REVIEW PAPER

Potentiality of agricultural adsorbent for the sequestering of metal ions from wastewater

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ABSTRACT: The expensive nature of metal ions detoxification from wastewater have restricted the use of conventional treatment technologies. Cheap, alternative measures have been adopted to eliminate metal contamination, and adsorptions using agricultural adsorbents seem to be the way forward. The use of agricultural adsorbents for cadmium (II), copper (II) and lead (II) ion removal has gained more interest in literature due to the level of contamination in water bodies. This review shed lights on the removal proficiency of various low–cost agricultural adsorbent for the elimination of cadmium (II), copper (II) and lead (II) ions, considering performance, surface modification, equilibrium adsorptive studies, kinetic characteristics, coefficient of correlation (R^2) and reuse. Furthermore, these agricultural adsorbents have displayed better performance when rivaled with commercial/conventional adsorbent. Observations from different adsorptive capacities presented owe their performance to surface area improvement/modification, pH of the adsorbent, ionic potential of the solution, initial concentration and elemental component of the adsorbent. However, gaps have been identified to improve applicability, sorption performance, economic viability, optimization, and commercialization of suitable agricultural adsorbents.

KEYWORDS: *Adsorption; Adsorption capacities; Agricultural adsorbent; Heavy metals; Wastewater*

INTRODUCTION

Portable water is one of the most significant resources to humanity and despite the relative abundance, there is a reduction in its availability because the percentage of salt water available is 97.5% compared to the total water present on earth (Rehman and Rehman, 2014; Tatiya, 2011; Thompson, 2009). There is increasing demand for water on a daily basis whereas all available water resources are gradually becoming contaminated and unsafe for use owing to the inadequate disposal of waste. The effort to provide adequate and proper treatment facility for homes having water related issues is challenging, and it also involves high – cost implication, hence, there is an urgent need for resourceful technologies that are attributed to low – cost efficiency, cheap maintenance and energy efficiency (Renge *et al.,* 2012).

Due to Industrialization, natural occurring metal may have increased relatively to the existing level experienced currently (Mireles *et al.,* 2012; Yaylalý – Abanuz, 2011; Wei and Yang, 2010). Moreover, it is important to note that the rate at which these toxic substances are absorbed in human tissues is faster than the rate at which they are eliminated through catabolism (Science Advisory Board, 2006). Activities such as petroleum refining, tanning, pesticide production, mining, paint manufacturing, electroplating, battery manufacturing, chemical production and metal processing introduce toxic substances in form of heavy

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metal contamination (Manzoor *et al.,* 2013; Banerjee *et al.,* 2012; Ahmaruzzaman, 2011; Kang, Lee and Kima, 2007). Traces of these heavy metals flow along with the waste gotten from these industries and are later discharged directly or indirectly into the environment regularly, especially in developing countries (Radjenovic and Medunic, 2014). There is a direct link between the level of environmental contamination and rate of contamination of water. Rainwater gathers contaminants while transiting through the atmosphere, local streams and rivers bodies absorbs these unwanted elements through surface runoff and discharges from industries and sewage effluents. These contaminated sources then percolate into the reservoirs that supply our drinking water (Alissa and Ferns, 2011), making it unfit for consumption as reported by Wu *et al.,* (2014) with which heavy metals (Hg, Cd, Pb, Cr, Cu and As) were discovered in Hongfeng and Baihua Reservoirs. Compilation of this review study was carried out in Nigeria during 2016.

Metal Essentiality

The proper metabolic function requires certain nutritional elements that are essential for survival. To maintain a healthy living, some metals are required either as a micro – nutrient or macro – nutrient. Certain metals with high nutritional value are fundamental to human existence, and they play a vital part in the biochemical or physiological process (NAS/IOM, 2003; IPCS, 2002). The relative nature of the essentiality concept states that some organisms may not need some metals that are fundamental requirements to humans.

The non–availability of sufficient amount of these elemental metals may result in adverse effects, increasing the vulnerability in human beings to toxic contributors and the risk associated with other metals. Metals such as Cr(III), Zn, Cu, Mn, Mo, Co, Fe, Se, Mg are nutritionally valuable to humans. Other metals which include Ni, V, B, Si, Pb, Hg, and As may not be needful to humans, but their adverse effect at low concentrations cannot be over – emphasized (NAS; IOM, 2003).

There are three groups of essential elements; the cationic metals, the anionic metals, and the inorganic complex. The cationic group comprises of Zn, Fe, Ca, Mn, Cr., the anionic group includes Mo, Se and the bio – inorganic complexes are Co complex and cobalamin (Violante *et al.,* 2010). The regulation of internal environment mechanism is different for each group,

and it is used to categorize the extent of health effect that may materialize and also the probable bioavailability of the metal (Soetan *et al.,* 2010; Aggett, 2007). However, the regulation of cationic intake and transfer occurs in the gastrointestinal tract of the liver (IPCS, 2002; Berkhin and Humphreys, 2001). The anionic group has increased solubility with water and their reaction with OH groups; S, P, N and O are reduced compared to the cations. Their rapid solubility makes them to be absorbed readily through the intestine, and the burden generated controlled by renal excretion (Barakat, 2011).

Distribution of metals

Ibrahim *et al.* (2006) made a remark that the uniqueness of metals affects their distribution potentials into specific tissues and organs. It displays a total reflection of the transport and accumulation mechanism. Metals retention in the human system can be linked to isolation in which some metals can be active/inactive for some period (Borowska and Brzóska, 2015). Metals such as cadmium and lead can be inherent in the system for years. In a research reported by Godt *et al.* (2006), several factors contribute to the increasing amount of cadmium in the body e.g. deficiency in calcium, Vitamin D, and the presence of trace elements such as copper and zinc. Cadmium interaction with these trace elements could be as a result of their molecular similitude (Naz *et al.,* 2005). Once cadmium is absorbed into the blood stream, it is transported in erythrocytes and attracts to protein fraction at an intracellular level (Godt *et al.,* 2006). Its transport mechanism is promoted by plasma metallothionein which occurs around the liver region when subject to exposure. The transport of cadmium can also be seen, even at low concentration, at an early stage of embryo formation which is induced through the placenta (Goyer, 1995). At heightened exposure, cadmium accumulates in the renal cortex and liver and later redistributed to the kidney through active synthesis of metallothionein in the liver (Satarug *et al.,* 2009). In line with this, Akesson *et al.* (2008) gave an overall remark that 50% of cadmium burden is located in kidneys, 20% around the muscles and about 15% eminent in the liver. In another report, (Wang and Du, 2013) iterates that at lower concentration, cadmium burden revolves around the brain and bone.

Copper, on the other hand, gain its control at the upper gastrointestinal tract through a variegated

homeostatic process comprising of both active and passive transport (Bost *et al.,* 2016). Olivares *et al.,* (2002) and Arredonado *et al.* (2000) explained that complex protein that is metallothionein-bound propagates the transport of copper. They further highlighted that exceeding the storage capacity of metallothionein may result to cell death. Many other factors facilitate the uptake of copper e.g. the presence of precipitating anions, fibre, fulvic acid dietary proteins and ascorbic acid (IOM, 2001). The pathway at which copper is distributed from the blood into the liver cannot be clearly understood, but Uauy *et al.* (2008) suggested that copper transportation is attributed to ceruloplasmin and cytochrome oxidase while its excretion is through biliary canaliculi (Wijmenga and Klomp, 2004).

Lead absorption occurs through inhalation and ingestion depending on the form and means of exposure (Babalola *et al.,* 2010). About 90% of lead absorbed is accumulated in the bone with a half-life ranging from 600 – 3000days while soft tissues such as liver, brain, and kidney are the custodian of the remaining 10%, having half – life of up to 40 – 50 days (ATSDR, 2007). The gastrointestinal tract acts as a medium by which lead enters the bloodstream. At first, attachments are made to the proteins located in the blood and later, they are transported to other parts (Gonick, 2011). In light of this, (Harmanescu *et al.,* 2011; Baby *et al.,* 2011) stated that the potential capacity of metals binding to proteins are limited, and the risk associated with target organs are escalated when the binding capacity is surpassed. Therefore, older adults are potential targets to metals that exhibit long half-lives.

Toxicity of metals

There are variations in the level of toxicity exhibited by different metals, and it is a representation of the collection of biochemical mechanism in which their effect and variability are made known (Kramer *et al.,* 2007). There are at least five metals that are carcinogenic while other effect includes cardiovascular disease (Alissa and Ferns, 2011), haematological, neurological, gastrointestinal, musculoskeletal, immunological effect (Tchounwou *et al.,* 2012) and alteration of epidermal systems (Sharma *et al.,* 2014).

Lead is being one of the three most hazardous metal, accumulates in the body causing severe damage to the central nervous system, bone marrow, kidney and liver (Tsoi *et al.,* 2016). Recent studies indicate that the rise

in mortality and systolic blood pressure has its root cause from elevated blood – lead levels (Hara *et al.,* 2014; McElvenny *et al.,* 2015). Elevated blood lead level could also bring about intelligential impediments, hearing impairment and alteration of puberty in girls (Gidlow, 2015). Jarup, (2003) also reported renal, hematopoietic and endocrine disease as a result of exposure to lead. Nelson *et al.,* (2011) sees lead as a potential contributor to osteoarthritis and osteoporosis.

Cadmium, on the other hand, instigates cancer, diarrhoea, damage to bones, kidney and mucus membrane. It also causes vomiting and affects hormone secretion (Godt *et al.,* 2006). Proliferating intake of nickel results in skin dermatitis, kidney damage, lung problems, pulmonary fibrosis whereas mercury causes nervous breakdown and protoplasm poisoning.

Accumulation of copper alters the function and structure of the brain and liver (Thiele, 2003). A widely recognized ailment known as the "Wilson Disease." – A situation where abnormal gene duplicates in other to promote development – is characterized by the accumulation of copper in the eyes, liver, and brain (Uauy *et al.,* 2008). Pandit and Bhave, (1996) also gave a remark that Tyrolean infantile cirrhosis and Indian childhood cirrhosis are as a result of heightened exposure to copper.

It is imperative to note that the organ/tissue that is affected by metal toxicity may be different from the ones where metal absorption is identified, and this may be as a result of the metal kinetics (NORD, 2016). This difference may apply to different species owing to the absorption, distribution and excretion variation. Also, the sensitivity to metals differs with age, sex, nutritional condition and genetics (Goyer *et al.,* 2003).

Interaction between biomass and ions

Global concerns have risen over heavy metal pollution discharged from various sources (Rangsayatorn *et al.,* 2004). These metals cannot be degraded nor destroyed, so they linger in the environment. Heavy metal presence in soils can be attributed to various environmental variables which include, but not limited to soil properties, parent material and human contribution such as irrigation and farming (Hu *et al.,* 2013). Mohammadpour *et al.* (2016a) in their report, outlined that the health risk to humans could be escalated as a result of masticating agricultural by – products gotten from contaminated soils. In addition,

proper knowledge of metal activities and speciation in soils helps to determine the rate at which metals are retained in soils and understand their ability to percolate into water bodies (Ghaemi *et al.,* 2015; Mohammadpour *et al.,* 2016b).

