.

Several previous studies have described the potential of plant as heavy metal bio-accumulator from contaminated soil and water. The studies have indicated the use of plants through phytoremediation technology is an alternative solution to treat heavy metal contaminated areas and can be used to remediate the environment. Table 1 and 2 summarizes the list of several plants and their part reported for heavy metals remediation. Each different plant has also different responses to different heavy metals exposure. Several plants are sensitive while other plants have a high tolerance to toxic metals. As a consequence of plant-metal interaction, numerous plants accumulate heavy metals from soil and have growth and development decreases. However, some plants have a high tolerance and can keep the growth and development as well under heavy metals stress.

## IV. DIFFERENT PART OF PLANT (STALK, HUSK, BAGASSE, FIBRE, SHELL AND STRAW) FOR REMOVAL EFFICIENCY OF HEAVY METAL

Various part of the plant including Stalk, Husk, Bagasse, Fibre, Shell, and Straw play an important role for removal of heavy metals. In this review, we are describing the various agricultural plants and their part as a waste for removal of heavy metals. In this constant, different types of agriculture plant stalk (sunflower, Zea maize, and corn) have been used as an adsorbent of several heavy metals in aqueous solutions [24]. A study reported by Zheng et al [25-26] the biosorption properties were improved by corn stalk. The husk is a part of agricultural residue, produced from several processes used in the removal of different metal ions in aqueous solution. A study reported by Wong et al. [27] used modified rice husk prepared by tartaric acid and carboxylic acid in removal of Cu (II) and Pb (II) ions adsorption reported 29 and 108 mg/g at $27\pm2^{o}$C. Bagasse, a composition of lignin, pentose and cellulose as main constituents, is an agricultural solid waste obtains from the sugar industry. Its absorption capacity was higher due to the presence of diverse functional groups such as carboxylic, carbonyl, amine and hydroxyl, which helps in the binding of metal ions through cation exchange on adsorptive sites [28]. Adsorption capacities of Bagasse for the different metal ions are given in Table 1. The composition of plant fibre is including cellulose, hemicellulose, lignin, pectin and extractives (fat, waxes, etc.). Various functional groups are also present in fibre which are responsible for adsorption of metal, carboxylic (including hemicelluloses, pectin, and lignin), phenolic (lignin and extractives), hydroxylic (cellulose, hemicelluloses, lignin, extractive, and pectin) and carbonyl group (lignin) [29]. Shells are the part of plant and used as low-cost adsorbents in removal of toxic pollutants from water. Ismaiel et al. [30] reported the potential of modified palm shell activated carbon in the removal of Hg (II) ions in aqueous solutions through batch-adsorption techniques. They observed that the efficiency of mercury removal increased with increasing contact time and increasing initial metal concentration. The increment of removal efficiency was found to be 83.33 mg/g at room temperature and pH 8, with a contact time of 3 hours while an initial concentration of 10-200 mg/L. Straw is mainly produced from the agricultural activities and mainly used in paper industry and as fodder for animals. The various study reported that different types of straw, such as wheat straw, barley straw, and rape straw, have potential in metal sequestration from wastewater. Biosorption potential of unmodified rice in the efficient removal of Cd (II) ions was reported by Ding et al [31]. The maximum biosorption capacity was noted 13.9 mg/g at pH range of 2.0-6.0. When 0.5% (w/v) rice straw was exposed to 50 mg/mL $CdSO_4$ solution with shaking at 150 r/min for 3 h, about 80% of aquatic cadmium was absorbed and the cadmium content in rice straw reached 8-10 mg/g. Gorgievski et al. [32] also reported the potential of wheat straw in the biosorption of $Cu^{2+}$, $Ni^{2+}$ and $Zn^{2+}$ ions from synthetic solution. Adsorption of heavy metal ion was influenced by the pH value and the adsorbent dosage. The study showed that the adsorption process increased with increasing adsorbent dose and pH values. Removal of metal more than 90% was obtained at pH 3.0-7.0. Metal ion biosorption is depending on insignificantly on pH but significantly on temperature.

