

## Adsorption Process of Heavy Metals by Low-Cost Adsorbent: A Review

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**Abstract:** In this article, the potential of various low-cost adsorbents for the removal of heavy metals from contaminated water has been reviewed. Various conventional methods for heavy metal removal such as precipitation, evaporation, electroplating and also ion exchange have been applied since previous years. However, these methods have several disadvantages such as only limited to certain concentrations of metals ions, generation large amount of toxic sludge and the capital costs are much too high to be economical. Hence, adsorption using low-cost adsorbents is found to be more environmentally friendly. Adsorption is the alternative process, for heavy metal removal due to the wide number of natural materials or agricultural wastes gathering in abundance from our environment. High adsorption capacities, cost effectiveness and their abundance in nature are the important parameters which explain why the adsorbent is economical for heavy metal removal. In this review, a list of adsorbent literature has been compiled to provide a summary of available information on a wide range of low cost adsorbents for removing heavy metals from contaminated water. The application of available adsorption models such as the isotherm, kinetics and thermodynamics as well as the influence of parameters on metal adsorption by low cost adsorbent shall be reviewed to understand the adsorption mechanism of low-cost adsorbents.

**Key words:** Adsorption • Heavy metals removal • Conventional methods • Low cost adsorbent

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### INTRODUCTION

Water pollution raises a great concern nowadays since water constitutes a basic necessity in life and thus, is essential to all living things. The fast-paced development of industries such as metal mining operations, fertilizers and paper industries and pesticides have deliberately discharged various types of pollutants into the environment especially in developing countries. The presence of various pollutants such as industrial effluents, mining and agricultural wastes, sewage and domestic wastes are continuously discharged into the water system and further affecting our ecosystem due to their lethal effects. Among other issues, water contaminations by heavy metals are more pronounced than other pollutants especially when heavy metals are exposed to the natural ecosystem. 'Heavy metals' refers

to any elements with the atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 [1]. Cadmium, zinc, copper, nickel, lead, mercury and chromium, are some examples of heavy metals which originate from activities of metal plating, mining, battery manufacture, petroleum refining and paint manufacturing [2, 3].

Heavy metals are non biodegradable pollutants and they are very difficult to eliminate naturally from the environment. Almost all heavy metal elements are highly toxic when their concentration exceeds their permissible limit in the ecosystem. High concentration of heavy metals may accumulate in the human body once they interrupt in human food chain and possibly in effect, cause severe health problems if the metals exceed the permitted concentration [4]. Zinc is one of trace elements essential for human health especially to protect against premature aging of the skin and muscles of the body but

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too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia [5]. Excessive intake of chromium by humans leads to hepatic and renal damages, capillary damage, gastrointestinal irritation and central nervous system irritation [6]. Lead has its environmental importance due to its widely known toxicity especially in industries such as storage-battery manufacturing, printing, fuel combustion and also photographic materials [7].

Owing to the toxic and adverse effects of heavy metals, most industries are advised to treat waste waters systematically so that the metal contents can be minimized in their wastes. Various conventional treatments have been applied for removing heavy metals such as chemical precipitation, ion exchange, filtration and electrochemical treatment, but most of these methods are only suitable for large scale treatments and incur high cost to be practiced. Generally, all these treatments lead to certain disadvantages such as incomplete removal of heavy metals, high-energy requirements and production of toxic sludge [8]. Numerous approaches have been studied for the development of more effective methods in removing metal pollution and the adsorption process is found to be more practicable over other techniques. Adsorption process is one of the easiest, safest and more cost-effective methods for heavy metal removal from industrial effluents [9, 10] and this process is already established as a simple operation and an easy-handling process [11].

Extensive studies have been undertaken in recent years with the aims of finding an alternative in the form of economic adsorbents for water treatment. Various types of natural materials or wastes have been utilized as adsorbents for the adsorption process due to their potential adsorption capacities; either used naturally or with some modifications. The removal of heavy metals by using low cost adsorbent is found to be more promising in long terms as there are many materials available locally and abundantly such as natural materials, agricultural wastes or industrial by-products which can be utilized as low-cost adsorbents. Previous research shows that there is growing interest of searching for a variety of materials as low cost adsorbents including sawdust [12], cocoa shell [13], rice husk [14], modified sawdust of walnut [15], papaya wood [16], maize leaf [17], rice husk ash and neem bark [18], fly ash [19] and tea-industry waste [20]. Hence, the conversion of these materials as low cost adsorbents is recognized as a potential and economic application for wastewater treatment. The increasing number of publications on adsorption using low cost adsorbents concludes the increasing interest in finding

suitable adsorbents for the adsorption process. In this article, an overview of the adsorption process using low cost adsorbents for heavy metal removal from different sources is presented by highlighting the applicability of adsorbents, optimum parameter and adsorption capacity. The main objective of this review is to provide a summary of information concerning the adsorption process using low-cost materials as adsorbents for heavy metal removal.

