



## The role of sawdust in the removal of unwanted materials from water

Alka Shukla<sup>a</sup>, Yu-Hui Zhang<sup>b</sup>, P. Dubey<sup>c</sup>,  
J.L. Margrave<sup>d</sup>, Shyam S. Shukla<sup>e,\*</sup>

<sup>a</sup> Southeast College, Houston, TX 77207, USA

<sup>b</sup> A&B Environmental Services, Houston, TX, USA

<sup>c</sup> Vikram University, Ujjain, India

<sup>d</sup> Chemistry Department, Rice University, Houston, TX 77251, USA

<sup>e</sup> Department of Chemistry, Lamar University, Beaumont, TX 77710, USA

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### Abstract

Sawdust, a relatively abundant and inexpensive material is currently being investigated as an adsorbent to remove contaminants from water. Chemical substances including dyes, oil, toxic salts and heavy metals can be removed very effectively with the organic material. This article presents a brief review on the role of sawdust in the removal of contaminants. Studies on the adsorption of various pollutants by different sawdust materials are reviewed and the adsorption mechanism, influencing factors, favorable conditions, etc. discussed in this paper. Some valuable guidelines can be drawn for either scientific research or industrial design.

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### 1. Introduction

Environmental pollution and its abatement have drawn keen attention for a long time. The problem of removing pollutants from water and waste water has grown with rapid industrialization. Heavy metals, dyes, oil and other salts, which are toxic to many living life and organisms, are present in the waste water streams of many industrial processes, such as dyeing, printing, mining and metallurgical engineering, electroplating, nuclear power operations, semiconductor, aerospace, battery manufacturing processes, etc. [1–4]. All of

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\* Corresponding author. Tel.: +1-409-880-8269; fax: +1-409-880-8270.

E-mail address: shuklass@hal.lamar.edu (S.S. Shukla).

them have faced increasing pressure regarding environmental and waste-related concerns as a result of the quantity and toxicity of generated waste waters. The waste generated in large volumes is high in pollutant load and must be cleaned before it is released. Many methods have been used to remove the dye component, oil pollutants, and heavy metals as well from the textile effluent, namely, membrane filtration [5], coagulation [6,7], adsorption [8–10], oxidation [4], ion exchange [10–16], precipitation [6,15,17,18], etc. have been reported in the literature, but few of them were accepted due to cost, low efficiency, inapplicability to a wide variety of pollutants.

The most widely used method for removing pollutants is coagulation and precipitation [6,7,15,17,18]. Heavy metals, for example, can be precipitated as insoluble hydroxide at high pH [19–21] or sometimes as sulfides [22,23]. A major problem with this type of treatment is the disposal of the precipitated waste. Another weak point is that in most time the precipitation itself cannot reduce the contaminant far enough to meet current water-quality standards. Ion exchange treatment is the second most widely used method for metal removal. This method does not present a sludge disposal problem and has the advantage of reclamation of metals. It can reduce the metal ion concentration to a very low level. However, ion exchange does not appear to be practicable to waste water treatment from a cost stand point [24]. Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water, but the high cost of activated carbon inhibits its large-scale use as adsorbent. Then, the need for effective and economical removal of unwanted materials resulted in a research for unconventional methods and materials that might be useful in this field.

The trace elements in water are so numerous that only a combination of various treatment processes can provide the effluent quality desired and only a non-specific process such as adsorption appears appropriate for their removal [1]. Scientists have, therefore, centered their interest on adsorbents research in recent years. The utilization of agricultural waste materials is increasingly becoming of vital concern because these wastes represent unused resources and, in many cases, present serious disposal problems. During the past decade, a great deal of attention has been given to methods of converting these materials into useful products. Among those, sawdust is one of the most appealing materials for removing pollutants, such as, dyes, salts and heavy metals, etc. from water and waste water. This study presents a brief review on the role of sawdust in the removal of unwanted materials from waters. Application and comparison of different methods are discussed and a number of references are available in this article. The principal, affecting factors and our recent study of sawdust adsorption are also discussed.

## **2. A brief review of the adsorption of unwanted materials by sawdust**

Numerous studies on adsorption properties of naturally occurring and low cost adsorbents, such as agricultural by products or natural fibers, have been documented. Namely, barley straw, tree bark, peanut skins, human hair, waste tire rubber, and moss peat [25], etc. have been reported in recent years. Studies have shown that sawdust, among the low cost adsorbents mentioned, is the most promising adsorbent for removing heavy metals, acid and basic dyes, and some other unwanted materials from waste water. Not only is sawdust

abundant, but also it is actually an efficient adsorbent that is effective to many types of pollutants, such as, dyes, oil, salts, heavy metals, etc. Many agricultural byproducts are little or no economic value, and some, such as sawdust, which are available in large quantities in lumber mills, are often present a disposal problem. The use of sawdust for removing pollutants would benefit both the environment and wood agriculture: contaminated streams would be cleaned, and a new market would be opened for the sawdust.

### *2.1. Removal of dyes, oils, and toxic salts from waters by sawdust*

A number of studies on the adsorption of dyes, toxic salts and oil from water using sawdust as an adsorbent have been reported [1,26–28]. Charred sawdust was acid-hydrolyzed (processed to remove sugars from the wood) and used to study its effectiveness in the removal of salts and dyes [1]. In one such experiment dyes were placed in standard joint bottles (50 ml) and pre-weighted sawdust was added. An electric shaker shook the bottles for 18 h. After settling the supernatant was collected and analyzed for its optical density by a Klett–Sommersion Colorimeter. It was found that acid-hydrolyzed sawdust residue is a useful material for removing contaminants such as dyes, toxic ions, and oil from waste water.

In another case, Ibrahim et al. [27] studied the factors affecting preparation of wood sawdust and used the obtained adsorbents for removal of anionic dyestuffs. Sawdust was modified by reacting with cross-linked polyethylenimine (CPEI) to create aminated adsorbent. Modified sawdust was added to acidic dye (pH 3.0) and shook for 30 min at 25 °C. The filtrate was collected and its concentration was determined with a UV spectrophotometer. The results showed that modification with CPEI increased the adsorptivity of the sawdust, since the CPEI introduced positive sorptive sites in the form of reactive amino groups onto the wood material, thus improving the sawdust reactivity and anionic dye uptake.