**Table 1: Agricultural Biomass and Their Heavy Metal Adsorption Capacity**

| ***Biomass*** | ***Metal, pH and Adsorption capacity (mg/g)*** | ***References*** |
|---|---|---|
| ***Stalk biomass*** | | |
| *Corn stalk (acrylonitrile modified); Corn stalk (raw)* | Cd (II), 7, 12.73; Cd (II), 7, 3.39 | 25,26 |
| *Sunflower stalk* | Pb (II), 5, 182; Cd (II), 5, 70 | 36 |
| *Zea maize stalk sponge* | Pb (II), 6±0.2, 80 | 37 |
| ***Husk biomass*** | | |
| *Bengal gram (Cicer arientinum) husk* | Cr (III), 2, 91.64 | 38 |
| *Coffee husk* | Cu (II), 4, 7.5; Zn (II), 4, 5.6; Cd (II), 4, 6.9; Cr (VI), 4, 7.0 | 39 |
| *Hazelnut husk carbon* | Cd (II), 5, 61.35 | 40 |
| *Rice husk* | Cr (III), 5-6, 30; Cu (II), 5-6, 22.5 | 41 |
| ***Bagasse biomass*** | | |
| *Agave bagasee( raw)* | Cd (II), 5, 14; Pb (II), 5, 36; Zn (II), 5, 8 | 42 |
| *Bagasse carbon* | Cd (II), 4.5, 38.03; Zn (II), 4.5, 31.11 | 43 |
| *Sugarcane; Sugarcane bagasse (untreated)* | Cr (VI), 1.9, 23.0; Pb (II), 5, 6.366 | 44,45 |
| ***Fiber biomass*** | | |
| *Agave sisalana (sisal fiber)* | Cd (II), 7, 1.85; Pb (II), 7, 1.34 | 46 |
| *Coconut fiber (with pristine)* | Hg (II), 2-10, 166.67 | 47 |
| *Citrus reticulata waste biomass (modified with NaOH)* | Pb (II), 5, 83.77; Co (II), 7, 95.55 | 48 |
| *Ficus carica fiber* | Cr (V), 3, 19.68 | 49 |
| *Palm kernel fibre* | Cu (II), 5.01, 20.12 | 50 |
| ***Shell biomass*** | | |
| *Annona squamosa* | Pb (II), 5, 90.93; Cd (II), 5, 71.0 | 51 |
| *Cashew nutshell* | Pb (II), 5, 408.6 | 52 |
| *Chrysophyllum albidum seed shell* | Pb (II), 5, 103.42 | 53 |
| *Pecan nutshell* | Cr (III), 5.5, 93.01; Fe (III), 4, 76.59; Zn (II), 5.5 107.9 | 54 |
| *Walnut shells (modified with ZnCl2)* | Hg (II), 5, 151.5 | 55 |
| ***Straw biomass*** | | |
| *Barley straw and Barley straw (modified with citric acid)* | Cu (II), 6, 4.64; Pb (II), 6, 23.20; Cu (II), 7, 4.64; Cu (II), 7, 31.71 | 56,57 |
| *Rape straw* | Cu (II), 5, 7.3 | 58 |
| *Wheat straw* | Cd (II), 6, 14.56; Cd (II), 6, 39.22 | 59 |

## V. OTHER AGRICULTURAL BIOMASS

Palm flower (*Borassus aethiopum*) treated with acid ($H_2SO_4$) and alkali (NaOH) was established as bio sorbent in the removal of Cr (VI) and Cr (III) ions from aqueous solutions. The maximum adsorption capacities were 6.24 mg/g (raw material) and 1.41 mg/g (acid-treated) regarding Cr (III) elimination. For Cr (VI) ion, the maximum uptake was 4.9mg/g (raw adsorbent) and 7.13 mg/g (acid-treated). The changes in functional groups in biosorption confirmed the experiment [33]. The use of weed as bio-adsorbent is a cheaper and eco-friendly technique in metal detoxification of the environment. In the above-mentioned biomass used in metal removal, some other materials like apricot stone, bael fruit, coir pith, and pine needles were also used in sequestration of various metals (Table 2). The adsorption performance of chemically modified cotton seed cake for lead (II) removal from aqueous solutions was tested. The adsorption capacity was found to be 115.86 mg/g, i.e., 5.3 times advanced than that of commercial activated carbon (21.69 mg/g) at $300^{o}$K. The adsorption procedure followed pseudo-second-order kinetics which confirms the chemisorption as a rate-controlling process [34]. Bouhamed et al. [35] studied $H_3PO_4$ activated Tunisian date stones, as a low-cost adsorbent for Cu (II) ion removal from aqueous solutions. The optimum results were found at about pH 5. The adsorption process followed pseudo-second-order kinetics. The data fitted the Langmuir and Dubinin-Radushkevich isotherm models. The monolayer adsorption capacity was recorded as 31.25 mg/g.

## VI. CONCLUSION AND FUTURE SCOPE

Burning of agricultural waste is a major cause of environmental pollution. Nowadays various techniques are used for agricultural waste management system including energy generation and compost formation. Toxic metal removal by agricultural waste is a sustainable way for environmental clean-up. Plants can be an alternative solution as a green technology to treat the heavy metal contaminated environment (soil, water, and air). According to previous studies, several plants have a high potential as heavy metals bio-accumulator and can be used for the removal process of heavy metals. Metal removal rate depends on the plant biomass harvested and metal concentration in harvested biomass. In the present scenario, heavy metal is a major problem for environment. The present study also referred that various agricultural waste can be used as an eco-friendly technology for heavy metal removal. As seen from the research literature related to the utilization of agricultural waste for removal of heavy metal as newer development technology. In future need to improve the utilization of agricultural waste for metal removal.

**Table 2: Other Agricultural Biomass Heavy Metal Adsorption**

| *Agricultural Biomass* | *Metal, pH and Adsorption Capacity (mg/g)* | *References* |
|---|---|---|
| *Apricot stone* | Pb (II), 6.5, 22.85; Co (II), 9, 111.11 | 60 |
| *Bael fruit* | Cr (VI), 2, 17.27 | 61 |
| *Bagasse pith (activated carbon)* | Co (II), 6, 153.6 | 62 |
| *Coir pith* | Co (II), 4.3, 12.82; Cr (III), 3.3, 11.56; Ni (II), 5.3, 15.95 | 63 |
| *Hibiscus rosa sinensis dye waste (HDW)* | Pb (II), 6, 90.909; Cd (II), 6, 103.093 | 64 |
| *Hydrilla verticilata* | As (III), 6, 11.65 | 65 |
| *Immobilized beads of Garcinia cambogia* | As (III), 6, 704.11 | 66 |
| *Parthenium hysterophorus and (modified with H2SO4)* | Cr (VI), 1, 24.5; Ni(II), 5, 17.24 | 67,68 |
| *Pine cone* | Pb (II), 5.2, 27.53 | 69 |
| *Salvinia cucullata (thermally activated weed)* | Cr (VI), 1.7, 247 | 70 |
| *Tea leaves (exhausted and exhausted)* | Pb (II), 1-6, 120.8; Zn (II), 1-6, 79.76 | 71 |

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