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A Review on Adsorption of Heavy Metals from Wood-Industrial Wastewater by Oil Palm Waste

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ABSTRACT

The use of heavy metals in the manufacturing industry over the past few decades has eventually contributed to a rise in the flow of metallic compounds into wastewater and has raised significant ecological and health threats to living things. Adsorption is an excellent way to treat solid waste effluent, offering significant benefits such as affordability, profitability, ease of operation and efficiency. However, the price of commercial adsorbent namely activated carbon has soared due to its high demand. There is also a green improvement in this method by turning the commercial adsorbent into agricultural waste. In Malaysia, the oil palm waste is such suitable material that can be utilized for making activated carbon, since they are ample and easy to find. Additionally, part of them is agricultural waste that cannot be consumed (i.e. leaves and fronds). Hence, this study aimed to analyse the potential of activated carbon from agricultural waste, namely oil palm waste, in reducing the levels of heavy metals in industrial wastewater.

Keywords: industrial wastewater, heavy metal, adsorption, activated carbon, oil palm waste

INTRODUCTION

Heavy metal is a collective term for the chemical elements that have an atomic density above 4 g/cm^3 (Aprile and Bellis, 2020; Abdullah, *et al.*, 2019). The heavy metals generated from industrial-based wastewater may contain a large number of elements. These elements can be divided into four major categories: (i) toxic heavy metals (Chromium (Cr), Lead (Pb), Zinc (Zn), Copper (Cu), Nickle (Ni), Cadmium (Cd), and Arsenic (As)) (Altowayti et al., 2020) (ii) strategic metals (Manganese (Mn) or Tungsten) (W)) (iii) precious metals (Silver) and (iv) radio nuclides (Uranium (U), Thorium (Th), Americium (Am)) (Wang and Chen, 2009). In terms of environmental threats, categories (i) and (iv) are more preferred for removal from the environment or from point source effluent discharges (Ahalya, 2003). Due to this threat, the Environmental Protection Agency (EPA) and world health organization (WHO) have regulated the maximum acceptable discharge level of concentrations for Zinc (Zn), Copper (Cu), Chromium (Cr), Lead (Pb), Nickel (Ni) and Manganese (Mn) which are 3.0 mg/L, 2.0 mg/L, 0.05 mg/L, 0.1 mg/L, 0.02 mg/L and 0.05-0.5 mg/L, respectively (ATSDR, 2012; EPA, 2016).

The presence of all metal elements cannot be seen with naked eyes in the polluted wastewater. However, it is often the root cause of various severe health issues. Metal toxicity is the term for the toxic effect of certain metals in certain forms and doses on life. The severity of the toxicity of heavy metals on health is highly variable and depends on varying parameters. They can easily carry the diseases that eventually pose significant hazards to the ecosystem health, especially human and animals. Therefore, extensive removal of toxic heavy metals from the environment has become an important challenge among researchers. Over the years, different approaches have been developed to extract the metal elements from wastewater by prioritizing simple, efficient and cost-effective techniques as a fundamental concept. The suggested methods include chemical precipitation, ion exchange, coagulation and flocculation, adsorption, and membrane processes (Shafiq *et al.*, 2018; Goher, 2015; Ahalya, 2005). However, the drawbacks of these methods include their high cost and lower adsorption capacity in the low concentration range, particularly in the range between 1 to 100 mg/L (Negm *et al.,* 2017; Rahman *et al*., 2014)

The selection method to be used in the treatment system usually depends on the wastewater characteristics. Each treatment has its own constraints, not only in terms of cost but also in relation to feasibility, efficiency, practicability, reliability, environmental impact, sludge production, operation difficulty, pre-treatment requirements and the formation of chemical residues (Crini and Lichtfouse, 2019; El Nadi and Alla, 2019). For adsorption, the main constraint is the cost of raw materials of activated carbon (AC). According to Research and market (2018) the top producer of AC which is China shows an increasing demand of AC starting from 2011. The market is booming further under the propulsion of national policy and demand growth, and the output of an average annual growth rate (AAGR) is estimated to maintain at least 5.0% during 2018 to 2023. In terms of prices, the cost of coal-based activated carbon increased by more than 20% from RM 3708/ton at the beginning of the year to around RM 4500/ton at the end of the year; the wood-based activated carbon prices increased by about 13.0%. This is mostly due to the increasing demand and higher production costs. In order to solve this problem, many researchers have adjusted the adsorption method by changing the utilization of commercial adsorbent to agricultural waste (Alalwan *et al.,* 2020; Yunus *et al.,* 2019; Saxena *et al*., 2017; Negm *et al.,* 2017, Demirbas, 2008).

In Malaysia, palm oil is a major agricultural industry which has helped to change the scenario of its agriculture and economy. Nevertheless, despite the obvious benefits, oil palm mills also significantly contribute to the environmental degradation. The Malaysian palm oil mills generate an abundance amount of lignocellulosic biomass derived from fronds, empty fruit bunches and trunks. Annually, about 36 million tons of these wastes are generated and most are either left in the plantations or burned illegally (Azemi *et al*., 2000). Recently, Oil palm waste has been widely used in AC by applying various activation methods and degrees of processing to have small, low-volume pores that increase the surface area and it is often used as bio-sorbent in the adsorption method. The present study discusses in systematic mode the types of heavy metals originating from wood-based industry, the effects of generated heavy metals towards living things and heavy metals removal by adapting oil palm waste as adsorbent and their future direction.

Wood-based industrial wastewater

Several studies show that the main factor to the ecological risk index comes from various anthropogenic influences, such as industrialization and urbanization (Demaku *et al*.,2020) Wood-based industry encompasses the production of sawn timber, veneer, panel products (including plywood, particleboard, chipboard, and fibreboard), mouldings, and builder joinery and carpentry (BJC), as well as furniture and furniture components (Malaysian Investment Development Authority, 2020). The wood-based panel sectors and furniture manufacturing usually differ in terms of water usage through the production process. Unlike pulp and paper production, the wood-based panel and furniture sectors are commonly considered to be a dry sector with low water consumption. Therefore, their discharge problems are often being neglected. Nevertheless, according to Maminska (2020) and Bouchareb (2020), wood production plants use between 300 m^3 per day and can generate up to ca. 600 MLN m^3 of wastewater every year. Results from Chu and Kumar (2020) assessments indicated that pollutant index of these industries on waste water discharge were significantly increased five folds between 2015 and 2017.

