ACID IMPREGNATED HONEYDEW RIND ACTIVATED CARBON FOR
CHROMIUM AND ZINC REMOVAL

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DEDICATION

Dedicated to my late grandparents who taught me the need of education in life. Also to my family, siblings and all beautiful souls who have kept my spirit boosted and who have not turned their backs every single day in this journey; rain and shine. To my husband and my dear kids Azraei, Khairie and Yasmin; thank you for the smiles and laughter.

May Allah s.w.t. shower countless blessings upon us hereafter.
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ABSTRACT

Heavy metal contamination in aqueous media and industrial discharges are among the significant environmental problems, which have to be encountered due to the toxic nature and the accumulation of these metal ions in the food chains. This study has upcycled an agricultural waste namely honeydew rind (HDR) as a precursor in activated carbon (AC) adsorbent preparation using chemical activation process for Cr(III) and Zn(II) removal from synthetic wastewater. Prior to the AC production, physicochemical characteristics of the HDR were analyzed by means of XRF, FESEM, TGA and FTIR. Optimization of sulfuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) of 10%–30% v/v impregnation agent generated honeydew rind impregnated activated carbon (ACS) and honeydew rind impregnated activated carbon (ACP). Optimization of carbonization temperature involved temperature of 430°C–490°C for H₂SO₄ and 450°C–510°C for H₃PO₄. Batch experiment study was conducted at constant value of 100 mL of synthetic wastewater, 125 rpm shaking rotation at ambient temperature. Brunauer-Emmet-Teller (BET), Langmuir and Freundlich were tested for isotherm adsorption while pseudo-first order and pseudo-second order were examined in kinetic behavior investigation. The column study was run under constant bed height, flow rate, inlet metal concentration of 25 cm, 16 mL/min, 1000 mL (Cr(III)); 400 mg/L (Zn(II)) respectively at ambient temperature. Boehm titration indicated that ACS and ACP are classified as acidic AC. The highest iodine number value (528.63 mg/g) and BET surface area (591.25 m²/g) were obtained by 20% v/v ACS and carbonized at 470°C. The highest iodine number value (1174.19 mg/g) and BET surface area (1272.38 m²/g) were achieved by 20% v/v ACP and carbonized at 490°C. Textural analysis produced an average pore diameter of 4.46 nm for the ACS and 2.92 nm for the ACP respectively. Batch adsorption analysis resulted in an optimum condition occurring at pH 4.5, 0.1 g of ACS and ACP, 40 minute contact time and 1000mg/L for Cr(III) and pH 5.5, 0.1 g of ACS and ACP with a 40 min contact time and 400 mg/L for Zn(II). Cr(III) maximum removal was 83.49% using ACS and 88.88% using ACP respectively while Zn(II) maximum removal was 81.55% using ACS and 84.13% using ACP respectively. It was demonstrated that high metal removal was achieved due to high range of metal concentration used in the study. Column adsorption
demonstrated breakthrough of 70 min and 100 min for Cr(III) and Zn(II), respectively. The regeneration study achieved three (3) adsorption cycles of the spent ACP. The present study was able to prove that the honeydew rind impregnated activated carbon is a promising adsorbent in Cr(III) and Zn(II) removal from synthetic wastewater solution. This study has also therefore confirmed that a relatively lower heating rate in the course of carbonization may manage to convert the HDR into its AC. Ion exchange and complexation were suggested to be the metals sorption mechanism.
ABSTRAK

Pencemaran logam berat media berair dan hasil buangan industri adalah salah satu masalah alam sekitar yang ketara disebabkan oleh sifat toksik dan pengumpulan ion logam ini dalam rantai makanan. Kajian ini telah menggunakan semula sisa pertanian, kulit tembikai susu (HDR) sebagai bahan pemula dalam penyediaan penjerap impregnasi karbon diaktifkan untuk penyingeiran Cr(III) dan Zn(II) daripada air sisa sintetik. Sifat kimia fizikal HDR terlebih dahulu telah dikaji menggunakan kaedah analisis XRF, FESEM, TGA and FTIR. Ujikaji pengoptimuman agen pengisitepuan asid sulfuric (H₂SO₄) dan asid fosforik (H₃PO₄) pada pencairan 10%–30% per unit isipadu air menghasilkan dua jenis karbon diaktifkan; karbon diaktifkan kulit tembikai susu ACS dan ACP. Analisis pengoptimuman suhu karbonisasi melibatkan jual suhu 430°C–490°C untuk H₂SO₄ dan 450°C–510°C untuk H₃PO₄. Analisis penjerapan kelompok telah dijalankan pada suhu sekitar mengikut ketetapan berikut; 100 mL isipadu air sisa sintetik dan 125 rpm putaran gencang. Persamaan Brunauer-Emmet-Teller (BET), Langmuir dan Freundlich telah digunakan untuk menguji keseimbangan isoterma sementara model tertib pertama dan model tertib kedua digunakan untuk pengujian kinetik. Analisis penjerapan turus dijalankan pada suhu persekitaran mengikut ketetapan berikut; tinggi padatan penjerap 25 cm, kadar alir 16 mL/min dan kepekatan influen 1000 mg/L (Cr(III)); 400 mg/L (Zn(II)). Pentitratan Boehm menunjukkan ACS dan ACP dikelaskan sebagai karbon diaktifkan yang berasid. Untuk ACS, nilai iodin yang maksimum (528.63 mg/g) dan luas permukaan BET (591.25 m²/g) telah diperolehi oleh ACS pengisitepuan asid sulfurik pada pencairan 20% dan karbonisasi pada 470°C. Untuk ACP, nilai iodin yang paling tinggi (1174.19 mg/g) dan luas permukaan BET (1272.38 m²/g) telah dicapai oleh ACP pengisitepuan asid fosforik pada pencairan 20% dan karbonisasi pada 490°C. Analisis tekstur menghasilkan purata diameter liang 4.46 nm untuk ACS dan 2.92 nm untuk ACP. Analisis penjerapan berkelompok menunjukkan keadaan optimum berlaku pada pH 4.5, 0.1 g ACS dan ACP, masa sentuhan selama 40 min dan 1000 mg/L untuk Cr(III). Keadaan optimum berlaku pada pH 5.5, 0.1 g ACS dan ACP masa sentuhan selama 40 min dan 400 mg/L untuk Zn(II).
Penyingkirkan Cr(III) maksimum didapati 83.49% menggunakan ACS dan 88.88% menggunakan ACP. Penyingkirkan maksimum Zn(II) sebanyak 81.55% menggunakan ACS dan 84.13% menggunakan ACP. Penyingkirkan logam yang tinggi diperolehi akibat penggunaan kepekatan logam yang digunakan di dalam kajian ini. Penjerapan turus menunjukkan takat muncul untuk Cr(III) ialah 70 min manakala 100 min untuk Zn(II). Analisis penjerapan-penyaherapan telah mencapai tiga (3) kitaran kebolehgunaan ACP. Kajian menekankan bahawa karbon diaktifkan yang dihasilkan daripada pengisitepuan kulit tembikai susu adalah penjerap yang berpotensi dalam penyingkirkan Cr(III) dan Zn(II) daripada larutan akueus. Selain itu kajian ini telah mengesahkan penggunaan suhu karbonisasi yang rendah dalam proses penghasilan karbon diaktifkan daripada kulit tembikai susu. Mekanisma pertukaran ion dan pengkompleksan telah dicadangkan dalam penjerapan logam-logam tersebut.
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A= adsorption, D= desorption

