

DESIGNING A BETTER BIO-ADSORBENT FROM SAWDUST FOR REMOVAL OF METAL IONS FROM WASTEWATER: A REVIEW ON VARIOUS MODIFICATIONS

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ABSTRACT: Sawdust-an abundantly available waste resource of timber industry has been valorized to effective biosorbent for wastewater treatment as indicated by literature studies. But use of raw sawdust for water clean-up activities has its own drawbacks which causes limitations to its widespread commercialization. Designing a quality adsorbent material from sawdust requires in addition to better adsorption capacity, better mechanical properties, stability, better selectivity for multi-pollutant systems and better reuse capacity. Surface modification techniques can ensure better physical and chemical properties which can finally lead to the development of an advanced adsorbent material from sawdust. An in-depth review is thus presented which is related to studies carried out on the role of raw sawdust for water clean-up activities, drawbacks associated with sawdust as a biosorbent, different modification methods adopted and finally their consequence on the physico-chemical/adsorption characteristics of the modified adsorbent. Although sawdust has the potential to remediate various water-based adsorbates but the present review has a focus on metal ions present in water bodies.

KEY WORDS: Sawdust; biosorbent; pretreatments; metal adsorbates; wastewater treatment

I. INTRODUCTION

The demand for use of green and low-cost technologies for obtaining clean water has paved the path for the more efficient adsorption process for treatment of wastewater [1,2]. Activated carbons manufactured from coal and petroleum-based sources have exhibited good adsorption properties for diverse types of pollutants and this has served as the basis for success of the adsorption technology. But the commercial activated carbons are expensive and regeneration processes often result in the degradation of their adsorption properties [3]. Waste products of industry and agriculture produced in abundance and having no economic utility have demonstrated good binding affinities for pollutants and are hence being effectively valorized into adsorbents for use in wastewater treatment [4].

Literature data pertaining to the development and use of low cost activated biosorbents for wastewater remediation have revealed the good adsorptive potential of the precursors from agricultural residues and wood by-products [5,6]. Various precursors have been demonstrated to have good adsorption properties; details of which are stated in the review [7]. The high efficiency of such precursors is attributed to the presence of favorable binding affinity of functional groups of cellulose, hemicellulose and lignin. Sawdust is produced at sawmills as a solid waste of the timber industry. The important characteristic of such waste is that it has no economic value and is either used to generate heat for cooking purposes or is used as commercially for packing purposes. As per a report published, approximately 1011 tones of sawdust are generated annually worldwide. Unscientific means of disposal has resulted in environmental problem [8]. Being lignocellulosic based, it has high carbon, low ash content and also appropriate "O" containing surface functional groups. Such features are required for a good adsorbent material. Research literature shows that the sawdust from various tree species like red fir, pine, cedar, teak, beach etc. has been valorized to effective biosorbent for removal of dyes, oil, salts, heavy metals, etc. Valorization of sawdust for effective water cleaning activities is beneficial to both the environment and to the timber industry. As per the review on sawdust as a biosorbent by Shukla et al., (2002) [8], the major qualities that have attracted its interest among the scientific community is their mass scale generation, no economic importance but has all the features of a good adsorbent. Such qualities have been corroborated by scientific work on the adsorption capacities of sawdust towards numerous water pollutants. But the raw sawdust has exhibited disadvantages like lower binding capacity and has also demonstrated a rise in COD levels in the wastewater due the release of organic compounds. Keeping in focus the huge potential exhibited by sawdust as a promising biosorbent as evident from literature, the present review has attempted to

highlight the role of modifications that can ensure better physical, chemical and textural properties. Secondly and more importantly, based on the disadvantages exhibited by raw sawdust as biosorbent, various modifications and pretreatments adopted by researchers have been critically discussed vis a vis their effect on the adsorption performance especially for metal ion adsorbates. Other likely factors bringing about a similar enhancement of adsorption capacity are also discussed. The prospects of carrying out modifications/pretreatments so as to bring about enhancements in surface texture and chemistry of the sawdust are interesting as it is a well-known fact that the fabrication of an advanced adsorbent material can ensure quality and economical water treatment.

Raw sawdust: Metal ion adsorption capacity; operating factors and underlying mechanism

A detailed survey of literature studies on untreated sawdust has revealed their biosorbent potential for removal of different metal ions from simulated water as can be evident from Table-1. Table-1 reveals that various tree species like maple, beech, poplar, linden, Mansonia, rubber wood, pines, mango, Meranti etc. have been experimented upon by researchers for development of the sawdust biosorbent. The Table-1 also reveals that the biosorption potential to remediate metal ions from water depends on various factors like pH, temperature, contact time, adsorbent dosage etc.

