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Review on Adsorption of Different Heavy Metals on Natural Adsorbent Sawdust

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Abstract: *Natural adsorbent i.e. Sawdust has been proved to be effective low cost adsorbent for removal of metals, dyes from their aqueous solutions. Sawdust is available in ample amounts in nearby area, so its use can be greener way of water purification. This paper reviews the findings of some researchers for the use of saw dust in different forms for heavy metal removal. Reported optimizing factors of adsorption, its isotherm analysis and kinetics are reviewed in this paper. It has been found that generally Langmuir and Freundlich adsorption isotherms fit well to batch experimental data. Pseudo-Second-order kinetic model best describe these processes. In some cases intraparticle and Elovich models are also used. Observations of effectiveness of Saw dust can be useful in future for designing water purification technology.*

Keywords: Adsorption, Sawdust, Heavy Metals, Adsorption Capacity, Isotherms, Kinetics

I. Introduction

Water pollution is biggest problem that world is facing today. In need of potable water new techniques of water purification are in demand. Scientists, Chemists, Environmentalist are aiming towards proper water treatment and management processes. Different sources for water contamination are industries, agriculture and human activities. Excessive levels of heavy metals causes problems to human beings and also ecosystems .Industrial effluents, agricultural ruff offs increase the levels of metals like Iron (Fe), Nickel (Ni), Cadmium (Cd) etc in water bodies and therefore their removal is necessary. Adsorption with natural adsorbents is attempted in last decades by researchers. This is an attempt to find efficient adsorbents to reduce the contamination. Many researchers tried saw dust of different trees as natural adsorbents. Many scientists reviewed the use of sawdust as adsorbent. (R. Chikri),(Renu, Agarwal, & Singh, 2017) This paper aims to summarize the different types of saw dusts, their use as adsorbent, their application by different researchers, their use to remove heavy metals .

1.1 Saw Dust as Good Adsorbent

Saw dust works as adsorbent because it has functional groups like -COOH, -OH, amide groups in which are responsible for chemisorption.(Renu, Agarwal, & Singh, 2017) .Saw dust is composed of lignin, Cellulose, hemicellulose (R. Chikri) . In process of adsorption on adsorbent, modifications in surface area is focused. This cheap adsorbent can be used also in its activated carbon form which can be prepared by chemical and physical activation methods

1.2 Adsorption Experiments with Saw Dust Adsorbent

Many researchers used Sawdust of different trees such as Beech sawdust for removal of Cu, Ni, Zn(Dragana Bozić, 2013), Sawdust of Walnut for removal of Lead, Cadmium and Nickel(Bulutyasemin, 2007), algae, sawdust of pine and Absol(Mehmet Emin Argun, 2007), modified oak sawdust by means of HCl treatment for removal of Zn, Cu, Pb, Ni and Cd(Mehmet Emin Argun, 2007), UAD, TAD & CAC

Adsorbent prepared from *Borassus aethiopum* (Adaji Idoko Johnson1, 2021), the wooden biomass of *Dalbergia sissoo for removal of Ni &Zn*(Samin Sirusbakht, 2017), Sawdust for removal of Cr(VI)(Samin Sirusbakht, 2017) . Batch experimental studies are carried out and best efficiency of saw dust is determined by optimizing factors like pH, contact time, adsorbent dose, etc a At optimized conditions different researchers reported maximum efficiency of the saw dust as follows

1. Ola Andersson (2016) reported the adsorption efficiency of algae, sawdust of pine and Absol (Sand, lime, cement and water) .Out of them percentage of adsorbed metals on sawdust in single-metal system is for Cu, Ni,

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Zn ,Cd ,Pb at 2mg/l is 81%, 60%, 66%, 74 %,98% and Percentage of adsorbed metals on sawdust, multi-metal system, for 2 mg/L percentage adsorbed is 85%, 53%, 65 %,19%, 96% on sawdust, i.e. sorption is of 65-90% of the metals at lower concentrations (0.2-2 mg/l).

