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Recent approach in heavy metals removal using plant derived bio-mass: A review

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***Abstract*—In the present scenario the water easily gets contaminated due to rapid industrialization and high population. Heavy metals have some severe deteriorating effects on environment as well as human lives. Therefore the eradication of heavy metals is necessary to protect the environment. Many researchers preferred bio-adsorbent generated from various biomass, as it is of low cost and high sustainability. This review mainly evaluates the recent approaches in the application of various bio-adsorbents in removal of noxious heavy metals for waste water treatment. The adsorption capacities of various heavy metals were investigated through different conditions such as adsorbent dose, pH, initial heavy metal concentration, and temperature in the literature study. Isotherm and kinetic study along with the maximum adsorption capacity were also specified. Basically, the bio adsorbent exhibits excellent evidence to remove single and multiple heavy metals from the aqueous medium.**

***Keywords*— Heavy metals, Bio-adsorbent, wastewater treatment, bio-adsorption.**

I. Introduction

Water is an essential resource for our daily need. The rapid population growth, agriculture, upgraded urbanization, and industries consume high amount of water and releases a huge amount of waste water as well[1]. Water pollution now became a major concern as it affects the environment in a destructive manner[2]. Generally water pollutants come from either point sources or dispersed sources[3]. Water pollutants mainly contain fertilizers[4], microorganisms[5], pharmaceutical waste[6], plastics[7], dyes[8], heavy metals, and several hazardous waste. This contaminant affects the quality of water and makes it unsafe for the drinking purpose. Therefore, the removal of pollutants from water is a prime factor for the wastewater treatment.

Among all the pollutants, heavy metals such as Chromium, Mercury, Lead, Cadmium, Arsenic, copper etc are toxic, insoluble in nature and highly responsible for water contamination[9]. These heavy metals have a tendency to bio-accumulate and cause several threats to living organisms. Water pollution by heavy metals has many origins, such as the exhaust gases from vehicles[10], mining[11], agriculture[12], and incineration of solid as well as liquid wastes[13].

Heavy metals also occur naturally, due to thermal springs, volcanoes[14], infiltration[15], etc. Some prevalent heavy metals have some serious toxicity rate and major health concern. The heavy metal Mercury cause serious health hazards like degradation of nervous and reproductive system, deafness, skin and eye problem, and have deteriorating effect on thyroid gland[16]. High exposure of Lead can cause damage to the kidney, liver and various nervous systems[17]. The toxic effect of Chromium has some severe health issues like renal failure, kidney damage, lungs cancer, and dermatitis[18]. The heavy metal Cadmium, being noxious having bad effects on the testicular tissue, kidney, heart, bones and liver of human beings[19]. The toxic effects of Arsenic are very critical. Beyond its maximum permissible limit can damage cardiovascular system, skin, stomach, central nervous system and results in cancer diseases[20]. Similarly, Copper can affect the abdomen, Lungs, and results in liver toxicity, diarrhea, and weakness[21]. Hence, it is necessary to remove heavy metals before discharging into water bodies.

Several techniques have been used for the removal of heavy metals from contaminated water such as, ultra filtration [22], coagulation- flocculation[23], membrane filtration[24], ion exchange[25], neutralization[26], solvent extraction[27] and adsorption[28]. Among all the techniques, adsorption has gained primary consideration for researchers due to its easy in operation, simple design, low cost, easy availability, reusability and higher removal efficiency for a broad range of pH.

There are many researches are performed on preparation of bio-adsorbent from the biomass which are used to remove heavy metal from waste water. Biomass includes plant residue such as seed[29,30], bark[31,32], peel[33,34], wood[35,36], leaf[37] and agricultural waste[38–40]. Plant materials mainly consist of cellulosic material which is efficient in adsorption of heavy metals from waste water. In past few years many studies have been performed on adsorption using biomass for heavy metal removal. Plant derived bio adsorbents, such as seed, root, bark, and peel successfully removed heavy metals from waste water. Agricultural waste has some significant role in heavy metals adsorption

II. BIO SORBENTS USED FOR HEAVY METAL REMOVAL

This section describes various reports on the uses of bio-adsorbents (Activated carbon) materials for the removal of heavy metal with the details about different parameters (sweet able pH, Initial heavy metals concentration, adsorbent dosage, and adsorption capacity) are given in Table 1. Table 2 shown comparison of various isotherm model, and kinetic models for activated carbon prepared from various bio-adsorbents.

