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Review Paper

Utilization of various Agricultural waste materials in the treatment of Industrial wastewater containing Heavy metals: A Review

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Abstract

The ability of agricultural solid waste such as Palm oil fuel ash, coconut shell, mangos teen, rice husk, corn cob and durian shell in the treatment of industrial waste water containing heavy metals in aqueous solution were reviewed. This Biosorbents has been found to serve as an alternative material to the conventional methods of wastewater treatment, and have the capability to compete favorably in eliminating heavy metal ions. The effects of important parameters such as maximum biosorption capacity, initial metal ion concentration, adsorbent dose, PH of the solution and equilibrium time were also shown. This review presents the use of available agricultural solid wastes as adsorbents to remove different pollutants and the effect of treatment on their efficiencies.

Key words*:* *Agricultural solid waste, biosorption, industrial waste water.*

Introduction

Discharge of waste water from industrial activity dealing with electroplating, normally released effluent containing heavy metals such as Cu(II), Pb(II), Zn(II), Ni(II), Cr(VI) etc. Generally, industrial waste water from plating factories is divided into two types, one from plating manufacturing process and from rinsing process. In developed countries, removal of heavy metals in wastewater is normally achieved by advanced technologies such as ion exchange resins, vacuum evaporation, crystallization, solvent extraction and membrane technologies[1, 2,3]. However, in developing countries, these treatments cannot be applied because of technical levels and insufficient funds[4]. Therefore, it is desired that simple and economic removal methods to beutilized in developing countries could be established. These by-products have influence the flow and storage of water and the quality of available fresh water. It is evident that waste water released from this activity activities is one of the major causes of environmental pollution, due to the presence of these heavy metals[4]. The term heavy means occurring or produced in large amount or in greater amount than normal and metal is a chemical element that is malleable and ductile usually solids. However, heavy metal exhibits metallic properties, and has a specific weight higher than 8 mg/cm^3. Furthermore, metals belonging to d-block elements of the periodic table have a specific gravity of not less than five times the specific gravity of water, and are termed as heavy metals.

The current findings add substantially to our understanding that, Heavy metal by its nature contains two most important characteristics namely, toxicity and persistency[5]. Because they do not degrade easily, unlike organic pollutants which are mostly biodegradable. Disposal of this wastewater containing such pollutants into receiving waters bodies can be toxic to both human and aquatic life[3]. Literatures have reports that, presence of heavy metals in water pose serious problems, because they may be mutagenic and carcinogenic[6-10]. Moreover, they can cause severe damage to human beings, such as dysfunction of kidney, reproductive system, liver, brain and central nervous systems[11]. The conventional methods for removing heavy metals, includes reverse osmosis, chemical precipitation and filtration, redox reactions, ion exchange electro chemical treatments, adsorption and evaporation[12]. Generally the use of the methods mentioned were reported to be expensive and inadequate, as they require high operational costs and gives minimal removal efficiencies. The cost of operations and inefficiency of those methods has led researchers to investigate alternative material that can compete favorably in terms of cost, efficiency and ease of operation, as such this paper will review the research conducted on the use of agricultural waste materials used as a low cost adsorbent in the treatment of effluent containing heavy metals.

Adsorption: This is a phenomenon commonly used in the gas phase, but can effectively be used for water and waste water treatment. Adsorption has a great advantage over other methods of water and wastewater treatment, especially when biomass is used. The major disadvantage in this process is its non-selective (i.e. it cannot isolate each pollutant and get it removed independently of one another) all contaminants are getting concentrated on the surface of adsorbent. Unlike ion exchange the processes are selective to the ions it needs to adsorb by selecting the ion in such a way that it is having affinity only that ion. Adsorption is understood to be a process involving interface accumulation or concentration of substances at a surface of the material.

