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Sawdust as Low-Cost Adsorbents for the Removal of Heavy Metals From Water

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Abstract: Sawdust is currently investigated as a sorbent to eliminate heavy metals from wastewater and other aqueous solutions. The raw material is relatively cheap and is available in abundance. Sawdust also helps to eradicate other contaminants, such as dyes, pesticides, phenols, toxic salts, etc. This literature discusses the elimination of heavy metals from wastewater through the help of sawdust. The composition of the sawdust, and the work done concerning the sorption of heavy metals, kinetics, adsorption isotherm, etc., are discussed in this study. The adsorption capacity of sawdust depends on the concentration of adsorbate, composition and characterisation of adsorbent, and the type of modifications. Also, the challenges faced during research are mentioned in this literature. More research should be done in this field to enhance the use of sawdust on large-scale cost-effectively.

Key words: Sawdust, adsorption, isotherm, kinetics, heavy metals.

Introduction

In the past 20 years, the world has seen swift growth in industrialisation and technology. This has led to an exponential rise in pollutant concentration in water bodies (Ahmaruzzaman, 2021). Climate change has added to complicating the situation, resulting in decreased pure water content (Wijayawardena et al., 2016). Contaminants such as toxic metal ions, dyes, organic pollutants, pesticides, detergents, and other organic substances play a massive part in increasing the water body's pollution content. Various researchers are working towards tackling these problems efficiently and cost-effectively. Numerous low-cost adsorbents, such as biochar (Ahmaruzzaman, 2021), fly ash (Gadore & Ahmaruzzaman, 2021), and nanocomposites (Liu et al., 2019, 2020) are being used to decrease the concentration of contaminants from water bodies.

Researchers have shown a greater interest in irradicating heavy metal contaminants from waste water bodies among the pollutants mentioned. As heavy metals are pretty toxic, neurogenic, carcinogenic, and teratogenic, they pose a severe risk to the entire ecosystem. The primary sources of heavy metals are semiconductors, printing press, cloth industries, aero technology, metallurgical engineering, battery production units, etc. (Chen et al., 1996; El Hajamet al., 2020; Gan et al., 2004). The waste produced in these units has a high contaminant concentration and should be treated effectively before releasing them into water bodies. To eliminate these pollutants, researchers are developing cost-effective and highly efficient materials. These are discussed in this literature.

The utmost procedures used for the removal of these impurities are precipitation and coagulation (Chen et al., 2018; Fu & Wang, 2011; Sis & Uysal, 2014; Tang et al., 2016). In the precipitation method, heavy metals are precipitated as hydroxides (mainly at high pH) (Tare & Chaudhari, 1987; Wang et al., 2018) or as sulphides (Ajmal et al., 1993; Zhou et al., 2019). However, the dumping of precipitation waste acts as a limitation for this process. Also, the precipitation alone cannot decrease the pollutant level to achieve water quality standards. The ion-exchange method is also used for removing heavy metals from wastewater (Bashir et al., 2019). In this method, the metal can be reclaimed, and secondary pollution from sludge can be avoided. This method is quite efficient as it reduces the heavy metal ion concentration significantly.

Nevertheless, this method is not used in extensive scale applications as it is not cost-effective. Activated carbon also faces a familiar problem (Zhang et al., 2021). Although it is highly effective for depleting trace elements from wastewater, the high cost is a problem to use as a large-scale adsorbent. So, researchers focus on cost-effective and efficient methods that are relatively useful for eliminating heavy metal ions from wastewater.

There are many trace elements present in water, and only by the combination of numerous treatment methods, the required standard water quality is obtained. The adsorption process can also be used to remove these contaminants, and this fact puts light on different types of adsorbents used for this process. One of the most effective adsorbents used is sawdust (Sikdar et al., 2021). It is a waste mainly obtained from wood industries and is quite appealing to remove harmful toxic contaminants such as dyes, heavy metals, etc. Sawdust is quite efficient and cost-effective. This literature discusses the role of sawdust in removing harmful heavy metals from water. The adsorption principle, affecting factors, and recent studies of sawdust sorption are also discussed.