Industries involved in metal machining operations require oil in large amount to cool and lubricate their equipment [1]. As a consequence, the waste water is contaminated with oil. Some oil can be skimmed but the emulsified oil is particularly troublesome to remove. Several methods, such as coagulation, are being considered to treat the emulsified waste. However, sawdust combined with hydrogen peroxide is more effective [1]. Hydrogen peroxide alone removes small amounts of oil but only with extensive shaking. As the addition of sawdust allows for a greater surface area and enhances oil flotation, oil removal can be greatly enhanced. Cost analysis of different coagulants has shown that sawdust treated with hydrogen peroxide would be much more cost efficient.

Sawdust can also be used for the removal of toxic salts from water; for example, denitrification walls amended with sawdust have proved effective in nitrate removal. Schipper and Vojvodic-Vukovic [26] used one of these walls to remove nitrates from groundwater. The denitrification wall was constructed by digging a trench that intercepted groundwater. The excavated soil was mixed with sawdust (30% (v/v)) as a carbon source then returned to the trench. Nitrogen levels in the wall and in the surrounding groundwater were monitored for one year. The denitrification wall successfully removed nitrates from water but did not provide long-term removal. Effectiveness of the wall depended on nitrate concentration not on the amount of carbon in the sawdust. Throughout the year, the wall proved to be very efficient even with the decrease in sawdust availability. This technique proved to be very useful in nitrate removal from groundwater.

## 2.2. Sawdust adsorption in the removal of heavy metals

The adsorption phenomenon has still been found economically appealing for the removal of toxic metals from waste water by choosing some adsorbents under optimum operation conditions. Sawdust both treated and untreated is effective in removal of heavy metals from water.

Our previous research [29] on the adsorption behavior of maple sawdust for the removal of heavy metals, such as copper and lead, presented some guidelines for the application of sawdust adsorption. In these studies, we investigated the adsorption behavior, capacity, and affecting factors, such as pH and sawdust dose, using untreated maple sawdust. Under optimized conditions, the percentage of metal removal by maple sawdust adsorption was over 90%; indicating sawdust is an appealing adsorbent for the removal of heavy metals. The applicability was also studied using packed columns, resulting in valuable guidelines for industrial design. The investigations are quite useful in developing an appropriate technology for designing a waste water treatment plant.

In 1998, Ajmal et al. [30] reported a study on the role of sawdust in the removal of Copper from industrial waste. The effects of contact time, pH, concentration, temperature, dose, particle size of the sawdust and salinity on the removal of copper were studied and valuable information presented in the report. It was reported that the efficiency for the removal of copper from real river water using sawdust was 63%, and it was thus concluded that the sawdust is an excellent adsorbent for copper removal from aqueous solution. Another report [2] showed that divalent copper and hexavalent chromium could be removed from solution with untreated red fir sawdust. In 1997, Raji and Anirudhan [31] published a study on chromium(VI) adsorption by sawdust carbon. They studied the adsorption behavior of rubber wood sawdust and tested the effecting factors, such as concentrations, pH and temperature. Under an optimized condition, an adsorption of 100% could be achieved.

Metals in the form of sulfates are of major concern in waste water from mining operations. They can be precipitated as sulfides and removed. A biological method of cleaning up contaminated water was developed at Idaho National Engineering and Environmental Laboratory [32]. A “sawdust reactor” was constructed by placing a layer of sawdust over mud in a rectangular vessel. Fungi present in the sawdust fed on the cellulose material and produced carbohydrates. These carbohydrates when pushed deeper into the mud fermented and formed organic acids. Oxidation of the acids by sulfate-reducing bacteria occurred and created an electron flow. This current reduced the sulfates present to sulfides and they were easily precipitated. The process can remove more than 90% of the metals present. When compared with the lime neutralization process usually used, the sawdust reactor would cost two-thirds less and produces less sludge. This method seems very promising and should be field-tested.

To enhance the capability and efficiency of sawdust adsorption, pre-treatment of sawdust may be needed. Untreated sawdust does not necessarily mean that the sawdust is used directly without any cleaning, size reduction or mechanical preparation. What treated sawdust means is that the sawdust has been treated or mixed with some other chemicals or materials before use. In the example of a sawdust reactor mentioned, it can be called that the sawdust was mechanically treated for a special purpose.

Research data has shown that sawdust treated with a special material or chemical can be significantly effective to the removal of a particular element and that treated sawdust had a higher capacity for ion removal. For example, scientific reports have shown that polysulfide treated sawdust was very effective for the removal of divalent cobalt from aqueous solution [33], while copper-impregnated sawdust is one material being considered and exhibits significant arsenic(III) removal [34].

Sawdust treated with phosphates has proven more effective for chromium removal as opposed to untreated sawdust [35]. Cr(VI) has also been removed from waste by using sawdust amended with clay [36]. Red mud derived from bauxite was added to a sawdust/grass mixture spiked with chromium. The clay/sawdust material was able to capture the chromium ions and prevent possible leaching of the ion or uptake by nearby plants. Cr(VI) bound to organic material was more difficult to capture. There was a slight increase in Cr concentration over time, however, due to the amount of chromium present in the red mud itself. The mixture did prove very useful in retaining the metal ions.

Raji and Anirudhan reported studies on the removal of lead(II) using polyacrylamide grafted sawdust [37] and polymerized sawdust [38]. In those studies, adsorption and desorption experiments were conducted, and various affecting factors tested. Research data showed that the treated sawdusts might be effectively used as sorbents for the removal of Pb(II) from aqueous media. The maximum removal of over 98% was reported. Earlier, they reported in 1996 a study on the removal of Hg(II) from aqueous solution by sorption on polymerized sawdust [39]. Mercury can also be removed by peanut hulls treated with bicarbonate [40]. The peanut hulls treated with bicarbonate acted as activated carbon that is a conventional sorbent for the removal of mercury from waters.