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<tr>
<td>AC</td>
<td>activated carbonization</td>
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<tr>
<td>ACHDP</td>
<td>activated carbon honeydew rind</td>
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<tr>
<td>ACP</td>
<td>phosphoric acid activated carbon</td>
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<td>ACS</td>
<td>sulfuric acid activated carbon</td>
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<td>chromium bounded to phosphoric acid activated carbon</td>
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<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
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<td>FESEM-EDX</td>
<td>field emission electron microscopy-energy dispersive x-ray</td>
</tr>
<tr>
<td>FTIR</td>
<td>fourier transformed infrared spectroscopy</td>
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<tr>
<td>H</td>
<td>hysteresis</td>
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<td>HDR</td>
<td>honeydew rind</td>
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<td>N₂</td>
<td>nitrogen</td>
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<tr>
<td>TGA</td>
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<tr>
<td>XRF</td>
<td>x-ray florescence analysis</td>
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<td>°C</td>
<td>degree Celcius</td>
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<td>Cr(III)</td>
<td>trivalent chromium ion</td>
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<tr>
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<td>empty bed contact time</td>
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<td>b</td>
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<tr>
<td>g</td>
<td>gram</td>
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<td>iodine number</td>
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<td>H₂SO₄</td>
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<td>H₃PO₄</td>
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<tr>
<td>n</td>
<td>affinity coefficient</td>
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<tr>
<td>mg/L</td>
<td>milligram per liter</td>
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<tr>
<td>mg/g</td>
<td>milligram per gram</td>
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<tr>
<td>minute</td>
<td>min</td>
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</tbody>
</table>


$q_e$  
sorption capacity at equilibrium

$q_{\text{max}}$  
maximum sorption capacity

$\mu m$  
micrometer

$nm$  
nanometer

SD  
standard deviation

pH  
potential of hydrogen

$pH_{\text{pzc}}$  
potential of hydrogen at point zero of charge

$R^2$  
correlation coefficient

rpm  
rotation per minute

t$_b$  
breakthrough point

t$_{\text{exh}}$  
exhausted point

Zn(II)  
divalent zinc ion
# List of Appendix

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CHAPTER 1

INTRODUCTION

1.1 Research background

The recent shift from an agricultural into a middle-income, knowledge-based economy observed in Malaysia has made its economy a role model for many developing countries. In its attempt to achieve the status of high-income and developed country by the year of 2020, the Malaysian government has clearly demonstrated its commitments towards stimulating a better growth in the manufacturing sector (Onundi et al., 2011). Manufacturing in these industries involve producing electronic products, chemicals, fertilizers, drugs and pharmaceuticals, dyes and batteries (Abbaszadeh et al., 2016).

Although each industry may have its own in-house waste management systems, releasing heavy metals in industrial discharge in huge amount into water drainage is deemed unavoidable. Some of them act as essential micronutrients for living things however at higher concentrations result in severe illness (Abbaszadeh et al., 2016). Upon realizing that the heavy metals have potential in contributing adverse impact on the environment and consequently on human health, it is equally realize that such industries can be harmful at the same time. Therefore, industrial activities in Malaysia reportedly contribute to one of the key environmental problems in relation to contamination of water drainage with thousands of industrial chemical compounds. A recent study carried out by Othman et al., (2014) reported the generation of waste containing heavy metals such as chromium, zinc, lead and nickel may originate from electroplating and metal treatment or fabrication industries which are located along the west coast of Peninsular Malaysia including major industrial areas like Klang Valley, Penang, Ipoh and Johor Bahru (Othman et al., 2014).
Unlike the organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Rahman et al., 2014). Even though some of these heavy metals are essential in trace amounts, they may however turn highly lethal at higher concentrations as in such conditions, they are capable of causing some incurable diseases (Kaur et al., 2013). Most of the metals are reported carcinogenic, teratogenic and may pose severe health problems like organ damage, reduced growth and development, nervous system impairments and oxidative stress (Lee et al., 2012). For instance, chromium may possibly result in liver damage, pulmonary congestion, oedema and skin irritation resulting in ulcer formation and zinc toxic property is capable of producing general symptoms such as retardation of growth in plants, fever and oedema of lungs in human beings (Gupta, 2014). Therefore, the presence of heavy metals in aquatic ecosystems has in the last few decades received widespread attention among scholars around the world owing to their potential risks towards human health and harmful effects on living organisms in general (Barakat, 2011).

It is of utmost importance to remove these metals from wastewater in order to prevent contamination of natural water bodies by effluents containing toxic metals. The issues have convinced environmental engineer and researchers to carry out extensive investigations into identifying more suitable method which may assist in the removal of heavy metals from wastewater before it enters public water stream. As the result, numerous studies have in recent years been conducted aimed at the removal of heavy metals from waters and wastewaters (Díaz-Muñoz et al., 2016; Kujundziski et al., 2015; Kyzas & Kostoglou, 2014; Rahman et al., 2014; Kikuchi & Tanaka, 2012). Various innovative treatment methods, namely ion exchange, reverse osmosis, electrolysis, oxidation and reduction, coagulation and flocculation, biodegradation, adsorption, membrane separations, and chemical precipitation are among some of the applications in wastewater treatment (Bilal et al., 2013) but they are reportedly costly (Nguyen et al., 2013). Other associated drawbacks are high sludge-production (coagulation and flocculation); high energy consumption and by-product formation (oxidation); adsorbent progressively deteriorating in capacity as number of cycles increases (adsorption) and the requirement of an optimal favourable environment (biodegradation) (Bilal et al., 2013).
Adsorption has presently become one of popular treatment techniques over the abovementioned methods for wastewater laden with heavy metals. Adsorption mainly uses commercial activated carbon (AC); however it requires the incorporation of expensive technology. Conventional commercial AC is derived from wood and coconut shell and a non-renewable resource; commonly coal, and therefore it has to compete with the energy industry as it is presently considered as a diminishing commodity (Cheung et al., 2012). Apart from that, its applications for multiple purposes have resulted in a steady rise observed in price of AC thus considered as an expensive. Hence, there is presently a need to employ waste materials as an alternative precursor to produce activated carbon.

Agricultural waste offers an effective, replacement for the non-renewable coal-based activated carbons due to their similar or better adsorption efficiency (Maheshwari & Gupta, 2016). Hence it has been considered as a better option for precursors of activated carbons from non-renewable source. Therefore, the need to find a new alternative precursor of AC has grown among the researchers by means of focusing on the use of alternative of non-conventional waste material. Adsorption was recently associated with new adsorbents such as biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials as they have been proved to be a potentially feasible alternative (El Zayat & Smith, 2013). Some of its advantages over other conventional treatments include, the need for a smaller area compares to a biological system, relatively lower sensitivity to diurnal variation and operational flexibilities (Vargas et al., 2011).