A. Seed

Mohib et al. (2018) investigated activated carbon synthesized from seeds of Melia azedarach and Albizia lebbeck trees for removing Pb and Cd metals in water solution. The synthesized activated carbon were characterized by FT-IR and SEM. The removal capacities of Pb and Cd were dependent on their pH, initial concentration and the quantity of adsorbents. Adsorption experiments have initial concentrations (40 mg/l) of both the Pb and Cd ions at a pH of 5 and temperature of 20°C. Langmuir isotherm was well fitted to the experimental data and kinetic study was done using pseudo second order kinetic model. Here the maximum adsorption capacity was noticed to be 3.25mg/g for Cd and 4.38mg/g for Pb while Albizia lebbeck tree prepared adsorbent was used and 4.20mg/g for Cd and 3.43mg/g for Pb when Melia azedarach trees prepared adsorbent was used.[30]

Alejandra et al. (2019) studied use of a black sapote seeds for synthesis of activated carbon as an adsorbent. These seed residues were chemically activated by H_3PO_4 and carbonized at 400-600^{0}C. The synthesized AC were characterized using IR, SEM, and Nitrogen - adsorption - desorption analysis. The dose of AC used was 5 g/L for heavy metals like Cr, Co, Fe and Pb. The highest removal efficiency seen at acidic pH (3 to 5) with initial concentrations 50 mg/L. It was seen that Cr was adsorbed in the max proportion, around 10 mg.g^{-1}, followed by Cu and Fe, Pb was adsorbed in a smaller amount of approximately 5 mg.g^{-1}. This adsorption is well suited to Langmuir-adsorption-isotherm and pseudo-second-order-kinetic model.[29]

B. Bark

Martini et al.(2019) studied the adsorption of Cr(III) on the bio adsorbents surface prepared from eucalyptus bark (EB). FT-IR and SEM were used in the characterization of adsorbent. The optimum conditions found at contact time of 100 min, adsorbent dosage 10 g.L^{-1}, pH of 3, and at 25^{0}C. It follows the Freundlich isotherm having R^2 =0.9758. Langmuir isotherm shows that adsorption capacity of this is 0.0263mg/g. The data was studied using pseudo-second-order kinetics model.[32]

Marina et al. (2021) studied the activated carbon from jambleng tree bark. The preparation of activated carbon was started by carbonization of jambleng tree bark at 400°C for 180 minutes . After completion of experiment the synthesis of activated carbon was experimented on the adsorption of Pb metal. SEM evaluates morphology of activated carbon, FTIR determines functional group, XRF determines composition and SAA evaluates surface area with pore size. The adsorption was about 57.28mg/gm. The adsorption process followed the Langmuir isotherm (R^2=0.619). Pseudo-second-order kinetic was highly sweet able to the adsorption process.*[31]*

C. Wood

Sujatha et al. (2019) studied the removal of Pb using AC prepared from Manilkara zapota tree wood. Activated carbon was prepared by using carbonization and activation. SEM, FTIR and XRD were used to characterize adsorbent. It was found that optimum adsorption was seen in case of acidic pH (pH 4), adsorbent dose of 0.2 gm and initial concentration of Pb about 60 mg/L. It follows Langmuir adsorption isotherm and pseudo-second-order kinetics. The max adsorption value was calculated to be 22.0618 mg/g[35].