Taking into account the pollution load of different soils, the geochemical accumulation index (Igeo), the pollution index (IPOLL) and their enrichment factor (EF) serves as indexing formulation used to evaluate and assess the degree of metal contamination in soils as indicated in Eq. 1:

$$I_{geo} = \log 2\left[C_n/(1.5 \times B_n)\right] \tag{1}$$

I_{geo} indicates the geochemical accumulation index, the metal concentration in bulk is denoted by C_n and B_n stands for the mean metal concentration (Gonzalez – Macias *et al.,* 2006).

The Enrichment Factor (EF) is obtained using Eq. 2:

$$EF = \left[(C_n/CFe)sample\right]/\left[(C_n/CFe)crust\right] \tag{2}$$

(C$_n$/CFe) Sample serves as the ratio of specific element concentration to that of Fe in a given soil sample while *(C$_n$/CFe) Crust* gives similar notation ration but on a sample that is not polluted (Pekey, 2006)

Modifying the I_{geo} formula produces the index of pollution which is expressed as Eq. 3:

$$IPOLL = \log 2\left[B_c/L_p\right] \tag{3}$$

B_c represents the bulk concentration while L_p stands for the lithogenous portion.

The presence of cadmium (Cd) in industrial effluents reaches humans through the food chain which tend to accumulate into toxic substances (Pandey *et al.,* 2008). Cadmium**,** being ranked the seventh most toxic heavy metal by the Agency for Toxic Substances and Disease Registry (ATSDR), is detected in steel production, cement production, battery manufacture, waste and combustion, refining, non – ferrous metal production and phosphate fertilizers (Thornton, 1992; Samarawickrama, 1983). Recently, (Kumar, 2012; Mutlu *et al.,* 2012; Bernard, 2008) pinpointed that once cadmium is absorbed into the body, its effect stays all through life while its environmental distribution remains in soils for decades. Cadmium exposure happens primarily through inhalation and ingestion. Toxicity derived from Cd leads to lungs damage and kidney dysfunction. According to the European Union

regulations, the allowable standard for Cd in drinking water source is 5 µg/L, while its concentration in non – polluted water bodies is often less than µg/L (Friberg *et al.,* 1986).

A most recent finding outlined Lead as a highly toxic metal whose unrestricted use has given rise to high environmental contamination, causing serious health problems globally (Raghad *et al.,* 2016). Its complexity in the mixture of compounds depending on the environmental condition makes its pollution complicated. Exposure to lead emanates from mainly industrial processes, domestic sources, food, smoking and drinking water. Initial exposures were linked to gasoline and paints, and its pollution extent has been further directed towards lead bullets, plumbing pipes, pewter pitches, toys, faucets and storage batteries (Thumer, 2002). Plants accumulate lead through their fixations to soils while the major means by which the uptake of lead is being transported into humans is either through food or by apparent flow into drinking water bodies (Goyer, 1990). (Jaishankar *et al.,* 2014; Okoro and Ejike, 2007) buttressed that the toxicity of lead is extremely high unlike other metals because it alters the physiological process of various living organisms and it does not take part in any biological function. In order not to jeopardize the health of humans, the Environmental Protection and Health Issues arm of the WHO advised that the permissible limit of lead in drinking water should vary between 3 – 10 µg/L (Pruss-Ustun *et al.* 2004; WHO 2000; Needleman 1999).

Copper being one of the most toxic compound known to mammals (Bowen, 1979) derive its visibility from copper compounds used for agricultural purposes, copper mining, electroplating companies and brass manufacturing industries (Nurchi and Vallaescusa, 2008). Copper sulphate used as an algicide for the elimination of blue – green algae found in water supply facilities is also a contributor to the accumulation of the contaminant. Its MAL in drinking water is 1 mg/L according to EU. Table 1 displays the MAL and health implication of various trace metals (Lenntech, 2016; GSDEP, 1993; ISDW–S, 1991).

Recent technologies used in water treatment

Different methods of heavy metals removal from water bodies and wastewater have been adopted which include membrane filtration, ion exchange/solvent extraction, electrochemical operations, reverse osmosis, coagulation/filtration, evaporation, electrolysis, chemical precipitation etc. (Yang and

Table 1: Maximum allowable limits (MAL) and health implication of trace metals

Trace metals	MAL for effluent discharge from industries mg/L				MAL for drinking water (mg/L)				Health implication
	WHO	Indian Standard			European Union standard	WHO	USEPA	Indian Standard IS 10,500	
	Inland surface water bodies	Marine coastal regions	Public sewers	Inland surface water bodies					
Arsenic	-	0.2	0.2	0.2	0.01	0.01	0.01	0.01	Cancerous, gastrointestinal disorder and causes liver tumors.
Cadmium	0.1	2.0	1.0	2.0	0.005	0.003	0.005	0.01	Causes cancer, dyspnoea and lung fibrosis.
Copper	0.05 – 1.5	3.0	3.0	3.0	2.0	2.0	1.3	1.5	Increased exposure causes stomach pain, irritation of the eyes, nasal cavity, mouth and headache.
Chromium	-	2.0	2.0	2.0	0.05	0.05	0.1	0.05	Causes tumor in lungs and cancers in humans.
Iron	0.1 – 1.0	3.0	3.0	3.0	0.2	0.2	0.3	0.3	Excessive intake result in hypertension, contraction of the blood vessel and rapid pulse rates
Lead	0.1	2.0	1.0	0.10	0.01	0.01	0.015	0.05	Causes anemia, joint and muscle ache, elevated blood pressure, kidney inflammation and a suspected carcinogen.
Manganese	0.05 – 0.5	2.0	2.0	2.0	0.05	0.5	0.05	0.1	Excessive accumulation causes redundant growth, fatigue, blindness and sexual impotence
Mercury	-	0.01	0.01	0.01	0.001	0.001	0.02	0.001	Excessive intake may result to diarrhea, headache and abdominal effects, loss of appetite, paralysis etc.
Nickel	-	5.0	3.0	3.0	0.02	0.02	0.1	0.02	Causes a decline in lung function, cancer of the lungs and acute bronchitis
Vanadium	-	0.2	0.2	0.2	-	1.4	-	-	May result in paralysis
Zinc	5.0 – 15.0	15.0	15.0	5.0	-	3.0	5.0	5.0	Causes discomfort and metal fume fever

McGarrahian, 2005; Gupta *et al.,* 2004; Nordberg *et al.,* 2007; Szpyrkowicz *et al.,* 1995; Birchler *et al.,* 1994; Tan and Sudak, 1992; Applegate, 1984; Judkins and Hornsby, 1978; Eliassen and Bennet, 1967). These processes generated productive results, but there are limitations with high energy requirements, incomplete removal, high operational cost, elaborate and sophisticated operations and the production of toxic sludge (Ahluwalia and Goyal, 2005a). Within the confines of different treatment methods, adsorption is seen as a user-friendly technique which is widely recognized for the abstraction of heavy metal contamination from water (Tripathi and Ranjan, 2015; Gunatilake, 2015; Lakherwal, 2014; Abas *et al.,* 2013; Geetha, 2013). Its flexibility in design and operation makes its process produce high-quality treated water (Fenglian and Qi Wang, 2011). Table 2 displays the pros and cons of several methods adopted in heavy metal removal (Ahmaruzzaman, 2009; Farooq *et al.,* 2008).

Adsorption

The vast deployment of the adsorption technique in pollution mitigation has been acknowledged, and the significance is well accredited in industries where food, chemical, petroleum and pharmaceuticals are produced (Abasi *et al.,* 2011; Sarin *et al.,* 2002). The definition of adsorption simply refers to a series of operations where the concentration of a particular component increase at the surface or juncture between two phases (Faust and Aly, 1987). The adsorption phenomenon was ascertained by Scheele in 1773 for the extraction of gases using carbon (Bhatnagar and Sillanpää, 2010; Mantell, 1951). Further observation was carried out by Lowitz in 1785 in which wood charcoal was used for the erratic removal of compounds found in water that produces colour and odour (Dabrowski, 2001). A Similar phenomenon was observed by Laroitz and Kehl in 1792 and 1793 respectively, using vegetables and animal charcoal respectively. However, Kayser in 1881 first introduced the phrase "Adsorption" to differentiate surface agglomeration from intermolecular intrusion, indicating that the adsorption phenomenon is all about surface accumulation of the material (Gupta *et al.,* 2009). The adsorption technique can be grouped into two namely; physisorption and chemisorption.

Table 2: Methods adopted for heavy metal removal

Treatment method	Advantages	Disadvantages
Ion–exchange	▪ Selects metals ▪ Intense regeneration of materials	▪ Expensive ▪ Removes fewer metals
Membrane process and ultrafiltration	▪ Production of reduced solid waste ▪ Consumes fewer chemicals ▪ Efficient (not less than 95% removal for single metal)	▪ High startup and operational cost ▪ Reduced flow rates ▪ Removal efficiency decreases over time ▪ Initial current density and solution pH ▪ Production of concentrated sludge
Chemical coagulation	▪ Sludge settlement ▪ Dewatering	▪ Very expensive ▪ Consumes large amount of chemicals
Electrochemical methods	▪ Selects metal ▪ Does not consume chemicals ▪ Extraction of pure metals is achievable	▪ High operational and startup cost
Chemical precipitation	▪ Incomplex ▪ Cheap ▪ Removal of most metals	▪ Production of sludge in large quantity ▪ Difficulty in disposal
Oxidation	▪ Rapid removal of toxic pollutants	▪ High energy requirement ▪ By – product formation
Ozonation	▪ Application is in gaseous state ▪ Volume reduction	▪ Reduced half-life
Biological Treatment	▪ Active in selected metals removal	▪ Commercialized technology still in view
Photochemical	▪ Produces no sludge	▪ By – products is formed
Fenton reagents	▪ Requires no energy when activating hydrogen peroxide ▪ Removal efficiency is high	▪ Produces sludge
Irradiation	▪ Efficiency at the laboratory is high	▪ Needs a lot of dissolved oxygen

Physisorption

This is described as physical adsorption that involves Van der Waals forces which do not require a considerable transformation in the electronic orbital arrangements of the species (Nabais, 2006). Physisorption produces equal energy potential emanating from the adsorbent and the adsorbate but greater than the condensation energy released by the adsorptive; thus, no activation energy is required. In cases of physisorption, the reactions are favoured at low temperatures; therefore, physisorption process decreases with increase in temperature (Al-Anber, 2011). Also, in physisorption, equilibrium exists between the fluid phase and the adsorbate resulting in multilayer adsorption. The operation of weak Van der Waals force makes physical adsorption a relatively non – specific process in which no attraction occurs between the molecules and the specific sites located at the surface of the solid, but the molecules are free to manoeuvre around the solid surface. This makes physical adsorption a reversible process (Somasundaran *et al.,* 2008) also, the materials adsorbed may dabber, forming layers of superimposed films on the adsorbent surface (Kong, 2009).