1.2 Problem statement

Agricultural waste was used as a precursor in various AC production (Anisuzzaman et al., 2015; Köseoğlu & Akmil-Başar, 2015; Nurdin et al., 2015; Angin, 2014; Mutah et al., 2013; Amalenei et al., 2012). However high concentration of chemical agents and high carbonization temperature was required during AC production to react with the lignocellulosic compounds in the material. Honeydew rind (HDR); a non-woody AC precursor contains cellulose (25.42%), hemicellulose (36.85%) and low lignin content (8.2%) thus requires lower acid concentration and lower carbonization
temperature. Therefore lower energy consumption in AC production form HDR (ACHDR) is an advantage.

A recent work has reported the potential of HDR biosorbent in lead, ferum and manganese removal from wastewater (Othman & Asharuddin, 2013). Hence, this study has carried out, in a way, a follow-up investigation and observation on upcycling of honeydew rind to its activated carbon. Cr(III) and Zn(II) which found in high concentration (150–450 mg/L) in effluent from tile and electroplating industries mining in Kluang and Ayer Hitam, Batu Pahat (Othman & Asharuddin, 2013) has embarked the selection in this study. Investigation of physicochemical properties has revealed both significant chemical compounds and physical behaviour are present in the native honeydew rind indicated its adsorption capacity. Hence previous study has triggered the potential of HDR with adsorption characteristic from a non-woody material.

By far, Cr(III) and Zn(II) removal in batch adsorption study at high range concentration (400 mg/L for chromium(III)) and (1000 mg/L for zinc(II) mg/L)) using ACHDR has not widely studied. Therefore, this study has provided an optimum experimental design and the affect of batch adsorption parameter on the metal removal from synthetic wastewater using ACHDR. Following from the investigation, determination of mechanism adsorption for chromium(III) and zinc(II) removal from the aqueous solution can be achieved for practical design and fundamental understanding of the adsorption systems (Foo & Hameed, 2012).

Previous studies have successfully proven the efficiency for non-woody agricultural waste-based AC from batch adsorption observations but unfortunately there is scant information on column application studies. Such arguments have sparked the interest to delve a deeper study. Therefore, assessing the performance of the ACs under the column apart is considered important for a wider range of applications. This has driven an operational model of activated carbon from honeydew rind bed-packed column for chromium(III) and zinc(II) removal in aqueous solution in order to manifest an extent of significant application of the carbon produced in this study.

In the present HDR or *Cucumis melo* rind was selected as a new alternative precursor for activated carbon adsorbent, specifically for chromium(III) and zinc(II) removal in wastewater. By means of selecting the waste material as a precursor to produce activated carbon, it may reduce the cost of waste disposal from its source (Umar *et al.*, 2015). Another contribution is it can be an alternative to overcome of
employing current commercial activated carbon which is estimated to increasing demand by 5-10% annually (Zaini et al., 2014). As a conclusion remark, this study redounded to a number of significant contributions in the converting agricultural waste research area as an alternative AC precursor in wastewater application.

1.3 The research objectives

The present study aims to utilize honeydew rind in wastewater application in order to produce its activated carbon. The objectives of the present study are:

(a) To investigate adsorptive properties of HDR namely surface morphology, lignocellulosic compounds, thermal characteristic, mineral content and surface functional groups.

(b) To observe the effect of impregnation agent concentration and carbonization temperature effect on surface morphology and characterize physicochemical properties of ACS and ACP.

(c) To study factors affecting chromium(III) and zinc(II) removal in batch adsorption, namely pH of synthetic water solution, mass of AC, contact time and metals concentration.

(d) To investigate the adsorption isotherms, adsorption kinetics in batch adsorption and the regeneration of honeydew rind acid impregnated activated carbon using column adsorption for chromium(III) and zinc(II) removal from synthetic wastewater by means of honeydew rind acid impregnated activated carbon.

1.4 Scope of research

HDR was used as the raw material in the preparation of sulfuric acid (H$_2$SO$_4$) and phosphoric acid (H$_3$PO$_4$) impregnated activated carbon adsorbent in the present study. The characterization and preparation of HDR as impregnated activated carbon precursor were carried out prior to the production of AC. H$_2$SO$_4$ was chosen because of its ability to produce high surface AC, user friendly and allow a low temperature
carbonization process. The process of carbonization was done in muffle furnace with limited oxygen supply to produce two types of activated carbon, namely honeydew rind H\textsubscript{2}SO\textsubscript{4} impregnated activated carbon (ACS) and honeydew rind H\textsubscript{3}PO\textsubscript{4} impregnated activated carbon (ACP). The study of chromium(III) and zinc(II) removal efficiency using the best ACS and ACP was done in batch adsorption parameter optimization. Determination of mechanism of the metal adsorption processes and adsorption kinetic were done. This was followed by the removal of heavy metals in synthetic wastewater using honeydew rind impregnation activated carbon in a continuous adsorption. In this experiment, a glass chromatography column was packed with only one AC based from removal efficiency result from batch adsorption study. Regeneration study of the exhausted carbon was attained for chromium(III) and zinc(II) removal. It is emphasized that throughout the present study, synthetic wastewater was utilized in all experiments.

1.5 Layout of thesis

This thesis is divided into five chapters and each chapter describes the sequence of this study. Chapter 1 consists of background, problem statement, objectives and scope of study. Chapter 2 reviews the affect of heavy metal, current wastewater treatment technology, agricultural waste based activated carbon, AC process and its relationship with the adsorbents performances, factors affecting batch adsorption. Isotherm and kinetic adsorption model investigation and previous column adsorption studies are also highlighted. Chapter 3 presents the methodology flow chart, description of honeydew rind collection, material preparation, instrumentation, chemicals preparation chromium(III) and zinc(II) stock solution and preparation of activated carbon from honeydew rind. The working condition range and experimental design in optimization of acids concentration and carbonization temperature, batch, isotherm, kinetic and column adsorption were included. Chapter 4 presents and discusses the analysis of data and result obtained from the experimental works. Chapter 5 presents the conclusions of the study.
CHAPTER 2

LITERATURE REVIEW

2.1 Industrial wastewater

Increased in industrial activities have generated of huge amount of polluted water containing a number of undesired products specifically harmful toxic matters which may potentially pollute the available fresh water (Gonzalez & Pliego-Cuervo, 2014). Small and medium enterprises involved in plating, polishing and metal-coating operations such as paint, motor vehicle parts and accessories manufacturing may significantly contribute to heavy metal water pollution (Issabayeva et al., 2010).

In this regard, it has to be highlighted that the precise qualitative estimations can be hard to derive partly owing to poor environmental control provisions along with difficulties of carrying out technical monitoring for small, often family run enterprises (Hashim et al., 2011). Due to the widely held belief and the findings of some recent studies that toxicants in water attributes affect living things, and the ecological lives as well as industrial activities. Therefore a huge concern in pollution control and industrial discharge management is now considered high priorities (Barakat, 2011). Although it is discharged through its own piping system, major concerns have been raised in relation to the safety of aquatics system and living things which may have to receive the wastewater from this source.