The wastewater generated from wood-based industries exerts harmful effects on the environment due to substantial concentrations of dangerous chemicals. Wide range of various substances are among which wood degradation products, wood extractives, heavy metals or even surfactants introduced during cleaning processes can be found (Kloch and Maminska, 2020). The existence of heavy metals presence in this type of industries is verified in different stages of related production on previous studies (Kloch and Maminska, 2020; Jones *et al*., 2019) Whereby, arsenic (Ar), copper (Cu), chromium (Cr), zinc (Zn), manganese (Mn) and Iron (Fe) are such metal elements that often associate (Rudi *et al*., 2020; Demcaka *et al*., 2019; Jones *et al*., 2019)

Heavy metals

Heavy metal can be categorized as essentials and non-essential toxic; however, they become noxious with long-term exposure or exceeding certain threshold concentrations. In general, heavy metals are non-degradable and some of them were toxic even at trace levels (parts per billion, ppb). The metal ions can bio-accumulate in the main systems of living thing and cause hazardous impacts to plants, animals, and humans (Abdullah *et al*., 2019).

Effect of heavy metals toward humans, plants and animals

With modern life, extensive use of heavy metal in the manufacturing and production industry resulted in metal ions reaching living organisms throughout the disposing wastes. Discharging heavy metals into the river caused the element to gradually accumulate at the bottom of the river. Subsequently, the accumulation of heavy metal will be re-released into the surface water due to environmental changes, such as sediment resuspension and reduction– oxidation reaction that will extensively increase the heavy metal concentrations. Ultimately, heavy metals are absorbed and bio-magnified in food chains, threatening the aquatic life and human health.

According to Sevim (2020), the exposure to heavy metal can lead to human death and disability. The study evinced the potential association between the heavy metal toxicity and cardiovascular disease. Elicit detrimental effects of heavy metals on the Cardiovascular system, resulting in pathophysiological changes, such as increased oxidative stress, inflammatory response, DNA damage, apoptosis, and atherogenic events, including hypertension, coronary and peripheral arteries abnormalities. In addition, heavy metals are often linked with carcinogenic effects. The International agency for Research on Cancer have categorized Arsenic (As), cadmium (Cd), chromium (Cr), and nickel (Ni) compounds as group 1 carcinogens (Kim *et al*., 2015; Kalagbor *et al*., 2019). The exposure to these heavy metals is associated with lungs, liver, nose and kidney cancers (Kalagbor *et al*., 2019).

The aforementioned heavy metals were essentials in some perspective ways (Yunus *et al.,* 2020). However, the toxicity of some essential heavy metals, such as copper (Cu), was also reported. Copper is a beneficial trace element for the growth and development of all known organisms, including humans and other vertebrates. Whereby, Cu acts as a co-factor of metalloenzymes (Pavelkova *et al*., 2018). Nevertheless, in China, a study by Bao (2020) found that copper gives acute and chronic toxicity effects to their commercially wild freshwater crayfish named Cambaroides dauricus (CD). The long-time exposure to sub-lethal levels of Cu in crustaceans impacted their survival, behaviour, and reproduction, which eventually change the population quantity.

Apart from human and animals, plants were also commonly affected by heavy metal pollution (Abazi *et al*., 2018). Irrigation is the main sources of heavy metal intake by plants; whereby, 27% of national and international vegetables or plants are being irrigated with wastewater, which includes sewage and industrial effluents (Latif *et al*., 2020). A pilot study from Hatamian (2020) determines the interaction of lead (Pb) and cadmium (Cd) on growth and leaf morphophysiological characteristics of European hackberry (Celtis australis) seedlings. The results shows that the Pb and Cd (5 mg L^{-1} for Cd and 15 mg L^{-1} for Pb) concentration significantly reduced new shoot growth, plant leaf area, SPAD value, leaf water conductance and leaf photosynthesis. Higher reduction was observed in new shoot growth and leaf water conductance over the interaction of 30 mg L^{-1} Pb levels.

In order to control the risks effects toward living things and environment, many countries have legislated limits for each of heavy metal disposal. In Malaysia Department of Environment is responsible in issuing Environment Quality Act 1974. Under industrial effluent sub-content, using regulation 2009, standard A prescribed the effluent discharge limit of heavy metal into any inland water within the catchment and standard B to any other inland water or Malaysian waters. Due to the rules and permissible limits, the industrial sector needs to ensure their effluent discharge is below than the allowable limits. Wastewater treatment plant (WWTP) which contains primary, secondary and tertiary treatment stages was developed to control the effluent rate released. This has attracted the attention of researchers to introduce a variety of more effective wastewater treatment methods in proportion to the industrial wastewater sector.

Method for removing heavy metals

To date, different processes to eliminate various metal elements from wastewater before entering into the water stream have been developed. The process is such ion exchange, coagulation and flocculation, adsorption, membrane filtration and chemical precipitation. These processes were usually positioned at different stages in WWTP. The descriptions of different process are given in Table 1 along with their advantages and disadvantages (Abdullah *et al*., 2019)

Researchers employ different efforts and approaches to show the efficacy of the process/method of wastewater treatment they perform. A study conducted by Kloch and Maminska (2020) stated that coagulation using aluminium sulphate ($Al_2(SO_4)_3$) was among the most popular treatment techniques that are utilized for wastewater treatment from the wood-based industry. The removal efficiency of organic compound is reported up to 50%; however, this technique is accompanied with the introduction of chemicals to the wastewater during treatment that caused secondary pollution and generated toxic sludge, such as Al that needs to be managed.

Meanwhile, membrane separation is widely used as an advanced technology in wastewater treatment due to its lenient operational conditions. However, the high operational costs and low efficiency has restricted the use of this treatment processes, especially in small and medium scales of the industrial sector (Zhu *et al*., 2019). Out of the mentioned methods, adsorption has been effectively applied in recent decades (Siyal *et al*., 2020). Continuous research has been conducted since adsorption is considered as a cost-effective and efficient technology as many adsorbents can be provided by forestry and agricultural residues (normally biomass) with one method of “dealing with waste by waste” (Esfahlan *et al*.,2020; Shahrakia *et al*., 2021).

Adsorption

Adsorption in aqueous solution is defined as unit operation that exploits the attraction of solutes (atoms, molecules or ions) in a liquid to a solid surface (Gabelman, 2017). In this process, the solid is called as adsorbent and the solute is known as adsorbate. In order to ensure the treatment process, the bonding interactions between adsorbent and adsorbate should eventuate. The exact nature of the bonding depends on the details on the species of adsorbent and adsorbate involved, but the adsorption process is generally classified as physisorption or chemisorption (Erkey, 2011)

Table 1. Different methods in removing heavy metals from wastewater (Abdullah et al., 2019)