#### **Toxicity and Sources of Heavy Metals in Waste Water:**

Heavy metals are a natural constituent on earth commonly known with properties such as having persistence, high toxicity and also serving as non-biodegradable pollutants when they accumulate in the ecosystem. Previous studies describe that heavy metals are applied to the group of metals and metalloids with atomic density greater than 4 g/cm<sup>3</sup> or 5 times or more and are greater than water [21-23]. Heavy metals can be classified into three different types including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am) [24].

Source of heavy metals that penetrate into the water system can derive from both natural and anthropogenic sources. The main source of heavy metal contamination involves urban industrial aerosols, solid wastes from animals, mining activities, also industrial and agricultural chemicals. Sometimes most heavy metals contaminate the water system through the various industrial activities or even from acid rain which breaks down the soils and rocks, releasing heavy metals into water resources [25]. Table 1 summarizes the variety of sources of heavy metal that exist in the environment [25] and the limits on the types and concentration of heavy metals that may be present in the discharged wastewater can be referred to the MCL(Maximum Contaminant Level) standards established by the USEPA [26].

The presence of heavy metals in the environment leads to a growing number of environmental problems such as the deterioration of several ecosystems due to its persistent accumulation. For instance, nickel is one of the carcinogenic elements which cause serious lung and kidney problems, aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis if exceeding its critical level [27]. Instead of nickel, lead might also cause damage to the kidney, liver and reproductive system. The toxic symptoms of nickel are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages [28]. The emission of heavy metals into the environment from mining operations [29, 30] will pollute the surface and also underground

Table 1: Various sources of heavy metal into the environment (Alluri *et al.*, 2007), (Babel and Kurniawan, 2003)

Heavy metal	Sources of heavy metals	Toxicities	MCL (mg/L)
Arsenic	Pesticides, fungicides, metal smelters	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Welding, electroplating, pesticide fertilizer, Cd-Ni batteries	Kidney damage, renal disorder, human carcinogen	0.01
Zinc	refineries, brass manufacture, metal plating, plumbing	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Paint, pesticide, smoking, automobil emission,mining, burning of coal	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.06
Mercury	Pesticides, batteries, paper industry	Rheumatoid arthritis, diseases of the kidneys, circulatory system and nervous system	0.0003

Table 2: Conventional treatment for heavy metal removals (O'Connell *et al.* 2008)

Conventional treatment	Advantages	Disadvantages
Ion exchange	Metal selective High regeneration of materials	High initial capital and maintenance cost
Chemical precipitation	Simple operation Non-metal selective Inexpensive cost	Large production of sludge High cost of disposal sludge
Membrane filtration	Less production of solid waste Low chemical consumption	High initial capital and maintenance cost Low flow rate
Electrochemical treatment	Metal selective Potential treat effluent > 2000 mg dm <sup>-3</sup>	High initial capital cost

water sources. This may lead to soil pollution and the increasing rate of pollution when mined ores are dumped on the ground surface for manual dressing [21]. When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissues [31]. Animals that graze on such contaminated plants and drink from polluted waters, as well as marine lives that breed in heavy metal polluted waters also accumulate such metals in their tissues and milk, if lactating [32]. All this acquire established wastewater regulations to minimize the human and environmental exposure to hazardous heavy metals.

**Conventional Process for Heavy Metal Removal:**

Numerous treatments on the heavy metal removal from contaminated water have already been applied years ago which can be divided into biological, chemical and physical processes. However, in most treatments, physical and chemical processes are more pronounced. The conventional method for heavy metal removal includes chemical precipitation, membrane filtration, ion exchange, reverse osmosis, electrodialysis, solvent extraction, evaporation, oxidation and activated carbon adsorption [33]. Chemical precipitation is the most widely used for heavy metal removal from inorganic effluents based on pH adjustment in a basic solution. However, the disadvantages of chemical precipitation are manifold the discharge of excessive sludge production that requires

further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates and the long-term environmental impacts of sludge disposal [34]. Coagulation-flocculation is also employed to treat wastewater with heavy metals by adding a coagulant during the coagulation process but this treatment might destabilize any colloidal particles and further result in sedimentation [35]. The advantages and disadvantages of the conventional method are listed in Table 2.