2.2 Heavy metals

Heavy metal is defined as elements with atomic weights of 63.5 g/mol—200.6 g/mol (Barakat, 2011). It is a chemical element in that has a relatively higher density; five times of specific gravity of water, classified toxic and harmful even in small amount
Generally, most of the heavy metals includes cadmium, chromium, copper, plumbum, zinc, mercury, manganese can be found both from the earth’s crust and oceanic sediments (Yus & Mashitah, 2014). Water stream is one of the transportation modes by means of which the heavy metals move from one place to another. Besides, heavy metals can be suspended by erosion and volcanic eruption sand ore exploitation. Anthropogenic sources are the resultant of activities of such rapid development in industrial activities, mineral combustible and waste dumps (Hashim et al., 2011).

Some of the heavy metals such as cobalt, zinc, chromium, copper, manganese are considered essential for the biological function (Yus & Mashitah, 2014). However, they have tendency to gradually increase in quantity in both the environment and living organisms through deposition and settlement. The accumulation in human’s bodies is carcinogenic and its consumption in excess may result in serious effects on inner organ damage, nervous system problems which eventually lead to the risk of death (Gautam et al., 2014). Table 2.1 samples some of the heavy metals which can be found in local industries discharge residue.

Table 2.1: Heavy metals found in various industries
(Gautam et al., 2014)

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<th>Industry</th>
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<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
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<th>Pb</th>
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<td>Pulp &amp; paper mills</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<td>Organic chemistry</td>
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<td>Flat glass &amp; cement</td>
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Table 2.2 summarizes toxicity of several heavy metals which may adversely affect human’s health.

Table 2.2: Toxicity heavy metals to human’s health

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Toxicities</th>
<th>Maximum contaminant level (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Skin malfunctions, visceral cancers &amp; vascular disease</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lo et al. (2012)</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Kidney damage, human &amp; carcinogenic</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lo et al. (2012)</td>
</tr>
<tr>
<td>Chromium (IV)</td>
<td>Headache, nausea, diarrhea &amp; vomit</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Miretzky &amp; Cirelli (2010)</td>
</tr>
<tr>
<td>Chromium (III)</td>
<td>Depression, lethargy, neurological signs such as seizures and ataxia</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Miretzky &amp; Cirelli (2010)</td>
</tr>
<tr>
<td>Cuprum</td>
<td>Linked to Alzheimer’s disease, Parkinson’s disease, and other neurodegenerative diseases with increased oxidative stress in the brain.</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bilal et al. (2013)</td>
</tr>
<tr>
<td>Lead</td>
<td>Abdominal pain, vomit, constipation</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lo et al. (2012)</td>
</tr>
<tr>
<td>Mercury</td>
<td>Rheumatoid arthritis, kidney failure, circulatory and nervous system damage.</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gupta et al. (2014)</td>
</tr>
<tr>
<td>Nickel</td>
<td>Dermatitis, nausea, chronic asthma, coughing</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lo et al. (2012)</td>
</tr>
<tr>
<td>Zinc</td>
<td>Headache, gastroenteritis, diarrhoea, vomit and increase thirst</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Maheshwari &amp; Gupta (2016)</td>
</tr>
</tbody>
</table>

2.3  Health effect of chromium to human

Property of chromium (Cr) is listed in Table 2.3. An oxide thin layer is formed to protect the metal below when exposes to oxygen. Cr is recognized as the important raw material in alloy industry such as stainless steel production, in chrome encrusting and in metal ceramics. The material plating was once widely applied in giving steel a polished silvery mirror glazing is widely used in dyes for plastic and to convey deterioration protection (Wlibur et al., 2012). Its salts are efficient for colouring glass in emerald green (Huang et al., 2016), producing synthetic rubies; as a catalyst in dyeing and in the tanning of leather and to make mold for the firing of bricks.

Table 2.3: Properties of chromium (Devi & Manonmani, 2015)
Chromium occurs in a number of oxidation states, but Cr(VI) and Cr(III) are of main environmental concern (Wlibur, 2012; Sud et al., 2008). Forms of Cr(VI) are as chromate ion, HCrO$_4$ predominant at pH < 6.5, or CrO$_4^{2-}$, prevalent at pH 6.5. Dichromate, Cr$_2$O$_7^{2-}$, predominant at higher concentrations (>10mM) and at pH 2–6. The main forms of Cr(III) in freshwater are Cr(OH)$_2^+$, Cr(OH)$_2$, Cr(OH)$_4^-$ and they are generally stable and kinetically inert (Gupta et al., 2014). Cr(III) is stable in acidic environment (Sulaymon et al., 2011).

Cr(III) is important in element trace for human beings and participates in the metabolism of lipids and glucose. The level of concentration exceeding 0.01 mg/L Cr(III) found to be toxic to fish, cause more structural perturbation in the human erythrocyte membrane, change the biological membrane permeability, which affects the function of receptors, ion channels and enzymes found in the erythrocyte membranes (Maheshwari & Gupta, 2016, Pan et al., 2013). Prolonged contact with high concentrations of Cr(III) can cause allergic skin reactions, cancer and DNA damage. Therefore, it is vital to ensure removal of Cr(III) from wastewater before disposal and amass in drainage. There have been only few reports on the Cr(III) removal in water treatment thus it is a huge concern on investigating an appropriate treatment method study of Cr(III) removal from wastewater (Pan et al., 2013; Duran et. al., 2011; Miretzky et al., 2010).

### 2.4 Health effect of zinc to human

Zinc (Zn) can be found in water, soil, air, and food items, and it is notably the most common trace in the earth’s crust. Table 2.4 lists the properties of Zn. It is reportedly bluish in colour and shiny metal in the pure or metallic form. Zinc is considered essential to our body as one of the nutritional requirements in trace quantity as a physiological function of living tissues and biochemical processes. It is an indicative element in enzymes participating in the synthesis and degradation of carbohydrates,
lipids, protein and nucleic acid as well as in the metabolism of other micronutrients. Zn is also a significant nutrient to plants’ growth.

Table 2.4: Properties of zinc (Sarkar, 2003)

<table>
<thead>
<tr>
<th>Colour</th>
<th>Atomic number</th>
<th>Atomic mass (g/mol)</th>
<th>Ionic radius (nm)</th>
<th>Density (g/cm³)</th>
<th>Oxidation state</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bluish</td>
<td>30</td>
<td>65.38</td>
<td>0.074</td>
<td>7.13</td>
<td>+2</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Dose recommendation of Zn for man, woman, children and infant on a daily basis is 15 mg, 12 mg, 10 mg and 5 mg, respectively (Roney & Osier, 2005). In the industrial sector, zinc has relatively wider applications such as steel and iron coating which helps preventing rust and corrosion during galvanizations; incorporate with other heavy metals to form brass and bronze alloys and in dry battery factories. Zinc sulfide and zinc oxide are recognized produce paints and ceramics (Sarkar, 2003).