Methods	Description	Advantages	Disadvantages
Precipitation	Metal ions is converted into insoluble precipitates of either hydroxide, sulphide, carbonate and phosphate by using chemical agents. The solid precipitate is later separated by filtration process	-Simple and easy method with high degree of selectivity -Precipitants are commonly inexpensive	-Does not suitable to treat water with high concentration of heavy metals -Requires high amount of precipitate agents -Produce large number of toxic sludge
Coagulation and flocculation	Coagulant with positive charge is present to reduce surface negative charge of particles and allow them to aggregate. The positive charges aggregates will then bind with anionic floacculant. The larger group formed will then be separated using filtration process	-Cost effectives if inexpensive coagulant is used - Easy operation	-Deficient metal ions removal - Need to be paired with precipitation method to gets the effective removal - Creating unwanted sludge
Adsorption	Highly porous, large surface area, active functional group of adsorbent materials is used to ensnare the metals elements ether using physical or chemical interactions.The adsorbents are later separated from solution by filtration process and undergo regeneration process.	- Extensive choices of adsorbents materials - Economical - Easy operation	-Due to Van der Waal’s forces nano-size adsorbents are unable to give encouraging results - Some of the adsorbents need to be modified for maximum adsorption capacity
Ion exchange	Resin with strong sulfonic acid group (–SO3H) or carboxylic acid group (–COOH) is mostly utillized in this process. Reversible exchange happened when H+ is released from the functional groups which ultimately allow complexation of metal with the free functional group	-Fast kinetic - Practical process - Uses low-cost materials and resin can be re-generated which resulted as economic method	-Fouling of metal ions on ion exchange media -Fit only in low concentration of metals - High responsive to pH value - Presence of free acids may result in low binding affinity

Classification of adsorption

The classification of adsorption is often described as physisorption and chemisorption. This classification depends on the strength of the interaction between the substrate and adsorbate. This interaction is determined during the isotherm and kinetic study. As for example, if the kinetic model is fitted to a pseudo second-order model, it assumes that two surface sites can be occupied by one adsorbate ion; these suggested that the adsorption is classified as chemisorption. (Abesekara *et al*., 2020)

Physisorption is a broad term that describes all weak electrostatic interactions including Van Der Walls, hydrogen bonding and the dipole dipole interactions between the sorbent and sorbate whereby the interactions are typically range from 0.2 to 4 kJ/mol (Sims *et al*., 2019). These bonds are considered the weakest of interactions and can be easily broken. Physisorption takes place at the low temperature and decreases with increasing temperature, as shown in Figure 1 (Milan, 2014; Mathew *et al*., 2016).

Chemisorption proceeds by exchange or sharing of electrons between the sorbate and sorbent to create a covalent or iconic bond (Kwon *et al*., 2011). In other words, chemisorption is based on chemical reactions between the adsorbate and the surface sites of the adsorbent (Patel, 2019). The strong chemical bond provided from adsorbate and adsorbent make it more difficult to reverse and requires more energy to remove the adsorbed molecules than physical adsorption does (Sarbu and Sebarchievici, 2017). Chemisorption first increases along with the temperature and there is an optimal strength of chemisorption (called “the volcano curve theory”) as shown in Figure 2 (Milan, 2014; Mathew *et al*., 2016). The differences between physisorption and chemisorption are summarized in Table 2 (Milan, 2014).

In general, chemisorption is more popular in heavy metal removal, because it has stronger interactions and higher adsorption capacity towards heavy metals (Khulbe and Matsuura, 2018).

Adsorption process

The adsorption process can be thought of as the separation of the adsorbent between the fluid phase and the adsorbent. If the solid and fluid are placed in contact for long time, an equilibrium distribution is reached and this equilibrium can be described quantitatively. The equilibrium behaviour is characterized by expressing the amount of adsorbate adsorbed as a function of partial concentration at a fixed temperature. Such equilibrium model was called isotherm (Gableman, 2017). The analysis of the isotherm data is important to develop an equation that accurately represents the results and which could be used for design purposes (Elsayed *et al*., 2020). The Langmuir and Freundlich isotherms

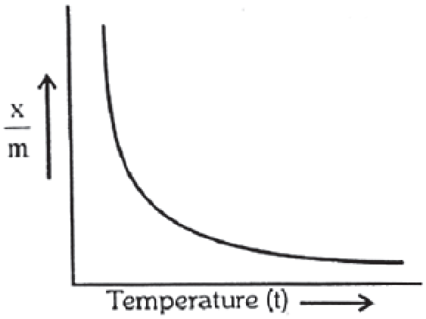


Figure 1. Adsorption isobar for physisorption

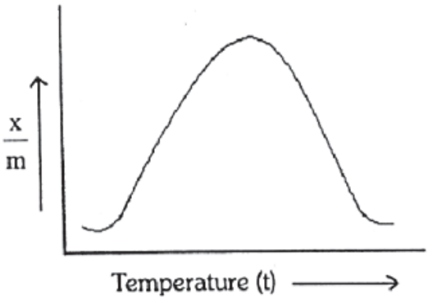


Figure 2. Adsorption isobar for chemisorption

Table 2. Comparison between physisorption and chemisorption

Properties	Physisorption	Chemisorption
Type of bonding forces	Van Der Wals	Similar to chemical bond
Adsorption heat	Low	High
Chemical change of adsorptive	None	Formation of a surface compound
Reversibility	Reversible	Irreversible
Activation energy	Very low	High
Formation of multi-layer	Yes	No

were two common isotherms used in the adsorption's studies (Table 3). The Freundlich isotherm is usually applied to characterize heterogeneous (multilayer) adsorption on the adsorbent surface, whereas the Langmuir isotherm was used to describe homogenous (monolayer) adsorption on the adsorbent surface (Duraisamy *et al*., 2020)

Factor Affecting Adsorptions

The interaction between adsorbate and adsorbent is influenced by some parameters, namely the operating parameters pH of solution, mass of adsorbent, and contact time (Othman *et al*., 2012). In order to evaluate the exact responses of these parameters under experimental conditions, batch sorption modelling is deemed pivotal.

Effect of contact time

Contact time is one of the major parameters that govern the adsorption processes. Determination of the optimum contact time for adsorption aims to determine the time needed by the adsorbent to absorb the maximum number of heavy metals. A study by Elsayed (2020) indicated that the removal percent of pollutants increases along with the contact time. According to Duraisamy (2020), this may due to the availability of greater biosorbent surface area at the opening of the adsorption of corresponding metal ions in the medium. Table 4 shows the summarization of previous study on the influence of contact time on adsorption of heavy metal removal.