Chemisorption

This is referred to as chemical adsorption where the adsorption process is propagated by chemical bonds forged between the adsorbent and the adsorbate. Energies are dissipated like that of chemical activity which may be endothermic or exothermic resulting in either small or large energy magnitudes. Its preliminary step requires enormous activation energy (Activated adsorption), which indicates that the pace at which equilibrium is attained may be reduced. Chemisorption process is favoured at high temperatures and the efficiency increases with increase in temperature (Ho *et al.,* 1993; Ho *et al.,* 1992). Usually, chemisorbed species can be removed from the surface either by extreme temperature conditions or high exhaustion or the application of chemicals on the surface.

The adsorption sites on the surface are usually occupied with layers formed by the chemo – adsorbed material (Kong, 2009). When the monomolecular layer covers the surface, the adsorbent is said to be essentially depleted. In addition, movement of molecules from one surface to the other is limited (Kong, 2009). The adsorption process is irreversible, and the chemical attributes of the adsorbent can be affected by surface dissociation whereas the original species cannot be recovered through adsorption (Guerrero – Ruiz *et al.,* 1985). Holistically, adsorption isotherms showcase two categories of adsorption namely; *(i)* reversible (comprising of physical adsorption and weak chemical adsorption) and *(ii)* irreversible (actively chemisorbed) (Al-Anber and Al-Anber, 2008; Al – Anber, 2007).

Occasionally, both physical adsorption and chemical adsorption may occur simultaneously or adversely, a film of molecule may undergo physisorption above an elemental chemisorbed film (Denizli *et al.,* 2000).

Linear forms of adsorption isotherm models

Mathematical simplicity has warranted the adoption of the linear forms of adsorption isotherm model to evaluate the isotherm parameter or the model that describes that best – fit adsorptive mechanism. Langmuir model can be represented in four linearized formats (Table 3) which will culminate in different parameter estimate. The most popular Langmuir model used in literature is the type II due to little deviations from the fitted equations (Ho, 2005; Kinniburgh, 1986).

Table 3: Linearized isotherm models

Isotherm Models		
Langmuir	Freundlich	Dubinin - Radushkevich
$(i)\ \dfrac{1}{q_e}=\left[\dfrac{1}{q_m K_L}\right]\dfrac{1}{C_e}+\dfrac{1}{q_m}$ $(ii)\ \dfrac{C_e}{q_e}=\dfrac{1}{q_m K_L}+\dfrac{C_e}{q_m}$ $(iii)\ \dfrac{q_e}{C_e}=K_L q_m - K_L q_e$ $(iv)\ q_e = q_m -\left[\dfrac{1}{K_L}\right]\dfrac{q_e}{C_e}$	$\ln q_e = \ln K_f + \dfrac{1}{n}\ln C_e$	$\ln q_e = \ln q_s - K_{DR}\varepsilon^2$

The equilibrium models outlined in literature that is adopted in adsorption can be grouped into mechanistic models and empirical equations. The mechanistic model explains the experiment behaviour of metal ion adsorption and also creates trends that can be used for prediction within the system. Other empirical models reported in literature that explains the single – solute adsorption mechanism are displayed in Table 4.

Commercial Adsorbents

Some adsorbents have been extensively explored for water pollution control. The important ones found in literature include zeolite, Silica gel, and activated carbon.

Zeolite

There are over 140 varieties of zeolites that are being utilized as adsorbent. 40 of them occur in their natural state and over 100 are synthetic products. Zeolites are aluminosilicate materials having silicon and aluminate ratios of 1 and affinity. They are practically used in the petroleum industry as catalyst, water softeners, production of molecular sieves and production of detergents. Several types of zeolite have been used as adsorbents for pollutant removal in areas of water treatment (Ellis and Korth, 1993; Okolo *et al.,* 2000; Metes *et al.,* 2004; Motsi *et al.,* 2009). Makki, (2014) applied zeolite A4 for Cd(II) and Pb(II) removal. Abdel–

Table 4: Different Biosorption models used in literature

Model Type	Model Equation	Notation	References
BET model (Multilayer adsorption)	$q_e = \dfrac{q_s C_{BET} C_e}{\left[1 + (C_{BET} - 1)\left(\dfrac{C_e}{C_s}\right)(C_s - C_e)\right]}$	q_s, q_e, C_s and C_{BET} are taken as the theoretical isotherm saturation capacity (mg/g), equilibrium adsorption (mg/g), Saturation concentration of adsorbate monolayer (mg/L) and the BET adsorption isotherm (L/mg) respectively	Brunauer *et al.* (1938)
Flory–Huggins	$\dfrac{\theta}{C_o} = K_{FH}(1 - \theta)^{\eta_{FH}}$	θ is the surface coverage potential, η_{FH} and K_{FH} are the model exponent and equilibrium constant	Flory, (1942); Huggins, (1942); Kaisheva *et al.* (1991); Vijayaraghavan *et al.* (2006)
Khan	$q_e = \dfrac{q_s b_k C_e}{(1 + b_k C_e)^{a_k}}$	a_k and b_k are the model exponent and constant respectively	Khan *et al.,* (1997),
Tempkin	$q_e = \dfrac{RT}{b_T} \ln A_T C_e$	b_T and $A_T (Lg^{-1})$ are Tempkin constants generated from the plot of q_e against $\ln C_e$	Tempkin *et al.* (1940); Aharoni and Ungarish, (1977); Vijayaraghavan *et al.,* (2006)
Koble-Corrigan	$q_e = \dfrac{A C_e^n}{1 + B C_e^n}$	The linear plot using trial and error method of optimization is used to derive Isotherm constants, A, B and n	Koble and Corrigan, (1952)
Frenkel–Hasley–Hill (FHH)	$\ln\left(\dfrac{C_e}{C_s}\right) = -\dfrac{\alpha}{RT}\left(\dfrac{q_s}{q_e^d}\right)^r$	α is the isotherm constant $(Jm^r .mole^{-1})$, d is interlayer spacing (m) and r is the inverse power of distance from the surface.	Hill, (1952)
Toth	$Q_e = Q_{max} \dfrac{b_T C_e}{\left[1 + (b_T C_e)^{1/\eta_T}\right]^{\eta_T}}$	Two constants are itemized, b_T and η_T. A Langmuir type of isotherm expression is obtained when $\eta_T = 1$	Toth, (1971); Vijayaraghavan *et al.* (2006)
Redlich–Peterson	$q_e = \dfrac{k_R C_e}{1 + a_R C_e^\beta}$	Redlich–Peterson parameters are itemized as k_R, a_R and β. The range of the exponent β spans between 0 and 1. When $\beta = 1$, the model transforms to Langmuir isotherm model	Redlich and Peterson, (1959); Preetha and Viruthagiri, (2005)
MacMillian–Teller (MET)	$q_e = q_s \left(\dfrac{k}{\ln(C_s/C_e)}\right)^{\frac{1}{3}}$	k is the isotherm constant	McMillan and Teller, (1951)

Salam *et al.,* (2011) did a similar research on Cu(II) ions. Pimraksa *et al.,* (2013) adopted synthesized zeolite for Cd(II) adsorption. Nah *et al.* (2002) utilized magnetically modified synthetic zeolite for Pb(II) removal. Meanwhile, Babel and Kurniawan, (2003) and Bose *et al.,* (2002) had earlier pinpointed the cation exchangeability of zeolite on Pb, Cd, and Cu removal. Their importance as adsorbents in water and wastewater treatment was discussed extensively by Wang and Peng, (2009).

Silica gel

Silica gels are categorized into three namely; low-density gels, intermediate and regular gel. The low-density gels possesses surface area ranging from 100-200 m^2/g. The intermediate gels are characterized with density range of 300 – 350 m^2/g, while the regular silica gel has a high surface area of 750 m^2/g. The various forms of gels possess good quality as adsorbents, and its versatility has been seen in many industries (Ahmed and Ram, 1992; Backhaus *et al.,* 2001). Modification of its properties to remove pollutants have been widely explored by many industries (Moriguchi *et al.,* 2005; Saad *et al.,* 2007; Wang *et al.,* 2009). Earlier research indicates that Katsumata *et al.* (2003) explored the usefulness of silica gel for Cd(II) removal. Bortoleto *et al.* (2004) obtained the concentration of Cd(II) ions using modified silica gel. Vaghetti *et al.* (2003) follow suit by removing Cu(II) ions using phenylenediamine propyl silica xerogel. Passo *et al.,* (2006) worked in similar area for Cu and Pb elimination.

Activated Carbon

All around the world today, activated carbon has gained recognition for the removal of pollutants from water and wastewater. In this vein, charcoal has been identified as the longest serving adsorbent known in wastewater treatment. Its production process involves dehydration, carbonization and subsequent activation of the parent material. The by–product has been characterized with porous surface structure with high surface area between 600 – 2000 m^2/g. The continuous use of activated carbon has developed productive results in the removal of various contaminants such as metal compounds (Perez-Candela *et al.,* 1995; Gabaldon *et al.,* 1996:2000; Sanchez-Polo and Rivera-Utrilla, 2002). Liu *et al.,* (2014) reported the progress of Cu(II) removal capacity using humic acid-impregnated activated carbon. Meanwhile, a holistic compilation of heavy

metal removal was previously reviewed by Goyal *et al.,* (2001). In addition, Ahn *et al.* (2009) reported Cd(II) removal using activated carbon treated with acid. Fan and Anderson, (2015) conducted similar research on Cu(II) and Cd(II) using granulated activated carbon. Activated carbon on Pb removal was also reported by several researchers (Karnib *et al.,* 2014; Dwivedi *et al.,* 2008; Goel *et al.,* 2005). Despite the relative abundance and productive use of activated carbons, there have been some restrictions on its applicability due to its high cost. Therefore, researchers are on the lookout for cheap and abundant form of adsorbent that can be applied to pollution control. As such, over some time now, attention have been diverted to the development and production of cheap alternative adsorbent using various raw materials that are abundant, possesses high carbon content and less difficult to activate (Moreno-Castilla and Rivera-Utrilla, 2001).

The use biosorbents for the elimination of heavy metals from water and wastewater have been reported by a number of publications. Concentrated and elaborate reports from Volesky's group is seen as one of the most impactful studies in areas of biosorption. Several aspects that contribute to heavy metal adsorption using biosorbent have been discussed in their review of which a number of them are cited in this article.

Kratochvil and Volesky, (1998) discussed ion exchange as the most prominent mechanism in adsorption. Volesky, (2007) reported the challenges and mysteries behind metal adsorption. Issues such as metal interaction, modeling of equilibrium studies, the drawbacks and future of adsorption were also mentioned in this review. Volesky, despite the abundant research towards adsorption, also iterated that the application of adsorption mechanism is just at the foundational level, stating that its future cannot be envisaged.

Apart from contributions from Volesky, other researchers provided recent review articles in similar areas that this article cannot help but discuss. For instance, Bhatnagar *et al.,* (2015) discussed the versatility of agricultural waste peels utilized for water cleansing. They reported the metal binding potentials for different fruit peels under different operational and experimental conditions. The mechanism of acid oxidation, ion exchange mechanism, and desorption characteristics are mentioned in their review. Furthermore, adsorption isothermal studies for

different fruit peels under different modified conditions are also presented in their study. Prior to the review publication stated above, Bhatnagar *et al.,* (2010) reported the accomplishments of coconut – based adsorbent in water treatment. Their report shed lights on the elimination of various pollutants such as dyes, heavy metals, phenolic compounds, inorganic anions and other miscellaneous pollutants from water. They also reported the production process, experimental methods, modification and adsorptive potentials of the said adsorbent.