Adsorption is a phenomenon which normally takes place in an interface of any two surfaces, such as gas-liquid, gas-solid, liquid-liquid or liquid-solid interface. Meanwhile on the process of adsorption, absorption can also take place, and is a process by which molecules or atom of one phase interpenetrates nearly uniformly in to another phase to form a solution[13]. Important models used in this system are adsorption isotherm which describes the adsorption behavior at equilibrium. Point of saturation is normally attained when no further adsorption can take place. Typically, the mathematical correlation, play an important role towards the operational design, modeling and practical application of the adsorption systems[14]. Recently, researchers have shown an increased interest in the use of adsorption reaction models to describe the kinetic process of the systems. Studies on the use of biomaterials such as adsorption of copper by Spent yeast[15], biointerface of copper, zinc, cadmium and lead[16], adsorption of Cu^{2+} from aqueous solution onto iron oxide coated egg shell powder[17], have yielded positive kinetic results with good correlations. The results of investigation by Ali et al[18] and Arief et al[19], show that, modified Oil Shale Ash and Ceratonia Siliqua Bark are promising adsorbent for removal of heavy metals with high correlation values which obey pseudo second order kinetic models. Biosorption of heavy metals from aqueous solutions generally, is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluent.

Activated carbon: Activated carbon also referred to activated charcoal or activated coal is a common term that Includes carbon material mostly obtained from charcoal. "Activated" at times is substituted by "active." By whatever name, it is a material with an exceptionally high surface area. There are three main physical carbon types. These are granular, powder and extruded (pellet). The three types of activated carbon can have properties modified by the application.

Activated carbon is often used in day by day life, for instance, in industrial activities such as, food production, medicine, pharmaceuticals, etc. In addition, one of the most significance of activated charcoal in pharmaceutical aspects, is it effectiveness. This makes it to be the most single available agent of emergency decontaminant in the gastrointestinal tract. It is mostly used after a person swallows any toxic drug or chemical. However, there are great advantages in the use of biomass. This is because; biomasses are renewable resource that has a steady and abundant supply, reliable and domestically produced especially those biomass resources that are by-products of agricultural activity. Moreover, its use is carbon neutral, can displace fossil fuels, and helps reduce GHG emissions while closing the carbon cycle loop. As the debate on food versus fuel intensifies, biomass can provide added income to farmers without compromising the production of main food and even non-food crops.

Among all physicochemical methods, Biosorption has emerged to be the most promising technique due to the ease of operation, comparable low cost of application and production of high-quality treated effluents[20]. Thus, recent research shows that adsorbents based on the agricultural wastes to remove different types of pollutants, such as micro particles of dry plant for adsorption of Pb(II) and Cd (II),Durian peels for adsorption of cadmium[21], neem leaf powder[22] , hazelnut husk[23], palm shell[24], dithiocarbamate modified chitosan bead[25], saw dust[26], tamarind wood[27], yeast biomass[28], aspergillus versicolor biomass[29], van apple pulp[30], orange peel[31], bamboo[32], physics seed hull[33], guava seed[34], guava leaf powder[35], Sargassum wightii biomass[36], holly sawdust[37] were reported to be very effective with high adsorption capacity. However, the pursuit in meeting the targets, using activated carbons suggest uneconomical on the side of polluters. Hence, it is of paramount importance to devise another means that can compete favorably with activated carbons, effectively, economically and environmentally friendly.

Adsorption using palm oil fuel ash: Palm Oil Fuel Ash (POFA) is a by product obtained by burning of palm oil fibers; empty fruit bunches and shells as fuel in palm oil mill boilers. It usually contains about 85% fibers,15% shells and empty fruit bunches are burned in boiler at a temperature of about 900-1000°C to produce energy for extracting process of crude palm oil. During this process, about 5% is obtained as ash waste and disposed in an open space which generates a lot of health hazard such as bronchi and lungs disease[38]. As a solution to these problems, many researchers have well examined the feasibility of using palm oil fuel ash as waste water remedy as shown in table 1.