Table-1: Performance of raw sawdust for removal of metal ions from wastewaters

Biosorbent	Metal ion	ads capacity	pH, Contact time	Isotherm applicable	Metal binding Mechanism	Reference
SD	Cr(VI)	24.63 mg/g	2, -	L	Electro-static attraction	[9]
SD	Cr(VI)	41.52mg/g	1, 1050min	L, F	Electro-static	[10]
SD (rubber)	Cr(VI)	4.87 mg/g	2, -	L	NA	[15]
SD	Cr(VI)	10.76 mg/g	2.6, 60m	L	Electro-static,	[20]
SD (Maple)	Cr(VI)	% removal -	2, 60min	F	Ion Exchange	[25]
SD(Turkish	Cr(VI)	5.50mg/g	3, 120min	L, F	Ion Exchange	[87]
SD	Cu(II)	3.742mg/g	7, 120min	L	NA	[11]
SD (Beech)	Cu(II)	4.5 mg/g	4, 20m	L	Ion exchange	[12]
SD	Cu(II)	57.14mg/g	5, 90min	L	NA	[16]
SD	Cu(II)	20.20mg/g	6, -	L, F	NA	[17]
SD (Meranti)	Cu(II)	37.17mg/g	6.6, 60m	L	Ion exchange and H ₂	[21]
SD (Cedar)	Cu(II)	294.12mg/g	6, 20min	L	Ion Exchange	[23]
SD (Maple)	Cu(II)	9.51mg/g	6, 39min	F	Ion Exchange	[24]
SD (Maple)	Cu(II)	1.79mg/g	7, 180min	L, F	Ion Exchange	[27]
SD(poplar)	Cu(II)	0.04mmol/g		L	Ion exchange	[29]
SD (fig)	Cu(II)	0.04mmol/g		L	Ion Exchange	[29]
SD(poplar)	Cu(II)	5.432mg/g	4	L	Electro-static attraction	[45]
SD (<i>Pinus</i>)	Cd(II)	7.35 mg/g	9, 20m	F	Electro-static,	[18]
SD (Beech)	Ni(II)	4 mg/g	4, 20m	L	Ion exchange	[12]
SD (Beech, linden, poplar)	Cu(II) Ni(II) Zn(II) Cd(II)	7-8 mg/g	3.5-5.5, 20min	L	Ion exchange	[13]
SD (poplar)	Cu(II) Zn(II) Cd(II)	0.040mmol/g 0.015mmol/g 0.005mmol/g	-	L, F	NA	[14]
SD	Pb(II)	39.50 mg/g	6, -	L	NA	[17]
SD (<i>Pinus</i>)	Pb(II)	% removal-	4, 40m	L	NA	[19]
SD (Meranti)	Pb(II)	37.04 mg/g	7, 60m	L	Ion exchange and H ₂ bonding	[21]
SD (<i>Caryocar</i>)	Pb(II)	89.10 mg/g	5, 70m	L	NA	[22]
SD	Pb(II)	145.04 mg/g	5, 70m	L	NA	[22]
SD (<i>Tabebuia</i>)	Pb(II)	95.31 mg/g	5, 70m	L	NA	[22]
SD (Maple)	Pb(II)	3.19mg/g	5, 180min	L, F	Ion Exchange	[26]
SD	Pb(II)	0.82 mg/g	5, -	NA	NA	[28]
SD + heat	Pb(II)	0.86 mg/g	5, -	NA	NA	[28]

SD (Beech)	Zn(II)	2 mg/g	4, 20m	L	Ion Exchange	[12]
SD(poplar)	Zn(II)	0.02 mmol/g		L	Ion Exchange	[29]
SD (fir)	Zn(II)	0.015 mmol/g		L	Ion Exchange	[29]
SD(Fir)	Au(III)	3.2mg/g	3, 5 min	L	Chelation	[43]