Effect of pH

The pH is the most susceptible parameter in the adsorption studies due to the fact that H^+ is a strongly competing adsorbent. The pH affects the specification of metal ions and the ionization of surface functional groups (Elsayed *et al*., 2020). In addition, pH is considered to play a vital role inside the adsorption system, especially in the aqueous solution, since it affects the character of each ion to be removed and the adsorbents (where

Table 3. Recent view on best fitted isotherm and kinetic model on heavy metal removal

Adsorption isotherm		Kinetic model		Sources
Langmuir	Freundlich	Pseudo first order model	Pseudo second order model	
x			x	Singh *et al*., 2020
	x		x	Sayed *et al*., 2020
	x		x	Duraisamy *et al*., 2020
	x		x	Beidokhti *et al*., 2019
x			x	Aguilar *et al*., 2019

Table 4. Efficient contact time on adsorption of heavy metals

Adsorbent	Heavy metals	Remarks	Source
Palm Kernel Shell	Chromium, Lead, Zinc and Cadmium	Highest contact time at 120 min	Baby and Hussein, 2020
Palm Kernel Shell	Cadmium	Highest contact time at 150 min, decreases at 180 min	Faisal *et al*., 2019
Pomegranate peel	Nickle	Sharply increased during the first 30 min; gradually achieved the equilibrium in 150 min	ElSayed *et al*., 2020
Kenaf Fibre	Iron, Manganese, Zinc, Arsenic, Copper, Nickle	The contact time will eventually reach a maximum value at a certain point and remain constant	Saeed *et al*., 2020
Mango Leaf	Chromium and Iron	Adsorption takes place at 120 min. of interaction time	Duraisamy *et al*., 2020
Coffee Shell	Lead	In the first 30 min. until min. 90 the adsorption rate is slow; however, from minute 90until min. 150 ultimately the absorption equilibrium occurs.	Juniar *et al*., 2019
Chestnut Shell	Chromium	An increase in adsorption was seen at initial 60-300 min thereafter remained constant	Singh *et al*., 2020
Jackfruit Peel	Lead and Cadmium	Range of between 15 minutes to 24 hours. Adsorption was rapid during the first 1 hour of contact but gradually decreases up to the point where equilibrium is achieved.	Ibrahim *et al*., 2020
Oil Palm Ash	Manganese	Within 80 min the system reached equilibrium	Chowdhury *et al*., 2011

the adsorption phenomena disappear and change to precipitation when the pHs is set to more than 7) (Saeed *et al*., 2020). Thus, in order to achieve the maximum adsorption capacity during the batch study, a well-defined pH range is usually identified. Numerous previous studies observed that the adsorption of metal ions was significantly increased as the pH shifted from low to high (Table 5).

Effect of adsorbent dose

The effect of the adsorbent mass usually determined the capacity of a solid adsorbent for a certain concentration of adsorbate in a solution. The availability of the exchange sites or surface area may contribute on the effect of adsorbent dose toward the adsorption capacity (Elsayed *et al*., 2020; Mahmudi *et al*., 2020). Table 6 shows the effect of adsorbent dose on removal capacity of heavy metals from previous study.

Activated Carbon

Large numbers of studies have been dedicated to find suitable and cheap adsorbents for the treatment or removal of heavy metal from wastewater. The concept of L-3 class (i.e. low cost, locally available, low technologically prepared and used) of adsorbents are the solutions that are being studied by many researchers worldwide (Baneerjee, 2020). The adsorbents investigated on heavy metal treatment in previous research include cellulose nanofibers, zeolites, carbon nanotubes, agro-industrial waste materials, granular or powdered activated carbon (AC), and modified AC (Shahrakia *et al*., 2021). Among which activated carbon (AC) is a popular adsorbent due to its high adsorption capacity owing to its porous structure and surface chemical groups. In addition, AC was also named as versatile adsorbent, since its performance characteristics can be tailored by varying the precursor, heating temperature and activation method (Gabelman, 2017).

In general, the surface areas of AC can be up to 3000 m^{2}g^{-1}, whilst the surface area of commercially available AC is approximately 1000 m^{2}g^{-1} as shown in Table 7. This high surface area results from the development of mainly microporous and mesoporous of different size and shape. Different pore size distribution influences the performance properties of the AC. Sudaryanto (2006) found that macro-pores have little contribution to the development of surface area. The AC pores are categorized by volume in accordance with the International Union of Pure and

Table 5. Effect of pH value adjustment towards the adsorption capacity of heavy metals

Adsorbent	Heavy metals	pH range	Optimum pH value	Adsorption capacity	Source
Pomegranate peel	Nickle	4 to 9	9	98%	Elsayed *et al*., 2020
Kenaf Fibre	Iron, Manganese, Zinc, Arsenic, Copper, Nickle	3 to 11	7	Between 5% to 30%	Saeed *et al*., 2020
Mango Leaf	Chromium and Iron	2 to 10	8	99% and 99.5%	Duraisamy *et al*., 2020
Palm Kernel Shell	Chromium, Lead, Zinc and Cadmium	2 to 6	6	60% to 80%	Baby and Hussein, 2020
Chestnut Shell	Chromium	2 to 12	7	78%	Singh *et al*., 2020
Banana Peel	Copper, Nickle and Lead	0.6 to 7.4	5.7 to 7.4	40%, 51% and 54%	Thuan *et al*., 2017
Jackfruit Peel	Lead and Cadmium	4 to 9	7	50% to 90%	Ibrahim *et al*., 2020
Pistachio Hull	Nickle	2 to 10	6	60% to 90%	Beidokhti *et al*., 2019
Oil Palm Ash	Copper	2 to 8	8	50% to 94%	Chowdhury *et al*., 2011
Oil palm Shells	Nickel, Lead and Chromium	3 to 10	8	Up to 70%	Rahman *et al*., 2014

Table 6. The effect of adsorbent dose on removal capacity of heavy metals from previous study

Adsorbent	Adsorbent Dose	Heavy metals	Removal capacity	Source
Mango Leaf	20 to 100 mg/L	Chromium and Iron	Chromium: from 93.4% to 99.6% Iron: from 89.4% to 99.4%	Duraisamy *et al*., 2020
Chestnut Peels	0.2 to 1.0 g	Chromium	60% to 79%	Singh *et al*., 2020
Banana Peels	0.9 to 2.4 g/L	Copper, Nickle and Lead	Copper:40%, Nickle: 51% and Lead: 54%	Thuan *et al*., 2017
Pistachio Hull	5 to 30 g/L	Nickle	66% to 76%	Beidokhti *et al*., 2019

Table 7. Surface area of commercial AC

Properties/Supplier	Commercially available activated carbon				
	HANYAN	HANYAN	Zhulin Carbon	Concept Ecotech	Innova Corporate
Starting materials	Coconut shell	Coal	Coal	Coconut Shell	Coconut Shell
Surface area (m^2/gm)	950-1500	500-950	900-1100	900-1350	400-1200

Table 8. Classification of pores by diameter

Types of pore	Diameter of pore	Characteristic of pore
Micropore	$D<2^oA$	Superimposed wall potential
Mesopore	$2^oA<D<50^oA$	Capillary condensation
Macropore	$D>50^oA$	Effectively Flat walled

Applied Chemistry (IUPAC 1972) classification system. Table 8 lists the classification of pores by their diameter.

Numerous kinds of carbonaceous materials can be utilized as AC; however, as shown in Table 8 coconut shell (CS) and coal are commonly used in industrial manufacturing to make commercial AC. Despite their ideal adsorption efficiency, high demand has required high investment costs in large-scale applications and led to escalation of their prices. Therefore, attention has been drawn to finding affordable and unconventional precursors, such as agricultural wastes.