Recently, Zhou *et al.,* (2015) did a state–of–the–art review of organic pollutant biosorption using agricultural wastes. They mentioned the different methods of preparing adsorbent generated from agricultural wastes. The review also covers the modification properties derived from chemical and physical alteration/activation and their surface characteristics. Furthermore, the study also focuses on the removal of dyes, antibiotics, pharmaceutical and other pollutants using agricultural sorbents. Optimization conditions, regeneration and future focus were also discussed. The study proposed molecular modeling as a way to predict adsorption mechanism. Fu and Wang, (2011) also did a holistic review of different treatment methods of eliminating heavy metals from wastewater. For explanatory and cost effective means of metal removal, this publication is recommended.

In another recent report by Purkayastha *et al.,* (2014), an elaborate view of Cd(II) removal using several adsorbents was discussed. This paper provided insight into cheap means of removing one of the most toxic metals present in water and also espouses the use of different adsorbents which include natural minerals, municipal and industrial wastes, agricultural adsorbents, animal and microbial biomass, fungi and algae. The article also stressed that special attention should be given to coagulation and precipitation, indicating that both methods can be economically efficient in practical scenarios.

Similar content was reported by Singha and Das, (2013) but towards Cu(II) removal using agricultural wastes. A compilation of publications on Cu(II) removal using agricultural adsorbent is presented in their review. The operational conditions, promotion of adsorptive mechanism, isothermal and equilibrium studies are the main focus of the review. Another review article with similar report (Bilal *et al.,* 2013) discussed the utilization of waste biomass for adsorbent in sequestering of Cu(II) from industrial wastewater. The review should be recommended to interested readers.

Preparing inexpensive adsorbent from waste materials is characterized by several advantages. Their viability mainly lies in their environmentally and economically friendly nature. Many low – cost adsorbent has been employed that utilized industrial, agricultural and municipal waste in the removal of metal ions in water and wastewater. Considering the increasing number of articles and the level of progress, taking into account the comprehensive conditions affecting the adsorption process and the need to provide relevant advances, this review tends to provide continuity by exploring recent publication with focus on the elimination of three prominent toxic metals namely Cu(II), Pb(II) and Cd(II) using agricultural adsorbents. Areas of adsorption which covers procedural pathways, isotherm models, kinetic and equilibrium adsorptive studies, modification, coefficient of correlation and desorption studies for different adsorbents are the primary direction of this review. Furthermore, the factors contributing to the adsorption of the aforementioned metals, drawbacks faced and prospects will be discussed as well. In order to demonstrate the potential capacity of the adsorbent in Cu, Pb, and Cd ion removal, this review tends to explore recent research articles within 10 – 15 years. The information contained in this review highlights the summary of methods that espouses the adsorptive potentials of several low – cost adsorbents with discussion of recent findings.

General consideration of Cd, Cu and Pb removal using agricultural adsorbent

(Haskem *et al.,* 2005; Bailey *et al.,* 1999) itemized that any agricultural product containing cellulose exhibit potentials for heavy metals absorption. The cardinal ingredients discovered in agricultural waste that are responsible for heavy metal absorption include simple sugars, hemicellulose, proteins, lignin, lipids and starch having a multiplicity of functional groups. The availability of these waste materials makes them eco-friendly, renewable, low in cost, abundant and the most viable alternative for heavy metal remediation. Also agricultural wastes, over the past decades have been seen as an alternative for activated carbon since its conversion into low – cost adsorbent is endowed with workable properties like low ash content and considerable hardness.

Elimination of Cd ions using agricultural wastes

(Cheng *et al.,* 2016) did an assessment on the adsorptive efficiency of various pyrolysed feedstock biochars on cadmium, at room temperature. A total 22 samples were considered which were mushroom waste, wulffia, lemna, rice straw, rice stubble, rice hush, rice root, water hyacinths stem, water hyacinth leaves, water hyacinth roots, legume straws, peanut husks, oil-tea camellia seed cake, soya bean straw and lavenda oil extraction residue. The cumulative report indicated that mushroom waste (without pulverization) has the lowest adsorption efficiency of 38.7% while soya bean straw achieved the maximum efficiency of 86.6%. The biochars used in the experiment had a Significant increase in adsorption capacity with peanut thick biochars having the highest cadmium removal efficiency of 99.2%. Optimum condition identified in the adsorptive capacity were pH value of 5, Cd initial concentration of (200mg/L). The equilibrium studies of peanut husk and peanut husk biochar all confirmed to Langmuir model with correlation coefficient (R^2) of peanut husk (0.9010), peanut husk biochar (0.9722). The Freundlich model correlation coefficient (R^2) observed for peanut husk and peanut husk biochar are (0.9212) and (0.9800) respectively.

Adsorption of Cd(II) from liquefied solution was performed using Sesame as biosorbent (Cheragi *et al.,* 2015). The experiments were carried out at temperature 25°C ± 1 using batch technique. The optimum uptake of Cd(II) recorded was 84.74mg/g at optimum conditions of pH 6.0, bed height of 2cm and discharge of 2.5mlmin^{-1}. The kinetics studies showed that pseudo – first – order and pseudo – second – order model serves as the best fit to describe the adsorption mechanism with R^2 values of 0.9929 and 0.9952 respectively. The experimental process revealed that the equilibrium adsorption capacity was attained in 30mins while using 201μm particle size.

Moubarik and Grimi, (2015) assessed the removal of Cd(II) from liquefied solution by vaporization of Olive stones and sugarcane bagasse. The corresponding experimental result revealed that equilibrium adsorption of Cd(II) was reached at 25mins for both samples. The removal efficiency recorded was 96% for both adsorbent. The kinetic studies could be illustrated using pseudo – second – order model. The optimum conditions recorded are initial pH of 7and experimental temperature of 298k.

Sedge (*Onosina bracteatum*) was used to remove of Cd from aqueous solution (Rao *et al.,* 2014). The

experiment performed showed a removal efficiency of 98.8%. The optimum sorption condition was obtained at pH 3.8. The equilibrium absorption was verified using the Langmuir model and it gave the best, considering all temperatures. The kinetics studies obeyed the pseudo – second – order model while the sorption of Cd(II) was seen as feasible and endothermic. The breakthrough capacity recorded was 46.2mg/g and exhaustive capacities was observed to be 99.0 mg/g. Desorption studies depicted a rapid process and within 70ml from the column 99.1% Cd(II) could be retrieved.

Iqbal *et al.* (2009) also analyzed Cd(II) removal using mango peel waste. Optimum sorption capacity of 68.92mg/g was recorded at 60 min. The equilibrium studies were best characterized using Langmuir isotherm model while the kinetics followed pseudo–second–order model. Desorption process showed that the adsorbent could be recycled 5 times without considerable loss in sorption capacity.

Furthermore, in a research by (Schiewer and Patil, 2008), Cd(II) removal was investigated using Pectin–rich fruit waste as biosorbents. The fruit waste materials mentioned in the study are lemon peels, orange peels, grape fruit peels, apple peels, apple cone, grape skins and apple kernel which showed rich content in pectin. The samples were modified with 0.1N HNO_3 for 6hours and allowed to undergo drying for 12hours at 38–40°C. Citrus peel performed better in the adsorption process. The equilibrium capacity was reached at 30 – 80mins with respect to particle size (0.18–0.9 mm). The kinetics studies were more explained using pseudo–second–order model while the equilibrium studies were buttressed with Langmuir model. The adsorption process was validated with R^2 values of 0.88. The maximum metal uptake of 0.67meq/g was observed at pH 5 using citrus peel.

Perez-marin *et al.* (2007) explored the use of orange waste to remove cadmium from aqueous solution The results obtained showed that the maximum adsorption capacity was found to be 0.40mmol/g at pH 4, 0.41mmol/g at pH 5 and 0.43mmol/g at pH 6. The analysis of the kinetics model responded to Elovish equation and the equilibrium data best fitted the Sips model. He further explained that data gotten fitted a non-linear regression. Benaissa, (2006) conducted a research to remove Cd(II) from aqueous solution using pea peels, broad bean medlar and fig leaves respectively. The result presented indicated that equilibrium sorption capacity was attained in 3hrs for medlar, peas and broad bean peels

respectively while fig leaves used 4h reaction time. Kinetic studies were fitted into Lagergren first-order rate model, pseudo – second – order model (Ho *et al.,* 2000) and the second order rate model equation and fig leaves gave a correlation coefficient (R^2) of (0.9876; 0.9988 and 0.7259) for the outlined models respectively. Medlar peels produced R^2 values of 0.9866, 0.9999, 0.4473 for the model respectively. Broad bean peels had R^2 values of 0.9266,0.9999, 0.4473 for the models respectively and peas peel gave R^2 values of 0.8886,0.9999, 0.9191 for the model respectively. The equilibrium studies were verified using Langmuir model with maximum sorption capacity of 147.71mg/g, 118.91mm/g, 98.14mg/g and 103.09mm/g for broad bean peel, peas peel, medlar peel and fig leaves respectively. The correlation coefficients R^2 values outlined are 0.9492, 0.9142, 0.9982, 0.9546 for broad beam peel, peas peels, medlar peel and fig leaves respectively.

Pino *et al.* (2006) considered the use of green coconut shell powder for the removal of cadmium. Result obtained showed that the maximum absorption capacity for a green coconut absorbent was 285.7mg/L. The best pH that favored the experiment was 7.0. Langmuir and Freundlich models both fitted when describing the equilibrium studies. Kinetics studies that best explained the experimental correlation was the pseudo – second – order paradigm.

Montanher *et al.* (2005) examined the use of rice bran for Cd(II) removal. The sample was first acidified using 0.1M $NaNO_3$ and 1.0M NaNO3, 0.1M NaCl and maintained to a pH of 3.0 using HNO_3. Maximum sorption capacity for Cd(II) was attained using NaCl as modifying agent. The result indicated that optimum condition was achieved at pH values around 5 – 6 for Cadmium. The increase in absorbent concentration (1 – 20mg/L) caused a decrease in metal removal efficiency as a result of agglomeration of the sample (absorbent) in the metal solution. He highlighted that for economy to be maintained, small batches of absorbent should be used. The result displays the analysis of the equilibrium studies using Langmuir and Freundlich model having good correlation coefficients R^2 of 0.9734. The Gibb's free energy studies had negative values as a confirmation of the feasibility of the sorption process. Singh *et al.* (2005) examined the removal of Cd(II) using rice polish derived from agricultural waste. The result showed that the optimum prerequisite for high Cd removal were pH 8.6, initial Cd concentration of 125mg/L and temperature 20°C, all with a yield capacity of

972mg/g. The equilibrium studies had Langmuir model applicability indicating the single–layer analysis of the adsorbate on the surface of the absorbent. The thermodynamics displayed a spontaneous and endothermic process.