A concentration level of higher than 5 mg/L zinc may cause a bitter, astringent taste to water, and it might precipitate as Zn(OH)₂ or Zn(CO)₃ in alkaline water to produce a milky turbidity. The toxicity is commonly warned by abnormal of growth in plants, zinc fever and edema of lungs in human beings (Moreno-Barbosa et al., 2013). Zinc is a threat to biological system as it can travel through the food chain via bioaccumulation. Polluted water with zinc can be related to numerous industrial disposal such as cell production industry, leather metal coating, steel, paper and pulp, agrochemicals, petrochemicals and fertilizer industries (Yao et al., 2016). It also enters water stream from the deterioration of galvanized iron pipes. Quite a number of studies have revealed these activities release zinc in high concentration from related industrial waste which in turn may result in the accumulation of zinc in the water bodies as untreated wastewater (Othman et al., 2016; Moreno-Barbosa et al., 2013; Othman et al., 2012; Lalhrualtuanga et al., 2011). Owing to these factors which appear to be threats, there is a necessity to eliminate Cr(III) and Zn(II) from untreated effluents in order to avoid the pollutants enter into natural water bodies.
2.5  Methods for removing heavy metals in wastewater

The necessity to employ suitable wastewater treatment to ensure it is safe before it is discharged to environment has widely been acknowledged among the researchers. Subsequently, numerous investigations with multiple degrees of success have been documented to date to manage water pollution as a result of serious and cooperative efforts among researchers in the field of wastewater treatment and management. Common methods for removing heavy metals from wastewater are physicochemical methods which include chemical precipitation (Maheshwari & Gupta 2016), chemical coagulation (Huang et al., 2016), ion exchange (Lee et al., 2016), electrochemical (Fu & Wang 2011), membrane filtration (Keng et al., 2013), adsorption (Devi & Manonmani 2015; Mishra 2014; Kyzas & Kostoglou, 2014) and biological treatment (Hashim, 2011). A comprehensive review of literature indicates that leading experts have unanimously concluded that these methods were found to have their own shortcomings and limitations in terms of being either ineffective, not employed for all processes that generate heavy metals bearing wastewater or expensive (Table 2.5).

At present, adsorption is recognized as an effective and economic method for heavy metals wastewater treatment. Despite of its disadvantages such as product recovery possibly requiring a special, expensive distillation (or extraction), adsorbent progressively deteriorating in capacity as number of cycles increases, adsorbent regeneration requiring a steam or vacuum source (Bilal et. al., 2013), adsorption is stated as notorious wastewater purification method for heavy metals removal. This method is preferably attributable on its advantage in low operational cost and spontaneous reaction during the remediation processes (Rahman et al., 2014; Gupta 2013). This process offers flexibility in design and operation, high treatment capacity, high removal efficiency and fast kinetic (Abbaszadeh et al., 2016). In addition, adsorption is occasionally reversible, reproducible and regenerated by suitable desorption process. It has wider applicability in the removal of diverse types of pollutants, environmental friendliness and exhibiting resistance to fouling from toxic pollutants and greater versatility (Barakat, 2011).
<table>
<thead>
<tr>
<th>Technique</th>
<th>Working Principle</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
</table>
| Chemical precipitation | • Involves the using of chemicals to cooperate with heavy metals ions with the purpose to form insoluble compound which can be separated from the water by sedimentation or filtration.  
• Ph value of 8 to 11 is essential to be retained in order to prolong the hydroxides precipitation in the medium. (Fu & Wang, 2011). | • A simple and inexpensive operation that is effective and most widely used in wastewater application (El-Zayat & Smith, 2013). | • Generates of huge quantity of relatively low-density sludge thus presents dewatering and disposal problems.  
• Insufficient treatment due to tedious in pH control for all types of metals contain in the polluted water (Keng *et al*., 2013).  
• Not a suitable metal removal method when the pollutant concentration is low (Mishra, 2014). |
| Coagulation and flocculation | • Coagulation destabilize colloids by offsetting forces that keep them disassociated with the aid of coagulants. Impurities are removed by neutralizing the charge of the particulate to form precipitates.  
• Flocculation takes place where by the particles binds together into large agglomerates with the aids of flocculants (Fu & Wang, 2011) and removed or separated by filtration, straining or floatation. | • Removes wastewater particulate and impurities efficiently (Hashim, 2011). | • Frequent maintenance and scrupulous chemical feed system monitoring to control the pH.  
• A careful operational routine is crucial by which overload dosing with coagulant to compensate for inefficient may produce a high amount of sludge.  
• Could result to uneconomical wastewater treatment in terms of chemical usage but it is expensive in terms of unwanted product (Drinan & Spellman, 2013). |
| Ion exchange        | • Employs ion-exchange resin; either synthetic or natural solid resin in heavy metals removal application (Díaz-Muñoz *et al*., 2016).                                                                                                                               | • Specific ability to exchange its ionic species through the cationic metals in metal wastewater treatment.  
• Cheap natural resin, whilst the synthetic form has wider application and more effective in heavy metals removal in wastewater. (Huang *et al*., 2014) | • Zeolites and montmorillonites ion-exchanger resin are limited compared to the synthetic resins (Kim *et al*., 2013).  
Generally applicable to remove heavy metals at low concentration due to the cost of replacing ion exchange resins prohibits the treatment of highly concentrated wastewater (Keng *et al*., 2013). |
Table 2.5: Working principle, advantage and disadvantage of wastewater treatment method

<table>
<thead>
<tr>
<th>Membrane filtration</th>
<th>Membrane filtration</th>
<th>Membrane filtration</th>
<th>Membrane filtration</th>
</tr>
</thead>
</table>
| **Membrane filtration** | • Adopt ultra filtration (UF), reverse osmosis (RO), nanofiltration and electrodialysis technology.  
  • Its operational technique based on pore size and molecular weight of suspended solids from organic solution pollutants; molecules with 5-20 nm and molecular weight of the separating compounds of 1000-100000 Dalton.  
  • UF membrane has larger pore sizes than the dissolved metal ions thus the ions are able to pass through easily. RO comprises a semi-permeable membrane, which filtered out the fluid by rejecting the contaminants (Fu & Wang, 2011). | • It is effective, easy operational, continuous throughput, low energy requirement, normal operating temperature, simple maintenance, flexible modular design and space saving technology. | • Consumes high power to pump the pressure required and high maintenance cost due to its membrane to be restored after certain operational time and low permeate flux (Hubbe et al., 2011). |

| **Adsorption** | A process of accumulation of ions at the interface between a solid phase and an aqueous phase.  
  • Involves mass transfer process, in which, pollutant in aqueous is transferred to the adsorbent solid surface bound by physical and chemical interactions. Pollutant in aqueous is known as adsorbate, while solid surface of adsorbent is known as adsorbent (Abdolali et al., 2014) | Effective and economic method for heavy metals wastewater treatment.  
  • Flexibility in design and operation, high treatment capacity, and fast kinetic (Abbaszadeh et al., 2016).  
  • Reversible, reproducible and regenerated by suitable desorption process.  
  • Wider applicability in the removal of diverse types of pollutants, environmental friendliness and exhibiting resistance to fouling from toxic and pollutants (Barakat, 2011). | Product recovery possibly requiring a special, expensive distillation (or extraction), adsorbent progressively deteriorating in capacity as number of cycles increases, adsorbent regeneration requiring a steam or vacuum source (Hashim et al., 2011). |
2.6 Adsorption mechanism

Adsorption is a process of accumulation of ions at the interface between a solid phase and an aqueous phase. Pollutant in aqueous is known as adsorbate, while solid surface of adsorbent is known as adsorbent. Adsorption involves mass transfer process, in which, pollutant is transferred to the adsorbent solid surface bound by physical and chemical interactions (Abdolali et al., 2014). Barakat (2011) highlighted three general steps involved in adsorption: (i) transportation of sorbate sorption to sorbent surface, (ii) adsorption on sorbent surface and (iii) transportation within the sorbent particles (Barakat, 2011).