Irrespective of the tree species, raw sawdust demonstrated varying potentials (5.50 mg/g to 41.52 mg/g) to bind to Cr(VI) as evident from studies carried out by different research groups [9, 10, 15, 20, 25, 87]. But in each of such study, highest adsorption capacity was observed at lower pH values of 1-3. The mechanism underlying the strong and better binding at lower pH values was proposed to be electrostatic attraction between the negative HCrO_4^- species and the protonated sawdust surface [9, 10, 20]. Usually higher temperatures were favorable for Cr(VI) adsorption thus revealing the chemical nature of the binding [15]. Surface functional groups was revealed to be OH, C=O and NO groups as per FTIR studies carried out on the sawdust surface [20]. Irrespective of tree species, adsorption for Cu(II) onto raw sawdust was found to range between 1.79 mg/g to 294.12 mg/g. The tree species studied ranged from beech [12], Meranti [21], Cedar [23], Maple [24, 27], Poplar [29, 45] etc. Operating pH for maximum Cu(II) adsorption was 4-7 and the mechanism of binding was proposed to be ion-exchange due to substitution of alkaline earth metals in the biosorbent with the metal adsorbates and protons present in the aqueous solutions. At a pH of 6, various researchers demonstrated varying values of Cu(II) removal viz. 99.39% [21] 94% [23] and 83.25 % [24]. In another study, highest Cu(II) removal of 63% was obtained under optimum operating conditions from a real wastewater [29]. Results obtained from adsorption experiments conducted on sawdust of various deciduous trees revealed faster kinetics with equilibrium reaching within 20 mins for Cu(II) [13]. Maximum Cu(II) removal efficiency was demonstrated to be 80% at pH 5. Sawdust from poplar wood revealed good remediation capacity and selectivity for Cu (II) and Zn (II) as compared to Cd(II) when used in an electroplating wastewater [14]. It was observed that metal adsorption capacity was increased by a corresponding increase in the sawdust dosage during the treatment process. But there was a steady increase in the COD levels in the water treated which is undesirable. In yet another study conducted by Ofomaja (2010) [16, 17], it was reported that maximum Cu(II) adsorption onto *Mansonia* sawdust was 57.14 mg/g [16], but when the experiment was conducted in wastewater containing both Cu(II) and Pb(II) using the same adsorbent, greater selectivity and binding was observed for Pb(II) (39.5 mg/g) as compared to Cu(II) (20.2 mg/g) at pH 6 [17]. Pb(II) adsorption onto raw sawdust ranged from 0.82 mg/g- 145 mg/g and the operating pH was reported to be 5 [17, 19, 21, 22, 26, 28]. Kaczala et al. [19] demonstrated good adsorption capacity of the biosorbent developed from untreated pine sawdust (*Pinus sylvestris*) from a real wastewater sample regardless of the presence of high organic loading and presence of suspended solids. Pb(II) removal of 99% could be ensured only after efficient pretreatment of the wastewater which was done by sedimentation and pH adjustments. In yet another study, sawdust from three different Brazilian species demonstrated an adsorption capacity of 95.31, 145.04 and 89.10 mg/g for Pb (II) from synthetic wastewater [22]. The same adsorbents when used to remediate battery industry wastewater having an initial Pb (II) concentration of 2.66 mg/L, showed that the final Pb (II) concentrations reduced to 2.49, 0.45 and 0.46 mg/L.

The various mechanisms as proposed by the different research groups viz. electrostatic, ion exchange and hydrogen bonding have been verified via batch adsorption studies while studying the effect of pH and via characterization techniques brought about by Fourier transform infrared (FT-IR) Raman, electron spin resonance (ESR) and the X-ray absorption spectroscopy (XAS) [35,36]. It is a well-known fact that efficient binding of metal adsorbates is a function of the chemical make-up of the biosorbent surface [37]. Researchers have identified the key surface functional groups of hydroxyl, carboxyl, carbonyl and phenolic on the surface of the sawdust biosorbent which are active binding sites [12, 14, 15, 34]. Such functional groups are the basic constituents of cellulose, hemi-cellulose and lignin moiety present in various lignocellulosic precursors [38] and are responsible for imparting polarity to the biosorbent [34]. In this respect, Argun et al. [39] reported that studied sawdust is composed of 41.5% cellulose, 32.7% hemi-cellulose and 22.8% lignin. Presence of polyphenolic compounds like tannin on the sawdust are believed to be active sites for attachment to metal ion pollutants. A review of the acidity constants [40,41] reveals that the surface of the sawdust is basically negative at a wide pH range of 3 to 10. This shows that the surface functional groups on the biosorbent can easily bind with the cationic metal ions present in aqueous medium thereby facilitating electrostatic interactions; and such have been demonstrated by various studies. Such ligands also are electron donators and based on the electron acceptor nature of the metal cations in aqueous suspension, an ion exchange interaction can also be inferred [40]. Ion exchange was also considered as a dominant mechanism by Sciban et al [14] who studied this phenomenon by monitoring the release of Ca^{2+} , Mg^{2+} , Na^+ , K^+ and H^+ from the biosorbent after the adsorption process. Involvement of ionic bonding was also revealed due to the release of smaller amount of H^+ in comparison to the other cations.

Besides the inherent surface chemistry of the sawdust biosorbent, the pH of the water medium has a definitive role on the binding characteristics towards the metal adsorbates [7]. pH results in ionization of the metal adsorbates with subsequent change in their solubility leading to their increased or decreased uptake onto the

surface of the sawdust biosorbent. Thus, with varying aqueous pH, the surface functional groups get protonated or deprotonated. In many instances, alkalinity of medium causes precipitation of the metal adsorbates. On the other hand, acidic medium not only protonates the surface functional groups but also, presence of increased protons may compete with the metal cations; hence causing lesser adsorption onto the sawdust biosorbent. A constant pH is thus desirable during the adsorption process; but this pH is known to vary with individual metal species as evident from Table-1. Thus, while Cr(VI) showed higher binding affinity at lower pH of 1-3, a higher pH is desirable for ensuring higher adsorption for Pb(II), Cu(II), Ni(II). A pH of 9 has been observed to have resulted in highest adsorption for Cd(II) [18].