Kolvankar et al. (2019) studied the preparation of activated carbon from coconut tree and its heavy metal removal capacity. Carbonization process was used to make activated carbon for Co(II) removal. Characterization was done using FTIR, XRD and SEM. It was seen that for optimal removal of Co(II) pH of 7.0, adsorbent doses of 0.5g and initial concentration of 50mg/L was needed. The adsorption data was highly adopted Freundlich isotherm. The max adsorption at optimum condition was seen to be 29.8507mg/g. Pseudo - second - order kinetic model was highly fitted to adsorption process[36].

D. Peel

Enniya et al. (2018) used the apple peels to prepare bio adsorbent for the removal Cr metal. Apple peel activated carbon was prepared using NaOH activation. Cr (VI) adsorption was studied in the initial concentration of 50mg/l while AC dose was taken to be 0.05gm/0.02L. FTIR and SEM techniques were used to describe the characterization of apple peel activated carbon. The maximum adsorption capacity could be achieved to be 36.01mg\g while pH was 2. It follows Freundlich isotherm (R^2=0.99). Pseudo-second-order model was set well to the experimental data.[33]

Wattanakarnsiri et al. (2022) showed that removal of Pb(II) and Cd(II) from waste water solution using activated carbon made from 3 types of peels such as Dragon fruit peel (DFP), Rambutal peel (RP) and Passion fruit peel (PFP). Adsorption was studied in the initial concentration of 100mg/L while adsorbent dose was taken to be 0.25gm/L with pH value of 4.the adsorption was seen to follow Langmuir adsorption and pseudo second order model. The maximum adsorbent capacities were 97.087mg (Pb^{2+})/g, 114.943mg (Pb^{2+})/g, 104.093mg (Pb^{2+})/g & 86.207mg (Cd^{2+})/g, 102.041mg (Cd^{2+})/g, 89.286mg (Cd^{2+})/g for DFP, RP, PFP respectively.[34]

E. Leaf

Juboury et al.(2019) studied Cu(II) removal using activated carbon prepared from palm leaf using co-precipitation method. FTIR, SEM and EDS were used to characterize the adsorbent. When 0.2gm/0.05L of adsorbent dose was used at pH of 5 maximum adsorption of 35.39gm/g was obtained for initial concentration of 50mg/L. It followed Freundlich isotherm & pseudo-second-order kinetic model.[37]

F. Agricultural residue

Zhao et al. (2020) prepared activated carbon using carbonization of corn stalk for removal of chromium from water. The characterization of activated carbon was done using

SEM, TEM, XRD and FTIR. The activated carbon showed high adsorption performance for Cr(VI), 89.5 mg/g of