Sawdust Composition

The composition of wood is quite heterogeneous, i.e., diverse and variable, depending on the tree species. So, to use wood (sawdust) for adsorption, researchers have focussed on finding the composition of wood. It was found that wood species typically have 37.1-51.1% of cellulose, 20-31% of hemicellulose, 19-30% of lignin, and nearly 2-5% of extractives (Mohammed-Ziegler et al., 2004). The three main components, cellulose, hemicellulose, and lignin, are mainly attached by hydrogen bonding. These sawdust components consist of functional groups such as hydroxyl, carboxyl, amide, and phenolic groups. The above-mentioned functional groups are instrumental in binding heavy metal ions and have high adsorption power (Fiset et al., 2000) (Sahmoune et al., 2016). Several researchers have reported the adsorption mechanism of heavy metal ions with the help of sawdust.

Adsorption of Heavy Metals

The adsorption process is mainly used to decrease the high pollution levels. Adsorption by sawdust is quite flexible, as it can remove diverse pollutants. In past years, sawdust is being used as an efficient adsorbent for heavy metals and other toxic pollutants. The studies of researchers are shown below.

Anna Witek Krowiak et al. (2013) experimented with measuring the capacity of untreated beech sawdust for effective adsorption of Copper (II) and Chromium (III) from water bodies. For Cu (II), sawdust exhibited an adsorption capacity of 30.23 mg g^{-1}, whereas, for Cr (III), it showed 41.85 mg g^{-1} of adsorption capacity. Raji et al. (1997) used bicarbonate-treated sawdust for effective elimination of Pb (II), Hg (II), and Cd (II) from water solutions. This adsorbent removed the heavy metals in the order Pb (II) > Hg (II) > Cd (II). The removal rate for Pb (II), Hg (II), and Cd (II) was 98.5%, 97.3%, and 95.2%, respectively.

Bulut et al. (2007) discovered that the adsorption of heavy metal ions hinges on the initial concentration of heavy metals, temperature, and contact time. They used the sawdust of walnut trees to remove metallic ions from water effectively. The sawdust showed effective eradication of Pb (II), Ni (II), and Cd (II) during water treatment. Modified holly sawdust, developed by Samarghandi et al. (2011) was used to remove nickel ions from aqueous solutions. This modified sawdust showed a very high adsorption capacity for Ni (II). This adsorbent showed a maximum adsorption capacity of 22.48 mg g^{-1} at a pH of 7.

Sawdust made from *Acacia leucocephala* showed various applications in the treatment of polluted water bodies. This was used for the effective removal of Pb (II), Cu (II), and Cd (II) (Munagapati et al., 2010). The sawdust worked in an optimum pH of 6.0, 5.0, and 4.0 with an adsorption capacity of 147.2 mg g^{-1}, 167.6 mg g^{-1}, and 185.2 mg g^{-1} for Cu (II), Cd (II), and Pb (II), respectively. Lim et al. (2008) studied sawdust made from *Pinus koraiensis*, to effectively remove Pb (II), Cu (II), and Zn (II) from water solution. This sawdust worked as an effective adsorbent and showed an adsorption capacity of 1.35 mg g^{-1} for Zn (II), 3.36 mg g^{-1} for Cu (II), and 7.74 mg g^{-1} for Pb (II).

In 2013, Kapur and Mondal (2013) developed sawdust from *Mangifera indica* to remove Cr (VI) from water bodies. The sawdust was entirely feasible and was an efficient method. They achieved 99.99% efficiency at an optimum pH of 2. At 298 K, the adsorption capacity for Cr (VI) showed around to be 10.85

mg g^{-1}. To remove Cu (II) from wastewater, Larous et al. (2005) used sawdust from local wood. It was found that raw sawdust, without any treatment, can also be used to remove Cu (II) from an aqueous solution. Also, Rahman and Islam (2009), removed Cu (II) using sawdust derived from maple trees. The sawdust showed an adsorption capacity of 9.5 mg g^{-1} for Cu (II) while working at an optimum pH of 6.