Table-1
Palm fuel ash used as biosorbent for the removal of metal ions from selected literatures

Adsorbate	q_{max}	Experimental parameter/result						Source
	(mg/g)	pH	T(^{0}C)	C_o(mg/L)	ET(min)	A.D(g/L)	Isothermal/kinetic model	
Cu(II)	18.86	5.5	30	100	-	0.2	L and K_2	39
Pb(II)	75.48	5	25	100 - 500	600	1.5	L and K_2	40
Zn(II)		5-6	25	20	-	3	K_1	41
Ni(II)	200	5	25		10	2.5	-	42
Cr(VI)	99%	1.5			150 – 300	5	F and K_2	43

Coconut shell used as biosorbent: Coconut shell is an agricultural waste and is available in very large quantities throughout the tropical countries of the world. In effort to reduce the effect of global and to safe guard the environment, the waste of this material has been utilized in the treatment of industrial waste water. More recently, has investigated the used of coconut shell in the removal of four different heavy metals and was found that (CNS) can be used as a low cost adsorbent for the removal of heavy metals in aqueous solution containing low concentrations of the metals[44]. Table 2 below, shows the adsorption capacity of coconut shell on the adsorption of different heavy metals at different experimental condition[45-49].

Mangosteen *(Garcinia mangostana L):* The mangosteen tree is widely found in several Asian countries, especially Thailand and Indonesia. It has been considered the "queen of fruits'' due to its pleasant taste apart from many functions for disease treatment[50]. For every 10 kg of mangosteen harvested, more than 6 kg of mangosteen peel is generated. The increasing popular consumption of mangosteen fruit has given rise to abundant abandoned mangosteen peel residue, which may be accessible in large quantities from the plants engaged in extraction of pulp juice or bioactive components from the fruit. Mangosteen peel wastes can therefore be explored as a new potential lignocellulosic precursor for activated carbons to derive more economic value[51] (table 3 Mangosteen (Garcinia mangostana L) used for the removal of Metal ions from selected literatures[52-55]).

Rice Husk: Rice husks are one of the most abundant agricultural wastes, accounting for about one-fifth of the annual gross rice, 545 million metric tons, of the world. It is apparent from this table that, every year large amount of rice husks is produced. The issue has grown in importance in light of recent environmental pollution, and as a matter of fact efforts have been made towards utilization of the burn husks under controlled temperature as a supplementary cementing and waste water treatment material[56]. Table 4 below is quite revealing in several ways the different heavy metals removed using rice husk as a potential adsorbent[57-61].

Table-2
Coconut shell used as biosorbent for the removal of metal ions from selected literatures

Adsorbate	q_{max} (mg/g)	Experimental parameter/result						Source
		pH	T (^{0}C)	C_o(mg/L)	ET(min)	A.D(g/L)	Isothermal/kinetic model	
Cu(II)	92.03	5-7	50	30	30	1	F	45
Pb(II)	0.02	10	30	0.5 – 5	30	0.5	F and K_2	46
Zn(II)	17.86	12	30	50	60	0.5	F and K_2	47
Ni(II)	0.21	9	-	2	-	1.05	-	48
Cr(VI)	40	4.6	-	10 – 200	100	1.5	L and K_2	49

Table-3
Mangosteen (Garcinia mangostana L) used for the removal of Metal ions from selected literatures

Adsorbate	q_{max} (mg/g)	Experimental parameter/result						Source
		pH	T(^{0}C)	C_o(mg/L)	ET(min)	A.D(g/L)	Isothermal/kinetic model	
Cu(II)	21.7	6.7	30	50 - 200	-	0.2	L	52
Pb(II)	3.56	5	25	20 - 250	30	1.5	L	53
Zn(II)	N.A	-	-	-	-	-	-	-
Ni(II)	0.102	3	27	25 - 150	15	0.5	L and k_2	54
Cr(VI)	24.5	4	20	25 - 100	120	0.6	L and K_2	55

Table-4
Rice husk used for the removal of Metal ions from selected literatures

Adsorbate	q_{max} (mg/g)	Experimental parameter/result						Source
		pH	T(^{0}C)	C_o(mg/L)	ET(min)	A.D(g/L)	Isothermal/kinetic model	
Cu(II)	1.046and6.277	5.5	-	2 – 50	-	1.0	L	57
Pb(II)	12.61	5.8	30	40	600	2.0	L	58
Zn(II)	12.41and20.08	4	25	25	-	1.0	L	59
Ni(II)	51.80%	6	25		180	20	L, F and K_2	60
Cr(VI)	1.25	1.7	-	24.8 – 50	-	-	-	61