Dyed sawdust is another very common modification to enhance the adsorption efficiency of sawdust material. Shukla and Sakhardande [11] reported a study on the removal of divalent Cu, Pb, Hg, Fe, Zn, Ni and trivalent Fe using untreated sawdust and sawdust treated with a reactive monochlorotriazine type of dye. The dyed materials showed better adsorption than the undyed materials for all metals used. In fact, dye-treated sawdust was used and proved useful long time ago for the removal of heavy metal ions from waste water [41].

Other organic materials can be added to sawdust when designing adsorption methods. Onion skin and corncob were used along with sawdust to remove metals from agricultural wastes, which are of current environmental concern [42]. Onion skin, polymerized corncob and sawdust were mixed and powdered to form a resin and used in packed columns. Static and dynamic equilibrium experiments were conducted. For the static analysis, 1 g of the resin and 100 ml of metal solution were allowed to sit overnight in a stoppered flask. Columns packed with the resin were used in the dynamic testing. Metal solutions were added to the column at a rate of 2–3 ml/min. The final and initial concentrations of the metal solutions were determined and the column was rinsed with dilute nitric acid to regenerate the resin. For the metal ions used the resin's removal capacity can be ranked:  $\text{Pb}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Cu}^{2+}$ . In the dynamic experiments, all metal ions were significantly removed. The percent ion removal for Zn, Ca, Mg, Mn and Pb was 75, 79, 71, 65 and 86%, respectively. The corncob-sawdust resin proved to be very economical and efficient for metal ion removal from waste.

Construction of wetlands to treat waste water containing metals is also being considered. Sawdust can be used to remove metals from these areas. Its effectiveness was compared with

that of *Sphagnum* peat in a 1990 journal article [43]. Sawdust and *Sphagnum* are present in constructed wetlands and would be very affordable to use.

Sawdust modified with iron hexamine gel has proved very efficient in the removal of several toxic metal ions [44]. Sawdust amended with the gel was used to filter various aqueous ion solutions. The gel was very stable and removed Hg(II), Pb(II) and Cr(VI) very well. Ni(II), Cd(II) and Cu(II) were also removed using the sawdust but not as efficiently. The sawdust was not able to adsorb Mn(II) or Zn(II).

### 3. Adsorption mechanism

Based on the behavior of heavy metal adsorption on sawdust, scientists have speculated that ion exchange and hydrogen bonding may be the principal mechanism for the removal of heavy metals [30]. There are a great deal of facts to support this speculation, including the components and complexing properties of the sawdust, the properties of heavy metals and the adsorption behavior, such as the effect of pH of the aqueous media.

It has long been recognized that heavy metal cations are readily form complexes with O-, N-, S-, or P-containing functional groups in polymer materials [45]. Although a detailed characterization of the nature of the binding sites on different sawdust materials was not conducted, from the nature of heavy metal ions and sawdust materials it can be speculated that ion exchange or hydrogen bonding may be the principal mechanism for the removal of heavy metal ions.

The cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds [41]. All those components are active ion exchange compounds. Lignin, the third major component of the wood cell wall, is a polymer material. Lignin molecule is built up from the phenylpropane nucleus, i.e. an aromatic ring with a three-carbon side chain. Vanillin and syringaldehyde are the two of other basic structural units of lignin molecule.

The lignin content of hardwoods is usually in the range of 18–25%, whereas that of softwoods varies between 25 and 35%. However, tropical hardwoods can exceed the lignin content of many types of softwood.

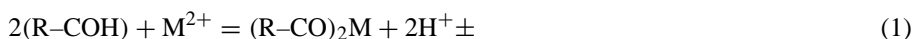
Tannins are complex polyhydric phenols which are soluble in water and have the property of precipitating protein (e.g. gelatin) from solution and converting hides into leather. They occur chiefly in hardwoods, and are also present in many barks, including softwoods barks, as well as in the leaves and fruits of some trees. Natural tannins are classified as either hydrolyzable or condensed tannins. The hydrolyzable tannins are esters of sugar (usually glucose) with one or more polyphenolic acids, commonly gallic, digallic, or ellagic acid. The basic unit of condensed tannins is, in many cases, catechin.

More extractive sites, such as N-, S-, and P-containing group, will be introduced to sawdust material when the sawdust is modified with some other materials, such as, dyestuff [41], hexamine [44], polyacrylamide [37,46], CPEI [27], or other chemicals [33,35]. Consequently, the binding ability of modified sawdust will be enhanced.

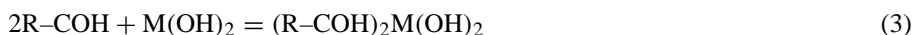
Based on the electron-donating nature of the O-, S-, N-, and P-containing groups in sawdust materials and the electron-accepting nature of heavy metal ions, the ion exchange mechanism could be preferentially considered. For instance, a divalent heavy metal ion

may attach itself to two adjacent hydroxyl groups and oxyl groups which can donate two pairs of electrons to the metal ion, forming four coordination number compounds and releasing two hydrogen ions into solution. It is then readily understood that the equilibrium is quite dependent on pH of the aqueous solution. At lower pH, the H<sup>+</sup> ions compete with metal cations for the exchange sites on the sawdust, thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions [15]. In most cases, the percentage of adsorption of metal ions increased with an increase in pH up to a certain value and then decreased with further increase of pH. Due to different properties of various heavy metal ions and different sawdust materials, the maximum adsorption took place in a slightly different pH range for different metals. In a certain pH range, for one specific heavy metal there may be a number of species present in solution, such as M, MOH<sup>+</sup>, M(OH)<sub>2</sub>, etc. At lower pH, the positive charged metal ion species may compete with H<sup>+</sup> and be adsorbed at the surface of the sawdust by ion exchange mechanism. With an increase in pH, metal ion species, mainly neutral, may be adsorbed by hydrogen bonding mechanism along with ion exchange. These mechanisms are shown in the following equations:

Ion exchange



Hydrogen bonding



(where R is the matrix of the sawdust).