2. Modified oak sawdust by means of HCl treatment Cu, Ni, and Cr showed adsorption percentage as 93%, 82% and 84%, for metal concentrations 0.1 to 100 mg/L.(Mehmet Emin Argun, 2007)
3. Using Sawdust as adsorbent percentage removal was 94.5% ± 0.3% for Pb^{+2} at pH5, in 1 hour contact time and with adsorbent dose of 7.5 g/L, (T.K. Naiya, 2008)
4. Beech sawdust adsorb Cu & Ni-4-4.5 mg/ g and Zn- 2 mg/g at pH>4 (Dragana Bozić, 2013),Simlarly Sawdust of Walnut saw dust removes Pb, Cd, Ni at equilibrium time of 60 minutes(Bulutyasemin, 2007).
5. Modified holly Sawdust showed q_{max} 18.86 mg/g at pH 7. for adsorption of Cr(VI)metal ions.(M. Shirzad Siboni, 2011).
6. Mohmmad Nurnabi et al, 2020 used Sawdust of *Albizia lebbeck* when used as sodium methylate, epichlorohydrin and n-dodecylamine modified adsorbent (DDA-SD)the observed adsorption q_{max} as 17.37 mg/g (for Pb^2) and 9.4 mg/g (Cu^{2+}) ions .
7. Daina Simon, 2020 reported use of pine sawdust to have maximum efficiency by stirring $NiCl_2$ solutions with pine sawdust for 24 h. and $NiCl_2$ and pine sawdust and sawdust mixture which is mixed with natural clay and biomass with adsorbed metals.
8. 8. For maximum removal of Chromium $^{+6}$ ions from solutions with sawdust optimum conditions reported are contact time 120 min., 50 mg/L concentration o and 4 pH value was 4 at 30°C temperature. (Ibrahim Yaagoub Erwa, 2016)

Following table no 1gives the summary of Sawdust adsorbents and their adsorption capacities

Metal	Adsorbent	q_{max}	Reference
Cu, Ni, Zn	Beech sawdust	Cu-4-4.5 mg/ g Ni-4-4.5 mg/ g Zn- 2 mg/g	(Dragana Bozić, 2013)
Cu, Cr	non-modified beech sawdust	Cu^{2+} -30.22 mg g^{-1} Cr^{3+} - 41.86 mg g^{-1}	(Witek-Krowiak, 2013)
Cr	Saw dust	Cr-50	(Ibrahim Yaagoub Erwa, 2016)
Pb Pb+HCl Pb+NaOH	pine bark	Pb-0.101 Pb+HCl-0.057 Pb+NaOH -0.071	(Sławomir Wierzbaa, 2019)
Ni	Pine saw dust	Cu- 19.59 Pb- 13.48	(Daiana Simón, (2020))
Pb^{2+} , Cu^2	Sawdust of *Albizia lebbeck* treated with sodium methylate and epichlorohydrin and n-dodecylamine	Pb^{2+} -17.37 mg/g Cu^2 -9.4 mg/g	(Mohammad Nurnabi, 2020)
Cr	The walnut shell, chestnut shell, wood	0.39–1.63 mg/g	(LUÍSA CRUZ-LOPES, 2020)

Table 1 gives the summary of Sawdust adsorbents and their adsorption capacities

Following table no2 gives the summary of Sawdust adsorbents and percentage removal of the metal

Metal	Adsorbent	% removal	Reference
Cu, Ni ,Cr	Modified oak sawdust by means of HCl treatment	Cu- 93%at pH 4, Ni- 82% at pH 8, Cr(VI) -84% pH 3.	(Mehmet Emin Argun, 2007)
Pb,Cd, Ni	Sawdust of Walnut		(Bulutyasemin, 2007)
Cu, Ni, Cr(VI)	HCl treated Oak Sawdust	Cu- 93% at pH 4 Ni- 82% at pH 8 Cr(VI)- 84% at pH 3	(Mater., 2007)

Zn, Cu, Pb, Ni and Cd	Algae, sawdust of pine and Absol (Sand, lime, cement and water	65-90%	(Andersson)
Pb(II)	Sawdust	94.5% ± 0.3%	(T.K. Naiya, 2008)
Hg ,Pb, Cd	Cottonwood &Pine wood	Cotton wood -Hg-50%, Pb- 70%, Cd-40% Pine wood -Pb-40%	(PESIC, 2017)
Zn, Cu, Pb, Ni and Cd	Algae, sawdust of pine and Absol	65-90%	(Andersson)