Agricultural wastes have been broadly utilized as biosorbents since they are inexpensive and abundantly available in large volumes as the residues from agricultural activities (Rudi *et al*., 2020; Pyrzynska, 2019). The sorption capacity of different biosorbents of plant origin whose efficiencies for the uptake of heavy metal have been reported previously include honeydew peels (Yunus *et al.,* 2019) grape (Melia *et al*., 2018), wheat (Melia *et al*., 2018), barley (Rajczykowski *et al*., 2018; Melia *et al*., 2018), coffee pulp (Aguilar *et al*., 2019), rice waste (Ravi *et al*., 2017; Garcia, 2018; El Nadi, and Alla, 2019; Obayomi, 2019;

Table 9. Adsorption capacity of biosorbents obtained from agricultural wastes on the removal of different metal elements

Adsorbents	Metal elements	Q_e (mg/g) or removal percentage (%)	Sources
Coffee Pulp	Chromium (Cr)	13.48 mg/g	Aguilar *et al*., 2019
White yam	Cadmium (Cd)	22.4 mg/g	Asuquo *et al*., 2018
Brassica Campestris waste stem	Nickle (Ni)	1.1 mg/g	Shaikh *et al*., 2018
	Chromium (Cr)	95 mg/g	
Canola seeds	Lead (Pb)	44.25 mg/g	Affonso *et al*., 2019
	Cadmium (Cd)	52.36 mg/g	
Rice husk	Zinc (Zn)	94.33 %	El Nadi and Abd Alla, 2019
	Chromium (Cr)	89.20 %	
Banana peel	Copper (Cu)	14.3 mg/g	Thuan *et al*., 2017
	Nickle (Ni)	27.4 mg/g	
	Lead (Pb)	34.5 mg/g	
Rice straw	Chromium (Cr)	97.12%	Kumar *et al*, 2017
Jackfruit peels	Lead (Pb)	10.1 mg/g	Ibrahim *et al*.,2020
	Copper (Cu)	17.5 mg/g	
	Cadmium (Cd)	20.0 mg/g	
	Manganese (Mn)	76.9 mg/g	
	Iron (Fe)	4.40 mg/g	
Pistachio Hull Waste	Nickle (Ni)	14 mg/g	Beidokhti *et al*., 2019
Ground Nut shell	Cadmium (Cd)	70.64%.	Vinaykumar *et al*., 2019
Pongamia Pinnata		79.9%.	
Onion skin		75.45%	
	Lead (Pb)	10.75 mg/g	

Bożęcka *et al*., 2020), ground nutshell (Obayomi, 2019; Garcia, 2018), white yam (Asuquo *et al*., 2018) and soya beans (Obayomi, 2019; Garcia, 2018). Table 9 shows the utilization of agricultural waste and their adsorption capacity on the removal of varied heavy metals.

Oil palm agriculture waste

In Malaysia, the main agricultural commodities grown are such oil palm, rubber, rice, cocoa and coconut. According to Malaysian Oil Palm Board (MPOB), Malaysia produced bisection of the world palm oil production and the production has increased up to 5.90 million hectares in 2019, approximately 0.9% in comparison to 5.85 million hectares in 2018. Among these numbers, Johor has the largest oil palm plantation area compared to other states in peninsular Malaysia, as tabulated in Table 10 (MPOB, 2019)

Malaysia, as the world's leading dealer in the palm oil industry, faces a difficult challenge in handling the palm oil waste. According to Lee (2017), for every 1 kg of crude palm oil produced, approximately 4 kg of waste are generated. Peninsular Malaysia recorded 77% of oil palm agriculture residue approximately 17 Mt as shown in Figure 3 (Hamzah *et al*., 2019). Palm kernel shell (PKS), fronds (OPF), trunk (OPT), leaves (OPL), mesocarp fibre, and empty fruit bunch (EFB) were among the aforementioned residues. The EFB, mesocarp fiber and PKS are collected during the pressing of sterilized fruits whilst OPF and OPL are available daily throughout the year when the palms are pruned during the harvesting of fresh fruit bunch for the production of oil. OPT is obtained during the replantation of the oil palm trees that occurred every 15-20 years (Marsin *et al*., 2018). Recently, abundant of research output proved that each part of oil palm waste could be converted into varieties of value-added products.

Oil palm waste as adsorbents

Globally, various technologies have been applied to convert the palm oil waste to bio-based products such as pellet for feedstock, fertilizers, fillers, bioplastics and adsorbent. In preparation as adsorbent, oil palm waste is usually treated under specific conditions. The activation can be done via physical or chemical activation, following the simplified structure presented in Figure 4.

For physical activation, two steps were involved. The first step is pyrolysis, where oil palm

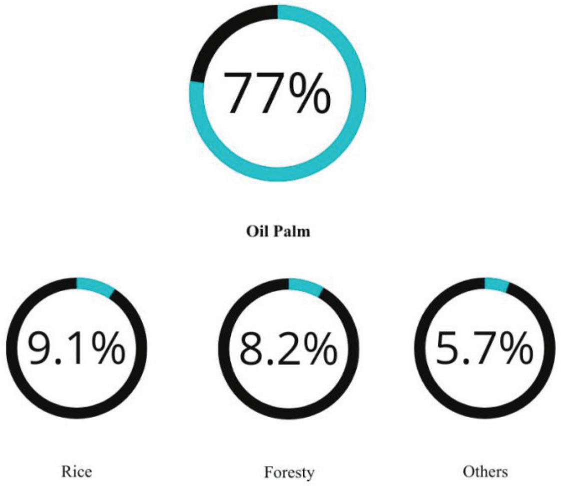


Figure 3. Total residues of different agriculture commodities in Malaysia (Hamzah *et al*., 2019)

Table 10. Oil palm planted area as December 2019 (MPOB, 2019)

State	Mature	Immature	Total	%
Johor	694,097	64,439	758,535	12.9
Kedah	81,794	8,927	90,721	1.5
Kelantan	127,221	44,124	171,345	2.9
Melaka	A 52,083	5,257	57,340	1.0
Negeri Sembilan	170,970	18,009	188,979	3.2
Pahang	668,236	100,161	768,397	13.0
Perak	363,813	43,790	407,603	6.9
Perlis	842	49	891	0.0
Pulau Pinang	13,445	355	13,800	0.2
Selangor	117,558	13,112	130,671	2.2
Terengganu	153,656	27,065	180,721	3.1
Sabah	1,353,812	190,669	1,544,481	26.18
Sarawak	1,419,295	167,378	1,586,673	26.9
Total	5,216,822	683,335	5,900,157	100.0