Sometimes it is hard to tell apart the two. Adsorption of metal ions from solutions by solid phase can occur with formation of surface complex between the adsorbed ligand and the metal. However, the sites on modified sawdust can also contribute to the adsorption process.

#### 4. Adsorption isotherms

The Langmuir and Freundlich isotherms were both used to describe observed sorption phenomena of various metal ions on sawdust materials [2,29–31,33,37,47]. The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. For a single solute, it is given by

$$\frac{x}{m} = \frac{V_m K C_e}{1 + K C_e} \quad (4)$$

However, the linear form of the equation can be written as

$$\frac{C_e}{x/m} = \frac{1}{K V_m} + \frac{C_e}{V_m} \quad (5)$$

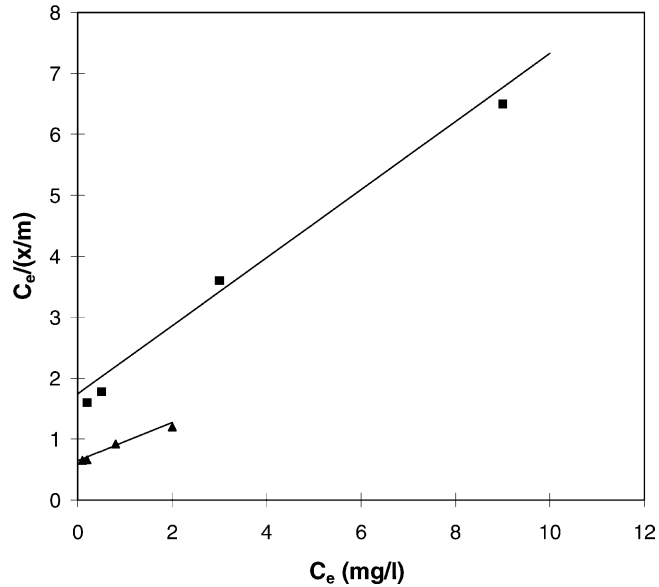


Fig. 1. Linear Langmuir isotherm for Cu(II) and Pb(II) sorption on maple sawdust. Sorbent concentration: 30 g/l; temperature: 23 °C; pH = 7.0; reaction time: 6 h. (□) Cu(II):  $C_e/x/m = 0.558 C_e + 1.743$ ; (△) Pb(II):  $C_e/x/m = 0.314 C_e + 0.646$ .

Where  $C_e$  is the equilibrium concentration of the solution,  $x/m$  is the amount adsorbed per unit mass of adsorbent,  $m$  is the mass of the sorbent,  $V_m$  is the monolayer capacity, and  $K$  is an equilibrium constant that is related to the heat of adsorption by equation:

$$K = K_0 \exp\left(\frac{q}{RT}\right) \quad (6)$$

where  $q$  is the heat of adsorption. Langmuir model can describe most adsorption phenomena of heavy metals on sawdust [30,31,37,38,40,47]. In most cases,  $V_m$  and  $K$  increase with temperature, suggesting that adsorption capacity and intensity of adsorption are enhanced a higher temperature. A linear plot from Eq. (2) can be drawn for a particular metal adsorption and the values  $V_m$  and  $K$  for the isotherms of the metal under study can be obtained by using least squares method. As example of this plots is shown in Fig. 1.

The Freundlich model, which is an empirical model used to describe adsorption in aqueous systems, was also used to explain the observed phenomena of metal adsorption on sawdust materials. The Freundlich isotherm is shown as the following equation.

$$\frac{x}{m} = K_f = C_e^{1/n} \quad (7)$$

The linear form of the equation can be written as:

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n \log C_e} \quad (8)$$



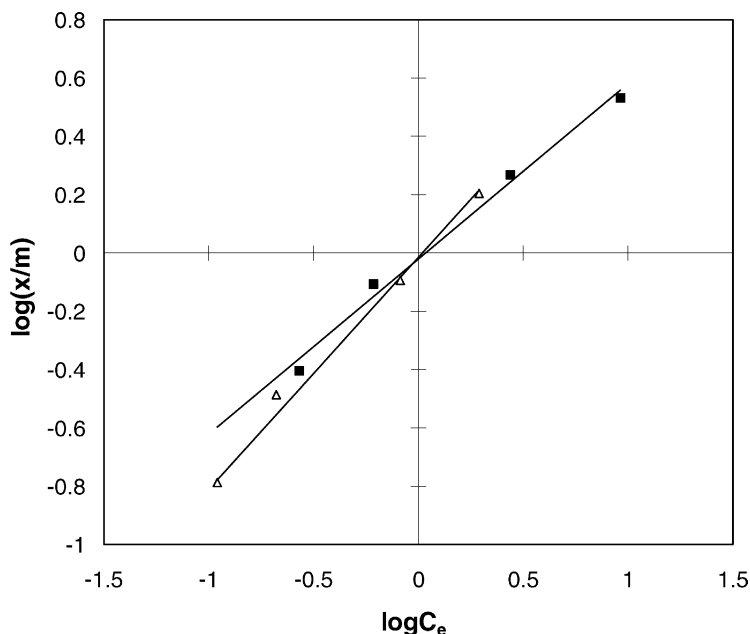


Fig. 2. Linear Freundlich isotherm for Cu(II) and Pb(II) sorption on maple sawdust. Sorbent concentration: 30 g/l; temperature: 23 °C; pH = 7.0; reaction time: 6 h. ( $\square$ ) Cu(II):  $x/m = 0.953C_e^{0.601}$ ; ( $\triangle$ ) Pb(II):  $x/m = 0.965C_e^{0.769}$ .

Where  $K_f$  is the measure of sorption capacity,  $1/n$  is sorption intensity and other parameters have been defined as in Eq. (4). A plot of  $\log(x/m)$  against  $\log C_e$  gives a straight line, the slope and intercept of which correspond to  $1/n$  and  $\log K_f$ , respectively. Freundlich plots for copper and lead sorptions on maple sawdust are shown in Fig. 2.