Drawbacks associated with raw sawdust as a biosorbent

Sawdust in its native form has demonstrated its potential as a low cost effective biosorbent not only for its wider availability as an uneconomic resource, lower processing cost but also for its better binding capacity as demonstrated by various researchers. But its usage as a biosorbent in aqueous solution has resulted in the simultaneous release of soluble organic compounds like phenolic components which are toxic thereby increasing the incidence of secondary pollution problems like generation of high COD, BOD, TOC etc. [17, 40, 42]. Such secondary contaminants may threaten aquatic life due to depletion of dissolved oxygen in aqueous streams. Also, use of sawdust biosorbent has created problems related to its physical stability and difficulties of its separation from wastewater. In many instances of experimental research work, it has been observed that biosorption efficiency and selectivity of raw sawdust decreases when applied under multi-pollutant systems as well as in real wastewater streams [14, 22, 29].

Modified sawdust: metal adsorption capacity; effect of modifications

It has been widely demonstrated that the surface of the biomass can be easily modified via chemicals so as to bring about changes related to its solubility, surface functionality thereby modifying its ion exchange capacity with the overall objective of improving its adsorption capacity [42]. Chemical treatment of sawdust irrespective of their source has shown significant improvement in their adsorptive uptake of the metal pollutants as demonstrated in Table-2. In a recent study, it was demonstrated that a chemically modified Dibetou sawdust demonstrated 99% Pb(II) removal as compared to 94% removal from raw sawdust under identical operating conditions [43]. The increase in the adsorption capacity has been explained [44] mainly due to:

- a. Changes in the surface of the sawdust biosorbent
- b. Improvement in ion exchange process
- c. Micro-precipitation of metal hydroxides in the pores of the sawdust.

The leaching of color and organic components from sawdust has been reduced effectively by pre-treatments and modification via chemicals like formaldehyde, alkalis and acids [44]. The chemicals identified to have been used by various workers are acids, bases, organics and polymers. Development of sawdust into effective nano-biosorbents and further functionalization has also helped in not only improvement in their adsorption capacity but also has curtailed the leaching of unwanted components into the waste waters. Also, magnetic nano-biosorbents fabricated from sawdust has helped in improved stability and separability from water medium after the adsorption process. A detailed literature study followed by discussion is given in the following section.

Table-2: Performance of modified sawdust for removal of metal ions from wastewaters

Biosorbent	Pre-treatment	Metal ion	ads capacity	pH, Contact time	Metal binding Mechanism	Refer ence
SD(Indian RoseWood)	Acid	Cr(VI)	10mg/g	3,	Ion exchange	[46]
SD (Rubberwood) + H ₃ PO ₄	Acid	Cr(VI)	44.05 mg/g	2, -	Ion exchange	[49]
SD(Aspen tree)+HCl	Acid	Cr(VI)	0.093mg/g	2	Ion exchange	[53]
SD(poplar) + H ₂ SO ₄	Acid	Cu(II)	13.495mg/g	5, -	Ion Exchange	[45]
SD (rubber wood) + H ₃ PO ₄	Acid	Cu(II)	5.729 mg/g	6,	Electrostatic attraction	[50]
SD+H ₃ PO ₄ +immobilised	Acid	In(III)	1.121 mg/g	3.5, -	NA	[47]
SD (Fig) +H ₃ PO ₄	Acid	Pb(II)	80.645mg/g	4,	Ion exchange	[48]
SD + acid	Acid	Pb(II)	0.37mg/g	5, -	NA	[28]
SD+H ₃ PO ₄	Acid	Pb(II)	1.45mmol/g	4,	NA	[51]
SD(Oak tree)+HCl	Acid	Cu(II)	3.22mg/g	4	NA	[39]
		Ni(II)	3.29mg/g	8		
		Cr(VI)	1.70mg/g	3		