Despite these methods being very costly, they contribute to most of the disposal problems and are even practicable for the treatment of water contaminated with heavy metals. The problems emerge during the conventional treatments which include high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary pollutants [36]. Apart from this, it is crucial to look for an alternative treatment to replace the conventional methods of removing heavy metal from polluted water sources.

**Adsorption Process:** Recently, the adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach for heavy metal removal. Adsorption is a fundamental process today due to its flexibility in design and simple operation instead of having to perform adsorptions that are perceived as impractical by most conventional techniques. The term “adsorption” refers as

a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions [26]. The advantages of the adsorption process in removing or minimizing the heavy metals even at low concentration enhance the application of adsorption as one practical treatment.

The effectiveness of the adsorption process is mainly influenced by the nature of solution in which the contaminants are dispersed, the molecular size and the polarity of the contaminant and also the type of adsorbent used. Adsorption also exists due to the attractive interactions between a surface and the species being adsorbed at certain molecular level [37]. Adsorption can be categorized into two; physical adsorption and chemisorption. Physical adsorption is a reversible phenomenon resulting from intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. Meanwhile, chemisorption is a result of the chemical interaction between the solid and the adsorbed substance. It is an irreversible phenomenon and is also called activated adsorption [38]. In terms of the temperature, high physical adsorption occurs at a temperature as close to the critical temperature of a given gas while chemical adsorption occurs at temperatures much higher than the critical temperature. Under certain conditions, both processes can occur simultaneously or alternately [39].

Some parameters should be considered during the adsorption process between adsorbent and adsorbate including the physical and chemical characteristics of adsorbent and adsorbate, the concentration of adsorbate in liquid solution, temperature, pH and also contact time [40]. pH is the most important factors than others as pH controls the distribution of charge on the adsorbent surface between the adsorbate ion. However, in most sorption studies point of zero charge ( $pH_{zpc}$ ) should be considered to be compared with pH as ( $pH_{zpc}$ ) determines the limitations of the adsorbent's pH.  $pH_{zpc}$  is the charge at the solid surface of adsorbent determined by the protonation and deprotonation of adsorbate ions. The surface charge density of surface depends on the specific metal ions which react directly with the adsorbent surface. For instance, when the pH value of solution is higher than  $pH_{zpc}$ , the surface charge of the adsorbent will be negatively charged and vice versa [41]. Otherwise, the increase of pH within a certain limit can increase the adsorption rate [42] but further increase in pH can decrease the adsorption rate as certain adsorbate ions in a particular range tends to be unaffected by pH [43].

Instead of pH, the adsorbent dose is another factor which influences the adsorption process. Based on assumption, when the adsorbent doses increase, the adsorption rate also increases. However, the adsorption rate can decrease if the adsorbent dose further increases, due to the presence of more occupied active sites when the concentration gradient of the adsorbate is kept constant [44]. Higher adsorption rate can be obtained once the temperature increases due to the increase of the surface area and the pore volume of adsorbent [45]. Initial metal concentration can be the driving force to overcome the mass transfer between the surface of adsorbent and the solution [46]. The initial metal concentration influences the adsorption rate based on the availability of the specific surface functional groups and the ability of the surface functional groups to bind metal ions (especially at high concentrations). Thus, any parameters influencing the adsorptive capacity of adsorbent should be considered during the adsorption process.

**Adsorption Mechanism:** Adsorption mechanisms are complicated as no simple theory adequately explains the adsorption of metal ions on the adsorbent surface. Previous studies have reported on the various models that describe the mechanism between the adsorbate and the adsorbent. The Langmuir model and Freundlich models are commonly used to describe the sorption isotherms while in terms of kinetics, the pseudo first order and pseudo second order kinetic models can be used to describe the sorption kinetics. The thermodynamics of the metal ion sorption can be explained based on thermodynamic parameters such as free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy changes ( $\Delta S^\circ$ ) based on the endothermic and exothermic sorption processes. Some empirical models of equation are listed in Table 3.