Plant Residue	Metals removal	Initial metal concentration	Adsorbent dosages	Adsorption capacity	pH	Reference
Albizia lebbeck seed	Pd	$40mg.L^{-1}$	-	$4.38\ mg.g^{-1}$	5	[31]
Albizia lebbeck seed	Cd	$40mg.L^{-1}$	-	$3.25\ mg.g^{-1}$	5	[31]
Melia azedarach tree seed	Pd	$40\ mg.L^{-1}$	-	$3.43\ mg.g^{-1}$	5	[31]
Melia azedarach tree seed	Cd	$40mg.L^{-1}$	-	$4.20mg.g^{-1}$	5	[31]
Black sapate seed	Cu	$50mg.L^{-1}$	$5gm.L^{-1}$	$10\ mg.g^{-1}$	3 to 5	[30]
Black sapate seed	Co	$50mg.L^{-1}$	$5\ gm.L^{-1}$	$8.2\ mg.g^{-1}$	3 to 5	[30]
Black sapate seed	Fe	$50mg.L^{-1}$	$5\ gm.L^{-1}$	$5.8\ mg.g^{-1}$	3 to 5	[30]
Black sapate seed	Pb	$50mg.L^{-1}$	$5\ gm.L^{-1}$	$5.1\ mg.g^{-1}$	3 to 5	[30]
jumbleng tree bark	Pb	$1000mg.L^{-1}$	$0.1\ gm.L^{-1}$	$57.28\ mg.g^{-1}$	-	[32]
Eucalyptus bark	Cr (III)	-	$10\ gm.L^{-1}$	$0.0263\ mg.g^{-1}$	3	[33]
coconout tree root	Co (II)	$50mg.L^{-1}$	0.5 g/0.1L	$29.8507\ mg.g^{-1}$	7	[37]
Manilkara zapota wood	Pb	$60mg.L^{-1}$	$0.2\ gm.L^{-1}$	$22.0618\ mg.g^{-1}$	4	[36]
apple peel	Cr (VI)	$50mg.L^{-1}$	0.05 gm/0.05 L	$36.01\ mg.g^{-1}$	2	[34]
Dragon fruit peel	Pb (II)	$100mg.L^{-1}$	$0.25\ gm.L^{-1}$	$30.64\ mg.g^{-1}$	4	[35]
Dragon fruit peel	Cd (II)	$100mg.L^{-1}$	$0.25\ gm.L^{-1}$	$33.04\ mg.g^{-1}$	4	[35]
Rambutal peel	Pb (II)	$100\ mg.L^{-1}$	$0.25\ gm.L^{-1}$	$19.84\ gm.g^{-1}$	4	[35]
Rambutal peel	Cd (II)	$100\ mg.L^{-1}$	$0.25\ gm.L^{-1}$	$35.92\ mg.g^{-1}$	4	[35]
Passion fruit peel	Pb (II)	$100\ mg.L^{-1}$	$0.25gm.L^{-1}$	$33.88\ mg.g^{-1}$	4	[35]
Passion fruit peel	Cd (II)	$100\ mg.L^{-1}$	$0.25\ gm.L^{-1}$	$30.16\ mg.g^{-1}$	4	[35]
palm leaf	Cu (II)	$50\ mg.L^{-1}$	0.2 gm/0.05 L	$35.39\ mg.g^{-1}$	5	[38]
corn stalk	Cr (VI)	-	$2.5\ gm.L^{-1}$	$89.5\ mg.g^{-1}$	4.5	[39]
luffa cylindrica	Cr (VI)	-	$1\ gm.L^{-1}$	$188.5\ 0mg.g^{-1}$	8	[40]
rice husk	Cr (VI)	$25\ mg.L^{-1}$	$2\ gm.L^{-1}$	-	6	[41]
rice husk	Pb (II)	$25\ mg.L^{-1}$	$2\ gm.L^{-1}$	-	6	[41]
rice husk	Zn (II)	$25\ mg.L^{-1}$	$2\ gm.L^{-1}$	-	6	[41]

TABLE I Different parameters value for Heavy metals adsorption

TABLE II Isotherm and kinetic models of various bio-adsorbent for heavy metals removal.

Plant Residue	Metal removed	Isotherm	R^2 Value	Kinetics	Reference
Albizia lebbeck seed	Pd	Langmuir	0.97	Pseudo -second -order	[31]
Albizia lebbeck seed	Cd	Langmuir	0.95	Pseudo -second -order	[31]
Melia azedarach tree seed	Pd	Langmuir	0.97	Pseudo -second -order	[31]
Melia azedarach tree seed	Cd	Langmuir	0.97	Pseudo -second -order	[31]
Black sapate seed	Cu	Langmuir	-	Pseudo -second -order	[30]
Black sapate seed	Co	Langmuir	-	Pseudo -second -order	[30]
Black sapate seed	Fe	Langmuir	-	Pseudo -second -order	[30]
Black sapate seed	Pb	Langmuir	-	Pseudo -second -order	[30]
jumbleng tree bark	Pb	Langmuir	0.61	Pseudo -second -order	[32]
Eucalyptus bark	Cr (III)	Freundlich	0.90	Pseudo -second -order	[33]
coconout tree root	Co (II)	Freundlich	0.96	Pseudo -second -order	[37]
Manilkara zapota wood	Pb	Langmuir	0.83	Pseudo -second -order	[36]
apple peel	Cr (VI)	Freundlich	0.99	Pseudo -second -order	[34]
Dragon fruit peel	Pb (II)	Langmuir	0.99	Pseudo -second - order	[35]
Dragon fruit peel	Cd (II)	Langmuir	0.99	Pseudo -second -order	[35]
Rambutal peel	Pb (II)	Langmuir	0.99	Pseudo -second -order	[35]
Rambutal peel	Cd (II)	Langmuir	0.98	Pseudo -second -order	[35]
Passion fruit peel	Pb (II)	Langmuir	0.99	Pseudo -second -order	[35]
Passion fruit peel	Cd (II)	Langmuir	0.99	Pseudo -second -order	[35]
palm leaf	Cu (II)	Freundlich	0.98	Pseudo -second -order	[38]
corn stalk	Cr (VI)	Freundlich	0.90	Pseudo -second -order	[39]
luffa cylindrica	Cr (VI	Freundlich	0.90	Pseudo -second -order	[40]
rice husk	Cr (VI)	Temkin	0.98	Pseudo -second -order	[41]
rice husk	Pb (II)	Temkin	0.95	Pseudo -second -order	[41]
rice husk	Zn (II)	Temkin	0.97	Pseudo -second -order	[41]