Durian peel as adsorbent: Durian (Durio zibethinus Murray) is one the most available agricultural waste materials found in the Southeastern Asian region. It belongs to the genus Durio, which is a member of the family Bombacaceae and consists of 28 species. Due to the high consumption of durians, massive amounts of the peels (as waste products) are disposed, causing a severe problem in the community. In the interest of the environment, researchers have study the ability of durian peel in removing heavy metal ions from aqueous solutions and were found to be very effective. Table 5 below, shows the adsorption capacity of durian peels in removing different heavy metals[62-65].

Corncob used for the removal of Metal ions: Corn or Maize, common name for the cereal grass widely grown for food and livestock fodder. Corn ranks with wheat and rice as one of the world's chief grain crops. The production of waste from this crops end up contributing to global warming, as the whole waste in burned in to ashes. While corncobs serves as important source of furfural, a liquid used in manufacturing nylon fibers and phenol-formaldehyde plastics, refining wood resin, making lubricating oils from petroleum and purifying butadiene in the production of synthetic rubber[66], it has also been investigate as a biosorbent material as shown from table 6 below[67-71].

Adsorption Models: Models have been used in adsorption processes to predict the capability of a certain adsorbent to remove a pollutant down to a specific discharge value. Depending on the time in which the mass of adsorbent is in contact with the pollutant, the result of their interaction will definitely come to equilibrium. i.e. the state whereby the biosorbent cannot longer adsorbed the pollutant. Therefore, the amount of pollutant adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount of material adsorbed onto the media can be calculated using the mass balance as shown in equation one below.

$$\frac{X}{M} = \frac{(Co-Ce)V}{M} \quad (1)$$

Where, X/M = equilibrium concentration on adsorbent at any time (mg/g), M = mass of the adsorbent used (g), V = volume of the solution (L), C_0 = initial concentration in sample (mg/L), C_e = equilibrium concentration in sample (mg/L)

Langmuir isotherm: This isa model suggesting monolayer adsorption,and assumes no interaction between the adsorbate molecules[72]. Thus, saturation happens when the heavy metal ion (pollutant) molecules fill the site where no more adsorption can occur at that site. This model can be described by the following form:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

Where q_e (mg/g) is the solid phase equilibrium concentration, qm (mg/g) is the maximum amount of adsorbate adsorbed at equilibrium, b (L/mg) are the Langmuir adsorption constant related to the free energy adsorption (L/mg) and C_e is Equilibrium concentration of adsorbate (mg/L). The linear form of this model can be expressed as shown below[73],

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} \quad (3)$$

Table-5
Durian peel used for the removal of Metal ions from selected literatures

Adsorbate	q_{max}	Experimental parameter/result						Source
	(mg/g)	pH	T(^{0}C)	C_o(mg/L)	ET(min)	A.D(g/L)	Isothermal/kinetic model	
Cu(II)	-	-	-	-	-	-	-	-
Pb(II)	7.49and8.43	5	30	10 – 30	120	0.01 - 0.13	L and K_2	63
Zn(II)	-	-	-	-	-	-	-	-
Ni(II)	12.1	6	-	50 – 500	300	-	L	64
Cr(VI)	10.67and63.78	7	30	25	30	10	L and K_2	65

Table-6
Corncob used for the removal of Metal ions from selected literatures

Adsorbate	q_{max}	Experimental parameter/result							Source
	(mg/g)	pH	T(^{0}C)	C_o(mg/L)	ET(min)	A.D (g/L)		Isothermal/kinetic model	
Cu(II)	1.77	5.0	-	-	-	350		L	67
Pb(II)	14.75	5.0	-	-	90	150		-	68
Zn(II)	79.21	5.0	70	-	-	3		L, T, F and K_2	69
Ni(II)	98%	4.0	-	1.0 - 10	30	0.5 - 5		F	70
Cr(VI)	90%	4.0	80	10	120	10		L and F	71

The essential characteristics of Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter (RL), and can be represented as shown in equation 4 below[74]:

$$R_L = \frac{1}{1+bC_o} \quad (4)$$

b = Langmuir adsorption constant related to the free energy adsorption (L/mg), C_o = the highest initial adsorbate concentration (mg/L).