**Adsorption Isotherm:** Sorption isotherm is used to describe the mechanism of how adsorbate ions interact on the surface of adsorbent. There are several isotherm equations available to analyze the experimental sorption equilibrium parameters, but the well known adsorption isotherm models used for single solute systems are Langmuir [47] and Freundlich isotherms [48]. Both adsorption isotherm models are found to be more suitable to describe the relationship between  $q_e$  (quantity adsorbed at equilibrium, mg/g) and  $C_e$  (concentration of adsorbates remained in the bulky solution at the equilibrium, mg/L).

Table 3: Adsorption models of the single-component system

Types of mechanism	Equations	Nomenclature	References
a) Adsorption isotherms	$q_e = \frac{q_{\max} b C_a}{1 + b C_a}$	$q_e$ is equilibrium metal sorption capacity, $C_e$ is equilibrium	Langmuir (1918)
i) Langmuir isotherms		solute concentration in solution, $q_{\max}$ and $b$ are Langmuir constants related to maximum sorption capacity (monolayer capacity) and bonding energy of adsorption	
ii) Freundlich isotherms	$q_e = K_f C_e^{1/n}$	$K_f$ is a biosorption equilibrium constant, $q_e$ is the sorption capacity, $n$ is a constant indicative of biosorption intensity	Freundlich (1906)
b) Adsorption kinetics		$q_e$ and $q_t$ are the sorption capacity at equilibrium and at time $t$ ,	Lagergren (1898)
i) Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$k_1$ is the rate constant of pseudo-second	
ii) Pseudo second order	$\frac{dq_t}{dt} = k(q_e - q_t)^2$	$q_e$ and $q_t$ are the sorption capacity at equilibrium and at time $t$ ,	Singh <i>et al.</i> , (1988)
		$k$ is the rate constant of pseudo-second order sorption	
c) Thermodynamics		$K_c$ is the equilibrium constant, $C_A$ is the solid phase concentration at equilibrium, $C_e$ is the equilibrium concentration	Kumar and Bandyopadhyay, 2006 (a)
Parameters	$K_c = \frac{C_A}{C_e}$		
	$\Delta G^\circ = -R \ln K_c$	$T(K)$ is the absolute temperature, $R$ is the gas constant (8.314 J/mol K), $\Delta G^\circ$ is the Gibbs free energy	Kumar and Bandyopadhyay, 2006 (b)
	$\ln k_e = \frac{\Delta S^\circ}{R} - \frac{-\Delta H^\circ}{RT}$	$\Delta H^\circ$ is the enthalpy change, $\Delta S^\circ$ is the entropy change	Aksu and Kabasakal, 2004

**Langmuir Isotherm:** Based on Langmuir adsorption theory, molecules are adsorbed at a fixed number of well-defined active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between the adsorbed molecules [47].

For Langmuir equation, it is written as:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1)$$

where  $q_e$  is the metal adsorption capacity of adsorbent and intensively depends on the physical and chemical properties of adsorbate and adsorbent. Langmuir isotherm can be explained based on the assumption; the adsorption process is only limited to mono-layer adsorption and reversible process when no interaction occurs between the molecules adsorbed on the active site and the neighboring sites [49]. This isotherm is suitable for representing chemisorptions on a set of distinct localized adsorption sites [50].

**Freundlich Isotherm:** Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is commonly used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents [49].

For Freundlich equation, it is written as:

$$q_e = K_f C_e^{1/n} \quad (2)$$

where  $K_f$  is the adsorption equilibrium constant while  $1/n$  is the heterogeneity factor which is related to the capacity and intensity of the adsorption and  $C_e$  is the equilibrium concentration ( $\text{mgL}^{-1}$ ). This model assumes that when the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases over the completion of the sorption centre of the adsorbent [51]. Langmuir and Freundlich isotherm models are frequently used for describing the short term and mono-component adsorption of metal ions by different materials [52, 53].