Karthikeyan et al. (2005) derived sawdust from rubberwood (*Hevea brasilinesis*) for the elimination of Chromium (VI) from wastewater. The researchers converted the sawdust into an activated carbon adsorbent and related it with commercially available activated carbon. It was found that sawdust turned into activated carbon showed higher efficiency and is relatively cost-efficient. Another low-cost sorbent is cedar sawdust. It was used to remove Cu (II) ions from wastewater. It showed an adsorption capacity of around 294 mg g^{-1} at around 298 K (Djeribi & Hamdaoui, 2008). Nordine et al. (2016) also removed Pb (II) using synthetic effluents such as pine, beech, and fir sawdust.

Meranti sawdust was used for the removal of Cu (II), Cr (III), Ni (II), and Pb (II) ions from wastewater. This adsorbent was entirely feasible and was readily available. The sawdust showed very high efficiency for the removal of heavy ions (Rafatullah et al., 2009). Yu et al. (2001) removed heavy metals such as Cu (II) and Pb (II), with an efficiency of over 90%. Maple sawdust was used as an adsorbent, and the adsorption capacity was 1.78 mg g^{-1} for Cu (II) and 3.18 mg g^{-1} for Pb (II). To measure the adsorption capacity, Freundlich and Langmuir isotherms were used. To remove Cr (VI) from aqueous solutions, Baral et al. (2006) used *Shorea robusta*, also known as Sal tree. This sawdust was quite adequate, and the adsorption capacity was up to 3.7mg g^{-1}. Back in 1992, Bryant et al. (1992) successfully removed Cu (II) and Cr (VI) from wastewater with the help of *Abies magnifica* sawdust.

Dyed sawdust is an alteration for enhancement of the adsorption capacity of the sawdust material. Shukla and Sakhardande (1992) removed heavy metals such as Cu (II), Pb (II), Hg (II), Fe (II). Zn (II), Ni (II), and Fe (III) using both untreated and treated sawdust. The sawdust was treated with monochlorotriazine type of dye. The study revealed that the treated sawdust showed a relatively higher efficiency. This was a proven method and used for heavy metal removal for a long time (Geay et al., 2000). Other modifications, such as onion skin and corncob, are added to sawdust to mainly remove heavy metal ions from agricultural waste (Odozi et al., 1985).

Factors like "contact time, pH, adsorbent concentration, initial metal concentration, adsorbate concentration, temperature, particle size (Park et al., 2010; Selvi et al., 2001), kinetics, thermodynamics (Michalak et al., 2013; Sahmoune & Yeddou, 2016), etc." affect the adsorption capacity of sawdust for the elimination of heavy metal ions from the aqueous solution. The process can be shown as an adsorption isotherm, and these isotherms help calculate sorption capacity, sorption intensity, and energy adsorption by linear regression (Shukla et al., 2002). This also focusses on the mechanism involved and the principles for removing heavy metal ions from wastewater and water bodies.

Adsorption Mechanism and Kinetics

The solute transfer in a solid-liquid adsorption process is categorised either by external mass transfer or by boundary layer diffusion, also called intraparticle diffusion, or by both. The dynamics of adsorption are explained by a four-step successive process, i.e., transportation of the solute from bulk solution by the liquid film to the exterior surface of the adsorbent; solute diffusion into the pore of adsorbent except for a small quantity of sorption on the external surface; parallel to the above step, there is the intraparticle transport mechanism related to the surface diffusion; adsorption of solute on the inner surfaces of the pores and capillary spaces of the adsorbent. The above stage is considered the equilibrium reaction, whereas the transport mechanism stage is relatively fast and negligible. The solute diffusion process is considered to be the slowest and is there for the rate-determining step of adsorption.

The adsorption process is expressed by various kinetics models, such as pseudo-first-order kinetics, pseudo-second-order kinetics, external diffusion model, and intraparticle diffusion model, shown in equations 1,2,3, and 4, respectively.