## 5. Factor affecting metal adsorption on sawdust

### 5.1. Effect of pH of the aqueous media

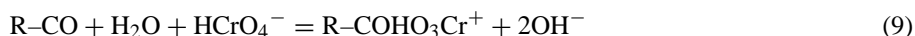
An important influencing factor for heavy metal adsorption on sawdust has been referred to as pH in most studies published in the literatures [31,37,38,44,46,47]. In a certain pH range, most metal adsorption increases with increasing pH upto a certain value and then decreases with further pH increasing. This is readily explained by the adsorption mechanism. Therefore, there is a favorable pH range for the adsorption of every metal on a certain sawdust material. Favorable pH ranges for some metal ions adsorbed by various sawdust materials are listed in Table 1. The effect of pH can also be explained in terms of  $pH_{zpc}$  of the adsorbent, at which the adsorbent is neutral. The surface charge of the adsorbent is positive when the media pH is below the  $pH_{zpc}$  value while it is negative at a pH over the  $pH_{zpc}$ . On the other hand at pH below the  $pH_{zpc}$ , the predominant metal species ( $M^{2+}$  and  $M(OH)^+$ ) are positively charged and therefore, the uptake of metals in the pH range below  $pH_{zpc}$  is

Table 1  
Favorable pH for the adsorption of various metal ions on different sawdust materials

Metal ions	Sorbent materials	Optimized pH range	References
Cd	Polyacrylamide-grafted sawdust, activated carbon	5–10	[47,48]
Co(II)	Rubber wood sawdust	6–8	[34]
Cr(III)	Rubber wood sawdust	7–10	[32]
Cr(VI)	Rubber wood sawdust, mango tree sawdust treated with hydrogen phosphate	1–3	[32,36]
Cu(II)	Sawdust	6	[31]
Hg(II)	Polyacrylamide-grafted sawdust, sawdust activated carbon, dyestuff-treated sawdust	4–10	[47,48]
Pb(II)	Polyacrylamide-grafted sawdust, sawdust activated carbon, polymerized sawdust	5–9	[38,39,47,48]

$H^+ - M^{2+}$  (or  $M(OH)^+$ ) exchange process explained by other authors as well [48,49]. With an increase in pH above  $pH_{zpc}$ , although the surface of the adsorbent is negatively charged, the adsorption still increases as long as the metal species are still positively charged or neutral. When both the surface charge of the adsorbent and metal species charge become negative, the adsorption will decrease significantly. The  $pH_{zpc}$  values for some sawdust materials as examples are given in Table 2.

According to the mechanism and the discussion of pH effect, the adsorption will lead to a decrease in pH as equivalent  $H^+$  will be released along with the adsorption. This is the case for most metal adsorption, but there is always exception. Some metals existing as negative species in solution, such as hexavalent chromium, may release hydroxide ( $OH^-$ ) instead of proton ( $H^+$ ) when they are adsorbed by sawdust materials, and therefore result in an increase in pH [31]. The following equations describe the chemical adsorption involving exchange with hydroxyl ions [50]:



### 5.2. Effect of adsorbent dose

It is apparent that by increasing the adsorbent dose the adsorption efficiency increases but adsorption density, the amount adsorbed per unit mass, decreases [31,37,51]. It is readily understood that the number of available adsorption sites increases by increasing the adsorption dose and it, therefore, results in the increase of removal efficiency. The decrease

Table 2  
 $pH_{zpc}$  values for different sawdust materials

Sawdust materials	$pH_{zpc}$
Polyacrylamide-grafted sawdust	5.9
Dyestuff-treated sawdust	5.9
Sawdust activated carbon	6.4
Polysulfide treated sawdust	4.3
Rubber wood sawdust carbon	5.8

in adsorption density with increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interaction, such as aggregation, resulted from high sorbent concentration. Such aggregation would lead to decrease in total surface area of the sorbent and an increase in diffusional path length [52]. Particle interaction may also desorb some of the sorbate that is only loosely and reversibly bound to the carbon surface.

### 5.3. Effect of particle size of the sawdust

Intraparticle diffusion study shows that particle size of the sawdust used greatly influences the adsorption rate [38]. Decrease in particle size would lead to increase in surface area and then increase in the adsorption opportunity at the outer surface of the sawdust materials. Besides adsorption at the outer surface of the sawdust there is also possibility of intraparticle diffusion from the outer surface into the pores of the material. The diffusional resistance to mass transfer is greater for large particles. Due to various factors, such as diffusional path length or mass transfer resistance, contacting time, and blockage of some diffusional path most of the internal surface of the particle may not be utilized for adsorption consequently the adsorption efficiency may be low.

### 5.4. Adsorption kinetics

The adsorption rate of heavy metals on sawdust has been studied by a number scientists [2,31,46]. Factors influencing the adsorption rate are mainly, among others, initial concentration, shaking speed and temperature. In most cases, at low initial concentration the adsorption of heavy metals by sawdust is very high, e.g. 95–99%, and reaches equilibrium very quickly. This indicates the possibility of the formation of monolayer coverage of the metal ions at the outer interface of sawdust and suggests that sawdust can remove most of the metal ions from water if their concentrations are low, say below 50 mg/l. At a fixed adsorbent dose, the amount adsorbed increased with increasing concentration of solution, but the percentage of adsorption decreased. In other words, the residual concentration of metal ions will be higher at a higher initial concentration of the metals under study. In the case of lower concentrations, the ration of initial number of metal moles to the available sorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration. At higher concentrations, however, the available sites of adsorption become fewer and subsequently the removal of metals depends on the initial concentrations. At higher initial concentration, it is not likely that metal ions are only adsorbed in a monolayer at the outer interface of sawdust. As a matter of fact, the diffusion of exchanging ions within sawdust particles may govern the adsorption rate at higher initial concentrations.