Adsorption study concerns the adsorbent, which is reacted with solutions containing varying quantities of the metal(s) of interest for a specified period of time using either batch or column techniques. The concentration range of adsorbate study should be imbriated with the concentration of environmental interest (Abdolali et al., 2014). The reaction time ought to approach an equilibrium, which is usually determined by kinetic experiment. The mixture of metal adsorbed adsorbent and solution is separated by centrifugation and/or filtration after a targeted contact time. The filtrate solution is analyzed by Atomic Absorption Spectroscopy (AAS) for the remaining metal ions while the metal adsorbed adsorbent is examined for its characteristic observation via various tools such as Field Emission Electron Microscopy (FESEM) and Fourier Transform Infrared (FTIR) spectroscopy. Batch adsorption and continuous adsorption are the two common types of adsorptions, which are employed in heavy metals metal (Gupta et al., 2014).

The understanding on metal adsorption mechanisms is crucial for the development of adsorption in aqueous system. The removal of heavy metals using activated carbon could involve several mechanisms such as physical adsorption, chemical adsorption, ion exchange, complexation, and electrostatic interactions (Díaz-Muñoz et al., 2016).
2.6.1 Physical adsorption

Physical adsorption, also called physisorption is based on intermolecular forces (Van der Waals) force between the adsorbate and functional groups on the carbon surface (Pyrzy´nska & Bystrzejewski, 2010). The driving force for this type of adsorption is the affinity of the adsorbate to the adsorbent. However physisorption is independent of the electronic properties of the adsorbent. Ion exchange of electrons does not occur results in less strongly adsorbate attached to a specific site on the adsorbent and thus this mechanism is reversible. Van der Waals forces exist not only between adsorbates and adsorbent but also among adsorbates. Because the adsorbate-surface interaction is weak in physisorption lateral interactions are very important for physisorbed molecules and can be as strong as the adsorbate—adsorbent interaction. Physical adsorption involves multilayer formation if the pores are close to the size of molecules. Therefore physically adsorbed adsorbate is free to move within the interface (Cecen & Aktas, 2012).

2.6.2 Chemical adsorption

Chemical adsorption, also called chemisorption is based on a strong force that allows the adsorption to occur at active sites on the carbon surface (Pyrzy´nska & Bystrzejewski, 2010). The forces of attraction that hold the metal ions onto the carbon surface are valence forces. Chemisorption involves exchange of electrons between specific surface sites and adsorbate, a chemical bond being formed. Chemically adsorbed adsorbates are not free to move on the surface or within the interface. It is irreversible and forms a specific interaction. Since the adsorbate is linked to the carbon surface by valence bonds, the adsorbate usually occupies certain adsorption sites on the surface thus monolayer adsorption is formed.

2.6.3 Ion exchange

Ion exchange is a chemical reaction in which free mobile ions on a carbon surface, the ion exchanger, are exchanged for different ions of similar charge in solution. Functional groups on carbon’s network structure undergo hydrolysis in aqueous
solution and form positively or negatively charged ion depending on to the pH of solution (Kumar and Jain, 2009).

\[ \text{RCOOH} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{RCOO}^- \] (2.1)

Cation exchanger containing negatively charged groups like sulphate, carboxylate, phosphate, benzoate and so forth are fixed to be the backbone materials and allow the passage of cations and rejects the anions. Anion exchanges contain basic functional groups, such as amine. There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously (Kumar & Jain, 2013). The mechanism of ion exchange involves replacement of protons, alkali, alkali earth or other cations present on the carbon surface by the heavy metal ions in the solutions as represented by the following equation (Kumar & Jain, 2013):

\[ \text{M}^{n+} + n\text{RCOO}^- \leftrightarrow \text{M(RCOO)}_2 + n\text{H}^+ \] (2.2)

Evidence presented by numerous researches on metal adsorption using AC has proven that this replacement phenomenon is taking place (Abdolali et al., 2014, El Zayat et al., 2013; Pan et al., 2013; Ahmaruzzaman, 2011; Miretzky et al., 2010; Sud et al., 2008). In such cases, it has been seen that the surface groups such as carboxyl, lactones an phenols render the AC surface polar and hydrophilic thereby facilitating the cationic species of metal ions (Gupta et al., 2014). Nguyen et al. (2013) reported that ion exchange might be the dominant mechanism in the removal of Cu(II), Zn(II) and Pb(II) using orange peel. A review on removal of Cd(II) from chemically modified plant waste AC has documented that ion-exchange was considered as a predominant mechanism in Cd(II) removal (Abdolali et al., 2014).

2.6.4 Precipitation

Precipitation occurs when cations and anions are combined to form insoluble ionic solid called precipitate. In metal removal from aqueous solution, metal precipitation is dependant closely to the pH value of the solution. This is to allow metal hydrolysis formation (M(OH)) which then will combine with negatively hydroxide ion (OH⁻)
from the solution. Research on the removal of Co(II) from aqueous solutions by green vegetable waste AC found that the adsorption favored precipitation of metal ions (Sabela et al., 2016). Runtti et al. (2014) observed removal of Fe(II), Cu(II) and Ni(II) via precipitation in addition to adsorption using chemically activated residue adsorbent at pH 6-8. The pH of solution was optimized in order to allow metal hydroxides formation (Cu(OH)$_2$ at pH 9; Ni(OH)$_2$ at pH 7.5) thus promoting the occurrence of metal precipitation. Co-precipitation of Cr(III) with Fe(OH)$_3$ was reported in a study of Cr(III) removal from oil palm AC which occur at the value of pH 9 (Rahman et al., 2011).

2.6.5 Complexation

Metal ions removals from the solution take place through complex formation on the carbon surface after the interaction between metal ion and functional groups. The removal of metal sorbate from solution may also happen through complex formation on the carbon surface after the interaction between sorbate species and active groups (Hashim et al., 2011). This mechanism was found uses polymeric nano-adsorbent whereby its exterior shell can be tailored (e.g., hydroxyl or amine-terminated) for adsorption of heavy metals. The interaction is responsible for the uptake of Cr(III) from aqueous solution (Qu et al., 2013). Nguyen et al. (2013) reported metal-carboxylate complexes formation in Cr(III) and Cu(II) removal using Cupressus lusitanica bark adsorbent as one of the interactions during adsorption. The other mechanisms are ion-exchange and precipitation.

2.7 Factors affecting adsorption

The adsorbate-adsorbent interaction is influenced by some parameters namely, operating parameters pH of solution, mass of adsorbent, contact time and metal concentration (Othman et al., 2012). In order to describe the response of the sorption systems to the changes caused by the variations in experimental conditions and the properties of the sorbents, batch sorption modelling is deemed pivotal (Patel, 2012; Ngah & Hanafiah, 2008). Table 2.6 compiles the affect of adsorption parameter on metal removal and adsorption capacity.
Table 2.6: Factors affecting adsorption using agro waste AC from previous study.