Elimination of Cu ions using agricultural adsorbent

Yargic *et al.,* (2015) conducted studies on the uptake of Cu(II) using chemically-treated tomato waste. Tomato waste treated with 3% v/v HCl solution. The removal efficiency was found to be 92.08%. The biosorption equilibrium was illustrated by the Langmuir and Freundlich isotherm models while the pseudo-first-order and pseudo-second-order kinetic models were employed to describe the biosorption kinetics. Luna *et al.,* (2015) used Adlai shell from Munoz, Nueva Ecija, Philippines as absorbent in the removal of Cu(II). The sample was activated by carbonization at 350°C for 120mins and soaked in 1M Nitric acid solution for 60mins. Kinetic rate constant varied from 0.158 to 0.0027 to 0.012gmg^{-1} as concentration increased, which showed that Cu(II) intake increased as concentration increased. The pseudo-second-order kinetic model confirmed the experiment with the coefficient of correlation values of the pseudo-second order kinetic equation and intraparticle diffusion of 0.999 and 0.9697 respectively. Langmuir and Freundlich isotherm equilibrium was used to evaluate the equilibrium distributions that indicated heterogeneous adsorption. Tan *et al.,* (2015) reviewed the application of different biochar for the removal of heavy metals present in water solutions. Different biochar including corn straw, canola straw, hardwood, peanut straw, soya beans straw and Spartina alterniflora (for Cu(II) ions only) were analysed taking into thought key factors affecting the adsorption process. Langmuir model was a better fit than the Freundlich model. Results for Cu(II) ion removal are given in Table 5.

Hawari *et al.* (2014) analyze the characteristics of olive mill solid residue and its application in remediation of copper (Cu^{2+}) from aqueous solution using a mechanistic study. It was observed that as temperature increase, removal capacity increases. The models used includes the R-P, Langmuir, Freundlich and D-R models.

Trakal *et al.,* (2014) analyze the removal of copper from aqueous solution using biochar via an effect of chemical activation using 2M KOH. Two samples were critically analyzed; A synthetic solution ($CuNO_3.3H_2O$) prepared with a background electrolyte (0.01M $NaNO_3$),

Table 5: Adsorption potential of some agricultural adsorbents in the removal of Cd(II) ions from aqueous solution

Adsorbent	Modifying agent	Experimental variables considered	Constants	Suited equilibrium model analysis (EMA)	EMA R^2 value	Kinetic model analysis (KMA)	KMA R^2 value	Optimum conditions	% Removal	Desorption	References
Cactus cladodes	-	Particle size, metal concentration, pH, dosage, Temperature, time	Agitating speed	Langmuir isotherm model	0.991	Pseudo–second – order	0.994	pH 5.8, Temp 30°C,	adsorption capacity 30.42mg/g	-	Barka *et al.*, 2013
Polyrhiza	-	pH, dosage, Contact time, initial concentration, temperature		Langmuir isotherm model	>0.995	Pseudo–second – order	>0.997	pH 4.0, 14.97 mg/g at 120mins, 36.0mg/g	-	52.83% recovered using 0.1M HCL	Meitei and Prasad, (2013)
Carpinus betulus tree leaves	-	pH, Initial concentration, dosages, temperature, particle size	Contact time (60min)	Sips model	0.99	Pseudo–second – order	0.999	pH 3.8, dosage 2g/L, Temp 25°C, particle size 0.12-0.17mm	64.46mg/g	-	Zolghamein *et al.* (2013)
Melon husk	H_2SO_4, NaHCO3	Initial concentration, dosage, contact time	pH	Freundlich Isotherm model	0.9953	Pseudo–second – order	$0.9984 - 1$	Dosage 0.3g/L, particle size 45 μ m	96.8% removal using 2.0mg/L	-	Giwa *et al.* (2013)
Chestnut shell	NaOH	Initial concentration, pH, Contact time	Temperature, Agitation	Freundlich Isotherm model	0.976	Pseudo–second – order	$0.989 - 1$	Natural pH (5 – 6), 25°C for 24h	98.3% removal using $P_{4\%-th}$ and $P_{8\%-th}$ pre – treated shells	-	Vazquez *et al.* (2012)
African bread fruit	Thioglycollic acid	Contact time,	pH, temperature and concentration	McKay and Poot intraparticle diffusion model	0.9088	Pseudo–second – order	$0.9999 - 1$	pH 7.5, 30°C for 10min	96% - 99% removal	-	Sonde and Odoemelam, (2012)
Modified orange peel	HNO₃	Dosage, Contact time, initial concentration	pH and temperature	Langmuir and Freundlich adsorption isotherms models	0.97	Pseudo–second – order	1	pH 5.0, 25°C for 30 mins	89.57% removal	-	Lasheen *et al.* (2012)
Modified wheat straw	Urea using Microwave radiation	Contact time, pH, temperature, Concentration	Dosage	Langmuir isotherm model	0.987	Pseudo–second – order	0.9984	pH 6.0 at 10 mins	39.22mg/g	-	Farooq *et al.* (2011)

and a solution obtained from Cu-contaminated. The prepared biochars (BC and BC$_{act}$) were able to remove Cu from synthetic and soil solutions respectively. Furthermore, chemical activation using 2M KOH significantly; i). Increased total pore volume. ii). Partly improved Cu sorption behaviour. iii). Enhanced the Cu removal from aqueous solution during the retention test over a period of time.

Application of straw ash from barley as a novel bioadsorbent for the removal of Ni(II), Cd(II), Cu(II) and Co(II) was explored by Arshadi *et al.,* (2014). The biomaterial utilized was obtained from cereal straw, barley straw and was activated thermally at 550°C. The results revealed that the amount of adsorption increases with increasing contact time. There was an increase in the initial heavy metal concentration at 25°C for 45mins. The adsorption of metals increases with increasing temperature in the solution. The best fit model that explained the equilibrium data was the Langmuir–Freundlich model with copper being the second metal largely removed while the kinetics followed the pseudo – second – order equation pattern.

Removal of copper by loofah fibers was experimented on by (Tang *et al.,* 2014). The dried fibers were shredded to 2 – 3mm pieces and pretreated with 30% NaOH solution in anhydrous ethanol at 298.15K for 48hours. 14.49mg/g was obtained as the optimum sorption capacity at a favorable pH of 8.0. In equilibrium studies, both Langmuir and Freundlich isotherm models fitted the equilibrium data, but a better linear correlation coefficient was obtained using the Langmuir model. The pseudo – second – order kinetic models was the best fit when considering the kinetics studies.

(Kong *et al.,* 2014) investigated removal of Cu(II) from solutions using raw and modified litchi pericarp. Modified litchi pericarp was prepared by mixing 5g of dried litchi pericarp with 50ml NaOH (0.1M) solutions for 24 h. The maximum sorption efficiency of modified litchi pericarp was found to be more than 97.5% at pH of 6, dose of 10.0g/L and 60minutes contact time. The modified litchi pericarp showed a sorption capacity increase of 23.7 mg/g when compared with raw litchi pericarp. Langmuir and Freundlich isotherm models analyzed the equilibrium of experimental data well while the pseudo-second-order kinetic model was used in describing adsorption kinetics of Cu(II).

Feng and Guo, (2012) carried out absorption of Cu(II), Pb(II) and Zn(II) using modified orange peels. The samples were modified chemically by soaking in ethanol,

NaOH, and NaCL$_2$ for 20h. The optimum pH value was 5.5 with absorption efficiencies of 93.7%, 99.4% and 86.6% for Cu(II), Pb(II) and Zn(II) respectively. The absorption capacities are given as 70.73mg/g, 209.8mg/g and 56.18mg/g for Cu(II), Pb(II) and Zn(II) respectively. Selectivity order is given as Pb(II) Ã Cu(II) Ã Zn(II). The experiment fitted well using Langmuir isotherm. Absorption mechanism is due to ion exchange.

Pellera *et al.,* (2012) analyzed the removal of Cu(II) from aqueous solution using biochars prepared from agricultural by-products such as rice husks, olive pomace, orange waste, and compost. Pyrolysis of biochars was done under oxygen-limited conditions according to Chen and Chen (2009). The chars produced were treated with HCl 1M for 12 h. with slurry separated by vacuum filtration. The optimum sorption conditions were pH in the range of 5–6 and 2–4 h. of contact time and adsorbent dose in the range of 5 – 12.5g/L. The adsorption kinetics was best fitted in the pseudo-second-order model while the equilibrium studies was best described by the Freundlich and linear isotherm models.

Hasfalina *et al.* (2012) studied the adsorption of copper (II) from aqueous solution using kenaf (*Hibiscus cannabinus,* L.) fibres in fixed bed column. Two models were adopted; the Thomas model and the bed depth service time (BDST) model throughout the experimental process. The result showed 47.27mg/g was the highest bed capacity which was obtained at 100mg/L of initial copper (II) concentration, flowing at a rate of 6ml/min. The breakthrough curve was best explained using the BDST model with percentage correlation coefficient not less than 91%.

Larous and Meniai, (2012) analyzed the removal of copper (II) from aqueous solution by agricultural byproducts – sawdust. After drying, activation was done using 1N H$_2$SO$_4$ at 150°C for 24hrs. The Cu removal efficiency increased from 46.22% (9.245mg/g) to 97.37% (19.475mg/g) when contact time increased from 5 to 60 min. It was also checked at 60mins (97.01%) and 120mins (97.37%). The maximum adsorption took place around pH 6.0. The amount of initial concentration of Cu (II) increased from 10 to 60mg/L and the amount adsorbed increased from 9.8652 to 37.334mg/g. The equilibrium data gathered conformed to Langmuir model while the kinetic trend followed the pseudo – second – order equation and the intraparticle diffusion model with correlation coefficient of 0.99962 and 0.99912 respectively.

(Chen *et al.,* 2011) analyzed adsorption of Cu(II) in aqueous solution using biochars prepared from pyrolysis of corn straw and hardwood. The corn straw biochar was prepared at a temperature of 600°C for 2hours under slow pyrolysis conditions while the preparation of other biochar was at 450°C under 5s retention time. The maximum sorption capacity was found to be 12.52mg/g and 6.79mg/g for corn straw biochar and hardwood biochar respectively. The Langmuir and Freundlich models were used to describe the equilibrium of experimental data, but a better coefficient of correlation value was obtained with Langmuir model ($R^2 = 0.999$). The adsorption kinetics corresponded to the pseudo-second-order kinetic models with coefficient of correlation (R^2) value of 0.988 as an explanation of the entire experimental process. Moreno-Pirajan and Giraldo, (2011) used activated carbon from pyrolysed potato peel in the removal of copper from aqueous solution. The experiments followed same processes employed in "adsorption of copper from aqueous solution by activated carbons obtained by pyrolysis of cassava peel" (Moreno-Pirajan and Giraldo, 2010). The optimum sorption capacity, in this case, was gotten as 74mg/g. Four three–parameter isotherms models were applied to verify the equilibrium trend represented by the adsorption capacity; Sips, Toth, Radke–Prausnitz and Vieth–Sladek models. The correlation coefficients (R^2) = 0.989511, 0.98716215, 0.986251911, 0.9767217 obtained in the experiments are in order of Radke–Prausnitz, Vieth–Sladek, Sips, and Toth respectively.