External mass transfer diffusion and intraparticle mass transfer diffusion models were used to evaluate the sorption kinetics. It has demonstrated that the sorption of heavy metal ions by polymerized materials is well described by intraparticle mass transfer model [53]. Due to the porous nature of sawdust materials the possibility of intraparticle transport of adsorbate within the pores is expected [54]. Experimental data has shown that both agitation and temperature affect the adsorption rate of metals on sawdust. Generally, the adsorption increases with increasing contacting time while the time for equilibrium would be decreased

by vigorous agitation when other conditions are kept constant. In a rapidly stirred batch reactor, the adsorbate species are most probably transported from solution to solid phase through intraparticle transportation which is often the rate control step in many adsorption processes. Increasing the stirring rate usually results in an increase in adsorption rate. The capacity of the adsorbent to adsorb metal ions increases with increase in diffusion coefficient at higher speed. The mobility of sorbing species can be increased at higher shaking speed and subsequently the sorption rate can be enhanced.

The adsorption rate and equilibrium adsorption level increases with increasing temperature. Thermodynamical parameters such as free energy change ( $G^\circ$ ), enthalpy change ( $H^\circ$ ) and entropy change ( $S^\circ$ ) can be calculated using the following equation [38,55,56].

$$\ln K_c = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} = \frac{\Delta H^\circ}{RT} \quad (10)$$

where  $K_c$  is equilibrium constant that is resulted from the ratio the equilibrium concentrations of the metal ion on the adsorbent and in the solution, respectively. The linear property of  $\ln K_c$  against  $1/T$  has been proven in a number studies on heavy metal adsorption by sawdust materials [33,46].  $G^\circ$  or  $S^\circ$  and  $H^\circ$  can be calculated from a plot of  $\ln K_c$  versus  $1/T$ . A negative  $G^\circ$  value indicates the process to be feasible and spontaneous nature of adsorption. A positive  $H^\circ$  value suggests the endothermic nature of adsorption and the  $S^\circ$  can be used to describe the randomness at the solid–solution interface during the adsorption. It has been found, in most cases, that the adsorption increases with increasing temperature. This is a direct consequence of (i) opening up the cellulose structure, (ii) enhancing the mobility and extent of penetration within the sawdust structure, and (iii) overcoming the activation energy barrier and enhancing the rate of intraparticle diffusion [27]. There is, however, a limit for maximum temperature at which solubilization of wood extractives with bound metal ions would probably occur, resulting in a low adsorption in solid phase. Therefore, a general temperature range is suggested to be 30–60 °C. Bryant et al. [2] discussed this effect in a scientific study on sorption of heavy metals by sawdust. Wood extractives are a broad class of low-molecular weight organic compounds that are soluble in polar or non-polar solvents [57]. The solubilization of these extractives will become significant at 60 °C. An important group of wood extractives are referred to as tannins, which is an indication of their tanning action on the proteins of hides [57]. Young et al. [58] have suggested that tannins serve as the primary site for divalent cations binding to wood.

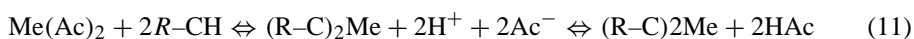
### 5.5. Effect of anions

Ionic strength is one of the important factors which influence the aqueous phase equilibrium. This effect has been intensively investigated by a number of scientists [29,30,33,38]. Generally, adsorption decreases with increasing ionic strength of the aqueous solution [33,59].

This effect may be ascribed to changes in the metal activity, or in the properties of the electrical double layer. According to surface chemistry theory, when two phases, e.g. sawdust particles and metal species in aqueous solution, are in contact, they are bound to be surrounded by an electrical double layer owing to electrostatic interaction. If the adsorption mechanism is significantly the electrostatic attraction adsorption decreases with

increase in ionic strength. Some inorganic anions, such as chloride, may form complexes with some metal ions and therefore, affect the adsorption process. In a study, Ajmal et al. [30] found that the effect of chloride on the adsorption of Cu(II) was very interesting. It was found that the presence of sodium chloride in the range of 0.25–5.0 g/50ml reduced the adsorption of Cu(II). This may be due to relative competition between sodium ions and copper species on the active centers of the sawdust. But after the critical concentration (above 5.0 g NaCl/50 ml), the percent adsorption sharply increased. The sodium chloride may act as an in situ regenerating agent for the sawdust via removal of oxygenated complexes as soluble chlorocomplexes, increasing thereby the number of adsorption sites and hence the Cu(II) adsorption.

In other studies, Yu et al. [29] investigated and compared the effect of inorganic anions and organic anions such as acetate on the metal adsorption by sawdust. The ion exchange hypothesis explains the better removal of some metals from acetate solution than from chloride, nitrate, or sulfate solutions because the removal of most metals from solution is inhibited by low pH. In all cases, the metal sorption was affected by the activity of hydrogen ions. The hydrogen ions in solution of strong acids like HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are almost completely dissociated, while it is only partially dissociated in acetic acid. Thus, the inorganic solution would have lower pH than HAc solution at equal concentrations of acid.



Metal ions could be removed from high pH acetate solution at an acid concentration where no further adsorption of them from nitrate or sulfate solutions would take place.

### 5.6. Selectivity of heavy metal adsorption

Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup> are the common cations present in water that may compete with heavy metal ions for adsorption and can affect the removal of heavy metals [33]. However, in general cations may follow an order of increasing selectivity for binding to organic matter of alkali metal cations < H<sup>+</sup> < alkaline earth cations < transitional group monovalent cations (e.g. Ag<sup>+</sup>) < transitional group divalent cations (e.g. Cu<sup>2+</sup> and Pb<sup>2+</sup>) < trivalent cations [60]. Therefore, heavy metals are preferably adsorbed provided in a tolerable concentration of light metal cations.

In fact, selective adsorption is possible by adjusting the adsorption conditions or modifying sawdust materials. According to the observation of pH effect on adsorption, adjustment Another way to achieve selective adsorption is to modify the sawdust materials with some chemicals. It is well known that the binding of cations to organic matter can be affected by the chemical nature of binding sites (e.g. carboxylic versus phenolic hydroxyl) and by the spatial arrangement of the potential binding sites. For example, carboxylic sites are more selective toward multivalent cations when the sites are attached to adjacent carbon atoms on a ring structure than when they are more widely spaced [60]. In addition, some metal cations preferentially form complexes with O-containing functional groups while others preferentially form complexes with N-, P-, or S-containing functional groups. Therefore, by modifying the sawdust material with chemicals which possess desired functional group, selective adsorption can be achievable.