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Metal</th>
<th>pH of solution</th>
<th>Mass of adsorbent (g/L)</th>
<th>Contact time (minute)</th>
<th>Metal concentration (mg/L)</th>
<th>Metal removal (%)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tea waste</td>
<td>Cr(III)</td>
<td>1-8 (5)</td>
<td>0.1-2.5 (1.0)</td>
<td>1-240 (120)</td>
<td>0.02</td>
<td>95</td>
<td>61.6</td>
<td>Duran (2011)</td>
</tr>
<tr>
<td>Tobacco dust</td>
<td>Cu(II)</td>
<td>4-5</td>
<td>1.0</td>
<td>1440</td>
<td>-</td>
<td>-</td>
<td>36</td>
<td>Bilal et al. (2013)</td>
</tr>
<tr>
<td>Papaya peel</td>
<td>Pb(II)</td>
<td>3-7 (5)</td>
<td>0.01-2 (0.1)</td>
<td>10-180 (120)</td>
<td>10-200 (120)</td>
<td>90-70.7</td>
<td>Abbaszadeh et. al (2016)</td>
<td></td>
</tr>
<tr>
<td>Banana peel</td>
<td>Cu(II)</td>
<td>5</td>
<td>5</td>
<td>60</td>
<td>10</td>
<td>-</td>
<td>4.08</td>
<td>Hossain et al. (2012)</td>
</tr>
<tr>
<td>Water melon shell</td>
<td>Zn(II)</td>
<td>4.5</td>
<td>0.2</td>
<td>240</td>
<td>10-500 (10)</td>
<td>80</td>
<td>6.08</td>
<td>Moreno-Barbosa et. al. (2013)</td>
</tr>
<tr>
<td>Oil palm shell</td>
<td>Ni(II)</td>
<td>5</td>
<td>1.0</td>
<td>40</td>
<td>6.06</td>
<td>50.9</td>
<td>15.97</td>
<td>Rahman et al. (2014)</td>
</tr>
<tr>
<td>Green vegetable</td>
<td>Cu(II)</td>
<td>2-8 (3.5)</td>
<td>0.1-0.6 (0.6)</td>
<td>0-120 (90)</td>
<td>1.5-5.0 (18)</td>
<td>97.36</td>
<td>75.93</td>
<td>Sabela et al. (2016)</td>
</tr>
<tr>
<td>Tamarix hispida</td>
<td>Zn(II)</td>
<td>2-10 (6)</td>
<td>1-20(10)</td>
<td>2-80 (50)</td>
<td>20-100 (100)</td>
<td>95.75</td>
<td>188.7</td>
<td>Khademi et al. (2012)</td>
</tr>
<tr>
<td>Tunisian date</td>
<td>Cu(II)</td>
<td>2-7 (5)</td>
<td>0.5</td>
<td>100</td>
<td>100</td>
<td>30</td>
<td>31.25</td>
<td>Bouhamed et al. (2012)</td>
</tr>
<tr>
<td>Crop straw</td>
<td>Cr(III)</td>
<td>2.5-5.0 (3.5)</td>
<td>0.1</td>
<td>120</td>
<td>5-35 (10)</td>
<td>-</td>
<td>330.0</td>
<td>Pan et al. (2013)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Pb(II)</td>
<td>2.5-6.5 (5.5)</td>
<td>-</td>
<td>0-150 (90)</td>
<td>40-140 (80)</td>
<td>45</td>
<td>143.45</td>
<td>Yao et al., 2016</td>
</tr>
<tr>
<td>Orange peel</td>
<td>Cu(II)</td>
<td>5</td>
<td>2</td>
<td>480</td>
<td>5-150</td>
<td>-</td>
<td>86.73</td>
<td>Bilal et al. (2013)</td>
</tr>
<tr>
<td>Grape seed</td>
<td>Cu(II)</td>
<td>5</td>
<td>25</td>
<td>120</td>
<td>25-1000</td>
<td>-</td>
<td>95</td>
<td>Bilal et al. (2013)</td>
</tr>
<tr>
<td>Palm date stone</td>
<td>Cr(III)</td>
<td>3.5</td>
<td>1</td>
<td>180-</td>
<td>-</td>
<td>-</td>
<td>120.5</td>
<td>Ahmed et. al. (2016)</td>
</tr>
</tbody>
</table>

Optimum value in bracket
2.7.1 pH of solution

Adsorbate-adsorbent interaction in aqueous solution system is influenced greatly by the pH value of the solution (Gundogdu et al., 2013). A number of research has been carried out on the effect of pH on metal adsorption using AC as adsorbent (Nowicki et al., 2015; Gundogdu et al., 2013; Sych et al., 2012). The pH was found to control the ionic activities including functional groups ionization and ionic state of metals species. Duran (2012) in a study revealed that the tea waste activated carbon adsorbent pH values fell in the acidic region and this shows dominance of acidic groups over basic groups. This is also related to Boehm titration, which proposed that the surfaces of adsorbents were rich in acidic groups. Cr(II) adsorption by using palm date stone AC was found best at 3.5 (Ahmed et al., 2016; Pan et al., 2013). Therefore, the knowledge on this value may help in deciding at which pH value one should work during adsorption studies.

A study carried out on palm shell activated carbon to remove Cu(II) in aqueous solutions concluded that the pH affected (Issabayeva et al., 2008) the metal ion removal. Adsorption at pH 5 was found relatively higher than pH 3. Such negative effect of acidic was assumed to be related with clogged pores due to the complex compound, hence the number of adsorption sites available for copper ions decreased.

2.7.2 Contact time

Contact time is also the significant factor that affects metals adsorption. According to Hossain et al. (2012), the influence of contact time on Cu(II) adsorption marked a swift rate of Cu(II) adsorption during the first 30 minutes, before Cu(II) removal became steady (Hossain et al., 2012). Abbaszadeh et al. (2016) studied Pb(II) removal using papaya peel AC with increasing time from 10 to 120 minutes. It was found that greater amount of adsorption as the contact time increased with maximum (93.22%) removal and it eventually became constant after 2 hours. The uptake trend became downward and steady after 2 hours indicating adsorption equilibrium has achieved.

In other study, in the beginning of the adsorption, a big number of empty active binding sites available during the early part of experiment and enormous of Cu(II) were rapidly attached on banana peel at a quick adsorption rate. Eventually, the amount of binding site decreased and the remaining empty surface sites were hardly adsorbed.
by Cu(II) due to the formation of repellent between the Cu(II) on the adsorbent surface and the aqueous phase (Zaini et al., 2014). This finding shows that optimal contact time is of utmost importance in order to obtain maximum adsorption interaction.

2.7.3 Mass of adsorbent

A study of Cu(II) adsorption using banana peel activated carbon has included adsorbent mass optimization experiments and revealed that the percentage removal was proportional to the mass of banana peel AC. At higher mass of AC, Cu(II) removal was observed to be decreasing. The highest Cu(II) removal (88%) was obtained through the initial Cu(II) concentration of 10 mg/L and dose of 5 g/L. Cu(II) adsorption onto banana peel was retarded when the incomplete aggregation among the available active binding sites were at higher doses and the shortage of active binding site at lower amount of adsorbent (Hossain et al., 2012).