SD(<i>Meranti</i>)+HCl	Acid	Cr(III) Ni(II) Pb(II) Cu(II)	37.87mg/g 35.97mg/g 34.26mg/g 32.05mg/g	6, 120min	NA	[52]
SD + base (NaOH)	Base	Pb(II)	0.89 mg/g	5, -	NA	[28]
SD (poplar) + NaOH	Base	Cu(II)	0.11mmol/g	-	Ion exchange	[29]
SD (fig) + NaOH	Base	Cu(II)	0.2mmol/g	-	Ion exchange	[29]
SD (poplar) + NaOH	Base	Zn(II)	0.242	-	Ion exchange	[29]
SD (fir) + NaOH	Base	Zn(II)	0.205mmol/	-	Ion exchange	[29]
SD(Turkish red pine)+NaOH	Base	Cr(VI)	10.72mg/g	3,	Ion Exchange	[39]
SD(Junifer fiber)+NaOH	Base	Cd(II)	29.54mg/g	5,	Ion exchange	[56]
SD(<i>Dalbergia sissoo</i>)+NaOH	Base	Ni(II)	10.47mg/g	5,	Ion exchange	[57]
SD(<i>Magnifera indica</i>)+NaOH	Base	Cr(VI)	12.78mg/g	2.6,60	Ion Exchange	[20]
SD(Coconut tree)+NaOH	Base	Cr(VI)	3.46mg/g	3,	Ion Exchange	[58]
SD(<i>Acacia Arabica</i>) +NaOH	Base	Cr(VI) Pb(II) Hg(II) Cu(II)	111.61mg/g 52.38mg/g 20.62mg/g 5.64mg/g	-	Surface complexation and ion exchange	[59]
SD +NaOH	Base	Cu(II)	19.475mg/g	6,	Ion Exchange	[60]
SD+NaOH	Base	Cr(VI)	20.70mg/g	3,-	NA	[61]
SD(Indian Rosewood)	formalde	Cr(VI)	9.2 mg/g	3, 60m	Ion exchange	[46]
SD (<i>S.Robusta</i>)+ HCHO	formalde	Cr(VI)	9.55mg/g	3.5,	Electro-static	[62]
SD (<i>Pinus sylvestris</i>)+ HCHO	formalde hyde	Pb(II) Cd(II)	22.22mg/g 19.08mg/g	5.5, 20 min	Ion Exchange	[63]
SD(Holly tree) +HCHO	formalde	Ni(II)	22.47mg/g	7,	NA	[64]
SD+dye	Dye	Cu(II)	8.07 mg/g	5.24, -	Chellation	[65]
SD+dye	Dye	Ni(II)	9.87 mg/g	5.16, -	Chellation	[65]
SD+dye	Dye	Zn(II)	17.09 mg/g	5.88,-	Chellation	[65]
SD + organic acid	Tartaric	Cr(VI)	10.72mg/g	3, 120	Ion	[87]
SD+polypyrrole	grafting	Cr(VI)	3.4 mg/g	3, -	Ion exchange	[72]
SD (rubber) + polyacrylamide	grafting	Cr(VI)	12.4 mg/g	3, -	Ion exchange	[75]
SD + xanthate+ ethane diamine	grafting	Cu(II) Ni(II)	1.00mmol/g 0.69mmol/g	NA	Electro-static attraction	[76]
SD + polyaniline composite	grafting	Cd(II)	430mg/g	6,	Ion Exchange	[77]
SD+polyacrylic +KMnO ₄	grafting	Cd(II) Cu(II) Ni(II)	168mg/g 104mg/g 97mg/g	pH-4.9- 5.9	Ion Exchange	[78]
SD+chitosan composite	grafting	Cr(VI)	122mg/g	2	NA	[79]
SD+methacrylic acid	grafting	Cr(III)	36.63mg/g	pH-7,	NA	[80]
SD+polyacrylamide	grafting	Cr(VI)	172.74mg/g	2	NA	[81]
SD (<i>Manilkara sp.</i>)+ EDTAD	grafting	Zn(II)	80mg/g	6,	Chelation	[82]
SD(Fir) +Fe ₃ O ₄ + 3 aminopropyltriethoxysilane	Magntise d	Au(III)	188.68mg/g	3, 5 min	Chelation	[43]
SD(Fir)+Fe ₃ O ₄	nanobios	Au(III)	16.45mg/g	3, 5	Chelation	[43]
SD +Fe ₃ O ₄ + chitosan	nanobios	Sr(III)	12.59mg/g	6.74,	Chelation	[83]
SD+urea+ZnCl ₂	Others	Cd(II)	909mg/g	pH-6	NA	[84]
SD(Spruce) + urea + ferric- oxyhydroxide	others	As(V)	9.25mg/g	pH- 6,120m	NA	[85]
SD(<i>Delbergia sissoo</i>) +Tween	others	Cr(VI)	71.4mg/g	pH-2,	Chellation	[86]

Pretreatment with acids, alkalis and organics

The different acids used for pretreatment of sawdust, as evident from literature studies are H₂SO₄, HCl and H₃PO₄ [39, 45, 46, 48, 49, 50, 51, 52, 53]. Sulphuric acid pretreatment has result in enhanced Cu(II) removal efficiency of 92.38% (Langmuir adsorption capacity of 13.95 mg/g) as compared to its unmodified counterpart which demonstrated 47.05% removal corresponding to an adsorption capacity of 5.432 mg/g under the same operating conditions of pH, dosage, temperature etc. [45]. It was reported that the binding mechanism was ion

exchange and surface complexation. Besides the adsorption capacity and metal removal rates, acid modification may have also changed the underlying binding mechanism. Modified surface chemistry may initiate the metal binding via surface complexation as well as exchange of metal ions with the acidic functionalities introduced via acid modification.