Moreno-Pirajan and Giraldo, (2010) investigated the removal of copper from aqueous solution using activated carbons gotten from pyrolysed cassava peel. The dried peels were impregnated with aqueous $ZnCl_2$ at different concentrations. The peels were modified by drying in air for 8 hours at a temperature of 383K and then pyrolysis treatment at constant heating rate of 10K/min and argon flow of 30 STP.cm^3/min at 823K, and 4 hours soaking time followed. Four three – parameter isotherms models were used in equilibrium studies, they include, Sips, Toth, Radke-Prausnitz and Vieth-Sladek isotherm models. The correlation coefficients (R^2) arrayed in descending order are 0.997698745, 0.978315, 0.978278 and 0.978123 for Sips, Vieth-Sladek, Toth, and Radke-Praisnitz models respectively with maximum sorption capacity of 55mg/g. Witek-Krowiak *et al.,* (2010) researched on the use of peanut shell to remove heavy metals from water

solution. Cu (II) and Cr (III) ions were the heavy metals in this research, using Langmuir and Freundlich (two – parameter models) and Redlich–Peterson and Sips (three – parameter models) models to examine data gotten from the tests. The analysis showed that for 1g of peanut shell, 25.39mg of Cu(II) and 27.86mg of Cr(III) were removed. The correlation coefficient $R^2 = 0.994$, 0.994, 0.992 and 0.9326 for Sips, Redlich–Peterson, Langmuir and Freundlich models respectively confirms a strong relationship between the experimental and model data. Moreso, the kinetics was best fitted using the pseudo – second – order model with R^2 value of 0.977.

Studies were also carried out on the use of cashew nut shell to remove Cu(II) ions present in water solutions as reported by SenthilKumar *et al.,* (2010). The results gotten from the test were analysed using Langmuir and Freundlich isotherm models. The study showed that the absorption capacity for Cu(II) ion is 20.00mg per 1g of bio sorbent at pH 5 in 30mins at 30°C, the results proved cashew nut shells to be effective. The experimental data best fitted the Freundlich model with correlation coefficient R^2 of 0.998. The adsorption kinetics was better explained using the pseudo – second – order model.

The removal of Cu(II) from aqueous solution using pine and base modified pine cone powder as biosorbent was experimented on by (Ofomaja *et al.,* 2009). Part of the substance was mixed with NaOH solution to attain the modified form. Optimum sorption occurred at pH of 5 and adsorbent dose of 8g/L with the modified pine cone removing more Cu(II) than the raw pine cone. The kinetic data was described by the intraparticle diffusion model and the pseudo-second-order kinetic model.

Liu *et al.,* (2009), used raw and acid pretreated bivalve mollusk shells as an absorbent for Cu(ii) removal in aqueous solution. Some part of the sample was treated with 1M H_2SO_4 for 60mins at 100rpm. The optimum contact time was below 90mins while optimum pH value varied with the type of solution given as 1.5 to 9.0 for industrial by-products and 5 – 9 for *S. cerevisiae*. The absorbent operated best at temperature between 15 – 40°C. The sorption was exothermic. The absorbent used high regeneration and reuse up to 12 cycles of sorption and desorption while still given 98.4% efficiency. The sorption capacity was 38.93mg/g and 138.95mg/g for raw and acid-pretreated bivalve mollusk shells.

Table 6: Summary of agricultural adsorbent and their capacity (As discussed by Tan *et al.,* (2015)

Feedstock	Pyrolytic temperature (°C)	Residence time	Adsorption temperature (°C)	Adsorption pH	Qmax (mg/g)	Isotherm	Kinetic model	References
Corn straw	600	2h	22 ± 2	5	12.52	Langmuir	PSO	Chen *et al.* (2011)
Canola straw	400	3.75h	25 ± 1	5	0.59	Langmuir	-	Tong *et al.* (2011)
Hard wood	450	<5s	22 ± 2	5	6.79	Langmuir	PSO	Chen *et al.* (2011)
Peanut straw	400	3.75h	25 ± 1	5	1.40	Langmuir	-	Tong *et al.* (2011).
Soya beans straw	400	3.75h	25 ± 1	5	0.83	Langmuir	-	Tong *et al.* (2011)
Spartina alterniflora	400	2h	25	6	48 ± 0.64	Langmuir	-	Li *et al.* (2013a)

Chestnut shell and grape seed activated carbons were also used as adsorbents for the removal of Cu(II) ions from water solutions (Özcimen and Ersoy-Mericboyu, 2009). Carbonization was achieved by impregnating the ordinary adsorbents with $ZnCl_2$ and adding carbon under heat in an atmosphere of nitrogen. Temperature and pH factors were investigated on the adsorption process optimum time using Langmuir and Freundlich models for data deciphering. The experimental data conformed to the Freundlich model with higher R^2 values. The experiment conducted proves the absorbents to be useful with an increase in adsorption capacity due to increase in pH, temperature and surface area. Other experiments found in literature where Cu(II) ions were eliminated are further discussed in Table 6.

Elimination of Pb ions using agricultural adsorbent
Yahaya and Akinlabi, (2016) made use of cocoa pod husk for the removal for the adsorption of lead. The fresh samples were collected from the Cocoa Research Institute, Nigeria. Chemical activation on the adsorbent was carried out using dilute HNO_3 for 24 h. Modification of the adsorbents was conducted using 7% (v/v) aqueous H_2SO_4 for 90mins. Further modification was done with $0.3dm^3$ of pyridine and 5.67g EDTA under reflux for 24hours. 94.6% and 98.2% removal efficiency at 50mins was recorded for unmodified and modified cocoa pod husk respectively. The kinetic studies best fits into the pseudo – second – order model with high R^2 value ranging from 0.9776 to 1. The thermodynamic studies produced values $5.499KJmol^{-1}$, 60.36KJ/mol and $212J/molK^{-1}$ as the free energy, enthalpy change and entropy change respectively. (Shi *et al.,* 2015) used arborvitae leaves to investigate heavy metal (Pb(II), Cu(II) and Co(II)) removal in aquatic environment. The conditions corresponding with single and competitive component absorption experiment was observed. The absorption ability of the leaf showed dependence on

the surface and pore diameter. Equilibrium was attained in 120mins while optimum adsorption for Pb(II) was 7.64mg/g, 3.38 mg/g for Cu(II), and 1.84 for Co(II). For the single component system, the order of adsorption was in accordance with the order of electronegativity value Pb(2.33) > Cu(1.90) > Co(1.88). The ternary component system showed a decrease in the adsorption capacity using the adsorbent from 35.84 to 9.32 mg/g, 7.94 to 3.07 mg/g, and 6.78 to 1.54 mg/g for Pb(II), Cu(II), and Co(II) ions respectively. The optimum pH value was 5.5. The experimental data was best arrayed with Langmuir model with correlation coefficient R^2 value of 0.974 and 0.992 for Pb(II) ions considering single and competitive ion adsorption respectively. Jane *et al.,* (2014) research on heavy metals adsorption using agroforestry waste derived activated carbon on the solutions containing the metals. Macadamia nut shells, baobab shells, pigeon pea husk, rice husk, moringa oleifera husks and marula stones were all to prepare activated carbon. The metals considered were Pb(II), Hg(II), Fe(II), Cu(II), Zn(II), Ni(II), Cd(II), Mn(II), Cr(II) and As(II). As pH increased from 4 to 6 the adsorption increased and all the activated carbons gave 60% absorption for Hg (II) for pH of 6. Absorption of Pb (II) also showed 22% increase in adsorption compared to commercial carbon for baobab shells, pigeon pea husk, moringa oleifera husks and marula stones. The adsorption processes fitted the Langmuir model and Activated carbons gotten from baobab shells, pigeon pea husk had better adsorption capacity compared with all other activated carbons. Chemically Modified cellulosic biopolymer generated from okra was used in the removal of heavy metal from wastewater (Singha and Guleria, 2014). Free radical polymerization using acrylonitrile (AN) and methacrylic acid (MAA) was employed to synthesize the biopolymers based graft copolymers; then the modified

Table 7: Adsorption potential of some agricultural adsorbents in the removal of Cu(II) ions from aqueous solution

Adsorbent	Modifying agent	Equilibrium model analysis	R^2 value	Kinetic model analysis	R^2 value	Optimum conditions	% Removal	References
Orange Peel	NaOH, CaOH, HNO$_3$	Langmuir isotherm model	>0.9930	Pseudo–second–order	0.9998	pH 6.6, Temp 30°C, adsorption capacity 289.0mg/g	94.6% but reduces to 85.2% after used 4 times	Feng et al. (2009)
Rubber (thevea brasiliensis) leaves	NaOH,	Langmuir isotherm model	>0.9962	Pseudo–second–order	>0.997	pH 4, 14.97 mg/g at 27°C	-	Ngah and Hanafiah, (2008)
Tamarind fruit shell	Hydroxyethyl methacrylate	Langmuir isotherm model	0.999	Pseudo–second–order	>0.99	64 mg/g at temp 303K and pH 6.	99.2% in 1h.	Anirudhan and Radhakrishnan, (2007)
Soya bean straw	Citric acid	Freundlich isotherm model	0.9914	-	-	0.64 mmol/g at pH 6	68.6% (0.069 mmol/g) and 22.5% (0.450 mmol/g) at C_o between 1 and 20mM	Zhu et al. (2007)
Hazelnut shells	-	Langmuir isotherm model	>0.98	Pseudo–second–order	0.99	0.104 mmol/g at pH 5-7	-	Demirbaş et al. (2007)
Sour orange Residue	NaOH	Langmuir isotherm model	0.99	Pseudo–second–order	-	21.7 mmol/g at pH 5.	-	Khormaei et al. (2007)
Ponkan mandarin peel	-	Dynamic conditions comprising of breakthrough points	-	-	-	1.31 mmol/g at pH 4.8 and temp 298±1K	Saturation Value of 1.30 mmol/g	Pavan et al. (2006)

cellulosic biopolymer was utilized in the elimination poisonous metal namely; Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+} from wastewater. The impacts of pH, contact time, temperature and metal particles fixation were considered in batch mode tests. Langmuir and Dubinin – Radushkevich (D – R) models were utilized to demonstrate the adsorption isotherm. The arrangement of monolayer limit q_m featured when utilizing Langmuir isotherm for Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+} were 1.209, 1.2609, 0.9623 and 1.295mmol/g, individually and the correlation coefficient R^2 values obtained were 0.9985, 0.9923, 0.9932 and 0.9972 respectively. The thermodynamic values "H° and "G° for metal adsorption on modified cellulosic biopolymer demonstrated that adsorption procedure was unconstrained and additionally exothermic in nature. According to (Ogunleye *et al.* 2014) activated carbon produced from banana stalk was used for the removal of Pb (II). The adsorbent was modified with phosphoric acid (H_3PO_4) at a ratio 1:1 (w/v). This was followed by the dehydration of the mixture at 105°C for 12 hours and then at 800°C in the absence of air for 2 h.; carbonization took place. The carbonized sample was cooled, filtered and mixed with 0.1 M HCl for 1 h.. The maximum percentage removal was at a percentage of 97.9% at equilibrium time of 120 minutes, and the optimum sorption capacity was 200mg/g at pH 8 and 250mg/L initial concentration. The pseudo – first and second – order and intra–particle diffusion models were employed in analyzing the kinetic data obtained while the Langmuir, Freundlich, Temkin and Dubini-Radushkevich isotherm models were used in the equilibrium studies of adsorption data. The results obtained from the research showed that the Langmuir model was the best fit model amongst the three model considered, obtaining a high correlation coefficient R^2 of 0.998. Pb (II) from aqueous streams was expunged using agricultural waste materials absorbents such as leaf base (petiole) and fiber of palm tree (Hikmat *et al.,* 2014). The BET surface area of the powder was measured prior and afterwards activated to petiole and fiber charcoal powders at 900°C. Variation of contact time (5 – 120 min), effect of pH (3.5 – 9), adsorbent weight effect (0.1g – 1.2g), effect of initial metal concentration (5mg/l) at a maximum removal percentage of 96% of Pb(II) using fiber. The Langmuir and Freundlich adsorption isotherm model was observed, but the Langmuir model did better with correlation coefficient R^2 value of 0.9974 and 0.9801 for petiole and fiber adsorbent respectively. The

investigated kinetics parameter showed that the pseudo-first-order model best fitted the experiment, displaying a correlation coefficient R^2 values of 0.9720 and 0.9773 for petiole and fiber respectively.