The value of R_L indicates the type of biosorption isotherm. If the separation factor is greater than unity ($R_L > 1$), it means the adsorption of metal ion is unfavorable. If it ranges between 0 and 1 ($0 < R < 1$), shows that adsorption is favorable. If the value of $R_L = 1$, the biosorption process is termed linear. Furthermore, if ($R_L = 0$), then the adsorption isotherm is irreversible[75].

Freundlich isotherm: This model suggests heterogeneous energetic surface site, followed by interaction between adsorbed molecules[76]. The linear form of Freundlich model is expressed as:

$$\log q_e = \log KF + \frac{1}{n \log C_e} \quad (5)$$

Where KF = is a constant related to the adsorption capacity and 1/n is an empirical parameter related to the adsorption capacity which varies with the heterogeneity of the material.

Having studied different articles, investigating the adsorption of various heavy metals, it has conclusively been shown that low cost adsorbents are very important, mainly because of their inexpensiveness and availability[77,78]. However, a considerable amount of literature has been publishedon the use of biosorbents, but its feasibility is mainly in developing and under developed countries[79].

Adsorption isotherm: This refers to the adsorption of adsorbate on the surface of adsorbent at constant temperature and pressure. The general modeling of sorption isotherms can be described in 4 particular cases[80].

The ''C'' isotherm: Figure 1a shows that the curve is a line of zero origin, which describes the ratio between the concentrations of the compound remaining in solution and adsorbed on the solid is the same at any concentration. This ratio is also known as distribution coefficient or partition coefficient K_d or K_p (L kg^{-1}). The ''C'' isotherm is frequently used as an easy-to-use approximation (for a narrow range of concentration or very low concentrations such as observed for trace pollutants) rather than an accurate description[81].

The ''L'' isotherm: This is a case whereby decrease in the ratio between the concentration of the compound remaining in solution and adsorbed on the solid takes place when the solute concentration increases, resulting in the production of concave curve (figure 1b). It proposes a progressive saturation of the solid which involve two sub-groups: i. The curve reaches a strict asymptotic plateau (solid showing a limited adsorption capacity), and ii. The curve has not reached any plateau (solid not shown clearly a limited sorption capacity).