adsorption capacity at an adsorbent dosage of 2.5 g/L and pH value of 4.5. The adsorption process follows Freundlich isotherm (R^2=0.90608) and shows second order kinetics.[38]

Kenechi et al. (2020) studied luffa cylindrica activated carbon for Cr(VI) removal. SEM was used for characterization of adsorbent. The adsorbent was prepared using chemical activation process. The optimum adsorption capacity of 188.50mg/g was seen in case of pH of 8 and adsorbent dose of 1gm. It undergoes Freundlich isotherm (R^2= 0.901) and Pseudo-first-order kinetic model.[39]

Priya et.al (2022) investigated removal of heavy metal from aqueous solution using rice husk. The removed heavy metals are Cr (VI), Pb (II) and Zn (II). The bio-adsorbent was prepared from rice husk powder and modified with 0.1N of HCl. For the pristine adsorbent FT-IR, SEM and EDX Characterisation were taken. The maximum percentage of removal of Cr, Pb, and Zn are 87.12%, 88.63%, and 99.28%, respectively in the optimum pH value of 6.0. Adsorbent dose was taken to be 2 gm/l for optimal adsorption. The adsorption followed Temkin and D-R isotherm models.[40]

III. CONCLUSION

Heavy metals are generally toxic and non degradable in nature, so even at very low concentration they can cause severe health hazard as well as environmental problems. Heavy metals like Mercury, Lead, Chromium, Cadmium, Arsenic, and copper have some serious health hazards which affect human lives in every possible way. Due to the noxious effect of heavy metals, it is required to remove them before discharging into aquatic body. Many researchers are using adsorption technique as it is highly efficient to remove heavy metals. Bio-adsorbent being easily available, low cost and abundant for removal of single and multiple heavy metals from waste water have gained a valuable consideration in past few years. This review is mainly based on the recent approach on noxious heavy metals removal using plant derived bio-adsorbent. Bio-adsorbent like seed, bark, peel, leaf, stalk, husk have been used for the heavy metals removal. We compared the various bio-adsorbent according to different parameters such as pH, initial concentration and adsorbent dose in our literature study. From the study we concluded that most of the bio-adsorbent removes heavy metals at acidic pH which is between pH 3 to pH 6. All these bio-adsorbent follows Langmuir and Freundlich isotherm model, out of which Langmuir isotherm model was followed in majority by bio-adsorbents. So, it can be suggested that the adsorption process involves one layer adsorption. From the isotherm model maximum adsorption capacity was also compared. Among all bio-adsorbent we found that corn stalk activated carbon has highest q_{max} value which is 188.50 mg/g. We also studied different kinetic models like pseudo-first-order and pseudo-second-order kinetic model, but most of the bio-adsorbent well fitted pseudo second order kinetic model. Moreover, our review mainly based on the application of various bio adsorbents for removal of heavy metals in a better economic and sustainable way in comparison to other adsorbents.

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