Ayyappan *et al.* (2005) made use of carbon obtained from pith, bagasse and saw dust collected from pulp, paper, and sugar industry respectively for the absorption of lead (Pb) from aqueous solution. Concentrated sulphuric acid was used to activate the materials and then placed in an oven at 150°c for 24 hours. The optimum absorption capacity was 2gd/m³ under conditions pH (5.0), 30mins contact time. Findings indicated that uptake of Pb(II) increased slowly and reached optimum level at 120 min. with piths based carbon. Saw duct carbon and bagasse carbon optimum uptake was above 90% of the same contact time. The adsorption isotherm explained in the study followed both Langmuir and Freundlich model. Kinetic modelling of data was performed using Largergren fist order rate equation. Desorption studies was also conducted using eluted 0.1M HNO_3 with 96% metal recovery. The carbon regeneration process was achieved by washing the sample with 0.1M $CaCl_2$

Bhattacharyya and Sharma, (2004) experimented on the adsorption of Pb (II) from water using mature Neem (*Azadirachta indica*) leaves. The adsorbent had an optimum removal efficiency of 93% at 300mins of agitation time. The first-order and second-order kinetics model were used to explain the adsorption mechanism, but the adsorptive performance corresponds to pseudo–second–order model. The equilibrium studies were described by the Langmuir and Freundlich isotherm models with correlation coefficient values of 0.99 respectively. Meanwhile, the dimensionless parameter R_L remained within the range 0.01 and 0.43. Wong *et al.,* (2003) analyzed the removal of lead (Pb) by means of a batch experiment using rice husk modified with tartaric acid. The sorption process relied on pH and displayed attributes of exothermic reaction. In his research, he mentioned the usability of rice husk in adsorption. Citric acid was also used at increased temperature to improve its adsorptive capacity. Citric acid was combined with cellulosic hydroxyl group forming a linkage which gives a carboxyl outcome. The cellulose content within the rice husk ranged from 28% – 36% which qualifies for transmogrification with carboxylic acids. The experiment is characterized by high sorption tendencies. Pseudo-second-order

model interpreted the kinetics of reaction better than pseudo-first-order model with evidence of high coefficient of correlation. This research has shown that modified rice husk with tartaric acid is a potentially material for Pb removal.

Parameters affecting heavy metal adsorption
pH effect

The pH of any solution to be considered for adsorption has an undeniable influence on metal intake. Within a certain range of pH, majority of adsorption increases with an increase in pH up to a value where a further increase in pH results in a decrease in adsorption. Park *et al.* (2010) explained that the pH has an effect on the surface charge of the adsorbent, speciation and degree of ionization of the metal ions, as well as causing competition between metal ions and solution. The significance of pH could be linked to the contribution of the functional group during metal adsorption (Kumar *et al.,* 2012). The pH_{zpc} of the adsorbent (the stage at which the adsorbent is neutral) may also serve as a contributing factor to the entire pH. Ahmaruzzamam, (2011) indicated the importance of the pH_{zpc} of the adsorbent. He explained that when the pH_{zpc} is higher than the pH of the media, it creates a positive surface charge on the adsorbent while in cases where the pH^{zpc} is lower than the pH of the media, a negative surface charge is seen on the adsorbent. Although, an increase in pH above the pH^{zpc} displays a negative surface charge, an increase in adsorption is obtain provided the metal species are neutral or charged. However, a decrease in adsorption is proof that both the metal species and the surface charge of the adsorbent are negatively charged.

Different authors have conducted several researches in the adsorption of divalent metals. They reported that an increase in adsorption is achieved with a corresponding increase in pH, with notable difference with pH values around 5 (Nhrchi and Villaescusa, 2008). Optimum removal has been reported for different divalent metals at pH 5.0. They include rice bran (Montanher *et al.,* 2005), nut shells (Basso *et al.,* 2002), papaya wood (Saeed *et al.,* 2005), black gram husk (Saeed *et al.,* 2005), sour orange residue (Khormaei *et al.,* 2007), cashew nut shell (Kumar *et al.,* 2012; Senthil – kumar *et al.,* 2012), watermelon rind (Liu *et al.,* 2012), Husk of *lathyrus sativus* (Panda *et al.,* 2008), soyabean meal waste (Witek – Krowiak *et al.,* 2013), pine cone powder (Ofomaja *et al.,* 2010). Also, optimal pH of 5.5

was obtained for grape stalks (Martinez *et al.,* 2006) and Chaff (Han *et al.,* 2005). Other studies reported increase in adsorption with varying pH; Grafted copolymerized orange peel [pH 2.0 – 5.5] (Feng *et al.,* 2011), potato peels [pH 2.0 – 6.0] (Taha *et al.,* 2011), hazelnut shell [pH 5 – 7] (Demirbas *et al.,* 2008), orange peel [pH 5 – 7] (Liang *et al.,* 2010).

Temperature effect

A substantial number of biosorption studies have been carried out by researchers on the effect of temperature on metal adsorption. Not only that temperature alters the solubility of the metals, but also the diffusion rate is affected (Park *et al.,* 2010). Therefore, temperature is also regarded as a contributor to metal adsorption owing to the different functional group of the agricultural adsorbent. However, many studies have discussed minimally the extent at which temperature can affect adsorption while some considered is at a certain range (Sahmoune *et al.,* 2011). The effect of temperature affects adsorption process either in endothermic or exothermic form. Exothermic adsorption was reported by Kumar *et al.,* (2012) using cashew nut shell to adsorb Cd(II) ions. He recorded a decrease in adsorption when temperature increased from 30°C to 60°C. El – Sayed *et al.,* (2011) also gave a similar report while using maize stalk for Zn(II), Cd(II) and Mn(II) adsorption. The adsorption capacity decreased from 52% to 38%, 34% to 16% and 39% to 13% for Zn, Cd, and Mn respectively when the temperature was increased from 25°C to 55°C. Han *et al.,* (2005) also discovered that an increase in temperature from 20°C to 30°C resulted in a reduction in the metal uptake using chaff. However, some endothermic cases have been reported in the literature. In Pb(II) and Cd(II) sorption using stalk sponge of Zea mays (Garcias – Rosales and Colin – Crus, 2010), an increase in adsorption 1.1 – 1.8 times were recorded when the temperature rose from 20°C to 40°C. Ozcan *et al.,* (2005) also reported a similar trend when *capsicum annuum* seed was used for Cu(II) sorption at an increased temperature of 20°C – 50°C. Banerjee *et al.,* (2012) reported similar tendencies in the adsorption of Cu(II) using watermelon shell. Nevertheless, a report was given by Park *et al*., (2010) with claims that heightened temperature may result in physical deformation of the adsorbent. In line with this, ambient temperature is mostly adopted in several adsorption studies.

Table 8: Adsorption potential of some agricultural adsorbents in the removal of Pb(II) ions from aqueous solution

Adsorbent	Modifying agent	Experimental variables considered	Constants	Suited equilibrium model analysis (EMA)	EMA R2 value	Kinetic model analysis (KMA)	KMA R2 value	Optimum conditions	% Removal	References
Soybean oil cake	K_2CO_3	Initial concentration, Contact time, Dosage, pH	Agitating speed, Dosage	Freundlich Isotherm model	0.9624	Pseudo – second – order	0.9995	pH 6.0, Temp 15°C,	Adsorption capacity 244.9mg/g	Erdem et al. (2013)
Ailanthus Excelsa tree bark	NaOH	pH, dosage, Contact time, initial concentration	-	Langmuir Isotherm Model	>0.944	Pseudo – second – order	-	pH 4.5, at 360mins, 22.72mg/g	-	Waghmare and Chaudhari, (2013)
flamboyant flower (*Delonix Regia*)	-	pH, Initial concentration, dosages, contact time	Temperature	-	-	Pseudo – second – order	0.9997	pH 5.0 at 60mins	-	Jimoh et al. (2012)
Cladophora rivularis	-	pH, contact time, temperature	Initial concentration, dosage	Freundlich Isotherm model	0.984	-	-	pH 4.0	97% Removal	Jafari and Senobari, (2012)
Verbenacea e leaves	Citric acid	Initial concentration Contact time	Temperature, dosage	Freundlich Isotherm model	0.946	-	-	5mg/l at 90mins	-	Tijani et al. (2011)
Date stems	Nitrate Solution	pH, initial concentration, dosage, temperature Contact time,	Agitation	Langmuir and Freundlich Isotherm models	0.978 and 0.979	Pseudo – second – order	1	pH 2 - 4, 30°C for 60min	97% Removal Adsorption capacity 5.15mg/g	Yazid and Maachi, (2008)
Coconut husk	-	initial concentration, temperature Contact time,	Dosage	Langmuir and isotherms models	0.987	Pseudo – second – order	0.910	30ppm, pH 5.0 for 30mins at 100oC	94%±3.2% Removal	Abdulrasaq and Basiru, (2010)
Birbira militia ferruginea leaves	H_2SO_4	pH, temperature, Concentration Contact time,	Dosage	Freundlich Isotherm model	0.9252	Pseudo – first – order	0.9998	pH 4.0 at 180 min. using 4g dosage	97.3% Removal	Mengistie et al. (2008)

Particle size effect

Metal adsorption capacity can be affected significantly by the total available surface area of the adsorbent, and this is a function of the particle size. The intra – particle diffusion model showcases how adsorption rate is significantly affected by particle size (Naeem *et al.,* 2007). A reduction in particle size would result in an increase in surface area and subsequent increase in adsorption capacity. Apart from the adsorption noticed at the surface of the adsorbent, there is likelihood of intra – particle diffusion from the surface of the pores of the adsorbent. Therefore, larger particles tend to produce resilience to mass transfer (Ahmaruzzaman, 2011). The internal surface area of the adsorbent particle may not be adequately utilized due to some deterrent factors such as resistance to mass transfer activities, time of contact and obstruction of diffusional pathway culminating to a reduced adsorption capacity. Notwithstanding, adsorption efficiency depends largely on the available surface area required for solute interaction.