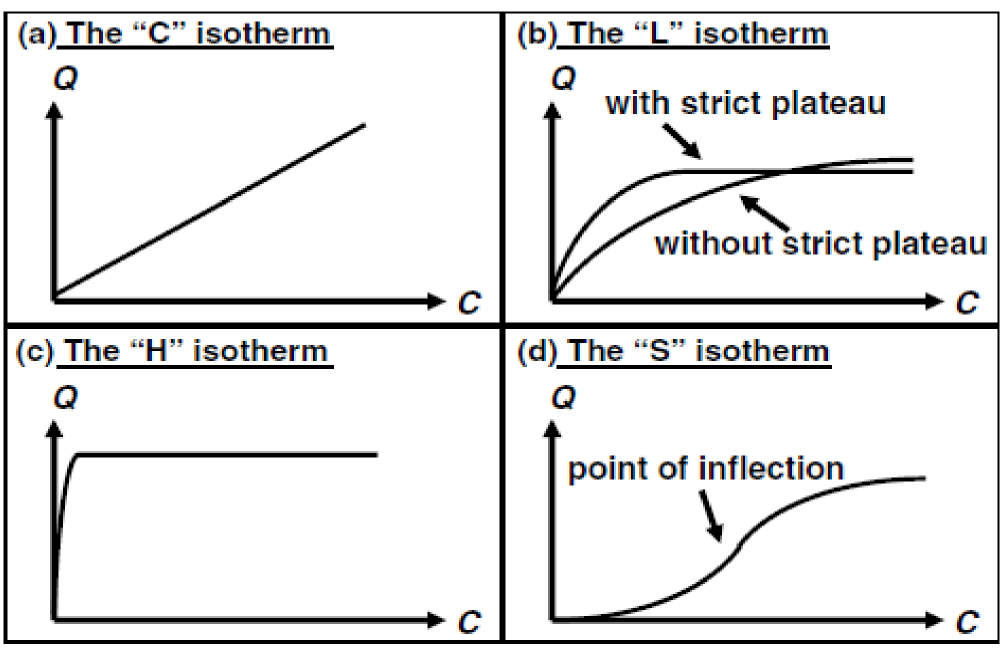

Figure-1
The four main types of isotherms[80]

The ''H'' isotherm: In this case the initial slope is very high (figure 1c), which is only a particular case of the ''L'' isotherm. Sometimes, compounds shows high affinity for solids to the extent that initial slope cannot be distinguished from infinity, which makes it distinguished from others[82].

The ''S'' isotherm: The curve in this type of isotherm has a point of inflection and so it is sigmoidal (figure 1d). Isotherms of this type are mostly as a result of at least two opposite mechanisms. Organic compounds (Non-polar) are a typical case: they possess low affinity with clays. Other organic compounds are adsorbed more easily as soon as clay surface is covered by these compounds[83,84]. However, Smith[85]examines that, one of the more significant findings to emerge from this study is that, this phenomenon is termed as cooperative adsorption and is also applied for surfactants[86]. Interestingly, the findings of the current study, support the previous research as regards to operative adsorption[87,88].

Adsorption kinetic reaction: Adsorption equilibrium needs to be supplemented with adsorption kinetics. In order to obtain a proper design of an adsorber. Several kinetic models such as pseudo-first order, pseudo-second order, saturation type, Weber and Moris as well as the Elovich model are available. The most predominant kinetic equations are pseudo first order and second order, and can be expressed as.

$$qt = qe(1 - \exp(-k_1 t)) \quad (6)$$

$$\frac{1}{qe-q} = \frac{1}{qe+k_2 t} \quad (7)$$

Where qt and qe(mg/g) are the amount adsorbedat a time t and equilibrium. Parameters $k_1$and k_2 are pseudo-first and second order rate constant[89].

Literatures such as adsorption intrinsic kinetics and isotherms of lead ions on steel slag[90], Adsorption of lead (Pb) from aqueous solution with Typha angustifolia biomass modified by $SOCl_2$ activated EDTA[91] Adsorption of lead ions from aqueous solution by using carboxymethyl cellulose- g -poly (acrylic acid) attapulgite hydrogel composites[92] Exploring the mechanism of lead(II) adsorption from aqueous solution on ammonium citrate modified spent Lentinus edodes[93], Biosorption of cadmium, lead and copper with calcium alginate xerogels and immobilized Fucus vesiculosus[94] the use of Mucor rouxii biomass[95]. Adsorption of lead and cadmium ions from aqueous solutions using manganoxide minerals[96] fly ash as low-cost adsorbents[97]. Removal of Cr(III) from model solutions by isolated Aspergillus niger and Aspergillus oryzae living microorganisms[98] and general treatment and classification of the solute adsorption isotherm[99] proves that pseudo-second order is more prevalent as compare to pseudo-first order models base on their kinetic studies. Furthermore, the trend proposes that heavy metal biosorption is chemisorption which is the rate limiting step and involves valence force sharing between sorbent and sorbate.

Conclusion

During the preparation of this article it was observed that many agricultural waste materials used as low cost adsorbent in the treatment of waste water were reported in hundredth of journal papers. This article has attempted to cover a wide range of those materials used in removing some selected divalent heavy metals. Parameters such as biosorption capacity of sorbent, biosorbent dose, initial concentration of metal ions, equilibrium time and PH of the solution were also presented. Furthermore, it also highlights the use of Langmuir adsorption isotherm and Freundlich isotherm modelsto determine the maximum capacity of biosorbents and effect of the physical and chemical properties on the adsorption capacity of the adsorbent. But the industrial application of those materials is still a dare; as such more studies are needed to transfer the process to pilot-plant scale.

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