## 6. Sawdust regeneration and packed column studies

To make the adsorption process more economical and practical it is necessary to regenerate the spent sorbent and pack the sorbent in a certain container, such as packed column. Studies on sawdust regeneration and dynamic adsorption of sawdust in packed column have been reported by a number scientists [29,35,37,46].

### 6.1. Regeneration of sawdust

The  $M^{2+}-H^+$  ion exchange is easily reversible, depending upon pH. In a study [29], sawdust samples which have been exposed to heavy metal solutions and adsorbed up to 97% copper and lead were stripped with 0.1 M  $HNO_3$  (pH  $\sim$  1.3). The heavy metal cations were almost completely removed from the sawdust after 6 h. These concentrations represent almost a complete exchange of  $H^+$  ions from the stripping acid to the sawdust. The regenerated sawdust samples were washed several times with distilled water until its pH reached the regular range. After dried in an oven at 101 °C, the regenerated sawdust was employed to adsorb heavy metals again. The results showed that the regenerated sawdust has even higher capacity for heavy metals than the untreated material dose. That may be due to the impurities of sawdust being removed after regeneration and more exchangeable surface area becoming available. A decrease in percent adsorption, however, was observed after a couple of cycles of regeneration, since a small fraction of adsorbed metals not recoverable by regeneration presumably represents the metals which are bound through stronger interaction [46].

As discussed, most metal adsorption results in a pH decrease of the aqueous solution. When the pH of the solution is low enough the adsorption will go in a reversed way, that is the metal ions will be stripped at an acidic condition. However, Cr(VI) is an exception. As described in Eq. (9), hydroxyl species are released from the process of Cr(VI) adsorption instead of hydrogen ions. In this case, decreasing the pH will favor the Cr(VI) adsorption on sawdust but not help strip Cr(VI) ions from sawdust. That is why NaOH was used for the desorption of Cr(VI) [31,35].

### 6.2. Packed column studies

Non-equilibrium adsorption was studied in packed columns [29,41,42]. In one study, Yu et al. [29] investigated the dynamic adsorption phenomena for copper and lead. In comparison of the two metals, the breakthrough point of copper appears much earlier than lead, and the slope of the copper curve is steeper than lead curve. This observation provides convincing evidence for the explanation of the proposed adsorption mechanisms noted before. The adsorption of copper on sawdust results mainly from the ion exchange, while the adsorption of lead is not only based on ion exchange, but also involves some static attraction. The individual and total capacities were also reported in this study. Comparing the individual metal ion operation equivalent capacity (0.036 meq./g S.D. for copper, and 0.03 meq./g S.D. for lead) with the mixture metal ions, it shows that the sawdust capacity keeps consistent regardless of individual or mixture components. The competition to bind sawdust for each component in mixture depends on the ion selectivity to sawdust.

## 7. Conclusions

The role of sawdust materials in the removal of pollutants from aqueous wastes has been investigated. The investigations are quite useful in developing an appropriate technology for waste water treatment. Some valuable information or guidelines can be drawn from the review and discussions.

Sawdust material has proven to be a promising material for the removal of contaminants from waste waters. Not only is sawdust abundant, but also it is really an efficient and economic adsorbent that is effective to many types of pollutants, such as, dyes, oil, salts, heavy metals, etc.

The ion exchange or hydrogen binding mechanism can very well explain the heavy metal adsorption by sawdust. Most adsorption can be modeled by Langmuir and Freundlich isotherms from which parameters such as sorption capacity, sorption intensity and energy adsorption can be calculated by linear regression.

The adsorption can be influenced by a number of factors, such as, adsorbent dose and size, contact time, agitation speed, temperature, pH and ionic strength of the aqueous solution, etc. Generally, percent adsorption increases with increasing adsorbent dose, contact time, and agitation speed although favorite conditions may be different for different materials and adsorptions. For each type of sawdust material, there is a neutral pH beyond which the sawdust will be either positively or negatively charged. This pH is very critical. For every heavy metal ions, there is a favorable pH range in which maximum adsorption was observed.

Desorption studies have shown the applicability to regenerate the sawdust used. Dynamic studies in packed column have shown that adsorption by sawdust materials is practicable. The process is economically feasible and easy to carry out. All those add more credits to sawdust materials for removing pollutants from waste waters.

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## References

- [1] A. Nag, *Process Safety Environ. Protection* 73 (1995) 299.
- [2] P.S. Bryant, J.N. Peterson, J.M. Lee, T.M. Brouns, *Appl. Biochem. Biotechnol.* 34/35 (1992) 777.
- [3] G. Mishra, M. Tripathy, *Colourage* (10) (1993) 35.
- [4] C.G. Namboodri, W.S. Perkins, W.K. Walsh, *Am. Dyestuff Rep.* 83 (1994) 17.
- [5] C.A. Brandon, J.S. Johnson, R.E. Mintura, J.J. Proter, *Text Chem. Color* 5 (1973) 134.
- [6] D. Lemordant, P. Letellier, M. Rumeau, C. Soma, *Text Month* 11 (1988) 41.
- [7] A. Nag, S.N. Mukherjee, *J. Surf. Sci. Technol.* 142 (1995).
- [8] G. McKay, H.S. Blir, J.R. Gardner, *J. Appl. Polym. Sci.* 27 (1982) 3043.
- [9] M.M. El-Zawahry, M.Sc. Thesis, 1991.
- [10] S.D. Faustt, A.M. Osman, *Adsorption Processes for Water Treatment*, Butterworth, Stockholm, MA, 1987.
- [11] S.R. Shukla, V.D. Sakhardande, *Appl. Polym. Sci.* 44 (1992) 903.