Kelly–Vargas *et al.,* (2012) investigated the sorption of metal using banana peel and discovered increased adsorption up to 12% with 1mm particle size than 2mm particle size. Amarasinghe and Williams, (2007) investigated particle size impact on the sorption of Cu(II) ions using tea waste. The experiment made use of particles of 575 μm, 925 μm and 1250 μm and the removal efficiencies recorded were 57%, 53%, and 41% respectively. Banerjee *et al.* (2012) reported similar experience of high adsorption efficiency using smaller particle sizes of watermelon. Contrarily, Taha *et al.* (2011) discovered that reduced particle sizes of potato peel did not alter the removal efficiencies of Cd(II) and Pb(II). Kaewsarm *et al.* (2008) conducted a similar study on the use of banana peel for Cd(II) removal and reported no noticeable effect when different particle sizes were administered. He also argued that increased adsorption attributed to smaller particle sizes may not be linked to their increased surface area. He further explained that irrespective of the particle size, grounded particles agglomerate to form similar thickness, making it difficult to observe its effect.

Effect of concentration

The initial concentration is also one of the pathways by which the migration of heavy metal to the surface of the adsorbent can be promoted (Taha *et al.,* 2011; Sahmoune *et al.,* 2011). A significant number of studies have been published to elucidate the effect of baseline concentration on metal adsorption using agricultural adsorbent. A common trend has been identified showing the relationship between maximum adsorption capacity and initial concentration. The trend explains increasing adsorption with increased initial concentration. Reddy *et al.* (2010) reported in increase in Pb(II) sorption from 12mg/g to 23mg/g with a corresponding increase in the initial concentration from 10 to 40mg/L. Kumar *et al.* (2012) reported a similar case in Cd(II) sorption from 2.671mg/g to 11.095mg/g in line with increased initial concentration from 10 to 50mg/L. This phenomenon could be as a result of increased collision between the agricultural adsorbent and the metal ion (Wang and Chen, 2010).

In contrast, the removal efficiency can be reduced as a result of increased initial concentration. Kannan and Vermaraj, (2010) identified that the adsorption sites on the surface of the adsorbent are responsible for this action. Kannan and Vermaraj, (2010) confirmed the behaviour with jack fruit seed in the adsorption of Cd(II). Notably, a reduction in adsorption was obtained from 66.28% to 22.43% with increased concentration of Cd(II) ions from 10 to 100ppm. Kumar *et al.* (2011) made a contribution by attributing the phenomenon to the reduced rate at which metal ions are transported to the adsorbent surface. Kumar *et al.* (2012) also confirmed the behaviour using cashew nut shell in the adsorption of Cd(II) ions. Concentration change from 10 – 50mg/L caused a reduction in metal efficiency from 80.13% to 66.57%. Ashraf *et al.* (2012) identified a similar scenario with Ni(II), Cu(II), Pb(II) and Zn(II) sorption using banana peel. A peak concentration of 150mg/L resulted in 63.23%, 68.10%, 79.55% and 92.52% removal efficiencies for Zn(II), Ni(II), Pb(II) and Cu(II) respectively. The minimum concentration used for the study (25mg/L) produced metal removal percentages of 82.36%, 84.63%, 86.81% and 94.80% for Ni(II), Zn(II), Pb(II) and Cu(II) ions respectively.

Effect of contact time

According to literature, some adsorption experiments tend to be quicker than the others. In a research conducted by Hossain *et al.* (2012) in the adsorption of Cu(II) ions unto banana peel, a quick adsorption was noticed during the first 30mins, accompanied by uniform removal rate of Cu(II) farther than 30mins until equilibrium was attained. Elmorsi *et al.* (2014) reported a similar case while using dobera

leaves for Pb(II) sorption. 83% removal efficiency was attained in the first 15mins. Shi *et al.* (2015) iterated similar incidence when arborvitae leaves were adopted for Pb(II), Cu(II) and Co(II) removal. They discovered increasing adsorption capacity with increasing contact time with which equilibrium was attained at 120mins. Desta, (2013) pointed out a rapid scenario where an initial increase was identified until optimal removal efficiency was reached within 60mins. In this case, teff straw was used to remove Pb(II), Cu(II) and Cd(II) and Cr(II). El–Ashtoukhy *et al.* (2008) investigated the effect of contact time in the adsorption of Pb(II) and Cu(II) removal using pomegranate peel. The research stated that maximum saturation was achieved in about 120min, but a decrease in adsorption was noticed until optimal sorption was reached. Shafaghat *et al.* (2012) used five plants adsorbents to investigate the sorption of Pb(II), Cu(II) and Cr(II) and discovered three of the adsorbent achieving maximum removal in 90mins. (Achak *et al.,* 2009; Srivastava *et al.,* 2006) gave an explanation that the saturation of the binding sites causes a repelling force occurring between the metal ion located at the adsorbent surface and liquid phase thereby making it uneasy for the remaining surface sites to undergo further binding. As such, metal adsorption tends to decrease gradually with increase in contact time. The resistance experienced when metals tend to bind while passing through the surface pores are substantial reasons why reduced adsorption is obtained at the later phase (Srivastava *et al.,* 2006). Shafaghat *et al.* (2012) supported the statement by attributing the rate of adsorption occurring in the later phase to the movement rate of metal ions from the external to the internal sites of the adsorbent particles.

Effect of ionic strength

Holistically, the rate of adsorption is inversely proportional to the ionic potential of the aqueous solution. It is as a result of alteration in metal activity or in the characteristics of the electric double layer. In my little knowledge about surface chemistry, when adsorbent particles interact with metal species in aqueous state, an electric double layer is formed around the particles and metal species. Electrostatic interaction triggers this layer, but a decrease in adsorption may result in an increased ionic strength if electrostatic bonding powers the adsorption process. Nguyen *et al.* (2013) espouses a statement that an ideal wastewater sample is characterized by different metal

ions, not just only heavy metals. Most of the metal ion found within are Ca^{2+}, Na^+, K^+, and Mg^{2+} but chemical compounds such as KCl, $MgCl_2$, $NaNO_3$ are introduced to examine the impact of ionic potential in adsorption efficiency. Fiol *et al.* (2006) investigated the effect of $NaClO_4$ and $NaCl$ on the adsorption efficiency using olive stone waste. He discovered that both compounds instigated a rapid decrease in metal sorption up to 70% except for copper. The reaction was affected more by $NaCl$ than $NaClO_4$. Villaescesa *et al.* (2004) also noticed a decrease in metal removal of Cu(II) and Ni(II) using grape stalk waste when $NaCl$ was introduced. The notable decrease in metal sorption, as reported by some authors, is as a result of competing Na^+ ions present during metal binding (Lee and Yang, 1997). Other authors are of the opinion that increase in ionic strength triggers a decrease in adsorption especially when there is electrostatic lure between the adsorbate and adsorbent (Stumm, 1996). El – Sayed *et al.,* (2011) reported a similar case with an indication that a reduction in metal adsorption efficiency is connected to an increase in ionic strength. They attributed the findings to reduced metal ion activity and increase in competing cations. Njoku *et al.* (2011) considered the effect of Ca^{2+} and Na^+ on the adsorption of metal ion and observed that Ca^{2+} affected the adsorption process more than Na^+ with reasons that divalent ions (Ca^{2+}) have stronger tendencies to compete for binding sites than monovalent ions (Na^+). On the contrary, Reddy *et al.* (2010) reported no considerable effect when adsorption of Pb(II) was conducted in the presence of Mg^{2+}, Ca^{2+}, Na^+, K^+ using *M. Oleifera* leaves.

CONCLUSION AND RECOMMENDATION

No doubt the performance of low–cost agricultural adsorbents is high in eliminating heavy metals, but one key relevant information to observe in all is that the effectiveness of any adsorbent is different for each pollutant, and this solely depends on the experimental conditions. Some of the low – cost adsorbent used for metal uptake are offshoot or byproducts of agricultural waste materials, and this has resulted in waste reduction and also a cut down in waste disposal cost. In this review, removal of Cu(II), Pb(II) and Cd(II) ions from aqueous solution using agricultural adsorbent have been rigorously studied. However, several limitations have been identified that needs to be addressed adequately.

1. In the literature, most researchers reported single–component metal adsorption using several adsorbents,

only a few conducted multi–component adsorption. However, limited data on the adsorption of metal pollutants combined with organic and other contaminants is available. Therefore, competitive metal adsorption needs to be addressed to encourage commercial application and production and also proffer solutions in areas of treatment of industrial wastewater being released into the environment, especially in developing countries.

2. It is imperative to note that amongst the abundant literature in adsorption studies, only a few reported adsorption using column operations. Most of the studies were conducted using batch operations. Therefore, adsorption using column operations should be performed in laboratories making use of these adsorbents to see their efficacy in commercial scale.

3. It is a known fact that metal adsorption is pH dependent. Although in most publication, the pH effect in relation to the initial pH of the solution is scarcely discussed. Most studies did not report the variation of the solution pH throughout the adsorption process.

4. Further investigation needs to be conducted to identify the component within the adsorbent compound that is responsible for metal attraction, development of functional group and surface area. Also, some death still exists in literature in identifying ways to enhance the metal attracting component so that increased adsorptive capacity can be attained.

5. Several procedures have been adopted in the literature towards the production and workability of low – cost agricultural adsorbent, yet there is a need to optimize the conditions required to produce modified agricultural adsorbent using various reagents.

6. To obtain maximum removal of selected metals, it is important to select and identify an appropriate agricultural waste as adsorbent that will provide efficient adsorbent – adsorbate interface.

7. Adsorption studies as seen in most article adopts single adsorbent, only a few considered hybrid composition in their research. Extensive studies are therefore required to investigate the potentials of hybrid adsorbents that can effectively enhance adsorption capacities.

8. In the literature, adsorbent surface modification serves as a condition for increased metal uptake and most investigations reported the surface area of the modified sample. The surface area translational phase from the ground raw sample to initial carbonization and subsequent chemical activation were not mentioned in any study.

9. Modifying an adsorbent can lead to the formation of new functional group, facilitate ion exchange mechanism and the development of new active binding sites. Various modification procedure on low – cost adsorbents made use of acids, base and other chemical reagents such as ethylenediamine, hydrogen peroxide, formaldehyde, methanol, etc. which has proven to enhance metal uptake efficiency. More attention should be geared towards the cost of modifying an adsorbent so that it's economic viability can be optimized.

10. Further studies on metal recovery and adsorbent regeneration need to be investigated in detail. Since indiscriminate dumping of industrial waste loaded with heavy metals is regarded as a big environmental problem that requires urgent attention, extensive research should be carried out to provide environmentally friendly disposal methods for metal – impregnated adsorbents. This will help in curbing environmental pollution and also promote the practicability of the adsorption process.

11. For any product to be economically feasible and commercially available, the cost implication is a key factor to be considered. Most articles did not report the cost of producing individual agricultural adsorbent that displayed high removal efficiency. The cost of production of individual adsorbent differs, taking into account its availability and processing conditions. However, adsorbents with high removal efficiency are suggested with conclusions on cost effectiveness and technical applicability. If these agricultural adsorbents are highly efficient in removing metal pollutants with supposed low cost, then the cost implication analysis using different low – cost adsorbent should be investigated on an industrial scale to estimate its cost efficiency and economic profitability.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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