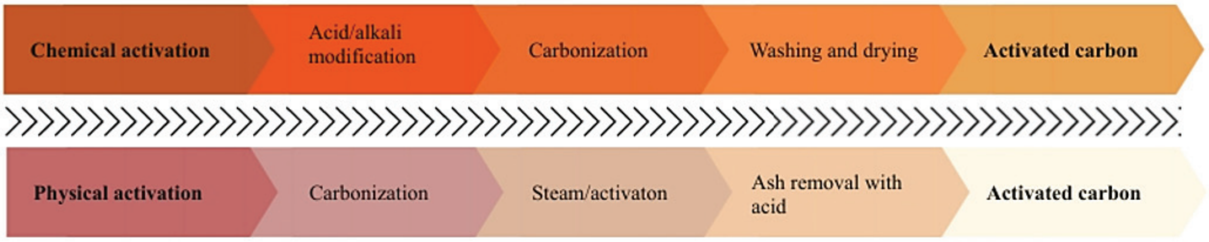


Figure 4. General method of chemical and physical activation for activated carbon

waste is carbonized and then followed with the carbon activation using steam or oxidation gases. Meanwhile, for the activation of carbon through chemical activation, the oil palm waste is saturated with activation chemical. The saturated chemical and raw materials are then simultaneously heated under various temperatures. After designated time, the raw materials are brought out and washed with distilled or hot tapped water (depends on the suggested method) to remove chemicals, and activated carbon is obtained. In general, chemical activation is preferred among researchers as it saves time and less activated carbon is burned (Yeow *et al*., 2021). Table 11 shows the process of activated carbon production steps from numerous sources of the previous research.

In terms of surface characterization, Scanning Electron Microscope (SEM) is commonly utilized as platform media in a way to identify the changes for pre- and post- development of pore structure. A study from Abu Sari (2014) made comparison on the morphology structure between oil palm empty fruit bunch (EFB) and rice husk biochars. The results show significant differences on both wastes (Figure 5 (a) and (b)). In comparison, the pores on rice husk biochar are not well shaped with diminished structure of pores. Small pores also were detected on the rough surface of rice husk biochar, while EFB provides more competent pore structures. Tobi (2019) also presented similar results of EFB, where EFB along with oil palm fronds developed pore networks of divine honeycomb pattern, compared to uneven pore development from palm kernel shell (Figure 6). This well-developed porous network is an indication of high surface area on which metal ions can be deposited.

Oil palm is made up from lignocellulosic material which is rich in carbohydrates in the form of starch and sugar and containing different compositions which making them excellent precursors for adsorbent (Ahmad *et al*., 2011). One of the most vital components of plant cell walls is β- D -glucopyranose units which has been identified in lignocellulosic materials. Each β-D - glucopyranose unit contains one primary hydroxyl group and two secondary hydroxyl groups that are commonly involved in chemical reactions (Vakili *et al*., 2014). The adsorbents obtained from various parts of oil palm biomass show different morphologies proportional to their composition, as shown in Figure 7 a, b and c, as they are transformed into adsorbents for the purpose of adsorption process.

In terms of the heavy metal removal, the contribution of electron pairs on the functional groups of the lignocellulosic will bind to form the heavy metal form complexes with metal ions in solution (Vakili *et al*., 2014). A study from Lim (2016) found that the chemically modified cellulose could potentially achieve efficient adsorption capacity of heavy metal ions, whereby, it can adsorb metal ions via ion exchange which contributed from the active sites present on them. Several other studys also have proven the potential of

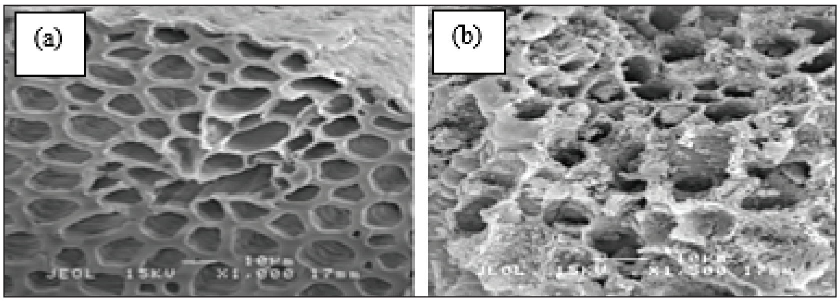


Figure 5. SEM image of (a) EFB biochar and (b) RH biochar 1000x magnification (Abu Sari *et al.,* 2014)