**Adsorption Thermodynamic:** Temperature is one of the important parameters for the sorption of metal ions related with the thermodynamics of the adsorption process. Generally, there are two common types, endothermic and exothermic sorption processes which are determined based on the increase or decrease in the temperature during adsorption. If the sorption increases with the increasing temperature, the sorption is an endothermic process whereas if the sorption decreases with the increasing temperature it is described as an exothermic process. The equilibrium constant obtained from Langmuir equation at various temperatures was used to determine the thermodynamic parameters such as enthalpy ( $\Delta H$ ), free energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ ) [54]. The free energy of adsorption ( $\Delta G_{\Delta}$ ) can be related to Langmuir adsorption constant by the following equations:

$$\Delta G^{\circ} = -RT \ln K_c \quad (3)$$

$$\ln k_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (4)$$

The value obtained from the thermodynamic parameters was computed to predict the nature of the sorption process. The adsorption of different heavy metal ions on different adsorbents are quite different and the thermodynamic parameters of the metal ion sorption are dominated by the nature of metal ion, nature of sorbents, solution conditions, ionic strength and experimental conditions.

**Adsorption Kinetics:** Contact time from experimental results can be used to study the rate-limiting step in the adsorption process in terms of the kinetic energy. The overall adsorption process can be controlled either by one or more steps such as pore diffusion, surface diffusion or a combination of more than one step. Lagergren's first order equation and Ho's second order equation are such examples of kinetic models commonly used to describe these adsorption kinetic models [55].

The pseudo first-order kinetic equation of Lagergren model is given as such equations [56]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

where  $q_e$  and  $q_t$  are the amount of adsorbed waste (mg/g) at an equilibrium and at any instant of time  $t$  (min), respectively and  $k_1$  is the rate constant of pseudo first

order adsorption operation ( $\text{min}^{-1}$ ). Pseudo first order equation refers to the assumption of the rate of change of solute uptake with time which is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time [57].

The pseudo second order kinetic equation is given as [58]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (6)$$

The pseudo second order model is based on the assumption that the rate limiting step may stem from the chemical adsorption involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate [59].

Tea waste has been investigated for the removal of Cu(II) and Pb(II) from wastewater under different optimized conditions of the initial metal concentration, adsorbent dose, pH solution and particle size [60]. The adsorbent to solution ratio and the metal ion concentration in the solution affect the degree of the metal ion removal. Maximum adsorption of Pb(II) was about 96% while 65% for Cu(II) achieved as the adsorbent dose per 200 ml of solution was increased from 0.25 to 1.5 g at different concentrations for Pb(II) and Cu(II), 200mg/L and 100mg/L. The adsorption increases when the electrolyte concentration increases. The highest metal uptake by tea waste occurred at 48 mg/g and 65 mg/g for Cu(II) and Pb(II) at pHs in the range of 5-6 respectively. The isotherm analysis of the adsorption data obtained at 22°C showed that the equilibrium data of Pb(II) and Cu(II) fitted both the Langmuir and Freundlich isotherms. Pb(II) showed higher affinity and adsorption rate compared to Cu(II) under all the experimental conditions. Kinetic studies reveal that Pb(II) and Cu(II) uptake was fast with 90% or more of the adsorption occurring within the first 15–20 min of contact time. The kinetic data fit the pseudo second order model with correlation coefficients > 0.999. The increase in the total adsorption rate and capacity of Pb(II) and Cu(II) was observed when smaller adsorbent particles were used.

The use of durian shell waste in the removal of Cr(IV) from synthetic wastewater is carried out [61]. Studies were carried out as a function of pH (2.5, 6.6 and 7.2), temperature (30°C, 40°C, 50°C and 60°C) and adsorbent dose (1-10g). Results have shown that the adsorption capacity of clay for the removal of lead increases with an increase in the temperature of the solution. The highest

adsorption capacity was 117 mg/g at 60°C. The adsorption process exhibited Langmuir and Freundlich behavior, indicated by the correlation coefficient ( $R^2 > 0.99$ ). High percentage of Cr (IV) ion removal at low pH of solution as the low content of Cr(VI) ions in solution was due to the reduction of Cr(VI) into Cr(III) by the lignocellulosic material in the durian shell. On modeling, the kinetic data fit the pseudo-first order model compared to the pseudo-second order model. The studies of the adsorption of Cr(VI) by the durian shell waste in terms of isotherms, kinetics and thermodynamics have confirmed the process which has endothermic ( $\Delta H^\circ > 0$ ), spontaneous ( $\Delta G^\circ < 0$ ) and irreversible ( $\Delta S^\circ > 0$ ) characteristics.