Table 2 gives the summary of Sawdust adsorbents and percentage removal of the metal

Adsorption Isotherm & Kinetic Models

To study this process different models like Freundlich isotherm, Langmuir isotherm models are employed. Similarly to explain the adsorption rate different kinetic models are applied. Following are linear form and nonlinear equations given in table .3- summary is as follows –

Kinetic & isotherm models	Equations	Terms
Pseudo first order kinetic model	$\log (qe-qt) = \log qe - (k_1 / 2.303)\, t$	qe and qt = quantity of the metal ions adsorbed (mg/g) on adsorbate
Pseudo second order kinetic model	$t/qt = 1/(K_2 qe^2) + t/qe$	K_2 = adsorption rate constant
Intra particle diffusion	$qt = K_1\, t^{1/2}$	K_1 (mg/g/min) and A=constant
The Freundlich isotherm	$\log q = \log K_f + 1/n \log Ce$	q_e =quantity of adsorbed metal ion per unit mass adsorbent, K_F = affinity of adsorbate towards adsorbent $(L/mg)^{1/n}$
Langmuir isotherm	$Ce/qe = 1/(qm.b) + Ce/qm$	qm = monolayer adsorption capacity b = Langmuir bio-sorption constant

Table 3 showing summery of kinetic models and isotherm models used in adsorption studies (Intidhar J Idan, 2017)

Adsorption of the different metals on sawdust adsorbents, their isotherm and kinetics is given below Table 4

Metal	Adsorbent	Isotherm	Kinetics	Reference
Cu, Ni, Zn	Beech sawdust	Langmuir equation	pseudo-second order	(Dragana Bozić, 2013)
Pb, Cd, Ni	Sawdust of Walnut	Freundlich &Langmuir isotherm models.	pseudo first,second order intraparticle diffusion	(Bulutyasemin, 2007)
Zn, Cu, Pb, Ni &Cd	algae, sawdust of pine and Absol (Sand, lime, cement and water	Freundlich and Langmuir isotherms	Pseudo second order	(Andersson)
Cu, Ni,& Cr	modified oak sawdust by means of HCl treatment	Langmuir and D-R adsorption isotherms	pseudo-second-order	(Mehmet Emin Argun, 2007)
Ni and Zn	the wooden biomass of *Dalbergia sissoo*		Pseudo-second-order kinetics	(Shatakshi Tiwari, 2021)
Chromium (VI)	Sawdust			(Samin Sirusbakht, 2017)

Pb^{2+} ,Cu^{2}	Sodium methylate treated Sawdust of *Albizia lebbeck* and epichlorohydrin and n-dodecylamine	Langmuir and D-R adsorption isotherms	pseudo-second-order	(Mohammad Nurnabi, 2020)

Table 4 Summary of the Isotherm & Kinetics of adsorption of metal on sawdust

Such Kinetic and isotherm modeling helps us to calculate different parameters such as sorption capacity, sorption intensity by plottong graphs and with linear regression and help to understand the mechanism involved in adsorption .

III. Mechanism Involved in Adsorption

Mehrnet Emin Argun et al,(2007) described the adsorption process as spontaneous and endothermic .These adsorptions are favored by exchange of Ca form sawdust with metal ions .(Dragana Bozić, 2013) .Normally chemisorption, covalent interactions take place. The similar results are reported by *D. sissoo* sawdust natural adsorbent for removal of Ni^{+2} and Zn^{+2}.(Shatakshi Tiwari, 2021)

IV. Conclusion

For lesser concentrations of heavy metal ion in water bodies, so old water treatment methods of metal removal cannot be applied here. From the review of the various application of sawdust, it proved that it is cost effective but modification in adsorbent is required The modifying agents can be heat, acids, bases, and other chemicals. So in future Saw dust can be effective low cost adsorbent capable of using in the water treatment. But in industry proper designs for industrial use are needed. Gap between experimntental and industrial use must be shortened. More efforts are required .There is vast scope for research in this field for successful implementation of adsorbents such as Saw dust. Modifications should be done in adsorbent and its environmental impact also should be checked. Future research should be carried out on the extension of batch tests.

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