In comparison to HCl pretreated sawdust, NaOH pretreated sawdust showed better adsorption capacity towards Pb(II) and Cd(II) [29]. It was postulated that base treatment helped in increasing the negative surface functionalities on the biosorbent surface which in turn resulted in higher cation exchange capacity (CEC) and hence higher binding to metal ions. As per a study [54], it was demonstrated that alkali pretreatment of agricultural wastes led to higher adsorption efficiency via eliminating the existing tannins [54]. In a study by Sciban et al., (2006) [44], textural and adsorption features of alkali pretreatment with NaOH and Na₂CO₃ were studied on sawdust of two varieties of wood: poplar and fir. Textural results revealed that irrespective of tree species, modified sawdust showed increased surface area (three times) as compared to that for unmodified sawdust. It was postulated that because of alkali modification, deacetylation of hemicellulose resulted in increase in the number of adsorption sites with consequent increase in the adsorption capacity. Adsorption capacity for Zn(II) increased fifteen times while the same for Cu(II) increased by five times as compared to their unmodified counterparts. Thus, Cu(II) and Zn(II) adsorption onto poplar sawdust was recorded as 6.9.2 mg/g and 12.70 mg/g respectively; while the same for fir sawdust was recorded to be 12.70 mg/g and 13.41 mg/g respectively. Besides ion exchange, it was postulated that microprecipitation of metal hydroxides onto the pore structure of sawdust occurred during the binding process. Another benefit that was testimony for alkali modification of sawdust was that leaching of color and other organic components decreased as compared to their unmodified counterparts. In yet another study [55], it was observed that NaOH pretreated sawdust of *Cedrus Deodar* tree demonstrated approximately four times higher adsorption capacity for Cd(II) (73.62 mg/g) as compared to its unmodified counterpart. In a study conducted by Min et al [56], sawdust of *Junifer* fiber after modification with 0.5M NaOH showed three times higher adsorption capacity for Cd(II) (29.54 mg/g) than its unmodified counterpart. The major reasons cited for enhanced adsorption performance was related to increase in surface area and porosity (brought about by swelling due to NaOH pretreatment) and increased surface functionality (brought about by de-esterification of ligno-cellulose by NaOH to carboxylate and alcohol). Similar explanation of increased surface functionality brought about de-esterification of cellulose/hemicellulose by NaOH pretreatment of *Dalbergia sissoo* sawdust was given by Shakirullah et al (2006) [57]. Such alkali modified sawdust showed good adsorption potential for Ni(II) (10.47 mg/g).

Among the different organics used to modify sawdust, use of formaldehyde is usually to immobilize water soluble components including color from sawdust [46]. Various studies have also demonstrated improved adsorption capacity of formaldehyde pretreated sawdust for metal adsorbates like Cr(VI), Pb(II), Cd(II) and Ni(II) [46, 62-64]. In a study by Taty Costodes et al., [63], formaldehyde modified sawdust of *Pinus sylvestris* tree showed 97.6% and 96% removal of Pb(II) & Cd(II) in less than 20 mins. Besides bringing about good removal efficiency, formaldehyde modified sawdust curbed the release of polyphenols thereby helped in curtailing secondary pollution problems. It was proposed that the metal adsorbates formed complex with the newly incorporated surface functional groups brought about by formaldehyde modification. The incorporation of dyes onto the sawdust was another modification method of improving its adsorption capacity [65-67]. The authors made a comparative study on the removal of various metal ions using raw and dye (Reactive Orange) modified sawdust. Better performance was demonstrated by the dye modified sawdust biosorbent. A hybrid biosorbent prepared from onion skin, corncob and sawdust was used for the treatment of agricultural waste waters via both static and dynamic modes of operation [68]. The trend observed for the adsorptive capacity towards the metal ions tested followed the order $Pb^{2+} > Ca^{2+} > Ni^{2+} > Zn^{2+} > Mg^{2+} > Cu^{2+}$.

Grafting

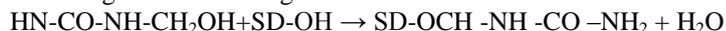
The process of grafting involves introduction of monomers and polymers onto the surface of sawdust. The aim is to incorporate additional surface binding sites so as to ensure improved adsorption performance [69, 70, 71]. Literature study reveals that grafting has been initiated by high energy radiation, photochemical or by chemical. Details of the procedure of grafting, properties of grafted adsorbents and their effects on the adsorption capacity can be assessed in a review [5]. Sawdust of various tree species have been successfully modified by grafting with polypyrrole [72], acrylamide [73,74,75], ethane diamine [76], polyaniline [77], polyacrylic chain [78], chitosan [79], methacrylic acid [80] and carboxylated polyacrylamide [81] and the resulting grafted sawdust biosorbent have demonstrated improved adsorption capacities for metal ions from waste waters. Acrylamide based sawdust biosorbent [73] followed by functionalization with ethylene diamine showed a Cr(VI) adsorption capacity of 45 mg/g corresponding to 91% removal efficiency. Polyaniline coated on sawdust demonstrated rapid Cd(II) removal capacity of 430 mg/g with a time frame of 20 mins [77]. Sawdust grafted with polyacrylic chain demonstrated approximately 15-40 times higher adsorption for Cd(II), Cu(II) and Ni(II) (168 mg/g, 104 mg/g and 97.3 mg/g respectively) as compared to its unmodified counterpart (76.1 mg/g, 46.9 mg/g and 39.8 mg/g respectively) [78]. Mango tree sawdust modified with chitosan composite showed Cr(VI) adsorption