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (1)$$

where 'k_1' is the pseudo-first-order rate constant, 'q_e' is the amount of solute in mg/g adsorbed at equilibrium, and 'q_t' is the amount of solute in mg/g adsorbed at any time 't'.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \quad (2)$$

where 'k_2' is the pseudo-second-order rate constant.

$$\frac{dC_t}{dt} = -k_s S(C_t - C_s) \tag{3}$$

where 'k_s' is the mass transfer coefficient, 'C_s' and 'C_t'concentrate on surface and solution, respectively, and 'S' is the specific surface area.

$$q_t = k_i(t^{\frac{1}{2}}) \tag{4}$$

where 'k_i' is the rate parameter of the intra-particle diffusion-controlled state.

Many researchers have studied the kinetics of adsorption by sawdust and most of them reported it to have pseudo-first-order kinetics (El-Saied et al., 2017), and the adsorption is pore-diffusion controlled (Semerjian, 2018).

Adsorption Isotherm

The Langmuir isotherm is used to show the adsorption mechanism of sawdust. This isotherm is shown when the adsorption occurs on a homogeneous surface with little interaction between the adsorbed molecules. For a single solute, the expression is given as,

$$\frac{x}{m} = \frac{V_m K C_e}{1 + K C_e} \tag{5}$$

Also, the linear form is expressed as

$$\frac{C_e}{x/m} = \frac{1}{K V_m} + \frac{C_e}{V_m} \tag{6}$$

where 'C_e' is the concentration at equilibrium, 'x/m' is the solute adsorbed per unit mass of adsorbent and K is the equilibrium's constant. The relation between 'K' and heat of adsorption 'q' is shown in the equation below.

$$K = K_0 e^{\frac{q}{RT}} \tag{7}$$

In equation 6, 'V_m' and 'K' are directly proportional to temperature. So, as the temperature rises, enhancement in adsorption capacity and intensity is seen. The Freundlich isotherm is often used to show adsorption in aqueous systems. It is also used to show heavy metal adsorption on sawdust. The isotherm is represented in the equation below.

$$\frac{x}{m} = K_f C_e^{\frac{1}{n}} \tag{8}$$

The linear form of the above equation is expressed as

$$\log\frac{x}{m} = \log K_f + \log C_e^{\frac{1}{n}} \tag{9}$$

where, 'K_f' is the sorption capacity, and '1/n' is the sorption intensity.

Another isotherm, the adsorption of heavy metals on sawdust, follows the Redlich-Peterson isotherm. It has three constants 'A', 'B', and 'β', where β is the heterogeneity factor and ranges from 0 to 1. The equation is expressed as

$$\frac{C_e}{x/m} = \frac{B}{A} + \frac{1}{A} C_e^{\beta} \tag{10}$$

This isotherm represents adsorption on a heterogeneous surface. If β approaches1, then this isotherm can be reduced into a Langmuir isotherm. With the help of curve fitting, the parameters A, B, and β are determined.

Future Prospectives

In this literature, the adsorption of heavy metal ions from wastewater by sawdust is studied. Sawdust is used as an efficient adsorbent, but the researchers have faced numerous limitations and challenges that should be addressed. The performance of the catalyst and the characterization results are not correlated in most of the research papers. The change in pH during adsorption was not reported in most of the cases. Also, the adsorption of heavy metals in the presence of organic and other pollutants is not studied. The sawdust should have a largescale application and should be cost-effective. In many literature works, researchers have not mentioned the cost, which mainly varies due to the type of adsorbent, availability, and the processing conditions. So, economic feasibility is a factor, which should be taken seriously during wastewater treatment. The regeneration of heavy metals that are adsorbed by sawdust should be studied in more detail. The recovery of these metals is quite crucial as this may lead to secondary pollution. Hence, more studies should be done on the green disposal of these contaminants. This will lead to the reduction of cost as well as environmental pollution.

Conclusion

Sawdust is mainly found as a by-product of agriculture or wood industries. With the help of certain modifications, it is turned into a cost-effective adsorbent and is used mainly for heavy metal removal. Researchers are currently focusing on various modifications of sawdust for enhancing its adsorbing capability. This literature summarises the work of various researchers done on removing heavy metals from wastewater. Various treatments on sawdust lead to enhanced adsorbing capacity. Different characteristics of sawdust are seen during different treatment methods. So, by controlling the operating parameters and sorbent characteristics, optimised biosorption parameters using sawdust can be obtained.

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