Banana peel was used for removal of Cu(II) from water [70]. Studies were carried out as a function of pH (1.18 to 13.5), particle sizes (600, 420, 300, 150, 75 and <75  $\mu\text{m}$ ), doses (0.05, 0.1, 0.2, 0.5 and 1 g), contact time (3hr) and temperature (30-70°C). Results have shown that the optimal conditions for adsorption are found at pH 6.5, size of particle less than 75  $\mu\text{m}$ , dose of 0.5g/100ml and 1-hour contact time. The adsorption capacity of banana peel for the removal of copper decreases with an increase in the temperature of the solution, indicates that the adsorption process was spontaneous. The adsorption and desorption equilibrium data were well described by Langmuir, SIPS and Koble-Corrigan models while kinetics data were elaborated by the pseudo-first order, Elovich and Intraparticle diffusion models. The maximum adsorption and desorption capacities were 20.37 and 32.40 mg/g, respectively as both processes can be described by the pseudo-first order kinetic.

Instead of the studies on the mechanism of the adsorption process, the type of adsorbent plays the most important role. Adsorption capacity depends on the activated carbon not relevant to be practiced nowadays due to its highly expensive cost of production and operations. Activated carbon also requires certain complexing agents to improve its removal performance for inorganic matters. Due to the problems mentioned previously, recent research interest has been looking for an alternative adsorbent with high regeneration capability, easy availability and cost effectiveness to replace the costly activated carbon. To date, hundreds of studies on the use of low cost adsorbents have been published. Agricultural wastes and natural substances have been studied as potential low-cost adsorbents for the treatment of wastewater plagued with heavy metals.

**Low Cost Adsorbents:** In recent years, efforts on searching for materials which are available in large quantities such as natural materials, agricultural wastes or

industrial by-products can be utilized as low-cost adsorbents. Low-cost adsorbent is defined as any material which is abundant in nature, or is a by-product or waste material from another industry [62]. An adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry [63]. Previous adsorption studies have been focused on plant wastes such as the maize leaf [17], rice husk ash and neem bark [18], orange peel [64], coconut husk [65] and tea waste leaves [66] which can be used either in their natural form or after some physical or chemical modifications. The conversion of these materials into adsorbents can help to reduce the cost of waste disposal and provide an alternative treatment to replace the commercial activated carbon [67-69]. Table 4 summarizes the findings of adsorption studies using various adsorbents.

**Factors Affecting the Adsorption of Heavy Metals:**

Various factors influence the adsorption capacity of potential adsorbents during the adsorption process. Previous researches have assumed that the efficiency of any adsorbent is strongly influenced by the physico-chemical characteristics of the solutions such as pH, temperature, initial concentration, contact time and also adsorbent dose. A large portion of adsorption studies has been compiled to investigate the relationship of these parameters.

**Effect of pH:** Adsorption of metal ions from the wastewater is mainly influenced by the pH of the solution. pH can influence the surface charge of the adsorbent, the degree of ionization also the species of adsorbate. In a particular pH range, most metal sorption is enhanced with pH, increasing to a certain value followed by a reduction when further pH increases. The dependence of the metal uptake on pH can be associated with both the surface functional groups on the biomass' cell walls and also the metal chemistry of the solution [71]. The pH value of the medium affects the equilibrium of the system [72], as the equation of pH can be written as Eq. (7):

$$pH = pK_a - \log \frac{[AH]}{[A^-]} \tag{7}$$

where  $[A^-]$  and  $[AH]$ , represent the concentration of deprotonated and protonated surface groups and the equilibrium constants  $pK_a$  resembled the carboxyl groups. The effect of pH in the metal ion uptake is also being investigated for the removal of Pb(II) ions in using the polkan peel [73]. The pH range within the range of 2.0-8.0