capacity of 122 mg/g [79]. Sawdust grafted with methacrylic acid showed 99.3% removal efficiency for Cr(III) corresponding to an adsorption capacity of 36.63 mg/g [80]. Sawdust grafted with carboxylated polyacrylamide showed high removal efficiency for Cr(VI) of 99% (corresponding to an adsorption capacity of 172.24 mg/g) [81]. A new chelating biosorbent was prepared by grafting of ethylene diamine tetra acetic dianhydride (EDTAD) on sawdust of *Manilkara* sp. using as modifying agent in order to introduce carboxylic acid and amine functional groups into the raw sawdust [82]. The incorporated surface carboxylic and amine groups resulted in improved adsorption performance for Zn(II) from synthetic and electroplating waste waters (80mg/g and 47mg/g respectively). The lower adsorption capacity of the developed biosorbent from the electroplating waste waters may have been due to competition with other cations like Ca^{2+} that are normally present in the waste waters. More recently, in a work carried out by Gao et al., 2018 [83], an effective adsorbent was fabricated via grafting of sodium lignosulphonate onto the surface of raw pine sawdust for assessing its potential to remove Hg(II) from wastewater. Results revealed high adsorption capacity of 164.77 mg/g for the studied aqueous pollutant but also demonstrated better reusability and desorption rates.

Magnetized sawdust nano-biosorbent

The drawbacks associated with the use of sawdust as biosorbent either via batch or column operation are the difficulties associated with the separation of the exhausted biosorbent from the processed water. Also, in column operations the flow of the wastewater through the sawdust biosorbent is very time consuming. Magnetic separation is very effective technique in the recovery of the solid biosorbent from waste waters where the lengthy column operation and filtration steps in batch operations are avoided. In this respect the binding of the sawdust onto the Fe_3O_4 nanoparticles via the hydroxyl and carboxyl functional groups will not only circumvent the solid-liquid separation problem, but will help in stabilizing the nanoparticles resulting in the development of a modified composite magnetic nano biosorbent having added features of nano size and increased surface area. Such added features will demonstrate enhanced adsorption efficiency for metal ions. Sawdust- Fe_3O_4 composite was prepared using a single iron precursor [84]. The micro-sized lignocellulosic sawdust particles served both as a template and a reducing agent for ferric ions. The composite was modified with 3-aminopropyltriethoxysilane and synthetic ligand (3,5-dinitrobenzoylthiocyanate). The modified composite showed increased selectivity toward Au(III). The surface area increased from 4.24 m^2/g in sawdust to 17.1 m^2/g in the modified composite. There was a corresponding increase in the adsorption capacity from 3.2 mg/g (sawdust) to 188.68 mg/g (composite). Cheng et al. [85] reported the modification of sawdust with magnetic Fe_3O_4 particle for the remediation of strontium from the aqueous solution using chitosan as a bridging agent between sawdust particle and Fe_3O_4 particle. The maximum adsorption capacity of the modified composite sawdust biosorbent was determined (12.59 mg/g) through Langmuir isotherm model. The magnetically modified sawdust had large surface area, high porosity and demonstrated ease in separation from aqueous solution after adsorption. Advanced biosorbents were fabricated from citric acid coated magnetic sawdust of olive tree [86]. Adsorption characteristics revealed the better performance of the composite adsorbent for the removal of Cu(II), Co(II) and Zn(II) (21.0, 14.4, 17.6 mg/g respectively) in contrast to olive sawdust for the same metal ions under identical conditions (3.5, 3.2 and 5.6 mg/g respectively).

Sawdust was modified with mono-methyl urea (MMU) in the presence of ZnCl_2 as a catalyst for remediation of Cd (II) from aqueous solution [87]. The MMU was found to interact with sawdust in the presence of ZnCl_2 according to the following reaction:



The modified biosorbent having newly incorporated functionalities demonstrated adsorption of 909 mg/g for Cd(II) with equilibrium reaching within 30 mins. The authors reported a decreasing trend of adsorption capacity for Cd(II) at lower pH ($\text{pH} < 6$) mainly because of the association of the biosorbent surface with H_3O^+ with subsequent inhibition of metal cations. *Picea Abies* (Spruce) sawdust chemically modified with urea and ferric oxyhydroxide [88] showed an As(V) removal capacity of 9.259 mg/g whereas the raw sawdust demonstrated negligible removal capacity. Sharma and Sharma [89] proposed the modification of *Sheesham* sawdust with Tween 20 and the same showed an efficiency of 71.4 mg/g for Cr(VI) adsorption from waste waters.