- [12] M.H. Abou-Shosha, N.A. Ibrahim, A. El-Halwagi, *Am. Dyestuff Rep.* 82 (1993) 41.
- [13] N.A. Ibrahim, M.H. Abou-Shosha, S. Farag, *Tinctoria* 9 (1994) 36.
- [14] S. Farag, M.H. Abou-Shosha, N.A. Ibrahim, *Tinctoria* 10 (1994) 48.
- [15] U. Forstner, G.T.W. Wittmann, *Metal Pollution in the Aquatic Environment*, 2nd Edition, Springer, New York, 1983.
- [16] C. Sarzanini, E. Mentaasti, V. Porta, in: M. Streat (Ed.), *Ion Exchange for Industry*, Ellis Horwood, Chichester, UK, 1988, pp 189–193.
- [17] J.C. Dean, F.L. Bosqui, K.H. Lanouette, *Environ. Sci. Technol.* 6 (1972) 457.
- [18] G.C. Cushnie, *Removal of Metals from Waste Water: Neutralization and Precipitation*, Noyes Publications, Park Ridge, NJ, 1984.
- [19] R.F. Weiner, *Plating* 54 (1967) 1354.
- [20] G.L. Culp, R.L. Culp, *New Concepts in Water Purification*, Van Nostrand Reinhold, New York, 1974.
- [21] Z. Zhou, Y. Xue, *Kuangye Gongcheng* 7 (1987) 24.
- [22] H.P. Larsen, J.K.P. Shou, L.W. Ross, *J. Water Pollut. Cont. Fed.* 45 (1973) 1682.
- [23] E. Mann, A. Denne, *Korresp. Abwasser* 33 (1986) 942.
- [24] R. Pinner, V. Crowle, *Electroplat. Met. Finish.* 3 (1971) 13.
- [25] D.K. Singh, D.P. Tiwari, D.N. Saksena, *Indian J. Environ. Health* 35 (1993) 169.
- [26] L. Schipper, M. Vojvodic-Vukovic, *J. Environ. Qual.* 27 (1998) 664.
- [27] N.A. Ibrahim, A. Hashem, M.H. Abou-Shosha, *Polyplast. Technol. Eng.* 36 (1997) 963.
- [28] G. McKay, J.P. Poots, *J. Chem. Biotechnol.* 30 (1980) 279.
- [29] B. Yu, Y.-H. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, *J. Haz. Mat.* B84 (2001) 83–94.
- [30] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, *Water Res.* 32 (1998) 3085.
- [31] C. Raji, T.S. Anirudhan, *Indian J. Chem. Technol.* 4 (1997) 228.
- [32] X.Y. Chem. Eng. (6) (1998).
- [33] T.S. Anirudhan, M.K. Sreedhar, *Indian J. Chem. Technol.* 5 (1998) 41.
- [34] C. Raji, T.S. Anirudhan, *J. Sci. Ind. Res.* 57 (1998) 10.
- [35] M. Ajmal, R.A. Rao, B.A. Siddiqui, *Water Res.* 30 (1996) 1478.
- [36] H. Goen, L. Qiao, *Water Sci. Technol.* 38 (1998) 17.
- [37] C. Raji, T.S. Anirudhan, *Indian J. Chem. Technol.* 4 (1997) 157.
- [38] C. Raji, T.S. Anirudhan, *Indian J. Environ. Health* 39 (1997) 230.
- [39] C. Raji, T.S. Anirudhan, *Indian J. Chem. Technol.* 3 (1996) 49.
- [40] C. Namasivayam, K. Periasamy, *Water Res.* 27 (1993) 1663.
- [41] R. Suemitsu, M. Osako, N. Tagiri, *Sci. Eng. Rev.* 27 (1986) 41.
- [42] T.O. Odozi, S. Okeke, R.B. Lartey, *Agric. Wastes* 12 (1985) 13.
- [43] R. Weider, *Water Air Soil Pollut.* 53 (1994) 391.
- [44] D.K. Singh, N.K. Mishra, *Pollut. Res.* 11 (1992) 187.
- [45] S. Ahrland, J. Chatt, N.R. Davies, *Chem. Soc. London Q. Rev.* 12 (1958) 265.
- [46] C. Raji, T.S. Anirudhan, *Indian J. Chem. Technol.* 3 (1996) 345.
- [47] C. Raji, G.N. Manju, T.S. Anirudhan, *Indian J. Eng. Mater. Sci.* 4 (1997) 254.
- [48] X. Ma, K.S. Subramanian, C.L. Chakrabarthy, R. Gou, J. Cheng, Y. Lu, W.F. Pickering, *J. Environ. Sci. Health A27* (1992) 1389.
- [49] M.O. Corapcioglu, C.P. Huang, *Water Res.* 21 (1987) 1031.
- [50] G.J. Alaerts, V. Jitjaturunt, P. Kelderman, *Water Sci. Technol.* 21 (1989) 1701.
- [51] S. Chand, V.K. Agarwal, P. Lumar, *Indian J. Environ. Health* 36 (1994) 151.
- [52] J.A. Perlinger, S.J. Eisenreich, in: R.A. Baker (Ed.), *Organic Substances and Sediments in Water*, Lewis, Michigan, 1991, p. 49.
- [53] M.J. Charrier, E. Guibal, J. Roussy, B. Delanghe, P. Le Cloirec, *Water Res.* 30 (1996) 465.
- [54] N.S. Rawat, D. Singh, *Asian Environ.* 14 (1992) 30.
- [55] W.R. Knocke, L.H. Hemphill, *Water Res.* 15 (1981) 275.
- [56] C. Namasivayam, K. Ranganathan, *Indian J. Chem. Technol.* 1 (1995) 351.
- [57] D. Fengel, G. Wegener, *Wood Chemistry Ultrastructure Reactions*, Walter de Gruyter, Berlin, 1984.
- [58] R.N. Young, G. McDonald, J.M. Randall, *J. Appl. Polym. Sci.* 23 (1979) 1027.
- [59] D.P.H. Laxen, R.M. Harrison, *Water Res.* 15 (1981) 1033.
- [60] O. Talibudeen, D.J. Greenland, M.H.B. Hayes (Eds.), *The Chemistry of Soil Processes: Cation Exchange in Soils*, Wiley, New York, 1981.