Table 4: Adsorption capacity of heavy metals using various adsorbents

Type of adsorbent	Optimum adsorption studies				q <sub>max</sub> (mg/g)	References
	pH	Dose (g/L)	Contact time (min)	Temperature (°C)		
Azadirachta indica Bark	Zn(II)	6	0.5	45	33.49	King <i>et al.</i> , 2007
Banana peel	Zn(II)	6.54			5.80	Annadurai <i>et al.</i> (2002)
	Ni(II)	6.89			6.88	
	Cu(II)	5.92			4.75	
	Pb(II)	5.89			7.97	
	Co(II)	6.66			2.55	
Cocoa shells	Pb(II)	2		<120	6.2	Meunier <i>et al.</i> (2003)
Durian shell waste	Cr(VI)	2.5			117	Kurniawan <i>et al.</i> (2011)
Neem sawdust	Cr(VI)	2	4	60	58.82	Vinodhini and Nilanjana Das <i>et al.</i> (2009)
Palm trees leave	Zn(II)	14.7		10		Fahmi and Abu (2006)
Rice husk	Zn(II)			60	19.617	Asrari <i>et al.</i> , (2010)
	Pb(II)			60	0.6216	
Rice straw	Ni(II)	5		90	35.08	El-Sayed G.O <i>et al.</i> , (2010)
	Cd(II)	6		90	144.19	
Sugarcane bagasse	Cr(VI)	2	5	180	23.8	Vinodhini and Nilanjana Das <i>et al.</i> (2009)
Modified sugarcane bagasse	Cd(II)	6		30	189	Junior <i>et al.</i> (2006)
Tea waste	Ni(II)	4			15.26	Malkoc and Nuhoglu (2005)

and the maximum biosorption occurred when the pH was between 2.5 and 5.0. This is because at lower pH values, the dissociation of carboxylic acids leads to the formation of carboxylate groups plus H<sup>+</sup> and an increase of pH value from 2.0 to 5.0, giving the increased amount of metallic ion biosorbed. Meanwhile, in the pH higher than 5.0, there is a drastic decrease in the metallic uptake due to the hydrolysis of the metallic ion that takes place. The effect of pH on banana peel has been investigated [70]. The pH of the adsorption capacities of Cu (II) was increased from 0.7 mg/g to 1.76 mg/g with the increase in pH from pH 2 to pH 6 which was because, free ion was available at pH below than 6. However, the adsorption capacity decreased after pH 6 to pH 12. To explain this, at low pH, the adsorption capacities lower than Cu ions compete with hydrogen ion for binding site on the adsorbent surface while at higher pH, Cu ions started to precipitate in the solution.

**Effect of Temperature:** Depending on the types of adsorbent used, temperature can affect the adsorption capacity of adsorbent. Temperature can change the adsorption equilibrium depending on the exothermic or endothermic nature of a process. Enthalpy, entropy and Gibbs free energy are such parameters that need to be determined before the spontaneity of the process can be inferred. Gibbs free energy ( $\Delta G^\circ$ ) is considered as the spontaneity indicator of a chemical reaction [74]. The relation between Gibbs free energy change, ( $\Delta G^\circ$ ), temperature and equilibrium constant,  $K_a$ , is given by Eq. (8):

$$\Delta G^\circ = -RT \ln K_a \quad (8)$$

The enthalpy,  $\Delta H^\circ$  and entropy,  $\Delta S^\circ$  changes on the adsorption process can be estimated from equilibrium constants as the function of temperature via Van't Hoff equation, as can be referred in Eq. (9):

$$\ln K_a = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

The percentage of As(V) adsorption by dried *Carpobrotus edulis* plant that increases with the increasing temperature from 25 to 40°C have been investigated [75]. The negative values of free energy change ( $\Delta G^\circ$ ) indicate the spontaneous nature of the adsorption and positive values of the enthalpy change ( $\Delta H^\circ$ ) suggest the endothermic nature of the adsorption process. This result is also supported by the increase in the value of uptake capacity of adsorbents with the rise in temperature. The increasing sorption capacity of the sorbent with temperature is due to the enlargement of pores and/or the activation of the sorbent surface has been revealed [76]. Additionally, the positive value of entropy ( $\Delta S^\circ$ ) shows the increased degrees of free active sites at the solid-liquid interface during the adsorption of As(V) onto dried plants.

**Effect of Contact Time:** The adsorption of metal ion by adsorbent also depends on the interactions of functional groups between the solution and the surface of adsorbent. Adsorptions can be assumed to be complete

when equilibrium is achieved between the solute of solution and the adsorbent. However, specific time is needed to maintain the equilibrium interactions to ensure that the adsorption process is complete. The effect of contact time on saw dust and neem bark for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions is observed [77]. The experiment measures the effect of contact time under batch adsorption's initial concentration and pH of 25 mg/L and pH 5 for Zn(II) while 10 mg/L and pH 6 for Cd(II) under contact time varied from 0 to 5 h. For the first 2 hours, the increased contact time enhanced the adsorption of both ions. However, the rapid adsorption initially affected the time needed to reach an equilibrium. For saw dust, the equilibrium time was 3 hr for both Zn (II) and Cd(II) adsorption while for neem bark, 3 and 4 hr were needed to reach the equilibrium for the adsorption of Zn(II) and Cd(II), respectively. Hence, 4 hr contact time was established as an optimum contact time for future studies.

The adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) metal ions on Meranti sawdust is observed taken 120 min as the optimum contact time during the studies [78]. The range of contact time varied from 1 to 180 min but the significant removal of different metal ions occurred during the first 20 min and no appreciable changes in terms of removal were noticed after 120 min. The adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions is initially high probably due to the availability of the larger surface area of the sawdust for the adsorption of these ions. For all subsequent experiments, the equilibrium time was maintained at 120 min which is considered sufficient for the removal of different metal ions by meranti sawdust.

**Effect of Adsorbent Dose:** Adsorbent dose is another parameter used to determine the capacity of adsorbent at a given concentration of the adsorbate. The effect of adsorbent dosage on bael tree (BT) leaf powder to adsorb Ni(II) from aqueous solutions is investigated [79]. The effects of adsorbent dosage were varied from 5 to 30 g/L under room temperature (30°C) and with initial concentration at 10 mg/L. Result obtained from this study describes the adsorption of Ni(II) which increases rapidly when the dose of BT leaf powder is increased from 5 to 20 g/L further explaining the large availability of the surface area at higher concentration of adsorbent. Any further addition of the adsorbent beyond this would not cause any significant change in the adsorption due to the overlapping adsorption sites of adsorbent particles.

The adsorption capacity for Pb(II) and Cd(II) is 1666.67mg/g and 1000.00mg/g using defatted Carica papaya seeds is recorded [80]. The increased biosorbent dosage gives a decreased amount of both metal ions adsorbed with Pb(II) being more adsorbed than Cd(II). However, the percentage of metal ion adsorbed was observed to follow a reverse trend. During this analysis, the optimum dosage of defatted Carica papaya seeds biosorbent is 0.5 gram showing a high percentage of metal ions adsorbed which is not significantly different from those obtained at higher dosage of biosorbent.

**Effect of Initial Concentration:** Initial concentration of metal ions can alter the metal removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions. Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases [81].

The Cr(VI) adsorption on sawdust as adsorbent is significantly influenced by the initial concentration of the aqueous solutions is observed [82]. During the study, the concentration of Cr(VI) was varied from 50 to 500 mg L<sup>-1</sup> at the initial pH 1 using a fixed dose of sawdust about 10 gL<sup>-1</sup>. However, once the equilibrium was achieved, the final value of solution pH had increased from 1.23 to 1.55 with an increase in the initial Cr(VI) concentration from 50 to 500 mg L<sup>-1</sup> confirming that the solution of Cr(VI) after the adsorption by adsorbent was a highly acidic medium. Results obtained show that the increase of the Cr(VI) concentration from 50 to 500 mg L<sup>-1</sup> decreased the percentage removal from 99.9% to 89.9% due to limitations of active sites on the adsorbent which become saturated above a certain concentration. The adsorption capacity increased from 4.98 to 41.45 mg g<sup>-1</sup> due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration. The rapid adsorption of Cu(II) using watermelon shell after 20 min before it proceeds at a slower rate and attains saturation has been investigated [83]. As the initial concentration of Cu(II) increased from 6, 10 and 20 ppm, the adsorption removal had decreased which was probably due to the fact that at lower concentration, almost all Cu(II) ions were adsorbed very quickly on the outer surface. However, further increase of the initial concentration of Cu(II) leads to the fast saturation of adsorbent.

## CONCLUSIONS

A review of various low cost adsorbents presented here shows the effectiveness and potential of the adsorption process by using low cost adsorbent for heavy metal removal. The adsorption capacity is dependent on the type of the adsorbent used and the nature of the waste water treated. More studies should be carried out for a better understanding of the process of low-cost adsorption instead of promoting the use of non-conventional adsorbents on a large scale. Adsorption studies include the structural studies of adsorbents, batch studies on the parameter that affects the adsorption, adsorption modeling such as isotherm, kinetics and thermodynamics, the recovery of metal ions and the enhancement of adsorption capacity through the modification of adsorbent.

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