Regeneration capacity of the sawdust biosorbent

Waste waters discharged from electroplating, tannery, battery industry etc. have been successfully treated by various researchers by using low cost and modified sawdust based biosorbent. The capacity of a biosorbent to be regenerated and reused makes the process not only economically viable eliminating the necessity of a new biosorbent but also solves the problem for disposal of the spent sawdust biosorbent which is yet another potentially hazardous waste; thereby making the process more environmentally friendly. There is also the possibility of recovery of the metal pollutants. A review of literature (Table-3) reveals that the regeneration of the metal loaded sawdust biosorbent has been possible by chemicals like acids (HCl, HNO_3) [26, 27, 43,44, 48, 66, 78, 80] and bases (NaOH) [10, 20, 59, 75, 79, 90] along with the simultaneous recovery of the metal ions. In all such studies, a continuous 4-5 adsorption-desorption cycle have been reported with < 10% decrease in the

efficiency of the sawdust biosorbent. This proves beyond doubt that the sawdust biosorbent has adequate stability for its repeated use for water treatment when applied on an industrial level. Table-3 further reveals the pH dependency of the regeneration and desorption process. With the exception of Cr(VI) loaded biosorbent which requires a basic medium, a majority of metal ions like Pb (II), Cu (II), Zn (II) Ni (II), Cr(III) etc. can be recovered from spent sawdust biosorbent using an acidic medium. Also, studies pertaining to the regeneration of the sawdust biosorbent, its reuse and recovery of the metal ions have established the metal loaded biosorbent acts as a cation exchanger thereby further establishing the ion exchange model for the binding of metal pollutants onto the sawdust biosorbent.

Table-3: Desorption of Metal Ions and Regeneration of the Sawdust Biosorbent

Biosorbent/ Adsorbate	Desorption medium	Metal recovery (%)	Ref
Sawdust/Cr(VI)	1N NaOH	95	[10]
Sawdust +Tartaric acid, Cr(VI)	NaOH	87	[87]
Magnifera indica/ Cr(VI)	1M NaOH	NA	[20]
Coconut tree sawdust/ Cr(VI)	0.01-1 NaOH	NA	[59]
Sawdust/ Cr(VI)	0.2 M NaOH	99.2	[75]
Sawdust/ Cr(VI)	NaOH	95	[79]
Sawdust/ Cr (III)	0.1M HCl	97	[80]
Sawdust/Zn(II), Cu(II)	0.1M HCl	33, 2	[28]
Fig sawdust/ Pb (II)	0.1M HCl	98	[48]
Sawdust/Cd (II), Cu(II), Ni(II)	HCl	98-99	[78]
Sawdust, Cu(II), Pb(II)	0.1M HNO ₃	> 98%	[27]
Dyed Sawdust/Cu(II), Ni(II), Zn (II)	0.5g/L HCl	>99	[66]
Phosphorylated Sawdust/In(III)	0.5M HCl	95	[44]

II. FUTURE PROSPECTS

Despite the promising potential of the use of sawdust as biosorbent, yet its application on an industrial scale has been far from reality. This can be attributed to factors like absence of specificity and selectivity of the biosorbent to mixed pollutant systems. Industrial waste waters are characterized by high variability of parameters linked to dissolved and suspended solid content, pH, co-existing ions, inorganic and organic contents. Various water environments like hard water, metal processing industrial effluents and high organic load in food processing waste waters may retard the performance of the sawdust biosorbent for cleanup operations. In this scenario, efforts are required to conduct tests under simulated multi-pollutant systems so as to assess the selectivity of the biosorbents prior to their industrial applications. More efforts need to address the development of better biosorbents having greater mechanical stability, resistance to chemical and microbial degradation, more favorable surface and porous properties via chemical modifications, grafting and immobilization techniques. Such endeavors will also help in improved adsorption and greater selectivity for target pollutants. Finally, studies should be directed for assessing the performance of sawdust biosorbent for various emerging micro-pollutants like the surfactants, chloro-alkanes, pesticides, drugs etc. Such pollutants have great environmental impact as they are noxious, having endocrine disrupting activities and their presence in very low concentration in water bodies makes their efficient removal difficult with the help of established technologies like membrane technology, photocatalytic oxidation etc.

III. CONCLUSION

The present study has focused on not only a detailed discussion on the literature studies conducted on sawdust of various tree species but also a detailed study is presented as to the various factors and the underlying binding mechanism affecting the efficiency of such biosorbent. The various drawbacks associated with using sawdust as biosorbent has not only been identified but definite steps that have been undertaken by various researchers to curtail them via different modification techniques have also been critically analyzed. Modified sawdust has also helped in improving the surface characteristics with simultaneous increase in the adsorption capacity. An understanding of the different underlying mechanism has helped in designing of a better biosorbent in sawdust. Regeneration of the spent sawdust biosorbent and its repeated use in wastewater treatment with minimum loss in its efficiency has demonstrated its adequate stability and economic viability of the process. Despite the economic and environmental benefits, the sawdust biosorbent has limited industrial application. Future research

directions should focus on designing of more robust and advanced biosorbent via modification of sawdust, assessing its performance for emerging micro-pollutants, multi-pollutant systems and behavior in waste streams from diverse sources like industry, agricultural and food processing plants.

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