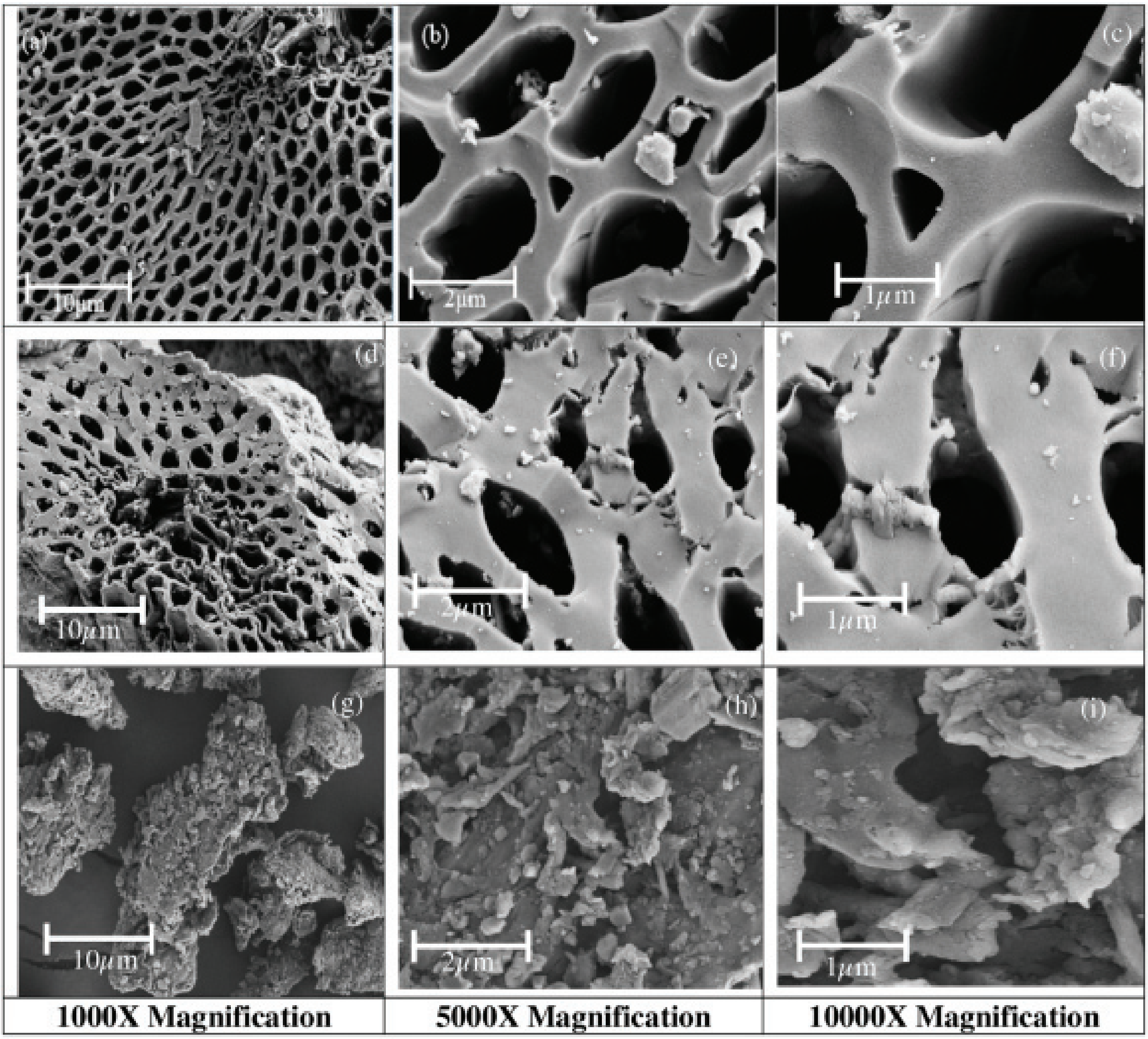


Figure 6. Micrograph image of EFB, palm oil fronds and kernel shells (1000X, 500X and 1000X) (Tobi *et al*., 2019)

different parts of oil palm waste as heavy metal removal in aqueous solution by using different types of modifications agents, as shown in Figure 8 (Barros *et al*., 2020; Baby and Hussein, 2020; Lim *et al*., 2016; Faisal *et al*., 2019).

Results have shown that chemically modifying waste improves the heavy metal removal and sorption capacity. The removal percentage was up to 99% (Figure 9). This waste can be modified by treating it with different chemical agents (e.g., alkalis, acids, organic compounds, etc.). Such chemical modification increases the level of metal uptake by releasing certain soluble organic compounds within the biomass (Vakili *et al*., 2014).

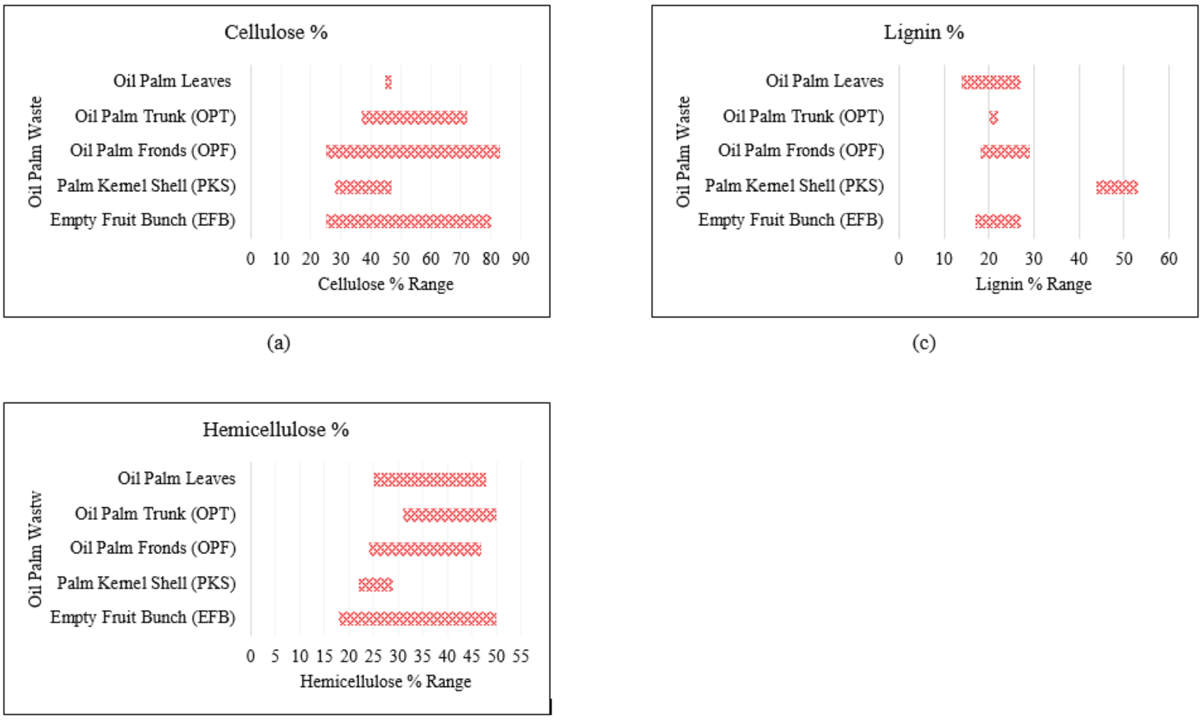
As in solid state, a study from Rasli (2017) shows their X-Ray diffraction (XRD) results indicating that the most prominent peak in the oil palm fronds is observed at 22.6º, which demonstrates the crystalline structure of the cellulose. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. The results also show (Figure 9) the crystalline index (CI) of 24.31% for the raw oil palm fronds, which progressively increased after alkali treatment (52.46%) and bleaching treatment (68.75%). The increment of this index was due to the progressive removal of the hemicelluloses and lignin.

On the other hand, as mentioned in factor affecting adsorption such factors (pH value, contact time, and AC dose) also implicate the adsorption capacities of oil palm waste AC. Therefore, in order to evaluate the oil palm waste AC responses toward these factors, Table 12 summarized the respective findings.

In the acquisition of high adsorption capacity, the optimum values of the factor influencing

Table 11. Method of oil palm waste AC production

Biosorbent	Preparation	Oven dried	Impregnation	Carbonization	Washing	Sizing	Utilization	Ref.
Empty Fruit Bunch	Cleaned	110 °C for about 24 hours	Soaked with concentrated H_3PO_4 at 1:1 (wt./vol.) in a 1500 mL beaker 30 minutes at room temperature	Muffle Furnace 400, 450, 500 and 550 °C 24 hours	Hot distilled water Left to dry in the oven overnight at 110 °C	0.5-1 mm	Adsorption of Nitric Oxide	Ahmad *et al*., 2020
Oil Palm Leaves and Shells	Washed with deionized water	Dry in an oven at 60 °C	Aqueous solution with concentrations of 0%, 11%, and 33% (*w/w*) 10 g of the sample impregnated in 100 mL concentration of H_3PO_4 Dried in an oven at 95 °C for 12 h,	Muffle Furnace 500 ◦C under a nitrogen atmosphere Heating speed of 10 °C/min	Hot and cold deionized water Until reached pH 7	N/A	Carbon source for electrode	Nasir *et al*., 2018
Oil Palm Trunk	N/A	105 °C for 24 hours	5 g of dried sample Impregnation ratio of H_3PO_4 between 0.5 and 3 Dried 100 °C for 24 h	450 °C for 6 min.	Washed with distilled water until the conductivity of the wash liquor became less than 50 µS	0.3 to 1.18 mm	Tanin removal	Lim *et al*., 2020
Palm Kernel Shell	N/A	N/A	Soaking it in a 0.1 N NaOH solution for 1 day	Pyrolysis at 380 °C	Washed with distilled water until achieved neutral pH	Ground using a ball mill for 24 h until a nanoparticle size was achieved	Adsorption of Cadmium	Faisal *et al*., 2019
Oil Palm Bagasse	Sample were cut into small pieces, washed thoroughly with water	Dried for 24 hours	0.5 g OPB/20 mL dimethyl sulfoxide (DMSO) stirred for 24 h at 120 rpm.	N/A	Ethanol and distilled water were used for washing the biosorbent, which was dried at room temperature	0.355, 0.5 and 1 mm	Adsorption of Nickle and Cadmium	Barros *et al*., 2020