The influence of adsorbent mass on the adsorption process of Zn (II) was proven using Tamarix hispida AC (Khademi et al., 2015). The removal of Zn(II) at a dose of 1 g/L was 21.7% improved to 95.75% when the adsorbent dosage was increased to 10 g/L. The author mentioned that adsorption efficiency with increasing adsorbents dose can be explained by the fact that the higher the dose of adsorbents in the solution, greater the availability of exchangeable sites for Zn(II) and greater the surface area would be. An adsorbent mass dependent experiment of 0.1 – 0.6 g adsorbent conducted in a Cu(II) removal study using green vegetable waste AC stated that increase of AC surface area and availability of more adsorption site that gradually improved the adsorption. However at higher dose the metal adsorbed per unit weight of adsorbent decreased means at higher adsorbent dose the solution ion concentration decreases to a lower value of qe, (amount adsorbed) indicating that adsorption sites remained unsaturated (Sabela et al., 2016). Based from the review, mass of AC in heavy metals removal from aqueous solution is one of the important adsorption parameter.

3.7.4 Metal concentration
Previous research have proved the influence of initial metal ion concentration in metal adsorption (Khademi et al., 2012; Wahi & Senghie, 2011; Moreno-barbosa et al., 2013; Ibrahim et al., 2010). Zn(II) adsorption onto the Tamarix hispida AC study at metal ions concentration of 20–100 mg/L resulted that degree of Zn(II) removal was decreased from 79% to 57% at respective concentration. The increase of initial Zn(II) concentrations resulted in a reduction of its adsorption percentage due to the limitation of available free sites for the adsorption of Zn(II). In fact, when the Zn(II) concentration was higher, the ratio of Zn(II) to the AC was greater, and therefore the percentage of Zn(II) removal was lower. Sorption capacity of Zn(II) at the selected conditions increased from 36.4 to 188.7 mg/g AC when the concentration of Zn(II) was increased from 20 to 100 mg/L. The enhancement of mass transfer rates occurs due to a higher Zn(II) gradient concentration at a higher initial Zn(II) (Khademi et al., 2012).

The influent of Pb(II) and Zn(II) concentration was investigated with different concentrations of 10–500 mg/L at constant 0.5 g of AC. The study concluded that at higher concentration (200–500 mg/L), the efficiency of adsorption process became poor confirming that initial concentration had an influence in the adsorption process. An assumption had been made that the saturation of micropores and mesopores of the watermelon shell and walnut shell AC could be attributed to the result (Moreno-Barbosa et al., 2013). Heavy metals removal using palm oil kernel shell AC resulted that the percentage of metal removal increased with the increase in metal initial concentration. It was found that at lower metal initial concentration (5 mg/l), Ni(II), Cu(II), and Cr(IV) removal were 12%, 26% and 10%, respectively. A pronounce increase in Cr(IV) removal (48%) was found at 35 mg/L. This study has resulted that more metal ions were left in the solutions at higher concentrations, and indicated smaller amount of available sites at higher concentration of metal ions in the aqueous solution (Wahi & Senghie, 2011).

2.8 Adsorption isotherm

Adsorption isotherm is a well-known instrument to comprehend the behavior of the adsorbent surface. It is an equation, which concerns with the quantity of pollutant
adsorbed onto the adsorbent surface and the equilibrium concentration of the solute in a solution at a given temperature (Kyzas & Kostoglou, 2014).

Brunnauer, Emmett and Teller, Freundlich and Langmuir are equilibrium isotherm model equations that are used to explain adsorption data in batch mode (Othman et al., 2012). It is of utmost importance to test the most suitable isotherm in order to access the success of the adsorbent in construct appropriate real application adsorption system designs. Isotherms BET portrayed the process more precisely if the adsorbent’s pores are filled with several layers of adsorbate (Lakovleva & Sillanpää, 2013). It is worth to try Freundlich isotherm since this isotherm is widely employed despite its rough approximation from thermodynamical point of view. The Langmuir isotherm assumes that adsorption happens at specific homogeneous sites within the adsorbent at the exclusion of any interaction between the adsorbed substances. These two isotherms employed reduced concentration approach, which contributes to the coverage of parameter equal to one as far as the pores are filled. Nevertheless, it is quite common for the data to not properly fit with the linear equation (Lakovleva & Sillanpää, 2013).

2.8.1 Brunauer, Emmett and Teller adsorption

Adsorbate molecules often form multilayer, in which, some are adsorbed on already adsorbed molecules and thus, the Langmuir isotherm is not valid. In 1938, Stephan Brunauer, Paul Emmett and Edward Teller developed an isotherm model that took this possibility into consideration. Hence, their model is known as the BET isotherm model (Lakovleva & Sillanpää, 2013).

Each additional layer of adsorbate molecules above the monolayer is assumed to equilibrate with the layer below it and layers of different thickness are allowed to coexist and take the following form (Othman et al., 2016):

\[
\frac{C}{(C_S - C_{eq}) q_m} = \frac{1}{K_B q_m} + \frac{K_B 1}{K_B q_m} \frac{C}{C_S}
\]  

(2.3)
In comparison with linear equation, \( y = mx + c \);

\[
y = \frac{C}{(C_s - C_q)q_m} \quad x = \left[ \frac{C}{C_s} \right] \quad m = \frac{K_B - 1}{K_B q_m} \quad c = -\frac{1}{K_B q_m}
\]  

(2.4)

Where \( q \) is the amount of metal ions adsorbed per specific amount of adsorbent (\( \mu g/g \)), \( C \) is the equilibrium concentration (\( \mu g/l \)), \( q_m \) is the maximum amount of metal ions required to form a monolayer (\( \mu g/g \)), and \( K_B \) is the constant BET adsorption (Danish et al., 2011).

### 2.8.2 Freundlich adsorption

The Freundlich isotherm is among the widely employed isotherm in the explanation of adsorption equilibrium as it is regarded as an empirical equation (Pan et al., 2013; Bello et al., 2010). In addition, the Freundlich model assumes that the adsorbent surface energy is heterogeneous and hence, the stronger binding sites are first occupied and the binding strength decreases with the increasing degree of site occupation. The following equation specifies the Freundlich isotherm (Giwa et al., 2012):

\[
q_e = K_F C_e^{\frac{1}{n_F}}
\]  

(2.5)

To linearize the equation, logarithms are taken.

\[
\log q_e = \log K_F + n_F \log C_e
\]  

(2.6)

where \( q_e \) = quantity adsorbed per unit mass \( \text{mol/g} \); \( C_e \) = equilibrium solution concentration \( \text{mol/L} \); \( K_F \) = \( L/g \) and \( 1/n = n_F \) = is empirical Freundlich constant. \( K_F \) (\( \text{mg/g (L/mg)}^{1/n} \)) is defined as the adsorption capacity of the adsorbent. \( 1/n \) is a measure of adsorption intensity or surface heterogeneity, which may become more heterogeneous as its value gets closer to zero (Albadarin et al., 2011).

It is stated that once the surface is covered, additional adsorbed species may still be accommodated. In this regard, multilayer adsorption is predicted. It should be noted that small organic molecules in water may distribute themselves between the
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