(a)

(c)

(b)

Figure 7. (a) Cellulose (b) hemicellulose and (c) lignin composition (%) of oil palm waste (Ahmad *et al*., 2011; Vakili *et al*., 2014; Marsin *et al*., 2018)

adsorptions were roughly in the same range without any significant differences, as seen in Table 12. In general, the relevance of metal ions toward the surface of the adsorbent is highly affected by the pH of the solution. Low values of the adsorption capacity were noticed in the strong acidic medium

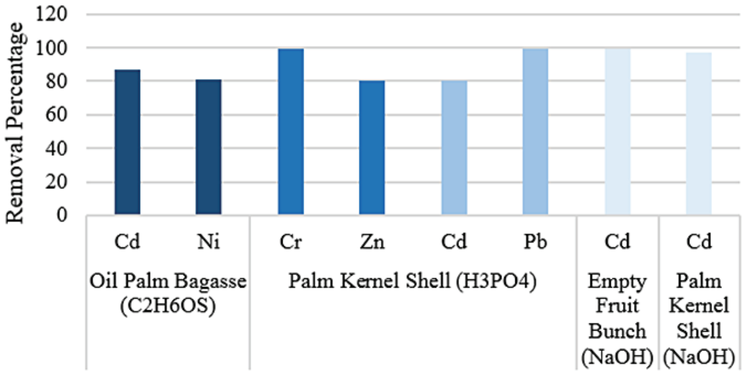


Figure 8. Modified oil palm waste-based adsorbent for heavy metal removal

Table 12. Optimum values of affecting factors for heavy metals adsorption using Oil Palm AC

Oil Palm AC	Heavy Metals	Factor affecting adsorptions (Optimum values)			Source
		pH value	Contact time	AC dose	
Palm Kernel Shell	Lead	4	60 min	1.5g	Baby and Hussein., 2019
	Chromium	6	60 min	1.5g	
	Cadmium	6	90 min	2.0g	
	Zinc	6	120 min	2.0g	
Oil Palm Leaves	Manganese	7	60 min	N/A	Alothman *et al.*, 2019
	Lead	6	60 min		
	Cobalt	7	60 min		
Oil Palm Ash	Manganese	7	80 min	N/A	Chowdhury *et al.*, 2011
Palm Kernel Shell	Chromium	6	120 min	0.25g	Baby and Hussien, 2020
	Lead				
	Zinc				
	Cadmium				
Palm Fruit Fibre	Lead	5	120 min	N/A	Ooia and Ong, 2019

(pH<7) due to the H^+ ions exchange hindrance, while the higher values of the adsorption capacity obtained in the weak acidic and neutral medium due to a greater ratio of positive metal ions (Baby and Hussein, 2020; Al Othman *et al.*, 2020). The data shows that the optimum pH value range is between 4 and 8. However, according to Baby and Hussein (2019) under basic conditions, formation precipitation of metal ions as their respective hydroxide can influence the adsorption results; therefore, selection of maximum adsorption under acidic environment below pH < 7 should also be considered.

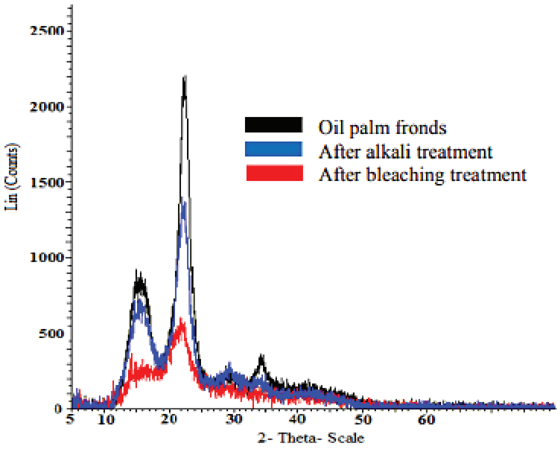


Figure 9. X-ray diffraction patterns for raw oil palm frond, after alkali treatment and after bleaching treatment (Rasli *et al.*, 2017)

In terms of contact time, the total value varies from 60 minutes to 120 minutes, before it approaches a static value after which no further change in uptake has been observed. The adsorption rate was found to increase as the adsorbent dosage escalated. By which the maximum number of active sites may be responsible for the removal of more ions at their surfaces (Baby and Hussein, 2020). In a period of time, the surface of adsorption sites was fully occupied; these reflected the equilibrium point of the system. The remaining vacant sites were difficult to be captured by metal ions due to the repulsive forces between the adsorbate, i.e. the metal present in solid and bulk phases. The adsorbent dose is crucial if research is conducted to adapt into the industrial WWTP system. The determination of AC dose will indicate the minimum possible dosage for the maximum adsorption of metal ions and gives initial theory of system design and costs. In general, Baby and Hussein (2019) suggested that adsorption is almost directly proportional to the amount of the adsorbent dosage

CONCLUSIONS

Considering that heavy metals are poisonous elements, releasing them into the environment as a result of industrial activity is a serious threat to human life and other living organisms. The current adsorption methods of heavy metal wastewater treatment are expensive due to the soaring demand of commercial activated carbon and also inefficient at low concentrations of metal ions. Converting agricultural waste into value-added adsorbents is a way to solve the disposal issue and substituting the conventional adsorbents. The utilisation of agricultural waste from oil palm as an adsorbent in Malaysia has gained recognition owing to its abundance, relatively low cost and rich in lignin, cellulose and hemicellulose. The physical and chemical modifications on oil palm waste are able to transform them into value added adsorbents with high adsorption capacity reaching up to 99% metals removal. The design of a suitable system that consumes the lowest amount of adsorbate that affects the cost is important as to be utilized in a real WWTP industrial system. Thus, the oil palm waste should be explored further in terms of factor affecting adsorption which ultimately will influence the adsorption rate, surface area and porosity.

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